Journal of the
ARKANSAS ACADEMY
OF SCIENCE

VOLUME 56
2002

Journal of the Arkansas Academy of Science, Vol. 56 [2002], Art. 1

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PAST PRESIDENTS OF THE ARKANSAS ACADEMY OF SCIENCE

Charles Brookover, 1917
Dwight M. Moore, 1932-33, 64
Flora Haas, 1934
H. H. Hyman, 1935
L. B. Ham, 1936
W. C. Mann, 1937
M. J. McHenry, 1938
T. L. Smith, 1939
P. G. Horton, 1940
I. A. Willis, 1941-42
L. B. Roberts, 1943-44
Jeff Banks, 1945
H. L. Winburn, 1946-47
E. A. Provine, 1948
G. V. Robinette, 1949
John R. Titter, 1950
R. H. Austin, 1951
E. A. Spessard, 1952
Delbert Swartz, 1953
Z. V. Harvallik, 1954
M. Ruth Armstrong, 1955
W. W. Nedrow, 1956
Jack W. Sears, 1957
J. R. Mundie, 1958
C. E. Hoffman, 1959
N. D. Buffaloe, 1960
H. L. Bogan, 1961
Truman McEver, 1962
Robert Shideler, 1963
L. F. Bailey, 1965
James H. Friboough, 1966
Howard Moore, 1967
John J. Chapman, 1968
Arthur Fry, 1969
M. L. Lawson, 1970
R. T. Kirkwood, 1971
George E. Templeton, 1972
E. B. Wittlake, 1973
Clark McCarty, 1974
Edward Dale, 1975
Joe Guenter, 1976
Jewel Moore, 1977
Joe Nix, 1978
P. Max Johnston, 1979
E. Leon Richards, 1980
Henry W. Robison, 1981
John K. Beadles, 1982
Robbin C. Anderson, 1983
Paul Sharrah, 1984
William L. Evans, 1985
Gary Heidt, 1986
Edmond Bacon, 1987
Gary Tucker, 1988
David Chittenden, 1989
Richard K. Speairs, Jr. 1990
Robert Watson, 1991
Michael W. Rapp, 1992
Arthur A. Johnson, 1993
George Harp, 1994
James Peck, 1995
Peggy R. Dorris, 1996
Richard Kluender, 1997
James Daly, 1998
Rose McConnell, 1999
Mostafa Hemmati, 2000
John Rickett, 2001

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The Arkansas Academy of Science recognizes the support of the following institutions through their Institutional Membership in the Academy.

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UNIVERSITY OF CENTRAL ARKANSAS, Conway
UNIVERSITY OF THE OZARKS, Clarksville
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COVER: Juvenile American alligator (Alligator mississippiensis) - Little Rock Zoo. Photo by Stan Trauth.

https://scholarworks.uark.edu/jaas/vol56/iss1/1
Arkansas Academy of Science 2002

April 5-6, 2002
86th Annual Meeting

University of Arkansas at Little Rock
FIRST BUSINESS MEETING  
UALR ETAS BUILDING ROOM 233  
APRIL 5, 2002

1. Call to Order: Dr. Walt Godwin, President-Elect of the AAS, called the meeting to order at 11:10 am. Dr. Godwin, presiding at meeting in place of Dr. John Rickett, President of the AAS, who missed the meeting due to health reasons. Dr. Goodwin provided an update on Dr. Rickett’s health status.

2. Historian’s Report: Henry Robinson reported that this is the 86th meeting of the Academy and the sixth time that the meeting has been held at the UALR campus. Previous meetings at UALR (or the same campus with previous names) were held in 1946, 1966, 1976, 1981, and 1987.

3. Local Arrangement Chair: On behalf of UALR, Steve Lindsey welcomed the members to the UALR campus. Steve recognized the hard work of the UALR faculty, staff, and students in preparing for the meeting.

4. Approval of Minutes: Minutes of last year’s business sessions at the Univ. of Central Arkansas were distributed and will be approved by vote at the second business meeting.

5. Treasurer’s Report: Joyce Hardin handed out copies of the 2001 AAS financial statement to the membership. The report indicated that the Academy had a net $950.31 budget loss for 2001, although this loss will likely be reduced to around $400 when all the Journal page charges are collected. The loss was attributed to a slight reduction in membership dues collected and a lack of profit from the 2001 annual meeting. Joyce provided details concerning the income and expenses for the year as well as information regarding journal costs. Bob Wiley was appointed Chairman of the Auditing Committee.

2001 FINANCIAL STATEMENT

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<td>Beginning Balance - January 1, 2002</td>
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INCOME:

1. ANNUAL MEETING                                            | $600.00  |

2. ENDOWMENT DONATIONS
   a. AAS Unrestricted                                       | $36.00   |

3. INTEREST (Endowment)                                     | $1,102.11|

4. INDIVIDUAL MEMBERSHIPS
   a. Associate                                               | $180.00  |
   b. Regular                                                 | $1,770.00|
   c. Sustaining                                              | $35.00   |
   d. Sponsoring                                              | $0.00    |
   e. Life                                                    | $475.00  |
   __________________________________________________________| $2,460.00|

5. INSTITUTIONAL MEMBERSHIPS                                | $1,400.00|

6. MISCELLANEOUS                                            | $6.40    |
Secretary’s Report

7. JOURNAL
   a. Miscellaneous Sales $3,577.76
   b. Page Charges $6,480.00
   c. Subscriptions $700.00
   TOTAL INCOME $10,757.76
   TOTAL EXPENSES $16,362.27
   COST OF JOURNAL
      PRINTER. CHARGE
      VOLUME COPIES PAGES $3,694.68
      36 (1982) 450 110 $5,233.28
      37 (1983) 450 103 $5,326.91
      38 (1984) 450 97 $5,562.97
      39 (1985) 450 150 $7,856.20
      40 (1986) 450 98 $6,175.20
      41 (1987) 450 116 $7,122.79
      42 (1988) 450* 116 $7,210.79
      43 (1989) 450* 119 $8,057.24
      44 (1990) 450* 136 $9,298.64
      45 (1991) 450* 136 $9,397.07
      46 (1992) 450* 116 $9,478.56
      47 (1993) 400 160 $12,161.26
      48 (1994) 450 270 $17,562.46
      49 (1995) 390 199 $14,725.40
      50 (1996) 345 158 $11,950.00
      51 (1997) 350 214 $14,308.01
      52 (1998) 350 144 $12,490.59
      54 (2000) 350 160 $14,149.07
   TOTAL VOLUME COST $14,974.78
   COST/COPY $49.21
   COST/PAGE $32.15

4. MISCELLANEOUS
   a. Ed Griffin Travel to AAS Conference (708) $250.00
   b. Doug James - Biota Project (709) $300.00
   c. Checking Account service charge $14.40
   TOTAL EXPENSES $564.40

5. NEWSLETTER
   TOTAL EXPENSES $0.00

6. OFFICE EXPENSES
   TOTAL EXPENSES $92.81

7. JOURNAL
   a. Stan Trauth - Editorial Consultation and Travel Volume 54 (710) $200.00
   b. Pinpoint Color Volume 54 (711) $14,149.07
   c. Joy Trauth - Editorial Consultant Volume 55 (714) $600.00
   d. Pinpoint Color Reprint forms (716) $25.71
   TOTAL EXPENSES $14,974.78

The Total Volume Cost equals the printer’s charge plus the editor, editorial assistant, and other miscellaneous charges.

- On Volume 42 the Academy received 560 copies, but the printer did not charge us for the extra 110 copies. For comparison purposes the calculated cost/copy is based on 450 copies.
- On Volume 43 the Academy received 552 copies, but the printer did not charge us for the extra 73 copies. For comparison purposes the calculated cost/copy is based on 450 copies.
- On Volume 44 the Academy received 535 copies, but the printer did not charge us for the extra 85 copies. For comparison purposes the calculated cost/copy is based on 450 copies.
- On Volume 45 the Academy received 594 copies, but the printer did not charge us for the extra 144 copies. For comparison purposes the calculated cost/copy is based on 450 copies.
- On Volume 46 the cost was greater than usual due to the high cost of a second reprinting of 54 copies by a different printer.

Journal of the Arkansas Academy of Science, Vol. 56, 2002

Published by Arkansas Academy of Science, 2002
6. **Journal Editor in Chief's Report:** Stan Trauth reported that Vol. #55 was available and asked members to take copies back to their respective campuses. Stan asked the Academy continue an allotment of $200 to cover costs incurred by the Editor-in-Chief. The motion, which was made and seconded and will be voted on at the second business session.

7. **Journal Managing Editor's Report:** David Saugey recognized the help of the 56 individuals, representing two countries (US and UK), nine states, 22 universities, seven agencies, and two organizations served as reviewers for Vol. 55. David requested $300 for Managing Editor expenses for Vol. 56. The motion was made and seconded and will be voted on at the second business session.

8. **Newsletter Editor:** Jeff Robertson reported on the status of the newsletter and requested a small amount of money to cover expenses for next year's newsletter. A motion to provide these funds was seconded will be voted on at the second business meeting.

9. **Arkansas Science Fair Association:** Dr. Godwin read a report from Mike Rapp who was not present since the state science fair was held in Conway on the same dates as the Academy meeting. Seven regional science fairs were held in March.

10. **Junior Academy of Science:** no report

11. **Intel Talent Search:** no report

12. **Committee Reports:**
   a. **Biota Committee:** no report
   b. **Constitution Committee:** no report
   c. **Development Committee:** David Saugey reported that he had compiled a notebook with potential companies and agencies that might be willing to provide support for the Academy. Over the course of the next year the committee will contact some of these sources.

13. **Old Business:** AAS Young Investigators Award Committee - Wayne Gray presented a proposal for the Academy to establish a Young Investigator award to recognize promising young scientists in Arkansas. Guidelines for the award were discussed. The proposal will be presented to the membership and discussed further at the second business meeting.

14. **New Business:** Problems concerning membership were discussed.

15. **Closing:** Dr. Godwin adjourned the meeting at 12:00 p.m.

**SECOND BUSINESS MEETING**

**UALR FRIBOURGH HALL ROOM 101**

**APRIL 6, 2002**

1. Dr. Walt Godwin, President-Elect of the AAS, called the meeting to order at 12:15 pm. Dr. Godwin, presided at meeting in place of Dr. John Ricketts, President of the AAS, who missed the meeting due to health reasons. Dr. Gary Heidt of UALR provided an update on Dr. Ricketts health status.

2. **Approval of Minutes:** MA motion to approve the minutes of last year's business sessions at the Univ. of Central Arkansas was seconded and approved.

3. **Historian's Report:** Henry Robinson reported that this is the 86th meeting of the Academy and the sixth time that the meeting has been held at the UALR campus. Previous meetings at UALR (or the same campus with previous names) were held in 1946, 1966, 1976, 1981, and 1987.

4. **Treasurer's Report:** Joyce Hardin provided copies of the 2001 AAS financial statement to the membership. The report indicated that the Academy had a net $950.31 budget loss for 2001, although this loss will likely be reduced to around $400 when all the journal page charges are collected. The loss was attributed to a slight reduction in membership dues collected and a lack of profit from the 2001 annual meeting. Joyce provided details concerning the income and expenses for the year as well as information regarding journal costs.

5. **Auditor's Report:** Bob Wiley introduced the members of his committee and confirmed the 2001 financial statement. A motion to accept the 2001 AAS financial statement, was seconded, and approved by unanimous consent of the membership.

6. **Journal Editor-in-Chief's Report:** Stan Trauth reported that Vol. #55 asked members to take copies back to their respective campuses. Stan asked the Academy continue an allotment of $200 to cover costs incurred by the Editor-in-Chief. The motion, which was made and seconded at the first business session, was approved. Stan mentioned that he is considering some minor editorial changes to update the style of the *Journal*. He reminded the membership to begin thinking about the next Editor-in-Chief, to replace himself in two years.
Secretary’s Report

Managing Editor’s Report: David Saugey reported that the review process for Vol. 55 went smoother and more timely than usual. He recognized the help of the 56 individuals, representing two countries (US and UK), nine states, 22 universities, seven agencies, and two organizations served as reviewers for Vol. 55. David mentioned the continuing problem that some authors do not submit manuscripts in the correct format. In the future manuscripts submitted in the proper format may be returned without review. David requested $300 for Managing Editor expenses for Vol. 56. The motion, which was made and seconded at the first business session, was approved.

Newsletter: Jeff Robertson was not present, but Dr. Godwin reported that Jeff had reported at the first business meeting and had requested a small amount of money to cover expenses for next year’s newsletter. A motion to provide these funds was seconded and approved.

Arkansas Science Fair Association: Dr. Godwin read a report from Mike Rapp who was not present since the state science fair was held in Conway on the same dates as the Academy meeting. Seven regional science fairs were held in March. A request for $400.20 was made to help cover some of the expenses for sending students and teachers to the International Science and Engineering Fair. A motion for the Academy to provide these funds was seconded and approved.

Junior Academy of Science: no report

Intel Talent Search: no report

Committee Reports:

a. Biota Committee: no report

b. Constitution Committee: no report

c. Development Committee: David Saugey reported that he had compiled a notebook with potential companies and agencies that might be willing to provide support for the Academy. Over the course of the next year the committee will contact some of these sources. David requested that the Academy provide $250 for purchasing stationary and for mailing costs. A motion was seconded and approved.

d. Nominations Committee: On behalf of the nominations committee, Dr. Scott Kirkconnell nominated Jeff Robertson for the office of Secretary. A motion to close nominations was seconded and Dr. Robertson was elected by acclamation. Dr. Kirkconnell nominated three individual for the office of Vice-President; Wil Braithwaite, Phoebe Harp, and Betty Crump. There were no additional nominations from the floor. A motion to cease nominations was seconded and approved. Ballots were distributed and the ballots were counted.

e. Science Education Committee: Dr. Hemmati reported that this committee had met on the previous day and several potential ideas for promoting science education were discussed. The committee will be developing these ideas over the coming year.

Old Business: AAS Young Investigators Award Committee - Wayne Gray presented a proposal for the Academy to establish a Young Investigator award to recognize promising young scientists in Arkansas. Guidelines for the award were discussed. After some discussion it was decided that the committee should consider further the details of the proposal.

Local Arrangement Chair: Steve Lindsey provided a recap of the meeting. The total registered attendance for the meeting was 209, including 95 students. Attendance at the banquet was 109. A total of 125 abstracts were presented including 21 poster presentations. Over 80% of the oral presentations utilized PowerPoint computer-generated slides. Steve recognized the hard work of the UALR faculty, staff, and students in preparing for and conducting the meeting.

Future meetings: Dr. Godwin announced that the 2003 AAS meeting will be held at the University of Arkansas at Fayetteville and the 2004 meeting will be held at Arkansas State University in Jonesboro. A bid from Hendrix College to host the 2005 meeting in Conway was accepted.

New Business: Dr. Godwin read a plaque to be presented to Dr. John Rickett, the AAS President for the past year. Unfortunately, Dr. Rickett was not able to attend the meeting due to health problems. Several members spoke of John’s devotion to the AAS over the years. A motion to provide funds for an in memoriam announcement for John was seconded and approved (Secretary’s note: Sadly, Dr. John Rickett passed away on April 6, 2002).

Dr. Kirkconnell announced the results of the election. Dr. Betty Crump will serve as the new AAS Vice-President.

Awards: Recipients of the student awards for best presentations were announced. Joyce Hardin will mail the certificates and checks to the winners.

Closing: Dr. Godwin assumed the office of AAS President for the next year. Dr. Godwin adjourned the meeting at 1:30 p.m.
APPENDIX A

2002 AAS Award Winners

GRADUATE STUDENT AWARDS

Environmental:
1st place: Gregory Eads
Occurrence of Tick-borne Disease at Arkansas Post National Memorial University of Arkansas at Monticello

Honorable Mention: Christopher Watt
Short-term Understory Vegetation Responses to Deer Exclosures at Arkansas Post National Memorial University of Arkansas at Monticello

Life Science:
1st place: Roger Redondo
Role of a Single Neuron in Turning While Crawling in the Marine Slug Tritonia Diomedea
University of Central Arkansas

Honorable Mention: Malcolm McCallum
A Forty-three Year Museum Study of Northern Cricket Frog (Acris crepitans) Abnormalities in Arkansas: Upward Trends and Distributions Arkansas State University

Physical Science:
1st place: Constance Meadors
Pressure and Flow Validation of a Second Generation Gas Extraction Probe for a Hybrid Rocket Gas Extraction System University of Arkansas at Little Rock

2nd: Steve R. Farmer
Simulation of Video Electric Single Particle Aerodynamic Relaxation Time Analyzers University of Arkansas at Little Rock

2nd: Steve Trigwell
Tribocharging of JSC Mars-1 Simulant Dust University of Arkansas at Little Rock

UNDERGRADUATE STUDENT AWARDS

Physical Science:
1st: Reason Cook
Potential Waves Arkansas Tech University

2nd: Mee-Lee Pritchett
An Electrostatic Deposition Engine for Making Pharmaceutical Tablets Using Pure Drug Powder Univeristy of Arkansas at Little Rock

3rd: Chris Hale
Cleavage Development Within a Folded Sequence of Jackfork Sandstone, Eastern Quachita Mountains, Arkansas University of Arkansas at Little Rock

Life Science:
1st: Nelly P. Norrell
The Role of Intracellular Acidification in Apoptotic Progression University of Central Arkansas

2nd: David R. Lyon
Patterns of Arthropods Inhabiting Epiphytes in a Temperate Deciduous Forest Hendrix College

3rd: Josh E. Kessler
Coccidian Parasites (Apicomplexa: Eimeriidae) of Select Rodents from Western and Southwestern Arkansas and Northeastern Texas Texas A&M - Texarkana

Environmental:
1st: Allison Boyer
The Ability of Soil Fungi to Degrade Glyphosate (Roundup) Hendrix College

2nd: Jessie K Fly
The Effects of Tree Species and Tree Age on Epiphyte Community Structure in a Temperate Deciduous Forest Hendrix College

3rd: Robert E. Swearingen
Interaction of Nutrients and Predators in an Arkansas Grassland Hendrix College

APPENDIX B

RESOLUTIONS

BE IT RESOLVED that we, the membership of the Arkansas Academy of Science, offer our sincere thanks to the University of Arkansas at Little Rock for hosting the 86th meeting of the Arkansas Academy of Science. In particular, we thank the local arrangements committee: Steve Leslie (Chair), Steve Grace, David Lindquist, Tom McMillan, Wil Braidwvate, Roger Hawk, and all of the student workers and staff who collectively contributed to a successful meeting. Appreciation is expressed for the use of the excellent facilities and the hospitality shown to us by all University of Arkansas at Little Rock personnel. The banquet was excellent, and we especially thank Dr. Alan Pounds for a stimulating presentation on "Global Warming and the Future of Biodiversity: Lessons From a Tropical Cloud Forest."

The Academy recognizes the important role played by session chairs and expresses sincere appreciation to Wayne
Gray, Wendi Williams, Brian Wagner, David Lindquist, Fred Hickling, Abhijit Bhattacharyya, George Harp, Richard Speairs, David Saugey, Don Bragg, and Roger Hawk. A special thanks is owed those individuals who devoted considerable time and energy to judge student papers: Al Adams, Wil Braithwaite, Betty Crump, Wayne Gray, Joe Guenter, Phoebe Harp, Bob Watson, and Bob Wiley.

The Academy appreciates the University of Arkansas at Little Rock for sponsoring the social, the Arkansas Environmental Federation for donating to undergraduate student awards and Sigma Xi for graduate student awards.

We express gratitude to the various directors of the science and youth activities which are supported or supervised by the Academy: Mostafa Hemmati, Chair of the Science Education Committee; Mike Rapp, Director of the Arkansas State Science Fair Association; Tom Palko, Director of the Junior Science & Humanities Symposium; Jim Murray, Director of the Intel Science Talent Search; and Rick Geraci and Mark Eakin, Co-Directors of the Junior Academy of Science. We wish to thank all those who served as directors at the regional science fairs and Junior Academy meetings: Kathryn Shinn, Beverly Meinzer, Marty Huss, Lynne Hehr, Darin Buscher, Dennis Miller, Jim Edson, Shane Willbanks, and Mike Rapp.

The continued success of the Academy is due to its strong leadership. We offer sincere thanks to our officers for another excellent year: John Rickett (President), Walt Godwin (President-Elect), Wayne Gray (Vice-President), Mark Draganjac (Past-President), Mike Soulsby (Secretary), Joyce Hardin (Treasurer), Stan Trauth (Journal Editor-in-Chief), David Saugey (Journal Managing Editor), Jeff Robertson (Newsletter Editor), and Henry Robison (Historian). In addition, the Academy expresses appreciation to all who contributed time and effort on various committees of the Academy.

We congratulate all who presented papers and posters at this meeting. Student participants are especially recognized since their efforts contribute directly to the future success of the Academy and the improvement and advancement of science in Arkansas.

Finally, the membership wishes to especially recognize President John Rickett. Over the years, John has had many significant roles in the Academy – Newsletter Editor, Secretary, Vice President, President, and numerous committees. In addition to formal roles, John has been the ultimate source of information regarding everyone and everything about the Academy. For his many years of dedicated service, both to the Academy and to the profession, the membership expresses its heartfelt concern and regret that John could not be here to participate in our 86th meeting.

Respectfully submitted this 6th day of April, 2002,
Mike Plummer, Chair
Perk Floyd, Member
Secretary's Report

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PROGRAM
Arkansas Academy of Science
86th Annual Meeting
April 5-6, 2001
University of Arkansas at Little Rock

SCHEDULE OF EVENTS

Friday, April 5, 2002
9:00 am - 3:00 p.m. Registration ETAS Lobby
8:30 a.m. - 10:30 a.m. Executive Committee Meeting ETAS 125L
11:00 a.m. - 12:00 p.m. First Business Meeting ETAS 233

Oral Presentations
1:30 p.m. - 2:30 p.m. Microbiology, Parasitology ETAS 233
1:15 p.m. - 2:30 p.m. Geology, Science Education ETAS 379
3:00 p.m. - 4:00 p.m. Aquatic Ecology ETAS 379
1:30 p.m. - 2:30 p.m. Atmospheric Chemistry ETAS 279
2:45 p.m. - 4:45 p.m. Chemistry ETAS 229
1:15 p.m. - 2:15 p.m. Mathematics ETAS 354
2:45 p.m. - 4:15 p.m. Physics ETAS 354
2:00 p.m. - 4:00 p.m. Poster Presentations ETAS Foyer & Earthquake Ctr
4:30 p.m. - 5:00 p.m. Science Education Committee Meeting ETAS 233
5:30 p.m. - 6:30 p.m. Reception / Social Mixer DSC 2nd Floor Concourse

6:30 p.m. - 8:00 p.m. Banquet DSC Meeting Rooms A & B
8:00 p.m. - 9:00 p.m. Keynote Address: J. Alan Pounds Dickenson Hall Auditorium Global Warming and the Future of Biodiversity: Lessons from a Tropical Cloud Forest Saturday, April 6, 2002
8:00 a.m. - 10:30 am. Invertebrate Zoology ETAS 233
8:00 a.m. - 10:45 am. Terrestrial Ecology ETAS 354
8:00 a.m. - 10:30 am. Vertebrate Zoology ETAS 262
8:00 a.m. - 10:30 am. Botany & Plant Biology ETAS 379
8:00 a.m. - 10:30 am. Inorganic Materials ETAS 229
8:00 a.m. - 10:45 am. Engineering ETAS 327
11:00 a.m. Second Business Meeting Fribourgh Hall 101

SECTION PROGRAMS
* Undergraduate **Graduate

ORAL PRESENTATIONS
Friday, April 5, 2002
Microbiology, Parasitology Location: Room 233

Time Topic
1:30 Chris T. McAllister, Charles R. Bursey and Stanley E. Trauth, Department of Biology, Texas A&M University-Texarkana, Texarkana, TX 75505. Department of Biology, Pennsylvania State University - Shenandoah Campus, Sharon, PA 16146; and Department of Biological Sciences, Arkansas State University, State University, AR 72467. PARASITES OF ENDEMIC PLETHODON SPP. (AMPHIBIA: CAUDATA) FROM ARKANSAS AND OKLAHOMA 2:15

2:45 Nelly P. Norrell, Fumiyu Kubo, G. Cory Morgan, Shane Melton, Dana K. Strassle, and Dr. Steven W. Runge, Department of Biology, University of Central Arkansas, Conway, Arkansas 72035. THE ROLE OF INTRACELULAR ACIDIFICATION IN APOPTOTIC PROGRESSION 4:30

E. Trauth2, (1) Environmental Sciences Ph.D. Program, Arkansas State University, P.O. Box 847, State University, AR 72467; (2) Department of Biological Sciences, Arkansas State University, P.O. Box 599, State University, AR 72467. SEVERE LEECH INFESTATION OF AN OZARK AMPHIBIAN COMMUNITY 5:30

Joshua E. Kessler and Chris T. McAllister, Department of Biology, Texas A&M University-Texarkana, TX 75505. COCCIDIAN PARASITES (APICOMPLEXA: EIMERIDAE) OF SELECT RODENTS FROM WESTERN AND SOUTHWESTERN ARKANSAS AND NORTHEASTERN TEXAS 6:00

BREAK 6:30

Journal of the Arkansas Academy of Science, Vol. 56, 2002
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<th>Time</th>
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<tr>
<td>1:30</td>
<td>Autumn R. Fernald, Stephen A. Leslie, and Jeffrey B. Connelly, University of Arkansas at Little Rock, Department of Earth Sciences, Little Rock, AR 72204. CARYOCARIS CURVILATA (ARTHROPODA, PHYLOCARIDA) FROM THE MAZARN SHALE, OUACHITA MOUNTAINS, PARON, ARKANSAS</td>
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<td>1:45</td>
<td>Alois J. Adams and Deborah L. Herden, Department of Physics and Astronomy, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, Arkansas 72204. PORTABLE PHYSICS MODULES IN STANDARDS-BASED INSTRUCTION</td>
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<tr>
<td>2:00</td>
<td>Deborah L. Herden and Alois J. Adams and Department of Physics and Astronomy, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, Arkansas 72204. THE ARKANSAS PHYSICS LENDING LIBRARY</td>
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<td>2:15</td>
<td>David Jamieson, Arkansas State University-Newport, Department of Biological Sciences, 7648 Victory Boulevard, Newport, Arkansas 72112. TEACHING DARWIN’S THEORY OF EVOLUTION AT THE TWO-YEAR COLLEGE</td>
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<td>3:00</td>
<td>Tobin Fulmer and Renn Tumilson, Department of Biology, Henderson State University, Arkadelphia, AR 71930. HAZARDS OF LOST FISHING GEAR TO WILDLIFE ON LAKES</td>
<td>Room 379</td>
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<tr>
<td>3:15</td>
<td>Malcolm L. McCallum, and Stanley E. Trauth, (1) Environmental Sciences Ph.D. Program, Arkansas State University, P.O. Box 847, State University, AR 72467; (2) Department of Biological Sciences, Arkansas State University, P.O. Box 599, State University, AR 72467. A FORTY-THREE YEAR MUSEUM STUDY OF NORTHERN CRICKET FROG (ACRIS CREPITANS) ABNORMALITIES IN ARKANSAS: UPWARD TRENDS AND DISTRIBUTIONS</td>
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<td>3:30</td>
<td>Benjamin A. Wheeler and Stanley E. Trauth, Environmental Sciences Ph.D. Program, Arkansas State University, P.O. Box 847, State University, AR 72467-0847; Department of Biological Sciences, Arkansas State University, P.O. Box 500, State University, AR 72467-0599. ABNORMALITIES IN THE OZARK HELLBENDER, CRYPTOBRANCHUS ALLEGIENSIIS BISHOPI</td>
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<td>3:45</td>
<td>James Daly, Bruce DeYoung, and Terry Hostetler, Department of Microbiology and Immunology, University of Arkansas for Medical Sciences, Little Rock, AR 72205. INFESTATION OF CROOKED CREEK SMALLMOUTH WITH YELLOW GRUB (CLINOSTOMUM MARGINATUM)</td>
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<td>1:30</td>
<td>Joseph D. Scott and David M. Chittenden, Department of Chemistry and Physics, Arkansas State University, State University, AR 72467. THE CHEMICAL COMPOSITION OF PARTICLES OF d ≤ 0.20 μm IN THE LOWER STRATOSPHERIC AEROSOL, SPRING 1998</td>
<td>Room 229</td>
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<td>1:45</td>
<td>Miah M. Adel, Interdisciplinary Sciences Research Center, Department of Chemistry and Physics, P.O. Box 4941, University of Arkansas at Pine Bluff, 1200 North University Drive, Pine Bluff, AR 71601. EXHAUST FALLOUT DISTANCES FROM THE INCIDENT-FREE INCINERATION AT THE PINE BLUFF ARSENAL</td>
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<td>2:00</td>
<td>Liz Null, Harding University, HU Box 12030, Searcy, AR 72149. HYDROXYL RADICAL REACTIONS WITH ALIPHATIC HYDROCARBONS</td>
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<td>2:15</td>
<td>Adam Jacoby and Lauren Gilbert, Harding University, HU Box 10592, Searcy, AR 72149. CHEMICAL KINETICS STUDIES OF THE REACTIONS OF HYDROXYL RADICALS WITH HYDROCARBONS</td>
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<td>2:45</td>
<td>Lesley White, Jennifer Faulkner, Dr. Mike Panigot, Department of Chemistry, Arkansas State University - Jonesboro, P.O. Box 419, State University, AR 72467-0419; Dr. Robert W. Curley, Jr., Division of Medicinal Chemistry, College of Pharmacy, The Ohio State University, 300 W. 12th Ave., Columbus, OH 43210-1291. EFFORTS TOWARD THE PREPARATION OF STEREORESELECTIVELY Beta-DUERATED HISTIDINE</td>
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<td>3:00</td>
<td>Amanda Caldwell, Jason Boggs, Robin Carlton, and Dr. Mike Panigot, Department of Chemistry, Arkansas State University - Jonesboro, P.O. Box 419, State University, AR 72467-0419. STUDIES IN THE SYNTHESIS OF C-GLYOSIDE DENDRIMERS - DIFFICULTIES AND SOLUTIONS</td>
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<td>3:15</td>
<td>Cecil A. Sorrells, Ali U. Shaikh, and V. M. Samokysyn, 1, 2 - Department of Chemistry, University of Arkansas at Little Rock, Little Rock, AR 72204; 3 Division of Toxicology, University of Arkansas for Medical Sciences, Little Rock. OXIDATION-REDUCTION CHARACTERISTICS OF CHLOROPHENOLS</td>
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<td>3:30</td>
<td>Anwar A. Bhuian, and Harry O. Brotherton, Department of Physical Science, Arkansas Tech University, Russellville, AR 72801; Chemistry Department, University of Louisiana at Monroe, Monroe, LA 71209. SOLID PHASE EXTRAC-</td>
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Published by Arkansas Academy of Science, 2002
**Arkansas Academy of Science**

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<tr>
<td>1:15</td>
<td>Fred Hickling and Danny Arrigo, University of Central Arkansas, UCA Math Department, Conway, Arkansas 72035. <strong>BOUNDARY VALUE PROBLEMS AND THE DARBOUX TRANSFORMATION</strong></td>
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<td>1:30</td>
<td>Brandon Lindley, University of Central Arkansas, Conway, AR 72035. <strong>TIME INDEPENDENT SCHRODINGER POTENTIALS</strong></td>
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<td>1:45</td>
<td>Garth Johnson and Bryan Gipson, University of Central Arkansas, UCA Math Department, Conway, Arkansas 72035. <strong>THE DARBOUX TRANSFORMATION OF THE VARIABLE WAVE SPEED EQUATION</strong></td>
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<td>2:00</td>
<td>Chad Fendt, University of Central Arkansas, UCA Math Department, Conway, AR 72035. <strong>SCHRODINGER'S EQUATION AND POTENTIALS USED TO MODEL $\alpha$-DECAY</strong></td>
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<td>3:15</td>
<td>A. Bhattacharyya$^1$, J. H. Masliyah$^2$ and J. Yang$^3$; $^1$Department of Applied Science, University of Arkansas at Little Rock, 2801 South University, ETAS 575, Little Rock, AR 72204-1099, $^2$Department of Chemical and Materials Engineering, $^3$Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta T6G 2G8, Canada. <strong>A MODEL OF OSCILLATORY LAMINAR ELECTRO-KINETIC FLOW IN LONG, CIRCULAR</strong></td>
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<td>3:30</td>
<td>Bao-An Li, Department of Chemistry and Physics, P.O. Box 419, Arkansas State University, Arkansas 72407. <strong>HIGH DENSITY BEHAVIOUR OF NUCLEAR SYMMETRY ENERGY AND HIGH ENERGY HEAVY-ION COLLISIONS</strong></td>
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<td>3:45</td>
<td>Bao-An Li, A. T. Sustich, M.A. Tilley and Bin Zhang, Department of Chemistry and Physics, P.O. Box 419, Arkansas State University, Arkansas 72407. <strong>PROBING THE ISOSPIN-DEPENDENCE OF MECHANICAL AND CHEMICAL INSTABILITIES IN NEUTRON-RICH MATTER</strong></td>
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<td>4:00</td>
<td>Rhonda Gregory and Tommy Nix, Harding University, HU Box 12369, Searcy, AR 72149. <strong>A DIFFERENTIAL CALORIMETRIC STUDY OF LYSOZYME</strong></td>
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**POSTER PRESENTATIONS**

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<td>3:45</td>
<td>Bin Zhang$^1$, C. M. Ko$^2$, Bao-An Li$^1$, Zi-Wei Lin$^2$, Subrata Pal$^3$, $^1$Department of Chemistry and Physics, Arkansas State University, P.O. Box 419, State University, Arkansas 72467; $^2$Cyclotron Institute and Department of Physics, Texas A&amp;M University, Mail Stop 3366, College Station, Texas 77843. <strong>DYNAMICAL $\chi^2$ PRODUCTION IN RELATIVISTIC NUCLEAR COLLISIONS</strong></td>
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<td>4:00</td>
<td>B. J. Bailey, Harding University, HU Box 12364, Searcy, AR 72149. <strong>THE QUANTUM MECHANICS OF THE ABSORPTION SPECTROSCOPY OF RUBIDIUM ISOTOPES USING INFRARED RADIATION FROM A DIODE LASER</strong></td>
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AMORPHOUS SILICON USING OPTICAL AND ELECTRON MICROSCOPY

John E. Urbanik and Thomas E. Nupp, Biology Department, Arkansas Tech University, Russellville, AR 72801. POPULATION STATUS OF INTERIOR LEAST TERNs OF THE ARKANSAS RIVER, ARKANSAS

Casey Milford and Brandon Willis, University of Central Arkansas, UCA Math Department, Conway, Arkansas 72035. EXACT SOLUTIONS TO APPROXIMATE EQUATIONS

Mary F. Kinney and Stephen C. Grace, Department of Biology, University of Little Rock, Little Rock, AR 72204. EFFECTS OF LIGHT INTENSITY ON PHENOLIC ANTIOXIDANT PRODUCTION IN TOMATO

Mary F. Kinney and Stephen C. Grace, Department of Biology, University of Little Rock, Little Rock, AR 72204. SEASONAL CHANGES IN POLYPHENOLS IN ECHINACEA ANGUSTIFOLIA

Jasa Holt, Arkansas State University, Dept. of Biological Sciences, Jonesboro, AR 72407. TRILLIUM VIRIDE IN THE STATE OF ARKANSAS

Matthew D. Lewis, Chris Kellner, Biology Department, Arkansas Tech University, Russellville, AR 72801; Steven Felker, James C. Bednax, Department of Biological Sciences, Arkansas State University, State University, AR 72467. SURVIVAL AND HABITAT USE OF PEN-REARED NORTHERN BOBWHITE AT CAMP ROBINSON WILDLIFE DEMONSTRATION AREA, ARKANSAS


Wendi J. W. Williams, Earth Science, University of Arkansas at Little Rock, 2801 S. University Ave., Little Rock, AR 72204. QUATERNARY MAAR VOLCANISM IN THE SOUTHERN RIO GRANDE RIFT, NEW MEXICO

Felton, William Joseph and Owens, Don R., Department of Earth Sciences, and Al-Shukri, Haydar, Department of Applied Science, University of Arkansas at Little Rock, Arkansas 72204-1008. MAGNETIC SURVEY OF THE OPELLO BRECCIA

Susan F. Baker, Rose McConnell, and Walter Godwin, School of Mathematical and Natural Sciences, University of Arkansas at Monticello, Monticello, AR 71656. CO-POLYMERS OF FURAN WITH PYRROLE OR THIOEPHENE: A SYNTHETIC STUDY

Amy Stefan, Crystal Newton, Nikki Herring, Rose McConnell, and Walter Godwin, School of Mathematical and Natural Sciences, University of Arkansas at Monticello, Monticello, AR 71656. PREPARATION OF NEW CATHESPIN D INHIBITORS

E. C. Gordon, T.C. Keading, L. R. Oliver, and T. A. Castille, Northeast Research and Extension Center, Keiser, AR 72351; University of Arkansas, Fayetteville, AR 72701, and RiceTec, Jonesboro, AR 72467. EFFECT OF TILLAGE AND HERBICIDE TREATMENTS ON REDVINE (BRUNNICHIA OVATA) SUBTERRANEAN MORPHOLOGY

Beatrice Kiranga, Chris M. Harrison, Lize Wilcox, Malay K. Mazumder, and David A. Lindquist. THE REACTION PRODUCTS OF DIETHYLLALUMINUM AMIDE WITH ACETONE AND SUBSEQUENT HYDROLYSIS TO FORM ALUMINA

David W. Clark and Robert S. Sikes, Department of Biology, University of Arkansas at Little Rock, Little Rock, AR 72204. FORAGING ACTIVITY AND ENERGY PROCUREMENT UNDER THE THREAT OF PREDATION

Stephany C. White, Carrie D. Day, David W. Clark, and Robert S. Sikes, Little Rock Zoo, 1 Jonesboro Dr., Little Rock, AR 72205. CHANGES IN ASSIMILATION EFFICIENCIES AS A FUNCTION OF DIET IN CAPTIVE OTTERS

Rajesh Sharma, David Caldwell, David A. Lindquist, Malay K. Mazumder, Department of Applied Science and Department of Chemistry, University of Arkansas at Little Rock, Little Rock, AR 72204. HIGH TEMPERATURE OXYGEN ION TRANSPORT USING PEROVSKITE-PHASE CERAMICS MEMBRANES

Greg Giuffria and K. C. Larson, Department of Biology, University of Central Arkansas, Conway, AR 72035. A COMPARISON OF FISH COMMUNITIES BETWEEN THE BUFFALO NATIONAL RIVER AND CROOKED CREEK USING AN INDEX OF BIOTIC INTEGRITY

Lee A. Elizondo, Department of Microelectronics-Photonics, University of Arkansas, Fayetteville, 72701; Hameed Naseem, Department of Electrical Engineering, University of Arkansas, Fayetteville, 72701. THE ROLE OF HYDROGEN IN ALUMINUM INDUCED CRYSTALLIZATION OF HYDROGENATED AMORPHOUS SILICON

ORAL PRESENTATIONS

Saturday, April 6, 2002
Invertebrate Zoology
Location: Room 233

Time
Topic
Location

8:00
Michael D. Warriner, Arkansas Natural Heritage Commission, 1500 Tower Building, Suite 323 Center Street, Little Rock, AR 72201; T. Evan Nebeker and Steven A. Tucker, Department of Entomology and Plant Pathology, Mississippi State University, Mississippi State, MS 35762. INSECT DIVERSITY IN AN EASTERN COTTONWOOD (POPULUS DELTOIDES) PLANTATION AND ADJACENT BOTTOMLAND HARDWOOD FOREST IN SOUTHEASTERN ARKANSAS

8:15
Chris T. McAllister, Rowland M. Shelley, and James T. McAllister, III, Department of Biology, Texas A&M University-Texarkana, Texarkana, TX 75505; Research Laboratory, North Carolina State Museum of Natural Sciences, Raleigh, NC 27607; and W. T. White High School, 1244 Forest Lane, Dallas, TX 75228. SOME MILLIPEDES (ARTHROPODA: DIPLOPODA) OF WESTERN AND CENTRAL ARKANSAS AND SOUTHEASTERN OKLAHOMA

8:30
David R. Lyon and Matthew D. Moran, Department of Biology, Hendrix College, Conway, AR 72032. PATTERNS OF ARTHROPODS IN HABITING EPIPHYTES IN A...
Arkansas Academy of Science

TEMPERATE DECIDUOUS FOREST

8:45
George L. Harp, Dept. of Biological Sci., Arkansas State Univ., State University, AR 72467. NEW DRAGONFLY RECORDS FOR NICARAGUA

9:00
Chris S. Harris, Chris T. McAllister, Rowland M. Shelley, and James T. McAllister, III, Department of Biology, Texas A&M University-Texarkana, Texarkana, TX 75905; Research Laboratory, North Carolina State Museum of Natural Sciences, Raleigh, NC 27607; and W. T. High School, 1244 Forest Lane, Dallas, TX 75228. MILLIPEDS (ARTHROPODA: DIPTEROPHOPODA) OF SEVEN COUNTIES OF THE WEST GULF COASTAL PLAIN OF ARKANSAS

9:15
Gerald F. Walah, 9 Yocum Road, Rogers, AR 72756; Brian F. Coles, 4202 Scottie Smith Drive, Jefferson, AR 72079. POLYGYRID LAND SNAILS (GASTROPODA, POLYGYRIDAE) OF ARKANSAS

9:30
Gregory K. Eads, Arkansas Post National Memorial, Gillett, AR 72055; Philip A. Tappe and Lynne C. Thompson, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. TACK SEASONALITY AND ABUNDANCE AT ARKANSAS POST NATIONAL MEMORIAL

9:45
Alexander J. D., Murray J. A., Department of Biology, University of Central Arkansas, Conway, AR 72035. MECHANICS OF TURNING WHILE CRAWLING IN THE MARINE SLUG TRITONIA DIOMEDA

10:00
Rondo R., Murray J. A., Department of Biology, University of Central Arkansas, Conway, AR 72035. ROLE OF A SINGLE NEURON IN TURNING WHILE CRAWLING IN THE MARINE SLUG TRITONIA DIOMEDA

10:15
Larry R. Hilburn and Lynita M. Cooksey, Department of Biological Sciences, Arkansas State University, P.O. Box 599, State University, AR 72467. GENETIC VARIABILITY IN ANOPHELES QUADRIMACULATUS SAY POPULATIONS FROM EASTERN ARKANSAS

Terrestrial Ecology
Location: Room 354

Time Topic
8:00 Jeremy L. Jackson, Shane Prescott, and J. D. Wilhide, Department of Biological Sciences, Arkansas State University, Jonesboro, AR 72401. PRELIMINARY EFFECTS OF WILDLIFE STAND IMPROVEMENTS AND LOW INTENSITY PRESCRIBED BURNS ON BAT POPULATIONS ON THE BUFFALO RANGER DISTRICT, OZARK NATIONAL FOREST, AR

8:15 James R. Samples, J. D. Wilhide, and Roger Buchanan, Arkansas State University, Department of Biological Sciences, Jonesboro, AR 72467. PRELIMINARY BAT SURVEY OF FORT CHAFFEE MTC

8:30 Pradeepa Rangarajan, Ali U. Shaikh, Gary A. Heidt, and David Clark, Department of Chemistry, and Department of Biology, University of Arkansas at Little Rock, Little Rock, AR 72204. DETERMINATION OF BILE ACID PROFILES IN SCAT SAMPLES OF WILD ANIMALS BY GAS CHROMATOGRAPHY - MASS SPECTROMETRY

9:45 Matthew J. Butler and Phillip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. UNDERSTORY HABITAT CHARACTERISTICS OF INDUSTRIAL FOREST STANDS USED BY FORAGING RED-COCKADED WOODPECKERS IN SOUTHERN ARKANSAS AND NORTHERN LOUISIANA

9:00 Matthew J. Butler and Phillip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. NEW DRAGONFLY RECORDS FOR NICARAGUA

9:15 Gerald F. Walah, 9 Yocum Road, Rogers, AR 72756; Brian F. Coles, 4202 Scottie Smith Drive, Jefferson, AR 72079. POLYGYRID LAND SNAILS (GASTROPODA, POLYGYRIDAE) OF ARKANSAS

9:30 Gregory K. Eads, Arkansas Post National Memorial, Gillett, AR 72055; Philip A. Tappe and Lynne C. Thompson, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. TACK SEASONALITY AND ABUNDANCE AT ARKANSAS POST NATIONAL MEMORIAL

9:45 Alexander J. D., Murray J. A., Department of Biology, University of Central Arkansas, Conway, AR 72035. MECHANICS OF TURNING WHILE CRAWLING IN THE MARINE SLUG TRITONIA DIOMEDA

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10:15 Larry R. Hilburn and Lynita M. Cooksey, Department of Biological Sciences, Arkansas State University, P.O. Box 599, State University, AR 72467. GENETIC VARIABILITY IN ANOPHELES QUADRIMACULATUS SAY POPULATIONS FROM EASTERN ARKANSAS

Vertebrate Zoology
Location: Room 262

Time Topic
8:00 Stanley E. Trauth, John C. Harshbarger, and Patrick Daniel, Department of Biological Sciences, Arkansas State University, P.O. Box 509, State University, Arkansas 72467. USE OF MINIATURE PLANTATIONS TO EXAMINE ACCELERATED STAND DEVELOPMENT IN Loblolly PINE PLANTATIONS: FIRST YEAR RESULTS

8:45 Matthew J. Butler and Phillip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. UNDERSTORY HABITAT CHARACTERISTICS OF INDUSTRIAL FOREST STANDS USED BY FORAGING RED-COCKADED WOODPECKERS IN SOUTHERN ARKANSAS AND NORTHERN LOUISIANA

9:45 Alexander J. D., Murray J. A., Department of Biology, University of Central Arkansas, Conway, AR 72035. MECHANICS OF TURNING WHILE CRAWLING IN THE MARINE SLUG TRITONIA DIOMEDA

10:00 Rondo R., Murray J. A., Department of Biology, University of Central Arkansas, Conway, AR 72035. ROLE OF A SINGLE NEURON IN TURNING WHILE CRAWLING IN THE MARINE SLUG TRITONIA DIOMEDA

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Vertebrate Zoology
Location: Room 262

Time Topic
8:00 Stanley E. Trauth, John C. Harshbarger, and Patrick Daniel, Department of Biological Sciences, Arkansas State University, P.O. Box 509, State University, Arkansas 72467. USE OF MINIATURE PLANTATIONS TO EXAMINE ACCELERATED STAND DEVELOPMENT IN Loblolly PINE PLANTATIONS: FIRST YEAR RESULTS
Secretary’s Report

DARTER ESTIMATES

8:15
Reon Tummison, Tommy Finley, Tobin Fulmer, and David Saugery, Department of Biology, Henderson State University, Arkadelphia, AR 71999 and U.S. Forest Service, Jessettville, AR 71949. BATS OF THE JESSIEVILLE RANGER DISTRICT, OUACHITA NATIONAL FOREST

8:30
Kelly S. Richey, David W. Allard and Chris T. McAllister, Department of Biology, Texas A&M University-Texarkana, Texarkana, TX 75505. A PRELIMINARY STUDY ON DISTRIBUTION OF FROGS AND TOADS (AMPHIBIA: ANURA) IN THE ARK-LA-TEX

8:45
Amanda C. Crnkovic; Museum of Life Sciences, Louisiana State University in Shreveport, One University Place, Shreveport, LA 71115-2399. THE DISCOVERY OF THE NORTHERN LONG-EARED MYOTIS, MYOTIS SEPTENTRIONALIS (CHIROPTERA: VESPERTILIONIDAE), IN LOUISIANA

9:00
Malcolm L. McCallum1, Robert G. Neal2 (vneal@cox-internet.com), and Stanley E. Trauthb (strauth@astate.edu), 1Environmental Sciences Ph.D. Program, Arkansas State University, P.O. Box 847, State University, AR 72467. 2Department of Biological Sciences, Arkansas State University, P.O. Box 309, State University, AR 72467. TAIL-COILING IN RINGNECK SNAKES: FLASH DISPLAY OR DECOY?

9:15
Mark F. Roth and Philip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. CHARACTERISTICS OF AMERICAN ALLIGATOR HABITAT AT ARKANSAS POST NATIONAL MEMORIAL

9:30
Christopher L. Watt, Mark F. Roth, and Philip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. AMERICAN ALLIGATOR DISTRIBUTION IN ARKANSAS

9:45
Mark F. Roth and Philip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. AMERICAN ALLIGATOR DISTRIBUTION IN ARKANSAS

10:00
Matthew J. Butler and Philip A. Tappe, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. RED-COCKADED WOODPECKER FORAGING HABITAT REQUIREMENTS ON INDUSTRIAL FORESTS IN SOUTHERN ARKANSAS AND NORTHERN LOUISIANA

10:15

Botany & Plant Biology

Time
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Topic
Staci Thomas, Texas A&M, Texarkana, 2600 N. Robison Rd., Texarkana, TX 75501. PURIFICATION OF POREWEED ANTIVIRAL PROTEIN COMPLEX
Don C. Bragg, USDA Forest Service, Southern Research Station, P.O. Box 3516 UAM, Monticello, AR 71656. CHECKLIST OF MAJOR PLANT SPECIES IN ARKANSAS NOTED BY GENERAL LAND OFFICE SURVEYORS
Jason A. Haley, Henderson State University, 1100 Henderson St., Arkadelphia, AR 71923; and Daniel L. Marsh, Greenwood, AR 72936. A DISTINCTIVE LEAFY LIVERWORT IN THE ARKANSAS OUACHITAS
Phillip A. Tappe and Christopher L. Watt, School of Forest Resources and Arkansas Forest Resources Center, University of Arkansas, Monticello, AR 71656. Gregory K. Eads, Arkansas Post National Memorial, Gillett, AR 72055. A VEGETATION INVENTORY OF ARKANSAS POST NATIONAL MEMORIAL
George P. Johnson, Biological Sciences, Arkansas Tech University, Russellville, AR 72801. ARKANSAS’ ORCHIDS: FREQUENCY AND DISTRIBUTION
Katherine C. Larson, Department of Biology, University of Central Arkansas, Conway, AR 72035; klarson@mail.uca.edu. CONTRASTING MOBILITY OF NATIVE AND EXOTIC HONEYSUCKLE VINES IN ARKANSAS
Alison Boyer, Department of Biology, Hendrix College, Conway, AR 72092. THE ABILITY OF SOIL FUNGI TO DEGRADE Glyphosate (RoundUp®)
Jessie K. Fly and Joyce M. Hardin, Hendrix College, 1600 Washington Avenue, Conway, Arkansas 72032. THE EFFECTS OF TREE SPECIES AND TREE AGE ON EPiphyte community STRUCTURE IN A TEMPERATE DECIDUOUS FOREST
Donald E. Culwell, Department of Biology, University of Central Arkansas, Conway, AR 72035. PILLWORT, An Elusive, But Thriving, Graminoid Fern
Michael P. Popp, University of Arkansas, Dept. of Ag. Econ. and Agribusiness, 217 Agriculture Building, Fayetteville, AR 72701; Terry C. Keisling, University of Arkansas HC 69, Box 51, Rover, AR 72860; Lanny O. Ashlock, University of Arkansas, 2301 S. University Ave., P.O. Box 391, Little Rock, AR 72203; Larry C. Purell, University of Arkansas, 276 Alltheimer Drive, Fayetteville, AR 72701; Paul A. Counce, University of Arkansas, RREC, 2900 Hwy. 130E, Stuttgart, AR 72160; David C. Amim Jr., Noble Foundation, Oklahorna; Patrick M. Manning, University of Arkansas, Dept. of Ag. Econ. and Agribusiness, 217 Agriculture Building, Fayetteville AR 72701; Eddie Gordon, University of Arkansas, NREC, Keiser, AR 72351. INNOVATIVE PRODUCTION METHODS ON WET CLAY SOILS FOR RICE AND SOYBEAN

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### Inorganic Chemistry

**Location:** Room 229

<table>
<thead>
<tr>
<th>Time</th>
<th>Topic</th>
<th>Authors</th>
</tr>
</thead>
<tbody>
<tr>
<td>8:15</td>
<td><strong>The Effect of the Native Oxide Layer on Photovoltaic Cells</strong></td>
<td>Richard Tanner, Lee Ketchum, and Anil Baral, Optoelectronic Materials Research Laboratory, College of Engineering, University of Arkansas, Fayetteville, AR 72701. Chastain, A. B. Wright, Department of Applied Science, University of Arkansas at Little Rock, AR 72204. Low boiling point solutions of metal salts for low temperature deposition of molybdenum and tungsten oxide films by spray pyrolysis.</td>
</tr>
<tr>
<td>8:30</td>
<td><strong>Electrodeposition of Chromium from Mixed Aqueous/Organic Chromium (III) Baths</strong></td>
<td>Anil Baral, Richard Tanner, Randy Stidham, Lee Ketchum, and Gustavo Rehder, Environmental Sciences and Engineering Programs, Arkansas State University, P.O. Box 1740, State University, AR 72467. Electrodeposition of chromium from mixed aqueous/organic chromium (III) baths.</td>
</tr>
<tr>
<td>8:45</td>
<td><strong>Aluminum Induced Lateral Crystallization of Amorphous Silicon</strong></td>
<td>Lee Ketchum, Dr. Robert D. Engelken, Richard Tanner, Anil Baral, Gustavo Rehder, Randy Stidham, Barrett Brown, and Chad Chastain, Optoelectronic Materials Research Laboratory, Department of Engineering, University of Arkansas, Fayetteville, AR 72701. Aluminum induced lateral crystallization of amorphous silicon.</td>
</tr>
<tr>
<td>9:00</td>
<td><strong>Optimizing Thermal Vacuum Evaporation of Thin Indium Sulfide Films for Use as Photoconductive and Photovoltaic Cells on Printed Circuit Board and Indium Tin Oxide-Coated Glass Substrates</strong></td>
<td>Randy Stidham, Dr. Robert Engelken, Gustavo Rehder, Richard Tanner, Lee Ketchum, and Anil Baral, Optoelectronic Materials Research Laboratory, Department of Engineering, Arkansas State University, P.O. Box 1740, State University (Jonesboro), AR 72467. Optimizing thermal vacuum evaporation of thin indium sulfide films for use as photoconductive and photovoltaic cells on printed circuit board and indium tin oxide-coated glass substrates.</td>
</tr>
<tr>
<td>9:45</td>
<td><strong>The Effect of the Native Oxide Layer on Metal Induced Crystallization</strong></td>
<td>Marwan Barghouti and Hameed Naseem, Dept. of Electrical Engineering, University of Arkansas, Fayetteville, AR 72701. The effect of the native oxide layer on metal induced crystallization.</td>
</tr>
<tr>
<td>9:45</td>
<td><strong>Chlorine Doped Cadmium Sulfide Thin Films for Solar Cell Application</strong></td>
<td>Maruf Hossain, Dr. Hameed A. Naseem, Dr. W. D. Brown, Dept. of Electrical Engineering, University of Arkansas, Fayetteville, AR 72701. Chlorine doped cadmium sulfide thin films for solar cell application.</td>
</tr>
</tbody>
</table>
S. University Avenue, Little Rock, Arkansas 72204. TRIBOCHARGING OF JSC MARS-1 SIMULANT DUST

10:00 A. S. Biris, C. U. Yurteri, M. K. Mazumder, R. A. Sims, P. H. Williams; University of Arkansas at Little Rock Applied Science Dept. ETAS 501, 2801 South University Ave., Little Rock, AR 72204. REDUCTION OF DENDRITE FORMATIONS TO IMPROVE THE APPEARANCE OF THE POWDER CURED FILMS FOR AUTOMOTIVE INDUSTRY


10:30 S. De, M. Pritchett, A. Rego, M. K. Mazumder, C. U. Yurteri, and R. A. Sims, Department of Applied Science, University of Arkansas at Little Rock, 2801 S. University Avenue, Little Rock, Arkansas 72204. ELECTROSTATIC MICROENCAPSULATION OF COMPOSITE PARTICULATE MATERIALS FOR MANUFACTURING AND ENVIRONMENTAL APPLICATIONS
Solid Phase Extraction of Pesticides with Determination by Gas Chromatography

Anwar A. Bhuiyan*  
Department of Physical Science  
Arkansas Tech University  
Russellville, AR 72801

Harry O. Brotherton  
Chemistry Department  
University of Louisiana at Monroe  
Monroe, LA 71209

*Corresponding Author

Abstract

A simple, rapid, and effective method for the extraction of fifteen organochlorine and organophosphorus pesticides based on the use of solid phase Bond Elut C-18 cartridges was studied as an alternative method to those based on extraction with organic solvents. Solid phase extraction is an attractive chromatographic sample preparation technology that reduces analysis time, costs, labor, and solvent consumption relative to traditional liquid/liquid extraction methods. The sample recoveries with the use of solid phase extractions were excellent for most pesticides. Analyte concentration by a factor as great as 1000-fold was achieved readily. The adsorbed pesticides were eluted from the solid phase by an organic solvent. The influence of the elution solvent was studied. The best recoveries were obtained using methanol. The detection of the pesticides was made using OV-17 megabore capillary gas chromatography (GC) with electron capture detection. Pesticide extraction efficiencies using C-18 cartridges ranged from 64-100%, with the exception of mirex which was 56% at 0.2 μg/L spiking levels. Recovery precision studies demonstrate that relative standard deviations range from 1 to 9%. The compounds were identified by comparing the retention time with that of a standard under the same GC conditions, and quantitation was accomplished by comparing the peak areas.

Introduction

The pesticides have conferred tremendous benefits on mankind both by controlling the arthropod vectors of serious human disease and by greatly increasing yields of many crops. There have been many reports of residues of persistent pesticides in air, rainwater, dust, rivers, the sea, and in the bodies of aquatic and terrestrial invertebrates (Edwards, 1973; Lincer, 1973; Duke, 1977). Those pesticides that are very persistent present a potential hazard to our environment. A large volume of work has been done on monitoring pesticides in the environment (Johnson and Ball, 1992). Pesticides will continue to be used in the production of food and fiber. Drastic reductions of pesticide usage would increase production costs and lower the quality of agricultural products.

Sample preparation strategies, while often excluded from method objectives, may be of equal or greater importance than other factors in improving the productivity of analytical methods. Sample preparation in modern instrumental analysis is often required for two reasons: clean up and concentration. The sample matrix frequently interferes with measurement. In many instances, the analyte concentration falls below the sensitivity range of the analytical method chosen. A faster, simpler, convenient, and efficient sample preparation method is a very important factor in improving the productivity of analytical methods. Solid phase extraction may be used in a variety of disciplines to provide faster and more efficient sample preparation. In addition to its broad capabilities, solid phase extraction has the advantages of being faster, safer, and more economical than many traditional sample preparation techniques. Reduced sample handling and transfer and the elimination of emulsions contribute to more reproducible results. Solid phase extraction is an emerging chromatographic sample preparation technology that reduces organic solvent consumption relative to traditional alternatives. It was reported that the recoveries with the use of solid phase extraction were excellent for most of the pesticides (Bolygo and Atreyia, 1991; Molto et al., 1990; Marvin et al., 1990; Brooks et al., 1990; Manes et al., 1990; Weigel et al., 2001; Sasano et al., 2000; Vandecasteele et al., 2000).

The purpose of this study is to develop simple, rapid, reliable, inexpensive procedures for the extraction and determination of different types of pesticides in water. Traditionally, liquid/liquid extraction has been used for the extraction of pesticides. This is very time consuming and involves costly high purity halogenated solvents. Also, halogenated solvents used in the procedure need to be disposed of in an environmentally acceptable manner. These extraction and concentration procedures make pesticides determination a time consuming and laborious analytical process with a large consumption of organic solvents. Any methods that can result in shorter analytical procedures and less use of organic solvents would be less
Solid Phase Extraction of Pesticides with Determination by Gas Chromatography

expensive and more environmentally desirable. A simple, rapid, and effective method for the extraction of organochlorine pesticides based on the use of Bond Elut C-18 cartridges was studied as an alternative method to those based on extraction with organic solvents. The recoveries with use of cartridges were excellent for most pesticides. Analyte concentration by a factor as great as 1000-fold was achieved readily. The adsorbed pesticides were eluted from the solid phase by an organic solvent. The best recoveries were obtained using methanol. The detection of the pesticides was made using OV-17 megabore capillary gas chromatography with electron capture detection. Isolation of the pesticides peaks from each other on the gas chromatograms was very satisfactory with the use of the OV-17 column. The compounds were identified by comparing the retention time with those of standards under the same GC conditions, and quantitation was accomplished by comparing the peak areas.

Materials and Methods

Reagents.--The following pesticide reference standards were obtained from Alltech Associates, Inc., Deerfield, IL: aldrin, dieldrin, endrin, HCB, heptachlor, heptachlor epoxide, and methoxychlor. Analytical standards of the pesticides endosulfan-1, endosulfan sulfate and mirex were obtained from Supelco, Inc., Bellefonte, PA. Metolachlor and trifluralin were obtained from AccuStandard, New Haven, CT 06511. Methyl parathion and metribuzin were obtained from Ultra Scientific, North Kingstown, RI 02852. All of the analytical standards were greater than 96% pure and EPA approved. Pesticide grade hexane, acetonitrile, methylene chloride, methanol, and ethyl acetate were obtained from Fisher Scientific, Fair Lawn, NJ. Redistilled industrial grade acetone and deionized water were used to clean all glassware and equipment.

Equipment.--The extraction of pesticides from the water samples was carried out using Bond Elut C-18 micropillars (0.5 mL volume tubes containing 50 mg of C-18 octadecyl sorbent (Varian, Walnut Creek, CA)). The samples were eluted under vacuum. A Hewlett-Packard 5880A Gas Chromatograph equipped with an electron capture detector was used to analyze the samples. The analytical column used was an OV-17 fused silica megabore (0.53 mm i.d.) column. The samples were injected using a 10-μL Hamilton syringe. The data were collected and processed using a Hewlett-Packard 5880A series GC terminal.

Stock Solutions.--Standard solutions of 20 μg/L were prepared for each of the 11 different organochlorine pesticides. These solutions were prepared in iso-octane and methanol. Further serial dilutions from the original solutions were made using methanol. The working standards were 0.2 μg/L for 11 organochlorine pesticides. Organophosphorus pesticide standards were prepared at 250 ppm in methanol. Further serial dilutions from the original solutions were made using methanol. The working standards were 250 μg/L with the exception of metolachlor which was 2.5 mg/L. One liter samples of distilled water were spiked with 1 mL of each of the standards to determine recoveries.

Extraction.--The extractions were carried out using a VAC-ELUT solid phase extraction system. Bond Elut C-18 columns (6 mL volume tubes containing 500 mg of C-18 octadecyl sorbent) were inserted into luer fittings, and the unused spaces were capped with plugs. A vacuum was applied and the sample eluents were collected in 10 mL volumetric flasks that were held under the columns in a stainless steel removable rack. All 15 standards were spiked into 1 L deionized water, each in duplicate, and then extracted through the C-18 cartridge to determine recoveries. One set of water samples was extracted directly while internal standards were added to a second set to monitor extraction efficiency. To determine the proper elution solvent, each of five duplicate spiked solutions was extracted with one of five different solvents. The C-18 cartridge was conditioned with methanol (10 mL) followed by 10 mL of deionized water. The column was not allowed to dry before the sample was added to the column. The water sample, 1 L, was slowly passed through the column using the vacuum. At no time from activation until the end of the retention were the columns allowed to go dry. After the sample had passed through, the vacuum was left on for 3 min to dry the column. The adsorbed pesticides were then eluted under vacuum with methanol (10 mL) into a volumetric flask. The extracted samples were stored in a freezer in small sample vials until GC analysis.

Water Sample Collection.--Thirty water samples were collected from different locations of Ouachita Parish from January to August. Water samples were taken from the top ten inches near the surface and placed in acetone rinsed wide-mouth quart jars fitted with aluminum foil under the lids. All samples were collected in duplicate. The sample were analysed for 11 organochlorine pesticides and 4 additional pesticides. The samples were extracted immediately after collection and stored in a freezer until analyzed.

GC Analysis.--Samples of 3 μL were injected in the splitless mode at 225°C. The instrument used for analysis was a Hewlett-Packard 5880A Gas Chromatograph equipped with a Ni-63 electron capture detector. The column used was an OV-17 megabore column. Operating parameters were as follows:

- Carrier gas = Nitrogen
- Oven Temperature = 180°C
- Injector Temperature = 225°C
- Detector Temperature = 320°C
The concentrations of the pesticides in the samples were determined by comparing their peak area with those of pesticide standards of known concentration. Corrections were made for percent recovery, which varied from sample to sample. The pesticides in the samples were identified by retention time.

**Results and Discussion**

Water samples were spiked at the 0.2 μg/L level with 11 organochlorine pesticides and at the 0.25 mg/L level with additional pesticides. Metolachlor was spiked at 2.5 mg/L level. Figures 1 and 2 show the chromatograms of the analysis of the pesticides after extraction from 1 L of water using SPE columns. The chromatograms were obtained using electron capture detection and contained no interfering peaks. Table I gives the average recoveries from six analyses of duplicate samples using SPE columns containing 500 mg of C₁₈ sorbent with 10 mL of acetonitrile, methylene chloride, ethyl acetate, n-hexane, or methanol as

![Chromatogram of 11 Chlorinated Pesticides](image)

**Fig. 1. Chromatogram of 11 Chlorinated Pesticides.** Column: OV-17 Megabore Column; Column Temperature: 180°C; Electron Capture Detector; 3 μL Sample. See text for experimental details.
eluents for pesticides from water spiked at the 0.2 µg/L level. The variation in recovery efficiency, as well as the low recovery of mirex, can be attributed to the diversity, in terms of polarity and volatility, of the compounds studied. The highest recoveries were obtained using methanol. Other solvents may have greater eluting power in reversed-phase chromatography but many are not water miscible. Acetonitrile & tetrahydrofuran are 100% miscible with water, are more non-polar than MeOH and have higher vapor pressure so they evaporate easily. Ethyl acetate may be a good solvent (due to high polarity) for the desorption of relatively polar compounds from the octadecylsilica.

Fig. 2. Chromatogram of 4 Additional Pesticides. Column: OV-17 Megabore Column; Column Temperature: 180 °C; Electron Capture Detector; 3 µL Sample. See text for experimental details.
Table 1. Recovery (%) of Pesticides from Water (Spiked at 0.2 µg/L) Using C-18 Bonded Silica and Different Eluents.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Acetonitrile</th>
<th>Methylene Chloride</th>
<th>Ethyl Acetate</th>
<th>n-Hexane</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methoxychlor</td>
<td>71</td>
<td>86</td>
<td>87</td>
<td>67</td>
<td>89</td>
</tr>
<tr>
<td>Endosulfan sulfate</td>
<td>87</td>
<td>85</td>
<td>72</td>
<td>60</td>
<td>87</td>
</tr>
<tr>
<td>Mirex</td>
<td>40</td>
<td>68</td>
<td>21</td>
<td>20</td>
<td>56</td>
</tr>
<tr>
<td>Endrin</td>
<td>60</td>
<td>77</td>
<td>57</td>
<td>55</td>
<td>73</td>
</tr>
<tr>
<td>Endosulfan-1</td>
<td>54</td>
<td>92</td>
<td>51</td>
<td>49</td>
<td>92</td>
</tr>
</tbody>
</table>

n = number of measurements = 6

while light petroleum (less polar) may be suitable for less polar materials. Methanol was chosen as the elution solvent, as it eluted most of the analytes from the cartridge and is water miscible. For a wide variety of compounds, successive elution with different solvents is also possible.

Table 2 shows the average recoveries and mean standard deviations obtained using C-18 solid phase extraction and elution with methanol (10 mL). These recoveries are in good agreement with those obtained using the methods reported by Rodier (1984) and the organization APHA (American Public Health Association, 1985). A comparison is shown in Table 3. The recovery efficiency used in evaluating the overall performance of the Bond Elut C-18 cartridge was tested by analyzing spiked distilled water samples. The recoveries reported were means of six duplicate analyses. The pesticide concentrations in water were maintained constant for all organochlorine pesticides (0.2 µg/L). All of the pesticides were extracted by C-18 with 64-100% recovery, except mirex, which was 56%. The standard deviations ranged between 1 and 9%. From the results, solid phase extraction results in higher recoveries than liquid-liquid partitioning for a large range of compounds. The molecular structure and the size of the apolar part of the molecule play an important role in the retention mechanism on reversed phase silica.

Solid-phase extraction occurs in four steps: column preparation or prewash, sample loading (retention), column post-wash, and sample desorption (elution). Recovery, calculated by comparing the original concentration to the concentration remaining after solid phase extraction, is a function of both retention efficiency and elution efficiency: recovery = retention efficiency x elution efficiency. For example, if retention is 50% efficient but elution is 100% efficient, the recovery measured is 50%. It is impossible to know whether reduced recovery was produced due to inefficient retention or inefficient elution or by a combination of both. For this reason retention and elution in solid phase extraction are said to be interdependent, and optimizing one without controlling the other can lead to a vicious circle of experiments.

Several factors such as sample pH, sample volume, sorbent mass, sample concentration, nature of the compound, and the attached functional groups may influence the retention. Once the conditions for elution are optimized, other factors can be optimized by trial and error. The residual water on the C-18 column is a disadvantage because it lowers the volatility of the eluted solvent under the nitrogen stream. Considerable care was taken in sample handling and analysis. Glassware was thoroughly cleaned with detergent, tap water, and deionized water as the usual laboratory routine required. Additionally, a methanol rinse was used to remove plasticizers or phthalates that might produce interfering or spurious peaks that may be incorrectly interpreted as a pesticide. The polypropylene extraction columns produced no interfering peaks. The extraction of pesticides from water with the octadecyl bonded porous silica requires less solvent than conventional solvent extraction methods.

Thirty samples of water from Ouachita Parish were analyzed for the following pesticides: aldrin, dieldrin, endrin, endosulfan 1, endosulfan sulfate, HCB, heptachlor, heptachlor epoxide, methoxychlor, mirex, lindane, metolachlor, metribuzin, methyl parathion, and trifluralin. The results are shown in Table 4. Twelve samples did not contain any detectable amount of pesticides. Eighteen of the samples contained detectable amounts of one or more
Solid Phase Extraction of Pesticides with Determination by Gas Chromatography

Table 2. Selected Pesticides, Their Retention Times (RT), Average Recoveries, and Sample Concentration.

<table>
<thead>
<tr>
<th>Compound</th>
<th>RT (min)</th>
<th>Recovery (%)</th>
<th>Conc. (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>4.26</td>
<td>79±5</td>
<td>0.2</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>8.61</td>
<td>91±6</td>
<td>0.2</td>
</tr>
<tr>
<td>Endrin</td>
<td>9.40</td>
<td>73±2</td>
<td>0.2</td>
</tr>
<tr>
<td>Endosulfan-1</td>
<td>6.74</td>
<td>91±9</td>
<td>0.2</td>
</tr>
<tr>
<td>Endosulfan sulfate</td>
<td>13.76</td>
<td>87±3</td>
<td>0.2</td>
</tr>
<tr>
<td>HCB</td>
<td>2.16</td>
<td>73±2</td>
<td>0.2</td>
</tr>
<tr>
<td>Heptachlor</td>
<td>3.83</td>
<td>73±1</td>
<td>0.2</td>
</tr>
<tr>
<td>Heptachlor epoxide</td>
<td>5.38</td>
<td>89±3</td>
<td>0.2</td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>24.12</td>
<td>89±3</td>
<td>0.2</td>
</tr>
<tr>
<td>Mirex</td>
<td>25.77</td>
<td>56±3</td>
<td>0.2</td>
</tr>
<tr>
<td>Lindane</td>
<td>2.23</td>
<td>76±2</td>
<td>0.2</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>4.38</td>
<td>100±3</td>
<td>2500.0</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>3.17</td>
<td>64±3</td>
<td>250.0</td>
</tr>
<tr>
<td>Methyl parathion</td>
<td>3.21</td>
<td>95±3</td>
<td>250.0</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>1.64</td>
<td>94±6</td>
<td>250.0</td>
</tr>
</tbody>
</table>

\( n = \) number of measurements = 6

Conclusions

The bonded-phase extraction columns are an alternative to the acid/base/neutral liquid-liquid extractions for isolation of pesticides from water for GC analysis. The bonded-phase method efficiently recovers a variety of organic pesticides having different functional groups in one step. In addition to involving less labor, time, glassware, and solvent, the method minimizes sample exposure of the technician to possibly hazardous samples. This aspect is
Table 3. Comparison Between the Reported Pesticide Recoveries from Water Using APHA, Rodier Methods, and This Study Using C-18 Bonded Porous Silica for Solid Phase Extraction.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>APHA</th>
<th>% Reported Recovery</th>
<th>Rodier</th>
<th>This study (using C-18)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>75 ± 6</td>
<td>70 ± 11</td>
<td>91 ± 6</td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td>90 ± 8</td>
<td>97 ± 7</td>
<td>91 ± 6</td>
<td></td>
</tr>
<tr>
<td>Endrin</td>
<td>106 ± 8</td>
<td>107 ± 9</td>
<td>91 ± 2</td>
<td></td>
</tr>
<tr>
<td>Endosulfan-1</td>
<td>92 ± 8</td>
<td>96 ± 6</td>
<td>73 ± 2</td>
<td></td>
</tr>
<tr>
<td>Endosulfan sulfate</td>
<td>94 ± 9</td>
<td>105 ± 6</td>
<td>87 ± 3</td>
<td></td>
</tr>
<tr>
<td>HCB</td>
<td>73 ± 11</td>
<td>86 ± 9</td>
<td>73 ± 2</td>
<td></td>
</tr>
<tr>
<td>Heptachlor</td>
<td>83 ± 10</td>
<td>73 ± 9</td>
<td>73 ± 1</td>
<td></td>
</tr>
<tr>
<td>Heptachlor epoxide</td>
<td>103 ± 8</td>
<td>90 ± 7</td>
<td>89 ± 3</td>
<td></td>
</tr>
<tr>
<td>Methoxychlor</td>
<td>90 ± 8</td>
<td>97 ± 10</td>
<td>89 ± 3</td>
<td></td>
</tr>
<tr>
<td>Mirex</td>
<td>90 ± 8</td>
<td>91 ± 8</td>
<td>56 ± 3</td>
<td></td>
</tr>
<tr>
<td>Lindane</td>
<td>108 ± 12</td>
<td>81 ± 10</td>
<td>76 ± 2</td>
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n = number of measurements = 6

important in view of the increasing demand for analysis of hazardous-waste-related samples. Using this method in the field would avoid the shipment, and possible breakage in transit, of potentially hazardous water samples. New sample preparation methods such as these complement the advanced analytical instrumentation already available today. The use of solid-phase extraction provides a rapid, efficient, and reproducible method for the simultaneous determination of pesticides in ground water and obviates the use of long sequential solvent extraction methods. The one step extraction and concentration procedure minimizes residue losses and the possible addition of contaminants. The simplicity of the analysis is complemented by good gas chromatographic results and a preconcentrated extract. The extract can then be analyzed immediately by mass spectrometry without the need for further removal of solvent.
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Reduction of Dendrite Formations to Improve the Appearance of the Powder Cured Films for Automotive Industry

A. Biris, C. U. Yurteri, M. K. Mazumder*, R. A. Sims, and P. H. Williams

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Abstract

The appearance of powder-coated films is dependent upon powder chemistry and spraying parameters. One of the most important physical factors controlling the powder film appearance is the microdeposition of the powder particles on the grounded substrate. During the electrostatic deposition of powder, the formation of dendrites and agglomerates was observed; these formations have an adverse effect on the final film appearance and their elimination may result in smoother and glossier films. Dendrites are generated due to bipolar charging and inter-particulate electrostatic attractive forces. The corona charging technique is mostly used in industrial powder coating applications. At low corona voltages (-40 to -60 kV) a greater degree of bipolar charging was observed compared to that at higher voltages (-80 to -100 kV). At the higher voltages, the increase in number of ions produces a more unipolar charging and higher charge-to-mass ratios. As the film builds up, the powder transfer efficiency decreases as the repulsion forces between oncoming charged particles and the already deposited powder layer increase. By controlling the deposition patterns, the final film appearance can be improved. The smoothest films were obtained when the voltage was ramped from -60 to -100 kV. Another method to reduce dendrite formations was to deposit powder particles charged unipolarly by first separating them from the oppositely charged ones by using a charge separator.

Introduction

Generally, the appearance of the powder-coated films is dependent upon the chemical properties of the powders but also on the deposition parameters. The charging technique is important because it is responsible for the charge level of the powder particles and also for how bipolar the particles will charge. The particle size distribution of the powder, the charge level, charging mechanism, electrical and geometrical aspects, and flow characteristics dictate the microdeposition of particles on the grounded workpiece (Adamiak, 2001).

Highly packed powder layers generate very smooth films with very glossy finishes, a conclusion previously shown by Mazumder et al. (2001). Unipolarly charged particles result in more uniform powder deposition on the substrate because of the mutual repulsion, while bipolar charged particles agglomerate and form dendrites due to particle-particle attraction. Agglomeration and dendrite formation is of concern to the automotive industry because dendrite formations degrade the appearance of cured films by generating an orange peel-like surface texture (King and Thomas, 1978).

This paper investigates the generation of dendrite formations and agglomerations on the surface of powder layers due to the bipolar charging characteristic of the powder. Some alternative charging and powder layer deposition methods are also presented. The effect of the dendrite formations on the film appearance is analyzed based on the charging and the deposition processes involved.

Materials and Methods

The experiments were performed in a computer controlled powder-coating booth, where the humidity and the temperature were monitored. The corona gun used for these studies is commercially available from Nordson Inc. The substrates were 10 cm x 30 cm electro-coated steel panels. The steel panels were electro-coated with a 25 μm thick polymer layer in order to emulate the automotive coatings for the clear coat particle deposition.

The powder that was studied is an acrylic with a narrow particle size distribution (PSD) of \(d_{10}=12, d_{50}=28, \text{and} d_{90}=40 \mu m\) and is typically used for the top clear coat in the automotive industry. The powder was fluidized for 15 minutes before each experiment and was transported pneumatically to the corona gun through a 1.0 cm diameter rubber hose. A charge separator was employed to measure the mass ratios of the positively and negatively charged or uncharged powder. It consists of two copper plates arranged in a V-shape. A voltage is applied between the two plates. The charged particles are fed from the top, and they move downward between the two plates. The positively charged particles move toward the negative plate, while the negative particles move toward the positive plate. Assuming that the...
air flow has low turbulence within the separator and with particle Reynolds numbers less than one (Stokes regime), the horizontal and vertical settling velocities of charged particles can be calculated by equating the weight and the electrostatic force of the particles with their drag forces.

The powder mass flow rate was 80 g/min, which allowed the deposition of 60 μm thick films in about 13 seconds. Once the powder was deposited, the panels were cured at 145°C for 30 minutes. The appearance of the coatings was tested with a BYK Gardner wave scan plus instrument which gives short (SW) and long (LW) wave and subnote parameters. SW and LW (on a scale from 0 to 99.9) are a measure of the film roughness and waviness, whereas subnote (on a scale from 0 to 600) is a parameter that integrates the first two and characterizes the overall appearance of the coating. The smaller these values, the better the film appearance. For each experiment 10 panels were sprayed, and the values reported are the averages.

**Results and Discussion**

Corona is the most common charging method used in the powder coating applications mainly because of the stable and consistent level of charge the particles acquire during this process. Once the particles become charged, they move to the grounded deposition system, driven by the electrostatic attraction forces.

In addition to the electrostatic forces, the aerodynamic forces produced by the air flow through the system are of great importance. These two forces cause the particles to move to the substrate. As the powder layer builds on the substrate, the electrostatic driving force is reduced because of the charge of this layer.

Besides the negative ions and electrons in a corona discharge there are also some positive ions generated. This along with tribocharging produces some positively charged particles. For higher negative corona voltages, the number of negative ions is much higher leading to a greater bulk charge-to-mass ratio (Q/M). The deposition pattern is highly dependent upon the charge polarity of the particles. If the powder is charged unipolarly, the particles with opposite polarity will tend to attract each other and form dendrites. Due to the fact that the deposition process is very dynamic, the airflow at the surface of the powder layer will probably retard the dendrites growth by causing them to break and to generate agglomerates.

As the voltage of the corona gun is increased, the number of negative ions increases with direct effect on the powder Q/M (Sims et al., 2001). The values of Q/M and ion current measured at -60, -80, and -100 kV corona voltages are plotted in Fig. 1.

The powder charge level variation with the corona voltage shows that the powder charge is higher as a larger number of ions are generated. The ratio of positive and negative particles was found for powder charged at different voltages, from -40 to -60, -80, and -100 kV. To determine the extent of unipolar charging, powder collected on electro-coated panels (2.5-3 grams) was blown off inside a charge separator, and the masses of powder deposited on the positive and negative plates and neutral are plotted in Fig. 2. The large amount of positively charged particles at -40 kV is believed to be caused by tribocharging during transport through the hoses. The low negative ion current generated by the corona gun at -40 kV is not enough to completely overcome this positive charge. Even at high voltages, some of the particles remain positively charged.

Some typical dendrite formations are shown in Fig. 3. Although it is very difficult to quantify the number of dendrite formations, an indirect measurement of the powder film layer unevenness can be made by analyzing the long wave and the short wave parameters of the cured films.

Figure 4 shows that the film roughness decreased as the...
voltage was increased. The best films were obtained at -100 kV. By increasing the negative voltage, the packing density increased with positive effects on the film appearance. As previously shown (Biris et al., 2001; Banerjee and Mazumder, 1996), the powder layer became coarser with time because only the large particles will have a high enough charge (charge of a particle is dependent on the diameter square) and momentum to overcome the electrostatic repulsion forces generated by the powder layer. In order to force the fine particles to deposit and to generate smoother films, the electric field between the corona gun and the plate was gradually increased. A 60 μm thick film was produced by spraying for a time period of 14 seconds while gradually increasing the voltage from -60 to -100 kV. The resulting field and the increased charge level of the fine particles allowed them to deposit on top of the powder layer. In another trial, the voltage was ramped in two steps. For the first half spraying period (7 seconds), the voltage was kept at -60 kV, and for the last 7 seconds, the voltage was rapidly increased to -100 kV. Fig. 4 shows that the films with the smoothest surface and best appearance were those generated while the voltage was uniformly ramped.

From Figs. 1, 2, and 4, it can be concluded that the appearance of the cured films increases as the particles are more unipolarly charged, which can be related to a smaller number of dendrite formations. A method of depositing unipolarly charged particles is by using the charge separator. The powder was charged at -100 kV inside the booth and blown off inside the charge separator. The surfaces of the powder layers deposited on the electro-coated panels, which were attached to the separator's plates, were very smooth, and no dendrite formations or agglomerates were observed. Results mean that by depositing unipolarly charged particles the roughness of the powder layers decreased. The experiments were carried out at three different voltages between the separator’s plates (10, 15 and 20 kV) and the appearance results are shown in Fig. 5. It can be observed that by increasing the voltage difference between the plates from 10 to 15 kV the films generated were smoother and had a higher packing density. A correlation between high packing densities and the improvement in the film surface smoothness has previously been shown. However, if the packing density of the particles is too high, the electric field within the powder layer can exceed the breakdown value, and back corona can occur. When the potential difference between the separator’s plates was increased to 20 kV, the appearance of the generated films was not as good as in the previous cases. Back corona onset and craters and pinhole-like formations were visible on the powder surface.

Conclusions

The microdeposition of powder particles on different substrates is an important factor for the appearance-related properties. At low voltages (-40 and -60 kV) a higher bipolar charging of the powder particles was observed. After the voltage was increased to -80 or -100 kV, most of the particles were unipolarly charged. The level of charge acquired by the powder particles was directly related to the free ion current generated by the corona discharge, therefore the voltage directly influences the microdeposition of particles and indirectly affects the appearance of the cured powder films. The particles were shown to form dendrites and agglomerates when charged at low voltage because the powder is bipolarly charged.

By ramping the corona voltage from -60 to -100 kV during the powder layer formation, the appearance of powder cured films was improved compared with the static spraying conditions (-60kV). When ramping the voltage, the fine particles acquire a high enough charge to deposit on the powder layer and to overcome the repulsion forces due to the already deposited particles.

The best appearance was obtained when the powder deposition was performed in a charge separator. The separator ensured the deposition of unipolar charged powder and reduced the dendrite formation process. It is believed that unipolarly charged particles, due to the mutual electrostatic repulsion, deposit uniformly over the surface of the grounded panels. The voltage between the charge separator’s plates that generated the smoothest powder films was found to be around 15 kV. Further increasing the voltage between the plates resulted in back corona onset that destroyed the fine film appearance.

Acknowledgements.—This work was partially supported by a EPA/EPSCOR grant.

Literature Cited


Reduction of Dendrite Formations to Improve the Appearance of the Powder Cured Films for Automotive Industry

Fig. 3. Typical dendrite formations.

Fig. 4. The appearance data for films generated at different voltages.

Fig. 5. The appearance data for films generated using the charge separator at different voltages.
Checklist of Major Plant Species in Ashley County, Arkansas Noted by General Land Office Surveyors

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Abstract

The original General Land Office (GLO) survey notes for the Ashley County, Arkansas, area were examined to determine the plant taxa mentioned during the 1818 to 1855 surveys. While some challenges in identifying species were encountered, at least 39 families and approximately 100 species were identified with reasonable certainty. Most references were for trees used to witness corners or lines. Prominent arboreal genera recorded in these early survey records included Quercus, Pinus, Carya, Liquidambar, Nyssa, Ulmus, Acer, Fraxinus, and Taxodium. A number of shrubs, vines, graminoids, and herbaceous species were also reported, including notable genera like Vaccinium, Lindera, Crataegus, Myrica, Rubus, Smilax, Vitis, Arundinaria, and Bidens. Even though very few GLO surveyors had formal training in plant identification, their familiarity with local and regional floras (undoubtedly supplemented by their field crew’s knowledge) contributed to the relative accuracy of the effort. Taxonomic discrepancies (e.g., shifting species names, delineation of new taxa since the survey was completed, obscure common names) have obscured a number of identifications in this study. Nevertheless, the GLO records are a valuable and systematic (statewide) source of information from a period of time that predates most formal botanical investigations.

Introduction

In the developing United States, land surveying was considered a highly prestigious profession. This recognition partially arose from an appreciation of the value of surveyed lands and respect for those applying this trade in a virtually unknown wilderness. Many of America’s “founding fathers” like George Washington and Thomas Jefferson spent at least some time surveying and contributed to our knowledge of early American landscapes (Spurr, 1951; Baldwin, 1958). However, the colonial metes and bounds system used by these early pioneers was considered inadequate for the rapidly expanding nation, prompting the government to initiate a rectangular approach to land surveying under the supervision of the General Land Office (GLO) (Stewart, 1935; Clement, 1958).

The Arkansas GLO survey started at the confluence of the Arkansas and Mississippi rivers in October of 1815 with the establishment of the 5th Principal Meridian (Nelson, 1997). The state’s Base Line (beginning at the confluence of the St. Francis and Mississippi rivers) intersected this meridian in a remote swamp in east-central Arkansas. Subdivision of Arkansas into townships and ranges started in lands already ceded by Native Americans. Statewide, the GLO survey took over three decades of continuous effort, with initial efforts completed by 1849 and some lines resurveyed as late as 1855 (Stewart, 1935).

One of the most important contributions of this surveying system was the codification of the practice, including how to mark corners and what observations to make along a traverse (Stewart, 1935). Government surveyors recorded information in their notebooks on estimated site productivity, witness trees, general forest types, major understory attributes, and other interesting features related to vegetation patterns. Prior to original land surveys, only a handful of observers had recorded any kind of environmental information in Arkansas, and these tended to be concentrated along major transportation corridors (e.g., navigable rivers or one of the few roads available) or near areas of geological interest (e.g., hot springs, mountains, mines).

While there are some issues with how the GLO survey notes can and should be used, they represent an invaluable asset if properly interpreted (Bourdo, 1956; Noss, 1985; Whitney and DeCant, 2001). Ecological researchers have long used GLO survey notes to help determine presettlement vegetation patterns in many areas of the country (e.g., Lutz, 1930; Howell and Kucera, 1956; Jones and Patton, 1966; Delcourt, 1976; Foti and Glenn, 1991; Nelson, 1997; Black and Abrams, 2001). A recent review of the published botanical resources of Arkansas (Peck and Peck, 1988) specifically listed the GLO records as a potential source of information. The study presented here provides a species checklist of the trees, shrubs, vines, and other...
notable plants of the Ashley County, Arkansas, area as interpreted from the GLO survey notes.

**Materials and Methods**

During the original period of surveying in Ashley County (1818 to 1855), at least 16 different GLO deputy surveyors officially traversed the region. Their transcribed notes were digitally scanned by the Arkansas Commissioner of State Lands and made publicly available on compact disks in 2000. These searchable GLO notes have been separated into boundaries, interiors, and plat maps. Boundary and interior records were identified for the townships in and bordering Ashley County. From these records, relevant information was transferred onto specially designed data sheets for later analysis. This paper reports only species identification, but most witness trees also had diameter and geographic coordinate data.

How taxonomically capable were the GLO survey crews? The seasonality of the Ashley County surveys (usually from November to April) placed their efforts during the dormant season, when many species are not readily identifiable. Presumably, early surveyors and their crews were familiar with local vegetation, even during leaf-off (especially for those species of commercial, nutritional, or medicinal value). No assessment of the accuracy of their taxonomic skills is possible, but for this effort, surveyor identifications were assumed to be reasonable. Surveyor plant names were then associated with potential scientific names, which led to another challenge: though many labels have transcended the years since being applied by the GLO surveyors, a handful of species did not have any common name equivalents in contemporary taxonomic references (e.g., Smith, 1988; Moore, 1999). Local botanical experts were consulted to determine the best interpretations of these taxa. In addition, some common names were liberally applied to species, thus necessitating an inclusive classification. Pin oak, for example, is the currently accepted common name for *Quercus palustris* Muenchh., but historically "pin" referred to the long, narrow leaves found on willow oak (*Q. phellos* L.), water oak (*Q. nigra* L.), and laurel oak (*Q. laurifolia* Michx.). Nuttall oak (*Q. texana* Buckley) was also listed as a pin oak candidate because it is locally common and closely resembles *Q. palustris* (which is not native to southeastern Arkansas).

**Results and Discussion**

At least 39 different families and over 100 species, subspecies, and varieties were recorded by the GLO surveyors in the Ashley County area (Table 1). Surveyors were not charged with detailed botanical assessment; rather, their instructions were specifically designed to expedite settlement by using the most convenient and healthy trees available (Stewart, 1935; Clement, 1958). This almost certainly resulted in the underestimation of the taxa present in the study region. Some species may also have been missed because of vagueness in common name application, thus subsuming additional candidates under the preferred options. For example, Table 1 lists *Crataegus berberifolia* T. & G. and *Crataegus crus-galli* L. as the most likely local candidates for "red haw," but Bush (1926) listed 23 different *Crataegus* as "red haw." Even though many of these *Crataegus* are not found in southeastern Arkansas, any inadvertent lumping would reduce the number of species recognized. Tree species were most commonly noted because they were used to mark important survey locations, but some shrubs, woody vines, grasses, and other herbaceous taxa were also identified. Unfortunately, a large portion of the study area's presettlement richness is incorporated under the unclassifiable labels in Table 2.

Nevertheless, study of the GLO notes will considerably supplement the available knowledge of vegetation patterns for an area that received very little botanical exploration prior to the 20th Century. Early expeditions by trained botanists in Arkansas (e.g., Owen, 1860; Harvey, 1881; Warder, 1881; Call, 1887-9; Bush, 1897) were often limited in extent and lacking detail, making it very difficult to recognize historical patterns. Contrast this to the GLO survey effort, which traversed the entire state on at least a one mile by one mile grid. The recently improved accessibility of Arkansas GLO notes, coupled with expanding interest in restoration ecology and ecosystem science, bodes well for research into historical vegetation patterns. For instance, it should be possible to construct maps of presettlement species distributions using the GLO records in much the same way as herbarium archives are used to develop a plant distribution atlas.

**Conclusions**

While most understory (and some canopy tree) species were not mentioned in the GLO notes, scores of arboreal and understory species were labeled with reasonable certainty in the Ashley County area. The systematic design of the GLO resulted in a spatially thorough canvassing of the landscapes, even if the taxonomic resolution was not as precise as if conducted by a trained academic botanist. Notwithstanding the uncertainty of some identifications, the original General Land Office surveys have considerable potential for the investigation of Arkansas flora years before most other efforts.

**Acknowledgments.—**I would like to recognize the deputy surveyors whose efforts in the early 19th Century made this work possible: Caleb Langtree, Nicholas Rightor, Abraham Bowman, Charles Moore, Lauretine Eiler, Jonas...

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Smith, Alexander Brookie, James Danley, Thomas Mathers, Charles Drury, Thomas Rector, John Wilson, Will Rector, John Clark, J.M. Conway, and J.E. Graham, as well as their often anonymous field crews. Eric Sundell (University of Arkansas at Monticello), Tom Foti (Arkansas Natural Heritage Commission), Carl Amason (Calion, Arkansas), and several anonymous referees graciously provided insights and reviews of this manuscript.

Literature Cited


# Checklist of Major Plant Species in Ashley County, Arkansas Noted by General Land Office Surveyors

Table 1. Surveyors' identifications, probable modern interpretations, and stratum of the plants identified to species in the Ashley County, Arkansas, area GLO survey records.

<table>
<thead>
<tr>
<th>FAMILY</th>
<th>Surveyor identification</th>
<th>Probable species</th>
<th>Strata code</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ACERACEAE</strong></td>
<td>box elder</td>
<td><em>Acer negundo</em> L.</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>maple</td>
<td><em>Acer rubrum</em> L. var. <em>rubrum</em></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Acer saccharinum</em> L.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Acer saccharum</em> Marsh. var. <em>floridanum</em> (Chapm.) Small &amp; Heller</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sugar maple</td>
<td><em>Acer saccharum</em> Marsh. var. <em>floridanum</em> (Chapm.) Small &amp; Heller</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>sugar</td>
<td><em>Acer saccharum</em> Marsh. var. <em>floridanum</em> (Chapm.) Small &amp; Heller</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Celtis laevigata</em> Willd. [ULMACEAE]</td>
<td></td>
</tr>
<tr>
<td><strong>ANACARDIACEAE</strong></td>
<td>sumac</td>
<td><em>Rhus glabra</em> L.</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>(flowertop sumac)</td>
<td><em>Rhus copallina</em> L.</td>
<td></td>
</tr>
<tr>
<td><strong>ANONACEAE</strong></td>
<td>pawpaw</td>
<td><em>Asimina triloba</em> (L.) Dunal</td>
<td>B</td>
</tr>
<tr>
<td><strong>AQUIFOLIACEAE</strong></td>
<td>holly</td>
<td><em>Ilex opaca</em> Ait.</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Ilex ambigua</em> (Michx.) Torr.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Ilex decidua</em> Walt. var. <em>decidua</em></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Ilex verticillata</em> (L.) Gray</td>
<td></td>
</tr>
<tr>
<td></td>
<td>black elder</td>
<td><em>Ilex decidua</em> Walt. var. <em>decidua</em></td>
<td>O</td>
</tr>
<tr>
<td><strong>ARALIACEAE</strong></td>
<td>prickle sumac</td>
<td><em>Aralia spinosa</em> L.</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Zanthoxylum clava-herculis</em> L. [RUTACEAE]</td>
<td></td>
</tr>
<tr>
<td><strong>ASTERACEAE</strong></td>
<td>Spanish needles</td>
<td><em>Bidens bipinnata</em> L. var. <em>bipinnata</em></td>
<td>U</td>
</tr>
<tr>
<td><strong>BETULACEAE</strong></td>
<td>alder</td>
<td><em>Alnus serrulata</em> (Ait.) Willd.</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>(swamp alder)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>water birch</td>
<td><em>Betula nigra</em> L.</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>(birch)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>water beech</td>
<td><em>Carpinus caroliniana</em> Walt.</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>hazel</td>
<td><em>Corylus americana</em> Walt.</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td></td>
<td><em>Hamamelis virginiana</em> L. [HAMAMELIDACEAE]</td>
<td></td>
</tr>
<tr>
<td>Plant Family</td>
<td>Scientific Name</td>
<td>List Position</td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------------------------------------------------------</td>
<td>---------------</td>
<td></td>
</tr>
<tr>
<td>horn beam</td>
<td><em>Carpinus caroliniana</em> Walt.</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>(horn beme)</td>
<td><em>Ostrya virginiana</em> (P. Mill.) K. Koch</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ironwood</td>
<td><em>Ostrya virginiana</em> (P. Mill.) K. Koch</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Carpinus caroliniana</em> Walt.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bignoniaceae</td>
<td><em>Catalpa bignonioides</em> Walt.</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>Catalpa</td>
<td><em>Catalpa speciosa</em> Warder</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bromeliaceae</td>
<td><em>Tillandsia usneoides</em> L.</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Spanish moss</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caprifoliaceae</td>
<td><em>Sambucus canadensis</em> L.</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>elder bushes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cornaceae</td>
<td><em>Cornus florida</em> L.</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>dogwood</td>
<td><em>Cornus foemina</em> P. Mill. <em>subsp. foemina</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>swamp dogwood</td>
<td><em>Cornus foemina</em> P. Mill. <em>subsp. foemina</em></td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Ebenaceae</td>
<td><em>Diospyros virginiana</em> L.</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>persimmon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ericaceae</td>
<td><em>Vaccinium arboreum</em> Marsh.</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>huckleberry</td>
<td><em>Vaccinium elliottii</em> Chapm.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(hackelberry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>whortleberry</td>
<td><em>Vaccinium stamineum</em> L.</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Vaccinium virgatum</em> Ait.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fabaceae</td>
<td><em>Gleditsia aquatica</em> Marsh.</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>locust</td>
<td><em>Gleditsia triacanthos</em> L.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Robinia pseudoacacia</em> L.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>honey locust</td>
<td><em>Gleditsia triacanthos</em> L.</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td></td>
<td><em>Gleditsia aquatica</em> Marsh.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pea vine</td>
<td><em>Galactia mohlenbrockii</em> Maxwell</td>
<td>U</td>
<td></td>
</tr>
<tr>
<td>Fagaceae</td>
<td><em>Castanea pumila</em> (L.) Mill. <em>var. pumila</em></td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>chinkapin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(multiple spellings)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>beech</td>
<td><em>Fagus grandifolia</em> Ehrh.</td>
<td>O</td>
<td></td>
</tr>
<tr>
<td>oak</td>
<td><em>Quercus</em> spp.</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>(many possible species)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>white oak</td>
<td><em>Quercus alba</em> L.</td>
<td>B</td>
<td></td>
</tr>
</tbody>
</table>

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## Checklist of Major Plant Species in Ashley County, Arkansas Noted by General Land Office Surveyors

<table>
<thead>
<tr>
<th>Species</th>
<th>Scientific Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>red oak</td>
<td><em>Quercus falcata</em> Michx.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus pagoda</em> Raf.</td>
</tr>
<tr>
<td>Spanish oak</td>
<td><em>Quercus falcata</em> Michx.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus pagoda</em> Raf.</td>
</tr>
<tr>
<td>overcup oak</td>
<td><em>Quercus lyrata</em> Walt.</td>
</tr>
<tr>
<td>black jack</td>
<td><em>Quercus marilandica</em> Muenchh.</td>
</tr>
<tr>
<td>swamp oak</td>
<td><em>Quercus michauxii</em> Nutt.</td>
</tr>
<tr>
<td>swamp white oak</td>
<td><em>Quercus michauxii</em> Nutt.</td>
</tr>
<tr>
<td>chinkpin oak</td>
<td><em>Quercus muehlenbergii</em> Engelm.</td>
</tr>
<tr>
<td>water oak</td>
<td><em>Quercus nigra</em> L.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus phellos</em> L.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus laurifolia</em> Michx.</td>
</tr>
<tr>
<td>pin oak</td>
<td><em>Quercus phellos</em> L.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus nigra</em> L.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus texana</em> Buckley</td>
</tr>
<tr>
<td></td>
<td><em>Quercus laurifolia</em> Michx.</td>
</tr>
<tr>
<td>willow oak</td>
<td><em>Quercus phellos</em> L.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus nigra</em> L.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus laurifolia</em> Michx.</td>
</tr>
<tr>
<td>post oak</td>
<td><em>Quercus stellata</em> Wang. var. <em>stellata</em></td>
</tr>
<tr>
<td></td>
<td><em>Quercus stellata</em> Wang. var. <em>paludosai</em> Sarg.</td>
</tr>
<tr>
<td>black oak</td>
<td><em>Quercus velutina</em> Lam.</td>
</tr>
<tr>
<td>(B. oak)</td>
<td><em>Quercus shumardii</em> Buckl.</td>
</tr>
<tr>
<td></td>
<td><em>Quercus pagoda</em> Raf.</td>
</tr>
<tr>
<td>sweetgum</td>
<td><em>Liquidambar styraciflua</em> L.</td>
</tr>
<tr>
<td>witch hazel</td>
<td><em>Hamamelis virginiana</em> L.</td>
</tr>
<tr>
<td>(witch hackle)</td>
<td></td>
</tr>
<tr>
<td>buckeye</td>
<td><em>Aesculus pavia</em> L.</td>
</tr>
<tr>
<td>hickory</td>
<td><em>Carya aquatica</em> (Michx. f.) Nutt.</td>
</tr>
<tr>
<td></td>
<td><em>Carya cordiformis</em> (Wang.) K. Koch</td>
</tr>
<tr>
<td></td>
<td><em>Carya glabra</em> (Mill.) Sweet var. glabra</td>
</tr>
<tr>
<td></td>
<td><em>Carya ovata</em> (P. Mill.) K. Koch</td>
</tr>
<tr>
<td></td>
<td><em>Carya texana</em> Buckl.</td>
</tr>
<tr>
<td></td>
<td><em>Carya tomentosa</em> (Poir.) Nutt.</td>
</tr>
</tbody>
</table>

### Hamamelidaceae

- sweetgum: *Liquidambar styraciflua* L.

### Hippocastanaceae

- buckeye: *Aesculus pavia* L.

### Juglandaceae

- hickory: *Carya aquatica* (Michx. f.) Nutt.
<table>
<thead>
<tr>
<th>Plant Family</th>
<th>Common Name</th>
<th>Scientific Name</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lauraceae</strong></td>
<td>spicewood</td>
<td><em>Lindera benzoin</em> (L.) Blume</td>
</tr>
<tr>
<td>LAURACEAE</td>
<td>(spice, spice bushes, swamp spice)</td>
<td></td>
</tr>
<tr>
<td>sassafras</td>
<td><em>Sassafras albidum</em> (Nutt.) Nees</td>
<td></td>
</tr>
<tr>
<td>LILIACEAE</td>
<td>greenbriar</td>
<td><em>Smilax spp.</em></td>
</tr>
<tr>
<td>LILIACEAE</td>
<td>(sawbriar)</td>
<td></td>
</tr>
<tr>
<td><strong>Magnoliaceae</strong></td>
<td>sweet bay</td>
<td><em>Magnolia virginiana</em> L.</td>
</tr>
<tr>
<td>MAGNOLIACEAE</td>
<td>(bay, bull bay)</td>
<td></td>
</tr>
<tr>
<td>poplar</td>
<td><em>Liriodendron tulipifera</em> L.</td>
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<tr>
<td><strong>Moraceae</strong></td>
<td>mulberry</td>
<td><em>Morus rubra</em> L.</td>
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<tr>
<td>MORACEAE</td>
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<td></td>
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<tr>
<td><strong>Myricaceae</strong></td>
<td>myrtle</td>
<td><em>Myrica cerifera</em> L.</td>
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<td></td>
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<tr>
<td><strong>Nyssaceae</strong></td>
<td>gum</td>
<td><em>Nyssa sylvatica</em> Marsh. var. <em>sylvatica</em></td>
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<tr>
<td>NYSSACEAE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>black gum</td>
<td><em>Nyssa sylvatica</em> Marsh. var. <em>sylvatica</em></td>
<td></td>
</tr>
<tr>
<td><strong>Nyssaceae</strong></td>
<td>tupelo gum (multiple spellings)</td>
<td><em>Nyssa aquatica</em> L.</td>
</tr>
<tr>
<td>NYSSACEAE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>black gum</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Oleaceae</strong></td>
<td>privet (red privet, white privet)</td>
<td><em>Forestiera acuminata</em> (Michx.) Poir.</td>
</tr>
</tbody>
</table>

Journal of the Arkansas Academy of Science, Vol. 56, 2002
<table>
<thead>
<tr>
<th>Plant Family</th>
<th>Common Name</th>
<th>Scientific Name</th>
<th>Surveyor Notation</th>
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<tbody>
<tr>
<td><strong>Ash</strong></td>
<td>ash</td>
<td><em>Fraxinus americana</em> L.</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>white ash</td>
<td><em>Fraxinus americana</em> L.</td>
<td>O</td>
</tr>
<tr>
<td><strong>Palmaceae</strong></td>
<td>palmetto</td>
<td><em>Sabal minor</em> (Jacq.) Pers.</td>
<td>U</td>
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<tr>
<td><strong>Pinaceae</strong></td>
<td>pine</td>
<td><em>Pinus echinata</em> Mill.</td>
<td>B</td>
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<tr>
<td></td>
<td>sycamore</td>
<td><em>Platanus occidentalis</em> L.</td>
<td>O</td>
</tr>
<tr>
<td><strong>Poaceae</strong></td>
<td>cane</td>
<td><em>Arundinaria gigantea</em> (Walt.) Muhl.</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>(large cane, small cane,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>switch cane, thin cane)</td>
<td></td>
<td></td>
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<tr>
<td><strong>Rhamnaceae</strong></td>
<td>supplejack</td>
<td><em>Berchemia scandens</em> (Hill) K. Koch</td>
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<td><em>Crataegus berberifolia</em> T. &amp; G.</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>haw</td>
<td><em>Crataegus crus-galli</em> L.</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>white thorn</td>
<td><em>Crataegus spp.</em></td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>(thorn)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>red root</td>
<td><em>Geum canadense</em> Jacq.</td>
<td>U</td>
</tr>
<tr>
<td></td>
<td>wild peach</td>
<td><em>Prunus persica</em> (L.) Batsch</td>
<td>B</td>
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<tr>
<td></td>
<td>black cherry</td>
<td><em>Prunus serotina</em> Ehrh.</td>
<td>O</td>
</tr>
<tr>
<td></td>
<td>plum</td>
<td><em>Prunus spp.</em></td>
<td>U</td>
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<tr>
<td></td>
<td>blackberry</td>
<td><em>Rubus spp.</em></td>
<td>U</td>
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<td><strong>Rubiaceae</strong></td>
<td>elbow wood</td>
<td><em>Cephalanthus occidentalis</em> L.</td>
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<td><em>Zanthoxylum clava-herculis</em> L.</td>
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<td></td>
<td><em>Aralia spinosa</em> L. [ARALIACEAE]</td>
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<td>Common Name</td>
<td>Scientific Name</td>
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<td>----------------------------------</td>
<td>---------</td>
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<td><strong>Salicaceae</strong></td>
<td>cottonwood</td>
<td><em>Populus deltoides</em> Marsh.</td>
<td><strong>O</strong></td>
</tr>
<tr>
<td></td>
<td>willow</td>
<td><em>Salix nigra</em> Marsh.</td>
<td><strong>O</strong></td>
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<td><strong>Symplocaceae</strong></td>
<td>laurel</td>
<td><em>Symlocos tinctoria</em> (L.) L’Her.</td>
<td><strong>B</strong></td>
</tr>
<tr>
<td><strong>Taxodiaceae</strong></td>
<td>cypress (cypress knees)</td>
<td><em>Taxodium distichum</em> (L.) Rich.</td>
<td><strong>B</strong></td>
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<tr>
<td><strong>Tiliaceae</strong></td>
<td>lynn</td>
<td><em>Tilia americana</em> L.</td>
<td><strong>B</strong></td>
</tr>
<tr>
<td><strong>Ulmaceae</strong></td>
<td>hackberry</td>
<td><em>Celtis laevigata</em> Willd.</td>
<td><strong>B</strong></td>
</tr>
<tr>
<td></td>
<td>swamp elm</td>
<td><em>Planera aquatica</em> (Walt.) Gmelin</td>
<td><strong>O</strong></td>
</tr>
<tr>
<td></td>
<td>water elm</td>
<td><em>Planera aquatica</em> (Walt.) Gmelin</td>
<td><strong>O</strong></td>
</tr>
<tr>
<td></td>
<td>elm</td>
<td><em>Ulmus alata</em> Michx.</td>
<td><strong>B</strong></td>
</tr>
<tr>
<td></td>
<td>sweet elm</td>
<td><em>Ulmus americana</em> L.</td>
<td><strong>O</strong></td>
</tr>
<tr>
<td></td>
<td>red elm</td>
<td><em>Ulmus rubra</em> Muhl.</td>
<td><strong>O</strong></td>
</tr>
<tr>
<td></td>
<td>slippery elm</td>
<td><em>Ulmus rubra</em> Muhl.</td>
<td><strong>O</strong></td>
</tr>
<tr>
<td><strong>Vitaceae</strong></td>
<td>grapevine</td>
<td><em>Vitis spp.</em></td>
<td><strong>U</strong></td>
</tr>
<tr>
<td></td>
<td>spice vine</td>
<td><em>Ampelopsis arborea</em> (L.) Koehne</td>
<td><strong>U</strong></td>
</tr>
</tbody>
</table>

*a* Sometimes the surveyors used multiple spellings for the same species—these names represent the most probable intended common names.

*b* Species nomenclature and interpretations from Smith (1988) and Moore (1999).

*c* Stratum codes (reported by GLO surveyors): **O** = overstory only; **U** = understory only; **B** = both.
Table 2. Unknown taxa with common names too vague to identify to family as provided by the original GLO surveys of the Ashley County area.

**Unknown understory taxa:**

<table>
<thead>
<tr>
<th>- weed</th>
<th>- grass</th>
<th>- fern</th>
</tr>
</thead>
<tbody>
<tr>
<td>- briars</td>
<td>- prairie grass</td>
<td>- moss</td>
</tr>
<tr>
<td>- bushes</td>
<td>- sedge grass (sidge)</td>
<td></td>
</tr>
<tr>
<td>- vines</td>
<td>- swamp grass</td>
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</tr>
</tbody>
</table>
Distribution of Clinostomum marginatum (Yellow Grub) Metacercaria in Smallmouth Bass Populations from Crooked Creek in North Central Arkansas

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Abstract

Four hundred thirty-three smallmouth bass (Micropterus dolomieui) were collected from ten sites on Crooked Creek in North Central Arkansas from just below the city of Harrison to the White River in the summers of 1988-90. Necropsy of these hosts for yellow grub (Clinostomum marginatum) metacercariae showed a range of mean abundance (average/fish) from 1.4 ± 1.9 (SD) at a far up stream site to 105 ± 368 at the White River juncture. An increasing mean abundance of C. marginatum was seen from the uppermost sites of the creek downstream to the White River. Relating stream mileage with mean abundance gave a correlation coefficient (r) of 0.78, with P = <0.01. Maximum abundance (maximum number of parasites in a single host from a site) ranged from 7 to 2500 and also showed a positive correlation with stream mileage (r = 0.77, P = <0.01). Prevalence (% fish infected) at the different sites ranged from 61 to 91% but showed no significant correlation with stream distance. The increasingly heavier infections seen in the downstream sites are not due to poor water quality but probably to the combination of the greater presence of the definitive host, the great blue heron, and large intermediate host (smallmouth) populations.

Introduction

Crooked Creek is located in the Ozark Plateau of North Central Arkansas. It begins above the city of Harrison and ends at the White River. It has a continuing series of riffles and pools, which makes it excellent habitat for smallmouth bass (Micropterus dolomieui). The stream dries up in the summer at Yellville, approximately 25 miles from the White River but emerges again just east of Highway 101, approximately 10 miles from the White River. Crooked Creek has an excellent smallmouth fishery, but the bass harbor some of the highest population densities reported for the metacercarial stage of Clinostomum marginatum, or yellow grub. This study was done to survey the distribution of the parasite population along the length of the stream in order to gain information regarding the ecology of the host-parasite relationship in a stream environment. Such information would be useful if control programs against yellow grub become feasible.

Clinostomum marginatum is a trematode that has a fish-eating bird as its definitive host and a snail and a fish as intermediate hosts (Olson, 1967). Fifty-six freshwater fish have been found to harbor the metacercarial form of this parasite (Hoffman, 1967). These larvae can be up to 0.5 cm in length and are called yellow grub because of their coloration. The presence of a large number of these worms in the flesh of the fish can make it undesirable as a food item. In Arkansas, yellow grubs are found in noticeable numbers in the tissues of stream bass, particularly the smallmouth (Micropterus dolomieui). Smallmouth previously taken from Crooked Creek have been shown to have high mean abundances (average number of parasites/fish) of 23 and 32.7 (Daly et al., 1987, Daly et al.1991) and the highest recorded abundances (number of parasites/individual fish) of 2500, 852, and 627 (Daly et al., 1991). During the course of an earlier study (Daly et al., 1987) it was noted that fish collected from upstream sites on the Creek were less infected than those collected from downstream sites. The aim of this study was to determine if a pattern of heavy infection exists from upstream to downstream sites.

Methods

Four hundred and thirty-three smallmouth bass (Micropterus dolomieui) were collected from ten sites on Crooked Creek in North Central Arkansas from below Harrison to the White River in the summers of 1988-90. The ten collection sites are as follows: Huzzah Creek (HU); Harmon 1, 2, and 3 (H1, H2, H3), which were 2 low water bridges on Crooked Creek Drive East and the main bridge on Harmon Road North; The city of Pyatt (P), at the juncture of Little Sugar Orchard Creek; Clear Creek (CC); Turkey (T), between Comal and Georges Creek; Georges Creek (G); The city of Yellville (Y), at Kelly's Slab; and the
Crooked Creek in North Central Arkansas

Fig. 1. Mean and maximum abundances of Clinostomum marginatum in smallmouth bass from ten sites on Crooked Creek. The light line is maximum abundance (heaviest infected fish) and solid line mean abundance (avg./fish). The maximum abundance of 2500 for the White River site is not included because it greatly exceeds the limits of the graph.

White River (WR). These sites were chosen for ease of access and well as their position on the stream. Bass hosts were all collected in Crooked Creek and none from the feeder streams. Mileage of each site, in respect to the White River as the terminus, can be found in Table 1. Mileage was determined by following the contours of Crooked Creek from maps in Streets and Trips 2001® from Microsoft and the Arkansas Atlas & Gazeteer. Mileage was determined by following the contours of the stream.

Bass were collected by rod and reel using live or artificial bait. Fish were placed on ice and later necropsied with all of the soft tissue of the host being examined. Metacercariae were removed to petri dishes with saline and counted. Parasite ecology terminology follows that of Bush et al. (1997) with maximum abundance meaning the most heavily infected individual host; mean abundance is the average number of parasites/number of hosts examined, and prevalence is the percent of fish infected/number of hosts examined. The term site in this paper refers to the collection area rather than parasitized area of host. T Tests and regression analyses (for r and P values) were done using Microsoft Excel, 1997.

Results and Discussion

Abundance and mean abundance of Clinostomum marginatum metacercariae in smallmouth increased as downstream distance increased (Table 1, Fig. 1). Regression analysis of mean abundance and site position gave an r of 0.78 and P = 0.008 and for maximum abundance, r = 0.8 and P of 0.007. Prevalence ranged from 61 to 91% with an overall prevalence of 79% for all smallmouth bass in the
Prior to doing so, we report the prevalence and mean abundances for each parasite species. Variance in the means in Table 1 imply a negative binomial rather than a normal distribution of yellow grub populations. This is indicated by a large standard deviation relative to the mean and is produced by many hosts having few or no infection while some hosts have large numbers of parasites. This is the rule for most parasitic relationships (Esch et al., 1990). In order to statistically test if significant differences occur using parametric procedures, a log transformation was done on the individual data where $X = \log(N) + 1$ with zero infestations assigned a 0 value. With these transformations, whereby the variance became much less than the mean, the Student T Test showed that most heavily infested sites (WR, T, GC, CC) were significantly different from the least infested sites (HU, H1, and H2) with $P$ values of less than 0.001.

Heavy infections of yellow grub of 2500, 852, and 627 grubs/host were found at the furthest downstream site, the White River, but heavy individual infestations of 179 and 144 were found at other sites as well (Table 1). It was not unusual to find smallmouth bass with 25 or more worms downstream from Pyatt to the White River, but such hosts were rare from the upstream sites at Huzzah and Harmon. Prior to this study the heaviest infection was found from a member of the catfish family (*Ictalurus nebulosus*) in Pennsylvania with 500 yellow grubs (Torres and Price, 1971).

Heavy infection, similar but less than that in Crooked Creek, was found in largemouth, smallmouth and spotted bass from Southwest Missouri streams (Taber, 1972). The spotted bass (*Micropterus punctulatus*) had the heaviest infections; one fish had 230 metaceriae and the 25 fish examined averaged 32.76 metaceriae/fish. Of the 25 smallmouth bass examined the prevalence was 88 percent, but the mean abundance was only 7.7. Heavy infections have also been reported in yellow perch (*Perca flavescens*) from lakes in Minnesota with 325 and 199 maximum infections (Elliott and Russert, 1949). In contrast to these reports and the present study the heaviest maximum abundance from a Ouachita stream in Arkansas, the Caddo, was only 30 metaceriae from 66 hosts (Daly et al., 1999). Mean abundances from three sites on that river were only 4.2, 9.9, and 2.8, upstream to downstream respectively. Yellow grub infections have been reported in fish from various geographic locations, but the data from Crooked Creek and the Caddo are unique in showing the variation of parasitism along a single stream.

Largemouth bass (*Micropterus salmoides*) were also examined from Crooked Creek and found to be infected. However, Crooked Creek is primarily a smallmouth bass stream, and there were too few (and some not at all) largemouth bass from individual sites to properly assess the yellow grub population in these hosts. Data from these fish

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### Table 1. Population parameters of *Clinostomum marginatum* in smallmouth bass from Crooked Creek, Arkansas (N = host numbers, STD = standard deviation).

<table>
<thead>
<tr>
<th>Site</th>
<th>Mileage</th>
<th>N</th>
<th>Prevalence</th>
<th>Mean Abundance</th>
<th>STD</th>
<th>Maximum Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>HU</td>
<td>0</td>
<td>10</td>
<td>80</td>
<td>2.1</td>
<td>2.8</td>
<td>10</td>
</tr>
<tr>
<td>H1</td>
<td>5</td>
<td>38</td>
<td>61</td>
<td>1.4</td>
<td>1.9</td>
<td>7</td>
</tr>
<tr>
<td>H2</td>
<td>8</td>
<td>45</td>
<td>62</td>
<td>2.2</td>
<td>3.2</td>
<td>11</td>
</tr>
<tr>
<td>H3</td>
<td>10</td>
<td>37</td>
<td>84</td>
<td>5.4</td>
<td>10.9</td>
<td>64</td>
</tr>
<tr>
<td>P</td>
<td>12</td>
<td>27</td>
<td>72</td>
<td>14.3</td>
<td>17.5</td>
<td>57</td>
</tr>
<tr>
<td>CC</td>
<td>24</td>
<td>43</td>
<td>84</td>
<td>19.0</td>
<td>24.0</td>
<td>92</td>
</tr>
<tr>
<td>T</td>
<td>31</td>
<td>107</td>
<td>91</td>
<td>83.0</td>
<td>28.3</td>
<td>179</td>
</tr>
<tr>
<td>GC</td>
<td>34</td>
<td>31</td>
<td>84</td>
<td>22.5</td>
<td>32.5</td>
<td>144</td>
</tr>
<tr>
<td>Y</td>
<td>45</td>
<td>44</td>
<td>86</td>
<td>9.4</td>
<td>14.2</td>
<td>76</td>
</tr>
<tr>
<td>WR</td>
<td>71</td>
<td>51</td>
<td>70</td>
<td>10.5</td>
<td>368.0</td>
<td>2500</td>
</tr>
</tbody>
</table>

Study. Prevalence did not show a significant correlation with stream distance ($r = 0.096, P = 0.79$). Variance of the means in Table 1 imply a negative binomial rather than a normal distribution of yellow grub populations. This is indicated by a large standard deviation relative to the mean and is produced by many hosts having few or no infection while some hosts have large numbers of parasites. This is the rule for most parasitic relationships (Esch et al., 1990). In order to statistically test if significant differences occur using parametric procedures, a log transformation was done on the individual data where $X = \log(N) + 1$ with zero infestations assigned a 0 value. With these transformations, whereby the variance became much less than the mean, the Student T Test showed that most heavily infested sites (WR, T, GC, CC) were significantly different from the least infested sites (HU, H1, and H2) with $P$ values of less than 0.001.
were not included in the present study because it was felt that the ecological niche for largemouth bass is different enough from smallmouth bass for its exclusion. Also, combining data from all sites for largemouth bass might also be misleading considering the variation at different sites found with smallmouth bass from this stream.

No correlation was found between fish length and infection of yellow grubs at each site or in toto. Sizes of the fish collected were relatively similar at all sites. It was noted that numbers of fish were more abundant, based on collection time, downstream than upstream but the stream is also smaller at the upstream sites.

It is generally assumed that poor water quality in aquatic environments leads to increased incidence of parasitism due to stress on hosts. The converse is seen for Crooked Creek where the highest infections are found at the sites of the best water quality as determined by Drope (1997). Pollution would not seem to be a factor with yellow grub infection in Crooked Creek. Crofton (1971), in a classic paper, reworked earlier nonparametric data on infection of a microcrustacean, *Gammarus*, with an acanthocephalan worm. Parasitism significantly decreased as distance on the stream increased from drainage into the stream from a duck farm. Ducks are the definitive host for this parasite. This decrease was presumably due to a dilution of the infective stages being passed by the birds. Downstream rather than upstream conditions must be more favorable for maximum transmission of *C. marginatum* with the proper proportion of bass, snail, and especially, great blue heron populations needed for heavy infection. Indirect evidence for the role of great blue herons is the marked drop in yellow grub infection at the Yellville site (Table 1, Fig. 1). Human activity is greatest in this area and may deter herons from feeding there thus decreasing the amount of parasite eggs entering the water and therefore reducing infection of snail hosts.

The importance of heavy yellow grub infection in Crooked Creek is several fold. Yellow grub is becoming a problem for catfish farmers in Oklahoma, Arkansas, and Mississippi (Mitchell, personal comm.). Daly and Singleton (1994) found fifty-four catfish of similar size from a pond in Northwest Arkansas to have a prevalence of 100% and a mean abundance of 31.7, values greater than most of the sites on Crooked Creek. Fish infected with too many grubs are rejected at the processing plant. The presence of a wild fish population serving as a yellow grub reservoir for farm fish complicates the control of this parasite. It can also be argued that the catfish might be a reservoir for infection of stream bass.

A use for heavy yellow grub infections would be as a source for experimental studies on this worm itself, and this has been done (Daly et al., 1987). The complexities of the life cycle of this and other trematodes make it difficult and economically unfeasible to obtain these parasites by laboratory cultivation. Finally, the Arkansas Game and Fish Commission considers the smallmouth bass fishery in Crooked Creek an important asset to Arkansas outdoor recreation. It is not known if bass populations are adversely affected by the parasite, but it might be speculated that heavy worm burdens must have an adverse effect on the host’s survival and may play a role in limiting smallmouth bass populations in streams with heavy infections.

ACKNOWLEDGMENTS.—This study was supported in part by the Arkansas Game and Fish Commission, which also supplied the necessary collecting permits.

**Literature Cited**


Taber, C. A. 1972. The yellow grub in centarchids of Southwest Missouri streams. Prog. Fish-Cult. 34:119.

Electrostatic Microencapsulation of Composite Particulate Materials for Manufacturing and Environmental Applications

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University of Arkansas at Little Rock
2801 S. University Avenue, Little Rock, Arkansas 72204

*Corresponding Author

Abstract

Electrostatic microencapsulation is a dry coating process where two powders, one containing the fines and the other relatively larger particles, are separately dispersed in air and pre-charged with opposite polarity, using corona charging for electrostatic coagulation. These oppositely charged core and guest particles experience attractive electrostatic forces and generate composite particles. Preliminary experiments of electrostatic microencapsulation were performed using Anionic Exchange Resin (AG 1-X8) as the host particle and Red Toner (Omega 4000) as the guest particles. An electrostatic microencapsulation tower has been designed for generation of composite particles using particles of different particle size distribution.

Introduction

Microencapsulation of particles with different sizes and compositions is widely used in many industrial, pharmaceutical, agricultural, and consumer product applications. Examples include controlled-release drugs, sustained-release pesticides, slow-release fertilizers, and triggered-release cosmetics. In most cases, the outer shell protects the encapsulated ingredients until the material is needed. The release mechanisms include mechanical, thermal, chemical, dissolution, and other processes. Most of the products are made from liquid phase dispersion commonly termed wet particle coating. In some applications, it is not desirable to have a protective outer shell completely covering the core material. In those applications, the encapsulating material must be highly porous, but stable. The porosity of the outer shell allows the inner core material to come in contact with the surrounding fluid. The outer shell and the inner core materials have two different functions. A cluster of particles from two different materials, serving as a composite material, can also be used to perform different functions.

In many cases, the encapsulation of particles must be made using a dry process. Electrostatic microencapsulation is a dry process in which core particles can be coated with fine particles of different materials. The method employs a mixing process (Fig. 1) with an oppositely charged relatively large size particle (called the host) and a fine particle (called the guest). The host forms the core and is coated with the guests, which form the outer layer. The electrostatic microencapsulation provides dry dispersion of powder and avoids mechanical mixing of the particles and generates composite particles by polydisperse coagulation of the precharged host and guest particles. Research in the field of dry particle coating shows that simultaneous fluidization and mixing improve the efficiency of the coating (Pfeffer, 2001) in comparison to many other mechanical devices, such as Mechanofusion™ or Hybridizer™, which primarily work by the application of shear force on the host and guest particles to make them coalesce. The electrostatic microencapsulation technique demands an effective precharging of the host and guest particles. Corona charging is an effective precharging method, which combines both field and diffusion charging methods. A corona discharge is

![Diagram](Fig. 1. Schematic of electrostatic microencapsulation technique to generate composite.)
generated by dielectric breakdown of air or other gases due the to non-uniform electrostatic field generated between a needle and a grounded plate. The corona discharge generates electrons, which promote field and diffusion charging of particles present in the corona region. Corona charging also generates a stream of ions, called an “ion wind”, from the point to the grounded plane. The corona gun (Fig. 2) is an effective device to disperse particles and generate highly charged particles. Powder is fed through a vibrating feeder into a diffuser. A regulated airflow through the diffuser conveys powder through a region rich in ions from a corona electrode, which is maintained at a high voltage and generates highly charged particles. The interparticle attachment force that holds the host and the guest particles is a summation of the London-van der Waals force, the electrostatic force, and the liquid bridge force (Hinds, 1999a). The above forces are dependent upon several factors including material, shape, surface roughness, relative humidity, and temperature. The London-van der Waals forces, which are short-range forces, are effective when two particles are very close to each other. These forces arise due to the random motion of electrons on the surface of the particle forming dipoles, which in turn induce an opposite polarity on the surface of another particle in close proximity. The resultant adhesive force between the particle and a plane surface can be estimated by the following equation:

\[ F_{adh} = \frac{(AD)}{12X^2} \]  

(1)

where \( A \) is the Hamaker constant, which depends on the material involved and ranges from \( 6 \times 10^{-20} \) to \( 150 \times 10^{-20} \) J for common materials, \( D \) is the diameter of the particle, and \( X \) is the separation distance, that depends on the surface distance of opposite charges.

The capillary force between a surface and a particle is created by the surface tension of the liquid drawn into the capillary space at the point of contact. The force between a particle and a plane surface at relative humidities higher than 90% can be estimated from the following equation:

\[ F_{bridge} = 2\pi \gamma d \]  

(3)

where \( \gamma \) is the surface tension of the liquid, and \( d \) is the diameter of the particle. For low humidity, the liquid bridge force is dependent on the curvature of the asperities at the point of contact and not the particle diameter.

In addition to long-range forces, the interaction of oppositely charged host and guest particles is dependent on polydisperse coagulation (Hinds, 1999b). The rate of change of number concentration of host and guest particles or of the rate of composite formation can be estimated from the following equation:

\[ \frac{dN}{dt} = -K_{12} \beta N^2 \]  

(4)

where \( N \) is the number concentration of particles, \( K_{12} \) is the coagulation coefficient (which is dependent upon particle diameter), and \( \beta \) is a correction factor dependent on particle charge and diameter. The coagulation coefficient for interaction of particles of two different sizes, \( d_1 \) and \( d_2 \), can also be estimated from the following equation:

\[ K_{12} = \pi (d_1 D_1 + d_2 D_2 + d_1 D_1 + d_2 D_1) \]  

(5)

where \( D_1 \) and \( D_2 \) are the diffusion coefficients of the two particles respectively.

The correction factor \( \beta \) for thermal coagulation of aerosols having charged particles \( +q_1 \) and \( -q_2 \) was estimated by Fuchs (1964) to be:

\[ \beta = \frac{\lambda_{12}}{\exp(\lambda_{12}) - 1} \]  

where \( \lambda_{12} = q_1 q_2 / (2\pi k T) \)  

(6)

The electrostatically induced bipolar coagulation is an efficient process to generate “tailored” particles by dispersing oppositely charged droplets and micro-mixing of particles inside the droplets.

**Materials and Methods**

Composite particles were generated using AG 1-X8 Resin (Catalogue No. 140-1441), manufactured by Bio-Rad Laboratories (Richmond, CA), as the host particles and Omega 4000 Red Toner, manufactured by AEG Olympia (Somerville, NJ), as the guest particles. These host and guest particles were chosen because of their ready availability and low cost. Corona charging of particles was performed to generate charged host and guest particles of opposite polarity. A corona-charging device (Nordson® Versa Spray®) was used, where the particles were exposed to

Fig. 2. A conventional corona gun (Bailey, 1998).
positively or negatively charged ions for a few seconds (Fig. 3). The ions collide with the particles, sticks to them, and cause the particles to attain the charge. The charged host and guest particles were then transferred into a steel tumbler for mixing. The charge decay characteristics of the particles were studied using an electrostatic voltmeter held close to the surface to monitor the surface potential. When the particles were sprayed with positive ions, the electrostatic voltmeter measured a positive surface potential and vice versa when sprayed with negative ions. The charge-to-mass ratio of the particles was measured.

Mixing of host and guest particles in different mass ratios were investigated. The mixing was performed in a stainless steel tumbler of 8 cm. diameter and 11 cm. long rotated at approximately 50 - 60 rev / min (Fig. 3). Experiments were performed using neutral host and guest particles, only charged guest particles and uncharged host particle, and oppositely charged host and guest particles. The host and the guest particles were tumbled for 10 to 20 minutes to form a loosely bonded composite powder. The mixture of loosely bonded composite particles were transferred to a metal panel and placed in an oven maintained at 100°C. The particles were then removed from the oven after 1, 3, and 5 minutes and observed under an optical microscope.

Results and Discussion

The particle size range of the as received resin and red toner powders (Table 1) was measured using MICROTRAC®. Both resin and red toner particles were widely spread with d_{50} of around 133 μm and 15 μm respectively. The MICROTRAC® was calibrated using fluorescent particles of 10 μm size (Duke Scientific), which showed a d_{50} of 10.13 μm (σ^2 = 2.28). As received uncharged resin (AG 1-X8) and red toner (OMEGA) particles were mixed at different mass ratios (95%-5%, 96%-4%, and 97%-3%) and cured in an oven.

The objective was to find the mixing ratio that would yield the lowest d_{50} of the cured composite to exclude the effect of tribocharging with the stainless steel container. The cured mixture of uncharged resin and toner powders of different mass ratios (95%-5%, 96%-4%, and 97%-3%) were dispersed in water and analyzed in MICROTRAC® (Table 2). It was found that a resin-red toner mass mixture of 95%-5% yielded the lowest d_{50} (104.77 μm) and hence this ratio was chosen to be the ratio for the charging studies.

Precharging of the resin and toner particles was done at +70kV or -70 kV and charge decay measurements were performed for approximately 360 seconds. The host and the guest particles were found to retain their charge (Fig. 4) while they are being transferred to the stainless steel tumbler for mixing. The charge-to-mass of resin and red toner was found to be + 0.5 μC/gm (corona charging + 70 kV) and - 1.3 μC/gm (corona charging - 70 kV) respectively. The mixing of precharged particles generated composites (Fig. 5) with d_{50} of close to 145 μm. The precharged particles were analyzed before (Table 3) and after (Table 4) being cured. No significant variation in d_{50} was observed due to curing, but significant change in d_{50} was observed between the uncharged (104.77 μm) and precharged (145 μm)

Table 1. Particle size distribution of resin and toner particles.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>AG 1-X8 (μm)</th>
<th>Red Toner (Omega) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{50}</td>
<td>55.43</td>
<td>9.94</td>
</tr>
<tr>
<td>d_{90}</td>
<td>133.80</td>
<td>15.60</td>
</tr>
<tr>
<td>d_{100}</td>
<td>180.05</td>
<td>21.17</td>
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</tbody>
</table>

Table 2. Particle size distribution of mixtures of uncharged resin and toner particles.

<table>
<thead>
<tr>
<th>Conditions of Mixing</th>
<th>d_{50}</th>
<th>d_{90}</th>
<th>d_{100}</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% Resin, 5% Red Toner</td>
<td>29.74</td>
<td>104.77</td>
<td>162.24</td>
</tr>
<tr>
<td>96% Resin, 4% Red Toner</td>
<td>42.50</td>
<td>138.07</td>
<td>174.95</td>
</tr>
<tr>
<td>97% Resin, 3% Red Toner</td>
<td>124.12</td>
<td>147.18</td>
<td>172.17</td>
</tr>
</tbody>
</table>
formulations at 95% - 5% ratios. The resin particles were found to be stable up to 150°C and did not melt or deform. The toner particles melted at a few degrees above 100°C resulting in coverage of the entire surface area of the resin particle (Fig. 5).

Conclusions

The preliminary experiments conducted with particles of \(d_{50}\) 15\(\mu\)m and 133 \(\mu\)m respectively did generate composite particles with a \(d_{50}\) close to 145\(\mu\)m. The composite particles had a single resin particle as the core and a cluster of red toner particles encapsulating the core.

Fig. 4. Charge decay characteristics of red toner (OMEGA) and Resin (AG 1-X8) particles corona charged at +70 kV or -70 kV.

Fig. 5. Optical microscope pictures of AG 1-X8 resin particles and red toner particles.

Table 3. Particle size distribution of mixtures of corona charged resin and toner particles before curing.

<table>
<thead>
<tr>
<th>Conditions of Mixing</th>
<th>(d_{\text{min}}) ((\mu)m)</th>
<th>(d_{\text{mid}}) ((\mu)m)</th>
<th>(d_{\text{max}}) ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% Resin, 5% Red Toner, Toner charged at -70kV</td>
<td>118.42</td>
<td>145.81</td>
<td>173.04</td>
</tr>
<tr>
<td>95% Resin, 5% Red Toner, Resin charged at +70kV, Toner charged at -70kV</td>
<td>104.40</td>
<td>142.57</td>
<td>178.27</td>
</tr>
</tbody>
</table>

Table 4. Particle size distribution of mixtures of corona charged resin and toner particles after curing in oven at 100°C for 5 minutes.

<table>
<thead>
<tr>
<th>Conditions of Mixing</th>
<th>(d_{\text{min}}) ((\mu)m)</th>
<th>(d_{\text{mid}}) ((\mu)m)</th>
<th>(d_{\text{max}}) ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>95% Resin, 5% Red Toner, Toner charged at -70kV</td>
<td>125.82</td>
<td>147.61</td>
<td>171.75</td>
</tr>
<tr>
<td>95% Resin, 5% Red Toner, Resin charged at +70kV, Toner charged at -70kV</td>
<td>123.28</td>
<td>146.69</td>
<td>173.78</td>
</tr>
</tbody>
</table>

These composite particles were found to be stable when dispersed in water. Based on these preliminary findings, an electrostatic microencapsulation tower (Fig. 6) has been constructed, where the host (100 to 500 \(\mu\)m) and guest (0.1 to 80\(\mu\)m) particles can be used to generate composite particles.

The electrostatic microencapsulation tower was designed to simultaneously disperse and charge host and guest particles using two corona guns (Nordson® Versa Spray®) held at a high voltage (one at + 70 and the other at...
- 70 kV). Negative and positive corona guns are used to generate oppositely charged host and guest particles. A grounded rotating screen was installed inside the tower at the middle of two charging corona guns. A screen was used to collect the composite particles at the bottom of the tower. A jet of air was used to dislodge the particles from the screen and the composite particles were cured to promote bonding.

ACKNOWLEDGMENTS.—This project was supported by a grant from the DOE/Pacific Northwest National Laboratory. We are grateful to Dr. Oleg Egorov for his support and guidance.

Literature Cited


Modeling of Electrofusion Coils for Performance Optimization

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Abstract

Modeling physical parameters provides a virtual design environment allowing the confirmation and optimization of electrofusion characteristics. Finite element incorporate physical parameters and their interactions along common boundaries defined within a model geometry. The electrofusion of polymeric piping is a widely accepted means of assembling piping systems with zero-leakage integrity. The key parameters in the fusion process are the coil resistance, the current passing through the coil and the time the current is applied. Modeling the coil and applying current to the model is accomplished using the MATLAB partial differential equations (PDE) toolbox. This paper presents the method of modeling and the results from changing the various fusion parameters such as time and current. Both the parameters and outputs are illustrated in various configurations.

Introduction

Electrofusion is a widely accepted means of joining polymer piping into a containment system. Specifically, resistive heating is utilized to change the state of polymers thereby joining two separate pieces into a system. A conductive coil is molded into a socket and a mating pipe is inserted to create a piping system. A large current (60-90 amps) is driven through the conductive coil to generate resistive heating, melt the plastic near the coil and pipe, and join the two elements into a system. The heat transferred to the surrounding polymer changes the state of the polymer from a solid to a liquid and joins separate pieces into a common system.

Modeling the electrofusion process provides a virtual design and development environment where the parameters of material properties, current and time can be simulated for performance optimization.

Materials and Methods

The piping electrofusion process, shown in Fig. 1, is accomplished by first joining separate pieces of pipe and fittings, creating a current loop through the joining region and creating a voltage drop to drive the current. The voltage drop is created using a transformer-based fusion machine designed to provide a constant potential across the coil even as the resistive load changes with temperature.

Modeling the electrofusion process is begun by drawing, to scale, the geometry of the pipe joining components shown in Fig. 2. The platform for modeling is the Partial Differential Toolbox (PDE) with MATLAB, available from The Mathworks, Inc., Natick, Massachusetts. The PDE toolbox allows various analysis configurations such as electrostatic, stress and heat transfer. The heat transfer mode is used to model the electrofusion process since the heat flux between the copper and surrounding polymer is analyzed. (One note of caution in that the PDE toolbox does not automatically assign units to each value. It is recommended that the designer choose a system of units, such as metric or imperial, and maintain those units throughout the modeling process).

The next step, after drawing the geometry of the electrofusion process, is to enter the PDE specification for each material. A choice of elliptic or parabolic FEM is made.
Modeling of Electrofusion Coils for Performance Optimization

Fig. 2. Geometry in PDE toolbox draw-mode.

Fig. 4. Energy generated by fusion machine.

Fig. 3. PDE specification parameters.

Fig. 5. Meshing during the FEM process.

depending upon the terms in the partial differential equation. In this case parabolic is selected to include material density (\( \rho \)) and heat capacity (\( C \)) in the analysis. The remainder of parameters are entered as shown in Fig. 3 for the copper coils. The copper PDE specification is shown due to the unique heat source (\( Q \)) property that must be calculated.

The heat source is calculated via data acquisition by measuring the power output (Watts) of the fusion machine during a typical fusion process. The data is transferred to MS Excel and a trendline is assigned. The trendline represents the energy (joules/sec) that is produced by the fusion machine during the electrofusion process as shown in Fig. 4 for a 4-inch coil. The energy is then divided by the volume of the copper wire in each coil to calculate the volumetric heat flux generated by the copper.

The mesh is then initiated after the PDE specifications are complete as shown in Fig. 5. After the mesh is completed, the solve parameters of fusion time, initial temperature (\( u(0) \)), relative tolerance and absolute tolerance are entered. The plot parameters are selected as shown in Fig. 6 and the simulation is executed. The results of the simulation are displayed and analyzed for dimensions of the polymer melt-zones and the maximum polymer temperature within each zone. As well, each of the fusion parameters are exactly repeatable and can be varied to demonstrate the affect of each polymer electrofusion process.

Results

The results of simulation are shown in Fig. 7 for a 4-inch pipe, socket and coil. The pipe and socket are made of...
displayed on the right side of the output. The melt-zone where the polymer bonded is the red color in the center of the image where the copper wire reached temperatures above 300°C.

One significant advantage of modeling and simulation is that some physical parameters can be changed while maintaining exact repeatability of other parameters. This is demonstrated in the output of a 4-inch polypropylene electrofusion where the fusion time was reduced from 105 sec to 75 sec as shown in Fig. 8. The maximum temperature reached in the center of the image is less than 250°C which is a result of decreasing the electrofusion time from 105 sec to 75 sec while all other parameters were not changed.

**Conclusions**

Modeling and simulation provides a virtual development environment free from requirements to change physical parameters in determining their affect. The flexibility of a virtual environment eliminates vast resources traditionally used to create new products and processes while shortening the development cycle.

Fig. 8. 4-inch polypropylene electrofusion (75 sec).

displayed on the right side of the output. The melt-zone where the polymer bonded is the red color in the center of the image where the copper wire reached temperatures above 300°C.

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Fig. 8. 4-inch polypropylene electrofusion (75 sec).

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Simulation of Video Electric Single Particle Aerodynamic Relaxation Time Analyzers

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Abstract

The simulation of physical parameters provides a virtual environment for the design and optimization of instrumentation. Applying physical laws and theorems to natural phenomena defines the behavior of analytical processes. Simulation provides a means for the adjustment of specific operating parameters while maintaining the repeatability of constant parameters. The Video Electric Single Particle Aerodynamic Relaxation Time Analyzer (VESPART) is an instrument that provides the diameter and charge-to-mass (q/m) ratio of particles. The simulation of the VESPART requires the modeling of the physical environment and application of modeling to simulations. Simulation includes characterization of the various natural forces that affect particle motion within the instrument. These natural forces can be modified to determine the impact each has on particle motion. The graphical user interface is created in MS Visual Basic providing an MS Windows compatible simulating environment. The output of the simulator is a virtual, illuminated particle track similar to the actual particle track acquired by the VESPART. This paper presents the parameters of simulation as well as the output virtual particle track. Also, the benefits of simulation are presented relative to research and development projects.

Introduction

The modeling and simulation of physical environments is an expanding and widely applied research area used in almost every segment of technology. Modeling and simulation allow the development of an advanced virtual research environment used to analyze physical parameters and optimize process applications without the modification of hardware and software. Specifically, modeling is introduced to establish operational parameters allowing computers to implement parameters as determined through simulation.

The Video Electric Single Particle Aerodynamic Relaxation Time (VESPART) analyzer concept creates an electric field that excites charged particle motion and captures the particle motion with a CCD camera (Mu 1994). The charged particle, size ranges 1 to 100 mm diameter, is introduced into one end of a flow chamber. At the other end of the flow chamber is a blower creating laminar flow conditions that gently guide the particle into the sampling volume. As the particle passes through the chamber, an applied electric potential, on the order of 20 \times 10^3 \text{ Volts peak-to-peak} and modulated at 50 to 255 Hz sinusoidal, excites particle motion. The horizontal component of the electric field (x-axis force) is over seven orders of magnitude greater than the vertical component of the electric field (z-axis force). The particle is driven by the strong horizontal electric field to create an amplitude and velocity phase of the oscillatory motion of the particle that are characteristic of the particle’s charge and diameter. The particles pass through the sampling volume of the flow chamber as it moves from one end to the other. The sampling volume is a 2\text{mm} \times 2\text{mm} flat area where the field of laser illumination intersects the focal-field of a CCD camera. As the particles pass through this region, the lasers are turned on for exactly two cycles of electric field to illuminate particle movement. The CCD camera and frame grabber acquires an image of the particle’s illuminated path and transfers the frame to C++ routines for analysis. The particle track amplitude and velocity phase calculations are solved, the charge and diameter of the particle are calculated, and data is stored and displayed. The input and output (I/O) of the VESPART to the host computer is accomplished via a serial cable from the CCD camera to the frame grabber in the computer. The instrument, in this configuration, is not portable and cannot be non-intrusively introduced into most process applications due to its bulky size, weight and manual adjustments.

The VESPART operation is simulated to allow the application of varying electric-field frequencies, airflow velocities, particle sizes, particle charges, chamber diameters and applied electric potential to analyze their affect on instrument charge-to-mass and diameter calculations (Farmer 2002).
Simulation of Video Electric Single Particle Aerodynamic Relaxation Time Analyzers

Materials and Methods

Modeling the physical environment facilitates the development of simulations by defining, developing and understanding the forces and their limitations driving the charged particle movement within the VESPART. Modeling also provides virtual design and development flexibility to alter physical parameters and analyze their affect on charged particle movement. The electric field, created by sinusoidally modulating the applied electric potential to the deflector plates, is modeled (in the DC state) to analyze the electric field driving forces, create a polynomial representation of these forces for simulation and to facilitate design and development of a smaller diameter flow chamber.

Modeling the VESPART electric field is accomplished using a commercially available software package, Lorentz 2D, available from Integrated Engineering Software, Inc., Manitoba, Canada. The Lorentz 2D software begins with a user interface to the geometry of the VESPART: a cylindrical tube (flow chamber) and two metal plates that match the radius of the chamber with 180-degree separation.

Next, ‘elements’ are placed along the geometry to divide the model into sub regions along the geometry’s boundaries. The Lorentz 2D uses the Boundary Element Method (BEM): BEM transforms differential operators defined in the geometry volume into integral operators defined on the geometry boundary. This makes the geometry ‘meshing’ simple, the calculations fast and utilizes precise integration to generate values. The VESPART chamber geometry, with boundary elements, is shown in Figure 1.

![Lorentz 2D VESPART Flow Chamber with Boundary Elements](https://scholarworks.uark.edu/jaas/vol56/iss1/1)

Fig. 1. Lorentz 2D VESPART Flow Chamber with Boundary Elements.
Fig. 2. Lorentz 2D Model of Electric Field (0.0955 meter plate separation) Volts/meter

The boundary conditions are modeled on the electric plates at -10kVDC potential to one plate and +10kVDC to the other. These physical parameters are applied to the VESPART chamber as it exists in original geometry. The original geometry has a flow chamber diameter of 0.0955 meters. After analysis, the DC electric field intensity is shown in Fig. 2 in 'solid' mode. The scale of electric field intensity is shown on the right side of the model where varying shades demonstrates the varying intensity of the electric field within the chamber. The high-intensity regions, represented by contrasting colors, are evident along the edges of the deflector plates; specifically at the corners of the plates. The corners of the deflector plates create the relatively high-intensity DC electric fields shown the Fig. 2.

The data from the Lorentz 2D graph is imported into Excel to interpolate linear curves and their outputs. The linear curves are used in the simulation to determine x- and z-component forces on the particle depending on where the particle is located in the flow chamber during simulation. The curves, shown in Fig. 3, represent the DC amplitude of the component force that the electric field exerts on the particle depending on the position and time relationship (elapsed time of simulation from \( t = 0 \) at the start) of the particle to the flow chamber.

During simulation, these DC-magnitude representations are utilized to develop the AC electric field driving forces on the particle along the x-axis direction by sinusoidal modulation while assigning polynomial representations of the electric field (volts/meter).
Simulation of Video Electric Single Particle Aerodynamic Relaxation Time Analyzers

Fig. 3. VESPART DC-Electric Field Representation

Results

The programming structure of the simulator was first developed using MATLAB, available from The MathWorks, Inc., Natick, Massachusetts. This provided confirmation of the algorithms and testing methodology before the user-interface version was programmed using Visual Basic 6.0 because of ease of creating the graphical user interface (GUI) as shown in Fig. 4.

The virtual particle track resulting from simulation is shown in Fig. 5. The six key points, shown as '*', represent the position of the particle used to determine particle phase lag and amplitude. The phase lag and amplitude are then used to determine charge-to-mass calculations.

Conclusions

The Lorentz 2D model provides a graphical representation of DC electric field values that, when sinusoidally modulated, create an AC driving force on the charged particle as it passes through the VESPART flow chamber. The graphical representation is characterized by polynomials and natural-log functions that are applied to the charged particle simulator for simulation and illuminated particle track capture. The illuminated particle track, identical to the track acquired by the VESPART, is stored in an Excel file for analysis. The simulator provides an important analytical virtual tool for the validation of application parameters and VESPART processing algorithms. Simulation requires minutes to complete and precisely repeats the physical parameters of particle charge, particle size, frequency, airflow velocity, chamber diameter and electric potential in each simulation. Modeling and simulation eliminate modification to the instrument's physical environment by providing a virtual design and development environment thereby eliminating the need for vast resources and eliminating potential repeatability errors.

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https://scholarworks.uark.edu/jaas/vol56/iss1/1
Steve R. Farmer and Robert A. Sims

<table>
<thead>
<tr>
<th>Input Electric Field Frequency (Hz)</th>
<th>{244 Hz Typical; Max 254} {Applied DC-Potential = 10kV}</th>
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<tbody>
<tr>
<td>Input Charge</td>
<td>{Select Charge Option Below After You Input All Data}</td>
</tr>
<tr>
<td>Input Particle Diameter (um)</td>
<td>{Diameter Range 5 to 98 um} {Ex: 42.0}</td>
</tr>
<tr>
<td>Input Particle Density (g/cc)</td>
<td>{Ex: 1.2}</td>
</tr>
<tr>
<td>Charge Options:</td>
<td></td>
</tr>
<tr>
<td>1. Input Particle Charge (fC)</td>
<td>Ex: 16.0</td>
</tr>
<tr>
<td>2. Input QbyM (uC/g)</td>
<td>Ex: .01</td>
</tr>
</tbody>
</table>

Fig. 4. Graphical User Interface

### Literature Cited


Simulation of Video Electric Single Particle Aerodynamic Relaxation Time Analyzers

Fig. 5. Virtual Illuminated Particle Track
The Effect of Tillage and Herbicide Treatments on Redvine (Brunnichia ovata) Subterranean Morphology

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Abstract

Redvine Brunnichia ovata (Walt.) Shinners is a perennial weed that reproduces from seed, rootstock, and rhizomes. Redvine infested areas that were exposed to different tillage practices, slicing techniques, and herbicide treatments were selected to excavate in order to observe rhizome and root morphology. When comparing tillage systems, deep tillage appeared to delay rhizome development following cultivation, but a characteristic branching occurred over time. Shallow cultivation (2.5 to 7.5 cm) concentrated rhizomes immediately below the depth of tillage; whereas, no-till areas concentrated rhizomes near the soil surface. Slicing the underground parts of redvine will not kill rhizomes if they are still attached to a live portion of the taproot. The same holds true for freezing and drying. Dicamba and glyphosate reduced the density of redvine rhizomes, but neither provided control of the entire underground plant structure. Nomenclature: dicamba, 3,6-dichloro-2-methoxybenzoic acid; glyphosate, N-(phosphonomethyl)glycine; redvine, (Brunnichia ovata (Walt.) Shinners) # BRVC1. Additional index words: Differential infestation, sensor applicator, dicamba, glyphosate, Glycine max.

Introduction

Redvine is a perennial weed that is native from south Illinois, Missouri to South Carolina, Florida, and Texas (DeFelice, 1998). Redvine grows in wetlands or nonwetlands (Reed, 1988). It reproduces from seed, rootstock, and rhizomes, and its above ground stems are deciduous and will regenerate yearly if undisturbed. This is not the case in production fields where the aerial portions are annually killed back to the soil surface. The establishment from seed is an erratic process and requires conditions that are favorable for the germination and establishment processes for an extended time period. Seed are not normally produced on the current year's growth; therefore, they are not produced in the growers' fields. The rootstock can be extensive and reach several feet into the soil. These deep rootstocks must be killed in order to effectively control redvine.

Redvine has been a problem in some agronomic fields for many years, but the increased acceptance of reduced tillage systems has allowed redvine and other perennial weeds to become more problematic (Elmore, 1984). Some studies have shown deep tillage can reduce groundcover levels of redvine (Elkins et al., 1996; Castillo et al., 1999). Conversely, shallow tillage operations can result in the spread of redvine and other perennial weeds and increase groundcover levels (Soteres and Murray, 1982; Castillo et al., 1998).

In an effort to better understand the morphological characteristics of rhizome and root systems, observations were made of subterranean redvine plant parts that had been exposed to different tillage practices, and experiments were conducted to determine the regeneration capacity of redvine and the effects of deep tillage and herbicide application on subterranean plant parts.

Materials and Methods

Redvine infested areas that were exposed to different tillage practices, slicing techniques, and herbicide treatments were selected to excavate in order to observe the rhizome and root morphology. Observations were made regarding rhizome and root location and regeneration. Although various soil series were located in the vicinity, all observations were confined to a Sharkey series (very-fine, smectitic, thermic, Chronic Epiaquerts).

Experiment 1.--Over years, observations were made of several fields where redvine was actively growing. No-till and conventionally tilled areas were selected. Notes and measurements were taken on redvine below ground morphology. These were utilized to construct stylized drawings illustrating the primary differences in growth habit.

Experiment 2.--Dicamba, 2.2 kg ai/ha, was applied to an established redvine population in the fall of 1997 at the Northeast Research and Extension Center (Lat. 33° 40' 27", Long. 90° 04' 24" W) at Keiser, AR. The experiment contained paired plots with two replications. Each treated and untreated plot contained thirty individual redvine clusters. A garden stake and red flag were placed at each cluster to mark the location for future evaluation. Visual
Fig. 1. Top view of redvine root severed within 2.5 to 5 cm of the soil surface. The rhizomes arise from adventitious buds near the top of the root.

control ratings were taken in the spring of 1998 and late summer of 1999. The plots remained undisturbed until August, 1999 when selected plots were excavated to observe redvine rhizomes and roots. A backhoe was used to create a flat, vertical surface near redvine plants, and small hand implements were used to remove soil from rhizomes and roots.

Experiment 3.--In February, 1998, redvine plants in the same area as Experiment 2 were sliced below the soil surface at depths of 7.5, 15, 23 and 30.5 cm. A metal bar 50.8 cm wide and 0.6 cm thick was beveled on one side and mounted on a tractor. The bar was pulled at the four slicing depths through areas where redvine plants were present. The experimental design was completely randomized with four replications. In August, 1999, observations were made as in Experiment 2.

Experiment 4.--Selected plots were excavated in October, 1999 from an experiment (Lat. 35° 39' 54" N, Long. 90° 10' 49" W) that included no-till, conventional, and moldboard plow treatments. The tillage treatments were also sprayed with dicamba at 2.2 kg ai/ha in the fall and glyphosate at 0.84 kg ai/ha applied at the V2 and repeated at the V6 stage of soybean [Glycine max (L.) Merr.] growth. Plots were excavated using a backhoe. Underground plant
Fig. 2. Regeneration of subterranean redvine growth after the plant is (A) severed at 30 cm, (B) subsequently years later, severed at 15 cm and (C) subsequently years later severed at a shallower depth of 7.5 cm. This figure illustrates the development of structures such as the one shown in D.

parts from a 15 cm depth by 76 cm wide by 58 cm long volume were collected. This process was repeated until only deep tap roots were occurring.

Experiment 5.--Two redvine infested fields (Lat. 35° 39' 55" N, Long. 90° 10' 57"W) had shallow fall tillage performed in October and November, 1999. Observations were made the next spring on the survival of underground plant parts that had at least 5 cm of underground stem exposed all winter. Stems which had newly developed leaves in the spring were considered alive. Various exposed rhizomes were pulled to determine if they were severed from the extensive underground plant parts.

Experiment 6.--A 16 ha field (Lat. 35° 43' 04" N, 90° 06' 36" W) with an extensive infestation of redvine was chosen for further evaluation of herbicide applications in the fall of 1998. Aerial photographs were taken in infra-red after the soybean leaves had dropped to provide a benchmark for the degree of redvine infestation. Glyphosate at 4.5 kg ai/ha was then applied by airplane. After soybean harvest, the producer planted wheat followed by a planting of soybean. The soybeans were planted in 48 cm rows which would allow a high clearance sprayer to be driven through the field prior to harvest after the soybean leaves had dropped. The experiment required the attachment of a Detectspray™ sensor applicator to the sprayer. The sensor applicator activates each nozzle as it passes over the green redvine foliage. This prevents areas void of redvine from being sprayed and reduces the per acre cost for an entire field. Subsequent infra-red photographs can be taken and analyzed using computer programs that can determine the reduction in ground cover compared to the benchmark infestation.

Results and Discussion

Experiment 1.--Redvine plants were observed to have an array of rhizomes emerging in many directions from adventitious buds located on the upper portion of the
The Effect of Tillage and Herbicide Treatments on Redvine (*Brunnichia ovata*) Subterranean Morphology

Fig. 3. Transverse cross-sectional view of the idealized redvine subterranean growth to illustrate growth habit when a field is converted to no-till from continuous shallow cultivation. First year comparison in spring before annual shallow tillage is (A) no till and (D) tilled; second year comparison under same conditions in spring is (B) no tilled and (E) tilled. Similarly, the third year is (C) no tilled and (F) tilled.

severed taproot (Fig. 1). From this array of rhizomes, additional rhizomes emerge at nodes along these underground stems creating a mass of subterranean growth. As above ground stems arise from other nodes on the rhizomes, dense clusters of vines can be formed.

Where deep tillage with a moldboard plow was used, the rootstock was severed at a depth of circa 23 to 30 cm (Fig. 2a). The rhizome and root portions that were severed were turned up and exposed to freezing and drying, which has shown to kill these rhizomes and roots (Castillo et al., 1998). It appeared that first year growth from the remaining taproot was in the form of stems that would emerge in late season (Fig. 2b). When the above ground stems were removed by shallow cultivation or harvesting equipment, multiple stems arose from adventitious buds on the stem (Fig. 2c-d).

Where shallow cultivation is followed by shallow cultivation or no-till, rhizomes tend to form quickly near the soil surface (2.5 to 7.5 cm). No-till areas seem to have larger rhizomes and above ground stems than areas that receive continuous shallow cultivation (Fig. 3a-c; Fig. 3d-f).

Shallow cultivation disturbs the surface of the soil and prunes the redvine rhizomes. Thus, the redvine rhizomes were found in areas immediately below the zone of cultivation. Conversely, rhizomes growing in no-till soils can be located closer to the soil surface and grow undisturbed.

Thus, the redvine does not have to regenerate plant parts that have been destroyed.

**Experiment 2.**—Visual ratings of treated plots showed 100% control in the spring of 1998 compared with 100% survival in the untreated plots. However, visual ratings in the summer of 1999 showed 100% survival in both the treated and untreated plots.

Excavation of rhizomes and roots revealed that some rhizomes had been killed back to their juncture with other rhizomes and the main root system. Certain rhizomes and roots that were not killed indicated that the herbicide may not be translocated in concentrations high enough to kill the entire root system in some cases.

New rhizomes emerged from nodes below the level of lethal herbicide concentration. It took almost two years for this regeneration to occur indicating that one herbicide application will give control, but only for about a year. If lethal concentrations of herbicide are not reaching the entire underground plant structure in one application, repeat applications are needed after regeneration in order to eliminate redvine by chemical means.

**Experiment 3.**—The conditions following the slicing of the redvine roots were moist with temperatures above freezing. The portion of the taproot above the slice survived and supported the rhizomes and the above ground stems attached to them. The portion of the taproot below the slice
Fig. 4. Typical subterranean redvine growth found after various combinations of tillage and herbicide treatments for a period of three years: conventional shallow tillage (A), no till (B), and moldboard plow (C) with no dicamba or glyphosate applied. Conventional tillage with glyphosate applied in season is shown in (D). No till in combination with dicamba in the fall is shown in (E) and in combination with glyphosate in season is shown in (F). The soil surface indicated by SS is always at the 0 cm depth. The average annual tillage depth (TD) varies at different field locations from approximately 5 cm to 10 cm. Observing the morphology of the subterranean redvine plant, the historical deep tillage depth (HDT) is readily determined. The depth of the moldboard plowing (MTD) is also readily determined by the morphology and in this study ranged from 30 to 35 cm deep.

began regenerating rhizomes from adventitious buds located immediately below the slice.

Thus, if conditions are favorable following the severing of the taproot both portions will live and continue to infest the area. If temperatures below freezing had occurred, or if dry conditions had occurred, the severed portions may have died. Castillo et al. (1998) were able to kill underground plant parts by placing them in a mixture of ice and water for 24 hours and reduced sprouting by 80% 20 weeks after planting when the parts had been air dried for 24 hours.

**Experiment 4.**—Plots tilled with a moldboard plow had considerably fewer rhizomes than other tillage treatments (Fig. 4). Observations showed that regeneration occurred from deep within the soil and took 2 to 3 years to produce a significant reinestation (Fig. 4c). It was obvious that deep tillage provided good control of redvine initially, but it did not eliminate the plant. However, multiple deep tillage operations might eliminate redvine over time by increasing the amount of subterranean biomass that would be exposed to the various climatic elements.

Conventional tillage resulted in a rhizome population that was less dense than no-till (Fig. 4a-b). Even though the
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Fig. 5. Typical redvine subterranean plant parts exposed by plowing in the fall of 1999. This photograph taken in the spring of 2000 shows that this plant had survived the winter.

Conventional tillage was shallow, rhizomes were killed in the tillage zone and had to be replaced. Conversely, rhizomes in the no-till plots generated new growth in addition to the existing plant structures, which allowed the underground plant structures to increase in number and size at all the upper soil levels.

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Dicamba and glyphosate were similar in their effects on redvine. The use of either herbicide reduced the rhizome density in both the conventional and no-till treatments (Fig. 4d-f). Although the herbicides provided a high percentage of control compared to no herbicide or tillage (Fig. 4b, e and f), there was not sufficient translocation of lethal concentrations of herbicide to kill the entire underground plant structure. These observations were similar to those in Experiment 2.

**Experiment 5.**—A typical plant that was considered alive is shown in Fig. 5. The 1999-2000 winter season exhibited temperatures below freezing a sufficient number of times to kill susceptible plant tissue. Temperatures reached 0°C or below 77 times, -5°C or below 45 times, -10°C or below 34 times, and -15°C or below 22 times (Fig. 6). It is obvious that these conditions were colder than those reported in Castillo’s greenhouse study (1999) where he obtained 100% mortality from 24 hours of 0°C in moist conditions. Therefore, if freezing is not killing the redvine in the field, there must exist a conditioning effect and/or a dry freezing effect under field conditions.

When the exposed rhizomes were pulled, those that were considered alive were attached to currently living plant parts that were still located underground. On exposed rhizomes that did not have new leaves, some were attached to underground living plant parts, and others were not. Those not attached to living underground plant parts were all found to be dead. Thus, it is obvious that without underground plant structures to supply moisture and energy, the above ground exposed rhizomes will die.

**Experiment 6.**—An adequate soybean stand was obtained following wheat, but the crop did not grow well after emergence due to the dry conditions which prevailed throughout the summer. A poor plant canopy allowed...
weeds to compete season-long and remain green after soybean maturity. This prevented any color differentiation among weed species present; thus, rendering sensor application and infra-red photographs useless for evaluation purposes. However, it was visually noted that redvine was still prevalent throughout the field and had not been totally eliminated by glyphosate at 4.5 kg ai/ha that was applied the previous fall.

Conclusions

Tillage systems influence subterranean redvine rhizome and root structures. Deep tillage applied over several years at different depths can create a characteristic subterranean branching structure. Shallow tillage (2.5 - 7.5 cm) creates a concentration of rhizomes immediately below the depth of plowing. The no-till systems that did not receive an application of herbicide allowed redvine root structures to proliferate, especially near the soil surface. The application of herbicides with perennial vine activity can reduce the density of redvine, but there does not appear to be adequate translocation to kill the entire underground plant structure with a single application.

Tillage systems that can sever redvine rhizomes and roots and expose them to air drying conditions can aid in controlling redvine. The rhizomes and roots that are severed from the underground plant structure may die from desiccation. Rhizomes that remain attached to the underground plant structure will survive the drying conditions, and freezing temperatures alone do not appear to affect them.

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Alumina and Synthesis Intermediates Derived from Diethylaluminum Amide, Benzaldehyde and Water

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Abstract

The reaction of diethylaluminum amide [Et₂AlNH₂] with benzaldehyde in toluene produces a solution of ethylaluminoxane polymer [EtAlO] and hydrobenzamide [PhCH=N(Ph)N=CHPh]. Alumina then is precipitated by the addition of water. Transition aluminas that may be useful in heterogeneous catalyst applications are obtained after calcining. Details of the chemistry of solution intermediates according to ¹H NMR and the properties of the alumina product according to surface area analyses and powder x-ray diffraction are described.

Introduction

Porous aluminas are valued as primary catalysts or as promoter supports for noble metal catalysts (Heck and Farrauto, 1995; Rase, 2000). Previously we reported a method to prepare porous aluminas from precursors synthesized by a series of reactions with alkylaluminum derivatives (Lindquist et al., 1996; Lindquist and Rooke, 2000). The general synthetic method involves three principal steps. Combination of triethylaluminum with a primary amine or ammonia in hydrocarbon solvent yields a diethylaluminum amide and an equivalent of ethane gas. An aldehyde or ketone then is added to produce ethylaluminoxane polymer, an imine, and a second equivalent of ethane. Addition of water results in precipitation of alumina precursor and a third equivalent of ethane. A generalized stoichiometry to prepare an aluminum oxide hydroxide precursor is shown by Equations (1)-(3).

\[
\begin{align*}
\text{Et}_2\text{Al} + \text{RNH}_2 & \rightarrow \text{Et}_2\text{AlNHR} + \text{EtH} \\
\text{Et}_2\text{AlNHR} + \text{R}’\text{C}=\text{O} & \rightarrow \text{EtAlO} + \text{R}’\text{C}=\text{NR} + \text{EtH} \\
\text{EtAlO} + \text{H}_2\text{O} & \rightarrow \text{AlO(OH)} + \text{EtH}
\end{align*}
\]

(1) (2) (3)

There are a number of variables possible in the synthesis scheme. For example, addition of two equivalents of water, in lieu of one equivalent by Equation (3), gives a precursor stoichiometry of \(\text{Al(OH)}_3\) instead of \(\text{AlO(OH)}\). Other potential variables include the use of different amines and aldehydes or ketones as reagents for Equations (1) and (2). Additionally, the imine product of Equation (2) may be subject to byproduct chemistry depending on its composition and on synthesis conditions. Herein we report details of the chemistry of intermediates when ammonia and benzaldehyde are used as reagents in Equations (1) and (2) respectively. The properties of the alumina obtained after calcining are compared with those of a commercial alumina.

Materials and Methods

Syntheses involving triethylaluminum or its derivatives were conducted under \(\text{N}_2\) or Ar atmosphere with an oil bubbler purge using Schlenk techniques. Benzaldehyde was obtained after two distillations in argon atmosphere. Triethylaluminum as a 25 wt% solution in toluene and Proton Sponge® [1,8-bis(dimethylamino)naphthalene] were used as received (Aldrich Chemical Co.). Anhydrous NH₃ from a cylinder (Delta Air Gas) was dried by passing it through a glass column containing KOH pellets. A commercial pseudoboehmite alumina was obtained (Alcoa Hi-Q 30) for purposes of comparison with aluminas synthesized.

The typical synthesis of an \(\text{Al(OH)}_3\) precursor using 2 equivalents of water is as follows. A 120 mL (0.23 mol) portion of 1.9M \(\text{Et}_2\text{Al}\) in toluene was transferred by cannula to a 250 mL Schlenk vessel equipped with a water reflux condenser, septum inlet, and \(\text{N}_2\) bubbler. Warning: Triethylaluminum is pyrophoric and must be handled using appropriate precautions. Anhydrous NH₃ was bubbled with a needle through the septum into the stirred solution maintained at 70°C. When gas evolution ceased, indicating reaction completion to form diethylaluminum amide [\(\text{Et}_2\text{AlNH}_2\)], the flask was cooled to 0°C in a water ice bath and NH₃ addition discontinued. With continued stirring, one equivalent of benzaldehyde (23.2 mL, 0.23 mol) was introduced by syringe over a period of 30 minutes. This was accompanied by vigorous ethane gas evolution. When the benzaldehyde addition was complete, the solution again was saturated with NH₃. With continued stirring, two equivalents of water (8.3 mL, 0.46 mol) were introduced by
Alumina and Synthesis Intermediates Derived From Diethylaluminum Amide, Benzaldehyde and Water

Fig. 1. $^1$H NMR spectrum of ethylaluminoxane and hydrobenzamide in toluene, proximate composition $[\text{EtAlO}]_{1.0}[\text{PhCH}=\text{NCH}(\text{Ph})\text{N}=\text{CHPh}]_{0.33}$.

syringe over a period of 30 minutes accompanied by gas evolution and precipitation of alumina precursor. Excess NH$_3$ was bubbled through the cold solution to saturate it. The flask was removed from the ice bath, capped with a loosely fitted stopper, and allowed to stand undisturbed for four days at room temperature. After four days, the alumina was filtered from the supernatant and washed with two 50 mL portions of toluene. Hydrobenzamide, recrystallized from diethyl ether, was recovered in 50% yield (11.4 g) from the evaporated supernatant filtrate and toluene washings (m.p. 101°C, literature same) (Strain, 1927). $^1$H NMR of hydrobenzamide (CDCl$_3$) 8 6.0 (s, 1 H), 7.2-7.5 (m, 13 H), 7.8-7.9 (m, 2 H), 8.6 (s, 2 H) ppm; $^{13}$C NMR $\delta$ 92.9, 127.5, 128.1, 128.8, 128.9, 131.3, 136.2, 160.9 ppm. Mass Spectrum (70eV) [m/e (relative intensity)]: [M$^+$$]$ 224 (5), 194 (100), 167 (10), 152 (3), 116 (16), 106 (10), 91 (80), 77 (20), 65 (13), 51 (19), 39 (13), 27 (12).

Alumina was calcined in a porcelain crucible in a muffle furnace. The atmosphere was humidified by bubbling air through a water containing gas dispersion bubbler at 50°C before passing the air into the furnace. The flow rate of air through the bubbler was sufficient to replace the furnace atmosphere a minimum of 2 times per minute. The temperature was ramped at a rate of 5°C/minute to a specified temperature and held for 3 hours before turning off the furnace.

The characterization methods employed for the alumina and precursors are as follows. Solutions during syntheses were monitored by $^1$H NMR using a Bruker 200 MHz FTNMR. The air and moisture sensitive NMR samples were prepared by repeated freeze-pump-thaw and glass sealed under vacuum with a torch. Hydrobenzamide, isolated from the product supernatant and recrystallized, was characterized by $^1$H and $^{13}$C solution NMR as well as
Fig. 2. Chemical transformations of hydrobenzamide under different conditions.

by mass spectrometry (Hewlett Packard 5890 series II GC with 5970 series mass selective detector) at 70 eV. Surface analyses of calcined alumina by N\textsubscript{2} adsorption and desorption isotherms were obtained with a NOVA-1200 gas physisorption instrument (Quantachrome Corp.). BET specific surface areas were calculated from 5 points of the adsorption branch of the isotherm (0.05 ≤ P/P\textsubscript{o} ≤ 0.30). Samples were outgassed overnight under vacuum at 250°C prior to surface analyses. X-ray powder patterns were obtained using a Rigaku Geigerflex x-ray generator equipped with a theta-theta goniometer and sample rotator (step size 0.05° 26, 1 second per step, range 10° to 75° 26).

Results and Discussion

*Imine Chemistry.*—Imines derived from ammonia are sensitive to further condensation (Layer, 1963). Thus, the isolated imine in this study was not benzylimine (PhCH=NH) which was expected from benzaldehyde according to Equation (2). Instead, hydrobenzamide [PhCH=NCH(Ph)N=CHPh] was recovered from the supernatant after precipitation of the alumina. Hydrobenzamide is the condensate of three benzylimine equivalents according to Equation (4).

\[
3 \text{PhCH}=\text{NH} \rightarrow \text{PhCH}=\text{NCH(Ph)N}=\text{CHPh} + \text{NH}_3 \quad (4)
\]
Alumina and Synthesis Intermediates Derived From Diethylaluminum Amide, Benzaldehyde and Water

Analysis of the reaction mixture prior to alumina precipitation with water also confirmed the presence of hydrobenzamide at this stage of the synthesis. Figure 1 is the $^1$H NMR spectrum of an aliquot collected after addition of one equivalent of benzaldehyde to the solution of diethylaluminum amide [i.e. completion of Equation (2)]. The broad resonances at 1.3 and 0 ppm in Fig. 1 correspond to the ethyl functions of the [EtAlO] polymer. The large singlet at 2.3 ppm is the methyl of toluene solvent. The signals from hydrobenzamide range from 6.0 to 9.6 ppm. Of particular interest is the acidic hydrogen of the central carbon of hydrobenzamide ($H_1$) seen at 6.0 ppm.

The acidic nature of hydrobenzamide has been found to promote byproducts if synthetic conditions deviated from those typically used as described in “Materials and Methods” above. Figure 2 summarizes our findings to date concerning these byproducts. The top of Fig. 2 shows the normal solution composition during a typical synthesis based on the NMR data presented in Fig. 1. If, however, the reaction medium is not kept cool during either the addition of benzaldehyde or the subsequent water addition, the solution turns a brown color. NMR and mass spectrometry analysis confirmed the presence of the thermal decomposition products shown on the left side of Fig. 2. Under another set of synthesis conditions, the right side of Fig. 2 shows what we found to be the most striking manifestation of the acidic properties of hydrobenzamide. The color changes from pale yellow to deep red when

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Fig. 3. N2 isotherms of aluminas calcined at 500°C for 3 hours in steam atmosphere a.) synthesized alumina b.) commercial alumina (Alcoa HiQ-30).
triethylaluminum, \( \text{[Et}_3\text{Al]} \) is added to the solution containing hydrobenzamide. The deprotonated aromatic anion of hydrobenzamide was implicated (Hunter and Sim, 1969). We tested this assumption by adding the nonchelating base, Proton Sponge\(^\text{TM} \) [1,8bis-(dimethylamino)naphthalene], instead of \( \text{Et}_3\text{Al]}. This also resulted in a strong color change, and as \(^1\text{H NMR} \) analysis confirmed, loss of the proton of the central carbon (\( \text{H}_b \) of Fig. 1) of hydrobenzamide. The byproducts of hydrobenzamide illustrated in Fig. 2, although interesting, are to be avoided in order to produce an alumina containing a minimum of organic impurities.

**Alumina Properties**.—Despite complications of byproducts, hydrobenzamide appears to exert a positive effect on alumina properties and may do so by functioning as a chelate during precipitation of the alumina. Relevant to our studies, Zeng and coworkers maximized the surface area for an alumina precipitated from an aluminum alkoxide precursor by coaddition of 1/3 equivalents of acetylacetonate, a bidentate chelate (Ji et al., 2000). The authors asserted that chelate coordination to aluminum centers induced defects in the alumina microstructure during precipitation. Moreover, they showed that additions of greater or lesser quantities of acetylacetonate were not as effective as 1/3 of an equivalent to enhance surface area. Coincidentally in our system, hydrobenzamide is formed in a ratio of 1/3 equivalents relative to aluminum. The serendipitous match of the ratio in our preparation with that found optimum by Zeng may help to explain the exceptional properties of our alumina.

Indeed, Fig. 3 shows the \( \text{N}_2 \) adsorption and desorption isotherms for our synthesized alumina and for Alcoa alumina, both calcined in steam atmosphere for three hours at 500°C. The larger pore volume of our alumina in comparison to the commercial alumina is readily apparent. The BET specific surface areas calculated for the synthesized alumina and Alcoa calcined alumina were 296 \( \text{m}^2/\text{g} \) and 228 \( \text{m}^2/\text{g} \), respectively.

In addition to having a high pore volume and surface area, it is desirable that alumina in catalysts be resistant to crystallization at elevated temperature. Crystallization results in a coarsened microstructure and diminished catalytic activity. Figure 4 illustrates the phase changes of the Alcoa Hi-Q-30 alumina, which typify a boehmite type precursor. The alumina maintains a boehmite \([\text{AlO(OH)}] \) phase after calcining at 300°C for three hours. At 400°C a phase change to \( \theta-\text{Al}_2\text{O}_3 \) occurs, and at higher temperatures, two discreet phase changes to \( \delta-\text{Al}_2\text{O}_3 \) and finally \( \gamma-\text{Al}_2\text{O}_3 \) at 1000°C are observed in Fig. 4. Temperatures and associated phases apparent from the patterns in Fig. 4 are consistent with those reported in the literature (Wefers and Misra, 1987). By contrast, the diffraction patterns of our alumina shown in Fig. 5 indicate a substantially more amorphous material at similar temperatures. After calcining to 1000°C a \( \gamma-\text{Al}_2\text{O}_3 \) phase is still retained, which is truly exceptional.

Based on favorably high pore volume, high surface area, and low crystallinity we are optimistic that our aluminas may supplant commercial aluminas in some applications. Studies are now underway to examine this potential for automobile emissions catalytic convertors. In addition we continue to seek further improvements in alumina microstructure and thermochemical stability through modified synthesis variables.
Fig. 5. Powder x-ray diffraction patterns for our synthesized alumina calcined at various temperatures.

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Bedrock Geology of West Fork Quadrangle, Washington County, Arkansas

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Abstract

A digital geologic map of West Fork quadrangle was produced at 1:24,000 scale using the geographic information system (GIS) software MapInfo. Data regarding stratigraphic relations observed in the field were digitized onto the United States Geological Survey (USGS) digital raster graphic (DRG) of West Fork quadrangle. The geology of West Fork quadrangle consists of sedimentary rocks of the Mississippian and Pennsylvanian systems. The Fayetteville Shale and Pitkin Formation represent the Mississippian system. The Hale, Boyd, and Atoka Formations represent the Pennsylvanian System. Each of these formations consists of members that were mapped at 1:24,000 scale, and this mapping effort represents the first time stratigraphic members were mapped utilizing digital technologies at this scale in West Fork quadrangle. The Hale Formation consists of the Cane Hill Member and the Prairie Grove Member. The Boyd Formation consists of the Brentwood Member, the Woolsey Member, the Dye Member, and the Kessler Member. The Atoka Formation in West Fork quadrangle includes the Trace Creek Member at its base. The overlying units of the Atoka Formation occur as unnamed alternating sandstone and shale units. The most prominent geologic structure in West Fork quadrangle is the Fayetteville Fault, which crosses the northwest quarter of the quadrangle. Several additional faults are associated with a fault zone surrounding the Fayetteville Fault. Another prominent normal fault was mapped striking east-west (downthrown to the south) in the southern part of the quadrangle.

Introduction

West Fork quadrangle (Fig. 1) is located near the center of Washington County, Arkansas and is named for the community of West Fork, which occupies the central portion of the quadrangle (Fig. 1). The quadrangle boundaries are 35°52.5'N 94°15.0'W (southwest), 36°00.0'N 94°15.0'W (northwest), 36°00.0'N 94°07.5'W (northeast), and 35°52.5'N 94°07.5'W (southeast).

Washington County is located on the south flank of the Ozark Dome (Croneis, 1930). The county occupies portions of two erosional plateaus formed along the southern portion of the Ozark Dome. The Springfield Plateau is defined by the top of the Boone Formation, a sequence of Lower Mississippian limestone and chert, whereas the higher Boston Mountains Plateau is formed by Upper Mississippian and Lower to Middle Pennsylvanian strata capped by the Middle Pennsylvanian Atoka Formation. The lithostratigraphic succession observed in West Fork quadrangle is shown in Figure 2 (Brown, 2000).

The landscape is a maturely dissected, dendritic drainage system dominated by the White River which flows north through the quadrangle (Fig. 3). Whereas upland areas throughout the quadrangle are heavily forested, excellent exposures of all lithostratigraphic units were observed in ravines associated with the West Fork of the White River and its tributaries, roadcuts along highways US 71 and Interstate Highway 540, and in on-going excavations produced by construction activities in the region.

The topography of the quadrangle is controlled by a number of units. The Wedington Member of the Fayetteville Formation is often expressed as an elevated bench on hilltops and caps some hills in the northwestern portion of the quadrangle. Prominent bluffs (ranging to 30 meters high) in many places in West Fork quadrangle are also associated with outcrops of the Pitkin Limestone. Finally, sandstone units of the Atoka Formation form bluffs and cap many of the mountaintops in the southern portion of West Fork quadrangle.

Previous Work.—The Carboniferous geology of the southern Ozark region has attracted worldwide interest because of exposures of the Morrowan Series at the base of the Pennsylvanian System and for the excellent outcrops of fossiliferous strata in proximity to the Mississippian-Pennsylvanian boundary (Frezon and Glick, 1959; Manger and Sutherland, 1984; McFarland, 1998). The geologic history and depositional dynamics of this interval continue to attract the attention of the geologic community as a means of investigating the interplay of tectonics and eustasy in the development of continental margin and foreland
basin sequences (Houseknecht, 1986; Viele, 1989; Ethington et al., 1989; Thomas, 1989; Viele and Thomas, 1989; Handford and Manger, 1990, 1993; Valek, 1999; Hudson, 2000; Anderson, 2001; Combs, 2001; Cooper, 2001). However, despite continued interest in the Carboniferous stratigraphy of northern Arkansas, no detailed mapping of the Carboniferous geology of West Fork quadrangle or its vicinity has occurred since thesis work.
could be used to determine the bedrock stratigraphy in these areas (J.T. King, 2001; M.E. King, 2001).

Locations of outcrop sites for individual stratigraphic members and observed geologic structures were determined using global positioning system (GPS) receivers capable of receiving differential corrections. These receivers typically have horizontal accuracy of approximately 5 m. For each outcrop or sample location, Universal Transverse Mercator (UTM) coordinates (eastings and northings relative to WGS 84 datum) were noted in the field notebook, and the location was indicated on the field map. A Garmin Etrex Summit with a built-in barometric pressure gauge was used to determine elevations.

A total of 486 field sites was recorded using these methods throughout West Fork quadrangle. These locations were recorded onto a 1:24,000 topographic map in the field, logged into the field book, and later entered into a spreadsheet database that facilitated their transfer to the GIS.

**Digital Mapping and Geographic Information System.** A GIS is a computer system that records, stores, and analyzes geospatial information. Information regarding field geologic relations was transferred from the field map to a digital raster graphic (DRG) of West Fork quadrangle using a “heads-up” digitizing method. Using this method, geologic contacts were drawn directly on the computer screen by moving the cursor over a digital raster graphic (DRG) of West Fork quadrangle and clicking the mouse button at short intervals to trace contacts onto the displayed topography (Sullivan, 1999). Each stratigraphic unit was digitized as a separate layer within the geographic information system such that the display of each layer could be toggled on or off. Faults were digitized as lines onto a separate layer as well. Once all stratigraphic units and geologic structures were digitized, map layers representing those stratigraphic units and geologic structures could be displayed hierarchically to generate the geologic map of the study area (Figs. 4 and 5). A legend for the map is presented as Figure 6. The final step in preparing the digital geologic map was to convert all data layers to several digital formats to ensure compatibility with popular GIS applications. Digital formats produced for this study were 1) MapInfo native format, 2) ArcView shape files, and 3) AutoCad DXF.

All data were archived on CD-ROM.

**Results**

In West Fork quadrangle, the Mississippian System is represented by, in ascending order, the Fayetteville Shale and the Pikin Formation (Simonds, 1891; Adams and Ulrich, 1904, 1905; Purdue, 1907; Croneis, 1930; Frezon and Glick, 1959; Haley et al., 1976; McFarland, 1998). The Mississippian System comprises a substantial portion of the

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**Methods**

Field mapping of West Fork quadrangle was conducted throughout the summer of 2000 accessing various locations from a network of county and state roadways or on foot. In areas of low relief where outcrops were poor or missing, a two-meter dutch augur was used to sample soil and weathered rock. Commonly, rock fragments and soil type

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**Fig. 2.** Generalized stratigraphic column of West Fork quadrangle, Washington County, Arkansas (adapted from Brown, 2000; M.E. King, 2001).
Fig. 3. United States Geological Survey 7.5-minute topographic quadrangle map of West Fork quadrangle, Washington County, Arkansas.
Fig. 4. Map showing bedrock geology northern half of West Fork quadrangle digitized onto West Fork quadrangle 7.5-minute digital raster graphic (DRG).
Fig. 5. Map showing bedrock geology southern half of West Fork quadrangle digitized onto West Fork quadrangle 7.5-minute digital raster graphic (DRG).
### Lithostratigraphy

<table>
<thead>
<tr>
<th>Formation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atoka Formation</strong></td>
<td>Marine sequence of mostly tan to gray silty sandstones and grayish-black shales; 5 - 200 meters thick.</td>
</tr>
<tr>
<td><strong>Trace Creek Member</strong></td>
<td>Dark-gray shale with some beds of sandstone; 20 - 32 meters thick.</td>
</tr>
<tr>
<td><strong>Kessler Limestone Member</strong></td>
<td>Bioclastic and oolitic limestone that contain abundant oncoliths, traces of clay-pebble conglomerate and minor amounts of calcareous sandstone; 1 - 3 meters thick.</td>
</tr>
<tr>
<td><strong>Woolsey/Dye Member</strong></td>
<td>Composed of terrestrial sediments comprised of dark-gray, fissile shale often interbedded with thin siltstones. A thin coal bed, called the Baldwin Coal, occurs near the top of the Woolsey. Dye - dark gray, marine shale. 2 - 40 meters total thickness.</td>
</tr>
<tr>
<td><strong>Brentwood Member</strong></td>
<td>Sequence of limestones separated by thick intervals of dark shale. The limestone has prominent cross bedding and contains quartz sand; 4 - 30 meters thick.</td>
</tr>
<tr>
<td><strong>Prairie Grove Member</strong></td>
<td>Composed of thin to massive, often crossbedded, frequently pitted (&quot;honeycomb weathering&quot;), limy sandstone or variously sandy limestone with lenses of relatively pure, crinoidal, highly fossiliferous limestone and oolitic limestone; 0 - 50 meters thick.</td>
</tr>
<tr>
<td><strong>Cane Hill Member</strong></td>
<td>Composed of dark gray silty shale interbedded with siltstone and thin bedded fine-grained sandstone; 0 - 30 meters thick.</td>
</tr>
<tr>
<td><strong>Pitkin Limestone Formation</strong></td>
<td>Represented by a fine to coarse grained, oolitic, bioclastic limestone; 5 - 30 meters thick.</td>
</tr>
<tr>
<td><strong>Upper Shale</strong></td>
<td>Black fissile shale with abundant small concretions; 3 - 12 meters thick.</td>
</tr>
<tr>
<td><strong>Wedington Member</strong></td>
<td>Gray to brown, fine-grained, very hard, sometimes calcareous sandstone. Upper 3cm often is a highly fossiliferous red limestone; 1 - 10 meters thick.</td>
</tr>
<tr>
<td><strong>Lower Shale</strong></td>
<td>Black fissile shale with large septarian concretions near the base; 50 meters.</td>
</tr>
</tbody>
</table>

#### Symbols
- **Contact**
- **Faults**

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Fig. 6. Legend to accompany geologic map of West Fork quadrangle (Figs. 4 and 5).
surface area of West Fork quadrangle (Figs. 4 and 5). Each formation of the Mississippian System contains marine fossils, thus indicating marine depositional environments throughout this portion of the stratigraphic succession.

The Fayetteville Shale was named for Fayetteville, Arkansas. Its type locality is in the valley of the West Fork of the White River in Washington County south of the city of Fayetteville (Simonds, 1891). The Fayetteville Shale is typically black to dark gray, organic-rich, and calcareous in places. It locally contains abundant septarian concretions ranging from a few inches to almost a meter in diameter, and some contain hydrocarbons and siderite cement. Benthic fossils, though rare, include brachiopods and mollusks. The Fayetteville Shale is better known for its fossil cephalopods – goniatites and orthoconic nautiloids. Ammonoids were often pyritized, with some silicified fossils also present (McFarland, 1998). The Fayetteville Shale is subdivided into two informally named stratigraphic units and one formal member: lower Fayetteville Shale (informal), the Wedington Sandstone (formal), and the upper Fayetteville Shale (informal).

The lower Fayetteville Shale is black fleshy shale. The base is not exposed in West Fork quadrangle. The lower Fayetteville Shale outcrops occur widely throughout the northern half of West Fork quadrangle (Fig. 4). Throughout this unit, small ironstone concretions of cobble size and smaller occur. The shale often weathers to expansive clay, resulting in damage to foundations of structures built on this shale. Streams incised into the lower Fayetteville Shale have deep, narrow channels with mud bottoms. Valleys floor by lower Fayetteville Shale are broad with low relief (Fig. 4). Rarely, the lower Fayetteville shale forms steep slopes where the overlying Wedington Sandstone protects it from weathering and erosion. Where the lower Fayetteville Shale is located on hillsides, mass wasting is commonly observed.

The Wedington Sandstone Member of the Fayetteville Shale is tan to gray, well-indurated, very fine- to medium-grained sandstone with an average thickness of 2 m (Fig. 7A). The thickest observed outcrop of Wedington Sandstone (approximately 10 m) is located on the north bank and bluff of the West Fork of the White River in the town of West Fork (Fig. 7B). The Wedington Sandstone is often capped by a thin layer of limestone (up to 5 cm thick) containing abundant brachiopods. The upper Fayetteville Shale is a black, fleshy shale that contains abundant iron concretions (< 0.2 m diameter). This informally-named member of the Fayetteville Shale is much thinner than the lower Fayetteville shale. The upper Fayetteville shale weathers quickly to expansive clay and is rarely observed in outcrop. The shale is usually identified by auguring 1 - 2 m and recovering clay mixed with abundant small concretions.

The Pitkin Formation is the uppermost formation of the Mississippian System in West Fork quadrangle (Easton, 1942; Tehan, 1976). The Pitkin Formation was named for exposures near Pitkin post office in Washington County, Arkansas (Adams and Ulrich, 1904). However, later study established that this exposure was not the Pitkin Formation, but the Brentwood Member of the Bloyd Formation (Tehan, 1976). Adams and Ulrich (1904) did note a cliff of Pitkin Formation exposed along what is now U.S. Highway 71 between Woolsey and West Fork, and this outcrop was later designated as the type section for the formation by Henbest (1953). Typically, the Pitkin Formation is an oolitic, bioclastic limestone containing fossils of crinoids, brachiopods, bryozoans, corals, bivalves, gastropods, cephalopods, trilobites, conodonts, and occasionally shark teeth. Chert occurs sometimes at either the top or bottom of the interval in some localities; an excellent example of the black chert of the Pitkin Formation was observed in the extreme central-western portion of West Fork quadrangle where the Pitkin Formation forms a natural dam on the Illinois River (Fig. 8).

In West Fork quadrangle, the top of the Pitkin Formation is an erosion surface with minor relief overlain unconformably by the Cane Hill Member of the Hale Formation (McFarland, 1998; Tehan, 1976). The lowermost unit of the Cane Hill Member is sometimes conglomerate with reworked clasts of the Pitkin Formation. This unconformable contact also represents the Mississippian – Pennsylvanian boundary (Handford and Manger, 1990, 1993).

The Pennsylvanian System in West Fork quadrangle is represented by, in ascending order, the Hale Formation, the Bloyd Formation, and the Atoka Formation (Simonds, 1891; Adams and Ulrich, 1904, 1905; Purdue, 1907; Croneis, 1930; Frezon and Glick, 1959; Haley et al., 1976; Handford and Manger, 1990, 1993; McFarland, 1998). The Pennsylvanian strata form the highest elevations in West Fork quadrangle.

The Hale Formation was named for Hale Mountain in the vicinity of Cane Hill, Washington County, Arkansas (Adams and Ulrich, 1903). The two members of the Hale Formation are (in ascending order) the Cane Hill Member and the Prairie Grove Member (Adams and Ulrich, 1905; Henbest, 1953; Cate, 1962). The Cane Hill Member is comprised of several lithologic components: a basal tan, very thin-bedded, medium grained, siliceous/calcareous sandstone or calcareous conglomerate containing limestone pebbles reworked from the underlying Pitkin Formation, alternating with very thin-bedded (< 0.15 m thick) siltstone and sandstone layers, often ripple-marked, and thick, tan, ripple-marked, medium grained, siliceous sandstone (Cate, 1962; Handford and Manger, 1990, 1993; M.E. King, 2001). The Prairie Grove Member is composed of thin to massive, commonly cross-bedded, calcareous sandstone or
Fig. 7. A) The Wedington Sandstone Member of the Fayetteville Formation. This well-cemented sandstone commonly forms a bench of two meters in West Fork quadrangle. Located at UTM (WGS-84) Zone 15 S 396222 3983128. B) Thick section (approximately 10 m) of the Wedington Sandstone Member of the Fayetteville Formation exposed in a park along the West Fork of the White River in the community of West Fork, Arkansas at UTM (WGS-84) Zone 15 S 393223 3976680.

sandy limestone with lenses of crinoidal and oolitic limestone. Occasional bryozoan bioherms (Hoaster, 1996) are observed within the Prairie Grove Member in West Fork quadrangle (Fig. 9). Prairie Grove Member outcrops typically have a mottled appearance when fresh. The contact of the Prairie Grove Member on the underlying
Cane Hill Member is considered unconformable (McFarland, 1998).

The Bloyd Formation was named from Bloyd Mountain, 14.5 km southwest of Fayetteville, Washington County, Arkansas (Purdue, 1907). The Bloyd Formation consists of (in ascending order) the Brentwood Limestone Member, the Woolsey-Dye Shale Members, and the Kessler Limestone Member (Purdue, 1907; Haley et al., 1976; McFarland, 1998).

The Brentwood Limestone Member is a succession of well-indurated, cross-bedded limestone beds separated by intervals of thin, dark shale (McGilvery, 1982).

The overlying Woolsey Member is composed of greenish gray silty shale in West Fork quadrangle and sometimes contains a one-meter thick, medium grained, siliceous sandstone layer. Plant fossils were observed in the Woolsey Member, as well as a coal bed known as the Baldwin Coal (McFarland, 1998) that is 0.2 m thick and appears to be continuous throughout West Fork quadrangle (J.T. King, 2001) and widespread in Fayetteville quadrangle (M.E. King, 2001) where it serves as a convenient marker horizon. The Woolsey Member weathers to expansive clay and forms gentle to moderate slopes. It is commonly observed in ravines and excavations and by auguring. Seeps and springs are common at the contact between the Woolsey Member and the Brentwood Member.

The Dye Member of the Bloyd Formation was observed in a roadcut of Interstate Highway-540 in West Fork quadrangle. It is a black fissile shale with thin beds of hard, fine grained, dark gray sandstone (Fig. 10). The Dye Member is not mappable on the 1:24,000 scale in West Fork quadrangle and therefore was lumped with the Woolsey Member during mapping.

The Kessler Limestone Member was observed throughout West Fork quadrangle. It was observed in roadcuts and as small bluffs up to three meters high on steep hillsides or forming a bench on moderate slopes. This limestone usually yields a strong smell of petroleum distillate and weathers to a dull tan to brown, crumbly surface. In some areas, it contains abundant sand. The top of the Kessler Limestone is a phosphatic conglomerate representing the unconformity between the Morrowan and
The Atoka Formation was named for the town of Atoka, Oklahoma (Taff and Adams, 1900). The Atoka is a series of tan to gray, silty sandstones and grayish-black shales. In West Fork quadrangle, the lowermost member of the Atoka is the Trace Creek Shale. It rests unconformably on the Kessler Limestone Member of the Bloyd Formation. The Trace Creek Shale is black, fissile shale with some thin beds of sandstone. This unit was rarely observed in outcrop but instead usually forms a moderate slope below the first sandstone of the Atoka Formation to the bluff or bench formed by the Kessler Limestone Member of the Bloyd Formation (Fig. 12).

Above the Trace Creek Shale Member, the Atoka Formation forms prominent bluffs composed of sandstone interbedded with shale slopes. The Atoka Formation caps the Boston Mountains in the southern portion of West Fork quadrangle. The Atoka Formation in West Fork quadrangle is typically fine- to medium-grained, well-indurated sandstone alternating with black shale. Many road cuts along Interstate Highway 540 in the southern third of West Fork quadrangle were carved out of the Atoka Formation.

**Structural Geology.**—West Fork quadrangle is situated on the southern flank of the Ozark Dome that is centered in southeast Missouri (Croneis, 1930). Regional dip of exposed strata is generally less than 5° to the south. Fractures were observed in outcrops of both Mississippian and Pennsylvanian strata, and these fractures were believed to result from brittle deformation related to flexure of the Ozark Plateaus and formation of the Ozark Dome during the Ouachita orogeny (Viele, 1989; Viele and Thomas, 1989; Hudson, 2000).

Fractures were observed on pavement outcrops of the Pitkin Formation (Mississippian) and the Brentwood Member of the Bloyd Formation (Pennsylvanian). Fractures on the surface of the Pitkin Formation have strikes of N90°E and N20°W. Fractures observed on the surface of the Brentwood Member of the Bloyd Formation in the bed of Winn Creek have strikes of N50°E.

Several faults were observed in West Fork quadrangle. The dominant structure in the quadrangle is the Fayetteville Fault, which crosses the northwest quarter of the quadrangle.
from southwest to northeast (Figs. 4 and 5). The Fayetteville Fault is a normal fault downthrown to the southeast. In West Fork quadrangle, the fault is poorly expressed because it occurs in weathered deposits of the Fayetteville Shale. A geologic worksheet (West Fork quadrangle) prepared by the Arkansas Geological Commission during preparation of the 1:500,000 geologic map of Arkansas (Haley et al., 1976, 1993) showed several parallel faults associated with the Fayetteville Fault, suggesting a broader fault zone associated with the Fayetteville Fault. These faults were apparently interpreted from lineaments observed on aerial photographs by Haley (Dr. D. Zachry, personal communication, 2002). However, focused efforts by the authors to locate field evidence for these faults proved difficult because the faults are wholly within deeply weathered profiles of the Fayetteville Shale. The faults are included in the present report as represented on the Arkansas Geological Commission worksheet compiled in conjunction with development of the state geologic map (Haley et al., 1976, 1993).

Other faults in West Fork quadrangle are oriented with northeast and east-west strikes (Figs. 4 and 5). A prominent fault in the southern portion of the quadrangle (Fig. 5) crosses Interstate Highway 540 with an east-west strike. This fault is downthrown substantially to the south such that south of the fault, the Mississippian section is no longer observed. However, the elevation of the Kessler Limestone (uppermost member of the Bloyd Formation) remains the same on the north and south sides of the fault. Thus, it appears that activity on this fault occurred prior to deposition of the Kessler Limestone.

Discussion

The stratigraphy of West Fork quadrangle is composed of alternating layers of shale, limestone, and sandstone in genetically related packages bound by prominent regional unconformities. These depositional series represent the
response of the sedimentary system of northwest Arkansas to fluctuating relative sea-level changes during the late Mississippian and Pennsylvanian Periods.

The Mississippian (Chesterian) Pitkin Formation rests conformably on the Fayetteville Shale. The Pitkin Formation represents a shallow-marine inner shelf environment (Handford and Manger, 1990). The end of this deposition was clearly a regressive phase that exposed the top of the Pitkin Formation subaerially and eroded it. North of West Fork quadrangle, in the Fayetteville quadrangle, the Pitkin Formation was completely eroded and the overlying Cane Hill Member of the Hale Formation (Pennsylvanian) was deposited unconformably on the Fayetteville Shale. Development of the Mississippian-Pennsylvanian unconformity is the major geologic event recorded by strata in West Fork quadrangle.

The Pennsylvanian Cane Hill Member of the Hale Formation was deposited across the eroded top of the Pitkin Formation as seas transgressed the erosional surface. Pebbles of Pitkin Formation were incorporated into basal Cane Hill Member deposits. However, relative sea-level rise over the top of the Mississippian-Pennsylvanian unconformity was apparently slight as the Cane Hill Member represents tidal deposits throughout its extent. Relative sea-level rise apparently continued with deposition of the Prairie Grove Member (Hale Formation) and Brentwood Member (Bloyd Formation). The Brentwood Member represents a broad transgression interrupted by lesser regressions and transgressions. A final regressive phase terminated Brentwood deposition (McGilvery, 1982). Following the regressive phase, the Morrowan Woolsey Member of the Bloyd Formation was deposited in a brackish
Fig. 12. Bloyd Formation – Atoka Formation contact. Road cut on the west side of Interstate Highway 540 shows the contact of the Kessler Limestone Member (Bloyd Formation) and Trace Creek Member (Atoka Formation) representing the Morrowan-Atokan. Location UTM (WGS-84) Zone 15 S 392505 3973721.

water environment that included deposition of the Baldwin Coal (McGilvery, 1982). Continued marine incursion during the Morrowan epoch is indicated by deposition of the Dye Member (a marine shale; Henbest 1953; McGilvery, 1982) of the Bloyd Formation unconformably on the Woolsey Member, culminating with deposition of the Kessler Limestone Member and eventual relative sea-level fall leading to development of the phosphatized, conglomeratic upper surface of the Kessler Member. This erosional conglomerate represents the Morrowan-Atokan unconformity. Finally, alternating deposition of nearshore marine and deltaic sandstone, shale, and siltstone of the Atoka Formation suggests renewed, minor, and fluctuating relative sea-level episodes in West Fork quadrangle during the Atokan epoch.

ACKNOWLEDGMENTS.—Geologic mapping of Fayetteville quadrangle was accomplished through a grant from the United State Geological Survey National Cooperative Geologic Mapping Program under assistance award #00HQAG0084.

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Bedrock Geology of West Fork Quadrangle, Washington County, Arkansas


Millipeds (Arthropoda: Diplopoda) of the Ark-La-Tex. I. New Distributional and State Records for Seven Counties of The West Gulf Coastal Plain of Arkansas

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Abstract

Unlike the Diplopoda of the Ozark Mountains region of north Arkansas, the millipeds of the West Gulf Coastal Plain of the state are poorly known. During the winter months of 2001-2002, we collected millipeds in four counties (Hempstead, Lafayette, Little River, and Miller) of southwest Arkansas and three counties (Columbia, Nevada, and Ouachita) of south Arkansas. We found the following species/subspecies Eurymerodesmus dubuis and Pseudopolydesmus pinetorum from Hempstead County; E. birdi birdi, E. mundus, Oxidus gracilis, and Pseudopolydesmus ? minor from Lafayette County; Aniuslus (Hakiulus) diversifrons diversifrons, P. pinetorum, and a possible new species of Tiganogona in Little River County; Abacion ? texense, E. mundus, O. gracilis, P. pinetorum, Thrinaxoria lampra, and a new species of Aniuslus (Hakiulus) from Miller County; Auturus louisianus louisianus, E. dubuis, Cambala minor, O. gracilis, P. pinetorum, and a female xystodesmid of the tribe Pachydesmidae from Cullman County; Virgoitillus minutus, C. minor, P. pinetorum, and A. I. louisianus from Nevada County; and P. pinetorum, Eurymerodesmus sp., Narcus americanus, and C. minor from Ouachita County. A new state record is documented for T. lampra from Miller County, and the finding of V. minutus in Miller and Nevada counties represents the southwesternmost distributional records for the genus and species. To our knowledge, all millipeds reported herein for Little River County are the first ever documented for that county, including a potentially new species of Tiganogona, a genus known previously from Carroll, Clay, Sebastian, and Washington counties, Arkansas, Lincoln Parish, Louisiana, and more distant locales in Missouri and Indiana.

Introduction

Although there has never been a consolidated listing of Arkansas millipeds, the fauna of the mountainous northwestern region was well collected by the late Dr. Nell B. Causey (1910-1979), who lived for many years in Fayetteville, Washington County. She collected extensively in that region of the state and amassed a large collection of millipeds (transferred to the Florida State Collection of Arthropods, Gainesville, upon her death), publishing numerous papers on these arthropods (Causey, 1950, 1951, and others). However, little collecting has been done in other parts of the state, particularly the Mississippi Valley and Gulf Coastal Plain of southern and southwestern Arkansas. (Shelley, 1990a). We have therefore focused our fieldwork on this relatively neglected area, particularly the southwestern corner of Arkansas near Texarkana (Little River and Miller counties). In the first in a series of reports on the millipeds of the Ark-La-Tex region, we report several new distributional records for Arkansas counties, including a new state record.

Materials and Methods

Between October 2001 and March 2002, we collected millipeds in four counties (Hempstead, Lafayette, Little River, and Miller) of southwest Arkansas and three counties (Columbia, Nevada, and Ouachita) of south Arkansas. The majority of specimens were taken from damp areas off trails in pine and hardwood forests by overturning decaying logs and leaf litter with potato rakes. Occasional millipeds were collected by peeling bark off rotting logs and stumps. At each locale, specimens were placed in individually labeled vials containing 70% ethanol and returned to the laboratory for preliminary processing and sorting. Millipeds were shipped to the third author (RMS) and identified to the lowest taxonomic level by examining aspects of the male genitalia (aperture and gonopods). Voucher specimens are deposited in the North Carolina State Museum of Natural Sciences (NCSM).

Results and Discussion

A total of 15 species and subspecies of millipeds, representing 11 genera, 11 families, and six orders was
found during our six-month survey; there were also two unidentifiable samples, one of juveniles of *Eurymerodesmus* and one of a female of the family Cleidogonidae. By far the most common order represented in our collection was the Polydesmida, the largest order in the class Diplopoda, with eight species in five families. The most common species was *Pseudopolydesmus pinetorum* (Bollman, 1888) collected from all seven counties surveyed. A complete list of taxa collected is presented below and annotated with distributional and ecological information.

**Annotated List**

Order Polydesmida
Family Xystodesmidae

*Thrinaxoria lampra* (Chamberlin, 1918). A male and female of *T. lampra* were collected in Miller County, 1.6 km S Genoa off St. Hwy 196 on 14 February 2002. This substantiates the prediction of Shelley (1984a) that it be listed as probable for southwestern Arkansas and constitutes new state records for both the genus and species. *Thrinaxoria lampra* is known from neighboring Caddo Parish, Louisiana (Shelley, 1984a), and from Longview, Gregg County, Texas (Shelley, 1990b). In addition, a female xystodesmid, assigned to the tribe Pachydesmini because of the large, thickened body and transverse sternal swellings between the legs, was collected from Logoly State Park in Columbia County on 19 December 2001. While geographically consistent with the known range of *T. lampra*, this individual is much larger than the female from Miller County and ones that we have collected in northeast Texas and has a different color pattern; furthermore, the sternal swellings are consistent with the genus *Pachydesmus* Cook (Hoffman, 1958). This genus comprises two species, *P. crassicutis* (Wood), with eight subspecies occurring east of the Mississippi River from Shelby County, Tennessee, and Baton Rouge, Louisiana, to southern South Carolina and Gaston County, North Carolina (Hoffman 1958; Shelley and Filka, 1979; Filka and Shelley 1980), and *P. clarus* (Chamberlin), which occurs west of the Mississippi in Beauregard, Grant, LaSalle, Lincoln, Natchitoches, and Rapides parishes, Louisiana, and Gregg and Newton counties, Texas (Hoffman, 1958; Causey, 1963; Shelley, 1990b). Additional collecting of males at this site will be necessary to confirm its identity.

Family Euryuridae

*Autorus louisianus louisianus* (Chamberlin, 1918). Specimens were taken from the Spring Branch trail at Logoly State Park, Columbia County, on 19 December 2001. Shelley (1982) revised the genus and summarized locales for Arkansas. All seven Arkansas counties reported previously for *A. l. louisianus* are south of the Arkansas River (Shelley, 1982). These are new county records and supplement its known range in south Arkansas.

Family Eurymerodesmidae

*Eurymerodesmus* sp. Juveniles not identifiable to species were collected from Poison Springs State Historical Park trail in Ouachita County. Additional collecting will be necessary in an attempt to obtain males for specific identity.

*Eurymerodesmus dubuis* Chamberlin, 1943. Adult males and juveniles of this species were found at Logoly State Park on 28 December 2001 and 3.2 km SW Spring Hill off State Hwy 353 in Hempstead County on 14 February 2002. Shelley (1990a) previously reported *E. dubuis* from Ouachita County. Hempstead County represents a new county record.

*Eurymerodesmus mundus* Chamberlin, 1942. Previous Arkansas locales for *E. mundus* include only two counties, Polk and Sevier, in the western part of the state (Shelley, 1990a). We collected five males of *E. mundus* on 14 February 2002 from the same Lafayette County locale noted herein for *E. b. birdi*. An additional male was taken on 14 February 2002 at the same site in Miller County reported for *T. lampra*. Although *E. mundus* has not been reported from Louisiana, we anticipate finding it in suitable habitat in the northwestern part of adjacent Caddo Parish.

Family Paradoxosomatidae

*Oxidis gracilis* (Koch, 1847). Juveniles of this common introduced species were taken on 17 February 2002 from Columbia County (Logoly State Park) and our Lafayette County site on 14 February 2002, and a male was collected in Doddridge, Miller County, on 1 March 2002. It should be expected in urban habitats throughout the Coastal Plain of southern Arkansas.

Family Polydesmidae

*Pseudopolydesmus minor* (Bollman, 1888). A small-bodied male of the genus *Pseudopolydesmus* was collected on 14 February 2002 at the Lafayette County site and is provisionally assigned to this poorly-known species. The specimen is clearly distinct from the more
common, larger-bodied P. pinetorum because of its small size and different gonopods. The genus Pseudopolydesmus occurs widely across eastern North America from James Bay, Ontario, to northern peninsular Florida and, east-west, from the Atlantic Ocean to the western periphery of the eastern forested biome from Texas to Nebraska. While the genus has not been revised, the species in the eastern half of the range have been reasonably well defined in faunal studies (Shelley, 1978, 1988; Hoffman, 1974, 1999), but the midwestern species, especially those occurring west of the Mississippi River, are poorly known, and modern drawings of the diagnostic gonopodal features are not available. This fauna thus needs comprehensive review, and lacking such, our determination is tentative.

Pseudopolydesmus pinetorum (Bollman, 1888). While our determination of P. minor is provisional, we are more confident about P. pinetorum because of the dactyloform process at midlength on the lateral side of the gonopodal telopodite. This is the most common species in woodlands west of the Mississippi River, and we found it throughout the winter study period from all the study sites in Columbia, Hempstead, Lafayette, Little River, Miller, Nevada, and Ouachita counties. Pseudopolydesmus pinetorum has been reported previously from extreme NE Texas in Bowie County (Stewart, 1969).

Order Spirostreptida
Family Cambalidae
Cambala minor Bollman, 1889. Numerous males, females, and juveniles of this species were collected on 28 December 2001 and 17 February 2002 from Columbia County, on 29 October 2001 from Ouachita County, and on 19 December 2001 in Nevada County. Members of the genus appear to prefer cool weather conditions, as noted by Shelley (1978, 1979) for the representatives in the southern Appalachian Mountains and eastern Piedmont Plateau. Identification is somewhat difficult since they possess small gonopods recessed internally, with both leg pairs on segment seven modified into gonopods.

Order Chordeumatida
Family Cleidogonidae
Unidentifiable Cleidogonidae. A single female representing an unidentifiable genus and species of cleidogonid was collected from Columbia County on 17 February 2002. It will be necessary to obtain males from this site to render a determination.

Tiganogona sp. A possible new species of Tiganogona was collected along the Waterfowl and Wildlife Way trails of Millwood State Park in Little River County on 24 November 2001, 19 December 2001, and 3 January 2002. Three males were encountered on the underside of decaying oak bark in flooded habitat. These specimens represent a significant generic range extension, as Tiganogona is previously known from northern and westcentral Arkansas (Carroll, Clay, Sebastian, and Washington counties), northcentral Louisiana (Lincoln Parish), and more distant locales in Missouri and Indiana.

Order Callipodida
Family Abacionidae
Abacion ?texense (Loomis, 1937). A female of Abacion was collected on 10 March 2002 in Miller County (Genoa site). Two species of Abacion are known from Arkansas, A. tessellatum Rafinesque and A. texense (Shelley 1984b), and we provisionally assign our specimen to the latter based on its small size and the fact that A. texense is the only species known from southwestern Arkansas. Previous Arkansas records (shown on a county dot map by Shelley 1984b, Fig. 12) are from Clark, Hempstead, and Pike counties, so Miller County constitutes a new county record. It is rather surprising that this is the only specimen of both the genus and species collected during our study, as Abacion is very common throughout the eastern United States, and A. texense is extremely abundant in Louisiana and eastern Texas.

Order Julida
Family Parajulidae
Aniulus (Hakilus) diversifrons diversifrons (Wood, 1867). A male and female of this subspecies was collected from the Millwood State Park trail sites in Little River County on 3 January 2002. It represents an additional species for an Arkansas county previously devoid of milliped records.

Aniulus (Hakilus) n. sp. A single male representing an undescribed species of this subgenus was collected at the Miller County site on 14 February 2002. More males are desirable to facilitate description. This specimen possesses a strong, spiniform epiproct, whereas the structure is short and blunt in other representatives of the subgenus. This is the first record of the subgenus for the county.

Family Blaniulidae
Virgulius minutus (Brandt, 1841). Two juvenile females of V. minutus were collected on 19 December 2001 from Nevada County and on 10 March 2002 from Miller County (Genoa site) under the bark of decaying pine stumps. The only previous record of the species in Arkansas was by Bollman (1888), who reported it from Little Rock, Pulaski County, and “Argenta,” which we cannot locate. As the species’ range includes much of the southeastern United States from Louisiana north to Illinois and Pennsylvania and east to North Carolina, our specimens are both new county records and the southwesternmost localities for V. minutus in the United States (Enghoff and Shelley, 1979; Enghoff, 1984).
Millipedes (Arthropoda: Diplopoda) of the Ark-La-Tex: I. New Distributional and State Records for Seven Counties of The West Gulf Coastal Plain of Arkansas

Order Spirobolida
Family Spirobolidae

Narceus americanus (Beauvois, 1805). Although N. americanus is very common in much of the eastern United States, it is less so west of the Mississippi River, and we only encountered one individual, an adult female from the Poison Springs site in Ouachita County during our six-month study period. It is one of the few millipeds that can be identified without an adult male.

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Millipeds (Arthropoda: Diplopoda) of Ark-La-Tex. II. Distributional Records for Some Species of Western and Central Arkansas and Eastern and Southeastern Oklahoma

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Abstract

We collected millipeds between November 2001 and March 2002 at several sites in the Ouachita Provinces of western (Garland, Hot Spring, Pike, and Polk counties) and central Arkansas (Pulaski County) and the Ouachita and Kiamichi Provinces of southeastern Arkansas (LeFlore and McCurtain counties). The following millipeds were found: Eurymerodesmus dubius, Auturus louisianus louisianus, Pseudopolydemos pinetorum, and Cambala minor in Garland County; Eurymerodesmus sp., A. l. louisianus, P. pinetorum, and juveniles of the family Parajulidae (tribe Aniulini) from Hot Spring County; E. dubius, A. l. louisianus, and juveniles of the family Cleidogonidae from Pike County; Brachycybe lecontei, A. l. louisianus, Abacion tesselatum, and P. pinetorum in Polk County; Eurymerodesmus pulaski, P. pinetorum, Auturus evides, G. minor, B. lecontei, and a possible new species of Cleidogona in Pulaski County; A. l. louisianus, Apheroria virginiensis ?reducta, P. pinetorum, Narceus americanus, and E. dubius in McCurtain County; and B. lecontei, A. l. louisianus, Eurymerodesmus b. birdi, A. ?tesselatum, and juveniles of the family Parajulidae (tribe Aniulini) in LeFlore County. Two new state records are documented for Oklahoma: B. lecontei (Planynogastrea: Andrognathidae), a record not only for the genus and species but also for the family and order; and E. dubius, the westernmost locality ever reported for the species.

Introduction

As part of an on-going worldwide effort to document the species within one of the poorest known arthropod classes, the Diplopoda, we continue our millipede recordings in various parts of the Ark-La-Tex region. Other than the concurrent report by McAllister et al. (2002), little collecting has been done in this area, particularly in Arkansas and Oklahoma, since the mid-1970’s, when the late Dr. Nell B. Causey effectively retired. We have therefore focused our fieldwork on this relatively neglected area, particularly western and central Arkansas and far eastern and southeastern Oklahoma. This paper, the second in a series of works on the fauna of the Ark-La-Tex, details several new distributional records for Arkansas and Oklahoma counties and two new state records for Oklahoma.

Materials and Methods

Between November 2001 and March 2002, we collected millipeds in five counties (Garland, Hot Spring, Pike, Polk, Pulaski) of western and central Arkansas and two counties (LeFlore and McCurtain) of eastern and southeastern Oklahoma. Most of the sites were off trails in state parks and in the Ouachita National Forest where there was an abundance of decaying logs and damp leaf litter, prime millipede habitat. Further methods for collecting and processing millipeds are described by McAllister et al. (2002). Voucher specimens are deposited in the North Carolina State Museum of Natural Sciences (NCSM), Raleigh, North Carolina.

Results and Discussion

A total of 11 species and subspecies of millipeds, representing nine genera, 10 families, and seven orders was found during our survey; there were also unidentifiable juveniles of Eurymerodesmus and individuals belonging to the families Cleidogonidae and Parajulidae (tribe Aniulini) that could not be assigned to genera. By far the most common order represented in our collection is the Polydesmida, the largest in the class Diplopoda, with seven species in four families. The most common species was Auturus louisianus louisianus, collected from four of five Arkansas counties and both Oklahoma counties surveyed. A complete list of taxa collected is presented below and annotated with distributional and ecological information.
Millipedes (Arthropoda: Diplopoda: Arlia-Tenebrionidae). Distributional Records for Some Species of Western and Central Arkansas and Eastern and Southeastern Oklahoma

Annotated List

Order Polydesmida
Family Xystodesmidae

Apheloria virginiensis reducta Chamberlin, 1939. Nine males of A. virginiensis were collected along the David Boren Trail in Beaver’s Bend State Park, McCurtain County, Oklahoma, in January and March 2002. Causey (1954) previously reported this millipede (a single male collected on 20 July 1954) from an unspecified locale somewhere in McCurtain County. Interestingly, the type locality of A. reducta is in the foothills of the Ozark Mountains at Imboden, Lawrence County, Arkansas (Chamberlin, 1939), over 400 km northeast of McCurtain County. Hoffman (1999) reduced reducta to subspecific status under A. virginiensis, the most widely ranging species in the genus, extending from the vicinities of Milwaukee, Wisconsin, and Montreal, Quebec, Canada, to southern Virginia and Kentucky and southeastern Oklahoma (Hoffman, 1999; unpublished specimens collected and examined by the second author). We provisionally assign our specimens to this race pending completion of a generic revision currently in progress by Dr. Hoffman. There is a third locality record for the state, a male, taken at Broken Bow, McCurtain County, by D. C. Arnold on 10 June 1982, in the collection at the Emerson Entomological Museum, Oklahoma State University. The presence of A. v. reducta in southeastern Oklahoma suggests occurrence in proximate parts of southwestern Arkansas and northeastern Texas, where the taxa are currently unknown, but more field work is necessary to determine whether the form occurs widely in the contiguous corners of these states or whether the McCurtain County samples represent an allopatric population. Apheloria v. reducta is a large-bodied species, dorsally black with yellow margins, and emits a fragrant aroma that smells sweet, like almonds or marachino cherries, because of the presence of benzaldehyde in the defensive secretions (Eisner, H. E. et al., 1963, 1967; Eisner, T. et al., 1963; Towers et al., 1972).

Family Eurymeredesidae

Auturus louisianus louisianus (Chamberlin, 1918). Specimens were taken from several locales, including the Pioneer Cemetery Historical Site (Pulaski County), the Queen Wilhelmina State Park, Lake DeGray State Park (Hot Springs County), Hot Springs National Park (Garland County), Daisy State Park and Crater of Diamonds State Park (Pike County), Choctaw Nation Historic site along St. Hwy. 1 (Talimena scenic drive) in LeFlore County, Oklahoma, just outside the Arkansas border, and Beaver’s Bend State Park. This millipede inhabited a variety of environments from sites dominant with pines and/or oaks to ones with mixed pines, oaks, and other hardwoods. Shelley (1982) revised the genus and summarized locales for Arkansas. All seven Arkansas counties reported previously for A. l. louisianus are south of the Arkansas River (Shelley, 1982). Hot Spring and LeFlore counties constitute new county records and supplement the known range in western Arkansas and eastern Oklahoma, respectively.

Auturus evides (Bollman, 1887). Auturus evides was collected in January 2002 from three sites south of the Arkansas River in Pulaski County, Arkansas, including Sweet Home, Boyle Park (western Little Rock), and Pinnacle Mountain State Park. It has the broadest distribution of any of the four species in the genus, extending from the vicinities of Minneapolis, Minnesota, and Champaign-Urbana, Illinois, to central Arkansas and eastern Oklahoma, primarily in the Mississippi Valley, and has been reported previously from Pulaski County at Camp Robinson, north of the Arkansas River (Shelley, 1982). Dowdy (1968) found A. evides exclusively in an oak–hickory forest; however, we collected specimens from predominantly pine areas.

Family Eurymerodesmidae

Eurymerodesmus sp. Juveniles not identifiable to species were collected from Pulaski County (Gilman Road site, Little Rock), Hot Spring Park (Lake DeGray State Park), Pike County (Crater of Diamonds State Park), Beaver’s Bend State Park (McCurtain County, Oklahoma), and Talimena State Park (LeFlore County, Oklahoma). These sites are well removed from each other with different habitat and elevations and probably involve a different species at each; additional collecting is necessary to obtain males for specific identifications.

Eurymerodesmus birdi birdi Chamberlin, 1931. Two males with juvenile phoretic mites (hypopi) were taken at Talimena State Park (LeFlore Co., Oklahoma) in March 2002. Shelley (1990) previously reported E. b. birdi from Bear Den Cave, vic. Talihina, LeFlore County, which is near our collection site.

Eurymerodesmus dubius Chamberlin, 1943. In Arkansas, adult males and juveniles of this species were found along the Mountain Top Trail (elev. 300 m) of Hot Springs National Park (Garland County) and at Lake Greeson/Daisy State Park (Pike County); two males were also taken beside the David Boren Trail at Beaver’s Bend State Park, McCurtain County, the first record of E. dubius from Oklahoma. The type locality is Delight, Pike County, Arkansas (Chamberlin, 1943), and specimens have been previously reported from Garland County (Hot Springs) and seven additional Arkansas counties (Shelley, 1990). More recently, McAllister et al. (2002) reported E. dubius from Hempstead County, Arkansas.

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Eurymerodesmus pulaski (Causey, 1950). The type locality for E. pulaski is just south of Sweet Home, Pulaski County, Arkansas (Causey, 1950), and the species was previously known only from this site and one near Little Rock (Shelley, 1990). We report E. pulaski from an additional Pulaski County site, the west summit trail off St. Hwy 300 (elev. 170 m) at Pinnacle Mountain State Park, which is about 31 km NW of the type locality. Shelley (1990) suggested that Pulaski County, particularly the area around Little Rock, should be meticulously sampled because at least three species may occur there.

Family Polydesmidae

Pseudopolydesmus pinetorum (Bollman, 1888). This is the most common species of the genus in woodlands west of the Mississippi River, and we found this millipede in Polk (Pioneer Cemetery Historical site), Pulaski (Pinnacle Mountain State Park), Hot Spring (Lake DeGray State Park), and Garland (Hot Springs National Park) counties, Arkansas, and McCurtain County, Oklahoma (Beaver’s Bend State Park). The latter locale represents a new county record for P. pinetorum. Stewart (1969) reported P. pinetorum from Bowie County in extreme NE Texas. This genus is badly in need of revision.

Order Spirostreptida

Family Cambalidae

Cambala minor Bollman, 1889. This species was found at only two sites, Pinnacle Mountain State Park (Pulaski County) and Hot Springs National Park, Garland County; previous records from Arkansas include Benton, Clay, Columbia, Howard, Ouachita, Polk, Randolph, Union, and Washington counties (Shelley, 1979). Our specimens represent new county records.

Order Chordeumatida

Family Cleidogonidae

Unidentifiable Cleidogonidae. Several juveniles representing either the genus Cleidogona or Tiganogona were collected from Pike County (Crater of Diamonds State Park). Males are necessary to render a determination.

Cleidogona sp. Two males of a probable new species of Cleidogona were collected off St. Hwy 365 just south of Sweet Home (Pulaski County). They belong to the “C. unita species group,” as defined by Shear (1972), and becomes the second representative of this assemblage along with C. unita Causey, which occurs in southern Illinois and western Kentucky. Studies on this and other potentially new cleidogonid species from the Ark-La-Tex region (see McAllister et al., 2002) are in progress, and those found to be truly new will be formally named and described.

Order Julida

Family Parajulidae

Unidentifiable Aniulini. Several juveniles of this tribe (unidentifiable genus and species) were collected at three sites, including Pulaski County (Little Rock, Gilman Road site), Hot Springs County (Lake DeGray State Park), and LeFlore County, Oklahoma (Chocotaw Nation Historic site). Additional collecting of males is necessary to determine their identity.

Order Callipodida

Family Abacionidae

Abacion tesselatum Rafinesque, 1820. We collected one male and three females of A. tesselatum from Polk County (Pioneer Cemetery Historical site) in March 2002. The species, which ranges from northern Iowa and southern Michigan to the Gulf Coast from Florida to Louisiana, was shown by Shelley (1984, Fig. 12) on a dot map to occur in Polk and other Arkansas counties: Benton, Cleburne, Cross, Jefferson, Stone, and Washington. It is surprising that we did not encounter this species more often as it is relatively common throughout its range. A lone female that we tentatively assign to A. tesselatum because of its large size (i.e., A. texense, a sympatric species, is typically smaller) was collected in March 2002 from Talimena State Park, LeFlore County. Abacion tesselatum would represent a new county record and only the second one from the state of Oklahoma; Shelley (1984, Fig. 12) showed the species in Craig County near the Kansas border. Authentic males of A. tesselatum from this site are necessary to confirm our preliminary identification.

Order Spirobolida

Family Spirobolidae

Narceus americanus (Beauvois, 1805). Although this millipede is very common throughout much of the eastern United States, it is less common west of the Mississippi River. During our five-month study, we encountered only one individual, in March 2002, an adult female from the David Boren Trail at Beaver’s Bend State Park, McCurtain County, Oklahoma. This millipede was taken beneath a decaying pine log that also harbored Eurymerodesmus sp. and A. v. ?reducta.

Order Platydesmida

Family Andrognathidae

Brachycybe lecontei (Wood, 1864). Gardner (1975) revised this family and summarized localities for this southeastern species, which occurs in Alabama, Arkansas, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee, and West Virginia. In Arkansas, B. lecontei is known from Benton, Izard, Logan, Polk, Saline, Scott, Stone, and Washington counties (Gardner, 1975). We also encountered it in Polk County (Pioneer Cemetery Historical site) and document a new county record for the state (Pulaski County, Boyle Park, Little Rock). Brachycybe lecontei occurs in the western tier of counties.
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along the Oklahoma state line (Benton, Washington, Scott, and Polk), and we officially extend it into Oklahoma (LeFlore County, Choctaw Nation Historic site just outside the Arkansas border), which constitutes new state records for the species, genus, family, and order. Our specimens display bright red paranota, in contrast to ones from the southern Appalachians, which are ivory colored. There appears to be a color gradient in *B. lecontei* with individuals becoming more reddish to the west, as the second author collected specimens from Cumberland Falls State Park, Whitley County, Kentucky, in June 2001, that were pink, an intermediate color.

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Co-polymers of Furan with Pyrrole or Thiophene: A Synthetic Study

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Abstract

The use of conductive polymers as a substitute for metallic conductors and semiconductors has attracted much attention in the literature. In particular, aromatic heterocyclic polymers constitute an important class since they possess chemical and electrical stability in both the oxidized (doped) and neutral (undoped) state. Doping a polymer allows one to vary its electrical, mechanical, optical, and thermal properties. The properties of these polymers are promising for their many technological uses such as antistatic coatings, solar cells, and electronic devices. Polyfuran is among the least common heterocyclic polymers. Polyfuran has been reported to be much less stable that either polypyrrole or polythiophene. The preparation of co-polymers of polyfuran with two percent pyrrole or thiophene is reported. The polymers are characterized by 1H NMR, IR, and ESR spectroscopy, and the electrical conductivity of the doped and un-doped synthetic polyfuran and co-polymers is provided.

Introduction

Electronically conducting polymers have attracted a great deal of attention from scientific and technological groups. There are many applications for conducting polymers in fields such as gas sensors (Nigorikawa et al., 1995), rechargeable batteries (Choi et al., 2001), electronic and optical devices (Nguyen and Potje-Kamloth, 1999), and corrosion inhibitors of metal substrates (Rajagopalan and Iron, 2001). In the U.S. many cities spend enormous resources maintaining bridges and high rise structures because of corrosion of the metal surfaces. Recently, conductive polymers have been shown to be very good corrosion inhibitors to metal substrates (Mikalo et al., 2001). For the past ten years polyaniline has generated tremendous interest as a corrosion inhibitor (Kumar and Sharma, 1998). Many investigators believe that redox forms of polyaniline help stabilize a thin oxide layer on the surface of iron (Dalas et al, 2000). Polypyrrole has also received attention due to its ability to inhibit corrosion of metal surfaces (Su and Iron, 2000; Ivanov et al, 2001). Unlike polyaniline, polypyrrole can be prepared even at neutral pH, which can be an advantage (Kang and Geckeler, 2000).

Polymers constructed of heterocyclic aromatic compounds, such as polypyrrole, polythiophene, polyaniline, have also been of particular interest due to their small band gap (1.4 - 3.2 eV) and doping capability. Doping a polymer with a small amount of a metal salt can greatly vary the conductivity of the polymer and so makes it useful in microelectronics and sensors (Kumar and Sharma, 1998). The electrical conductivity of these polymers, both neutral and doped, seems to depend on the degree of disorder in the solid state, including the disorder caused by the dopant (Mikalo et al, 2001; Ivanov et al, 2001).

Fig. 1. Polyfuran in the more stable head to tail configuration.
Polyfuran (Fig. 1) is an aromatic heterocyclic polymer that is fairly uncommon and ill-defined. However, as a five-membered heterocycle polyfuran should have electrical and optical properties similar to polypyrrole and polythiophene, with variations due to the differing electronegativity of the heteroatoms (Ivanov et al., 2001). In 1997, ours was the first reported chemical synthesis of polyfuran from the monomer using a mild oxidizing agent, pyridinium chlorochromate (McConnell et al., 1997). Polyfuran has been shown to be much less stable than polypyrrole with respect to ring opening by nucleophilic reagents (Fig. 1) especially in the oxidized, doped state (Distefano et al., 1991). However, molecular modeling, via HyperChem, indicated that polyfuran can be greatly stabilized either by introducing small amounts of pyrrole or thiophene units throughout the polymer. Co-polymerization techniques to form primarily polypyrrole and polyacilene composites have been used to create stable materials with a wide variety of properties (Aubert et al., 1999; Dalas et al., 2000; Rajagopalan and Iron, 2001). We have therefore synthesized polyfuran and co-polymers (polyfuran with 2% pyrrole and polyfuran with 2% thiophene) in both the doped and undoped states. The \(^1\)H NMR and IR spectra of these polymers show them to be almost completely aromatic with little or no ring opening.

**Materials and Methods**

The \(^1\)H NMR spectra were collected on a Bruker 200 MHz AC 200 superconducting spectrometer. The spectral data was processed by NTONMR software produced by TeleMag. The NMR samples of the polymers were solutions utilizing deuterated dimethyl sulfoxide (DMSO-d\(_6\)) as a solvent with tetramethylsilane (TMS) as an internal standard. The FTIR spectroscopy was performed on a Bio-Rad FTS-40 FTIR spectrophotometer with the samples prepared as KBr pellets. Electron Spin Resonance (ESR) spectra were recorded on a Varian E-4 spectrometer. Direct current electrical conductivity was measured of each copolymer as a pressed pellet of the dry polymer powder by a method described by Lyding et al. (1988). All chemicals were purchased from Aldrich Chemical Company Inc. The tetrahydrofuran (THF) solvent was refluxed and distilled over sodium just prior to use. The furan, pyrrole, and thiophene were also freshly distilled and inhibitor free.

The synthesis of polyfuran was achieved by the following method. In an oven dried flask inhibitor free furan (100 mL) was added to 40 mL of a 0.29 M PCC solution in dry, freshly distilled, tetrahydrofuran (THF) with or without doping agent (0.1 mg silver p-toluene sulfonate). The mixture was refluxed for 2 hours and then stirred at room temperature for 12 hours, resulting in a black, tar-like precipitant. Excess furan and THF were evaporated under reduced pressure. To remove the PCC from the product, the precipitant was repeatedly dissolved in 50 mL dimethyl sulfoxide (DMSO) and re-precipitated by the addition of 200 mL THF. The slurry was stirred for 5 minutes, and then the precipitated polymer was allowed to settle to the bottom of the flask. The mother liquors were then decanted. This re-precipitation process was repeated until essentially all the PCC was recovered from the decanted THF (a minimum of four times). The product was then washed three times with THF (200 mL) and dried under vacuum. (Average yield = 4.2±0.5 grams).

A similar approach was taken for the preparation of copolymers of furan and pyrrole or thiophene. For the copolymers of furan with pyrrole, two percent inhibitor free pyrrole was added, along with the furan, to the 0.29M PCC solution in freshly distilled THF. For the co-polymers of furan with thiophene, two percent inhibitor free thiophene was added instead. The mixture was refluxed for 2 hours and then stirred at room temperature for 12 hours, resulting in a brown to black solid. Excess furan and THF were evaporated under reduced pressure. To remove the PCC from the product, the precipitant was repeatedly dissolved in 35 mL dimethyl sulfoxide (DMSO) and re-precipitated by the addition of 200 mL THF. The slurry was stirred for 5 minutes, and then the precipitated polymer was allowed to settle to the bottom of the flask. The mother liquors were then decanted. This re-precipitation process was repeated until essentially all the PCC was recovered from the decanted THF (a minimum of five times). The product was then washed three times with THF (200 mL) and dried under vacuum. (Average yield = 5.1±0.5 grams).
Results and Discussion

Synthesis.--Polyfuran, like polypyrrole and polythiophene, is a conjugated planar aromatic polymer (Fig. 1). Little research on polyfuran has been reported in the literature compared to that of polypyrrole and polythiophene. The synthesis of polyfuran was first reported in 1984 but only by electrochemical means (Ohsawa et al., 1984). However, the electrochemical formation of polyfuran required an applied potential of > 3 volts. This potential was found to be too oxidizing for the resulting polymer, which decomposed oxidatively. In 1990, Zotti et al. found polyfuran could be formed with a somewhat lower voltage using a Ni(bipy)32+ catalyst and an electro-reduction technique. In 1993, Glenis et al. found that polyfuran could be made by electrochemical polymerization of the tetramer, at a lower potential of 0.75 volts. Glenis et al. (1993) used a variety of dopant anions (i.e. CF3SO3-, BF4-, ClO4-, and PF6-) in their preparations of polyfuran. They found that the polymer color and structure (according to the IR spectra) to be greatly influenced by the nature of the dopant anion. In 1997, we reported the chemical synthesis of polyfuran from the monomer using a mild oxidizing agent, pyridinium chlorochromate (McConnell et al., 1997). During synthesis, polyfuran is believed to be much less stable that polypyrrole with respect to ring opening by nucleophilic reagents, such as water (Fig. 2). Therefore, we took great care to utilize anhydrous conditions. We utilized a similar approach in the preparation of the co-polymers of furan with 2% pyrrole and furan with 2% thiophene. The pyridinium chlorochromate serves as an extremely mild oxidizing agent. In each case essentially all the pyridinium chlorochromate was recovered from the product by repeatedly dissolving the polymer in a small amount of dimethyl sulfoxide (DMSO) and then precipitating it with the addition of cold tetrahydrofuran (THF). In some cases the dopant, 1 mL of a solution containing 0.1 mg/mL silver p-toluene sulfonate in DMSO, is added along with the oxidizing agent. The furan co-
Co-polymers of Furan with Pyrrole or Thiophene: A Synthetic Study

polymer products vary in color from brown to shiny black, depending on the dopant and pyrrole or thiophene added.  

$^1$H NMR spectra were used to detect ring opening by comparing aromatic hydrogen signals to aliphatic hydrogen signals.

$^1$H NMR Spectra.—The $^1$H NMR spectra of all the synthetic co-polymers show significant peak broadening typically seen in polymer spectra. The $^1$H NMR spectra of polyfuran, prepared using PCC, display primarily aromatic signals ($\delta$ 7.420, 7.740, 8.066, 8.581). However, about 5% ring opening was detected through aliphatic signals (in addition to DMSO-d$_6$ solvent signals). When two percent thiophene is combined in the polyfuran polymer the aromatic portion of the spectra increases in complexity (with signals at $\delta$ 7.132, 7.412, 7.787, 8.336, 8.594, 8.865). However, the amount of ring opening was decreased to 3% as observed through relative intensities of aliphatic signals. When two percent pyrrole was used in preparation of the polyfuran the aromatic portion of the $^1$H NMR spectra is further complicated (signals at $\delta$ 7.094, 7.421, 7.549, 7.787, 8.023, 8.322, 8.510, 8.589, 8.861, 9.116). However, the observation of about 1% aliphatic signals in the $^1$H NMR also indicated that only a trace amount of ring opening occurred during the reaction. This demonstrates that the introduction of small amounts of pyrrole or thiophene into the polyfuran matrix helps to prevent ring opening and loss of aromaticity during the polymerization process.

IR Spectra.—The infrared spectra of polyfuran (Fig. 3) has some bands that are characteristic of the monomer (1585, 1535, 1438, 1200, 1160, 1060, 940, and 730 cm$^{-1}$). Additional bands shown in the IR of polyfuran at 1165, 1090, and 1030 cm$^{-1}$ were attributed to C-H bending and stretching, and additional bands at 953, 790 and 630 cm$^{-1}$ were contributed to aromatic C-H out of plane bending. These bands are consistent with IR spectra reported of polyfuran prepared by electrochemical means (Zotti et al., 1990; Glenis et al., 1993). Some ring opening was suggested by a band at 1740 cm$^{-1}$ in the IR spectra of polyfuran. This

Fig. 4. Infrared transmission spectra of polyfuran with 2% pyrrole.
Fig. 5. Infrared transmission spectra of polyfuran with 2% thiophene.

band was reduced significantly and disappeared completely in several of the IR spectra of co-polymers of furan with 2% pyrrole (Fig. 4) or 2% thiophene (Fig. 5). Figure 6 shows sample IR spectra of polyfuran (PF) doped with silver p-toluene sulfonate. The band at 1740 cm\(^{-1}\) (attributed to ring opening) has been significantly reduced. This is also the case in the IR spectra (Figs. 7 and 8) of doped polyfuran with 2% thiophene (PF-T2) and doped polyfuran with 2% pyrrole (PF-P2).

**ESR Spectra.** Polyfuran and the co-polymers of polyfuran, both the neutral and doped forms, containing either 2% pyrrole or 2% thiophene were examined by electron resonance spectroscopy (ESR). The room temperature ESR spectra of polyfuran (PF) exhibits a Gaussian signal (\(\Delta H_{pp} = 0.79 G\)) with a spin concentration of \(8.2 \times 10^{10}\) spins/mole. In the polyfuran doped with silver p-toluene sulfonate, the Gaussian signal (\(\Delta H = 0.68 G\)) was significantly reduced. In the polyfuran co-polymers produced with 2% thiophene (PF-T2), the \(H^1\) line width was 0.75G in the undoped polymer and 0.70G in the doped polymer. A similar observation is made in the co-polymers produced with 2% pyrrole (PF-P2) in that the \(H^1\) line width was 0.71G in the undoped version and 0.65G in the doped co-polymer. Polyfuran and the co-polymers all have \(g\) values ranging from 2.0011 to 2.0014 which indicates that unpaired electrons of the conjugated carbon backbone structures are most likely responsible for the ESR signals. No \(g\)-value anisotropy is observed in any of the co-polymers.

**Electrical Conductivity.** The electrical conductivity at 25\(^\circ\)C for polyfuran prepared through chemical polymerization using pyridinium chlorochromate is \(1.3 \times 10^{-6}\) S/cm for the neutral polymer and \(1.2 \times 10^{-3}\) S/cm for polyfuran doped with silver p-toluene sulfonate. The electrical conductivity of the furan-thiophene co-polymer (PF-T2) was \(2.1 \times 10^{-4}\) S/cm in the undoped form (Table 1) and \(1.1 \times 10^{-2}\) S/cm in the doped form. This increase in

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Fig. 6. IR spectra of polyfuran doped with silver p-toulene sulfonate.

Electrical conductivity was also observed in the doped furan-pyrrole co-polymer (from $1.5 \times 10^{-2}$ S/cm for the undoped polymer to $3.5 \times 10^{-2}$ S/cm for the doped co-polymer). In general the electrical conductivity is higher for the co-polymers and is further increased when the dopant is introduced into the polymer matrix. The apparent increase in conductivity is attributed to an increase in the stability of the polymer and a higher degree of backbone conjugation. This is supported by the spectral data of the co-polymers.

Conclusions

Although polyfuran is predicted to be a good conductive polymer, polyfuran is much less stable than polypyrrole and polythiophene with respect to ring opening by nucleophilic reagents, especially in the oxidized, doped state. We have demonstrated that not only can polyfuran be produced in good quantity through chemical polymerization, but that excessive ring opening can be avoided through the use of anhydrous conditions during the polymerization process. Also, the quality of the polymer is improved and ring opening minimized by the introduction of small amounts of thiophene or pyrrole into the polymer matrix. Under these conditions the use of silver p-toulene sulfonate as a dopant does not decrease the stability of the co-polymers. The absence of g-value anisotropy in the ESR and the correlation between the increase in electrical conductivity with polymer stability may indicate that the charge transport occurs primarily along the conjugation of the carbon backbone.

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Fig. 7. IR spectra of polyfuran-2% thiophene doped with silver p-toluene sulfonate.

Baskett, and Kenya Powell were also generously supported by the Science Information Liaison Office (SILO) of Arkansas by SILO Undergraduate Research Fellowships (SURF).

Literature Cited


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Fig. 8. IR spectra of polyfuran-2% pyrrole doped with silver p-toluene sulfonate.


Table 1. Electrical Conductivity of Pressed Pellets of Polyfuran and Copolymers at 298 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity, S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyfuran</td>
<td>1.3 x 10^{-6}</td>
</tr>
<tr>
<td>PF-T2</td>
<td>2.1 x 10^{-4}</td>
</tr>
<tr>
<td>PF-P2</td>
<td>1.5 x 10^{-3}</td>
</tr>
<tr>
<td>Polyfuran - doped-Ag</td>
<td>1.2 x 10^{-3}</td>
</tr>
<tr>
<td>PF-T2 - doped-Ag</td>
<td>1.1 x 10^{-2}</td>
</tr>
<tr>
<td>PF-P2 - doped-Ag</td>
<td>3.4 x 10^{-2}</td>
</tr>
</tbody>
</table>

PF-T2 = polyfuran with 2% thiophene
PF-P2 = polyfuran with 2% pyrrole
doped-Ag = addition of silver p-toluene sulfonate
Preparation of Novel Hydroxyethyl Amine Isosteres as Potential Cathepsin D Inhibitors

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Abstract

Cathepsin D is a lysosomal aspartic protease found in all mammalian cells and is considered to be one of the main catabolic proteinases. Cathepsin D has been suggested to play a role in the metastatic potential of several types of cancer. A high activated cathepsin D level in breast tumor tissue has been associated with an increased incidence of relapse and metastasis. High levels of active cathepsin D have also been found in colon cancer, prostate cancer, uterine cancer, and ovarian cancer. Hydroxyethyl isosteres with cyclic tertiary amine have proven to be clinically useful as inhibitors of aspartyl proteases similar to cathepsin D in activity, such as the HIV-1 aspartyl protease. We have undertaken the design, via computer molecular modeling, and the synthesis of (hydroxyethyl)amine isostere inhibitors, which are similar to potent inhibitors of the aspartyl HIV-1 protease. We now report the preparation of six compounds that contain novel hydroxyethyl isosteres with cyclic tertiary amines.

Introduction

Aspartyl proteases are among the most biologically important proteolytic enzymes. Some of the more serious medical problems, such as cardiac disease, AIDS, Alzheimer’s disease, as well as colorectal and breast cancer, and other cancers, either result directly from, or are characterized by, uncontrolled aspartyl protease activity (Mimoto et al., 2000; Moore et al., 2000; Nakaya et al., 2001; Messmer et al., 2001). The HIV-1 aspartyl protease, which is responsible for the maturation of HIV into the infectious viral particles (Darke and Heff, 1994), has become an important therapeutic target for treatment of acquired immunodeficiency syndrome (AIDS) (Debnath, 1999; Alterman et al., 1998; Backbro et al., 1997; Hulten et al., 1997).

Cathepsin D is an aspartyl lysosomal protease similar to the HIV-1 aspartyl protease in substrate specificity. Cathepsin D is clearly involved in the process of tumor invasion and metastasis (Thorpe et al., 1998; Vetticka et al., 1997; Laury-Kleintop et al., 1995; Losch et al., 1996; Mordente et al., 1998; Reig et al., 1996). In fact, cathepsin D has recently emerged as a prognostic indicator in several cancers, including breast cancer (Thorpe et al., 1998), prostate (Mordente et al., 1998), and colon (Reig et al., 1996). Also cathepsin D has recently been associated with the development of Alzheimer’s disease (Moore, 2000). Specific proteinase inhibitors, useful in investigations of the mechanisms and pathways of intracellular protein degradation, could lead to the development of therapeutic agents for treatment of many types of carcinomas, as well as Alzheimer’s disease.

Pepstatin, renin, cathepsin D, and recently the HIV-1 aspartyl protease are among the best characterized aspartyl proteases. All of these proteases are inhibited by pepstatin A (Kratzel et al., 1998; Kratzel et al., 1999; Scholtz et al., 1994), a pentapeptide like compound which contains two unusual α-amino acid statines [(3S,4S)-4-amino-3-hydroxy-6-methylheptanoic acid]. Pepstatin, which contains a reactive hydroxyl group, forms the tetrahedral intermediate by reacting with the essential carboxyl group in the active site of the protease (Rich and Bernatowicz, 1985; Payne et al., 1991). Although pepstatin A was found to be a potent inhibitor of the HIV-1 aspartyl protease, the peptidic nature of the inhibitor resulted in poor bioavailability. In order to improve bioavailability and improve in vivo half-life, recent work has focused on smaller inhibitors that contain a non-peptide functionality in place of the peptide bond cleavage site of the substrate (Skulnick et al., 1997; Reich et al., 1996). The use of hydroxyethyl isosteres with cyclic tertiary amines has led to compounds with enhanced oral absorption (Smith et al., 1997). In recent years the (R)-hydroxyethylamide insert was incorporated as a key component of many clinically used, highly potent, HIV-1 protease inhibitors. Initially several compounds that contain hydroxyethyl amine isosteres with flexible alkyl amines were developed (Beaulieu et al., 1997), but they suffered limited in vivo half-lives and were not therapeutically useful.
Preparation of Novel Hydroxyethyl Amine Isosteres as Potential Cathepsin D Inhibitors

Molecular modeling [HYPERCHEM] has shown that a six member ring forming the tertiary amine may be able to orient the backbone of the inhibitor toward a bioactive conformation while providing more of a non-peptide functionality which greatly improves the half-life of the inhibitor in vivo. A comparison of the structural and stereochemical requirements of the S$_3'$, S$_2'$, and S$_1'$ as well as the S$_1$, S$_2$, and the S$_3$ subsites of cathepsin D along with projected interactions with various inhibitor side chains suggests modifications which may be introduced to improve potency. Several investigators have shown, through crystallographic studies or molecular modeling, that either a cyclohexyl group of a reduced phenylalanine or the phenyl group of a phenylalanine-type statine (hydroxystatin) or hydroxystatin amine is easily positioned in the S$_1$ site of the HIV-1 aspartyl protease (Payne et al., 1991; McConnell et al., 1991). Other studies show that a bulky amine or amide might fit reasonably well into the S$_2'$ and S$_3'$ sites (Paul et al., 1995). Therefore, we set out to synthesize compounds that contain a peptide portion to accommodate the S$_1$, S$_2$, and S$_3$ subsites and a non-peptide hydroxystatin isostere portion with a cyclic tertiary amine to accommodate the S$_1'$, S$_2'$, and S$_3'$, enzyme subsites. The general structure of our synthetic target is shown in Figure 1.

**Materials and Methods**

Anhydrous solvents were “anhydrous grade” from Aldrich Chemical Company. Dry solvents were distilled from sodium just prior to use. All other solvents were HPLC grade. Reagents were purchased from Sigma-Aldrich Chemical Company. Thin layer chromatography (TLC) was run on Whatman PE SIIL G/UV 250 µm silica gel plates. Column chromatography was run on either Aldrich TLC grade silica gel 2-2.5 µm particle size BET surface area ~500 m$^2$/g, average pore diameter 60Å, or Sigma Sephadex LH-20, lipophilic, bead size 20-100 µm. The $^1$H NMR spectra were collected either on a Bruker 200 MHz AC 200 superconducting spectrometer or on a Hitachi 60 MHz R1200 RS NMR spectrometer. $^1$H NMR of final compounds and major intermediates were collected on the 200 MHz spectrometer, while the spectra of minor intermediates were collected on the 60 MHz NMR spectrometer. The spectral data were processed NTNMR software produced by TeleMag.

**BOC-L-phenylalaninal (1).--**Commercially available BOC-L-phenylalanine methyl ester (10.2 g, 36.5 mmol) in 200 mL dry tetrahydrofuran (THF) was chilled to -80°C under a N$_2$ atmosphere. The cold solution was slowly treated with 92 mL (91.25 mmol, 2.5 equivalents) of 1 M diisobutyl aluminum hydride (DIBAL) in hexanes over 20 minutes. The mixture was stirred at -80°C under N$_2$ for four hours. The reaction was quenched by the addition of 100 mL 0.01 M aqueous HCl. The mixture was then partitioned between the layers of dichloromethane (400 mL) and 5% aqueous sodium potassium tartrate (400 mL). The aqueous layer was extracted with another 400 mL of dichloromethane. The organic layers were combined and washed three times with 250 mL portions of distilled water. The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to produce a colorless viscous oil. The crude aldehyde was purified by silica gel flash chromatography using dichloromethane as the mobile phase, (final mass 5.80 g). TLC (CH$_2$Cl$_2$) R$_f$ = 0.39. $^1$H NMR (CDCl$_3$/TMS, 60MHz) δ 1.0 (9H, s), 2.3 (2H, d), 4.1 (1H, m), 4.9 (1H, m), 6.9 (5H, s), 9.9 (1H, s).

**3(S)-BOCamino-4-phenyl-1-butene (2).--**A precooled (0°C) solution of triphenylmethyl phosphonium bromide (12.8 g, 0.035 mol) in 50 mL dry THF was slowly treated over 10 minutes with 20 mL of 1.6 M n-butyl lithium (0.032 mol) under N$_2$ atmosphere. The solution was stirred for four hours at 0°C. A solution of BOC-L-phenylalaninal (5.0 g, 0.020 mol) in 25 mL dry THF was added. The mixture was allowed to warm to room temperature and was refluxed for 24 hours under N$_2$ atmosphere. The reaction was cooled and then quenched by the addition of 100 mL 0.01 M aqueous HCl saturated with NaCl. The mixture was extracted three times with 200 mL portions of ether. The

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Fig. 1. Target molecules with peptide and non-peptide portions.
organic layers were pooled, dried over anhydrous MgSO₄, and concentrated under reduced pressure to give a white powder (3.5 g). TLC (ether/hexanes, 1/1, v/v) Rf = 0.36. ¹H NMR (CDCl₃/TMS, 60MHz) δ 1.0 (9H, s), 2.2 (2H, d), 4.2 (1H, m), 4.9 (1H, m), 5.1 (2H, d, J=10 Hz), 5.3 (1H, m), 6.9 (5H,s).

3(S)-BOCamino-4-phenyl-2-oxirane (3a).--A solution of 5.5 g (4 equivalents, 32 mmol) meta-chloroperoxybenzoic acid (MCPBA) in 200 mL methylene chloride was mixed with a solution of 2.0 g (8 mmol) 3(S)-BOCamino-4-phenyl-1-butene (2) in 100 mL methylene chloride. The mixture was stirred at room temperature for 24 hours. The mixture was then filtered and concentrated under reduced pressure. The oily residue was partitioned between the layers of ether (400 mL) and distilled water (400 mL). The organic layer was removed and saved. The aqueous layer was extracted with another 400 mL ether. The ether layers were combined, washed with distilled water (400 mL), 5% aqueous NaHCO₃ (400 mL), and distilled water again (400 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to produce a mixture of epoxide diastereomers (1.5 g). The diastereomers were separated by silica gel (grade 710, 4.20 μm, surface area 480 m²/g) column chromatography (column size 4" dia. x 5' length) using 10% ethyl acetate/hexanes as the mobile phase.

3(S)-BOCamino-4-phenyl-2(R)-oxirane (3a).--0.597 g. TLC (35% ethyl acetate/hexanes) Rf = 0.21. ¹H NMR (CDCl₃/TMS,200MHz) δ 0.9572 (9H, s), 2.451 (2H, d), 3.525 (2H, d), 3.705 (1H, d of t), 4.531 (1H, m), 4.715 (1H, m, exchangeable), 7.105 (5H,s).

3(S)-BOCamino-4-phenyl-2(S)-oxirane (3b).--0.535 g. TLC (35% ethyl acetate/hexanes) Rf = 0.18. ¹H NMR (CDCl₃/TMS,200MHz) δ 0.9805 (9H, s), 2.401 (2H, d), 3.529 (2H, d), 4.203 (1H, d of t), 4.502 (1H, m), 4.675 (1H, m, exchangeable), 7.059 (5H,s).

3(S)-BOCamino-4-phenyl-1-N-piperidine-2(S)-butanol (4a).--A solution of 3a (1.0 g, 3.1 mmol) in 100 mL dry THF was treated with 1.0 mL (10 mmol) piperidine. The solution was refluxed for 48 hrs. The mixture was then cooled to room temperature, concentrated under reduced pressure to about one half its volume, and partitioned between ethyl acetate (200 mL) and 5% aqueous sodium potassium tartarate (200 mL) containing 1.0 g NaCl. The organic layer was washed with distilled water (100 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure to give a white solid (0.867 g). The crude product was purified by silica gel column chromatography (2.5 cm x 60 cm length) using 50% ethyl acetate/hexanes as the mobile phase to give 0.673 g. TLC (50% ethyl acetate/hexanes) Rf = 0.34. ¹H NMR (CDCl₃/TMS,200MHz) δ 0.9990 (9H, s), 1.859 (4H, t), 2.330 (4H, t), 2.456 (2H, d), 2.927 (2H, d), 3.892 (1H, d of t), 4.501 (1H, d of t), 4.935 (1H, m, exchangeable), 7.125 (5H,s).

3(S)-amino-4-phenyl-1-N-piperidine-2(S)-butanol dihydrochloride (5a).--0.55 g of 4a was dissolved in 50 mL cold (0°C) 2 M HCl in chloroform. The mixture was stirred at 0°C for 1 hour. Cold diethyl ether (250 mL) was added to induce precipitation of the product. The liquid was decanted, and the precipitant was washed twice with cold ether (100 mL). The crude solid was dissolved in 20 mL methanol and then recrystallized by the addition of 250 mL cold ether. The white solid was again washed twice with cold ether (100 mL) and dried under reduced pressure (0.46 g). TLC (10% ethanol/ethyl acetate) Rf = 0.35 ¹H NMR (D₂O, 60MHz) δ 1.7 (2H, t), 1.9 (4H, m), 2.2 (4H, t), 2.5 (2H, d), 2.9 (2H, d), 3.7 (1H, m), 4.5 (1H, m), 7.1 (5H,s).

3(S)-amino-4-phenyl-1-N-pyrrolidine-2(S)-butanol dihydrochloride (5b).--0.55 g of 4b was dissolved in 50 mL cold (0°C) 2 M HCl in chloroform. The mixture was stirred at 0°C for 1 hour. Cold diethyl ether (250 mL) was added to induce precipitation of the product. The liquid was decanted, and the precipitant was washed twice with cold ether (100 mL). The crude solid was dissolved in 20 mL methanol and then recrystallized by the addition of 250 mL cold ether. The white solid was again washed twice with cold ether (100 mL) and dried under reduced pressure (0.47 g). TLC (10% ethanol/ethyl acetate) Rf = 0.23 ¹H NMR (D₂O, 60MHz) δ 2.0 (4H, t), 2.3 (4H, m), 2.6 (2H, d), 3.0 (2H, d), 3.8 (1H, m), 4.4 (1H, m), 7.0 (5H,s).

General Procedure for Preparation of Carboxbenzoxo-
amino acids (6a-c).--A solution of the appropriate amino acid (0.050 moles) in 250 mL 1 M aqueous NaOH was chilled to 0°C and slowly treated (over 1 hour) with (0.055 moles) benzyl chloroformate. The mixture was stirred for three hours at 0°C, allowed to slowly warm, and stirred...
Preparation of Novel Hydroxyethyl Amine Isosteres as Potential Cathepsin D Inhibitors

Carbobenzyo-L-alanine (6a).--TLC (ethyl acetate/hexanes, 1/1, v/v) Rf = 0.35. 1H NMR (CDCl3/TMS, 60MHz) δ 2.3 (3H, d), 2.7 (2H, d), 3.8 (3H, s), 4.5 (2H, m), 4.7 (1H, m), 5.0 (1H, m), 5.4 (2H, s), 6.9 (5H, s), 7.3 (5H, s).

Carbobenzyo-L-valine (6b).--TLC (ethyl acetate/hexanes, 1/1, v/v) Rf = 0.20. 1H NMR (CDCl3/TMS, 60MHz) δ 2.2 (3H, d), 2.7 (2H, d), 3.7 (3H, s), 4.6 (2H, m), 4.7 (1H, m), 5.0 (1H, m), 5.3 (2H, s), 7.0 (5H, s), 7.3 (5H, s).

Carbobenzyo-L-leucine (6c).--TLC (ethyl acetate/hexanes, 1/1, v/v) Rf = 0.29. 1H NMR (CDCl3/TMS, 60MHz) δ 1.5 (6H, d), 2.2 (3H, m), 4.0 (2H, m), 5.3 (2H, s), 7.3 (5H, s).

General Procedure for Preparation of Carbobenzylo-dipeptide methyl esters (7a-c).--A cold (-10°C) solution of 0.015 mole of the appropriate carbobenzylo-amino acid (6a-c) in 20 mL anhydrous dimethyl formamide (DMF) was treated with 2.0 mL (0.015 mole) anhydrous triethylamine. After 10 minutes the cold solution was treated with 1.2 mL (0.014 mole) ethyl chloroformate. The mixture was stirred for 1 hour at -10°C and then combined with a precooled (0°C) solution containing 2.6 g (0.015 mole) L-phenylalanine methyl ester hydrochloride and 2.0 mL (0.015 mole) triethylamine in 20 mL anhydrous DMF. The mixture was stirred at 0°C for 3 hours, allowed to warm to room temperature, and stirred overnight. The mixture was then partitioned between the layers of ethyl acetate (200 mL) and aqueous 1 M NaOH (150 mL). The organic layer was washed with distilled water (150 mL), aqueous 1 M HCl (150 mL), and distilled water under reduced pressure. The organic layer was dried over anhydrous magnesium sulfate and evaporated under reduced pressure.

Carbobenzyo-L-alanyl-L-phenylalanine methyl ester (7a).--TLC (chloroform) Rf = 0.18. 1H NMR (CDCl3/TMS, 60MHz) δ 2.3 (3H, d), 2.7 (2H, d), 3.8 (3H, s), 4.5 (2H, m), 4.7 (1H, m), 5.0 (1H, m), 5.4 (2H, s), 6.9 (5H, s), 7.3 (5H, s).

Carbobenzyo-L-valyl-L-phenylalanine methyl ester (7b).--TLC (chloroform) Rf = 0.27. 1H NMR (CDCl3/TMS, 60MHz) δ 1.5 (6H, d), 2.3 (1H, m), 2.6 (2H, d), 3.7 (3H, s), 4.6 (2H, m), 4.7 (1H, m), 5.0 (1H, m), 5.3 (2H, s), 7.0 (5H, s), 7.3 (5H, s).

Carbobenzyo-L-leucyl-L-phenylalanine methyl ester (7c).--TLC (chloroform) Rf = 0.38. 1H NMR (CDCl3/TMS, 60MHz) δ 1.2 (6H, d), 2.2 (3H, m), 2.7 (2H, d), 3.6 (3H, s), 4.6 (2H, m), 4.7 (1H, m), 5.0 (1H, m), 5.5 (2H, s), 7.0 (5H, s), 7.2 (5H, s).

General Procedure for Preparation of Carbobenzyo-dipeptide acids (8a-c).--A solution of the appropriate carbobenzyo-dipeptide methyl ester (0.010 to 0.015 mole) in 100 mL methanol was mixed with 50 mL aqueous 1 M NaOH. The mixture was stirred overnight at room temperature. The resulting mixture was diluted with 200 mL distilled water and acidified to pH 3.0 with aqueous 6 M HCl. The mixture was then concentrated to about one half volume under reduced pressure. The cloudy mixture was extracted twice with ethyl acetate (150 mL). The organic layers were combined, washed with distilled water (150 mL), dried over anhydrous magnesium sulfate, and then evaporated under reduced pressure.

Carbobenzyo-L-alanyl-L-phenylalanine (8a).--TLC (chloroform) Rf = 0.18. 1H NMR (CDCl3/TMS, 60MHz) δ 2.3 (3H, d), 2.7 (2H, d), 4.6 (2H, m), 4.9 (1H, m), 5.0 (1H, m), 5.4 (2H, s), 6.9 (5H, s), 7.5 (5H, s), 10.8 (1H, m).

Carbobenzyo-L-valyl-L-phenylalanine (8b).--TLC (chloroform) Rf = 0.27. 1H NMR (CDCl3/TMS, 60MHz) δ 1.2 (6H, d), 2.2 (3H, m), 2.7 (2H, d), 4.5 (2H, m), 4.8 (1H, m), 5.0 (1H, m), 5.3 (2H, s), 7.0 (5H, s), 7.4 (5H, s), 11.0 (1H, m).

Carbobenzyo-L-leucyl-L-phenylalanine (8c).--TLC (chloroform) Rf = 0.38. 1H NMR (CDCl3/TMS, 60MHz) δ 1.2 (6H, d), 2.2 (3H, m), 2.7 (2H, d), 4.5 (2H, m), 4.7 (1H, m), 5.0 (1H, m), 5.5 (2H, s), 7.0 (5H, s), 7.4 (5H, s), 11.2 (1H, m).

General Procedure for Coupling Cbz-dipeptide to 3(S)-amino-4-phenyl-1-N-piperidine (or pyrrolidine)-2(S)-butanol (9a-f).--A precooled solution (-15°C) of the appropriate carbobenzylo-dipeptide (8a-c) (0.35 mmol) in 10 mL anhydrous DMF was treated with 56 μL (0.40 mmol) triethylamine. The mixture was allowed to react at -15°C for 30 minutes and was then treated with 34 μL (0.35 mmol) ethyl chloroformate. The mixture was stirred under N2 atmosphere for 1 hour at -15°C. A precooled (0°C) solution containing 0.32 mmole of either 5a or 5b in 25 mL anhydrous DMF and 125 μL (1.0 mmole) triethylamine was then added to the mixed anhydride of the Cbz-dipeptide. The combined mixture was stirred under N2 at 0°C for 4 hours, allowed to warm to room temperature, and stirred overnight at room temperature. The mixture was partitioned between the layers of ethyl acetate (250 mL) and 0.01 M aqueous NaOH. The organic layer was removed and saved. The aqueous layer was extracted again with another 250 mL ethyl acetate. The organic layers were pooled, washed with distilled water (100 mL), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure.

3(S)-Cbz-L-alanyl-L-phenylalaninylamino]-4-phenyl-1-N-piperidine-2(S)-butanol (8a)--0.157 g. TLC (10% ethanol/ethyl acetate) Rf = 0.17. 1H NMR (DMSO-d6, 60 MHz) δ 1.7 (2H, d), 1.9 (4H, m), 2.0 (4H, t), 2.5 (4H, m), 2.7 (2H, d), 3.1 (2H, d), 3.7 (1H, m), 4.6 (3H, m), 5.0 (1H, m), 5.4 (2H, s), 6.9 (5H, s), 71 (5H, s), 72 (5H, s).

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3(S)-(Cbz-L-Valyl-L-phenylalanlylamino)-4-phenyl-1-N-pipеридине-2(S)-бутанол (9a). -0.135 g. TLC (10% ethanol/ether-acetate) Rf = 0.23. 1H NMR (DMSO-d6, 60 MHz) δ 1.3 (6H, d), 1.5 (2H, t), 1.8 (4H, m), 1.9 (4H, t), 2.5 (3, m), 2.7 (2H, d), 3.1 (2H, t), 3.7 (1H, m), 4.6 (3H, m), 5.0 (1H, m), 5.4 (2H, s), 6.8 (5H, s), 7.1 (5Hs), 7.4 (5H, s).

3(S)-(Cbz-L-Leucyl-L-phenylalanlylamino)-4-phenyl-1-N-piperidine-2(S)-butanol (9c). -0.128 g. TLC (10% ethanol/ether-acetate) Rf = 0.26. 1H NMR (DMSO-d6, 60 MHz) δ 1.3 (6H, d), 1.5 (2H, t), 1.8 (4H, m), 1.9 (4H, t), 2.5 (7, m), 2.7 (2H, d), 3.1 (2H, d), 3.7 (1H, m), 4.6 (3H, m), 5.0 (1H, m), 5.4 (2H, s), 6.9 (5H, s), 7.3 (5Hs), 7.5 (5H, s).

3(S)-(Cbz-L-Alanyl-L-phenylalanlylamino)-4-phenyl-1-N-pyrrolidine-2(S)-butanol (9e).-0.167 g. TLC (15% ethanol/ether-acetate) Rf = 0.23. 1H NMR (DMSO-d6, 60 MHz) δ 1.3 (6H, d), 1.7 (4H, m), 2.0 (4H, m), 2.4 (4H, m), 2.9 (2H, d), 3.3 (2H, d), 3.8 (1H, m), 4.3 (6H, m), 5.0 (1H, m), 5.3 (2H, s), 6.8 (5H, s), 7.1 (5Hs), 7.5 (5H, s).

3(S)-(Cbz-L-Leucyl-L-phenylalanlylamino)-4-phenyl-1-N-pyrrolidine-2(S)-butanol (9e).-0.117 g. TLC (15% ethanol/ether-acetate) Rf = 0.35. 1H NMR (DMSO-d6, 60 MHz) δ 1.3 (6H, d), 1.7 (4H, m), 2.0 (4H, m), 2.4 (3, m), 2.8 (2H, d), 3.2 (2H, d), 3.8 (1H, m), 4.7 (3H, m), 5.0 (1H, m), 5.3 (2H, s), 6.8 (5H, s), 7.2 (5Hs), 7.5 (5H, s).

General Procedure for Preparation of 3(S)-(Acetyldipeptide-amino)-4-phenyl-1-N-piperidine-2(S)-butanol hydrochloride (10a-f).- A solution of the carbobenzoxy protected compound (9a-f) (0.20 mmol) in 250 mL methanol and 1 mL 0.01 M aqueous HCl was treated with 0.505 g pre-moistened 10% Pd-C to form a slurry in a 3 neck flask. H2 gas was bubbled (1 atm) through the rapidly stirring mixture at room temperature for three hours. The mixture was then filtered to remove the catalyst, and the solvent was evaporated under reduced pressure. The crude amine hydrochloride was dissolved in 10 mL dimethyl sulfoxide (DMSO) and treated with 125 µL (0.10 mole) triethylamine. The mixture was stirred at room temperature for 30 minutes. Acetic anhydride (95 µL, 1.00 mmol) was added, and the mixture was stirred overnight at room temperature. Cold diethylether (200 mL) was added to precipitate the product. The liquid was decanted, and the white solid was washed three times with cold ether (100 mL). The crude product was purified by Sephadex LH-20 column chromatography (column size 5 cm dia. x 80 cm) using methanol as the mobile phase.

3(S)-(Acetyl-L-Alanyl-L-phenylalanlylamino)-4-phenyl-1-N-piperidine-2(S)-butanol (10a). -0.52 g. TLC (1-butanol/H2O/acetic acid, 15/2/1) Rf = 0.67. 1H NMR (methanol-d4, 200 MHz) δ 1.689 (2H, d), 1.987 (4H, m), 2.010 (4H, t), 2.305 (3H, d), 2.210 (2H, s) 2.462 (4H, m), 2.597 (2H, d), 3.715 (1H, m), 4.610 (3H, m), 4.984 (3H, m), 6.949 (5H, s), 7.212 (5Hs).

Results and Discussion

Our synthetic plan of the potential cathepsin D inhibitors involved three phases: (a) preparation of the protected hydroxyethyl amine isostere portion (b) preparation of the carbobenzyox protected dipeptide portion and (c) condensation and deblocking of the peptide and non-peptide portions. The hydroxyethyl amine isosteres were prepared from a tert-butoxycarbonyl (BOC) chiral amino aminooalkyl epoxide (Scheme 1). The novel chiral aminooalkyl epoxides were first reported by Evans et al. (1985) and have been subsequently used successfully in the preparation of...
Preparation of Novel Hydroxyethyl Amine Isosteres as Potential Cathepsin D Inhibitors

Scheme 1

several HIV-1 aspartyl protease inhibitors with hydroxyethyl amine isosteres (Fassler et al., 1996; Barrish et al., 1994). The alkene was prepared from a protected chiral aminoaldehyde by reaction with a ylide (triphenyl phosphonium methylide). The olefin was converted to the chiral epoxide with meta-chloroperoxybenzoic acid (MCPBA) in methylene chloride. This reaction takes place with retention of stereochemical configuration at the α-carbon of the protected aminoaldehyde. The ylide attack on the diastereotopic faces of the aldehyde is nonspecific, and the epoxide obtained is a separable mixture of isomers easily distinguished by NMR adsorption on the C2 proton (δ 3.7 and 4.1) (Evans et al., 1985). Separation of the diastereomers was accomplished by silica gel column chromatography using ethyl acetate/hexanes (23% v/v) as the mobile phase. Normally the 2S,3S epoxide is utilized to prepare HIV-1 protease inhibitors with the desired R-hydroxyethyl amine isostere (Fassler et al., 1996; Barrish et al., 1994). However, since the S-hydroxyethyl amine isostere is reported to be the more active isomer for cathepsin D inhibition (Kick, 1997), we utilized the 2R,3S protected amino epoxide in our synthesis (Scheme 1). Piperidine or pyrrolidine was used as a nucleophile in the preparation of the cyclized tertiary amines. The BOC protecting group was removed from the primary amine with non-aqueous acid (2 M HCl in chloroform).

Preparation of the protected peptide portion of the target molecules was accomplished in the following manner. A basic solution of the chosen amino acid was condensed with benzyl chloroformate to provide, after acidification and purification, the carbobenzoxy (Cbz) protected amino acid. The Cbz-amino acid was then coupled to a separate amino acid methyl ester by a mixed anhydride coupling technique utilizing ethyl chloroformate. The C-terminus of the Cbz protected dipeptide methyl ester was then deblocked in aqueous sodium hydroxide, followed by acidification (Scheme 2). In the third phase of our synthesis, the Cbz-protected dipeptide was condensed with ethyl chloroformate and then reacted with the basified primary amine of the hydroxyethyl amine isostere portion (Scheme 3). The Cbz protecting group of the resulting compound was then removed and replaced with an acetyl group. The final product was purified by sephadex HP chromatography and characterized by TLC and 1H NMR.

Conclusions

Our synthetic route shows a great deal of promise for the future synthesis of similar hydroxyethyl amine isosteres. The synthetic inhibitors will be screened for their inhibition of cathepsin D first by spectrophotometric assay techniques, and then detailed kinetic data will be determined by more
sensitive fluorometric techniques (Kick et al., 1997). The inhibition constants for these synthetic compounds will be reported in the near future.

ACKNOWLEDGMENTS.—The authors wish to thank the National Cancer Institute at NIH for their generous support of this research project (Grant No. 1 R15 CA86933-01).

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Preparation of Novel Oxyethyl Amine Isosteres as Potential Cathepsin D Inhibitors


Pressure and Flow Validation of a Second Generation Gas Extraction Probe for a Hybrid Rocket Gas Extraction System

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Abstract

A gas extraction system (GES) has been designed for use with the hybrid rocket facility at the University of Arkansas at Little Rock (UALR) for spectroscopic analysis of rocket plumes. While monitoring gas flow-rate and pressure, the GES extracts gases from the hybrid rocket plume and transports them to a mass spectrometer. This paper describes design and construction of a gas extraction probe (GEP) prototype capable of extracting gases directly from the plume. Gas dynamics equations were used to design two venturi-type GEP, converging and converging-diverging. The probe was tested with air to verify design assumptions. Flow rate through the U-arm and pressures for each probe were measured and compared.

Introduction

The University of Arkansas at Little Rock's (UALR) labscale hybrid rocket (Shanks and Hudson, 1994) facility is shown schematically in Fig. 1. A hybrid rocket motor employs a cylindrical, hollow, solid fuel grain through which oxygen flows. It combines advantages of a liquid propellant motor (start-stop-restart, throttle capabilities, and safety) with those of solid propellant motors (less complexity and higher propellant density). Hybrids use solid fuels, such as hydroxyl-terminated polybutadiene (HTPB) and methyl methacrylate, and they burn at high temperatures. These two factors may lead to undesirable exhaust constituents (Meadors et al., 2000).

NASA's John C. Stennis Space Center (SSC) has done extensive research in the area of plume spectroscopy (Tejwani, et al., 1996). One of SSC's priorities for its hybrid rocket programs is identification of constituents and amounts present in the exhaust gases. By making measurements along the plume, SSC will be able to monitor rocket engine health and meet EPA requirements. NASA currently uses Computational Fluid Dynamic (CFD) models to predict concentrations of exhaust constituents. Validating NASA's computer model of hybrid rocket combustion and
flow will satisfy EPA requirements with more realistic safety factors on the rocket's performance envelope. If large-scale hybrid rockets are used for propulsion, the environmental effects due to exhaust must be quantified.

SSC also uses the non-invasive instrumentation and measurement techniques to monitor and diagnose failed components. NASA studies indicate that plume spectroscopy can be successfully used in monitoring the levels of metals that may be found in the plumes of rocket motors (Tejwani et al., 1996). It is possible to monitor the health of the engine during operation and, by quantifying metals detected in the plume, determine excessive wearing of engine components. This method of monitoring the engine aids in inspection and flight certification of the Space Shuttle Main Engine (SSME). It may also be used to monitor future hybrid flight systems.

The long term goal for this project is to continuously extract gases from the hybrid rocket plume and transport them to a mass spectrometer (see Fig. 1). The probe will be inserted in the plume so as to minimally disturb the flow pattern. The pressure differential between the U-arm inlet and the nozzle exit will drive a secondary metered flow through the probe's U-arm. A "T" junction removes plume constituents in small amounts and transports via capillary tubing and transports them to a mass spectrometer (see Fig. 2). This paper focuses on the design of the gas extraction probe (GEP).

Materials and Methods

Gas Extraction System Design.--The gas extraction system consists of a gas collection unit (GCU), a gas flow line (GFL), and a Finnegan 5100B mass spectrometer (see Fig. 1). The GCU removes gases from the plume of the hybrid rocket and transports them to the mass spectrometer via the GFL.

The GES is designed to meet hybrid rocket plume and mass spectrometer interface requirements. For plume insertion, the design specifications of the GES are minimal flow disturbance and continuous sampling. Temperature, pressure, and Mach number are determined from the hybrid rocket plume. The hybrid rocket plume has a 3000°C temperature (Teague, et al., 1996), 30 psi (206.8 kPa) stagnation pressure, and a Mach number varying between 0.5-1.5. Mass spectrometer interface requirements are 20-25mL/min inlet flow rate and 0.19-0.09 psi (1.3-66 kPa) vacuum pressure.

Gas Collection Unit 2.--In GCU-1 a low variable pressure differential produced high flow rates through the U-arm. To achieve target flow rates through the U-arm (Meadors and Wright, 1999), a second GCU is designed with a new probe that provides a small constant pressure differential. The second GCU employs the same venturi function as GCU-1 (see Fig. 2).

Gas Collection Probe 2.--Using one-dimensional, isentropic, compressible flow assumptions (Potter and Foss, 1982; John, 1984), gas collection probe-2 (GCP-2) is designed to achieve ideal mach numbers, pressure, and flow rates. The ideal conditions will yield a stable pressure output for a variety of Mach inputs and very small constant pressure differential with a shock in the exit area (see Fig. 3).

Computer analysis of standard gas dynamic equations (John, 1984) that demonstrate pressure and area as a function of Mach number is done to create Mach and pressure profiles along a convergent-divergent nozzle and determine the best area ratios to meet ideal conditions. Two cases considered are Mach less than one at the throat and Mach equals one at the throat.

Given Mach number, M, stagnation pressure, P₁, and specific heat, γ, the static pressure is given by

\[ P = P₁ \left[ 1 + \frac{\gamma - 1}{2} M^2 \right]^{\frac{\gamma}{\gamma - 1}}. \]  \hspace{1cm} (1)

The ratio between current area, A, and the area at which Mach number is 1.0, A", is given by

\[ \frac{A}{A"} = \frac{1}{M} \left[ \frac{\gamma + 1}{2} \frac{1 + \frac{\gamma - 1}{2} M^2}{\gamma} \right]^{\frac{\gamma + 1}{2(\gamma - 1)}}. \]  \hspace{1cm} (2)
The area ratios and pressures were determined by equations 1 and 2 (John, 1984). Static and back pressures are used to calculate the area before the throat. The areas up to the shock are calculated by varying static pressure. The static to back pressure ratio is used to solve the exit plane mach number which is used to calculate exit area to throat area ratio. Once the shock is reached the converging section does not change.

To calculate the second case the shock is moved along the nozzle from the throat to exit plane. Since isentropic properties do not apply across a shock, given the Mach number, M1, before the shock and γ (John, 1984), the Mach number after the shock is given by

\[ M_2 = \sqrt{\frac{M_1^2 + \frac{2}{\gamma - 1}}{\frac{2\gamma}{\gamma - 1} M_1^2 - 1}}. \]  

Given M1 the stagnation pressures across the shock are characterized by

\[ \frac{P_2}{P_{1t}} = \left[ \frac{\gamma + \frac{1}{2} M_1^2}{1 + \frac{\gamma - 1}{2} M_1^2} \right]^\frac{1}{\gamma + 1} \left[ \frac{1}{\gamma + 1} \frac{2\gamma}{\gamma - 1} M_1^2 - \frac{\gamma - 1}{\gamma + 1} \right]^\frac{1}{\gamma - 1}. \]  

The backpressure, inlet, exit, and throat area are factors considered and varied in analysis. Inlet and throat areas were selected and the exit area varied. The Mach number and static pressures were plotted along the nozzle. The inlet area was then varied to see its effect on the exit conditions. Finally, the throat area was varied to gain the best possible inlet and exit conditions. The best computed area ratios are inlet to throat of 1.15 and exit to throat of 2 (see Fig. 4).

GCP-2 is designed with variable inlet Mach numbers 0.2-1.0 and a stagnation pressure of 30 psi (206.8 kPa). GCP-2 is made of aluminum with an inlet diameter of 2.64 cm, a throat diameter of 1.09 cm, and an exit diameter of 3.56 cm, yielding an inlet to throat ratio of 5.67 and an exit to throat ratio of 10. For design purposes these ratios are twice the ideal ratios. The probe has two sets of holes drilled and tapped with 1/16 NPT in the diverging section. Two holes are on each side of the probe 1.4 cm apart. One set of the holes is 0.51 cm from the throat and the other is 1.91 cm from the exit plane. The probe is 6.35 cm long (see Fig. 5).

U-arm. --GCU-2 is designed with two U-arms. The U-arm is designed similar to the old carburetor venturi meter (see Fig. 2). Gases enter the probe and flow through the U-arm (Meadors and Wright, 1999). Assuming frictionless flow through the U-arm, the volumetric flow rate, Q, is expressed as a function of pressure difference, P1-P2, by using Bernoulli's equation (Bertin, 1984). The volumetric flow rate through the arm is characterized by

\[ Q = A \left( \frac{2(P_1 - P_2)}{\rho} \right). \]  

One U-arm is made of 0.123 cm I.D. 316 stainless steel tubing and instrumented with two 2100 GP Motorola pressure transducers to measure pressure at the taps. The pressure transducers are connected to the U-arm by "T" junction Swage-lock fittings. The second U-arm is instrumented with a 43600 Honeywell inline mass flow meter to measure flow rate (see Fig. 2).

Gas Flow Line. --The gas flow line is connected to the U-arm with the pressure transducers only. The GFL is connected to the U-arm by a "T" junction. Since the GFL is the mass spectrometer interface, capillary tubing reduces to
molecular flow. Molecular flow is characterized as

\[ c_{mp} = \sqrt{\frac{2kT}{m}} \]  

where \( k \) is Boltzmann's constant and \( T \) is the absolute temperature. The GFL is made of 0.25 cm I.D. stainless steel capillary tubing.

**Experimental.—**GCU-2 was constructed. A 0.33cm diameter pressure-regulated nozzle was placed 2.54 cm from the inlet of the probe. While inlet air pressure was varied, pressure and flow measurements were taken at the taps (see Fig. 6). The output of the pressure transducers was conditioned and converted to voltage using LM741 op-amps. The voltages were measured with a hand-held multimeter.

Given the pressure measurements, volumetric flow through the U-arm was calculated using equation 5 and compared with measurements (see Table 1). The Mach numbers at the taps, M1 and M2, were calculated by substituting static pressures in equations 1 and 2. After \( P_1 \) and \( A^* \) were eliminated from these equations, M1 and M2 were solved simultaneously. The stagnation pressure, \( P_o \), was computed directly from equation 1.

**Results and Discussion**

Data collected from GCU-2 is shown in Table 1. The Mach numbers and pressure ratios at the taps were plotted along the nozzle to compare with ideal and best design conditions (see Fig. 7). It can be seen that as the flow in the unit increased, the pressure ratio stabilizes representing choked flow and a shock in the diverging section. Choked flow in the nozzle is achieved over a range of inlet Mach numbers (0.2-1.0). However, as the shock moves toward the exit plane, the flow rate and pressure fluctuate signifying conditions predicted by computer analysis (see Fig. 4). Controlling the location of the shock could further control the flow rate.

The pressure differential versus the Mach number at tap one was plotted (see Fig. 8). As inlet pressure and Mach number increased, the pressure differential decreased. The small changes in pressure in the nozzle produce reduced flow through the U-arm and a stable range of flow rates. With constant flow rates in the U-arm, the pressure and flow rate into the mass spectrometer can be controlled.

The volumetric flow through the U-arm was predicted using equation 3 and measured with an in-line mass flow meter. The predicted flow was higher than the actual flow. The connection of the flow meter to the taps resulted in losses of pressure drop across the flow meter. The flow measurements provide qualitative confirmation of the design.

**Conclusions**

The prototype, GCU-2, qualitatively verified the design concept. Pressure and flow measurements were taken to validate the design concept and generate preliminary design information for the next iteration. GCP-2 verified that with a shock in the U-arm, constant flow and pressure into the mass spectrometer or other measuring devices can be achieved over a range of inlet pressures. A high and low flow probe can be designed to transport gases from the rocket to the mass spectrometer. Pressure measurements at the GFL should be taken to confirm flow rate into the mass spectrometer.

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collaboration and assistance in the design of the GCU. We would like to thank Armand Tomany for fabrication of the prototype and for assistance in setting up the flow experiments. This work is supported by the Arkansas Space Grant Consortium through Collaborative Research Project grant and student fellowship. This work is also supported by NASA through a GSRP Fellowship.

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Fig. 6. Experimental Setup

Fig. 7. Mach Number and Pressure Along Diverging Section.
Pressure and Flow Validation of a Second Generation Gas Extraction Probe for a Hybrid Rocket Gas Extraction System

Fig. 8. Pressure Differential versus Mach Number.

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Table 1. Data for GCU-2.
Profitability of Variable Rate Phosphorus in a Two Crop Rotation

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Abstract

The purpose of this study is to examine the profitability of variable rate phosphorus application on a rotation of rice (Oryza sativa) and soybeans (Glycine max) on fields comprised of clay and silt loam soils. Phosphorus was chosen because 1) farmers have recently been advised of the benefit of phosphorus applications on rice as well as soybeans, 2) recommended phosphorus application rates vary greatly between clay and silt loam soils and across rice and soybeans, and 3) the residual effects of phosphorus applications in a crop rotation affect the appropriateness of variable rate technology (VRT).

A three phase simulation, regression and mathematical optimization analysis was conducted to determine within a ten year planning horizon the conditions under which the profitability of variable rate phosphorus applications exceeded the profitability of uniform rate technology. Results showed that in general, VRT is not profitable when fields are comprised of only the three studied silt loam soils. However, VRT was found to be profitable in most cases when even small percentages of clay were added to the soil mix in the field. Adoption will likely also be a function of farm size. Farmers earning relatively small returns to VRT on a small area are not as likely to adopt the technology as larger operations with similar per hectare returns.

Introduction

The silt loam, sand and clay soils of the Arkansas delta are home to 4.4 million acres of irrigated cropland. Major irrigated crops include rice, cotton, and soybeans (AAAS, 1999). Of these crops, rice and soybeans are often grown in rotation so that residual effects of management practices from one year to the next may be important. In the past, phosphorus was not generally recommended for rice grown in Arkansas for two reasons. First, the availability of phosphorus under the flooded conditions associated with upland rice is difficult to predict, it is very common for flooded soils to provide adequate levels of phosphorus for rice as the soils become reduced causing the dissolution of iron (III) and manganese (IV) phosphate minerals (Hossner and Baker, 1988). Second, residual phosphorus levels from the soybean portion of the rotation are already adequate for rice production on many soils (Beyrouty et al., 1991). Recent research, however, has shown that applied phosphorus (P₂O₅) can improve the chances of attaining optimal rice yields on alkaline silt loam soils (Wilson et al, 1999). Yet, a similar recommendation has not been made for clay soils.

Further, while adequate levels of phosphorus are advantageous, excess phosphorus in the soil may indirectly decrease yields due to micronutrient imbalances. This new information suggests that phosphorus management in rice production may be beneficial, especially when rice fields are comprised of both silt loam and clay soil.

Variable rate technology (VRT) can be defined as changing the application rate of an input across a field so as to meet nutrient requirements for production. By contrast, uniform rate technology (URT) ignores spatial variation in input requirements and leads to a single rate input application on the entire field. Much economic research has focused on VRT in recent years (see Lambert and Lowenberg-DeBoer (2000) for a compilation of economic studies). Some VRT studies focused on single, monoculture crops such as cotton (Yu et al., 1999) and corn (English et al., 1999, 2001; Lowenberg-DeBoer, 1998; Roberts et al., 2000) or single nutrients such as nitrogen (English et al., 1998, 1999; LaRuffa et al., 2001; Taylor et al., 1998; Thrikawala et al., 1999) and phosphorus (Yang et al., 1999; Yu and Segarra, 1999). While the focus of these studies typically was on productive capacities or
Profitability Of Variable Rate Phosphorus In A Two Crop Rotation

profitability, some studies also discussed environmental concerns (English et al., 1999; Prato and Kang, 1998). Many studies (e.g., Babcock and Pautsch, 1998; English et al., 1998; Lowenberg-DeBoer, 1998; Prato and Kang, 1998; Watkins et al., 1998) suggest that the economic feasibility of VRT is linked to the inherent spatial differences of variable properties within a field (i.e., texture, fertility, and water holding capacity). Economic feasibility requires that benefits of VRT are greater than all the costs associated with VRT. This condition usually holds only for a limited range of input cost to crop price ratios, a specified amount of soil quality variability within a field, or both.

The purpose of this study is to examine the impact of variable rate phosphorus in a rice and soybean rotation. The objective is to evaluate the profitability of variable rate phosphorus application in fields with various proportions of silt loam and clay soils. Other evaluation criteria, such as environmental concerns, are reserved for future study. This research thus addresses under what conditions variable rate phosphorus is economically viable for rice and soybean production in regions facing similar conditions as those modeled.

Materials and Methods

This study extends previous research efforts of VRT benefits in agricultural production (see Lambert and Lowenberg-DeBoer (2000) for full compilation). This study compares URT to VRT phosphorus applications in a 1:1 rice and soybean crop rotation. As in previous studies (English et al., 1999; Lowenberg-DeBoer, 1999; Prato and Kang, 1999; Yu and Segarra, 1999), biophysical simulation data and hypothetical field combinations of multiple soil series are used for analysis. Sensitivity analysis on input and crop prices is utilized to examine price effects on optimal phosphorus application rates and economic feasibility of VRT.

This section progresses by 1) describing assumptions made regarding producer behavior, 2) outlining the production environment, 3) presenting the simulation framework, 4) delineating the functional form of required response equations, and 5) outlining optimization procedures.

Study Assumptions.—Four assumptions are made. First, variable rate application of phosphorus on a given field involves the following processes. Geographical information system (GIS) software produces a prescription nutrient plan based on the results of soil sampling. Application equipment with variable rate controllers (many types are available, but all use similar methods) interprets the prescription nutrient plan and applies product at appropriate rates site specifically. Second, VRT technology and field variability are assumed to be such that VRT is accurate enough to spatially match nutrient requirements with actual applications. It is understood that today’s technologies are precise only to engineering constraints of the width of the applicator boom currently 60-foot or 90-foot swaths and many fields are likely more variable than this. Thus said, results may suggest a greater return to VRT application than may currently be feasible on the hypothetical fields in this study. Third, application rates of all other inputs (such as nitrogen for example) are applied on all soils at a constant (or uniform) recommended rate rather than at a variable rate. Finally, simulations reflect potential conditions in Arkansas County, Arkansas, a leading rice and soybean production area in the state, where four commonly found soils—Calloway (fine-silty, mixed, active, thermic Aquic Fragiudalfs), Calhoun (fine-silty, mixed, active, thermic Typic Glossaquolls), Crowley (fine, smectitic, hyperthermic Typic Albaquolls), and Sharkey (very-fine, smectitic, thermic Chromic Epiaquerts)—were selected for this study. Soil properties including physical, chemical, and cultural characteristics are assumed to be homogeneous throughout the soil series. These soils are often found scattered throughout any given field in Eastern Arkansas (USDA, SCS, 1972).

Production Environment.—The three silt loam soils, Calloway, Calhoun, and Crowley, are considered similar in natural fertility and yield potential. Generally low in organic matter and natural fertility, these soils are expected to respond well to fertilizers and lime with similar potential for yields across soils (USDA, SCS, 1972). The Sharkey clay soil may be characterized as medium in organic matter and high in natural fertility; however, under similar nitrogen management, rice yields are expected to be lower than on the silt loam soils (USDA, SCS, 1972). Further, Sharkey soil currently has a zero phosphorus application recommendation for rice in Arkansas. Applied phosphorus and yield are, therefore, expected to exhibit a positive correlation in silt loam soils and a negative correlation in clay soils.

Crop Simulation.—The Environmental Policy Integrated Climate, or EPIC, model can be used to simulate crop production, soil erosion, water quality aspects, environmental concerns and ramifications of management practice changes over multiple years under varying weather conditions (Mitchell et al, 1995). Rice and soybean production practices such as tillage, planting, spraying, irrigating, and harvesting were adapted from field practices listed in Arkansas crop production budgets (Windham, 1999a, 1999b) and simulated in EPIC over a thirty-year period. A 1:1 rice-soybean rotation, representative of Arkansas county producer practices was followed (Norman, R. J. Personal communication). While applications of all inputs other than phosphorus were held constant at recommended rates, simulation runs were generated on the
four soils using 13 different phosphorus fertilizer rates ranging from 0 to 107.6 kg ha⁻¹ on each crop over a thirty-year planning horizon. A wide range of application rates was used to be able to adequately estimate the impact of phosphorus on crop yields. Three general phosphorus management strategies were followed. In the first, phosphorus rates were varied over both rice and soybean portions of the production process. In the second, the recommended phosphorus rate (Windham, 1999a) was used on the rice portion of the rotation where high and low phosphorus rates were used on soybeans. In the third, the recommended phosphorus rate (Windham, 1999b) was used on the soybean portion of the rotation where high and low phosphorus rates were used on rice. These three strategies were used in an attempt to capture the carryover effects of nutrient applications for different crops. As a result, 39 phosphorus treatments were developed. Due to duplications, 2 strategies were discarded leaving 37 different treatment combinations. These 37 combinations were replicated on each of the four soils, producing 148 total treatments. Over the 30-year production period, EPIC generated 4,440 observations (or 2,220 each for rice and soybeans) on over two hundred production and environmental variables.

Functional Form of Response Equations.—While crop production is a function of many factors including weather, soil moisture, tillage, variety, pesticide, soil quality, and timing of practices, this study utilizes only a few of the over two hundred variables of the EPIC model to focus on the profitability of variable rate phosphorus. Here, yield of a given crop is a function of soil phosphorus, applied phosphorus, and total available water. Soil phosphorus available at the beginning of any period is a function of previous period levels of soil phosphorus, applied phosphorus, phosphorus runoff, and phosphorus uptake by the crop. Finally, phosphorus runoff in any given period is a function of current amounts of soil phosphorus, applied phosphorus, total available water, and crop uptake of phosphorus. The following generalized equations, assumed to include the same variables for both rice and soybean crops, are thus used to evaluate the profitability of phosphorus driven yields:

\[
Yld_t = f(SP_t, AP_t, W_t) \tag{1}
\]

\[
SP_t = g(SP_{t-1}, AP_{t-1}, \text{Runoff}_{t-1}, UP_{t-1}) \tag{2}
\]

\[
\text{Runoff}_t = h(SP_t, AP_t, W_t, UP_t) \tag{3}
\]

where \(Yld_t\) is yield, \(SP\) is soil phosphorus, \(AP\) is applied phosphorus, \(W\) is total available water, Runoff is phosphorus runoff, \(UP\) is crop uptake of phosphorus, and \(t\) designates the time period—a production year. Using data from EPIC runs with the different phosphorus application rates, parameters are estimated for equations 1 to 3 and used to solve for profit maximizing phosphorus applications on each of the four soil series.

Optimization Procedures.—Once estimated, equations 1 to 3 serve in a mathematical optimization program, General Algebraic Modeling System (GAMS) (Brooke et al., 1998) to maximize discounted net revenue over a ten-year planning horizon for each of the soils. Net revenue was a function of total revenue (crop price times yield) less costs of production (price of phosphorus times the amount of phosphorus applied), VRT custom hire plus all other production costs specified in the enterprise budgets of Windham (1999a,b). The ten-year planning horizon was chosen to evaluate any phosphorus carryover effect between rice and soybean.

To determine the profitability of VRT on fields with combinations of different soils, the following two scenarios were established for the ten-year planning horizon 1) maximize profit by choosing variable phosphorus application rates across soils within a field for rice and soybean (referred to as the VRT system) and 2) maximize profit when phosphorus application rates are fixed at uniform rates according to the soil most prevalent in the field (referred to as the URT system). Profitability is calculated by adding discounted net revenues (yield times price less cost of production) across the ten-year planning horizon. Further, these net revenues are adjusted for their time of occurrence by adjusting each year’s net revenue as if these cash flows occurred all at the same time. This eliminates effects of cash flow timing across the different scenarios and is thus a preferred method of evaluation. The results are returns to the production of soybeans and rice as if all production had occurred today and are called the net present value (NPV). These are cumulative returns to land, management and risk over the planning horizon. A rice price of \$0.189 kg⁻¹, a soybean price of \$0.239 kg⁻¹, a phosphorus price of \$0.55 kg⁻¹, VRT costs of \$9.88 ha⁻¹, and a discount rate of 8.0 percent per annum were used. The VRT cost is the custom hire of variable rate phosphorus application on a field. In Arkansas, most custom application firms charge a flat fee per acre. The custom rate is not a function of within field soil variability (Daniels, M. Personal communication). Differences in NPV across the VRT and URT systems over the ten-year planning horizon were calculated to determine returns to VRT adoption on fields characterized by combinations of the three silt loam soils only and combinations of silt loam and clay soils.

Optimization runs in GAMS were performed using various price levels to determine the sensitivity of phosphorus application rates across soils. Four prices (current and five year low, high and average prices) were used for rice and soybeans. Three prices (five year low, high and average prices; in this case average and current prices were the same value) were used for phosphorus. Two values were used for the discount rate. This resulted in 96 different
Results and Discussion

Intermediate results of crop simulation and functional form are presented first. Subsequently, the optimization work in GAMS is presented and discussed to provide answers for the study objectives.

**Crop Simulation.**--The EPIC simulated yields were compared to actual farm yields reported for Arkansas County. EPIC soybean yields ranged from 1,211 kg ha\(^{-1}\) to 3,093 kg ha\(^{-1}\) and are similar to 1994-1998 average county yields reported for irrigated soybean (AASS, 1999). EPIC rice yielded between 4,338 kg ha\(^{-1}\) and 6,305 kg ha\(^{-1}\). These yields are slightly lower than typical rice yields in Arkansas County from 1994 to 1998 (AASS, 1999). Applying too little or too much phosphorus with the wide range in application rates in the model may have affected these observed yields.

**Functional Form of Response Functions.**--EPIC generated panel data for over 200 variables with thirty annual observations each. A general linear model for panel data was used to estimate equations 1 to 3 (Hsiao, 1991). All equations were tested for heteroskedasticity and serial correlation using procedures outlined in Greene (1995). The model was adjusted for heteroskedasticity (Greene, 1995). The estimated equations took the following functional forms:

\[
Yld_i = f(C, SP_b, AP_p, W_p, SP^2_b, AP^2_p, W^2_p)
\]

adj. \(R^2\): Rice = 0.64 Soybean = 0.70

\[
SP_i = g(C, SP_{r1}, AP_{r1}, Runoff_{r1}, Yld_{r1})
\]

adj. \(R^2\): Rice = 0.87 Soybean = 0.89

\[
Runoff_i = h(C, SP_p, AP_p, W_p, Yld_p)
\]

adj. \(R^2\): Rice = 0.71 Soybean = 0.82

where \(C\) is an intercept term and other variables are as defined above. Note that for equations 5 and 6, substituting \(Yld\) for EPIC’s \(UP\) variable led to better results. Also, as expected (Mitchell et al., 1995), the yield equation 4 for both rice and soybeans exhibited a quadratic functional form. Equations 5 and 6, the soil phosphorus and phosphorus runoff equations, respectively, showed a linear fit as expected from previous research (Daniel, T. Personal communication). Many of the parameter estimates were significant at the 99 percent confidence level, with signs and magnitudes of all coefficients as expected. Detailed results are available from the authors upon request.

**Optimization.**--First, the phosphorus application rates that maximize NPV for the VRT system are presented. Subsequently, returns to the adoption of VRT are assessed by comparing URT to VRT phosphorus applications on fields in two ways. First a field is assumed to be composed of combinations of only the three silt loam soils as variation of soil characteristics across the three silt loam soils is expected to be minimal. Next the field is assumed to have combinations of all four silt loam and clay soils. In this case, within field soil variation across silt loam and clay soils could lead to a higher return to VRT than fields comprised of silt loam soils only.

**Optimal Phosphorus Application Rates for Each Soil.**--Equations 1 through 3 were placed in GAMS to determine the optimal (or steady state uniform) phosphorus application

<table>
<thead>
<tr>
<th>Crop</th>
<th>Rice</th>
<th>Average Annual Yield (kg ha(^{-1}))</th>
<th>Soybeans</th>
<th>Average Annual Yield (kg ha(^{-1}))</th>
<th>Rotation NPV ($ ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>Applied Phosphorus (kg ha(^{-1}))</td>
<td></td>
<td>Applied Phosphorus (kg ha(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Calloway 52.7</td>
<td>6,759</td>
<td>40.6</td>
<td>2,354</td>
<td>3,511</td>
</tr>
<tr>
<td></td>
<td>Calhoun 67.2</td>
<td>6,658</td>
<td>40.8</td>
<td>2,354</td>
<td>3,341</td>
</tr>
<tr>
<td></td>
<td>Crowley 50.4</td>
<td>6,204</td>
<td>37.0</td>
<td>2,555</td>
<td>2,921</td>
</tr>
<tr>
<td></td>
<td>Sharkey 2.2</td>
<td>6,103</td>
<td>10.1</td>
<td>2,018</td>
<td>2,192</td>
</tr>
</tbody>
</table>

1These are the phosphorus application rates for rice and soybeans that maximized discounted net present value of production on each soil.

2Discounted Net Present Value (NPV) is calculated by adding discounted net revenue values across the ten-year planning horizon. Discounted net revenues are calculated by subtracting costs from revenues in each of the ten years and discounting each year’s net revenue by the appropriate discount factor; these are cumulative returns to land, management and risk over the planning horizon. A rice price of $0.189 kg\(^{-1}\), a soybean price of $0.239 kg\(^{-1}\), a phosphorus price of $0.55 kg\(^{-1}\), VRT costs of $9.88 ha\(^{-1}\) and a discount rate of 8.0 percent per annum were used.
rate that would maximize NPV on each soil series. Table 1 presents the resulting phosphorus rates, yields and dollar amounts that maximized NPV on each soil. As expected for silt loam soils, the optimal phosphorus rate on Calloway and Crowley soils were similar. Unexpectedly, optimal phosphorus rates for rice were much higher on Calhoun soils. This may be an EPIC modeling issue but is still considered within normal ranges (Norman, 2000). Phosphorus rates on the Sharkey soils for rice and soybeans were 2.2 and 10.1 kg ha\(^{-1}\), respectively. Although phosphorus rates of zero were expected, this too is within a normal range (Norman, 2000). As expected, the yields on the silt loam soils are higher than those on the Sharkey clay soil.

Surprisingly, optimal phosphorus application rates were insensitive to price or discount rate changes. NPV varied with price ratios but values were consistently positive or consistently negative across the different price and discount rates used. Only magnitudes differed. Likely the variability in prices was too narrow over the five year period studied (1995-1999) to materially affect results. Therefore, only results using 1999 values are reported. A rice price of $0.189 kg\(^{-1}\), a soybean price of $0.239 kg\(^{-1}\), a phosphorus price of $0.55 kg\(^{-1}\), VRT costs of $9.88 ha\(^{-1}\) (AASS, 1999; Randlemann, R. Personal communication) and a discount rate of 8.0 percent per annum were used.

**Impacts of Alternative Phosphorus Rates on Yields and Returns on the Four Soils.**—Once these optimal uniform application rates were determined for each soil, simulations using equations 4 through 6 were run with alternative (that is rates not optimal for a given soil) phosphorus application rates to estimate yields using uniform rates to capture the effect of sub-optimal application rates across soils. This analysis was conducted to determine what happens to yields and NPV if sub-optimal phosphorus rates are used on each of the four soils. This situation could occur when one phosphorus application rate (say the rate for the Calloway soil) is used across a field that is comprised of multiple soils (a field of Calloway, Calhoun and Sharkey, for example).

Three different uniform rates, abbreviated as \(U_1\), \(U_2\), and \(U_3\), were developed on the basis of the optimal uniform rates that maximized NPV shown in Table 1. \(U_1\) was calculated by taking the average optimal phosphorus rates for Calloway and Crowley silt loam soils. This new \(U_1\) rate (that is, 51.6 kg ha\(^{-1}\) on rice and 38.7 kg ha\(^{-1}\) on soybeans) is appropriate for a field with either Calloway or Crowley silt loam soils. \(U_2\) and \(U_3\) represent the appropriate uniform phosphorus rates for fields with a Calhoun silt loam soil and a Sharkey clay soil, respectively. These rates are the same optimal application rates shown in Table 1 for Calloway (67.2 kg ha\(^{-1}\) on rice and 40.3 kg ha\(^{-1}\) on soybeans) and Sharkey clay (2.2 kg ha\(^{-1}\) on rice and 10.1 kg ha\(^{-1}\) on soybeans) soils.

Table 2 shows the yield and economic losses that occur when \(U_1\), \(U_2\) and \(U_3\) are misused on each of the four soils. Silt loam soils yields and NPV were most negatively impacted when \(U_3\) was utilized because applied phosphorus was too low. For example, NPV fell from $3,506 ha\(^{-1}\) to $918 ha\(^{-1}\) when phosphorus application rates were changed from \(U_1\) to \(U_3\) on the Calloway soil. Similarly, compared to the optimal phosphorus rate application, yields and NPV on the Sharkey clay fell dramatically under \(U_1\) and \(U_2\) rate applications because phosphorus applications were too high.

### Table 2. Estimates of Yield and Net Present Value (NPV) Losses Under Non-Optimal Phosphorus Application Rates.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Rice (kg ha(^{-1}))</th>
<th>Soybeans</th>
<th>NPV ($ ha(^{-1}))</th>
<th>Rice (kg ha(^{-1}))</th>
<th>Soybeans</th>
<th>NPV ($ ha(^{-1}))</th>
<th>Rice (kg ha(^{-1}))</th>
<th>Soybeans</th>
<th>NPV ($ ha(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calloway</td>
<td>N/A(^3)</td>
<td>N/A</td>
<td>N/A</td>
<td>6,406</td>
<td>2,286</td>
<td>3,398</td>
<td>4,741</td>
<td>1,950</td>
<td>918</td>
</tr>
<tr>
<td>Calhoun</td>
<td>6,456</td>
<td>2,219</td>
<td>3,115</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>287</td>
<td>1,345</td>
<td>211</td>
</tr>
<tr>
<td>Crowley</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>5,901</td>
<td>2,286</td>
<td>2,748</td>
<td>4,438</td>
<td>2,017</td>
<td>764</td>
</tr>
<tr>
<td>Sharkey</td>
<td>2,875</td>
<td>672</td>
<td>-839</td>
<td>2,471</td>
<td>605</td>
<td>-1,230</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

1. NPV calculations are as defined in Table 1.
2. \(U_1\) represents an average rate appropriate for Calloway or Crowley silt loam soils (51.6 kg ha\(^{-1}\) on rice and 38.7 kg ha\(^{-1}\) on soybeans). \(U_2\) and \(U_3\) represent the appropriate rates for Calhoun silt loam (67.2 kg ha\(^{-1}\) on rice and 40.3 kg ha\(^{-1}\) on soybeans) and Sharkey clay (2.2 kg ha\(^{-1}\) on rice and 10.1 kg ha\(^{-1}\) on soybeans) soils, respectively.
3. N/A indicates that the (appropriate) uniform phosphorus application rate is applied in that case (for example, \(U_1\) is the rate appropriate for the Calloway soil) and, therefore, no losses result. Yield and NPV values are the same as those presented in Table 1.
Table 3. Returns to Variable Rate Technology (VRT) on Fields of Silt Loam Soils

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Field Combination (percent)</th>
<th>Calloway</th>
<th>Crowley</th>
<th>Calhoun</th>
<th>NPV$<em>{VRT}$ - NPV$</em>{U1}$</th>
<th>NPV$<em>{VRT}$ - NPV$</em>{U2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>60 20</td>
<td>20 20</td>
<td>20</td>
<td>-13</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>40 40</td>
<td>40 20</td>
<td>20</td>
<td>-9</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>20 60</td>
<td>20 20</td>
<td>20</td>
<td>-5</td>
<td>N/A</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>50 25</td>
<td>25 25</td>
<td>25</td>
<td>2</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>25 50</td>
<td>50 25</td>
<td>25</td>
<td>3</td>
<td>N/A</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>60 0</td>
<td>40 0</td>
<td>40</td>
<td>27</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>40 20</td>
<td>40 20</td>
<td>40</td>
<td>31</td>
<td>N/A</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>20 40</td>
<td>40 40</td>
<td>40</td>
<td>35</td>
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<tr>
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<td>50 50</td>
<td>50</td>
<td>54</td>
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<td>0 50</td>
<td>50 50</td>
<td>50</td>
<td>59</td>
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</tr>
<tr>
<td>12</td>
<td></td>
<td>20 20</td>
<td>60 60</td>
<td>60</td>
<td>N/A</td>
<td>3</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>0 40</td>
<td>60 60</td>
<td>60</td>
<td>N/A</td>
<td>5</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>10 20</td>
<td>70 70</td>
<td>70</td>
<td>N/A</td>
<td>-20</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>5 25</td>
<td>70 70</td>
<td>70</td>
<td>N/A</td>
<td>-17</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>20 0</td>
<td>80 0</td>
<td>80</td>
<td>N/A</td>
<td>-44</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>0 20</td>
<td>0 0</td>
<td>0</td>
<td>N/A</td>
<td>-32</td>
</tr>
</tbody>
</table>

1Silt loam soils are Calloway, Calhoun and Crowley series in this example.

2NPV calculations are defined in Table 1. Uniform rate applications are described in Table 2.

3N/A is not applicable because these NPV would result only from uniform phosphorus rate applications that a farmer would not normally use given the majority of the soil in the field.

**Profitability of VRT**—Once the relationships between phosphorus application rates, yields, and NPV were established for the four soils individually, the effects of URT and VRT phosphorus applications on fields comprised of more than one soil could be tested. A series of 135 hypothetical one-hectare fields was created. Each of these fields was comprised of various amounts of two, three, and all four soils (see authors for details on soil combinations in the fields). Comparisons of NPV from using VRT (the appropriate application rate for each soil in the field) versus using a uniform phosphorus rate (the rate appropriate for the soil that represented the largest proportion in the field) were then made for each hypothetical field.

Results were first analyzed on fields with different combinations of silt loam soils only. As these soils have similar characteristics, large returns to VRT were not expected. While Table 3 does not provide a complete listing of the returns to VRT for all possible silt loam field combinations, it does highlight the general results. On fields comprised of combinations of the three silt loam soils, results showed that VRT provided greater returns than using one uniform rate (URT) under two conditions. First, VRT was superior to U7 when Calloway and/or Crowley soils made up between approximately 50 and 75 percent of the field. As more and more Calloway and/or Crowley were present in the field, the difference between VRT and U7 narrowed. As shown in scenarios one through eleven, Crowley soil has a lessened sensitivity to the average uniform phosphorus application rate U7. So that when a field is comprised of 25 to 50 percent Calhoun, net returns to VRT will increase as the proportion of Crowley in that field increases. As Crowley and Calloway are similar soils, these results were unexpected. However, as the difference in profitability is small, this raises little concern and does not affect our general conclusions. Once Calloway and Crowley made up more than 75 percent of the field, VRT was no longer more profitable than U7. Second, VRT was superior to U2 when a field consisted of 50 to 60 percent Calhoun. As more Calhoun enters the field, VRT becomes less attractive compared to U2. The same condition applies for the makeup of the remaining soils. While these results do show there may be possible returns to VRT on silt loam soils, the 10 year net returns to VRT are small (reaching a maximum at just under $60 ha$^{-1}$) and the range of soil combinations where these benefits may be found are limited.
Table 4. Profitability of Variable Rate Technology (VRT) on Fields of All Soils

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Field Combination (Percent)</th>
<th>NPV&lt;sub&gt;VRT&lt;/sub&gt; - NPV&lt;sub&gt;U1&lt;/sub&gt; ($ ha&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>NPV&lt;sub&gt;VRT&lt;/sub&gt; - NPV&lt;sub&gt;U2&lt;/sub&gt; ($ ha&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>NPV&lt;sub&gt;VRT&lt;/sub&gt; - NPV&lt;sub&gt;U3&lt;/sub&gt; ($ ha&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Calloway 99, Crowley 0, Calhoun 0, Sharkey 1</td>
<td>31</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2</td>
<td>Calloway 0, Crowley 99, Calhoun 0, Sharkey 1</td>
<td>N/A</td>
<td>11</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td>Calloway 0, Crowley 0, Calhoun 99, Sharkey 1</td>
<td>N/A</td>
<td>32.12</td>
<td>N/A</td>
</tr>
<tr>
<td>4</td>
<td>Calloway 98, Crowley 0, Calhoun 0, Sharkey 2</td>
<td>-5</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>Calloway 0, Crowley 98, Calhoun 0, Sharkey 2</td>
<td>N/A</td>
<td>0</td>
<td>N/A</td>
</tr>
<tr>
<td>6</td>
<td>Calloway 0, Crowley 0, Calhoun 98, Sharkey 2</td>
<td>N/A</td>
<td>5.02</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>Calloway 97, Crowley 0, Calhoun 0, Sharkey 3</td>
<td>N/A</td>
<td>29</td>
<td>N/A</td>
</tr>
<tr>
<td>8</td>
<td>Calloway 0, Crowley 97, Calhoun 0, Sharkey 3</td>
<td>49</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>9</td>
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<tr>
<td>10</td>
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<td>N/A</td>
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<tr>
<td>11</td>
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<td>12</td>
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<td>104.72</td>
<td>N/A</td>
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<tr>
<td>13</td>
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<tr>
<td>14</td>
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<tr>
<td>15</td>
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<td>42</td>
<td>N/A</td>
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<tr>
<td>19</td>
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<td>N/A</td>
<td>90</td>
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</tr>
<tr>
<td>20</td>
<td>Calloway 1, Crowley 1, Calhoun 0, Sharkey 97</td>
<td>N/A</td>
<td>12</td>
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</tr>
<tr>
<td>21</td>
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<td>N/A</td>
</tr>
<tr>
<td>22</td>
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<td>-14</td>
<td>N/A</td>
</tr>
<tr>
<td>23</td>
<td>Calloway 0, Crowley 2, Calhoun 0, Sharkey 98</td>
<td>N/A</td>
<td>-23</td>
<td>N/A</td>
</tr>
<tr>
<td>24</td>
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<td>-4</td>
<td>N/A</td>
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<tr>
<td>25</td>
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<td>-40</td>
<td>N/A</td>
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<tr>
<td>26</td>
<td>Calloway 0, Crowley 1, Calhoun 99, Sharkey 0</td>
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<td>-45</td>
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<tr>
<td>27</td>
<td>Calloway 0, Crowley 0, Calhoun 1, Sharkey 99</td>
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<td>-35</td>
<td>N/A</td>
</tr>
<tr>
<td>28</td>
<td>Calloway 0, Crowley 0, Calhoun 0, Sharkey 100</td>
<td>N/A</td>
<td>-66</td>
<td>N/A</td>
</tr>
</tbody>
</table>

1 Soils are Calloway, Calhoun and Crowley silt loam and a Sharkey clay.
2 NPV calculations are defined in Table 1. Uniform rate applications are described in Table 2.
3 N/A is not applicable because these NPV would result only from uniform phosphorus rate applications that a farmer would not normally use given the majority of the soil in the field.

Clay soils introduced a greater degree of phosphorus response variability to the field and therefore suggested a larger range of soil combinations over which VRT might be profitable. In fact, as seen in scenarios 7 through 21 in Table 4, VRT was superior to URT in these mixed fields when the proportion of Sharkey was greater than two percent and less than 98 percent. The full range of positive returns to VRT (not shown in Table 4) were roughly $1.00 ha<sup>-1</sup> to $1,003.00 ha<sup>-1</sup>. The authors note that in this case the range for which VRT is profitable may be extreme and an artifact of the modeling process. However, it does support the idea that VRT can be profitable where soil characteristics, that are important to rice and soybean production processes, are diverse within a given field. Given the broad differences in nutrient requirements between the clay and silt loam soils, application rates desired for one soil series could have devastating effects on yields and thus NPV of other soil series. When the clay rate was applied to silt loam soils, yield decreased more than when other silt loam application rates were applied. However, when a silt loam rate was applied to Sharkey clay, yields decreased dramatically. Thus there was much to be gained by applying the proper phosphorus rate to each portion of the field.
Table 5. Summary of Comparison of Variable Rate Technology (VRT) to Uniform Rate Technology (URT)

<table>
<thead>
<tr>
<th>Soils in the Field</th>
<th>When VRT is Superior to URT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calloway and Crowley</td>
<td>Never</td>
</tr>
<tr>
<td>Calhoun and all Calloway/Crowley combinations</td>
<td>Superior to U1 when Calloway/Crowley mix is between 50 and 75 percent of field</td>
</tr>
<tr>
<td>Calhoun and all Calloway/Crowley combinations</td>
<td>Superior to U2 when Calhoun is between 50 and 60 percent of field</td>
</tr>
<tr>
<td>Sharkey and all Calloway/Crowley/Calhoun combinations</td>
<td>Superior to U1, U2, and U3 when amount of Sharkey in the field is between 3 and 97 percent</td>
</tr>
</tbody>
</table>

Conclusions

This paper describes some of the results of a study of the profitability of VRT of phosphorus on a rice and soybeans rotation. Yields were found to be responsive to phosphorus application rates. This suggested that in fields comprised of multiple soils, variable rate applications of phosphorus could improve net returns over returns attributed to uniform rate applications alone. However, VRT was found to produce higher net returns than URT only when sufficient variation existed within a field. Cases of sufficient variation (summarized in Table 5) included situations where 1) Calloway and/or Crowley made up between 50 and 75 percent of the field (VRT provided greater net returns than application of the U1 rate), 2) Calhoun composed between 50 and 60 percent of the field (VRT provided greater net returns than application of the U2 rate), and 3) the proportion of Sharkey was between three and 97 percent of the field (VRT provided greater net returns than application of any of the U1, U2, and U3 rates alone). In general, returns to VRT were small on silt loam fields, less than $60 ha⁻¹ over a ten-year planning horizon, whereas gains to VRT reached as high as $1,000 ha⁻¹ on fields containing both silt loam and clay soils over the same planning horizon.

While this paper gives some indication of the potential profitability of VRT applications of phosphorus in rice and soybeans rotations, it is still unclear how many farmers are likely to adopt the technology. Ongoing efforts of soil scientists at the University of Arkansas are expected to lead to a better understanding of the soil composition of the cropland in major Arkansas crop production regions. With this information, areas where VRT adoption is most likely to occur could be identified as those meeting the criteria outlined above. Adoption will likely also be a function of farm size as farmers earning relatively small returns to precision farming on a small area are not as likely to adopt the technology as larger operations with similar per hectare returns. Finally, further research on the effect of different rice/soybeans rotations on nutrient carryover may affect the applicability of VRT on an annual basis.

Literature Cited


Assessing spatial break-even variability in fields with two or more management zones. J. Agric. Appl. Econ. 33:551-565.


Stability and Optimization of Photoconductivity in Thermally Vacuum Evaporated Indium (III) Sulfide Thin Films

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Abstract

Long term stability of photosensitivity versus time in indium (III) sulfide thin films thermally vacuum evaporated onto photocell-patterned printed circuit boards varies sensitively with several factors including contact metal type, contact metal diffusion and electromigration into the semiconductor, doping, and encapsulation method. Because of the significant photoconductivity and relative low toxicity and environmental impact of this compound semiconductor, it is important to better characterize these dependences toward commercial applications. We will report on measurements of photoconductivity vs. time as functions of such factors and evolving methods to stabilize this photoconductivity.

Introduction

Indium (III) sulfide, In$_2$S$_3$, is a photosensitive semiconductor with potential for various commercial applications because of its low toxicity and environmental impact, reasonable cost ($\$3.42/g – Cerac, Inc.), and ease of deposition as a thin film (Barber et al., 1997). It is an n-type semiconductor with 2.0 eV indirect bandgap and exhibits significant photoconductivity (Yu et al., 1999). There has been considerable recent interest in In$_2$S$_3$ and In$_2$S$_x$O$_{3-x}$ as possible safer alternatives to CdS for use as window materials in photovoltaic cells (Bayón et al., 1998). The Arkansas State University Optoelectronic Materials Research Laboratory is working on developing large area printed circuit boards (PCB’s) containing a two-dimensional array of indium sulfide-based photocells for use in applications involving laser activation of computer or control commands.

The board consists of conductive photocell-patterned contacts, In$_2$S$_3$ as the photosensitive semiconductor film, and electronic interfacing components. The semiconductor film is deposited onto the photocell-patterned contacts by thermal vacuum evaporation. The semiconductor increases in electrical conductance in response to illumination with photon energies greater than the 2.0 eV bandgap of In$_2$S$_3$. Thus, when low power laser light strikes a photocell, it produces a proportional photovoltaic, which can be amplified and used as an input signal for the computer or control interface.

Thermally vacuum evaporated thin films of this semiconductor on photocell-patterned contacts exhibit a photovoltaic versus time stability that depends on several variables. These include contact material, doping, and encapsulation of the films.

The stability of the photovoltage was investigated using different contact materials such as bare copper, solder-coated copper, gold-on-nickel-coated copper, ITO-on-glass, and graphite. Underlying semiconductor films of bismuth (III) sulfide and tin (II) sulfide and polyurethane, indium (III) oxide, and molybdenum (VI) oxide encapsulant films were also investigated in an effort to enhance the photosensitivity and/or the stability of the In$_2$S$_3$ films on photocell patterns.

Materials and Methods

Copper, the standard material used in PCBs, was the first material to be tested. Solder (63% Sn / 37% Pb) and gold-on-nickel are common barrier coatings for underlying copper contacts and were also investigated. Indium tin oxide (ITO – 0.9 In$_2$O$_3$ / 0.1 SnO$_2$, 15 ohms/square) coated glass was obtained commercially from Applied Films and patterned by photolithography and etching methods. Graphite ink (Aquadag®) was applied to glass substrates in-house to produce graphite contact patterns. Indium (III) sulfide (In$_2$S$_3$ - 99.99%) was purchased from Cerac. Bismuth (III) sulfide (Bi$_2$S$_3$ - 99.999% - Cerac) and tin (II) sulfide (SnS - 99.9% - Alfa Aesar) were used in some instances as photoconductive barrier films between the PCB and upper In$_2$S$_3$ layer. Polyurethane, molybdenum (VI) oxide (MoO$_3$ - 99.95% - Alfa Aesar), and indium (III) oxide (In$_2$O$_3$ - 99.9% - Alfa Aesar) were investigated as encapsulants. The photocell patterns used on substrates with metal and ITO contacts were the basic interdigitated photocell layout shown in Fig. 1A, while two closely spaced parallel contact stripes were used with graphite (Fig. 1B).

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Fig. 1A. Photocell contact pattern used with bare copper, solder-coated copper, gold-on-nickel-coated copper, and ITO.

Fig. 1B. Photocell contact pattern used with graphite.

Fig. 2. Typical photovoltage vs. time waveform.
Fig. 3. Measurement and data acquisition schematic diagram.

Fig. 4. Stability of photovoltage for In$_2$S$_3$ on bare copper contacts over time.
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Fig. 5. Variation of gross stoichiometry of In$_2$S$_3$ film as a function of distance from copper contacts.

With lowering pressures, the boiling and sublimation points of any material decrease. Thus, In$_2$S$_3$ was easily evaporated at approximately 10^-3 torr (in a TM Vacuum Products, Inc. Smartjar™ thermal evaporation system) by applying current and voltage to a molybdenum boat in which the semiconductor powder was placed. A substrate with photocell-patterned contacts was positioned above the boat. Since the temperature of the substrate was just above room temperature and considerably lower than the vaporization point of the material, the semiconductor condensed on the board forming a thin film, the thickness of which was controlled by a rate monitor (XTC/2 - Inficon). By using up to three different boats and shutters and controlling the applied voltage and current, it was possible to evaporate up to three different materials as separate layers without breaking vacuum.

A Bi$_2$S$_3$ or SnS barrier film was evaporated before the In$_2$S$_3$ layer in some cases. Sometimes MoO$_3$ or In$_2$O$_3$ was also evaporated after the In$_2$S$_3$ layer as an inorganic encapsulant. Polyurethane was painted over the In$_2$S$_3$ film as an organic encapsulant in other instances. All of these materials are minimally toxic and minimally environmentally impactive. Bi$_2$S$_3$ and SnS are also photoconductors (Johnson et al., 1999; Mishra et al., 1989) with nearly equal 1.3 eV bandgap; Bi$_2$S$_3$ is n-type and SnS is p-type.

To produce the photovoltage signal which was proportional to photoconductance, a bias of 15 VDC was applied across the photocell while a low power (1 mW) red (635 nm) solid-state laser was modulated on-and-off at 1 kHz and illuminated the sample. The photovoltage waveform (Fig. 2) produced by this process was amplified using a variable gain amplifier (Fig. 3). To reduce electrical noise, grounded metal foil encased most of the sample as a shield. A multimeter with computer interface was used as a data acquisition system to provide information required to plot graphs of photovoltage versus time and to indicate the stability of the films.

Results and Discussion

Indium sulfide evaporated onto bare copper contacts yielded a signal that initially increased in magnitude over time. After this initial period of increase, the signal often fluctuated (Fig. 4). The well-known diffusion of copper (d’Heurle and Ho, 1978; Baglin and Poate, 1978) doped the semiconductor with acceptor levels (as is common with copper sensitization of photoconductivity in CdS (Bube, 1960)) and increased the signal, as was seen initially. Eventually the diffusion could cause a conductive copper or
Fig. 6A and 6B. Electromigration of copper into semiconductor film evidenced by the dark region near the contacts in the electron microscope photographs.

Fig. 7. Stability of photovoltage for In$_2$S$_3$ on solder-coated copper contacts over time.
Copper sulfide bridge across the contacts, shorting the photocell. To further investigate the diffusion and electromigration of copper into the film, energy dispersive X-ray analysis/spectroscopy (EDS) was performed by Dr. Susan Kerber, Material Interface, Sussex, WI. Figure 5 shows the atomic percentages of different elements in the semiconductor film at various distances from the copper contacts. The EDS analysis confirmed the suspicion that the copper diffused into the film. At 3 and 10 μm from the metal contacts, the atomic percentages of copper were surprisingly high (48.43% and 14.35%, respectively). Scanning electron microscope photographs (Fig. 6A and 6B) illustrate the diffusion of copper; the copper/copper sulfide region can be seen as a dark area close to the metal contact. The percentages of oxygen were also significant throughout the film. This indicates the possibility that In₂S₃ reacted with or absorbed/adsorbed atmospheric moisture or oxygen, which could have contributed to the fluctuations of the photosignal over time.

In an attempt to block the copper diffusion into the film, In₂S₃ was evaporated onto solder-coated copper contacts. The same initial increase and fluctuations were observed, but the magnitude of the signal decreased slightly over time (Fig. 7). EDS analysis was also performed on this sample (Fig. 8). It indicated that copper was still diffusing into the film, which is consistent with the previous assumption that the copper was doping the semiconductor, causing the signal to increase initially. Tin and lead also diffused into the film to a much lesser extent and could be responsible for the subsequent slight decrease in signal. Once again, oxygen was detected in the film.

Gold and nickel are known to be more stable chemically than copper and more effective than solder in preventing copper diffusion, thus In₂S₃ was evaporated onto gold-on-nickel-coated copper contacts. Once again, the sample exhibited an initial increase followed by minor fluctuations of the photosignal (Fig. 9). It is possible to see in the EDS data of Fig. 10 that copper was still diffusing into the semiconductor film. Also, the large amounts of oxygen again indicate a potential partial oxidation or hydrolysis of the film into In₂O₃, In(OH)₃, and/or In₂S₃O₅x as was seen in previous EDS analyses.

Bi₂S₃ and SnS were investigated as underlying photoconductive barrier films for the In₂S₃ film. This was an attempt to further block the copper diffusion and increase overall photoconductance. Plots of photovoltage versus time...
for a Bi$_2$S$_3$/In$_2$S$_3$ film on bare copper and solder-coated copper contacts are shown in Fig. 11. Photovoltage versus time data for these films behaved similarly to that for In$_2$S$_3$ films on bare copper and solder-coated copper contacts films. SnS as a barrier film yielded an initial decrease of photovoltage followed by a considerably more stable signal (Fig. 12). The sharp peaks seen on the graph are transient electrical/electromagnetic noise spikes interfering with the photosignal.

Since copper diffusion could not be conclusively eliminated using coatings of various metals or semiconductor barrier films, In$_2$S$_3$ was evaporated onto ITO-on-glass contacts (Fig. 13). This film yielded an initial increase in signal, as had the films with copper contacts. This indicates that the copper diffusion wasn’t solely responsible for the initial transient increase in signal. Another plausible explanation for the initial increase in photosignal could be the transient filling of an impurity or defect level ("trap state") within the bandgap by the photo-excited electrons and/or holes that fall from the conduction band and/or valence band and get trapped in this band, thus decreasing the initial free carrier concentrations (Rose, 1978). As increasing numbers of trap states become filled, less-and-less additional free carriers become trapped, more stay in the bands as free carriers, and the conductivity increases. Once the impurity or defect level is filled, there is no further increase in signal, since the concentrations of free holes and electrons remain the same under steady state conditions. This conjecture is supported by the fact that the photosignal decreased in magnitude when the laser was moved from the illuminated area to a previously unilluminated location on the same photocell. Indium sulfide on graphite contacts produced a small steady increase in signal over time (Fig. 14). Very small fluctuations of the signal were due to electrical noise.

Polyurethane was applied to an In$_2$S$_3$ film on solder-coated copper contacts after evaporation (Fig. 15). The initial decrease in photosignal illustrated on the graph was probably due to the drying of the polyurethane. After this initial decay, it was once more possible to see a slight increase of the photovoltage over time. The polyurethane coating prevented reactions with the atmosphere, and the small fluctuations that were common on the unencapsulated In$_2$S$_3$ on solder-coated copper contacts vanished.

In$_2$O$_3$ was evaporated onto In$_2$S$_3$ on solder-coated copper contacts as an inorganic encapsulating film. This
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Fig. 10. Variation of gross stoichiometry of In$_2$S$_3$ film as a function of distance from gold-on-nickel-coated copper contacts.

Fig. 11. Stability of photovoltage for In$_2$S$_3$ on bare copper and solder-coated copper contacts over time with Bi$_2$S$_3$ as a photoconductive barrier film.
sample produced a very small photovoltage with a poor signal-to-noise ratio which hindered accurate measurements. Annealing In$_2$O$_3$ at 500°C for about 5 minutes converts the oxide layer into a fully oxidized transparent film, but the PCB will withstand only up to 200°C for short periods of time before deteriorating. Annealing for different intervals of time at 200°C was attempted, but resulted in no major improvement in the photosignal.

A multi-layer (Bi$_2$S$_3$/In$_2$S$_3$/MoO$_3$) film was evaporated onto solder-coated copper contacts. Bismuth sulfide was used as a barrier film and molybdenum oxide as an encapsulant. The photovoltage decreased very sharply initially, but then stabilized and increased slightly (Fig. 16). The abrupt vertical drop on the graph was due to the change in scale setting of the multimeter.

Conclusions

Barrier layer methods used to eliminate copper diffusion from the contacts into evaporated In$_2$S$_3$ thin films were ineffective. EDS analysis showed that solder and gold-on-nickel coatings on the underlying copper did not block the electromigration of copper and led to some additional tin, lead, and gold diffusion. A photoconductive SnS barrier film underneath the In$_2$S$_3$ film reduced photovoltage fluctuations, whereas the Bi$_2$S$_3$ barrier film resulted in no improvement in long-term stability. ITO-on-glass contacts, despite the initial transient instability, produced a very stable subsequent signal. The sample with graphite contacts had the best long-term stability of all tested samples and warrants further investigation. Evaporated inorganic encapsulants were not totally transparent and reduced the photosignal considerably. A clear coat of polyurethane on In$_2$S$_3$ appeared effective in further stabilizing the photoconductivity and protecting the integrity of the film. A more detailed investigation of the absorbance of the encapsulant films is required for further improvement in photoconductive signal magnitude. Table 1 is a summary of results for all off the different experiments conducted to investigate the stability of In$_2$S$_3$ films on photocell patterns.

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Fig. 13. Stability of photovoltage for In$_2$S$_3$ on ITO-on-glass contacts over time.

Fig. 14. Stability of photovoltage for In$_2$S$_3$ on graphite contacts over time.
Fig. 15. Stability of photovoltage over time for In$_2$S$_3$ with polyurethane encapsulation.

**Literature Cited**


![Graph showing stability of photovoltage over time for In$_2$S$_3$ with Bi$_2$S$_3$ as a photoconductive barrier film and MoO$_3$ as an encapsulant.](image)

**Fig. 16.** Stability of photovoltage over time for In$_2$S$_3$ with Bi$_2$S$_3$ as a photoconductive barrier film and MoO$_3$ as an encapsulant.

**Table 1. Summary of Experiments and Results.**

<table>
<thead>
<tr>
<th>Contact Material</th>
<th>Signal Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare copper</td>
<td>Initial increase/decrease</td>
</tr>
<tr>
<td>Solder-coated copper</td>
<td>Initial increase/fluctuations</td>
</tr>
<tr>
<td>Gold-on-nickel</td>
<td>Initial increase/fluctuations</td>
</tr>
<tr>
<td>ITO-on-glass</td>
<td>Initial increase/stable</td>
</tr>
<tr>
<td>Graphite</td>
<td>Stable</td>
</tr>
<tr>
<td>Solder-coated copper with Bi$_2$S$_3$ barrier film</td>
<td>Initial increase/fluctuations</td>
</tr>
<tr>
<td>Bare copper with Bi$_2$S$_3$ barrier film</td>
<td>Increase</td>
</tr>
<tr>
<td>Solder-coated copper with SnS barrier film</td>
<td>Initial increase/fluctuations</td>
</tr>
<tr>
<td>Solder-coated copper with polyurethane encapsulant</td>
<td>Initial decrease/increase</td>
</tr>
<tr>
<td>Copper with Bi$_2$S$_3$ barrier film and MoO$_3$</td>
<td>Initial decrease/stable</td>
</tr>
</tbody>
</table>

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Effect of Charge on the Deposition of Electrostatically Charged Inhalable Aerosol in Lung Model

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Abstract

Inhalable drugs are widely used for treating lung diseases such as asthma, emphysema, and cystic fibrosis. The aerosol particles in these inhalable drugs may be charged electrostatically. The deposition of these inhaled therapeutic aerosol particles in the different regions of the lung depends on the particle aerodynamic diameter, electrostatic charge distribution, particulate number density, breathing rate, aerodynamics of the lung, ambient temperature, and relative humidity (RH). The primary mechanisms for lung deposition of inhaled particles are impaction, gravitational settling, diffusion, interception, and electrostatic attraction. To simulate lung deposition, electrostatically charged aerosol particles are introduced through a throat section into a glass bead lung model. The E-SPART analyzer was used to measure aerosol deposition as a function of the particle charge and size. Experiments were carried out to determine the increase in deposition efficiency as a function of the net charge-to-mass ratio (Q/M) of aerosol particles. Using a fairly monodisperse aerosol of 5.0 μm count median aerodynamic diameter, it was found that the total deposition efficiency increased from 54% to 91% when Q/M increased from 0.5 to 9.67 μC/g. The data show that enhanced delivery of the therapeutic aerosol in the lung can be achieved by controlling the electrostatic charge on the inhaled aerosol particles.

Introduction

Inhalable drugs are widely used for treating lung diseases such as asthma, emphysema and cystic fibrosis. Localized delivery of drugs to the pulmonary tract has become an increasingly important and effective therapeutic method. Several studies show the clinical advantage of inhalation aerosols over systemic therapy for the treatment of lung disorders. Relatively small doses are required for effective therapy, since delivering small doses of active ingredients directly to the lung effectively targets the drug, thereby maximizing therapeutic effect. Lower dosage regimens may provide considerable cost savings, especially with expensive therapeutic agents. The efficiency of a therapeutic aerosol is mainly determined by the amount of drug reaching the target site, which in turn depends on the particle size, charge distribution, particulate number density, and the breathing rate, aerodynamics of the lung, and ambient temperature and relative humidity (RH). The primary mechanisms for inhaled particle deposition are impaction, gravitational settling, diffusion, interception and electrostatic attraction. Electrostatic charge has been shown to influence the deposition of inhaled particles within the lung (Balachandran et al., 1991; Melandri et al., 1983). It was found that with an increase in charge on the inhalable particles, there was an increase in the fraction of drug reaching the periphery of the pulmonary tract. Drug residence time and therefore duration of effect at the site of action is a function of the rate of pulmonary clearance and pulmonary absorption, which in turn are determined by several factors, including the physicochemical properties of the drug, such as molecular weight, dissolution rate, partition coefficient, and charge. The therapeutic effect and the duration of this effect are determined not only by the drug dose and its pulmonary clearance, but also by particle-to-particle interactions (Bailey et al., 1998; Balachandran et al., 1997). These pulmonary drugs are inhaled from dry powder inhalers, metered dose inhalers, spinning disk aerosol generators, atomizers, or nebulizers. The overall success of an aerosol delivery system is determined by its components, the mechanism of dispersion, and patient compliance. The challenges encountered with aerosol drug delivery include the control of particle size, distribution, and the reproducibility of dose uniformity.

The various sections of the experimental setup (Fig. 1) to study the deposition were the spinning disk aerosol generator, hollow cast larynx section, glass bead lung model, sampling chamber, and the particle analyzer E-SPART (Mazumder et al., 1991). A spinning disk aerosol generator is used to produce aerosol particles in the range of 1-2.5 μm. The ring electrode around the spinning disk of the aerosol generator charges the particles, and by varying the voltage the magnitude and polarity of charge of the particles can be changed. Aerosolizing a liquid solution produces the inhalable particles generated by the spinning disk aerosol generator.
Effect of Charge on the Deposition of Electrostatically Charged Inhalable Aerosol in Lung Model

Fig. 1. Shows the site-specific deposition system to study the effect of charge on drug particles in surrogate lung models.

generator. The liquid solution is injected as a continuous stream at a constant flow rate onto a spinning disk. Due to the high velocity of the spinning disk liquid droplets are produced, which form an aerosol cloud. The droplets are charged through induction charging. The airflow stream carries this cloud.

The inhalable charged particles enter the hollow cast throat section and the glass bead lung model (Fig. 2), where they are deposited. A multi-layer granular bed filter was designed to approximate the deposition characteristics of the bronchial and alveolar regions of the human lung. The sizes of the beads were selected to correspond to the sizes of different bronchial orders as given in the Olson model of the lung (Gao, 1994). The cross-sectional area of the filter increases as bead size decreases so that the calculated Reynolds number through the beads is equal to that specified in the Olsen model for the corresponding bronchial and trachobronchial orders. The airflow velocity decreases by a factor of 250 in an actual human lung as air reaches the lower regions of the lung. This is a result of the increase in total cross-sectional area due to the large number of airways. The particles in the different regions can be analyzed for the aerodynamic diameter and charge-to-mass ratio (Q/M) distributions using the E-SPART. From the different regions of the glass bead lung model, the particles enter the sampling chamber connected to the E-SPART particle analyzer, which measures the size and charge distributions of particles in the aerodynamic diameter range of 1-25 μm.
Fig. 2. Shows hollow cast larynx section and glass bead lung model.

Materials and Methods

To generate the test aerosol, a solution of 2% emery oil and 98% alcohol was prepared. Changing the percentage of emery oil in the alcohol solution controlled the particle size. The liquid solution was fed to the spinning disk aerosol generator to produce inhalable aerosol particles of specific size. By applying voltage on the ring electrode, the particles acquired charge. When +30 volts were applied on the ring electrode, particles with an average Q/M of -4.21 μC/g were obtained. When -30 volts are applied, particles with a Q/M of +9.67 μC/g were obtained. Test aerosols with well-characterized size and charge distributions entered the hollow cast larynx section where the large particles deposited (Wesley et al., 2000; Schlesinger et al., 1977). The particles then entered the glass bead lung model. The particles, depending on their size and charge, deposited in the various sections of the model. The particles from the different sections of the glass bead lung model were sampled to determine the particle size and charge distribution. The E-SPART sampled the particles from the sampling chamber at a rate of 3 lpm.

Results and Discussion

Figures 3-8 show the particle size distributions (PSDs) of the aerosol particles from the glass bead lung model. Lognormal distribution was selected empirically to fit the wide range and skewed shape of aerosol size distributions. Keeping all variables such as airflow and liquid solution flow rate constant, the aerosol cloud was fed from the aerosol generator through the three layers of the glass bead model and its PSD was measured. When the particle number density was high, there was mutual repulsion between the particles, and they deposited on the glass beads and the wall. However, if the particle number density was low, the image force acting on the particle due to the presence of glass beads and the wall was the principal force responsible for particle deposition.

Figure 3 shows the PSD of particles coming from the spinning disk aerosol generator as measured by the E-SPART. The number of particles was found to decrease from 18136 to 8184 (Fig. 4) when measured for 5 min at the inlet and outlet. Thus the efficiency of deposition was found to be only 54%, and the remaining 46% of the particles...
Effect of Charge on the Deposition of Electrostatically Charged Inhalable Aerosol in Lung Model

Fig. 3. PSD of uncharged particles from the spinning disk aerosol generator. The aerosol particles have a CMAD = 4.8 μm and MMAD = 5.5 μm, which was measured by the particle analyzer ESPART.

passed through the glass bead lung model. The aerosolized particles from the spinning disk aerosol generator were fairly monodisperse. Figures 5 and 6 show the PSD of positively charged particles from the spinning disk aerosol generator and from the model. The PSD after the particles passed through the lung model was wider. The number of particles was found to decrease from 14998 to 1294, increasing the deposition efficiency to 91%. Similarly, it was found that for negatively charged particles the particle count fell from 15727 to 1036, resulting in an efficiency of 93%.

Conclusions

The particle deposition was found to be dependent on the distribution of particle charge and size. Due to the image forces or the mutual repulsion of the particles, the deposition is found to increase. By controlling the charge and particle size distributions of the drug particles, it may be possible to control their deposition in the various regions of the lung.

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Fig. 4. PSD of uncharged particles collected after the aerosol passed through the first three sections of the lung model. Particle CMAD = 4.5 μm and MMAD = 6.9 μm.

Fig. 5. PSD of positively charged particles collected from the spinning disk aerosol generator. Particle CMAD = 4.8 μm and MMAD = 4.9 μm.
Fig. 6. PSD of positively charged particles collected after the aerosol passed through the first three sections of the lung model. Particle CMAD = 3.9 μm and MMAD = 4.6 μm.

Fig. 7. PSD of negatively charged particles collected from the spinning disk aerosol generator. Particle CMAD = 4.9 μm and MMAD = 5.1 μm.
Fig. 8. PSD of negatively charged particles collected after the aerosol passed through the first three sections of the lung model. Particle CMAD = 4.7 µm and MMAD = 5.1 µm.
The Chemical Composition of Particles of \(d < 0.20 \mu \text{m}\) in the Lower Stratospheric Aerosol, Spring 1993

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Abstract

The majority of the mass of stratospheric aerosol collected during the spring of 1993 consisted principally of particles of \(d > 0.20 \mu \text{m}\) containing a mixture of \(\text{H}_2\text{SO}_4\) and \((\text{NaK})_2\text{SO}_4\). However, the composition of the more numerous particles with \(d < 0.2 \mu \text{m}\) was very different. X-ray emission spectra (EDS) of individual particles indicated that there were three different chemical populations of small particles. The most numerous population was almost all C with only traces of S and Na. The second population contained metal sulfates and chlorides, possibly accreted to a C-containing matrix. The third population consisted of S- and Cl-containing species and trace amounts of Na and K ions. The number of equivalents of metal ion was much less than that of S and Cl was not ionic, but was covalently bonded, perhaps to a C matrix.

Introduction

The chemical composition and the phase of the stratospheric \(\text{H}_2\text{SO}_4\) aerosol affect the rates of heterogeneous reactions involving \(\text{N}_2\text{O}_5\), \(\text{HNO}_3\), and Cl-containing species. It is possible that the reaction rates are affected by trace constituents in the aerosol. Direct injection of particulate matter and \(\text{SO}_2\) influence the particle surface area at which heterogeneous reactions are catalyzed. The normal stratospheric aerosol particle is composed of \(\text{H}_2\text{SO}_4\) and, occasionally, \((\text{NH}_4)_2\text{SO}_4\) which results from neutralization of the acid by trace \(\text{NH}_3\) carried up from the troposphere (Junge and Manson, 1961; Bigg, 1975; Mossop, 1963, 1965). Two processes have had a significant effect on the stratospheric aerosol during the last quarter of the 20th century, injection of S and Cl species by violent volcanic eruptions and the injection of C particles by high flying jet aircraft.

The eruptions of El Chichón in March-April, 1982 injected S and Cl species into the stratosphere. Between April and December, 1982, Woods et al. (1985) sampled by impactor the cloud generated by these eruptions. In April and May, particles containing halite crystals were collected along with the majority sulfuric acid particles. The halite containing particles were irregular in shape while the sulfuric acid particles were spherical. In samples collected later in the year, no halite crystals were observed. The samples of April and May which had contained halite were reexamined to find that the NaCl had, in the interim, been converted to \(\text{Na}_2\text{SO}_4\) by reaction with \(\text{H}_2\text{SO}_4\):

\[
2 \text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2 \text{HCl} \quad (1)
\]

The 1991 Mount Pinatubo eruption injected 30 MT of \(\text{SO}_2\) into the stratosphere (McCormick et al., 1995) and, possibly, hydrothermal fluids and silicates. This eruption caused the greatest perturbation of the stratospheric aerosol in this century. Chittenden and Scott (unpubl.) analyzed six samples of stratospheric aerosol particles collected at altitudes of 19 - 21 km during April and May of 1993, 21 months after the eruption. The particles were neutralized by ammonia immediately after collection. The majority of the neutralized particles of \(d > 0.20 \mu \text{m}\) were composed of \((\text{NH}_4\text{NaK})_2\text{SO}_4\) while a small minority of those from 21 km contained only \((\text{NH}_4)_2\text{SO}_4\). Most or all of the ammonium ion arises from the ammonia neutralization of \(\text{H}_2\text{SO}_4\) originally in the collected particles.

The majority of the particles had been originally either a slurry of \((\text{NaK})_2\text{SO}_4\) in \(\text{H}_2\text{SO}_4\) or particles composed of a \((\text{NaK})_2\text{SO}_4\) core surrounded by \(\text{H}_2\text{SO}_4\). The \((\text{NaK})_2\text{SO}_4\) was not simply the small core of a predominantly \(\text{H}_2\text{SO}_4\) particle but the principle component of these particles. The particles from 19 km had a mean chemical equivalent ratio \((\text{NaK})_2\text{SO}_4/\text{H}_2\text{SO}_4\) of 1.70 while those from 21 km had a ratio of 1.08 (see Table 1). It was assumed that the Mount Pinatubo eruption contributed the metal ions. Only a minority of particles collected from 21 km contained only \(\text{H}_2\text{SO}_4\).

Pueschel et al. (1992) and Blake and Kato (1995) have documented the increase in submicron graphite particles in the lower stratosphere since the introduction of high altitude supersonic aircraft with the greatest increase at the latitudes of the most heavily traveled airlines.

The present study describes the search for submicron particles collected at an altitude of 20 km whose X-ray
The Chemical Composition of Particles of d < 0.20 μm in the Lower Stratospheric Aerosol, Spring 1993

Table 1. Chemistry of two groups of small (d<0.20 μm) particles compared to two groups of large particles (d≥0.20 μm).

<table>
<thead>
<tr>
<th>Group</th>
<th>Low metal with d&lt;0.20 μm</th>
<th>High metal with d&lt;0.20 μm</th>
<th>d≥0.20 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Altitude (km)</td>
<td>20</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>Sample Population, N</td>
<td>32</td>
<td>20</td>
<td>391</td>
</tr>
<tr>
<td>Mean equivalent ratios</td>
<td>(Na+K)/(S+Cl)</td>
<td>0.28 ± 0.16</td>
<td>1.15 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>(Na+K)/Cl</td>
<td>0.35 ± 0.18</td>
<td>7.65 ± 6.66</td>
</tr>
</tbody>
</table>

* - no Cl detected

spectra exhibited relatively prominent peaks for C, Cl, or S that remained in the stratosphere 21 months after the Mt. Pinatubo explosion.

Experimental Methods

For each sampling in this study the collector assembly, a modification of that used by Snetsinger, et al. (1987), consisted of a metal ring across which were stretched three 75 μm Pd wires and two 500 μm Pd wires. A 3000 μm diameter transmission electron microscope (TEM) grid with a carbon coated thin polymer backing was attached to the 75 μm wire impactors at two points. The assemblies were flown on NASA ER-2 aircraft for inertial sampling of aerosols. Aircraft speed at collection was 200 m/s. During collection, the rings were extended outside the aircraft boundary layer for 2 minutes. Collections were made during April and May 1993 at 37°-38° N latitude, 121°-122° W longitude, and altitudes of 18.8 km - 21.3 km. Immediately after collection, the samples were returned to and sealed inside modules which contained ammonia vapor. The sulfuric acid component was neutralized to form ammonium sulfate crystal(s) of density little different from the droplet from which it was formed.

Elemental Analysis.—Quantitative elemental analyses of several hundred spheroidal particles with 0.20 μm > d ≥ 0.10 μm were performed using the energy dispersive X-ray spectra (EDS) generated by irradiating individual particles with the electron beam of a JEOL JEM-100CX scanning transmission electron microscope (STEM) in the SEM mode at Arkansas State University (ASU). The areas under the X-ray peaks for the elements of interest (A_i where i = Na, k, S, or Cl) were calculated using the MicroEDS program of Dapple Systems, Inc. on the ASU system. The atomic ratios Na/S and Na/Cl are functions of the ratios of areas, A_{Na}/A_S and A_{Na}/A_{Cl}, respectively. The ratios K/S and K/Cl are calculated in a similar fashion. The areas must be corrected for absorption of X-rays by the particle and the detector window. Since the two standard correction models (Goldstein et al., 1992) for quantitative analysis from X-ray spectra are designed for samples with a flat surface, they were incapable of yielding usable absorption correction factors for a spheroidal particle because they over-correct for the lighter elements. To determine a correction algorithm standard aerosol samples of pure Na_2SO_4 and pure K_2SO_4 were prepared by atomizing saturated aqueous solutions at ~50°C. A TEM grid was passed through the suspended cloud of droplets. The grids were stored in a desiccator and later examined in the same manner as the sample grids. From the EDS of the standard particles, the correction factors, f_i, for the area ratios as a function of mean particle cross sectional diameter were determined. The correction factors were applied to EDS peak area ratios for each particle to calculate the atomic ratios of metal (M=Na or K): M/S = (A_{M}/A_{S}) f_{M/S}. s. The same factor can be used for both the S and Cl ratios since their K X-ray energies are so close that their attenuation as they pass through the particle is essentially the same, so M/Cl = (A_{M}/A_{Cl}) f_{M_S}.

The composition of particles of d < 0.20 μm collected from 20 km was more difficult to determine than that of larger particles because the sample-to-background signal ratio of their electron induced X-ray emission spectra was usually very low. The Hitachi S-4000 SEM and its associated EDS system at the NASA Ames Research Center (ARC), Mountain View, CA, yields spectra with sample-to-background signal ratios for low Z elements far superior to...
the ASU system. Qualitative chemical analysis was performed at ARC on 12 particles of diameters from 0.12 μm to 0.17 μm, which had exhibited no detectable concentration of elements of Z > 10 when analyzed in the ASU system. In all analyses, a background spectrum was taken by moving the electron beam to a vacant area of the backing lying within 2 μm of the particle and recording the spectrum from that area.

**Measurement of Particle Size.**--The diameters of particles were obtained either by measuring the size of the particle's image directly from the CRT display of the SEM's secondary electron image (SEI) at magnifications of up to 100,000 X or by measuring the image on a magnified scan of a Polaroid photograph of the SEI. The lengths of the major axis, a, and minor axis, b, of particles were measured to the nearest 10 nanometers. The uncertainty in measured d =[(a+b)/2] values was < 10% for particles with d > 0.10 μm.

**Results**

The 20 km sample was unusual in that particles of d < 0.20 μm were far more numerous than the sample's larger particles and more numerous than all particles collected at 19 km and 21 km. The majority of these particle contained no detectable quantity of elements with Z > 10 but a small fraction of these particles contained detectable Cl. Of the hundreds of particles analyzed, 54 yielded X-ray spectra with at least one peak well above background level (Fig. 1) as well as an indication of the presence of C. Average analyses, in ratios of chemical equivalents of metals (Na and K) to chemical equivalents of nonmetals (S and Cl) for two differing populations of particles, those with low metal contents and those with high metal contents, are presented in Table 1. The 12 particles which were analyzed qualitatively at ARC contain only C in appreciable concentration, although there is some indication of the presence of a small amount of S in most of these particles (Fig. 2).

**Conclusions**

The particles of d < 0.20 μm collected at 20 km were different from the larger particles in their chemical makeup, in that they contained little or no H₂SO₄. There were three different chemical populations among these small particles, two very unlike the larger particles, one similar to them. Most of the smaller particles analyzed contained only C in detectable quantities. It is possible that the matrix of all smaller particles is graphite. The other two populations contain detectable quantities of S and/or Cl.

The high metal particle population exhibits some similarity to the larger particles, having a mean chemical equivalent ratio (Na+K)/(S+Cl) ~ 1, leading to the conclusion that they are essentially alkali metal sulfates and chlorides. They may be simply salt crystals or, perhaps, ions adsorbed on or mixed in with a carbon matrix. Since (Na+K)/(Cl) > (Na+K)/(S+Cl), the sulfate is the dominant anion. They differ from the larger particles in that they lacked H₂SO₄. The presence of H₂SO₄ would result in the equivalent ratio being < 1 and the chloride ion being converted to volatile HCl.

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![Fig. 1. EDS spectrum of Cl-containing particle. Background, containing the Si and Cu-L peak from X-ray detector and TEM grid, has been subtracted and the baseline has been smoothed.](image1)

![Fig. 2. EDS spectrum of carbon particle. The darker line is the sample spectrum; the lighter line is the background spectrum.](image2)
The low metal particles are even more interesting. The 
\( \frac{(Na+K)}{(S+Cl)} \ll 1 \) and since \( \frac{(Na+K)}{(S+Cl)} \sim \frac{(Na+K)}{Cl} \), Cl is the dominant nonmetallic species. This leads to the conclusion that the majority of the Cl is not ionic. It is possible that Cl atoms produced by photochemical decomposition of the HCl produced by reaction (1) reacted with the C containing particle matrix to form covalently bonded Cl species.

**Acknowledgments.**—This research was supported by the National Aeronautics and Space Administration’s EPSCoR grant NCCW-0055, a SILO Undergraduate Research Fellowship, and Arkansas State University. The authors wish to thank Ms. Katherine Kato and Dr. David Blake of the ARC, Dr. Sherry Cady of Portland State University, and Dr. Stan Trauth of the ASU EM facility for their help with electron microscope procedures.

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Modification of Surface Properties of Polymeric Materials

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Polymeric materials are successfully used in virtually all industries ranging from semiconductors, and coatings, to household appliances, automotive, and biomedical implants. Polymers generally have excellent bulk physical and chemical properties. However, certain properties of polymers such as low surface energy, low wettability, and high electrical resistivity sometimes limit their applications. Changing the bulk formulation of the polymers can alter some of these properties, but in general this is not acceptable as it can affect “desirable” bulk properties. Surface modification techniques have been used to alter polymer surfaces without affecting the bulk properties of the material. Most polymers have very high surface and bulk resistivity, which causes static charge problems in many applications. One such application is powder coating where the accumulation of excess charge causes an adverse impact on the appearance of the powder layer. Similarly, the buildup of static charge during processing and application of polymer films in packaging industries is often harmful to sensitive electronic components such as those used in the computer industry. Charge buildup may be reduced by surface modification to control the surface resistivity. In this work, atmospheric plasma treatment was used to modify the surface resistivity of polymers. The surface resistivity of polyethylene film decreased from $1.28 \times 10^{16} \, \Omega / \square$ to $5.73 \times 10^{15} \, \Omega / \square$ at 18% RH.

Abstract

Introduction

In the last few decades synthetic polymers have replaced several materials, such as metals, and have extended their application to many innovative processes. This is due to their superior physical and chemical characteristics such as high strength to weight ratio, corrosion resistance and chemical inert nature. They are also relatively inexpensive and easy to process. At the same time some of these properties impose a limitation on applications in several new and high technology areas. Thus it is required that their surface properties be modified to suit a particular application without affecting their bulk properties. One such application is the use of conductive plastic packaging for protecting semiconductor chips against electrostatic discharge.

Surface modification is quite often used to create surfaces with properties considerably different from that of the bulk of the polymeric materials. Since the polymer surfaces are non-reactive, and surface modification involves chemical alteration of the surface layer, it requires the generation of high-energy species such as radicals, ions, and molecules in an excited electronic state to promote a surface reaction. This is achieved by techniques such as flame, plasma, UV, laser, X-ray and γ-ray, electron beam, ion beam, and corona treatment.

Plasma treatment is one of the most widely used surface treatment techniques. Plasma can be defined as a mixture of charged and neutral species, such as electrons, positive ions, negative ions, radicals, neutral atoms and molecules. During plasma treatment, the composition and structure of a few molecular layers at or near the surface (approximately 10 nm) is modified due to the action of the energetic particles. This has been used to alter surface properties of polymers such as adhesion to metals and to other polymers, wettability, and printability, without changing their bulk properties (Briggs, 1982; Garbassi et al., 1996; Wu, 1982; Chan, 1994a, 1994b).

Typically most polymeric materials have extremely high electrical resistivity. Though high electrical resistivity of polymers is required in certain applications, such as insulative shielding on cables; it may be an undesirable property in other areas. The high surface resistivity can cause static charge problems in applications such as powder coating where typical powder paints (epoxy, acrylic, urethane or polyester) have high surface resistivities ($\rho > 10^{14} \, \Omega / \square$). During the electrostatic powder deposition process, the highly resistive powder layer does not allow the electrostatic charge to decay at a rate fast enough to avoid the formation of back corona. The accumulation of excess charge has an adverse impact on the appearance of the powder layer (Cross, 1987; Bailey, 1998; Mazumder, 1998). Similarly, the buildup of static charge during processing and application of polymer films in the packaging industry is often harmful to sensitive electronic components such as those used in computers. Many times the buildup of static
charge in the polyethylene packaging film damages the semiconductor chips (Fowler, 2001). This damage can be avoided by decreasing the surface resistivity of polymer films.

Various approaches have been utilized to decrease resistivity of polymers (Fowler, 2001; Ha, 2000). The electrical resistivity can be decreased by deposition of a thin layer of conductive polymer on the surface or by microencapsulation. Changing the chemical formulation could also decrease the resistivity of polymers. Long chain amines, such as POE, are used as anti-static agents. They are added to the bulk formulation during polymer synthesis. These additives have surfactant like structure with a polar head and a hydrocarbon chain. They migrate to the polymer surfaces where they form a micelle-like structure. The micelles act as moisture traps increasing the conductivity of the surface (Rosen, 1997). The above-mentioned approaches are not very well accepted due to cost and/or contamination considerations.

Previous studies on plasma treatment of polyethylene have shown the modification of chemical-surface structure to render the surface more hydrophilic (Liston et al., 1993; Foerch et al., 1993). A more hydrophilic surface will adsorb more moisture on the surface making it more conductive. Thus plasma treatment could decrease the electrical resistivity of polymer surfaces. The plasma treatment of polymers has been intensively studied using low-pressure plasmas, but very little work has been reported on plasma treatment under atmospheric conditions. In this work atmospheric plasma was used for surface modification of low-density polyethylene film.

**Materials and Methods**

A plasma reactor was built for surface modification of polymer films with air as plasma gas. A low-density polyethylene (LDPE) film (100 mm thick), obtained from Fisher Scientific, was used for plasma treatment. The polymer film was exposed to plasma in the reactor, as shown in Fig. 1. The reactor is composed of a plasma generator and a grounded aluminum panel as an electrode. The plasma generator consists of a 200 mm long hemispherical Poly methyl methacrylate (PMMA) tube with 100 mm diameter stainless steel wire as the electrode. A high voltage (10 kV) AC power supply was used for generation of plasma. The surface resistivity of plasma-treated and untreated LDPE film was measured at various relative humidities to assess the effect of plasma treatment.

The polymer sample was plasma treated for 0.16, 0.5, 1, 2, 5, and 10 min, successively. After each treatment the film was exposed to an environment of known RH for 5 min in an environmental chamber before the surface resistivity was measured. RH values in the chamber were maintained within +/- 1% of the desired RH in the range of 50 – 90%.

The surface resistivity of a film was measured using the setup shown in Fig. 2. A surface resistivity instrument (Model 8009 by Keithley Instruments) was used along with an electrometer (Model 6517 of Keithley electrometer) in this setup. The measurements were also performed inside the environmental chamber.

**Results and Discussion**

The surface resistivity of a polyethylene (LDPE) film was...
measured at different relative humidity values varying between 18% and 90%. The surface resistivity was found to decrease with increasing humidity. The surface resistivity declined from 1.28x10^16 Ω/□ at 18% RH to 2.73x10^12 Ω/□ at 90% RH. The sample was plasma treated for 10 sec, and the surface resistivity was measured again. The surface resistivity was mainly observed for treatment times of less than 2 min (Fig. 4). An atomic force microscope (AFM) was used to characterize of surface roughness of treated and untreated sample. Plasma treated sample was found to be rougher than untreated sample (Fig. 5).

The decrease in surface resistivity with increasing relative humidity for the untreated sample could be due to formation of a conductive moisture layer over the sample surface. The change in surface resistivity with plasma treatment could be a result of processes at three different levels.

On the physical level, plasma treatment causes a change in the morphology of the surface. It distorts the surface leading to formation of micro-dents, which increases the surface roughness and the effective surface area. An increase in surface area results in more moisture adsorption, thereby increasing the surface conductivity. The AFM characterization of the plasma treated surface and the untreated surface substantiates the argument about the increase in surface roughness.

The change in surface chemistry of a polymer surface due to plasma treatment has been investigated in detail by several researchers (Wu 1982; Chan 1994a). Plasma treatment in air can generate several oxygen and nitrogen functionalities on the surface. It causes the uptake of oxygen by polymer surfaces leading to the formation of C-O-C (or C-OH), C=O and O-C-O groups. The plasma treatment is also known to increase the O/C ratio. More highly oxidized carbon increases with an increase in the O/C ratio. Initially the oxygen adds preferentially to specific carbon atoms unless no further C=O bonds can be formed. Further oxygen adds to the carbon that has already reacted leading to the formation of O-C=O species. Since the plasma treatment was carried out in air, the nitrogen also adds to the polymer as amine functional groups (C-NH2, C-NHR, C-NR2) and imines (C=N). These groups cause the increase in surface energy that makes the surface hydrophilic. The increase in surface energy results in the adsorption of more moisture on the surface making it more conductive. Besides the addition of polar functional groups, the plasma treatment also causes graphitization of the polymer surface, which strongly affects the electrical conductivity. There was a significant difference in surface resistivity of the plasma treated and the untreated sample at 18% RH. That could be due to the breaking of C-C bonds in polyethylene and the introduction of polar groups from the air making the surface hydrophilic. At higher RH there is not much difference in surface resistivity of plasma treated and untreated films. This could be due to attaining saturation in adsorption of the moisture layer. Longer treatment times, such as 5 or 10 minutes, could result in excessive chain scission leading to a layer of short chain oxidized material on the surface which has been referred as low-molecular-weight oxidized
Modification of Surface Properties of Polymeric Materials

Material (LMWOM) by many researchers. The role of LMWOM on the polymer surface has not been very well understood (Chan, 1994a). There have been contradictory reports about their function of this material. But longer treatment time and higher RH are conducive to the formation of LMWOM.

On a molecular level the decrease in resistivity may also be explained on the basis of changes in electronic surface states. The addition of oxygen may create both occupied and unoccupied surface states that could change the Fermi level. A small concentration of nitrogen could create additional unoccupied surface states that again could change the Fermi level, bringing it closer to conduction band.

Conclusions

Surface modification of the low-density polyethylene (LDPE) substrates was carried out using plasma treatment to lower the electrical resistivity. Plasma treatment decreased the surface resistivity of polyethylene film from $1.28 \times 10^{16} \Omega \cdot \square$ to $5.73 \times 10^{15} \Omega \cdot \square$ at 18% RH. The LDPE surface was plasma-treated for 0.16, 0.5, 1, 2, 5, and 10 minute successively. In all the cases it was found that the surface resistivity of plasma treated LDPE was lower than an untreated surface. The major change in resistivity was observed within the first two minutes of plasma treatment. The effect of plasma treatment on surface resistivity of LDPE was also assessed at different RH. The surface resistivity of plasma treated sample was found to be lower than that of untreated sample at all RH values tested. This study has shown the feasibility of using plasma surface modification for controlling electrical resistivity of polymer surfaces.

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Fire Effects on Three Trophic Levels in a Central Arkansas Grassland

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Abstract

We studied the effect of a late growing-season fire on the plant and foliar arthropod communities in a naturally occurring grassland. In central Arkansas, these grasslands are common on south-facing slopes where shallow soils and hot/dry weather conditions during the summer cannot support the growth of a forest community. Patches of grassland were burned in the autumn (4 November, late growing season), often the time of natural fires in Arkansas, and compared to unburned areas. Fire increased the biomass of forbs and decreased the biomass of grasses, although overall biomass was not different between treatments. Among the foliar arthropods, herbivores were significantly reduced by burning, especially the Homoptera. Carnivorous arthropods as a whole were not affected by burning, although spiders showed a small but significant reduction. The response of arthropods to fire occurred almost one year after the burn, showing that fire effects can be delayed for a substantial period of time. This experiment shows that fire occurring during the natural burning period in Arkansas can have substantial effects on grasslands communities. The response of plants in Arkansas is similar to that of plants in nearby grasslands on the Great Plains and southeastern United States which also show a great increase in forbs under late growing season burning regimes. The changes seen in this experiment demonstrate that the suppression of fire by humans has probably modified the structure of Arkansas grasslands. With the increasing use of fire as a management tool in Arkansas, changes to grassland systems are likely to be profound.

Introduction

Fire is the major abiotic disturbance event that is important in structuring North American prairies (Bragg, 1982). In the absence of fire, many prairie habitats undergo succession to forests (Bragg and Hulbert, 1976; Collins and Wallace, 1990; Knight et al., 1994; Sparks et al., 1999). In addition to preventing the encroachment of trees, fire has profound effects on other components of grassland plant communities, and it can alter nutrient cycles (Collins, 2000; Briggs and Knapp, 1995; Blair, 1997). For instance, in the tallgrass prairies of central North America, frequent fire tends to increase the dominance of C₄ grasses at the expense of C₃ grasses and forbs (Collins et al., 1998; Knapp et al., 1998). However, the timing of fire can cause substantial variation in this response. In North American tallgrass prairies, fire in the spring, the traditional season of burning by cattle producers, tends to reduce forbs and promote the growth of grasses (Gibson and Hulbert, 1987; Svejer and Browning, 1988; Biondini et al., 1989), whereas summer fires tend to do the opposite, increasing the abundance of forbs at the expense of grasses (Pfeiffer and Steuter, 1994). In the southeast United States, growing season fires appear to be more effective than dormant-season fires in maintaining prairie habitat (Boyer, 1990; Glitzenstein et al., 1995) including the pine-grassland communities of the western Ouachita Mountains (Sparks et al. 1999), which are near our field site.

Fire also has varied direct and indirect effects on animals. The most ubiquitous macroscopic animals in most grassland communities are arthropods (Redak, 2000). Studies investigating fire effects on grassland arthropods have found both positive (Evans, 1984, 1988; Moya-Raygoza, 1995) and negative (Amburg et al., 1981; Seastedt, 1984; Anderson et al., 1989; Fay and Samenus, 1993) effects. Anderson et al. (1989) found a significant decline in insects immediately after a burn whereas Swengel (1996) found that infrequent fire promoted butterfly abundance. It is known that some arthropods such as fire beetles (Buprestidae) are promoted by fire (Whelan, 1995), but others may be at greater risk of predation in burned habitat due to exposure. Nagel (1973) found an increase in herbivore biomass after a spring grassland burn, but above-ground arthropod species fared worse than the more abundant soil arthropods.

In Arkansas, fires historically tended to occur during the late summer and early autumn (Foti and Glenn, 1991; Masters et al., 1995) when high temperatures and low rainfall (National Weather Service, Little Rock) increase the potential for ignition and fire spread. Sparks et al. (1998) studied the effects of fire season on vegetation in a western Arkansas grassland. Species diversity and stand species
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Richness were greater in burned stands than in unburned control stands. Although they set out to determine the effects of fire season on plant communities, no overall community attributes differed between late growing-season and late dormant-season burns. However, late growing-season fires decreased density of warm-season (C₄) plant species (Sparks et al., 1998).

Here we report the results of a study on the effects of fire on the vegetation and associated foliar arthropod community in the growing season following a prescribed burn during the late growing season. We examined the entire plant-foliar arthropod community to determine how different functional groups are affected by burning.

Materials and Methods

In the spring of 1999, 12 2 m x 2 m experimental plots were established within grassland patches in northeastern Conway Co. near Center Ridge, Arkansas. Grassland patches ranged in area from approximately 20 m² to 105 m² and were surrounded by closed canopy Quercus - Carya (Oak-Hickory) forest. Therefore, each larger grassland patch contained one 2 m x 2 m plot that was monitored during the course of the experiment. The grasslands were located on a south-facing slope (elevation 186 m) in an eastern extension of the Ouachita Mountains.

The most common plant species is the native grass, little bluestem (Schizachyrium scoparium) which co-occurs with other grasses (mostly dropseed, Sporobolus spp.) and numerous forb species. The most abundant secondary species are lanceleaf coreopsis (Coreopsis lanceolata), venus looking-glass (Specularia perfoliata), false garlic (Nothoscordum bivalve), toothwort (Dentaria laciniata), and sunflower (Helianthus spp.).

To determine the pre-burn conditions of the plots and to verify similar community attributes between treatment and control plots (before manipulation), we classified all plants to species level every two weeks for the entire 1999 growing season (Feb. to Oct.). These measurements were used to determine plant species diversity within the plots. Once per month we also measured arthropod abundance by placing a single 30 cm x 30 cm wooden plate painted with Tangletrap (Tanglefoot Co., Grand Rapids, Michigan) in each plot. Captured arthropods were counted and classified to order and trophic level. Finner classification was not possible with these samples as the Tangletrap tends to severely damage fine structures (e.g., wings, bristles, etc.), which are necessary for identification.

On 4 November 1999, we successfully burned six grassland patches and the experimental plots within those patches with a kerosene drip torch. This date corresponds to the end of the dry season (late growing season). The other six grassland patches (and imbedded experimental plots) remained unburned. The following growing season (2000), we monitored plant and arthropod communities with the same methods as the pre-burn samples. We also employed additional, more destructive, post-burn sampling techniques to more thoroughly measure plant and arthropod parameters. Once in June and once in September 2000, we removed all above-ground plant biomass in a randomly selected 1 m² quadrat within each plot. Plants were sorted according to species, dried, and massed. To more thoroughly sample arthropods at the end of the experiment, the entire plots were sampled by D-vac to remove as many arthropods as possible. Arthropods were counted and classified according to order and trophic level.

There was much heterogeneity between plots so that most plants were not found in every sample area, and it was impractical to analyze the treatment response of individual plant species. We therefore analyzed the plants by broad growth form groups (i.e. grasses and forbs) between treatment and control plots.

For dependent variables measured multiple times over the two years of the study, we performed repeated measures MANOVA. If the repeated measures analysis was significant, we analyzed individual dates to determine what time of year the treatment response was occurring. Plant biomass and the final arthropod samples, for which we did not have pre-treatment measurements, were analyzed by one-way ANOVA. Data sets that showed significant heteroscedasticity were log10-transformed prior to analysis, after which no data set violated this ANOVA assumption.

Results

In June 2000, there was no significant effect of fire on total plant biomass, grass biomass, or forb biomass (one-way ANOVA, Fig. 1A). However, by the September sample, grass biomass was reduced in burned plots (one-way ANOVA, F₁,10 = 5.87, P = 0.036) whereas forb biomass was greater in burned plots (one-way ANOVA, F₁,10 = 7.46, P = 0.021). Total plant biomass was similar between burned and unburned plots (Fig. 1B). There was no change in plant diversity between burned and unburned plots during the course of the experiment.

When measured over time, herbivorous arthropods were reduced by burning (repeated measures ANOVA, between-subject effects: F₁,10 = 9.44, P = 0.017, Fig. 2A), indicating that herbivores were generally greater in control plots over time. Analysis of herbivore abundance only during the 1999 seasons (pre-treatment) was non-significant showing that the response occurred after the prescribed burn. Only the final sample period had significantly higher herbivore abundance (one-way ANOVA, F₁,12 = 29.92, P = 0.001, Fig. 2A). Carnivorous arthropod abundance over time was not affected by burning (repeated measures ANOVA, F₁,10 = 0.001, P = 0.973, Fig. 2B), although the
number of carnivores captured in the sticky traps was small. There were significant time effects for both herbivorous (Wilk's Lambda = 0.052, F_{1,9} = 21.80, P = 0.001) and carnivorous arthropods (Wilk's Lambda = 0.160, F_{5,4} = 6.30, P = 0.022), indicating seasonal changes in abundance (Fig. 2). The final D-vac sample showed that herbivorous arthropods were significantly reduced in burned plots (F_{1,9} = 11.96, P = 0.006, Fig. 3) while carnivorous arthropods were unaffected by burning (F_{1,9} = 1.23, P = 0.293, Fig. 3). Among individual orders of arthropods, only Homoptera and Araneae significantly declined in burned plots (one-way ANOVA, Fig. 3). No taxa or trophic level showed a positive response to burning.

Discussion

The prescribed burn had significant effects on plant growth, with forbs benefiting and grasses being adversely affected. The dominant grass in this system is little bluestem (S. scoparius), which accumulates large amounts of litter from previous years that covers the ground. The elimination of this detritus by fire, along with increased nitrogen released and direct fire damage to S. scoparius, probably allowed forbs to grow more vigorously (Knapp and Seastedt, 1986). The reduction in grass biomass was opposite from what is seen in many prairie habitats in the Great Plains; there a single burn tends to increase grass growth (Gibson and Hulbert, 1987; Anderson, 1990; Collins and Gibson, 1990). However, many prairie studies used spring burns whereas our burn was in the late growing season. In prairies of the Great Plains, late growing season burns cause similar plant responses as seen in this study (Howe, 1994; Pfeiffer and Steuter, 1994). In other studies in the southeastern United States, the response of a growing season burn appears similar this study with an increase in forb growth (Sparks et al., 1998, 1999). Therefore, it appears that across a large geographic area, late growing season burns have similar effects on plant communities.

Previous studies of fire effects on arthropods have been equivocal with some positive and some negative responses (see introduction). We found that some arthropod groups were reduced, and this effect was strongest among herbivores. However, no arthropod order or trophic level increased in abundance when burned. Carnivores are generally more mobile than herbivores, as herbivores are more closely associated with their host plant (Bernays and Chapman, 1994). Therefore we suggest carnivores are less affected by disturbance or can recover more quickly. In addition, the areas we burned were relatively small, which could also have allowed mobile carnivores to recolonize quickly.

It is also interesting that the effect on herbivores was not indicated until the final sample period (almost one year after the burn), showing that fire effects can occur well after the disturbance event. The significant negative effect on Homoptera is expected because these groups oviposit on their host plant stems, which would be severely damaged by fire. Other herbivorous groups that oviposit in the ground (e.g. Orthoptera) were not significantly affected.

The link between herbivore abundance and plant growth is important. The increased forb growth may have been caused directly by fire, but also could have been caused indirectly by reduced herbivory in burned plots. Therefore when examining fire effects on plants, the indirect role of herbivores needs to be considered as well. For instance, in tallgrass prairie, bison preferentially graze on areas recently burned (Coppedge and Shaw, 1998), feed exclusively on C$_4$ grasses, and subsequently change the plant communities in profound ways (Hartnett et al., 1996, 1997; Collins et al., 1998; Knapp et al., 1999). Since arthropod herbivory can also cause significant changes in plant communities (Brown, 1988; Brown et al., 1987, 1998), herbivory and arthropods interact to affect plant communities needs to be more thoroughly investigated.

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Literature Cited


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Fig. 1. Effects of fire on total plant biomass, grass biomass, and forb biomass in A) June and B) September following an autumn burn. * indicates significant differences (one-way ANOVA).
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Fig. 2. Effects of fire on abundance of A) herbivorous and B) carnivorous arthropods captured in sticky traps over the course of the experiment. Abundance data is presented per trap (0.09 m²). Effects on herbivorous arthropods were significant (repeated measures MANOVA). * indicates sample period where significant differences exist (one-way ANOVA).
Fig. 3. Effect of fire on the arthropods captured in a D-vac sample of entire plot (9 m²) at the end of the experiment. * indicates significant differences (one-way ANOVA). Dip = Diptera, Hom = Homoptera, Hym = Hymenoptera, Col = Coleoptera, Ara = Araneae, Ort = Orthoptera, Herb = Herbivorous Arthropods, Carn = Carnivorous Arthropods.


Svejcar, T. J. and J. A. Browning. 1988. Growth and gas exchange of Andropogon gerardii as influenced by burning. J. Range Manage. 41:239-244.


Oxidation-Reduction Characteristics of Chlorophenols in an Aprotic Medium

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Abstract

Eighteen chlorophenols, containing from one to five chlorine atoms on the benzene ring at various positions, have been studied by cyclic voltammetric methods to evaluate their oxidation-reduction characteristics in an aprotic medium. The compounds were dissolved in dimethylsulfoxide containing 0.10 M tetrabutylammonium perchlorate as the supporting electrolyte and were then both oxidized and reduced on a glassy carbon electrode. The results indicate that phenols oxidize in a one-step process to phenoxium ion which dimerizes to quinone ether. The ether can be reduced back to phenol in a two-step reduction process. The oxidation potential of the chlorophenols varies with the number and the position of the chlorine substitution. It may also have a relationship with the toxicity of the compound. The main purpose of this study is to understand how chlorophenols, classified as environmental pollutants for their toxicity and carcinogenicity, are oxidized by cytochrome P450 in the metabolic activation process in living systems.

Introduction

Chlorophenols are classified as environmental pollutants by the Environmental Protection Agency (USEPA, 1979) since many of them are toxic, and some of them are carcinogenic (Lewis, 2000). The major sources of these compounds are pulp and paper mills (Kristiansen et al., 1994), petrochemical refineries (Rogers et al., 1996), plastic and glue manufacturers (Pavlov and Terentyev, 1965), coke plants and leachate from municipal waste dumps (Gilman et al., 1982). Many chlorophenols are produced in the environment by reactions between phenol and chlorine during municipal water treatment (NTP, 1985). Significant in vivo generation of some chlorophenols, such as pentachlorophenol, in living systems occurs through metabolism of hexachlorobenzene (Stewart and Smith, 1986) or hexachlorocyclohexane (Munir et al., 1984), which are ubiquitous environmental pollutants.

Because of the acute toxicity and carcinogenicity of chlorophenols, considerable research has been conducted to detect these compounds in aqueous environments (Terashima et al., 2002). Among them, photochemical, chemical and enzymatic methods are not very successful due to their lack of sensitivity, complexity, and limitation to only a few chlorophenols. More successful methods are gas chromatography (G.C.) and gas chromatography-mass spectrometry (GC/MS), high performance liquid chromatography (HPLC), and electrochemical methods coupled with HPLC.

In aqueous solution of pH 5 and above, most chlorophenols exist in the ionic form. In living systems, however, chlorophenols tend to be absorbed primarily in the adipose tissues in the molecular form because of their low solubility in water. The major target organs for pentachlorophenol toxicity and carcinogenicity include the liver, kidney, hematopoietic tissues, pulmonary system, and central nervous system. It is a general cytotoxic agent because of its ability to uncouple mitochondrial oxidative phosphorylation (Weinbach, 1954). In addition, pentachlorophenol undergoes cytochrome P450-dependent metabolic oxidation in vitro and in vivo to genotoxic tetrachlorobenzenediols and tetrachlorobenzozquinones, which have been shown to react with protein and DNA-derived nucleophiles (Juhl et al., 1985; Ehrlich, 1990). Some chlorophenols, such as 2,4,6-trichlorophenol and pentachlorophenol, undergo oxidative metabolic activation and partial dechlorination by mammalian peroxidases to 2,6-dichloro-1, 4-benzoquinone and tetrachloro-1, 4-benzoquinone, respectively (Samokysyn et al., 1995, Weise et al., 1999). It is expected that all chlorophenols will act in a similar manner in living systems. Since chlorophenols differ significantly in their toxicity (Lewis, 2000), it is important that their general oxidation-reduction characteristics be investigated in order to understand any relation between their relative ease of oxidation by enzymes and toxicity.

Eighteen chlorophenols, containing chlorine substitution of one to five in various positions on the benzene ring, have been studied in an aprotic medium to mimic the hydrophobic situation in various organs of living systems. The chlorophenols chosen have one to five chlorine substitutions, as listed in Table 1.
Oxidation-Reduction Characteristics of Chlorophenols in an Aprotic Medium

Table 1. List of chlorophenols used for the present study.

<table>
<thead>
<tr>
<th>Compound Name</th>
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<tbody>
<tr>
<td>Phenol</td>
</tr>
<tr>
<td>2-chlorophenol</td>
</tr>
<tr>
<td>3-chlorophenol</td>
</tr>
<tr>
<td>4-chlorophenol</td>
</tr>
<tr>
<td>2,3-dichlorophenol</td>
</tr>
<tr>
<td>2,4-dichlorophenol</td>
</tr>
<tr>
<td>2,5-dichlorophenol</td>
</tr>
<tr>
<td>2,6-dichlorophenol</td>
</tr>
<tr>
<td>3,4-dichlorophenol</td>
</tr>
<tr>
<td>3,5-dichlorophenol</td>
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<td>2,3,4-trichlorophenol</td>
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<td>2,3,6-trichlorophenol</td>
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<tr>
<td>2,4,6-trichlorophenol</td>
</tr>
<tr>
<td>2,3,5,6-tetrachlorophenol</td>
</tr>
<tr>
<td>2,3,4,5-tetrachlorophenol</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
</tr>
</tbody>
</table>

Perchlorate (TBAP) was used as the supporting electrolyte to make the solution conducting for voltammetric measurements of Faradaic current as a function of applied voltage.

Materials and Methods

All 19 chlorophenols were purchased from Supelco (Bellafontaine, PA) with 98% or greater purity and were used without further purification. DMSO (spectroscopic quality) and TBAP (99.9% purity) were obtained from Fisher Scientific. Glassy carbon electrodes (GCE), saturated calomel electrodes (SCE) and platinum electrodes were obtained from Bioanalytical Systems (Lafayette, IN). A Bioanalytical Systems Model 100-A Electrochemical Analyzer was used to record all cyclic voltammograms in conjunction with a Model DMP-40 (Houston Instruments) plotter. Prior to use, the GCE was polished with alumina sol (Buehler, IL) followed by rinsing with distilled water to assure a clean surface.

A 100.0 mL of 0.10 M TBAP in DMSO solution was dehydrated by stirring with about 5 g of molecular sieve (Union Carbide, Plainfield, NJ) for an hour. The solution was filtered quickly into a 100 mL volumetric flask and sealed tightly. Exactly 10.0 mL of the solution was taken in a cell in which the electrodes (GCE — working electrode, SCE-reference electrode, platinum wire — counter electrode) were assembled. A cyclic voltammogram was taken between +1.00 volts and –2.00 volts versus SCE (the entire potential range of the GCE) to determine the response of the electrode in terms of dissolved oxygen. The solution was then deoxygenated by bubbling high purity nitrogen for 15 minutes to obtain a clean background response (with no visible peak in the entire potential range). About 10 mg of a chlorophenol was added to the solution and dissolved completely by bubbling nitrogen for five minutes. The nitrogen flow was then diverted and held to just above the solution as a cyclic voltammogram was taken throughout the entire potential range to observe the electrochemical response of the chlorophenol. A series of cyclic voltammograms was taken for each chlorophenol at the potential scan rates varying from 10 mV/sec to 1.0 V/sec. GCE was polished periodically as needed in order to ensure reproducibility of the peaks as well as to minimize electrode contamination prior to using another chlorophenol. The oxidation and reduction potentials were estimated at 85% of the peaks due to oxidation of phenol and the reduction of the oxidized products of phenol.

Results and Discussion

A typical cyclic voltammogram of chlorophenols, using 2,6-dichlorophenol as the representative, is shown in Figure
Fig. 1. Cyclic voltammogram of 2,6-dichlorophenol in 0.10 M tetrabutylammonium perchlorate in dimethylsulfoxide performed at a scan rate of 0.10 volt/sec. Five repeated scans were performed without renewing the GCE surface between 1.00 volt and -2.00 volt versus SCE.

The starting potential is 0.00 volt vs. SCE, which is close to the rest potential of the chlorophenol. The rest potential is defined as the potential at which no current is flowing when the electrodes are assembled into the experimental solution. All of the chlorophenols were found to have the rest potential between 0.00 volt and 0.100 volt versus SCE. At the rest potential, no electrochemical change (due to oxidation or reduction) occurs. As the potential was scanned to the positive direction, the compound was oxidized. When the potential reached 1.00 volt, the GCE reached its most positive limit. The potential was then scanned backward (to reduce the oxidized products) until it reached the most negative limit of the electrode. The cyclic potential scan was repeated four times. In the first scan, two oxidation peaks appeared, at 0.24 volt and 0.62 volt. On the reverse scan, several peaks appeared, at 0.46 volt, 0.18 volt and at -0.92 volt. After repeated scans, the oxidation peak at 0.24 volt disappeared, whereas the peak at 0.62 volt grew bigger and then became reproducible. We conclude that the peak at 0.24 volt was due to either an impurity or electrode contamination as it did not appear on another cyclic voltammogram run with fresh 2,6-dichlorophenol (Figure 2). The peak at 0.62 volt was assigned to the oxidation of the phenol. Moreover, this peak is diffusion controlled. Cyclic voltammograms at various scan rates ranging from 10 mV/sec to 1000 mV/sec showed a linear relationship when the peak current was plotted as a function of the square root of the scan rate.

It is well documented that phenols tend to foul the electrode surface rapidly, causing poorly shaped peaks (Wang and Li, 1989). Based on the results of previous observations (Hemmerich, 1983), we conclude that a one-
Oxidation-Reduction Characteristics of Chlorophenols in an Aprotic Medium

**Fig. 2.** Cyclic voltammogram of 2,6-dichlorophenol in 0.10 M tetrabutylammonium perchlorate in dimethylsulfoxide performed at a scan rate of 0.10 volt/sec. Five repeated scans were performed without renewing the GCE surface. Two scans were performed without renewing the surface between 0.60 volt and -2.00 volt.

electron oxidation took place at 0.62 volt. On the reverse scan, the peak at 0.46 volt is typical of reduction of a thin film deposit, producing a soluble species which further reduces at 0.18 volt. Figure 2 shows the cyclic voltammogram where the potential was switched backward at 0.60 volt (before oxidation of the phenol occurred) when no peak appeared at 0.46 volt. This observation unequivocally confirms that the peak at 0.62 volt is indeed due to the oxidation of the phenol. It also proves that this peak is reproducible, and electrode fouling is not as severe in DMSO as observed in aqueous solution. All chlorophenols studied behave in a similar manner, showing only one peak due to oxidation in the positive potential range, although the magnitude of this potential changed according to the number and the position of chlorine substitutions. Based on our results, we conclude that 2,6-dichlorophenol undergoes oxidation-reduction processes as shown in Fig. 3. At 0.62 volt, phenol undergoes oxidation to form a stable phenoxyl radical intermediate (I), which dimerizes to form a quinone ether (II). The ether forms a deposit on the electrode surface and then is reduced, successively at 0.46 volt to form a phenol ether (III) and then at 0.18 volt to form phenol again. At -0.92 volt, phenol probably undergoes an aromatic ring reduction which is oxidized again at 0.0 volt (on reverse scan) to phenol. The entire oxidation-reduction process is electrochemically irreversible (the separation between oxidation and reduction peaks for phenol is 0.44 volt, much larger than 0.059 volt predicted by theory of cyclic voltammetry), although the process is chemically reversible. No attempts
Fig. 3. Proposed reaction mechanism of oxidation and reduction of 2,6-dichlorophenol in dimethylsulfoxide.
Oxidation-Reduction Characteristics of Chlorophenols in an Aprotic Medium

Table 2. Comparison between toxicity and oxidation potential of chlorophenols. The toxicity is presented as LD$_{50}$ in mollusk.

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Toxicity ($LD_{50}$, mg/kg)</th>
<th>Oxidation potential (volt vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
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<td>0.78</td>
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<tr>
<td>2-chlorophenol</td>
<td>345</td>
<td>0.63</td>
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<td>3-chlorophenol</td>
<td>521</td>
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<td>4-chlorophenol</td>
<td>1373</td>
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</tr>
<tr>
<td>2,3-dichlorophenol</td>
<td>2376</td>
<td>0.65</td>
</tr>
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<td>2,4-dichlorophenol</td>
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<td>0.75</td>
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</tr>
<tr>
<td>3,4-dichlorophenol</td>
<td>1684</td>
<td>0.52</td>
</tr>
<tr>
<td>3,5-dichlorophenol</td>
<td>Not available</td>
<td>0.70</td>
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<tr>
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<td>0.15</td>
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<td>Pentachlorophenol</td>
<td>117</td>
<td>0.18</td>
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</table>

have been made to isolate and confirm the formation of various intermediate products in this oxidation-reduction scheme since the chemical isolation process is extremely tedious and some intermediates are relatively unstable to extract at room temperature.

The oxidation potential and toxicity of various chlorophenols are listed in Table 2. An interesting pattern between the two parameters is observed. First of all, the oxidation potentials of all chlorophenols are less positive than that of phenol itself, indicating that they are more easily oxidized. Our observation is in agreement with results obtained in aqueous solution (Terashima et al., 2002), although it is in contrast to another study (Rodgers et al., 1999). Second, there appears to be an empirical relationship between the toxicity and the oxidation potential of chlorophenols when they have the same number of chlorine substitutions. For example, two tetrachlorophenols show a trend where greater toxicity (low LD$_{50}$ in mollusk) is associated with less positive oxidation potential, which means the compound is easier to oxidize. This trend is followed among trichlorophenols and to some extent among dichlorophenols. However, the trend is reversed among monochlorophenols. Further studies need to be conducted to establish such a relationship.

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Revised Bedrock Geology of War Eagle Quadrangle, Benton County, Arkansas

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Abstract

A digital geologic map of War Eagle quadrangle (WEQ) was produced at the 1:24000 scale using the geographic information system (GIS) software ArcView® by digitizing geological contacts onto the United States Geological Survey (USGS) digital raster graphic (DRG). The geology of WEQ consists of sedimentary rocks of Ordovician (Cotter, Powell, and Everton Formations), Devonian (Clifty Formation and Chattanooga Shale), and Mississippian (St. Joe-Boone, Batesville, and Fayetteville Formations) systems. Impoundment of Beaver Lake in 1966 inundated most Ordovician rocks cropping out in WEQ, but all three formations were present in isolated outcrops along the present shoreline of the lake. The St. Joe Limestone was mapped as a separate unit from the Boone Formation throughout WEQ and all four members of the St. Joe Limestone were observed, lending credence to suggestions that the St. Joe Limestone should be elevated to formation status. The Hindsville Member of the Batesville Formation and the Fayetteville Formation were mapped in an isolated outcrop along the extreme eastern boundary of WEQ. All formations within WEQ were highly fractured, and some prominent lineaments may represent faults with minor displacement. Several new normal faults were mapped in the central-eastern portion of the quadrangle, and the most prominent structural feature in the quadrangle was the northward extension of the Fayetteville Fault (also known as the Price Mountain Fault), which bisects the quadrangle from southwest to northeast.

Introduction

War Eagle quadrangle (WEQ) is located in the southeastern corner of Benton County, Arkansas. The quadrangle lies from 36° 22' 30" to 36° 15' 00" North latitude and from 94° 00' 00" to 93° 52' 30" West longitude (Fig. 1). The quadrangle was named for War Eagle Creek and War Eagle Mill, each located near the southern boundary of the quadrangle (Fig. 2). Previous mapping within the quadrangle was conducted prior to inundation of the White River valley to create Beaver Lake in the northern half of WEQ (Fig. 2). In the 40 years since the last mapping effort in WEQ (Staley, 1962), changes in stratigraphic nomenclature reassigned some stratigraphic members to different formations whereas other members were nominated to be elevated to formation status. Thus, revised mapping in WEQ was undertaken with the aim of delineating field relations of exposed sedimentary strata in the context of modern stratigraphic nomenclature. In addition, geologic structures within WEQ were reinterpreted in the context of the plate tectonic paradigm and its relation to the geologic history of Arkansas (Houseknecht, 1986; Hudson, 2000) and the Ozark Plateaus. This report presents results of field mapping and revision of the geology of War Eagle quadrangle. A new, digital geologic map was produced from field data utilizing the geographic information system (GIS) software ArcView.

Branner (1940) and Croneis (1930) described the Ozark Plateaus physiographic province of northwest Arkansas. The Ozark Plateaus province comprises the Salem, Springfield, and Boston Mountain plateau surfaces (from oldest and topographically lowest to youngest and topographically highest). The Salem Plateau and Springfield Plateau are separated by the Eureka Springs escarpment, which rises 137 m above the general level of the Salem Plateau. The Boston Mountains escarpment separates the Springfield and Boston Mountain Plateaus (Croneis, 1930; Fig. 3). WEQ is located mostly on the Springfield Plateau with a small portion of the White River valley at the extreme northern limit of the quadrangle within the Salem Plateau. The Ozark Plateaus province is a portion of a structural dome believed to have been formed by regional tectonic warping during the assembly of Pangea in the late Paleozoic (Guccione, 1993; Hudson, 2000). Though structurally a part of the Ozark Dome, the Salem and Springfield plateaus consist of nearly horizontal beds of Paleozoic sedimentary rocks. Ordovician rocks form the foundation of the Salem Plateau, whereas Mississippian and Devonian rocks form the Springfield Plateau (Guccione, 1993; Fig. 4).

The topography of WEQ is controlled by the type of rock cropping out in the area. Steep, regolith-covered slopes...
are typically developed within the Boone Formation (Mississippian), and near-vertical to overhanging cliffs are typically associated with outcrops of the St. Joe Formation. The Chattanooga Shale (Devonian) forms gentle slopes and broad terraces, whereas the Everton, Powell and Cotter Formations (Ordovician) form both gently and steeply sloped terrains.

Most stream valleys within WEQ are v-shaped and carry mainly intermittent or disappearing streams. Exceptions to this are the Van Hollow Creek, Rambo Creek, Devil’s Gap Creek, War Eagle Creek, and two unnamed streams feeding War Eagle Creek. The entire quadrangle is located in the drainage basin of the White River.

Previous Investigations.--Branner (1891) discussed topographic features, hydrology, and the stratigraphy of Benton County, Arkansas. Croneis (1930) provided a similar stratigraphic description, but also outlined the major structural features (e.g., Price Mountain Fault, now known as the Fayetteville Fault and Glade Fault) located within the study area.

The geology of the WEQ is known only from the 1:500,000 geologic map of Arkansas (Haley et al., 1976), Eureka Springs-Harrison 30 minute quadrangle folio at
Fig. 2. USGS Digital Raster Graphic (DRG) of War Eagle quadrangle, Benton County, Arkansas.
Fig. 3. Physiographic provinces of Arkansas (modified from Adamski et al., 1995). Note: Province divisions only show general boundary locations.

1:100,000 scale (Purdue and Miser, 1916), and an unpublished geologic map (Staley, 1962) at 1:24,000 scale.

In 1962, Staley mapped WEQ as a master's thesis project in the Department of Geology at the University of Arkansas (Fayetteville). A geologic map and cross-section were produced, but the map was never published; the only known copy of Staley's (1962) WEQ geologic map was located after an extensive search of holdings in the Department of Geosciences and the University of Arkansas library. Staley's (1962) map was important to this study because it predated construction of Beaver Dam and inundation of the White River Valley to create Beaver Lake (Black, 1979). Thus, the single remaining copy of his map was the only detailed source of information regarding geology and stratigraphy of areas of WEQ now inundated by Beaver Lake. For the map produced in the present study, sub-lake geology was taken directly from Staley's (1962) map. The accuracy of Staley's (1962) work was evaluated by comparing his mapped formations in areas still above lake level to those mapped during the present study.
Quinn (1963) discussed the Price Mountain Fault (Fayetteville Fault) along with other northeast trending faults in northern Arkansas. He believed that groundwater movement along these faults caused dissolution of carbonate beds along the fault plane. Dissolution opened voids that allowed the overlying material to slowly subside and form "subsidence structures". He also believed that anticlines existed between and parallel to the subsidence structures. Gibbons (1962) concluded that fractures striking N70°E and N7°E indicated a northwest-southeast compressional force, leading Quinn (1963) to conclude that a compressional force from the northwest-southeast direction was responsible for the faulting and folding observed in WEQ. In addition, Gibbons (1962) documented another system of fractures trending N30°W and N55°E that were not cut by the earlier system. Gibbons believed these fractures were indicative of a later north-south compression. Based upon Quinn's (1963) work, Clardy (1964) discussed the subsidence structures of Price Mountain Syncline and the relationship with a parallel anticline (Cove Creek Anticline). Staley (1962) also included this structural framework in his work on WEQ.

In a petrographic study of calcite twin lamellae, Chinn (1967) and Chinn and Konig (1973) suggested that rocks of northern Arkansas had been subjected to north-south compression but could not identify conclusive evidence validating Quinn's hypothesis for an earlier compressive stress from northwest-southeast.

### Materials and Methods

Field reconnaissance throughout WEQ was performed with the aid of a Brunton compass, rock hammer, and digital camera. Field measurements were recorded on topographic maps, aerial photographs, and in a field notebook. Satellite imagery (Landsat Thematic Mapper) obtained from the Center for Advanced Spatial Technologies (CAST) at the University of Arkansas was also examined to help determine fracture and fault orientations (Fig. 5). Field investigations were completed by accessing WEQ by automobile, on foot, and by boat around the margins of Beaver Lake. Use of a boat to circumnavigate the lakeshore proved essential in mapping geologic contacts and investigating geologic structures; a number of new stratigraphic relationships and geologic structures (faults) were discovered from shipboard observations.

**Digital Mapping and Geographic Information System.**—A digital geologic map of WEQ was developed for this project by digitizing geologic contacts and observed faults from field maps onto a digital raster graphic (DRG) of WEQ. The digitizing technique involved drawing contacts directly on the computer screen by moving the cursor over the DRG and clicking the mouse button at short intervals to

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Fig. 4. Generalized stratigraphic column of War Eagle quadrangle.
Fig. 5. Landsat Thematic Mapper image with prominent lineaments highlighted. Note there appear to be several superimposed sets of lineaments in this area. Image taken from Arkansas Interactive Mapper (http://www.cast.uark.edu/local/mapper) developed by the Center for Advanced Spatial Technologies, University of Arkansas.
trace contacts onto the displayed topography. Each stratigraphic unit was digitized as a separate layer within the geographic information system such that the display of each layer could be toggled on or off. Faults were digitized as lines onto a separate layer as well. Each layer was then displayed hierarchically to depict the geology of the study area (Figs. 6, 7, 8).

Results

All rock types cropping-out within WEQ are of sedimentary origin. The dominant lithic types are limestone, dolostone, sandstone, shale, and chert. Strata of Ordovician, Devonian, and Mississippian age were exposed throughout WEQ (Fig. 4). Silurian-age rocks are absent throughout the quadrangle as a result of erosion or non-deposition.

The Ordovician System in WEQ is represented by (in ascending order) the Cotter Formation, Powell Formation, and Everton Formation. The Cotter Formation is composed mostly of medium gray to light brown to bluish gray weathered dolomite with thin layers and nodules of chert (Simonds, 1891; Hopkins, 1893; Adams and Ulrich, 1904; Purdue and Miser, 1916). The chert ranges in color from white through diverse shades of gray. Many of the nodules are banded and a few are oolitic. Thin (<0.5 m) to thick (~8 m) beds of microcrystalline dolomite alternate with intervals of argillaceous, oolitic and quartz sand-bearing units throughout the formation. The sand intervals occur as thin lenses, thinly interbedded (<0.5 m), or as thicker individual beds (> 1 m) within the dolomite (Holland, 1987). Stromatolitic mounds are sometimes present (Staley, 1962). Intraformational conglomerates (0.075 m to 4.5 m thick) of chert and dolomitic pebbles are sporadically distributed throughout the formation (Staley, 1962). Since
impoundment of Beaver Lake, only the uppermost 1 m to 12 m of the Cotter Formation are still visible in a few locations around the lake shore (Figs. 6 and 7).

The Powell Formation lies unconformably on top of the Cotter Formation. It is light gray to tan dolomudstone with orthoquartzite lenses. Shale is more abundant than in the underlying Cotter Formation. An undulating green shale layer, 0.05 m to 0.46 m thick, marks the base of the formation (Manger, 1988). Absence of chert in the Powell Formation helps differentiate it from the Cotter Formation. Like the Cotter Formation, Powell Formation outcrops in WEQ were limited to the northern half of the quadrangle where it commonly occurred near lake level (ca. 341 m above sea-level). The observed thickness of the interval ranged from 6 m to 24 m. Staley (1962) reported measurements up to 31 m, but the lower portions of this section are presently below lake level and therefore inaccessible. Staley (1962) also reported differences in elevation of outcrops that he attributed to folding, but more likely resulted from minor faulting.

The Everton Formation was subdivided by Purdue and Miser (1916) into three different members. These units are the Sneeds Limestone Lentil, Kings River Sandstone, and an upper member composed of magnesium-free limestone and sandstone. Studies by Giles (1930), McKnight (1935), Frezon and Glick (1959), and Suhm (1970 and 1974) redefined the different members of the Everton Formation. The only unit present in WEQ was the Kings River Sandstone Member. The Kings River Sandstone Member is thin bedded, saccharoidal, quartz sandstone cemented by calcium carbonate. Grains are subangular to rounded and fine- to medium-grained. Beds are friable to non-friable and are cross-bedded and often ripple marked with occasional channels. Sedimentary structures and stratal geometries
suggested deposition in nearshore, beach, and coastal dune environments (Dr. D. Zachry, pers. comm., 1999). The creation of Beaver Lake inundated most outcrops of the Everton Formation in WEQ. Presently, outcrops are observed only along the lakeshore of the east-central portion of the quadrangle, and these average only 2 m thick (Figs. 6 and 7). Staley (1962) reported a maximum thickness of 12 m near Rambo Creek and an average thickness of approximately 5.5 m throughout WEQ.

The Devonian System in WEQ is represented by the Clifty Formation and the Chattanooga Shale. The Clifty Formation is white to yellow-brown orthoquartzite ranging in thickness from <1 m to 2.5 m. The surface of the Clifty Formation is heavily burrowed (Fig. 8) and represents a probable nearshore (shallow littoral) setting (Dr. D. Zachry, pers. comm., 1999). The Clifty Formation is widespread throughout the quadrangle except in the northwestern portion (Figs. 6 and 7). It is observed to be mainly massively bedded sandstone with discontinuous chert layers in a few places. It is unconformable with the Everton Formation or Powell Formation where the Everton Formation is absent.

The Chattanooga Shale is a black to brownish-black, fissile, carbonaceous, pyritic shale with a maximum observed thickness of 15 m and average thickness between 6 m and 9 m. The Chattanooga Shale correlates with the Chattanooga and Woodford Shale of Oklahoma (Frezon, 1962) and the type Chattanooga Shale of Tennessee (Cooper et al., 1942). The basal unit of the Chattanooga Formation is the Sylamore Member (a mature, thin bedded, phosphatic pebble-bearing orthoquartzite that commonly displays a chert breccia at its base; (Hall, 1978; Hall and Manger, 1978)). Nowhere in the WEQ did the Sylamore Member lie in direct contact with the Everton Formation. It has been proposed that the Chattanooga Shale was deposited as shelf mud with the Sylamore Member sandstone representing an early transgressive, shallow-water, near-shore accumulation (Swanson and Landis, 1962).

The Mississippian System in WEQ is represented by the St. Joe Formation and the Boone Formation, the Hindsville Member of the Batesville Formation, and the Fayetteville Formation. The first appearance of the name St. Joe Limestone was in Hopkins (1893) for the basal chert-free unit within the Boone Formation. Girty (1915) assigned the St. Joe Limestone as a member of the Boone Formation. However, in 1934 Cline proposed to raise the St. Joe Member to formation status. While working on the Chouteau Group in Missouri (equivalent to the St. Joe in Arkansas), Mehl (1960) identified the following members (in ascending order): the Bachelor Member, the Compton Member, the Northview Member, and the Pierson Member. Subsequent work by McFarland (1975), Shanks (1976), Manger and Shanks (1977), and Shelby (1986) reordered the classification to bring the St. Joe Limestone to formation...
status including the Bachelor, Compton, Northview, and Pierson as members. This convention was followed for this study. Staley (1962) did not recognize the St. Joe Limestone as a formation and subsequently did not map the formation, but included it with the overlying Boone Formation. For this study, the St. Joe Formation was mapped as a separate stratigraphic unit throughout WEQ (Figs. 6 and 7). The thickness of the St. Joe Formation ranges from 9 m to 15 m in WEQ. The St. Joe Formation formed near vertical to overhanging cliffs in the areas where it cropped out, especially along the margins of Beaver Lake. The contact between the Bachelor Member of the St. Joe Formation and Chattanooga Shale is an unconformity. The rest of the members of the St. Joe Formation are conformable (Manger, 1988).

The Boone Formation was named by Branner (1891) for exposures in Boone County, Arkansas. The classification scheme for northwest Arkansas divides the unit into two informal intervals and a capping oolitic member (Fig. 4). The two informal members are the Upper and Lower Boone. The type of chert development is the primary means for characterizing these units. The Lower Boone has dark gray to black penecontemporaneous chert that occurs in nodules and beds disrupting bedding of the limestone in an anastomosing fashion (Manger, 1988). The Upper Boone interval has light gray to gray diagenetic chert that was formed by silica replacing carbonate sediment after deposition. The Short Creek Oolite is the only formally recognized member of the Boone Formation. Development of the oolitic unit is sporadic throughout northern Arkansas (Shelby, 1986) and was not observed in WEQ. The Lower Boone Formation is a fine-grained, grain-supported, calcarenite consisting mainly of bryozoan detritus, while the Upper Boone is more grain-dominated than the Lower Boone (Shelby, 1986). The Boone Formation is the most widespread of the rocks cropping out in WEQ, occurring as the surface cover over 63% of the quadrangle. The Boone Formation has an approximate average thickness of 91 m. The Boone Formation displayed many karst features. Sinkholes and blind valleys with disappearing streams are present throughout the study area. Dissolution of the St. Joe Formation and subsequent collapse of the overlying Boone Formation formed these sinkholes.

The Hindsville Member of the Batesville Formation was named by Purdue and Miser (1916) for exposures located near Hindsville, Madison County, Arkansas. Grayson (1976) proposed the Hindsville Member be elevated to formation status in order to distinguish it from the Batesville Formation. However, because outcrops of Hindsville strata are restricted to a single locality in WEQ, there is insufficient evidence to permit evaluation of Grayson’s (1976) proposal. Thus, Hindsville strata observed in WEQ are considered a member of the Batesville Formation. The contact between the underlying Boone Formation and Hindsville Formation is marked by a basal mudstone. Chert pebbles reworked from the Boone Formation are found throughout the lower portion of the formation. Hindsville Member limestones are light gray to gray in color. The only outcrop of the Hindsville Member in WEQ is located in Sections 29 and 32, T19N, R27W. A recent road cut provides an excellent exposure of an approximately 7.5 m section (Fig. 9) of the Hindsville Member.

Simonds (1891) named the Fayetteville Shale for exposures near Fayetteville, Washington County, Arkansas. At the type locality, the Fayetteville Shale consists of 1) a lower black, fissile, non-silty shale unit, 2) Wedington Sandstone Member, and 3) an upper interval of lighter colored, less fissile, silty to sandy shale. The only unit present in WEQ is the lower black, fissile shale (Handford
Formations and Manger, 1990, 1993). The Fayetteville Shale lies uncomformably on the Hindsville Member of the Batesville Formation. The unit is approximately 6 m thick in WEQ.

Structural Geology.—Northwest Arkansas is situated on a sable midcontinent craton that consists of a Precambrian basement of igneous rocks overlain by Paleozoic strata. The controlling influence on the structure in the southern portion of the craton was the assembly of Pangea during the latest Paleozoic, resulting in development of the Ouachita Mountains and Ozark Dome (Smith, 1977; Houseknecht, 1986; Hudson, 2000). Throughout the study area the geologic formations are typically horizontal with a slight dip to the south (<5°). Occasionally, a few disjunct blocks have dips greater than 5°, especially in the vicinity of faults. However, these are not representative of the regional dip.

Quinn (1959) proposed a system of northeast trending folds throughout northwest Arkansas that were presumed to result from compressional tectonics. Staley (1962) used Quinn's model of northeast trending folds by including the Cove Creek Anticline in the northwest portion of WEQ. However, Staley (1962) determined the existence of the Cove Creek Anticline from dip angles less than 2°. Field investigation during revised mapping of WEQ failed to produce evidence of the Cove Creek Anticline within WEQ. Quinn's (1963) later subsidence structure hypothesis involved karstification of underlying carbonates and subsequent subsidence along faults without the need for compressional tectonics. As an example, Simonds (1891) named the Price Mountain Syncline for inward dipping beds near Price Mountain, Washington County, Arkansas. The Price Mountain Syncline trends along the trace of the Fayetteville Fault, but appears to terminate before entering WEQ. Solution features are present near Rocky Branch Marina in Sections 11 and 2, T19N, R13W of WEQ. Thus, this area appears to have been down-dropped by dissolution of underlying carbonates. Resulting gravity faults bound this feature (Fig. 6). Clardy (1964) discussed similar structures associated with the Fayetteville Fault and Price Mountain Syncline.

Compression and tension have produced systematic joint and fault patterns in northwestern Arkansas. Analysis of satellite imagery shows a series of lineaments believed to be expressions of regional joint patterns (Fig. 5). Lineament trends measured in WEQ were N30°E, N90°E, N7°W, N40°W, and N55°E.

The Fayetteville Fault bisects WEQ from the southwest to the northeast (Figs. 6, 7), and is the most prominent structure in the quadrangle. Simonds (1891) named the Fayetteville Fault for a fault trace exposed in Fayetteville, Washington County, Arkansas. In WEQ the strike of the Fayetteville Fault is N30°E and the fault appears to be discontinuous along strike. The Fayetteville Fault is a near-vertical normal fault down-thrown to the southeast, but the vertical displacement is difficult to determine. The Fayetteville Fault is exposed in an area northwest of Rocky Branch Marina in Section 2, T19N, R28W (Fig. 6). In this area Staley (1962) did not discover the exposure of the fault and mapped it incorrectly to the southeast.

In the Glade Creek area (Sections 26 and 25, T20N, R28W), a normal fault is present (Fig. 6). This fault is downthrown to the northwest. Staley (1962) mapped this area before the Glade Fault was accepted to be a part of the Fayetteville Fault system. By mapping these faults separately it was necessary for Staley (1962) to incorporate additional faults to explain the stratigraphy, and this complicated the
Revised Bedrock Geology of War Eagle Quadrangle, Benton County, Arkansas

structural interpretation by adding additional faults without field evidence.

The Clifty Fault is located in the eastern quarter of the quadrangle (Figs. 6 and 7) and has a slightly curving east-west trend. The fault is downthrown to the south and is displaced approximately 15 m.

Van Hollow branch of Beaver Lake is located in the central portion of the map and is the location of two newly described normal faults (Figs. 6 and 7). The first fault trends in a curving northeasterly direction (approximately N70°E) and has an approximate displacement of 17 m (Fig. 10A). The fault is downthrown to the south. The second fault trends N60°W and is downthrown on the northern side with a displacement of approximately 4.5 m (Fig. 10B).

Another fault located along the Devil's Gap branch of Beaver Lake was identified during this project. The sense of displacement and strike of this fault are similar to the second fault in Van Hollow several kilometers to the west, suggesting these structures may be genetically related (Fig. 7).

Conclusions

Exposed stratigraphy within WEQ is Ordovician-Mississippian and generally horizontal (Figs 6 and 7). The impoundment of Beaver Lake covered much of the Ordovician section previously mapped by Purdue and Miser (1916), Staley (1962), and Haley et al. (1976). However, important revisions of the geologic map of Staley (1962) included 1) separating and mapping the St. Joe Formation as a distinct stratigraphic unit, 2) separation of the Bachelor Member from the Chattanooga Formation and assigning it as the basal member of the St. Joe Formation, 3) revision of fault locations and documentation of several new faults, 4) mapping the Hindsville Formation within WEQ, and 5) mapping the Fayetteville Shale within WEQ.

Observed jointing and faulting patterns coincide with previously mapped trends. The control of joint and fault patterns on topography and drainage patterns throughout the quadrangle was made apparent from satellite imagery. The Fayetteville Fault is discontinuous and was previously mapped incorrectly in the Rocky Branch Marina and Glade Creek areas. All of the faults in WEQ are normal faults (implying extensional tectonics) and are difficult to follow in the Boone Formation regolith.

Utilizing digital mapping techniques had many advantages over conventional styles of mapping. Once field-mapping data are entered into digital format and incorporated into a geographic information system, they are more easily manipulated and merged with geologic maps of adjoining quadrangles.

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Revised Bedrock Geology of War Eagle Quadrangle, Benton County, Arkansas


Epidermal Papilloma in an Ozark Hellbender
(Cryptobranchus alleganiensis bishopi) from the Spring River of
Northern Arkansas

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Abstract

An Ozark hellbender (Cryptobranchus alleganiensis bishopi) with multiple, large, warty skin lesions was collected in the Spring
River, Fulton County, Arkansas, in 1994. The specimen was a female, 560 mm in total length, and had a mass of 1,947 g.
Tissues were formalin-fixed, and three lesions were processed for histopathology. The normal skin at the tumor margins had
a stratified squamous epidermis overlying a loose, well-vascularized, heavily pigmented dermis. Poison glands and mucous
glands extended from the epidermis into the dermis. The lesions, in contrast, were masses of epidermal cells up to 100 times
thinner than the normal epidermis. They consisted of long, thick, branching epidermal pegs separated by thin fibrovascular
papillae. The base of the lesions and all pegs had sharp boundaries bordered by a basement membrane, ruling out invasion.
Tumor cells were differentiated into scattered glandular structures suggestive of dermal glands. Cells within the pegs were
poorly organized. Nuclei usually contained basophilic granules. Mitotic figures were numerous. By electron microscopy, the
cells appeared to be pulling apart except where held together by desmosomes. The sum of the above observations is consistent
with a pathological diagnosis of epidermal papilloma.

Introduction

Amphibian tumors, in general, are rare in wild populations (Sheremetieva, 1965; Elkan, 1976; Asashima et al., 1982; Oka et al., 1992); their occurrence was reviewed by Asashima et al. (1987). Non-invasive, papillary epidermal neoplasms (known as “epidermal papillomas”) have been infrequently reported. A review of the literature dating from 1955 through 1999 revealed that relatively few studies (< 30) have addressed the occurrence of skin lesions in salamanders. Most of these investigations have focused on the Japanese newt, Cynops pyrrhogaster (Salamandridae), in which the presence of spontaneous skin papillomas have been well studied (Honma and Murakawa, 1967; Bryant, 1973; Pfeiffer et al., 1979, 1989; Asashima and Komozaki, 1980; Asashima et al., 1982, 1985; Asashima and Oinuma, 1982; Asashima and Meyer-Rochow, 1988; Oka et al., 1992). In this newt, the prevalence of papillomas varies both seasonally and geographically (Oka et al., 1992). In North America, a high incidence of neoplastic skin lesions is known from the tiger salamander, Ambystoma tigrinum (Ambystomatidae), collected in sewage lagoons in northwest Texas (see Rose, 1976, 1977, 1981; Rose and Harshbarger, 1977; Harshbarger et al., 1989).

Two studies have identified skin neoplasms within the families of primitive salamanders (Hyobranchidae and
Cryptobranchidae). In the Aomori salamander (Hyobius lichenatus) from northern Japan, the incidence of skin papillomata was 0.67% (N = 7) in 1,050 individuals examined (Asashima and Meyer-Rochow, 1988). Within the giant salamanders (Cryptobranchidae), data are available on squamous cell papillomas in a single specimen of the Japanese giant salamander, Andrias davidianus japonicus (Frye et al., 1989), from northern Japan.

The Ozark hellbender, Cryptobranchus alleganiensis bishopi (Caudata: Cryptobranchidae), is a large aquatic salamander whose range is restricted to rivers and streams in the Ozark Mountains of southwestern Missouri and northeastern Arkansas (Conant and Collins, 1998). In the following, we report the first incidence of epidermal papilloma in the Ozark hellbender, a salamander whose recent population declines (Trauth et al., 1992, 1993) have gone unresolved. This observation also represents the second report for any type of neoplasm for Cryptobranchus (see Cosgrove and Harshbarger, 1971).
Fig. 1. Photographs of a living adult Ozark hellbender (Cryptobranchus alleganiensis bishopi) illustrating major skin lesion areas on the body and tail. A. Left lateral view of salamander showing a massive globular tumor mass. Line = 100 mm. B. Close up of the enlarged tumor embedded within rugose skin. Line = 25 mm; A indicates region from which tissue section shown in Fig. 3A was obtained. C. Rump and left thigh revealing large continuous papillomal region. Line = 25 mm; B and C indicate tissue sections shown in Fig. 3B and C, respectively.
Materials and Methods

On 3 October 1994, one of us (PD) collected a female *C. a. bishopi* possessing multiple skin lesions from the Spring River (Fulton County), Arkansas, in the vicinity of Bayou Access (T21N, R5 W, Sec. 33). The specimen was returned to the lab and photographed (Fig. 1); this was soon followed by the removal of small tissue samples from several skin lesion areas (dorsal tail surface, left lateral body surface, and left rear leg surface). The animal was fed live minnows and/or small crayfish and remained alive in a chilled aquarium until being sacrificed (in a 10% chloretone solution) on 15 February 1995. (The preliminary biopsied sites had successfully healed during the approximately 4.5 months in captivity.) Upon death, additional tissue samples were taken throughout the body; all samples were fixed in either 10% formalin or 2% glutaraldehyde (the latter for studies using transmission electron microscopy—TEM). The hellbender was fixed in 10% formalin, preserved in 70% ethanol, and deposited into the Arkansas State University herpetological collection as voucher specimen ASUMZ 20081. At the time of death, the salamander measured 560 mm in total length, 392 mm in snout-vent length, and had a mass of 1,947 g.

Routine histotechnical techniques (Presnell and Schreibman, 1997) were employed to prepare the tissue samples for light microscopy (LM). In brief, these steps included dehydrating tissues in a graded series of ethanol concentrations, clearing the tissues in xylene, and embedding in paraffin. Paraffin tissue blocks were then oriented so that sectioning would yield either sagittal or transverse sections that were cut into serial strips (at a thickness of 8μm). Sectioned tissue was affixed to slides using Haupt’s adhesive, stained with hematoxylin, counterstained with eosin (H&E), and then enclosed with glass coverslips. For TEM, tissue samples were fixed in 2% glutaraldehyde in 0.1 M sodium cacodylate buffer for 2 hr and postfixed in 1% osmium tetroxide. After four rinses in cacodylate buffer, the tissues were passed through a graded series of acetones, infiltrated, embedded in Mollenhauer’s Epon-Araldite Mixture number 2 (Dawes, 1988), and sectioned with a diamond knife. Sections were picked up on copper grids for examination and were stained with uranyl acetate (3% aqueous) and lead citrate. TEM images were recorded on Kodak SO 163 electron image film with a JEOL 100 CXII TEM-SCAN electron microscope. A voucher set of stained tissue slides is deposited at the Registry of Tumors in Lower Animals (RTLA) located in the Department of Pathology at George Washington University Medical Center (Washington, D.C.) and was assigned the accession number RTLA 6035.

Results

**Gross Morphology.**—Clusters of papillary epidermal neoplasms (epidermal papillomas) were scattered along much of the body surface of the tumor-bearing Ozark hellbender. Conspicuous anterior body lesions included those incorporating the right eye and several patchy, light-colored ovoid lesion clusters atop the head (Fig. 2A). A large, highly-vascularized, globular, flesh-colored tumor (approximately 50 X 35 mm in size) protruded from the left dorsolateral, rugose surface of the body approximately midway between the fore and hind leg. Posterior to this large lesion was a broad, continuous papillomatous area on the rump. The rump patch appeared as a low, smooth, multilobate cluster of lesions; the tumorous skin appeared lighter in pigmentation compared to the surrounding normal skin. The papillomatous dorsal surface of the left hind leg was similar in appearance to the rump region.

**Light Microscopy.**—The histology of normal skin in *C. a. bishopi* revealed a mostly homogenous epidermis 5 - 8 cell layers in height comprised of stratified squamous (Fig. 2B) and a highly-vascularized dermis embedded with conspicuously- large, epidermal mucous glands and granular (poison) glands. Pigmented melanocytes (chromatophore cells) were evident lying along the adnexal epidermal boundary (basal lamina) as well as being scattered throughout the dermosubcutaneous tissue. Nuclei of epidermal cells were mostly round or oval in shape. In contrast, lesions from three regions of the tumor-bearing Ozark hellbender shown in Fig. 3 revealed a striking proliferation of the epidermal cells in masses as much as 100 times the thickness of normal skin. When viewed across section using LM (Fig. 3), the tumor tissue was seen to consist of long, thick, branching epidermal pegs separated by thin, fibrovascular papillae. Tumor cells were presummably derived from the stratum granulosum layer; these cells also exhibited a wide range of nuclear and cytoplasmic irregularities. Mitotic figures, observed primarily in the stratum basale cells of normal skin, were not confined to this layer in the tumor tissue. A well-defined corneal layer was absent on the surface of the large tumor (Fig. 3A). In some instances, irregularly-grouped epidermal glands appeared to be squeezed into regions between proliferating cell pegs (Fig. 3B and C). Many of these secrerory glands had hypertrophied to such as much as eight times their normal diameter. The growth pattern of tumor cells within some epidermal pegs was that of individually-segregated masses of well-differentiated glandular compartments, reminiscent of glands lying within the dermis. In most cases, the base of the lesions as well as individual epidermal pegs had well-defined limiting boundaries bordered by a basement membrane. In one area tumor cells had breached the basement membrane and
Epidermal Papilloma in an Ozark Hellbender (*Cryptobranchus alleganiensis bishopi*) from the Spring River of Northern Arkansas

Fig. 2. Head region (A) and cross section of normal skin (B) of *Cryptobranchus a. bishopi* shown in Fig. 1. Line in A = 25 mm; arrow points to right eyeball enveloped by tumorous tissue. Line in B = 100 μm; E = epidermis; GG = granular gland; ME = melanocyte; MG = mucous gland.

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Fig. 3. Photomicrographs of neoplastic lesions from the dorsolateral body wall (A), left thigh (B), and rump region (C) of Cryptobranchus a. bishopi. Line in A = 2 mm for A - C.
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Fig. 4. Electron micrographs of tumorous epidermal cells (A) and normal epidermal cells (B) in *Cryptobranchus a. bishopi*. In A, large intercellular spaces (S) are numerous; in contrast, B reveals small intercellular regions. D = desmosome in A (indicated by pointers in B).
were invading the connective tissue, in a manner characteristic of squamous cell carcinoma.

_Electron Microscopy._—The ultrastructure of epidermal cells of tumors revealed enlarged intercellular spaces between cells (Fig. 4). Subcorneal cell clusters characteristically exhibited cytoplasmic pedicles joined by desmosomes (Fig. 4A and B). Although electron-dense, cytoplasmic inclusions were observed, most cells possessed evacuated spheres containing membranous fragments and cellular debris. Thus, the appearance of the tumor cells was suggestive of tissue being stretched or torn apart (Fig. 4A).

**Discussion**

Spontaneous epithelial tumors account for nearly half of all tumors reported for amphibians (Asashima et al., 1987). With the addition of the Ozark hellbender, three salamander species (including _A. tigrinum_ and _C. pyrrhogaster_) are known to exhibit papillomas. The neoplasms found in the Ozark hellbender were similar to the epidermal papillomas described and illustrated by Asashima et al. (1987) and Pfeiffer et al. (1989) for _C. pyrrhogaster_. Our ultrastructural analysis in _C. a. bishopi_ indicated the presence of similar intercellular spaces and associated intercellular bridges with desmosomal attachments; these cytoplasmic characteristics are also described for tumor cells in _C. pyrrhogaster_ (Pfeiffer et al., 1989).

**Acknowledgments._**—We thank David Weingold, M.D. (Jonesboro, Arkansas), for his assistance in the histological examination of tissues. This research was partially supported by NIH Contract Number NO1-CB-77021 awarded to J.C.H.

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Epidermal Papilloma in an Ozark Hellbender (Cryptobranchus alleganiensis bishopi) from the Spring River of Northern Arkansas


Effects of Welding Electropolished Stainless Steel as Used in Ultra-Pure Fluid Delivery Systems for the Semiconductor and Pharmaceutical Industries

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Abstract

In the semiconductor and pharmaceutical industries, care is taken to prevent any contribution to product contamination or corrosion from the fluid delivery systems. Electropolished 316L stainless steel has become the industry standard due to its superior corrosion resistance. However, welding of the tubing often leads to discoloration in the heat affected zone (HAZ) which can lead to corrosion. Electropolished specimens from various lots of 316L stainless steel tubing were welded under identical parameters, but with varying concentrations of oxygen leaked into the argon purge gas during the welding, simulating on-site welding conditions. Various levels of discoloration were observed in the HAZ after welding. The chemical composition and thickness of the discoloration and an adjacent clean reference area on each specimen were analyzed by Auger Electron Spectroscopy. The cause of the discoloration was due to an iron-enriched oxide layer in the HAZ in the sensitizing temperature range. The thickness and level of discoloration depended upon the concentration of oxygen in the purge gas. The presence of this oxide layer is due to the rapid growth kinetics of FeO compared to that of Cr2O3. The composition of the original steel was found to be only a minor factor in the extent of the discoloration.

Introduction

The purity of chemicals and gases used in the semiconductor and pharmaceutical industries has been subject to heavy scrutiny to minimize contamination, corrosion, or particulate generation. Similarly, the methods of fluid distribution are also now being subjected to the same scrutiny. Due to its superior corrosion resistance and low carbon content (Cormia, 1993), electropolished 316L stainless steel has become the industry standard, especially where extensive welding is to occur. Although strict specifications have been developed (Cormia, 1993) to ensure quality for semiconductor grade tubing, concerns have been expressed by the manufacturers and vendors of tubing regarding the often observed discoloration in the heat affected zone (HAZ) near the weld joint, often referred to as the sensitizing region. Examples of weld zone discoloration on 316L stainless steel are shown in Figures 1 and 2.

Type 316L is used where extensive welding is to occur; it has lower levels of carbon (0.03% max. versus 0.08% for type 316) to reduce the tendency toward carbide precipitation at the grain boundary during welding. In this process, carbon diffuses to the grain boundary in the sensitized region forming chromium carbide precipitates (Cr23C6) which deplete the regions adjacent to grain boundaries of the necessary chromium for passivity.

In order to produce a smooth surface with a uniform chromium-enriched oxide layer that is chemically inert and corrosion resistant, the tubing is subjected to electropolishing and passivation. In electropolishing, iron is selectively removed from the surface, enriching the chromium level. Passivation follows, which oxidizes the surface with a strong oxidizer, usually nitric acid. The resulting finished surface in now smooth and free from machining marks, grooves, and pits, which may be sites for corrosion.

Welding of Type 316L stainless steel is usually performed by pulsed-arc gas tungsten-arc (GTA) welding, also known as tungsten inert-gas (TIG) welding. In the welding process, an arc discharge takes place between the tungsten electrode and the base metal, and metal fusion takes place without the use of a filler. The weld head forms an enclosed chamber that is filled with an inert gas, commonly argon, to protect the molten weld metal from air during the process. Since the welding involves the melting of the base metal itself, the chemical composition of the base metal is important. Variations in difficulty in the weldability
Effects of Welding Electropolished Stainless Steel as Used in Ultra-Pure Fluid Delivery Systems for the Semiconductor and Pharmaceutical Industries

Fig. 1. Example of Heat Affected Zone discoloration on 316L electropolished stainless steel as viewed under a fluorescent lamp.

of different lots of Type 316L have been observed (Burgardt and Heiple, 1986) resulting in deviations of the weld bead from a perfect circle (known as meander) and/or excess discoloration in the HAZ.

Susceptibility to intergranular corrosion in the HAZ of welded stainless steel has been known for a long time (Uhlig and Revie, 1985) and attributed to the formation of chromium carbide. The low carbon content steels (labeled with an L suffix) were developed to attempt to eliminate this problem. However, work on Types 304L and 316L showed pitting corrosion in the HAZ that was dependant upon the extent to which the HAZ was oxidized (Joshi and Stein, 1972), and increased corrosion in the HAZ when exposed to aggressive gases (HCl, WF₆) that was the result of varying the oxygen leak into the argon purge during welding (Henon and Jekel, 1989). More recent work (Grant et al., 1997) showed the amount of surface etching and pitting was directly proportional to the amount of heat tint present in the HAZ and that the blue ring observed in the HAZ may result from manganese that has been vaporized during welding and redeposited in the HAZ causing preferential corrosion. Other work showed that slight variations in the composition of the alloying elements in Type 316L can have an effect on the welding characteristics (Pollard, 1988) and that there existed variations in the oxide layer thickness and chromium content across the weld zone region, even for no discernable discoloration.

The objectives of this study were therefore to determine the nature of the discoloration in the HAZ and determine exactly how much the extent of discoloration depended upon the composition of the steel.

Materials and Methods

Five different heat lots of 6.35 mm diameter Type 316L stainless steel tubing were used in this study. The lots included a typical “normal” heat (labeled V20892), an Electron Beam Remelt (labeled EBR R3040), a heat lot having a higher than normal tendency to oxidize in the HAZ (labeled Trouble 1 V30110), a heat lot characterized as having severe weld bead meander (labeled Trouble 2 V30112), and a lot with a higher than normal chromium concentration (specified as 16 - 18 wt %) (labeled High Chrome 432958). The elemental bulk compositions of each
lot as given by the suppliers are shown in Table 1. The welding was performed in a high purity gas fabrication shop at Intel Corporation, Hillsboro, Oregon. A mixing panel was constructed to control accurate ratios of O₂:Ar, and ratios were checked with a Delta-F Platinum Nanotrace O₂ analyzer. A total of 73 runs was performed including runs to establish the welding parameters. After welding, each tube was classified according to the extent of oxidation in keeping with the recommendations in ASTM Standard D1729-96. Acceptability is defined and the weld considered “color free” when no ring is observed when viewed with a fluorescent lamp of know wattage or a 3 volt halogen lamp at a distance of 46 - 61 cm. A sampling plan was established after review of the experiment’s objectives with an Intel Corporation statistician (Cohen, 1995 unpub.). A total of 29 welded tubes were chosen for the analysis, covering all the different heats and purge gas levels. The sampling plan is shown in Table 2. The tubes were cleaned with deionized water and dried by blowing cryogenic argon for three minutes through each tube. For the AES analysis, the tubes were cut to approximately ½ inch in length. Each sample was cut along its axis to expose the inner diameter surface. The cutting was performed using an ultrasonically cleaned, stripped hacksaw blade of fine cut to minimize heat build up in the tubing. The AES experiments were performed on a VG Scientific Microlab 310-F equipped with a field emission source and a background pressure of 10⁻¹₀ torr. The samples were analyzed with an electron beam energy of 10 kV and sample current of 50 nA at a magnification of 10000x. The analysis area was approximately 5 μm square in size. The relative atomic concentrations for each specimen were obtained by measuring the elemental peak-to-peak heights in each spectrum and normalizing with sensitivity factors. The sensitivity factors used in the quantification were obtained from a NIST certified standard of Type 316 stainless steel (SRM 1155). The depth profiles were acquired utilizing an EX05 scanning ion gun using research grade argon ions at an energy of 3 kV, 1 μA, rastered over a 4 mm² area. The argon etch rate was calibrated against a thermally grown layer of Ta₂O₅ of 1000 Å thickness on Ta.
Table 1. Bulk elemental compositions of the 316L stainless steel lots as supplied by the vendor

<table>
<thead>
<tr>
<th>Element</th>
<th>Normal V40639</th>
<th>EBR R3040</th>
<th>Trouble 1 V30110</th>
<th>Trouble 2 V30112</th>
<th>High Cr 432958</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.020</td>
<td>0.029</td>
<td>0.018</td>
<td>0.017</td>
<td>0.015</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.001</td>
<td>0.001</td>
<td>---</td>
<td>---</td>
<td>0.033</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.002</td>
<td>0.009</td>
<td>0.004</td>
<td>0.004</td>
<td>0.003</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.590</td>
<td>0.005</td>
<td>0.400</td>
<td>0.690</td>
<td>0.530</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.027</td>
<td>0.001</td>
<td>0.024</td>
<td>0.026</td>
<td>0.022</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.009</td>
<td>0.005</td>
<td>0.010</td>
<td>0.011</td>
<td>0.007</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.010</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Manganese</td>
<td>1.310</td>
<td>0.030</td>
<td>1.510</td>
<td>1.640</td>
<td>1.600</td>
</tr>
<tr>
<td>Iron</td>
<td>67.030</td>
<td>66.838</td>
<td>66.174</td>
<td>65.166</td>
<td>63.634</td>
</tr>
<tr>
<td>Cobalt</td>
<td>0.030</td>
<td>0.030</td>
<td>0.100</td>
<td>0.150</td>
<td>0.071</td>
</tr>
<tr>
<td>Copper</td>
<td>0.032</td>
<td>0.002</td>
<td>0.280</td>
<td>0.470</td>
<td>0.200</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2.170</td>
<td>2.180</td>
<td>2.050</td>
<td>2.160</td>
<td>2.580</td>
</tr>
</tbody>
</table>

Table 2. Experimental sampling plan. The number of specimens analyzed from each heat lot is indicated.

<table>
<thead>
<tr>
<th>O₂ content</th>
<th>Pass/Fail criteria</th>
<th>Oxidation level</th>
<th>Normal V40639</th>
<th>EBR R3040</th>
<th>Trouble 1 V30110</th>
<th>Trouble 2 V30112</th>
<th>High Cr 432958</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Pass</td>
<td>None</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Pass</td>
<td>Light</td>
<td>2</td>
<td>1</td>
<td>NA</td>
<td>NA</td>
<td>2</td>
</tr>
<tr>
<td>6.3</td>
<td>Pass</td>
<td>Medium</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>31.6</td>
<td>Fail</td>
<td>Heavy</td>
<td>NA</td>
<td>NA</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

The oxide layer thicknesses, defined as the depth at which the oxygen signal falls to half-maximum, are reported as $T_{\text{ox}}$ equivalent thicknesses, as accepted by the SEMATECH protocol (SEMASPEC, 1993a). The maximum Cr:Fe ratio was determined in the oxide layer and is used as an indication of the effectiveness of the electropolishing (SEMASPEC, 1993b). Typically this value is greater than 1.5:1 and occurs at about the midpoint of the oxide thickness.

Results

The results of the AES analysis of the surface in the HAZ and reference area of each specimen are reported in Figs. 3 - 12. Each plot shows the relative atomic concentration of a particular element for the reference and HAZ areas of each specimen as a factor of O₂ exposure in the purge gas. The Cr:Fe ratios and oxide layer thickness for each specimen are reported in Figures 13 and 14, respectively.

Discussion

The levels of discoloration optically observed in the HAZ for the various levels of oxygen in the purge gas were similar for all the heat lots. However, there were significant differences detected in the results of the AES data for certain elements among the different heat lots that correlated with the bulk elemental compositions. These differences may have an effect on the long-term corrosion resistance or on the corrosion susceptibility to severely corrosive environments.

The Cr:Fe ratios in the HAZ were on average slightly higher for the high chromium concentration heat lot (432958) and the EBR heat lot (R3040) than the other heats. The relative chromium and iron concentrations in the HAZ were significantly higher in the EBR heat (R3040) for all
Fig. 3. Silicon concentration variation for different levels of O₂ in weld purge gas.

Fig. 4. Phosphorus concentration variation for different levels of O₂ in weld purge gas.

Fig. 5. Sulfur concentration variation for different levels of O₂ in weld purge gas.

Fig. 6. Carbon concentration variation for different levels of O₂ in weld purge gas.

Fig. 7. Tin concentration variation for different levels of O₂ in weld purge gas.

Fig. 8. Oxygen concentration variation for different levels of O₂ in weld purge gas.
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Fig. 9. Chromium concentration variation for different levels of O₂ in weld purge gas.

Fig. 10. Manganese concentration variation for different levels of O₂ in weld purge gas.

Fig. 11. Iron concentration variation for different levels of O₂ in weld purge gas.

Fig. 12. Nickel concentration variation for different levels of O₂ in weld purge gas.

Fig. 13. Cr: Fe ratios for different levels of O₂ in weld purge gas.

Fig. 14. Oxide layer thickness for different levels of O₂ in weld purge gas.
Table 3. Table of free energy of formation of respective oxides in 316L stainless steel.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta G^\circ \text{f} ) (kcal/mole O(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298 °K</td>
</tr>
<tr>
<td></td>
<td>873 °K</td>
</tr>
<tr>
<td>2Cr + 3/2O(_2) = Cr(_2)O(_3)</td>
<td>-249.2</td>
</tr>
<tr>
<td>Ni + 1/2O(_2) = NiO</td>
<td>-51.4</td>
</tr>
<tr>
<td>Fe + 1/2O(_2) = FeO</td>
<td>-57.6</td>
</tr>
<tr>
<td>2Fe + 3/2O(_2) = Fe(_3)O(_4)</td>
<td>-175.5</td>
</tr>
<tr>
<td>3Fe + 2O(_2) = Fe(_2)O(_3)</td>
<td>-238.5</td>
</tr>
</tbody>
</table>

Oxygen exposures. The nickel concentration was also higher in the HAZ for the high chromium heat (432958) and the EBR heat (R3040). However, significant amounts of silicon and manganese were detected in the HAZ of all the specimens except for the EBR heat (R3040). This data correlates with the bulk composition. Tin was also detected in the HAZ for each heat except for the EBR heat (R3040), although it was not detected initially in the bulk. The effects of tin and silicon on the corrosion performance of electropolished stainless steel are not known at present, but are not immediately considered a problem. However, the amounts of manganese detected were significant (up to 12 relative atomic %). Manganese has a relatively high vapor pressure compared to the other major constituents of stainless steel. AES analyses taken 1 mm apart starting from the edge of the weld zone performed on a specimen of heat lot V30110 with the highest level of discoloration showed the manganese concentration reached a maximum at a point 6 mm from the weld zone, well past the observed discoloration in the HAZ (typically 1.5 to 3.5 mm from the weld bead). Manganese was detected at a very low concentration in the base metal (0.03 wt. %) of the EBR heat (R3040) compared to the other heats (1.31 - 1.64 wt. %), but no manganese was detected for the EBR heat (R3040) in the HAZ. The data suggests that the presence of manganese by itself cannot be the cause for the oxidation in the HAZ of weldments.

Copper was prominent in the bulk analysis (0.47 wt. %) for the Trouble 2 heat (V30112), which had a bead meander problem when welded. Copper was detected in the HAZ of this heat (0.5 - 0.7 at. %). The role of copper in the mechanism of bead meander is therefore a target for further study.

A direct correlation between the amount of discoloration in the HAZ and the amount of oxygen in the purge gas was observed. All of the tested samples welded with a concentration of 1.2 ppm O\(_2\) in the purge gas showed a degree of oxidation low enough to pass the in-house QC optical inspection, but levels above that produced optically observable discoloration that was proportional to the amount of oxygen in the purge gas and resulted in thicker oxide layers.

The Cr:Fe ratios were significantly reduced in the HAZ of all the specimens and tended to decrease with increasing oxygen concentration in the purge gas. The AES data showed the chromium concentration in the HAZ was considerably less than the reference area, whereas the iron concentration was higher for all the specimens.

At the high temperatures used in the welding process, it would be expected that the chromium would preferentially oxidize to form Cr\(_2\)O\(_3\) over iron in the vicinity of the weld zone (Kubaschewski and Evans, 1958). Temperature gradient calculations showed the temperature in the vicinity of the HAZ (1.5 - 3 mm from the weld) was approximately 873 K. The standard free energies of formation (\( \Delta G^\circ \text{f} \)) of the relevant oxides (Kubaschewski and Evans, 1958) at 289 K and at 873 K are shown in Table 3. Observation of the data shows that the \( \Delta G^\circ \text{f} \) for Cr\(_2\)O\(_3\) is far more negative and therefore more thermodynamically stable than for FeO, Fe\(_2\)O\(_3\), and Fe\(_3\)O\(_4\). However, the chromium and iron are not in their standard states, but their concentrations are relatively high so that it is assumed their activities are equal to their mole fraction and the directions of the reactions hold true.

It was expected that Cr\(_2\)O\(_3\) would be formed on the surface of the stainless steel in the vicinity of the weld zone, but this was not the case observed in the HAZ in this study. Therefore the presence of an iron oxide top layer in the HAZ needs to be explained.

Recent literature (Tuthill and Avery, 1999) proposes that in the sensitized region at this temperature, chromium diffuses to the surface of the metal, leaving a chromium
Effects of Welding Electropolished Stainless Steel as Used in Ultra-Pure Fluid Delivery Systems for the Semiconductor and Pharmaceutical Industries

depleted/iron enriched layer just under the surface which is more susceptible to corrosion. Close examination of the AES depth profiles in this study do not support this hypothesis, showing in some cases the chromium concentration is depleted from the surface throughout the oxide layer.

It was suggested by Betz et al. (1974) that the presence of an iron oxide layer in this temperature range is due to the rapid growth kinetics involved with the formation of FeO, compared to that of Cr₂O₃ and the other iron oxides. The growth rate of FeO has been reported to vastly exceed that of Cr₂O₃ and Fe₂O₃ (Birchenall, 1971) and as Cr₂O₃ and Fe₂O₃ have similar crystal structures and mutual solid solubility indicates a slower growth rate for Cr₂O₃ than FeO. The iron-enriched zone in the HAZ is postulated to be caused by this rapid growth of FeO at the surface.

Conclusions

The discoloration in the HAZ commonly observed in welded electropolished stainless steel is caused by contamination by O₂ of the argon purge gas used during welding and is a function of the concentration of O₂ in the purge gas. It was determined that the nature of the discoloration was a thick iron enriched oxide layer, with the severity of the discoloration proportional to the thickness of the oxide layer. The extent of discoloration was also affected by the chemical composition of the original steel. The EBR heat showed the lowest concentration of contaminants such as sulfur and phosphorus in the bulk, although no correlation between the level of discoloration and the presence of these contaminants was observed. Significant amounts of manganese were detected in the HAZ of all the specimens, although again the level of discoloration was not dependent on the manganese concentration. No evidence of carbide precipitation at the grain boundaries for the worst discolored cases was observed, which would rule this mechanism out as being the cause for the higher susceptibility for corrosion. It is postulated that the iron rich layer in the HAZ is due to the kinetics of the formation of iron oxide over that of chromium oxide in the sensitizing temperature range found in the HAZ. Levels of 1.2 ppm O₂ and below do not appear to affect the degree of oxidation in the samples that passed the QC inspection. Electron Beam Remelting the steel, although producing a composition that did not show a higher chromium composition in the bulk, showed a HAZ with lower chromium depletion than the other heats after welding.

It is recommended that future work be performed to determine if similar results are obtained among other alloys of the Type 300 series and of different alloys.

Acknowledgments.—The authors would like to thank Mr. Ralph Cohen of Intel Corporation for supplying the tubing and performing the welding.

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Bats of the Jessieville Ranger District, Ouachita National Forest, Arkansas

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Abstract

During July and August 2000 and 2001, mist nets were set concentrated on three drainages in the Jessieville District of the Ouachita National Forest: North Fork Ouachita River (ten sites), Irons Fork Creek (five sites), and Muddy Creek (two sites). A total of 83 bats representing seven species was caught during 20 evenings (43 net nights). Sampled habitats included pools in road ruts, intermittent streams, man-made ponds on ridgelines, a wet road rut fed by a seep, small drainages that flowed only after a heavy rain, a standing pool in a clearing, and larger streams. Eastern red bats (Lasiurus borealis) were caught 64 times. Other bats caught included three evening bats (Nycticeius humeralis), eight eastern pipistrelles (Pipistrellus subflavus), two hoary bats (Lasiurus cinereus), three northern long-eared myotis (Myotis septentrionalis), one big brown bat (Eptesicus fuscus), and two Seminole bats (Lasiurus seminolus). A juvenile Seminole bat, only recently volant, represents the first documentation of likely reproduction of this bat in Arkansas.

Introduction

Occurrence and diversity of bats has been studied in several areas of Arkansas (Harvey and McDaniel, 1983; Heath et al., 1983, 1986; Steward et al., 1986; Saugey et al., 1988, 1989; Wilhide et al., 1998b; Caviness and James, 2001) but little work has been done in that part of the Ouachita Mountains north of Lake Ouachita. This study was undertaken to determine the distribution and diversity of species in that area and to check for the possible presence of the endangered Indiana bat (Myotis sodalis). Studies of the Indiana bat in hibernacula in Arkansas indicate a decline of 59% in the numbers roosting in the state over the last 20 years (Harvey, in press).

Materials and Methods

Study Site.--The general boundaries of the study site were State Highway 298 to the south, Highway 27 to the west, generally Forest Service (FS) road 11 to the north, and a gas ROW pipeline to the east (Fig. 1). Sites were located on three drainages in the district: North Fork Ouachita River (ten sample sites, sites 1-10 on Fig. 1), Irons Fork Creek (five sites, 11-15 on Fig. 1), and Muddy Creek (two sites, 16 and 17 on Fig. 1). Ten sites occurred in Garland County, two in Perry County, two in Yell County, and three in Montgomery County. Most sites were in Township1N in Ranges 21-23W.

A variety of habitats was sampled, including pools in road ruts, pools in intermittent streams, man-made ponds (upland sites), a wet road rut formed by a small seep, small ponds, and larger drainages that contained water only after a heavy rain, pools formed in depressions after a heavy rain, and larger streams.

The following list of sample sites corresponds with numbered sites shown on Fig. 1.

1) Garland Co., North Fork Ouachita River at Forest Service Road 154; SW% S1 T1N R21W, 30 July 2000. One net across the river at the road, another about 50 m upstream over a canopied pool.


4) Garland Co., man-made pond near Potato Hill Road; S4 T1N R21W, 19 and 24 July 2000. Pond intermediate in size to sites 2 and 3.

5) Garland Co., Little Creek on FS 119; S13 T1N R22W, 1 August 2001. One net on the north side of the stream, another downstream (south side of FS 119) in a canopied flyway.

6) Garland Co., Bear Creek on Forest Service road 225; S8 T1N R21W, 7 August 2001. Site dark due to overcast skies, full moon rising about 2330h. One net by the concrete low-water bridge, and one about 10 m downstream. The road was a good flyway, but the stream flyway was occluded by several trees felled during an ice storm that occurred in December 2000.

7) Garland Co., Ouachita River on access road off FS 119; S13 T1N R22W, 2 and 6 August 2001. Larger stream with open flyway located near site 6. The river was about 15
Fork Creek
Published by Arkansas Academy of Science, 2002

Yell

11. over a new crossing with some rain: made in the afternoon and an overcast sky at night on the second date.

8) Garland Co., Little Creek at FS 35720, off FS 11; S11 T1N R22W, 31 July 2001. One net along the concrete low-water bridge and another downstream in the canopied flyway.

9) Garland Co., FS J30B and J30D near their intersection; S22 T1N R22W, 30 July 2001. Upland site, two nets over road ruts that contained water from a recent rain: a small one on J30D, and one the width of the road on J30B (a depression over a culvert).

10) Garland Co., North Fork of the Ouachita River at State Highway 298; S33/34 T1N R22W, 8 August 2001. Three nets set at the bridge and downstream. Water willow (Justicia americana) common in streambed.

11) Garland Co., FS 78-2 off FS 11; and 1.3 km W of this site off FS 11; S5, 8 T1N R22W, 26 July 2001. Afternoon rains made numerous scattered pools and produced flow in intermittent streams. Net placed in a road rut/stream crossing with some canopy and flyway just onto FS 78-2 (N side of FS 11 in immediate area is a large clearcut). A second net over a new pool in a 0.4 ha clearcut on the south side of FS 11.


Pools at the bridges appeared to be the only water source for the area.

13) Yell Co., Irons Fork Creek at FS 11 and 148, 23 July 2001. One net over ruts on FS 148 near the creek and another over the creek.

14) Garland Co., Redbank Creek on FS 736; S18 T1N R22W, 24 July 2001. One net over a dirt road with wet ruts fed by a small spring, and another net across a pool at the concrete bridge. Flyway along the road narrowed at sites of water.

15) Montgomery Co., Irons Fork Creek at State Highway 298; S35/36 T1N R23W, 12 July 2001. Two nets were set, one on either side of the east bridge (two bridges occur near each other). Site revisited 17 July 2001 due to rain and lightning possibly disturbing bat activity during the first sampling: two nets, one on the north side of each bridge.

16) Montgomery Co., Muddy Creek at State Highway 27; S13 T1N R24W, 19 July 2001. One net was set west and one east of the bridge.

17) Montgomery Co., Muddy Creek at State Highway 298; S36 T1N R24W, 11 and 18 July 2001. Two nets were set over two pools on the north and south sides of the bridge. Water willow surrounded pools, good flyway available.

Standard mist nets were used to sample diversity of bats at each sample site. In addition, a night-vision scope was used to watch bats as they foraged, to observe their behavior.
Table 1. Measurements for bats captured during July and August 2000 and 2001 in the Jessieville Ranger District, Ouachita National Forest, Arkansas.

<table>
<thead>
<tr>
<th>Species</th>
<th>Sex</th>
<th>Time of Capture (CDT)</th>
<th>Weight (g)</th>
<th>Length of forearm (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>n</td>
<td>X</td>
</tr>
<tr>
<td>Lasiurus borealis</td>
<td>M</td>
<td>2039-2345 h</td>
<td>28</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2117-2355 h</td>
<td>14</td>
<td>11.2</td>
</tr>
<tr>
<td>Lasiurus cinereus</td>
<td>M</td>
<td>2130-2355 h</td>
<td>1</td>
<td>21.4</td>
</tr>
<tr>
<td>Lasiurus seminolus</td>
<td>M (ad)</td>
<td>2200 h</td>
<td>1</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>M (juv)</td>
<td>2220 h</td>
<td>1</td>
<td>7.0</td>
</tr>
<tr>
<td>Pipistrellus subflavus</td>
<td>M</td>
<td>2200-0003 h</td>
<td>3</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>2140-2210 h</td>
<td>4</td>
<td>4.6</td>
</tr>
<tr>
<td>Myotis septentrionalis</td>
<td>F</td>
<td>2230-2330 h</td>
<td>3</td>
<td>5.9</td>
</tr>
<tr>
<td>Eptesicus fuscus</td>
<td>M</td>
<td>2140 h</td>
<td>1</td>
<td>13.3</td>
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<tr>
<td>Nycticeius humeralis</td>
<td>M</td>
<td>2100-2340 h</td>
<td>2</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Results and Discussion

One objective of this study was to survey for the endangered Indiana bat (Myotis sodalis). However, only the northern long-eared myotis (Myotis septentrionalis) represented that genus during the study.

The species caught most frequently (64 individuals – 77% of total bats) was the eastern red bat (Lasiurus borealis). Other bats captured included the evening bat (Nycticeius humeralis), the eastern pipistrelle (Pipistrellus subflavus), the hoary bat (Lasiurus cinereus), the northern long-eared myotis (Myotis septentrionalis), the big brown bat (Eptesicus fuscus), and the Seminole bat (Lasiurus seminolus). The Ouachita River drainage produced individuals of all species collected. However, only eastern red, pipistrelle, and hoary bats were captured on Muddy Creek. Only an eastern red and a Seminole bat were collected from the Iron Fork drainage. Part of the reason for this difference is that more sample sites occurred in the Ouachita River drainage due to accessibility. Both sites on Muddy Creek had open flyways, but some
Further, the later were bigger, but bright, River drainage. The Ouachita River drainage included a greater diversity of sites: along the river, along smaller creeks feeding the river, and permanent upland ponds (the only locations at which the northern long-eared myotis and big brown bat were captured).

Inadvertent captures included one cottonmouth (Agkistrodon piscivorus), two green sunfish (Lepomis cyanellus), and several dobsonflies, dragonflies, and beetles (especially Scarabeidae). These were removed from the nets to reduce the chances that bats would detect the nets.

Bright moonlight and lightning may explain inactivity of bats near nets on several occasions. No bat was caught at sites 7, 9, 12, 15, and 17 when these conditions were noted. At sites 8 and 11, bats were captured on a moonlit night, but only in a shaded flyway. At site 6, bats were caught early (about 1700h) before a net became moonlit, whereas other bats were captured at the site later but only in a shaded flyway. Site 7 was revisited, and the bright moon rose about 2330h. One eastern red bat was captured before and one after the moonlighted the area (the net had been shaded by the trees). At site 5, the moon rose about 2330h and was bright, but 11 captures were made prior to that time, when the area was dark.

Female eastern red bats captured during this study averaged slightly larger than males (Table 1). Many of the subadults captured were males, apparently lowering the average size of males. Interestingly, males tended to be captured more often in early evening, and females in the later evening (Table 2).

All species combined, males were taken more often than females (49 males versus 25 females). However, only females were caught of the northern long-eared myotis. Further, the larger number of eastern red bats biased the sample, but four species (hoary, Seminole, big brown, and evening bats) were represented only by males. Because the time of sampling represents the beginning of the normal mating period, males may be more active and more likely to be captured. Males were becoming scrotal by mid-July and most males captured by late July to early August were scrotal and enlarged.

Eastern Red Bat (Lasiurus borealis).--Although considered to be a common species in Arkansas, the eastern red bat has received little research attention (Saugey et al., 1998). This species was captured in all drainages and was believed to be the species observed foraging in the early evening at all sites. Sixty-four individuals were caught at sites 1, 4-8, 10, 11, 13, 14, 16, and 17, representing almost all habitats sampled.

Researchers often are frustrated by bats flying to and over a net, apparently aware of its presence. The distress calls of several bats may offer a distraction to detection and avoidance of the net, therefore captured bats were held in a bag positioned near the net. Like Saugey et al. (1998), we observed that other bats became curious about vocalizations coming from the bag, and occasionally these bats became entangled in the net. Further, efforts to remove eastern red bats from a net attracted and resulted in capture of additional bats, apparently curious about the events at the net.

A night vision scope was used to observe the behavior of bats during sampling periods. Well after dark at site 10, two eastern red bats were observed foraging just under the bridge for Hwy 298. They flew between the bridge supports and occasionally flew out over the grassy roadside to forage, but when approaching the net set in the area, they flew over it.

In late July, the night vision scope provided interesting observations of a swarm of eastern red bats at Site 1 on the Ouachita River. By dusk, eastern red bats (identified when they briefly came down to drink) could be seen above clearings. With early nightfall, there was no activity near the nets but, with the aid of the night vision scope, many L. borealis were seen flying just under the canopy. With increasing darkness, these bats gradually descended until some were captured. Groups of 2-3 consistently were seen flying together along the creek bed, and occasionally these hit the nets as a group. Often, these were young bats of the same age (based on similar epiphyseal closure of finger bones, and forearm measurements). This could mean that siblings born this season still were flying together at the time of capture.

Similar "cluster catches" were comprised of an adult female and one or two scrotal males, all of different forearm lengths. Perhaps this represented the beginning of mating, which occurs in August and September (Sealander and Heidt, 1990). Saugey et al. (1989) made a similar
observation regarding eastern red bats, as well as evening bats (Saugey et al., 1988).

Mating aggregations of large numbers of bats have been called "swarms" and some researchers have caught from dozens to >100 *L. borealis* during swarming (Cassidy et al., 1978; Saugey et al., 1998). More eastern red bats may be caught at such times simply because they locally are more numerous. Observations with the night vision scope revealed additional explanations for more numerous captures: (1) interests of the bats are focused more on mating than detection of minor irregularities (nets) in the environment, and (2) the background ultrasonic noise may make it more difficult to echolocate nets in the environment.

**Evening Bat (Nycticeius humeralis).**--The evening bat was taken in the Ouachita drainage (3 individuals) at Sites 2 and 10. These sites represent an upland man-made pond and a larger stream. One individual escaped the holding bag prior to collection of data, but the other two were males.

**Eastern Pipistrelle (Pipistrellus subflavus).**--The eastern pipistrelle was caught in the Ouachita River and Muddy Creek drainages (8 individuals) at sites 10, 16, and 17. The smaller specimens (Table 1) were juvenile females that had not yet replaced the grayish juvenile pelage with the buffy adult coloration.

**Hoary Bat (Lasiurus cinereus).**--The hoary bat was caught in the Ouachita River and Muddy Creek drainages at sites 3 and 16. Site 3 was a man-made pond and an upland site, but site 16 was a larger creek. The individual from site 3 was caught at 2130h, and the other specimen was taken at 2355h. Sometimes considered to be a late flyer, this bat often is taken prior to 2400h (Caire et al., 1986; Saugey et al., 1989).

**Northern Long-eared Myotis (Myotis septentrionalis).**--The northern long-eared myotis was taken in the Ouachita River drainage (three individuals), at sites 2 and 3. These sites were man-made ponds at higher elevations along ridge lines. This species was believed to be rare in Arkansas (Harvey and McDaniel, 1983) until Wilhide et al. (1998b) found them to be common in their study of ridgetop ponds in the Ozarks. All three specimens caught in the present study were females (Table 1).

Wilhide et al. (1998b) noted that <2% of 770 banded bats were recaptured on subsequent nights. It is not known whether a bat, once captured and escaped, will be recaptured in the same net the same night. On 24 July 2000 at Site 3, capture of a northern long-eared myotis may support this possibility. An undamaged mist net had been set up (bats sometimes are able to chew their way free if left in a net long enough). At 2130h, a northern long-eared myotis was removed from the highest section of the net, but it was unexplainably soaking wet. Perhaps the bat had crashed into the water at another time, regained flight, then experienced the net for the first time while wet. However, there was a new hole at the bottom of the net near the water. It was deemed probable that an earlier capture of the bat at that spot caused the net to sag into the water, wetting the bat. The bat then chewed out and flew away, only to return and be caught in an upper bag of the net.

**Big Brown Bat (Eptesicus fuscus).**--The big brown was caught in the Ouachita River drainage at Site 4, which was a man-made pond. Although not captured in the mist nets, several big brown bats were observed roosting in the bridge at Site 10 over the Ouachita River at State Highway 298.

**Seminole Bat (Lasiusus seminolus).**--In Arkansas, the Seminole bat was known primarily from southern counties until Wilhide et al. (1998a) extended the range northward by documenting specimens from Baxter and Franklin counties. Specimens collected from other counties (Heath et al., 1983; Heath et al., 1986; Saugey et al., 1989) all were adults. The species is presumed to be migratory due to its seasonal distribution and the presence of individuals north of the range of Spanish moss (*Tillandsia usneoides*), the purported preferred roost for the species (Barbour and Davis, 1969). Menzel et al. (2000), however, found that Seminole bats in South Carolina roosted during the summer on small branches of pines away from Spanish moss. Thus, it is not clear whether the few specimens previously collected from Arkansas represent individuals that have moved north of their breeding range.

Seminole bats were captured in the Ouachita and Iron Fork River drainages at Sites 1 and 11. A juvenile specimen collected 26 July 2001 from a small tributary to Rock Creek in the Iron Fork drainage (Site 11, Table 1), had recently become volant, and therefore represents the first inference of reproduction of this bat in Arkansas. Similarly, Barkalow and Funderburg (1960) suggested probable breeding in North Carolina based on finding immature Seminole bats. The Arkansas site was an intermittent stream with small canopy flyway adjacent to a large clearcut area.

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**Literature Cited**


Distributions and Geographical Relationships of the Polygyrid Land Snails (Mollusca, Gastropoda, Polygyridae) of Arkansas

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Abstract

The Arkansas distributions of land mollusks of the family Polygyridae are presented based on the results of a state-wide survey and a critical review of published and unpublished locality records. Six of the 45 species previously recorded for Arkansas are excluded because they were misidentified, do not have established populations in the state, or are found only as fossils. Four others are not mapped because of a lack of recent distributional data or because the specific status of a form is unclear. There is a predominant pattern of occurrence limited to the northern, northwestern, or western parts of the state. The northwest has rock outcrops, including the limestone and dolomite outcrops of the Ozark Mountains, extensive broadleaf woodland cover, and has suffered less disturbance from agriculture than the southeast, which results in more suitable land mollusk habitats in the northwest. Secondary patterns are apparent for species that are of widespread or sporadic distribution throughout the state, or found only in the eastern part of the state. Compared to adjoining states, Arkansas has a high diversity of polygyrid snails, exceeded only by Tennessee (59 species) and Texas (40 species). The highest number of co-occurrences is between Arkansas and Missouri (94.1%) and Arkansas and Oklahoma (92.3%). Arkansas shares 36.9% of species with states that border the eastern side of the Mississippi River and 63.1% with states that border the western side of the river. These data illustrate the dominance of the Ozark/Boston Mountains fauna on Arkansas land snail distribution plus what could be regarded as a secondary mid-western element.

Introduction

Gastropod land mollusks of the family Polygyridae form a conspicuous, diverse, and in some cases abundant, component of woodland invertebrate land faunas, with many species of highly restricted distribution. There are approximately 160 species of polygyrids in the eastern United States (Hubricht, 1985); they are classified into two subfamilies and represent approximately 30% of the eastern United States land mollusks. The evolutionary significance, conservation priorities, and several aspects of polygyrid biology have been discussed by Emberton (1988, 1991, 1995).

Forty-five of the 144 terrestrial mollusks reported for Arkansas (Coles and Walsh, 1999) are in the family Polygyridae. An earlier report listed 35 polygyrid species of a total of 107 (Gordon, 1980). Both reports indicate that, as in the eastern United States as a whole, polygyrids represent approximately 30% of the Arkansas snail fauna, including species endemic to the state or of highly restricted distribution (Pilsbry, 1940; Hubricht, 1985; Robison and Smith, 1982; Coles and Walsh, 1995). We have further reviewed published distribution reports on the family Polygyridae and present new distribution records by county based on them, museum specimens, and our state-wide survey.

Materials and Methods

Species identifications were made from descriptions given by Baker (1939), Pilsbry (1940), Hubricht (1961), Cheatum and Fullington (1971), Leonard (1959), and Emberton (1988, 1991, 1995), and by reference to collections in the Field Museum of Natural History, Chicago, and the Academy of Natural Sciences of Philadelphia, Philadelphia. The taxonomic revisions of Emberton (1995) and revised names given by Turgeon et al. (1998) are incorporated in the list of Arkansas species.

Distributional maps of species in Arkansas were compiled at the county level. The following sources were used: collections made by the authors at over 400 sites, the unpublished collection of David Causey in the University Museum, University of Arkansas, Fayetteville; and distributions given by Pilsbry (1940), Hubricht (1985), and Emberton (1988, 1991). Thus, all counties of Arkansas have been included in map preparation, and all major habitat types (Coles and Walsh, 1999) have been sampled. Voucher material in the authors' collections will be deposited in the University Museum, University of Arkansas at Fayetteville, and the Field Museum of Natural History, Chicago.

The number of species in the Ozark Plateau (including the Boston Mountains, Ouachita Mountains, West Gulf Coastal Plain, and Mississippi River Alluvial Plain (including Crowley's Ridge and Grand Prairie) was determined in order
Distributions and Geographical Relationships of the Polygyrid Land Snails (Mollusca, Gastropoda, Polygyridae) of Arkansas

Fig. 1. Distributions of polygyrid species in Arkansas, Subfamily Polygyrinae. A. Daedalochila leporina (Gould, 1848), B. Linisa texasiana (Moricand, 1833), C. Millerelix dorfiulliana (I. Lea, 1838), D. Millerelix jacksoni (Bland, 1866), E. Millerelix deltoidea (Simpson, 1899), F. Millerelix simponi (Pilsbry and Ferriss, 1907), G. Millerelix peregrina (Rehder, 1932), H. Millerelix sp. nov., I. Mesodon elevatus (Say, 1821), J. Mesodon zaletus (A. Binney, 1837), K. Mesodon clausus (Say, 1821), L. Mesodon thyroidus (Say, 1816), M. Patera binneyana (Pilsbry, 1899), N. Patera denticulata (Rehder, 1932), O. Patera indianorum (Pilsbry, 1899), P. Patera kiowaensis (Simpson, 1888), Q. Patera perigrapta (Pilsbry, 1894), R. Inflectarius inflectus (Say, 1821), S. Inflectarius dentatus (Sampson, 1889), T. Inflectarius magniflum (Pilsbry and Ferriss, 1907), U. Stenotrema pilsbryi (Ferriss, 1900), V. Stenotrema labrosum (Bland, 1862), W. Stenotrema stenotrema (Pfeiffer, 1842), X. Stenotrema uncirosum (Pilsbry, 1900), Y. Stenotrema blandianum (Pilsbry, 1903), Z. Euchemotrema fraternal imperforatum (Pilsbry, 1900), ZZ. Euchemotrema leai aliciae (Pilsbry, 1893).

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Fig. 2. Distributions of polygyrid species in Arkansas, Subfamily Triodopsinae. A. Triodopsis cragini Call, 1886, B. Triodopsis hopetoniensis (Shuttleworth, 1852), C. Triodopsis neglecta (Pilsbry, 1899), D. Neohelix divesta (Gould, 1848), E. Neohelix alleni alleni (Sampson, 1883), F. Neohelix albolaris bogani Emberton, 1988, G. Webhelix multilineata (Say, 1821), H. Xolotrema fosteri (F.C. Baker, 1932), I. Xolotrema carolinense (I. Lea, 1834), J. Xolotrema occidentale (Pilsbry and Ferriss, 1907), K. Xolotrema denotatum (Férussac, 1821)

to evaluate patterns of distribution.

The numbers and distributions of polygyrid mollusks in states that border the Mississippi River and those adjacent to Arkansas, and the numbers common to Arkansas and these states were taken from Pilsbry (1940), Leonard (1959), Cheatum and Fullington (1971), Hubricht (1985), Emberton (1988, 1991), and the authors’ collections. The number of species/km² was calculated for each state as an estimate of the area available for polygyrid habitat.

Results

Revised list of Arkansas Polygyridae.——The family Polygyridae is represented in Arkansas by two subfamilies, 13 genera, and 39 species (Figs. 1 and 2). We listed 15 genera and 45 species of polygyrids from Arkansas in our earlier review of the literature (Coles and Walsh, 1999). Six of the species given in that report are deleted from the list for the following reasons and are omitted from the analysis that follows.

1. Triodopsis vultuosa (Gould, 1848) was reported from Benton, Washington, Crawford, Sebastian, and Nevada counties by Sampson (1894). At that time, Triodopsis cragini was treated as a form of T. vultuosa and it is possible that Sampson did not distinguish between the two species (Pilsbry, 1940).

2. Stenotrema caddoense (Archer, 1935) was first described as Polygyra (Stenotrema) caddoense by Archer (1935). Pilsbry (1940) reported it as Stenotrema unctiferum caddoense from Caddo Gap, Montgomery County. Archer (1948) continued
to recognize it as a separate species. However, Hubricht (1972) found its shell morphology to be within the natural variation of *S. uncinatum*, a fact mentioned by Pilsby (1940), and placed it under *S. uncinatum*. This view is supported by our examination of specimens from Arkansas.

3. *Linisa triodontoides* (Bland, 1861) was reported from Washington and Sebastian counties by Sampson (1893). Hubricht (1985) pointed out that *L. triodontoides* may be confused with *Linisa texastia* and that *L. triodontoides* is found only south of Arkansas in Texas, Louisiana, and Mississippi. Based on size and apertural dentition, all populations of *Linisa* that we have examined from Arkansas are *L. texastia*.

4. *Patella roemerii* (Pfeiffer, 1848) was reported from Arkansas by Gordon (1980). We have been unable to find other reports of this species in Arkansas and have not found it in our collections. Pilsby (1940), Hubricht (1985), and Cheatum and Fultong (1971) listed it only from central Texas and one county in southern Oklahoma.

5. *Pristolella berlandieriana* (Moricand, 1833) was reported from "Washita Springs", Arkansas, by A. Binney in 1851 (Pilsby, 1940). A shell of this species is in the Cousey collection at the University Museum, University of Arkansas, Fayetteville (Catalog Number 95-1-2000), but the collection site is not given in the notes of Dr. Causey. We have been unable to find "Washita Springs" in Arkansas on maps as early as 1840. The town of Washita is in Montgomery County near Lake Ouachita. An extensive search in the Washita/Lake Ouachita area failed to produce this species, which we believe to be adventive in Arkansas. The nearest documented distribution is in southern Texas (Hubricht, 1985).

6. *Allogona profunda* (Say, 1821) was reported by Hubricht (1983) as a fossil from Phillips County. This is an eastern and mid-western species (Hubricht, 1985), with fossils distributed along the Mississippi River from Illinois to Louisiana. We have not found living specimens in Arkansas.

**Species of Uncertain Taxonomic Status.**—The taxonomic status of two species of *Millerelix* in Arkansas requires confirmation.

1. *Millerelix lithica* Hubricht, 1961 was described from Stone County by Hubricht (1961) as being similar to *Millerelix dorfeuilliana* but distinguishable on the basis of apertural dentition, notably the shape of the parietal lamella. Our searches in the region of the type locality have failed to find populations of *Millerelix* that consistently conform to Hubricht's description of *M. lithica*. Branson (1970) showed that *Dorfeuilliana* is a highly variable species. We have stated previously (Coles and Walsh, 1999) that the shell characteristics of *M. lithica* fall within the variability of *Dorfeuilliana*. However, Emberton (1995) retained *M. lithica* as a valid species without comment. We retain *M. lithica* as a valid species because we regard it as an unwise to equate it with *Dorfeuilliana* in the absence of critical morphological and anatomical data. Therefore, the distribution of *Dorfeuilliana* (Fig. 1C) should be regarded as that of a potential aggregate of the two forms.

2. *Millerelix sp. nov.* was reported as an undescribed new species by Coles and Walsh (1999). A detailed description of this form has been prepared (Malacological Bull., in review).

**Geographical Distribution of Polygyrids in Arkansas.**—The distributions of Arkansas polygyrids by county are given in Figs. 1 and 2. Inspection of the maps suggests that many species are restricted to the northwestern part of the state (e.g., *Stenotrema labrosum*, Fig. 1IV). A few species exhibit restriction to western (e.g., *Triodopsis cragini*, Fig. 2A), northern (e.g., *Mesodon elevatus*, Fig. 2I), and eastern (e.g., *Xolotrema denotatum*, Fig. 2K) Arkansas or are cosmopolitan (e.g., *Mesodon denotatum*, Fig. 1L and *Inflectarius inflectus*, Fig. 1R). On a sectional basis, the greatest number of species occurred in the north and west. Species diversity, as number of species/km², also followed this pattern (Table 1).

**Comparison with Other States.**—The number of polygyrid species in Arkansas is compared with those reported from surrounding states in Table 2. Only

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**Table 1.** Species number and species density of polygyrids in four physiographic areas of Arkansas.

<table>
<thead>
<tr>
<th>County</th>
<th>Area</th>
<th>No. of Species</th>
<th>Species/km²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozark Plateau</td>
<td>21</td>
<td>37,143</td>
<td>29</td>
</tr>
<tr>
<td>Ouachita Mts.</td>
<td>18</td>
<td>33,937</td>
<td>30</td>
</tr>
<tr>
<td>West Gulf Coastal Plain</td>
<td>16</td>
<td>28,620</td>
<td>16</td>
</tr>
<tr>
<td>Mississippi River Alluvial Plain</td>
<td>20</td>
<td>35,569</td>
<td>14</td>
</tr>
</tbody>
</table>

---

*Journal of the Arkansas Academy of Science, Vol. 56, 2002*
Table 2. Number of polygyrid species in Arkansas and surrounding states, with the percentage of polygyrid species they have in common with Arkansas.

<table>
<thead>
<tr>
<th>State</th>
<th>Number of Polygyrid Species</th>
<th>% of Polygyrid Species in Common With Arkansas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tennessee</td>
<td>59</td>
<td>20.3</td>
</tr>
<tr>
<td>Arkansas</td>
<td>39</td>
<td>-</td>
</tr>
<tr>
<td>Texas</td>
<td>40</td>
<td>17.5</td>
</tr>
<tr>
<td>Mississippi</td>
<td>27</td>
<td>48.1</td>
</tr>
<tr>
<td>Oklahoma</td>
<td>26</td>
<td>92.3</td>
</tr>
<tr>
<td>Missouri</td>
<td>17</td>
<td>94.1</td>
</tr>
<tr>
<td>Louisiana</td>
<td>16</td>
<td>75.0</td>
</tr>
<tr>
<td>Kansas</td>
<td>15</td>
<td>80.0</td>
</tr>
</tbody>
</table>

Table 3. Number of Polygyrid species, percentage in common with Arkansas, and species density in states north to south along the Mississippi River.

<table>
<thead>
<tr>
<th></th>
<th>No. of Polygyrid Species</th>
<th>% of Species in Common With Arkansas</th>
<th>No. of Species/ km² (\times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>East of the Mississippi River</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wisconsin</td>
<td>8</td>
<td>37.5</td>
<td>0.55</td>
</tr>
<tr>
<td>Illinois</td>
<td>11</td>
<td>47.6</td>
<td>1.43</td>
</tr>
<tr>
<td>Kentucky</td>
<td>39</td>
<td>30.8</td>
<td>3.73</td>
</tr>
<tr>
<td>Tennessee</td>
<td>59</td>
<td>20.3</td>
<td>5.40</td>
</tr>
<tr>
<td>Mississippi</td>
<td>27</td>
<td>48.1</td>
<td>2.19</td>
</tr>
<tr>
<td>(\bar{x} = 28.8)</td>
<td></td>
<td>(\bar{x} = 36.9)</td>
<td>(\bar{x} = 2.66)</td>
</tr>
<tr>
<td>West of the Mississippi River</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minnesota</td>
<td>7</td>
<td>28.6</td>
<td>0.32</td>
</tr>
<tr>
<td>Iowa</td>
<td>11</td>
<td>54.5</td>
<td>0.75</td>
</tr>
<tr>
<td>Missouri</td>
<td>17</td>
<td>94.1</td>
<td>0.66</td>
</tr>
<tr>
<td>Arkansas</td>
<td>39</td>
<td>-</td>
<td>2.83</td>
</tr>
<tr>
<td>Louisiana</td>
<td>16</td>
<td>75.0</td>
<td>1.27</td>
</tr>
<tr>
<td>(\bar{x} = 18.0)</td>
<td></td>
<td>(\bar{x} = 63.1)</td>
<td>(\bar{x} = 1.17)</td>
</tr>
</tbody>
</table>

Tennessee, with 59 species, and Texas, with 40 species, have more polygyrid species than Arkansas. Tennessee and Mississippi have the fewest number of species in common with Arkansas. West of the Mississippi River, Texas shares only 17.5% of its species with Arkansas. Several aspects of these comparisons are misleading. Most of the 40 polygyrid species of Texas occur in the southern part of the state (Cheatum and Fullington, 1971). The seven species that occur in the northern part of Texas, *Linisa texasiana*, *Daedalochila lepirona*, *Millerelix dorfeuilliana*, *Mesodon throroidus*, *Triodopsis cragini*, *Neohelix divesta*, and *Euchemotrema leai aliciae*, also occur in Arkansas. However, Cheatum and Fullington (1971) reported few species from western Texas and its panhandle, so these data will have to be re-evaluated.
when further collections are made.

Similarly, the numbers for Tennessee and Kentucky include polygyrids that are present in the distinct molluscan faunas of the southern Appalachian and Cumberland Mountains. The western third of Tennessee has only 20 reported polygyrid species and shares 50% of them with Arkansas. The western third of Kentucky has 15 reported species and shares 66.7% of them with Arkansas. When so adjusted, Tennessee, Kentucky, Mississippi, and Louisiana share similar numbers with Arkansas.

Table 3 shows the numbers of polygyrid species, percentage of species held in common with Arkansas, and the number of species per state normalized for state area for states immediately to the west and east of the Mississippi River. This analysis shows that Arkansas has high diversity (third in abundance of species/km²) and highest diversity for states bordering the west side of the Mississippi River. There are also greater numbers of species and greater species density in states east of the Mississippi River, while those west of the river have a greater percentage of species in common with Arkansas.

**Endemic species.**--Several species appear to be endemic to Arkansas in the Ozark and Boston Mountains:

1. *Millerelix peregrina* (Rehder, 1932) was reported by Robison and Smith (1982) from Izard, Marion, Newton, Searcy and Stone counties. We found it in Carroll County.

2. *Millerelix sp. nov.* (Coles and Walsh, in review) has been found in Madison, Newton, and Searcy counties. This species has been identified as *Millerelix peregrina* by earlier workers. We found specimens in the Causey collection at the University of Arkansas Museum and the Hubricht collection at the Field Museum of Natural History.

3. *Patera crenchi* (Rehder, 1932) was reported by Robison and Smith (1982) from Izard and Yell Counties. We found it in Searcy and Scott counties.

4. *Xolotrema occidentale* (Pilsbry and Ferriss, 1907) was not listed by Robison and Smith (1982). We found it in Stone and Independence counties.

5. *Inflectarius magazinensis* (Pilsbry and Ferriss, 1907), listed by Robison and Smith (1982), continues to be found only on Mt. Magazine in Logan County. It was listed as a threatened species by the U.S. Fish and Wildlife Service (1989) with a recovery plan published in 1994.

**Species of limited distribution.**--The following species are of limited distribution in Arkansas:

1. *Millerelix deltoidea* was reported from Polk County and eastern Oklahoma by Hubricht (1985).

2. *Millerelix simpsoni* was reported from Polk County and eastern Oklahoma by Hubricht (1985).

3. *Stenotrema pilsbryi* (Ferriss, 1900) was reported from Polk County and eastern Oklahoma by Hubricht (1985).

4. *Webbelix multilaterrita* (Say, 1821) was found in Newton and Phillips counties by the authors. It was reported as a fossil from Crittendon County by Hubricht (1985). The species is common in the northern Midwest.

5. *Xolotrema carolinense* (I. Lea, 1834) is an eastern species reported by Hubricht (1985) for Clark and Ouachita counties. We have not found it in Arkansas.

![Fig. 3. Physiographic regions of Arkansas with number of polygyrid species in each: 1. Ozark Plateau (29 species); 2. Ouachita Mountains (30 species); 3. West Gulf Coastal Plain (16 species); 4. Mississippi River Alluvial Plain (14 species).](image)

**Discussion**

The results detailed above indicate several facts concerning distribution of Arkansas polygyrid land mollusks: 1. Arkansas hosts a diverse polygyrid fauna; 2. the greatest number of species occurs in the Ozark and Boston Mountains. Fewest numbers occur in the West Gulf Coastal Plain and the Mississippi River Coastal Plain (Fig. 3); and 3. there is a tendency for Arkansas to show more similarity in polygyrid assemblage to states immediately west of the Mississippi River, than to those immediately east of the river. These observations support our assertion, made on the basis of the entire Arkansas land snail fauna (Coles and Walsh, 1999), that the diversity of Arkansas land snails is due to intrinsic diversity of species in the Ozark and Boston Mountains in the northwestern part of the state.

General aspects of this predominantly north-westerly distribution should be examined in more detail. The northwestern and southeastern halves of the state coincide with the boundary of the Mesozoic/Cenozoic rocks and the consequent differences in land use and natural vegetation communities. Thus, the north-west has rock outcrops,
including the limestone and dolomite outcrops of the Ozark Mountains, extensive broadleaf woodland cover, and has suffered less disturbance from agriculture than the southeast, resulting in more suitable land mollusk habitats occurring in the north-west of the state. For example, the distribution of *Stenotrema labrosum* (Fig. 1V) shows the most significant northwestern distribution of Arkansas polygyrids. Our collecting experience suggests that this species is restricted to the north-west because it requires woodland sites with boulder outcrops, including rock piles of woodland and upland stream valleys. Such habitats are absent from the east, south-east, and extreme south-west of the state. Conversely, *Inflectarius inflectus* (Fig. 1R) occurs throughout the state and much of the southeastern United States (Hubricht, 1985) and in many woodland sites. The pattern of predominant north-western distribution is, thus, better regarded as the result of intrinsic geographical localization enforced by geology, vegetation, and land use.

Similarly, the easterly distribution of *Xolotrema fosteri* also appears to be due to availability of suitable riparian woodland in the east of the state, although a population of this species was found under rubbish in the back yard of a home in West Fork in western Washington County. The national distribution of this species (Hubricht, 1985) shows a pattern consistent with riparian distribution in the south. Other factors that have to be considered when judging the validity of these analyses are that collecting efforts have varied from state to state and that published records are incomplete for Minnesota, Wisconsin, Iowa, and western Tennessee (Hubricht, 1985).

Distribution by humans can also confound biogeographical data. The distribution of *Triodopsis hopetomensis* (Fig. 2B) appears to be a case in point. This species of the southeastern United States was not recorded in Texas by Cheatum and Fullington (1971) or for Arkansas by Hubricht (1985). We have found it to be a common urban snail in eastern Texas and several localities in Arkansas, likely as a result of human transport.

The observation that Arkansas shares more species of polygyrid mollusks with states immediately to the west of the Mississippi River than with those immediately to the east of the river gives some support to the hypothesis that there is what should be regarded as a "mid-western" assemblage of land snails. This pattern of distribution has been identified for *Vertigo meramecensis* and *Gastrocopta rogersensis* (Gastrocopta, Pupillidae) that have disjunct distributions in northwestern Arkansas, Missouri, western Illinois, eastern Iowa, and southeastern Wisconsin (Nekola and Coles, 2001). The United States distributions of *Neoheleis alleni* and *Millerelix dorfeuilliana* (Hubricht, 1985) suggest a similar pattern.

Whatever the causes of land snail distribution in Arkansas, sites in northwestern Arkansas that have high land snail diversity should be regarded as being of high conservation priority.

**Acknowledgments.**—We are grateful to the staff of the Arkansas Game and Fish Commission, the Ozark Saint Francis and Ouachita National Forests, the Nature Conservancy of Arkansas, and private land owners who have given permission to collect snails on their lands. In particular, we wish to acknowledge the assistance of G.O. Graening of the Nature Conservancy, Fayetteville, Gregg Butts of the Arkansas State Parks, Douglas Zoller of the Arkansas Field Office of the Nature Conservancy, Cindy Osborne of the Arkansas Natural Heritage Commission, George Oviatt of the Buffalo National River, and Nancy McCartney of the University Museum, University of Arkansas, Fayetteville.

**Literature Cited**


Gordon, M. E. 1980. Recent mollusks of Arkansas with
Distributions and Geographical Relationships of the Polygyrid Land Snails (Mollusca, Gastropoda, Polygyridae) of Arkansas


Beetle Diversity in an Eastern Cottonwood (Populus deltoides Bartr.) Plantation and Adjacent Bottomland Hardwood Forest in Southeastern Arkansas

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Abstract

Within the Lower Mississippi Alluvial Valley (LMAV), some lands cleared of bottomland hardwood forests have the potential to return to forest as a result of private sector and government interests in Populus cultivation. Specifically, monoculture plantings of eastern cottonwood (Populus deltoides Bartr.) represent an important component of many recent afforestation efforts in the region. The impact establishment of such monocultures will have on native insect communities in the LMAV is relatively unknown. To evaluate this, beetle (Coleoptera) diversity, abundance, and functional distribution were examined within an intensively managed eastern cottonwood plantation and nearby bottomland hardwood forest in southeastern Arkansas. Beetles were sampled in both settings over the summer of 2000 using Malaise traps. When compared to the heterogeneous bottomland hardwood forest, the beetle morphospecies assemblage collected from the plantation was one characterized by lower species diversity and a depauparate xylophagous and fungivorous beetle fauna. Over half of all beetles trapped in the eastern cottonwood plantation were species considered to be economic pests of Populus.

Introduction

The Lower Mississippi Alluvial Valley (LMAV) has undergone widespread deforestation as a result of clearing for agriculture, resulting in a loss of approximately 75% of the original forested wetlands that once occurred across this region (Stanturf et al., 2000). As a result of agricultural conversion, lands once covered by bottomland hardwood forests are now used to produce such crops as cotton and soybeans. However, some of this land has the potential to return to forest through developing private sector interest in the production of alternative timber/wood fiber resources and federal incentive programs (Wetlands Reserve Program) to restore bottomland hardwood forests (Stanturf and Portwood, 1999; Stanturf et al., 2000). Although seemingly divergent, both ventures share an intertwined interest in the cultivation of eastern cottonwood (Populus deltoides Bartr.).

Recently, economic interest has developed in the southern U.S. for fast growing tree species, such as eastern cottonwood, that can be intensively managed in monoculture settings (plantations, fiber farms) to produce a short rotation woody crop (Stanturf et al., 1998). Eastern cottonwood is the fastest growing commercial forest tree native to North America, with average rotations of only six to 12 years, and is well suited for use as a harvestable resource on former cropland in the LMAV (Stanturf and Portwood, 1999). Uses of eastern cottonwood range from fiber (pulp and paper), biomass energy, to carbon sequestration. Currently, several timber companies have established short rotation woody crop programs and pilot projects in areas across the south.

Plantings of eastern cottonwood have also been recognized as potentially effective tools in the afforestation of bottomland hardwood forests on marginal agricultural land (Stanturf et al., 2000). Traditional bottomland hardwood forest restoration has relied upon single species plantings of heavy-seeded oak based on the idea that light-seeded tree species would later colonize the plantation, enhance diversity, and provide suitable habitat for wildlife (King and Keeland, 1999). Research indicates that development of forest structure under such a system takes a long time (Twedt et al., 1999); colonization by other plant species is often unreliable (Allen, 1997); and opportunities to manipulate the developing stand are limited (Stanturf et al., 2000). In contrast, fast growing plantations of eastern cottonwood, interplanted with oak seedlings, have been shown to provide the forest structure required by some species much more rapidly than oak plantings alone (Twedt and Portwood, 1997).

Establishment of eastern cottonwood plantations on former agricultural lands does have the potential to provide habitat for a range of plant and animal species. Although plantations may provide more favorable habitat conditions for some species than cropland, studies have indicated that
eastern cottonwood plantations represent lower quality habitat when compared to natural bottomland hardwood forests (Christian et al., 1998; Twedt et al., 1999). As eastern cottonwood plantations may become a more common component of the LMAV landscape, studies need to be conducted to determine what other taxa might utilize these “new forests.”

Terrestrial insects represent a fundamental, but understudied, component of the LMAV ecosystem. Insects are tied to a diverse array of microhabitats, are known to play a number of important roles (pollination, nutrient cycling) in forest systems (Janzen, 1987; Packham et al., 1992), and represent a vital food base for other organisms (Greenberg and McGrane, 1996). Excluding a few pest species, little research has been conducted regarding how land use and management affect terrestrial insect species diversity and abundance in the LMAV.

Although additional research concerning insects is needed within this region, there are obstacles to this kind of work. One such obstacle is the often overwhelming diversity of insect species that can be collected, making timely, cost effective processing and identification difficult (Disney, 1986). As an alternative to sampling all insect species, assemblages of select species representing different ecological or functional roles have been suggested for use as monitoring tools or indicators of habitat change (Kremen et al., 1993). Beetles (Coleoptera), in particular, are considered well suited for such uses as they display a wide range of functional roles (herbivores, predators, fungivores), are easily sampled through a variety of trapping methods, and good taxonomic information exists for many families (Hutcheson and Jones, 1999). In that light, the objective of this study was to compare the species diversity, abundance, and functional composition of beetles inhabiting an intensively managed eastern cottonwood plantation and adjacent bottomland hardwood forest in southeastern Arkansas.

**Materials and Methods**

**Study Site.**—This study was conducted from April to October 2000 on Choctaw Island, just west of Arkansas City, Arkansas (Desha County), along the flood-prone bateau lands of the LMAV. A large, intensively managed eastern cottonwood plantation and nearby secondary bottomland hardwood forest on the island served as study sites. The plantation was established early in 1998 (February) on land previously used to produce soybeans. Eastern cottonwood cuttings, planted in rows on 3.6 x 3.6 meter spacing, were used to establish the plantation. During the summers of 1998 and 1999, workers disced and mowed between rows of trees to reduce the shading effects of competing vegetation. The plantation also received infrequent aerial applications of insecticide in an effort to control populations of the cottonwood leaf beetle (Chrysomela scripta F.), a major economic pest of Populus (Morris et al., 1975).

During the winter of 1999, the plantation was interplanted with oak seedlings in conjunction with a National Resources Conservation Service pilot project examining the feasibility of incorporating eastern cottonwood into bottomland hardwood afforestation efforts. Oak seedlings were planted along every other row of the plantation. Discing and mowing were discontinued in 2000.

At the time the study was conducted, the plantation was in its third growing season and contained trees ranging in height from 4 to 6 m. Other than eastern cottonwood and oak seedlings, vegetation within the plantation consisted mainly of trumpet creeper (Campsis radicans (L.) Seemen), passionflower (Passiflora incarnata L.) vines, and Johnson grass (Sorghum halepense (L.) Pers.). A mature bottomland hardwood forest, dominated by willow oak (Quercus phellos L.), cherrybark oak (Q. falcata Michaux), American sweetgum (Liquidambar styraciflua L.), sugarberry (Celtis laevigata Willd.), and red maple (Acer rubrum L.), adjacent to the plantation was also sampled.

**Insect Sampling and Analyses.**—Beetle sampling was conducted using Malaise traps. Malaise traps are tent-like structures that passively trap insects and funnel them up into a collecting head filled with a killing agent (Townes, 1972). Samples of Malaise trapped beetles have been shown to be characteristic of recognizable communities and strongly related to habitat variables up to 50 m from traps (Hutcheson, 1990; Hutcheson and Jones, 1999). Two Malaise traps, spaced 100 m apart, were placed in the plantation and forest. Malaise traps were placed at least 50 m into each site. Collecting containers were filled with 75% ethanol mixed with a small amount of ethylene glycol to reduce evaporation of the ethanol. All traps were operated continuously from April to October. Insects were removed from traps every two weeks. All beetles collected were identified to family and sorted to morphospecies. To compare beetle trophic structure, collected morphospecies were assigned to one of five functional groups: (1) predacious, (2) herbivorous, (3) fungivorous, (4) xylophagous, or (5) omnivorous.

Beetle morphospecies diversity was evaluated using rarefaction. Rarefaction estimates the number of species in a random subsample to the entire sample (Simberloff 1972). The resulting value can then be interpreted as a measure of diversity because the technique takes into account both species richness and abundance (Niemelä et al., 1993; Spence et al., 1997). Over the course of our study, trap contents from both sites were lost at certain sampling periods due to vandalism and high winds. Rarefaction was used as it compensates for sampling errors and uneven catch.
Table 1. Beetle families and number of morphospecies collected from an eastern cottonwood plantation and adjacent bottomland hardwood forest in southeastern Arkansas.

<table>
<thead>
<tr>
<th>Family</th>
<th>Number of Morphospecies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Forest</td>
</tr>
<tr>
<td>Staphylinidae (Rove beetles)</td>
<td>16</td>
</tr>
<tr>
<td>Cerambycidae (Long-horned beetles)</td>
<td>15</td>
</tr>
<tr>
<td>Elateridae (Click beetles)</td>
<td>14</td>
</tr>
<tr>
<td>Chrysomelidae (Leaf beetles)</td>
<td>13</td>
</tr>
<tr>
<td>Scarabaeidae (Scarab beetles)</td>
<td>13</td>
</tr>
<tr>
<td>Buprestidae (Metallic woodboring beetles)</td>
<td>7</td>
</tr>
<tr>
<td>Curculionidae (Snout beetles and true weevils)</td>
<td>7</td>
</tr>
<tr>
<td>Coccinellidae (Ladybird beetles)</td>
<td>5</td>
</tr>
<tr>
<td>Erotylidae (Pleasing fungus beetles)</td>
<td>5</td>
</tr>
<tr>
<td>Mordellidae (Tumbling flower beetles)</td>
<td>4</td>
</tr>
<tr>
<td>Cleridae (Checkered beetles)</td>
<td>4</td>
</tr>
<tr>
<td>Lampyridae (Firefly beetles)</td>
<td>3</td>
</tr>
<tr>
<td>Eucnemidae (False click beetles)</td>
<td>3</td>
</tr>
<tr>
<td>Bostriichidae (Horned powder-post beetles)</td>
<td>2</td>
</tr>
<tr>
<td>Cantharidae (Soldier beetles)</td>
<td>1</td>
</tr>
<tr>
<td>Cucujidae (Flat bark beetles)</td>
<td>1</td>
</tr>
<tr>
<td>Melandryidae (False darkling beetles)</td>
<td>1</td>
</tr>
<tr>
<td>Oedemeridae (Pollen-feeding beetles)</td>
<td>1</td>
</tr>
<tr>
<td>Pyrochroidae (Fire-colored beetles)</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>116</strong></td>
</tr>
</tbody>
</table>

Results and Discussion

A total of 1,941 individuals representing 137 beetle morphospecies was collected from the two sites. Morphospecies representing nineteen beetle families were trapped, with the greatest number collected from the bottomland hardwood forest (Table 1). Staphylinidae, Cerambycidae, Elateridae, Scarabaeidae, and Chrysomelidae dominated trap samples from the bottomland hardwood forest. By comparison, trap samples from the eastern cottonwood plantation contained a less diverse complement of families, mostly dominated by Elateridae, Chrysomelidae, and Cerambycidae. Overall, most families collected from the plantation contained fewer morphospecies than their counterparts in the forest. The exception to this was the Coccinellidae, with trap samples from the plantation containing nearly twice the number of morphospecies as those from the forest.

Species diversity, as estimated by rarefaction, was higher in the bottomland hardwood forest than in the eastern cottonwood plantation (Fig. 1). Very few morphospecies were shared between the two sites, with the forest containing a larger, and more diverse, complement of morphospecies than the plantation, which was characterized by a smaller, but still unique assemblage. Dissimilarity in morphospecies assemblages between the two sites was underscored by the low Morisita-Horn value of 0.33.

Both sites, forest and plantation, also differed in terms of equability of species abundances. Dominance by a single morphospecies in the eastern cottonwood plantation is evident in the rank abundance plots comparing morphospecies abundance distributions (Fig. 2). The plot
Beetle Diversity in an Eastern Cottonwood (Populus deltoids Bartr.) Plantation and Adjacent Bottomland Hardwood Forest in Southeastern Arkansas

![Graph showing beetle morphospecies diversity](image)

Fig. 1. Beetle morphospecies diversity, as estimated by rarefaction, in an eastern cottonwood plantation and adjacent bottomland hardwood forest.

for the plantation shows a high value at the intersect with the y-axis, indicating dominance by a single species and fewer morphospecies of intermediate abundance. The shallow slope of the forest plot indicates a greater degree of equitability among morphospecies abundance. Plot length further underscores the differences in numbers of morphospecies collected at both sites.

At both sites, predaceous and herbivorous beetles accounted for most of the morphospecies collected in Malaise traps (Table 2). Herbivorous beetles accounted for over 60% of the individuals collected from the plantation site, whereas that functional group only accounted for 38% of the total catch from the forest. Conversely, trap samples from the forest contained larger numbers of xylophagous beetles than samples from the plantation. Fungivorous beetles, although collected from the forest, were absent from plantation trap samples.

Research comparing forest plantations (conifer, broadleaved hardwood) to natural forest has often indicated a trend toward lower species diversity in the plantation setting (Deharveng, 1996; Fahy and Gormally, 1998; Ananthakrishnan, 2000). Herbivorous insects, pest species specifically, also tend to be more abundant in monocultures due to abundant food supplies and fewer natural enemies (Moore et al., 1991; Bragança et al., 1998; Zanuncio, 1998). These broad assertions are applicable to the results we obtained concerning beetle morphospecies diversity and abundance in the eastern cottonwood plantation.

During their first two years, intensively managed eastern cottonwood plantations are managed essentially as field crops. Areas surrounding the trees are cleared of competing vegetation (discing, mowing, herbicides), and outbreaks of insect pests are often treated with applications of insecticide. Based upon our personal observations of a number of plantations (newly planted to harvest age) in Arkansas and Mississippi, these areas tend to remain relatively simple habitats. During the first two to three years, plantations are generally characterized by little canopy cover and an open understory composed of grasses, forbs, and vines. Accumulations of leaf litter and dead woody material are scarce. On most sites, crown closure does not take place until the fourth or fifth growing season. After closure, ground vegetation tends to remain relatively simple. Dead woody material, outside of small diameter branches and the occasional wind-felled tree, is also limited.

Our results, especially those regarding species diversity, appear to be reflective of these structurally simple habitat conditions and are particularly applicable to the early stages of plantation development. Lack of certain habitat features within these plantation settings most likely played an important role in the absence of certain beetles from our trap samples. In particular, beetles known to be associated with dead wood for some portion of their life-cycle either occurred in much smaller numbers in plantation trap

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Fig. 2. Rank abundance plots for beetle morphospecies collected from an eastern cottonwood plantation and adjacent bottomland hardwood forest.

Table 2. Number of individuals, representing various trophic roles, collected from an eastern cottonwood plantation and adjacent bottomland hardwood forest in southeastern Arkansas.

<table>
<thead>
<tr>
<th>Trophic Role</th>
<th>Forest</th>
<th>Plantation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herbivorous</td>
<td>452 (38.2%)</td>
<td>459 (60.6%)</td>
</tr>
<tr>
<td>Predaceous</td>
<td>297 (25.1%)</td>
<td>200 (26.4%)</td>
</tr>
<tr>
<td>Xylophagous</td>
<td>283 (23.9%)</td>
<td>95 (12.5%)</td>
</tr>
<tr>
<td>Fungivorous</td>
<td>125 (10.6%)</td>
<td>0 (0)</td>
</tr>
<tr>
<td>Omnivorous</td>
<td>26 (2.2%)</td>
<td>4 (0.5%)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>1183 (100.0%)</td>
<td>758 (100.0%)</td>
</tr>
</tbody>
</table>

Since many xylophagous beetle species feed on dead wood, their presence in an area is based to a great extent upon the presence of suitable host material (Martikainen et al., 1999; Martikainen et al., 2000). Consequently, for diversity of these species to be maintained dead woody material, in various stage of decay, must be present. This is a resource that is often lacking in eastern cottonwood plantations, but is present in natural bottomland hardwood forests. Since trees within intensively managed plantations are often harvested after only 10 to 12 years, opportunities for increased loads of dead wood are minimal. In addition, following harvest, little wood often remains on site. Decreased diversity of dead wood associated organisms will potentially represent a long-term feature of intensively managed eastern cottonwood plantations.

Conversely, the homogeneous nature of the eastern cottonwood plantations provided highly suitable habitat for Populus pest species. Of the total number of herbivorous beetles trapped in the plantation, 73% were cottonwood leaf beetles. By comparison, trap samples from the bottomland hardwood forest contained twice as many herbivorous beetles, with numbers more equitably distributed among those beetles that are known to feed upon wood-decaying fungi. Absent from plantation samples were members of the Erotylidae, many of whose members feed on a range of fungi, from mushrooms to hard bracket fungi (Goodrich and Skelley, 1994).

...
Beetle Diversity in an Eastern Cottonwood (Populus deltoides Bartr.) Plantation and Adjacent Bottomland Hardwood Forest in Southeastern Arkansas

those morphospecies. Coccinellids, reported egg and larval predators of the cottonwood leaf beetle (Morris et al., 1975), accounted for over 50% of the predaceous beetles collected from that site. The influence of habitat homogeneity also applied to xylophagous beetles trapped in the plantation. The most commonly collected xylophagous beetle from the plantation was another Populus pest, the poplar borer Saperda calcarata Say. Overall, both the cottonwood leaf beetle and poplar borer accounted for 51% of all individuals collected in the plantation.

Comparison of a young eastern cottonwood plantation and a mature bottomland hardwood forest is not a completely balanced comparison. However, achieving a balanced comparison would be difficult, as intensively managed eastern cottonwood plantations are typically harvested after only 10 to 12 years and so will never achieve the same level of structural diversity a mature, natural forest possesses. What our study provides is preliminary insight into major differences between the two habitats as far as beetles are concerned. Populus plantations, even as they reach late rotation, will be unable to provide the range of microhabitats (abundant dead wood, large amounts of leaf litter) that are available in natural forests. For some groups, such as xylophagous and fungivorous insects, this will translate into lower quality habitat, or even a complete lack of suitable habitat. From our limited data, it is apparent that such homogeneity can shape the composition of beetle trophic groups, providing abundant food for some and little suitable resources for others. Ultimately, in terms of native beetles, intensively managed eastern cottonwood plantations will represent a new and unique component of the LMAV landscape.

Conclusions

Based upon these data, an intensively managed eastern cottonwood plantation appears to represent lower quality habitat when it comes to supporting the diversity and abundance of beetle species comparable to that of bottomland hardwood forest. The plantation does support a unique assemblage of beetle species, but it is one shaped by the high homogeneity of a monoculture setting and therefore not necessarily characteristic of the more heterogeneous bottomland hardwood forests that once occurred across the LMAV. Plantations have the potential to host a wider range of beetle species, particularly those managed jointly for fiber production and bottomland hardwood restoration, especially if dead wood is allowed to accumulate and plant diversity is allowed to increase in these settings.

Acknowledgments.—We acknowledge the cooperation and assistance of Jeff Portwood of Crown Vantage in providing access to Choctaw Island. William D. Jones provided a great deal of assistance in the collection and processing of insect samples. The contributions of Terry Schiefer of the Mississippi Entomological Museum at Mississippi State University in beetle identification were invaluable. This project was funded in part by the Mississippi Agricultural and Forestry Experiment Station and through contributions to the Poplar Pest Management Program by Westvaco and International Paper.

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GENERAL NOTES

Hazards of Fishing Gear to Wildlife of Lakes in Arkansas

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Fishermen in Arkansas cover many kilometers (km) of shoreline and hectares of water while angling. The many lakes in Arkansas support much fishing pressure, resulting in a large amount of lost line, baits, and lures that eventually lie along shorelines. Fishing lines that are snapped off or cut and thrown away by fishermen usually wash onto shore. Crank baits, plastic baits such as worms, jig skirts, salamanders, and lizards, and other types of floating lures may be lost or thrown out and eventually mix with debris on the shore.

Many waterfowl species forage along shorelines and in the adjacent water; whereas diving ducks, coots, and grebes forage underwater near shorelines in search of aquatic vegetation and insects (Bellrose, 1976). Shorebirds forage for insects, fish, and other aquatic animals along shorelines (Tacha and Braun, 1994), and raccoons (Procyon lotor) and river otters (Lutra canadensis) search these areas for crayfish, frogs, other small animals, injured waterfowl, persimmons, and other fruits (Lotze and Anderson, 1979; Sealander and Heidt, 1990; Larivière and Walton, 1998). Most lures are made to look realistic enough to entice fish into biting or ingesting them, and they may inadvertently get the same but undesired response from birds or raccoons.

In Vermont and New Hampshire, anglers have exchanged lead sinkers for nontoxic alternatives to protect birds from lead poisoning they may get by picking up lost sinkers (National Wildlife, World Edition, 2002, 40(3):63). State wildlife magazines are reporting the problems of lost line and baits (e.g., the death of a Great Blue Heron by entanglement in discarded line in Nebraskaland Magazine, 2002, 80(1):9) and pelicans have been reported entangled or hooked on lost lines or baits when diving for food (Wildlife Conservation, 2002, 105(2):8). In Sweden, cormorants have been found drowned in fishing nets (Engstrom, 1998). Obviously, the problems of unintentional damage to wildlife by fishing equipment are global.

Our objectives were to quantify the frequency of baits and line along selected heavily-fished shorelines, and to search for indications that wildlife of DeGray Lake might be ingesting or snared in such materials. Also, we contacted people involved with wildlife rehabilitation via electronic mail to obtain observations of wildlife-bait problems witnessed on other bodies of water in Arkansas.

Study Area.-The field portion of this study was done on DeGray Lake, Clark and Hot Spring counties, in southwest Arkansas. DeGray is a 5,587 hectare (ha) impoundment that was created in 1972 by the U.S. Army Corps of Engineers via the damming of the Caddo River. The lake has 333 km of shoreline and is a popular fishing area renowned for its largemouth bass (Micropterus salmoides), hybrid bass (Morone saxatilis x chrysops), crappie (Pomoxis sp.) and other game fishes. Many access points provide opportunities for fishing along these shorelines. The shorelines of this lake generally are rocky and have fairly dense, brushy cover, with the exception of areas maintained by the Corps of Engineers and state park land. There also are many small coves on the lake that support dense brush and harbor heavy concentrations of debris that wash up after periods of high water. Debris include limbs, logs and other organic matter, as well as trash (bottles, plastic bags, cans) and other various anthropogenic refuse – including fishing line and baits.

We walked portions of the shoreline of DeGray Lake, focusing on heavy use areas such as the lodge and marina areas, and near State Highway 7. Search efforts were conducted during May 2000, and from January 2001 until March 2002, and focused on areas of debris and latrine sites of raccoons. Areas searched extended from the edge of the water up the shore into brush where debris was found, with each section of shoreline searched twice. Areas that contained large amounts of debris especially were targeted. Baits and some lines discovered at these areas were photographed, then were placed into ziplock bags.

E-mail requests for information relating to injuries to wildlife due to fishing gear were sent to several state wildlife rehabilitators, local university biology departments, state parks, and wildlife refuges.

A total of 20.3 km of shoreline was searched between January 2001 and March 2002, with samples collected from 20 sites, and a total of 40 baits found. The majority of baits recovered were soft worm, salamander, or lizard types (52.5%) with the remainder of the sample composed of hard spinner baits, crank baits, and other hard plastic lures.

On one 1.7 km section of shoreline near State Highway 7, we found 19 lines and 13 lures, and along the shoreline of...
DeGray State Park Marina, we found 10 lines and 20 lures. An average of 3.0 lines and 2.0 lures per km was calculated over the study area.

Some baits were found at the edge or floating in the water. Several hard baits were found with line still attached and tangled in small trees and bushes on shore. Hard baits often had rusted hooks, and some were hanging from debris in a manner that would easily snare mammals or birds that encountered them. Many of these baits were suspended from bushes and hung down 0.5 meters (m) or less above the ground.

Plastic worms sometimes still retained hooks that could impale an animal if the animal attempted to chew or swallow the lure. A majority of the lines found were lying along the shore well out of the water, and many of them were tangled up into balls. Some lines were found stretched out as much as 3-4 m.

Latrine sites of raccoons tended to be located on logs or on bent willows adjacent to the water and could consist of one to several defecations. Nineteen latrine sites were discovered within a 4 km stretch of shoreline in the area of DeGray State Park Marina. Numbers of latrine sites of raccoons averaged 1.4 per km along these same shorelines which had been searched for baits.

In the summer of 2000, a raccoon latrine found along the levee of DeGray Lake on State Highway 7 contained seeds of persimmon (Diospyros virginiana) and the remains of a plastic worm that had passed through the digestive tract of the raccoon. In January 2001, a latrine located on a bent willow tree (Salix nigra) on a peninsula of the island containing DeGray Lodge contained persimmon seeds and most of a plastic worm that had remained intact during its passage through the raccoon. In January 2002, in this same general area, a latrine was found with 3 pieces of a green plastic worm embedded in the dropping. Overall, 10.7% of latrines (3 of 28) contained plastic worms whereas 17.9% contained remnants of paper towels and plastic kitchen and trash bags (5 of 28).

E-mail responses documented additional incidents involving wildlife and fishing gear in Arkansas. In particular, waterfowl and birds that forage in and around water were noted to have come in contact with these hazards.

K. Nichols and his wife were on Lake Dardanelle in 2000 and observed a man pulling a net from the water that contained at least 10 drowned diving ducks identified as lesser scaup (Aythya affinis). The dead ducks were removed and discarded into the water. In early 2002, J. Wilson of Tennessee found a Northern Flicker (Colaptes auratus) tangled in fishing line on the banks of the Mississippi river (which he untangled and released). “Years ago” S. Rhodes of North Little Rock discovered a young barn swallow (Hirundo rustica) at Beaverfork Lake near Conway (Faulkner county) that had been caught in fishing line. Within 15 minutes after being freed, the swallow recovered and flew away. In 2000, D. G. Krementz of the Arkansas Cooperative Fish & Wildlife Research Unit rescued a mallard (Anas platyrhynchos) and a pelican (Pelecanus erythrorhynchos) at Bella Vista that had injuries due to fishing hooks. The mallard had been hooked on its beak, and the pelican was hooked on its leg. H. & M. Parker related a story about finding a common loon (Gavia immer) at Millwood Lake that had been snagged by the wing on a trotline.

It is obvious from the data from DeGray Lake that many fishermen lose or throw away baits and lines and these items end up on shorelines and in bushes where they become a hazard for wildlife. The discovery of remains of a plastic worm in feces at each of three latrine sites of raccoons is evidence that soft baits are ingested with adequate frequency for concern. Baits with hooks hanging in brush along shorelines have a potential of snagging wildlife that pass by.

Education concerning the problem of discarded or lost fishing gear on wildlife could help convince anglers to never intentionally discard gear, which should help decrease the frequency of damage or losses of wildlife due to encounter events. Further, interested groups might organize volunteer cleanup campaigns along rivers or lakes, specifically targeting lures and line. Campaigns around some Arkansas lakes managed by the Army Corps of Engineers already are effective in collecting various forms of trash. We believe that lures and line also should become a focal point of cleanup and education.

In addition, fishermen using nets should avoid setting their nets in areas in which diving ducks presently can be seen foraging. Trotlines should be removed from the water as soon as the fisherman ceases to use them, and current state regulations require daily checking of trotlines (Arkansas Fishing Regulations 2002). Following these suggestions and regulations more carefully can help reduce losses of non-target wildlife.

ACKNOWLEDGMENTS.—We thank the Army Corps of Engineers for allowing us to conduct an aspect of this study along the shorelines of DeGray Lake. K. Nichols, J. Wilson, S. Rhodes, D. G. Krementz, and H. and M. Parker provided details of their encounters with wildlife affected by fishing gear. L. Slater of HAWK (Helping Arkansas Wild “Kritters”) provided logistic support.

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Mammalian Species 587:1-8.
Habitat and Abundance of the Ouachita Darter (*Percina* sp. nov.)

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The Ouachita darter (*Percina* sp. nov.), a morphologically distinct form of the longnose darter (*Percina nasuta*), is endemic to the Ouachita River drainage and is considered an undescribed species (Robison and Buchanan, 1988; Robison, 1992). Most records of occurrence are from the upper Ouachita River within the boundary of the Ouachita National Forest. The U.S. Forest Service considers the Ouachita darter a sensitive species and Robison and Buchanan (1988) considered it a species of special concern. Historically, the Ouachita darter has been captured in low numbers, and there is limited ecological information available on habitat preferences or abundance. Since the darter occurs in low numbers within a relatively large river, it is difficult to capture and estimate abundance with confidence. The objectives of this study were to develop a methodology for estimating population levels of the darter and define the preferred habitat of the Ouachita darter based on water depth, velocity, and substrate composition.

In the late spring of 2000, a preliminary survey of 35 sites on a 9.6-km section of the Ouachita River between Pine Ridge and Shirley Creek campground, Montgomery County, AR indicated certain habitat characteristics associated with the Ouachita darter (Table 1). We used this preliminary data to identify reaches of likely habitat in an effort to concentrate our sampling as we continued downstream in the following year. During the summer of 2001, we sampled a 6.5 km section of the Ouachita River between Shirley Creek campground and the bridge at Arkansas Highway 379.

This section of the river was floated in a canoe to classify each macrohabitat type as run, riffle, or pool in mid-May, 2001. Locations and lengths of each habitat were determined with a Trimble Geo Explorer (GPS) and widths were measured with a Bushnell Yardage Pro 400 range finder. We measured water temperature, dissolved oxygen, nitrate, conductivity, turbidity and pH by towing a Hydrolab Datasonde 4 behind the canoe.

Based on our preliminary survey, we identified preferred habitat as reaches with emergent, semi-aquatic macrophytes growing along the edge of runs (primarily water willow, *Justicia* sp.). These reaches and adjacent habitat immediately upstream and downstream were sampled by snorkeling on the last week of July and the first week of August. Three snorkelers started at the downstream

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Table 1. Habitat type and water quality at sites with Ouachita darters in the preliminary survey of the Ouachita River between Pine Ridge and Shirley Creek in 2000.

<table>
<thead>
<tr>
<th>Habitat type(^a)</th>
<th>pH</th>
<th>Conductivity (µS)</th>
<th>Velocity (m/s)</th>
<th>Ouachita darters observed(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run</td>
<td>7.3</td>
<td>44.5</td>
<td>0.38</td>
<td>3</td>
</tr>
<tr>
<td>Run</td>
<td>7.2</td>
<td>67.6</td>
<td>1.25</td>
<td>6</td>
</tr>
<tr>
<td>Riffle</td>
<td>7.2</td>
<td>71.0</td>
<td>0.42</td>
<td>5</td>
</tr>
<tr>
<td>Riffle</td>
<td>7.2</td>
<td>72.2</td>
<td>0.75</td>
<td>+2</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td>7.2</td>
<td><strong>63.8</strong></td>
<td><strong>0.70</strong></td>
<td><strong>Total=16</strong></td>
</tr>
</tbody>
</table>

\(^a\) Most sites with Ouachita darters also had clean gravel substrate.

\(^b\) Over thirty other sites were also surveyed but Ouachita darters were not found.

---
ends of these reaches and proceeded upstream for 20 minutes while counting Ouachita darters (providing one person-hour of effort). Basin Area Stream Survey methodology was followed to characterize the physical variables along a transect in the center of each macrohabitat (Clingenpeel and Cochran, 1992). We also characterized microhabitat at the point where the density of Ouachita darters was the highest in a particular site. Variables included water depth, water velocity at the standard 6/10 total depth and at maximum depth (close to where darters live), and a visual estimate of substrate composition.

When Ouachita darters were observed, we used a seine (3.0 m x 1.8 m with 5-mm mesh) and a Smith-Root Model 12 backpack electrofisher to capture them. The two approaches were used singly and in combination to maximize capture. We also returned to site 4, a reach of high Ouachita darter density based on the initial snorkel survey, to conduct a mark/re-sight population estimate. Fish were captured by a “herding” technique that involved a snorkel and a set-seine. Two individuals held a seine perpendicular to the current and the seine was tilted back until it was lying flat on the substrate. The lead-line of the seine was buried in the substrate to restrict darters from escaping under it. A third individual, 4 to 5 m upstream, located a Ouachita darter by snorkeling and then gradually directed the fish into the seine. The seine was quickly raised once the darter

<table>
<thead>
<tr>
<th>Variable</th>
<th>Mean</th>
<th>Standard deviation</th>
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<tr>
<td>pH</td>
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<td>0.2</td>
</tr>
<tr>
<td>Conductivity (μS)</td>
<td>67</td>
<td>0.4</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>26</td>
<td>0.5</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>5.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Nitrate (mg/L)</td>
<td>0.32</td>
<td>0.05</td>
</tr>
<tr>
<td>Dissolved Oxygen (mg/L)</td>
<td>8.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 2. Means and standard deviations of water quality variables in the Ouachita River between Shirley Creek and AR Hwy 379 in May, 2001 (n=24).

Fig. 1. Macrohabitat types and sites where Ouachita darters were found in the Ouachita River between Shirley Creek and AR Hwy 379. All riffles and runs were snorkeled except the farthest downstream and Ouachita darters were found in all that are identified by site numbers.
Table 3. Numbers of Ouachita darters observed during one person-hour of snorkeling and associated habitats at seven sites on the Ouachita River between Shirley Creek and AR Hwy. 379 in the summer of 2001. Microhabitat was from the point of highest darter density in each site. Because depth and velocity were typically zero at both banks along macrohabitat transects, we presented the means of these variables with and without the data from the banks (standard deviations in parentheses). Column totals or means with standard deviations in parentheses are also shown.

<table>
<thead>
<tr>
<th>Site</th>
<th>Sample area (m²)</th>
<th>Ouachita darters observed</th>
<th>Percent cobble</th>
<th>Depth @ 6/10</th>
<th>Velocity @ 6/10</th>
<th>Velocity @ max</th>
<th>Macrohabitat with banks</th>
<th>Macrohabitat without banks</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(cm)</td>
<td>(cm)</td>
<td>depth</td>
<td>Percent cobble</td>
<td>Depth @ 6/10</td>
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<tr>
<td>1</td>
<td>80</td>
<td>18</td>
<td>60</td>
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<td>0.12</td>
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<td>(0.09)</td>
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<td>0.12</td>
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<td>(0.06)</td>
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<td>(8.9)</td>
<td>(3.7)</td>
<td>(0.10)</td>
<td>(8.2)</td>
<td>(8.08)</td>
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</table>

a Based on two person-hours of sampling.

b This site was selected for a mark/re-sight, population estimate resulting in an estimate of 32 darters (90% C.I. = 13 to 51).

c Physical habitat was not measured at site 7 but visual observations were consistent with other sites.

was inside. This process was repeated until there were no Ouachita darters observed by the individual snorkeling. Captured darters were placed into a bucket until they were marked with a subcutaneous injection of fluorescent green dye in the suborbital epidermis. The marked fish were released back into the area where they were captured. Approximately two hours later, we snorkeled the area to search for marked individuals. The number of marked and unmarked individuals was recorded. We used Chapman's modification of the Peterson method to estimate population abundance and associated 90% confidence limits (e.g. Van Den Avyle and Hayward, 1999).

The 6.5 km section of the Ouachita River between Shirley Creek Campground and Highway 379 bridge was characterized by short riffle and run habitats (total of 870 m) that were separated by long pools (Fig. 1). During the 2001 float, there was little measurable variation in water quality along the study reach of the river. For example, the mean nitrate concentration was 0.32 mg/L with a standard deviation of only 0.05 mg/L (Table 2). We identified four
vegetated runs that were characteristic of the habitat that held Ouachita darters in the spring of 2000. During our snorkeling surveys, no Ouachita darters were found in these reaches. However, Ouachita darters were present in transition zones between riffles and runs.

A total of 74 Ouachita darters as observed at seven of the ten run sites within the study area (Fig. 1 and Table 3). The number of Ouachita darters per site (for sites where the darters were observed) ranged from 2 to 18 versus a range of 2 to 6 for the 2000 study in the reach immediately upstream. Microhabitats usually consisted of the upstream end of a run with slight surface agitation due to the adjacent riffle. The mean depth and velocity at maximum depth of the microhabitat was 22 cm and 0.15 m/s, respectively. Microhabitats contained a higher percentage of cobble than the transect line at the middle of the predicted macrohabitat (Table 3). The mean substrate composition of microhabitats with Ouachita darters was 60% cobble and 40% gravel versus 43% cobble and 47% gravel for the associated runs.

Ouachita darters used the cobble substrate for cover when approached. Consequently, continuous slow snorkeling was less effective than intermittent snorkeling (moving to the edge of visibility, then waiting 20-30 seconds for the darters to emerge from cover before moving again). Seining where the darters were observed, resulted in only one darter captured after 16 attempts (2.5 person hours). Similarly, we only captured two darters with the use of electricity (8 person hours). Herding the darters while snorkeling resulted in 10 captures in 3 person hours of sampling. We successfully marked and released 8 Ouachita darters and counted 10 during the re-sight attempt. Only 2 of these were marked, thus we estimated the population for the 28 m² area to be 32 with 90% confidence limits of 13 to 51. The mean length of the thirteen captured darters was 50 mm and ranged from 43 to 54 mm.

The Ouachita darter occupied a similar microhabitat at each site and was rarely seen outside of this microhabitat. The darters preferred upstream edges of runs in late summer when the water level was low (discharge was around 1.4 m³/s). Records from 1942 to 2000 at the nearby Mount Ida gauging station show that discharge exceeds 0.9 m³/s 90% of the time and exceeds 7.0 m³/s 50% of the time (USGS, 2001). Low water level, characteristic of late summer, reduces the areal extent of preferred microhabitat and concentrates the Ouachita darters.

The microhabitat preference that we found, contrasts with the pool habitat suggested by Robison and Buchanan (1988) for late summer habitat. It also differs from what we found during higher spring flows in 2000 (two significant rain events occurred during the 2000 sampling). The discrepancy is most likely due to temporal variations in the availability of preferred habitat. We found the darters in microhabitats that invariably included slight surface agitation and a high percentage of cobble substrate.

Substrate size and arrangement are among the most important microhabitat features for several darter species (Hlohoswkyj and Wissing, 1986). The cobble habitat, where the darters were concentrated, was free from the sedimentation that was common in nearby habitats without Ouachita darters. This absence of sediment provided interstitial spaces, which the Ouachita darters frequented for cover. This common response of Ouachita darters was rare among the other seven species of darters observed. It seems that clean cobble substrate may constitute a critical summer habitat for this species. The clean gravel substrates that were typical of where Ouachita darters were found in the previous spring were abundant at that time of year.

Excessive sedimentation resulting from careless land-use practices may significantly reduce availability and suitability of clean cobble substrate (Danielson, 1991). Berkman and Rabeni (1987) found that sedimentation from bank and channel erosion was pervasive in Ozark streams, and it altered densities of benthic, riffle-inhabiting, insectivorous and herbivorous fishes. Riffles and runs adjacent to and immediately downstream of the eroded bank observed in this study (Fig. 1) contained a high degree of sedimentation. These riffles and runs had few darters that were common elsewhere in the river and no Ouachita darters. A similar pattern was observed in the 2000 study. Low water levels can also reduce the extent of preferred habitat if velocity becomes too low to keep the substrate clean. Lobb and Orth (1991) found riffle and run habitats to be the most sensitive to reductions in flow.

Structure, such as course substrate, within a habitat can also reduce capture efficiency (Parsley et al., 1989). The substrate and the evasive behavior of the Ouachita darter may explain the low capture efficiency of seines and backpack electrofishers. Both techniques resulted in Ouachita darters hiding in interstitial spaces or swimming away from captors more than other darter species. Consequently, the herding technique was the most efficient way to capture this species. Once the preferred habitat was identified, we were able to capture 10 darters in an hour (3 person hours). Our approach met the assumptions of the Peterson method. However, the lower limit of the population estimate was 13, which was less than the known number of darters present (8 marked and 8 unmarked). This artifact resulted from a small sample size and the low number of recaptures.

The estimated population of 32 Ouachita darters in 28 m² should be considered an upper range of density rather than typical, because the darters were concentrated into small areas of preferred habitat during the late summer and we selected a site with high density to maximize our chances of estimating a confidence interval. Extrapolation to estimate darter abundance for the entire 6.5 km study reach

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involves a significant assumption. We only observed 9 Ouachita darters in our initial snorkel survey of site 4, yet our population estimate was 32. If one assumes that our sight success was similar for the 74 fish observed at other sites, then the entire reach probably had about 260 Ouachita darters. That abundance constitutes an extremely low darter density for a 6.5 km reach of river. However, only 870 m (13.3%) of the river was riffle or run habitat. When one considers that the identified microhabitat was less than a quarter of the riffle and run macrohabitat, it seems that densities of this species in its preferred habitat were low, but not extremely low, compared to other darter species.

Kessler and Thorp (1993) found that microhabitat studies provide basic ecological information needed for management plans. In the case of the Ouachita darter, microhabitat analysis helped explain sampling difficulties and indicated vulnerability to sedimentation and low streamflow. We conclude that late summer is the most efficient season to sample the Ouachita darter and that a multi-scale approach is needed.

**Literature Cited**


Coccidian Parasites (Apicomplexa: Eimeriidae) of Select Rodents of Western and Southwestern Arkansas and Northeastern Texas

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*Corresponding Author

McAllister et al. (1991b) provided several new host and locality records of coccidia from a survey of 147 rodents from five states in the southwestern and western United States (Arizona, Colorado, New Mexico, Texas, and Utah). In addition, several taxa of rodents from northcentral, western, and southwestern Texas have been reported to harbor previously described and/or new species of *Eimeria* or *Isospora* (McAllister and Upton, 1988, 1989a, b; Ford et al., 1990; Levine and Ivens, 1990; McAllister, et al., 1991a; Upton et al., 1992; Duszynski and McAllister, 1993). However, to our knowledge, nothing has been previously documented on the coccidian parasites of rodents from northcentral Texas, and rodents from all of the 75 counties of the state of Arkansas have been entirely neglected in coccidial surveys. As part of an ongoing study on the ecology of select rodents of the Ark-La-Tex region, we surveyed rodents for coccidia from four counties of northcentral Texas and two counties of western and southwestern Arkansas.

Between August 2000 and February 2002, 30 rodents (see Table 1) were collected with baited Museum Special® snap-traps and Sherman live traps and examined for coccidial parasites. They were returned to the laboratory and killed by cervical dislocation. A portion of the intestinal contents and feces was removed from each rodent, placed in vials containing a small volume of 2.5% (w/v) aqueous potassium dichromate, and stored briefly at room temperature (ca. 23°C). Samples were screened twice for coccidia following flotation in Sheather's sugar solution (specific gravity = 1.30). Negative samples were discarded and those samples containing unsporulated oocysts were allowed to sporulate for up to one week at room temperature in Petri dishes containing a thin layer of 2.5% potassium dichromate. Upon sporulation, oocysts were concentrated again with Sheather's and identified using a compound microscope equipped with Nomarski interference-contrast (DIC) optics. Oocysts were 30 days old when examined.

Voucher specimens of hosts are deposited in the Arkansas State University Museum of Zoology (ASUMZ). Rodent common and family names follow Wilson and Cole (2000).

Of the 30 rodents examined, five (23%) were found to be harboring at least one of four eimerians (Table 1). Of the infected rodents, only one (20%) hispid cotton rat (*Signodonta hispidis*) had a multiple infection of two coccidian species. Although no new host records are reported, we document three new geographic records for coccidia (Table 1).

*Eimeria langebarteli* Ivens, Krudener, and Levine, 1959 has been reported previously from the Texas mouse (*Peromyscus attwateri*) and the white-ankled mouse (*Peromyscus pectoralis*) in Hood and Kimble counties, Texas, respectively (Duszynski and McAllister, 1993). This coccidian has now been reported from at least six species of *Peromyscus* and *Reithrodontomys* from the southwestern United States and Mexico (Ivens et al., 1959; Redeker et al., 1985; Duszynski et al., 1992) (see Table 2). Herein, we report the coccidian species in Arkansas for the first time. Our Polk County site on Rich Mountain (8 km NW Mena at Blue Haze Vista Overlook off St. Hwy 88), represents the northern and easternmost geographic distributional record ever reported for *E. langebarteli* in the United States (Table 2).

*Eimeria lancasterensis* Joseph, 1969 is one of the most prevalent coccidians infecting the rodent family Sciuridae. It has been reported previously from eastern fox squirrels (*Sciurus niger*) in northcentral Texas (McAllister and Upton, 1989a) and Nebraska (Spurgin and Hnida, 2002) and eastern gray squirrels (*Sciurus carolinensis*) in Massachusetts (Joseph, 1969, 1972) and Florida (Forrester et al., 1977). McAllister (unpublished data) also found *E. lancasterensis* during December 1988 in five of five (100%) *S. carolinensis* from Franklin (1/1), Madison (1/1), Pulaski (2/2), and Scott (1/1) counties, Arkansas, which represents a new state record for the coccidian. Bowie County, Texas, is a new county record for *E. lancasterensis*.

*Eimeria sigmodontis* Barnard, Ernst, and Dixon, 1974 was originally described from *S. hispidis* in eastern Alabama (Barnard et al., 1974). This coccidian has also been reported from the same host in Dallas and Johnson counties, Texas (McAllister et al., 1991a) and Payne County, Oklahoma (Faulkner and Lochmiller, 1997). We report *E. sigmodontis* in Arkansas *S. hispidis* for the first time.

*Eimeria webbae* Barnard, Ernst, and Dixon, 1974 was originally described from *S. hispidis* in eastern Alabama (Barnard et al., 1974). Additional reports of *E. webbae* include infections in populations of *S. hispidis* in northcentral Texas (McAllister et al., 1991b) and northeastern Oklahoma (Faulkner and Lochmiller, 1997).
Table 1. Rodents surveyed for coccidia from counties of Arkansas (AR) and Texas (TX) and the *Eimeria* species collected.

<table>
<thead>
<tr>
<th>Rodent taxa</th>
<th>Locality*</th>
<th>Prevalence**</th>
<th>Eimeria spp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geomyidae</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Geomys breviceps</em></td>
<td>BC</td>
<td>0/4 (0%)</td>
<td></td>
</tr>
<tr>
<td>Muridae</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Mus musculus</em></td>
<td>LRC</td>
<td>0/1 (0%)</td>
<td></td>
</tr>
<tr>
<td><em>Neotoma floridana</em></td>
<td>LRC</td>
<td>0/1 (0%)</td>
<td></td>
</tr>
<tr>
<td><em>Oryzomys palustris</em></td>
<td>CC</td>
<td>0/1 (0%)</td>
<td></td>
</tr>
<tr>
<td><em>Peromyscus attwateri</em></td>
<td>PC</td>
<td>1/4 (25%)</td>
<td><em>E. langebarteli</em></td>
</tr>
<tr>
<td><em>Peromyscus leucopus</em></td>
<td>CC</td>
<td>0/1 (0%)</td>
<td></td>
</tr>
<tr>
<td><em>Reithrodontomys fulvescens</em></td>
<td>CC</td>
<td>0/3 (0%)</td>
<td></td>
</tr>
<tr>
<td><em>Reithrodontomys humulis</em></td>
<td>MC</td>
<td>0/1 (0%)</td>
<td></td>
</tr>
<tr>
<td><em>Sigmodon hispidis</em></td>
<td>CC &amp; LRC</td>
<td>2/9 (22%)</td>
<td><em>E. sigmodontis</em></td>
</tr>
<tr>
<td></td>
<td>LRC</td>
<td>1/9 (11%)</td>
<td><em>E. webbae</em></td>
</tr>
<tr>
<td>Sciuridae</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Sciurus carolinensis</em></td>
<td>BC</td>
<td>2/2 (100%)</td>
<td><em>E. lancasterensis</em></td>
</tr>
<tr>
<td><em>Sciurus niger</em></td>
<td>BC</td>
<td>2/2 (100%)</td>
<td><em>E. lancasterensis</em></td>
</tr>
</tbody>
</table>

*Locality abbreviations: LRC (Little River Co., AR); PC (Polk Co., AR); BC (Bowie Co., TX); CC (Cass Co., TX); MC (Marion Co., TX); RRC (Red River Co., TX).

**Number infected/number examined (%)**.

In conclusion, of the 27 species of rodents found in Arkansas (Sealander and Heidt, 1990), only five species (19%) have now been examined for coccidia, and three were found to harbor infections. A similar situation exists for Arkansas bats, as only one of 16 species (6%) has been surveyed previously (McAllister et al., 2001). We suggest additional Arkansas rodent taxa be examined to include larger sample sizes and additional locales in other counties in an effort to further characterize their coccidian parasite communities.

We thank the Arkansas Game and Fish Commission for Scientific Collecting Permit No. 3029. We also thank the TAMU-T Summer 2001 Vertebrate Field Biology class (particularly Beverly Allen) for assistance with collecting and Dr. Steve J. Upton (Kansas State University) for providing some helpful information. Drs. John Johnson and Gene Mueller (TAMU-T) aided in obtaining travel support for the senior author.
Table 2. Summary of the rodent hosts and localities for *Eimeria langebarteli*.

<table>
<thead>
<tr>
<th>Host</th>
<th>Locality*</th>
<th>Prevalence**</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Peromyscus attwateri</em></td>
<td>Hood Co., TX</td>
<td>4/5 (80%)</td>
<td>Duszynski and McAllister, 1995</td>
</tr>
<tr>
<td></td>
<td>Polk Co., AR</td>
<td>1/4 (25%)</td>
<td>This report</td>
</tr>
<tr>
<td><em>P. boylii</em></td>
<td>Chihuahua, MX</td>
<td>2/4 (50%)</td>
<td>Ivens et al., 1959</td>
</tr>
<tr>
<td><em>P. leucopus</em></td>
<td>Socorro Co., NM</td>
<td>4/17 (24%)</td>
<td>Reduker et al., 1985</td>
</tr>
<tr>
<td><em>P. pectoralis</em></td>
<td>Kimble Co., TX</td>
<td>5/6 (83%)</td>
<td>Duszynski and McAllister, 1995</td>
</tr>
<tr>
<td><em>P. truei</em></td>
<td>Baja California, MX</td>
<td>12/37 (32%)</td>
<td>Reduker et al., 1985</td>
</tr>
<tr>
<td></td>
<td>Cochise Co, AZ</td>
<td>2/2 (100%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Los Angeles Co., CA</td>
<td>2/21 (10%)</td>
<td></td>
</tr>
<tr>
<td><em>Reithrodontomys megalatis</em></td>
<td>Madera Co., CA</td>
<td>3/4 (75%)</td>
<td>Duszynski et al., 1995</td>
</tr>
<tr>
<td></td>
<td>San Bernardino, Co., CA</td>
<td>1/1 (100%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ixtlan District, MX</td>
<td>2/7 (29%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Veracruz, MX</td>
<td>1/2 (50%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zacatecas, MX</td>
<td>1/3 (33%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nevada de Toluca, MX</td>
<td>1/3 (33%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>= 41/116 (35%)</td>
<td></td>
</tr>
</tbody>
</table>

*Number infected/number examined (%).

---

**Literature Cited**


**Forrester, D. J., J. D. Shamis, G. L. Huff, and J. W.**


Parasites of Four Species of Endemic *Plethodon* from Arkansas and Oklahoma

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The Caddo Mountain salamander, *Plethodon caddoensis* Pope and Pope, 1951, is restricted to the Caddo and Ouachita Mountains of Howard, Montgomery, Pike, and Polk Counties of western Arkansas; the Kiamichi slimy salamander, *P. kiamichi* Highton, 1989, is known only from the Kiamichi and Round Mountain outcroppings of Polk County of western Arkansas; the Rich Mountain salamander, *P. ouachitae* Dunn and Heinze, 1933, occurs on Rich Mountain and adjacent ridges of the Ouachita Mountains of Polk County, Arkansas, and eastern Oklahoma; the southern redback salamander, *P. serratus* Grobman, 1944, exists in four isolated populations, west-central Arkansas and southeastern Oklahoma, central Louisiana, central and southeastern Missouri, and the Piedmont and Blue Ridge provinces of northeastern Georgia, adjacent Alabama, eastern Tennessee and western North Carolina (Highton et al., 1989; Conant and Collins, 1998; Trauth et al., 2003). To our knowledge, there is only one report (Winter et al., 1986) of parasites from *P. caddoensis* and *P. ouachitae*, and Arkansas populations of *P. serratus*. The purpose of this note is to report additional parasites from *P. caddoensis*, *P. ouachitae*, and *P. serratus*, and for the first time, parasites from *P. kiamichi*.

Between December 1988 and February 2002, 72 plethodontid salamanders were collected by hand from several counties within the Ouachita National Forest of Arkansas and Oklahoma: *P. caddoensis* from springs or abandoned mines and *P. kiamichi*, *P. ouachitae*, and *P. serratus* from beneath decaying logs and leaf litter in seepage areas of deciduous forest habitat. Salamanders were placed in individual bags and transported on ice to the laboratory where they were killed within 48 hr of capture by prolonged immersion in a dilute chloroquine® solution. Methods for salamander necropsy, coccidial isolation, and preparation and staining of blood smears and helminths follow McAllister and Upton (1987) and Upton et al. (1993); preparation of mites follows McAllister et al. (1995d).

Collection sites, sample size, mean ± 1 SD snout-vent length (SVL) in mm, and host accession numbers for voucher specimens deposited in the Arkansas State University Museum of Zoology (ASUMZ) for each species are listed in Appendix 1. Selected voucher specimens of parasites were deposited in the U.S. National Parasite Collection (UNSPC) and their accession numbers are listed in Table 1.

Of the 72 salamanders collected, 32 (44%) harbored parasites 11 (39%) *P. caddoensis*, four (25%) *P. kiamichi*, seven (88%) *P. ouachitae*, and 10 (50%) *P. serratus*. Blood smears were negative for intraerythrocytic hematozoa and viral and/or rickettsial inclusions. Parasites found in this study with their intensity of infection are listed in Table 1.

*Cepedietta michiganensis* (Woodhead, 1928) Corliss, de Puytorac, and Lom, 1965, was originally described as *Haptophrya michiganensis* by Woodhead (1928). Joy and Tucker (2001) have summarized hosts and localities. In Arkansas, it has been reported from the western slimy salamander (*P. albagula*), Fourche Mountain salamander (*P. fourchensis*), and *P. ouachitae* (Winter et al., 1986; McAllister et al., 1993). *Plethodon serratus* represents a new host record for *C. michiganensis* and Oklahoma a new locale for the parasite.

One of the *P. kiamichi* (ASUMZ 18982, male, 65 mm SVL, collected on 23 April 1993) was found to be passing eimerian oocysts in the feces. Unfortunately, only a few oocysts were present and not enough completed sporulation to allow for specific identification; however, oocysts of this isolate clearly contained four sporocytes, a taxonomic characteristic of the genus *Eimeria*. *Plethodon kiamichi* represents a new host record for *Eimeria* sp. This is only the fourth time a coccidian has ever been reported from plethodontid salamanders (Saxe, 1955; McAllister et al., 1993; Upton et al., 1993).

*Cylindroatraenia idahoensis* (Waitz and Mehra, 1961) Jones, 1987 was originally described from the Coeur d’Alene salamander, *Plethodon idahoensis* from Kootenai County, Idaho (Waitz and Mehra, 1961). It has been reported from Jordan’s redcheek salamander, *P. jordani* from North Carolina (Dyer, 1983; Jones, 1987) and the western redback salamander, *P. vehiculum* from Oregon (Panitz, 1969). *Plethodon caddoensis*, *P. ouachitae* and *P. serratus* represent new host records for *C. idahoensis*. The Ouachita National Forest of Arkansas and Oklahoma are new locality records for *C. idahoensis*.

*Batracholandros magnavulvaris* (Schad, 1960) Petter and Quentin, 1976 was originally described as *Oxyuris magnavulvaris* by Rankin (1937) from the red-spotted newt (*Notophthalmus viridescens*) and several species of plethodontid salamanders from Buncombe County, North Carolina. It
Table 1. Parasites of endemic *Plethodon* spp. from Arkansas and Oklahoma.

<table>
<thead>
<tr>
<th>Host species</th>
<th><em>P. caddoensis</em></th>
<th><em>P. kiamichi</em></th>
<th><em>P. ouachitae</em></th>
<th><em>P. serratus</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number examined</td>
<td>(28)</td>
<td>(16)</td>
<td>(8)</td>
<td>(20)</td>
</tr>
</tbody>
</table>

Parasite Number of infected hosts and intensities (mean ± 1SD, range) USNPC Accession No.

**Protista**

- *Cepedietta michiganensis***
  - Number: 4 (50%)
  - USNPC Accession No.: 84342, 92564, 92565

- *Eimeria sp.*
  - Number: 1 (6%)*

**Cestoidea**

- *Cylindrotaenia idahoensis***
  - Number: 9 (32%)*
  - USNPC Accession No.: 84300, 84339, 84340

- *Nematoda*

  - *Batracholandros magnavulvaris***
    - Number: 3 (38%)*
    - USNPC Accession No.: 92042

  - *Cosmocercoides variabilis*
    - Number: 1 (4%)*
    - USNPC Accession No.: 84256

  - *Oswaldocruzia euryceae*
    - Number: 2 (13%)*
    - USNPC Accession No.: 84254

**Arthropoda**

- *Hannemania sp.*
  - Number: 2 (7%)
  - USNPC Accession No.: 84341

*New host records.

**New locality record (Ouachita National Forest, Arkansas and/or Oklahoma).**

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has been reported from the Ouachita dusky salamander, *Desmognathus brillleyorum*, *P. caddoensis*, *P. fourcenhensis*, *P. ouachitae*, and *P. serratus* from Arkansas (Winter et al., 1986; McAllister et al., 1995d), and many species of salamanders from other North American locations (hosts and localities summarized by Joy and Tucker, 2001). The Ouachita National Forest of Oklahoma is a new locality record for *B. magnavulvaris*.

*Cosmocercoides variabilis* (Harwood, 1930) Travassos, 1931 was originally described from Woodhouse’s toad, *Bufo woodhousii* collected in Texas (Harwood, 1930). It has been reported from the ringed salamander, *Ambystoma annulatum* from Arkansas (McAllister et al., 1995b) and various other hosts (see Baker, 1987). It should be noted that a similar species, *Cosmocercoides dukae*, a parasite of gastropods, has been reported from numerous amphibians (Baker, 1987). The major difference between the two species is the number of caudal papillae: *C. dukae* with 12 pairs of plectenes (Holl, 1928); *C. variabilis* with 14-20 pairs of plectenes (Harwood, 1930). Because our specimens had 16 pairs of plectenes, we have assigned them to *C. variabilis*. *Plethodon caddoensis* and *P. ouachitae* represent new host records for *C. variabilis*.

*Oswaldocruzia euryceae* Reiber, Byrd, and Parker, 1940 was originally described from the three-lined salamander, *Eurycea longicauda guttulineata* collected in Georgia (Reiber et al., 1940). It has been reported from *P. caddoensis*, *P. ouachitae*, and *P. serratus* (Winter et al., 1986). *Plethodon kiamichi* represents a new host record for *O. euryceae*.

Larval intradermal mites, *Hannemania* sp. was found encapsulated in three species *P. caddoensis*, *P. ouachitae*, and *P. kiamichi*. Because only larvae were found, specific identity was not possible. *Hannemania* sp. has also been reported in Arkansas on *D. brillleyorum* (Loonis, 1956; Winter et al., 1986; McAllister et al., 1995d), graybelly salamanders, *E. multiplicata griseogaster* (McAllister et al., 1995c), and pickerel frogs, *Rana palustris* (McAllister et al., 1995a). *Plethodon kiamichi* represents a new host record for larva of *Hannemania* sp.

In summary, nine new host records and three new locality records are reported for parasites of four endemic species of *Plethodon* from the Ouachita Province of Arkansas and Oklahoma. Our survey supports Aho’s (1990) suggestion of a depauperate noninteractive community structure observed in helminth communities of most amphibians and reptiles.

We wish to thank the Oklahoma Department of Wildlife Conservation and Arkansas Game and Fish Commission for Scientific Collecting Permits Nos. 3172, 1480 and 1048 to C.T.M. and S.E.T., respectively. We also thank the Arkansas State University Natural History Class (Spring 1991), Mr.
Appendix 1. Voucher specimens of host salamanders (ASUMZ accession numbers) and collection localities in Arkansas and Oklahoma.

<table>
<thead>
<tr>
<th>Species</th>
<th>SVL ± 1 SD mm (range)</th>
<th>ASUMZ</th>
<th>Localities and sample sizes (parentheses)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>P. caddoensis</em></td>
<td>42 ± 4 (32-47)</td>
<td>18519-18520</td>
<td>Montgomery Co., AR; T3S, R27W, S26 (n = 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Polk Co., AR; T4S, R29W, S6 (n = 23)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T3S, R29W, S26 (n = 23)</td>
</tr>
<tr>
<td><em>P. kiamichi</em></td>
<td>57 ± 16 (27-73)</td>
<td>17575-17585; 17661-17663</td>
<td>Polk Co., AR; T1S, R32W, S31 (n = 16)</td>
</tr>
<tr>
<td><em>P. ouachitae</em></td>
<td>49 ± 9 (29-59)</td>
<td>19492</td>
<td>Hot Spring Co., AR; T5S, R20W, S31 (n = 7)</td>
</tr>
<tr>
<td><em>P. serratus</em></td>
<td>40 ± 6 (27-49)</td>
<td>19491; 26396-26402</td>
<td>Perry Co., AR; T3N, R20W, S27 (n = 1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pike Co., AR; T6S, R25W, S14 (n = 3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Polk Co., AR; T1S, R32W, S10 (n = 3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>LeFlore Co., OK; T1S, R32W, S7 (n = 2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>McCurtain Co., OK; T5S, R25E, S10 (n = 4)</td>
</tr>
</tbody>
</table>

David Saugey (U.S. Forest Service), and Dr. David W. Allard (TAMU-T) for assistance in collecting, and Dr. Steve J. Upton (Kansas St. Univ.) for examining some salamanders for coccidia.

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Parasites of Four Species of Endemic Plethodon from Arkansas and Oklahoma


Reiber, R. J., E. E. Byrd, and M. W. Parker. 1940. Certain new and already known nematodes from Amphibia and Reptilia. Lloydia 3:125-144


Concentrations of American Alligator Populations in Arkansas

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In the early 1800's the American Alligator (Alligator mississippiensis) population was estimated at three million for the United States (Woodward and Marion, 1978). However, by the early part of the 20th century, increased land conversion to agriculture and commercial exploitation caused alligator numbers to plummet (McIlhenny, 1935). The Arkansas Game and Fish Commission (AGFC) enacted a regulation to protect the alligator in 1961. In 1967 the American Alligator was listed as an endangered species throughout its range (U.S. Fish and Wildlife Service, 1967). At that time the alligator population was estimated to be only in the thousands (Woodward and Marion, 1978). Concern over the fate of the alligator stimulated strong interest in its conservation and biology. In January 1977 it was down listed to Threatened status. In 1987 the U.S. Fish and Wildlife Service removed the American Alligator from the endangered species list and announced the animal as fully recovered throughout its range.

The American Alligator is seen as a classic success story of the Endangered Species Act. Currently, the American Alligator is listed as "Threatened due to similarity of appearance" by the U.S. Fish and Wildlife Service and is listed as Endangered by the Arkansas Game and Fish Commission. This listing ensures control of legal trade of alligator hides and products.

According to a questionnaire mailed to state wildlife agencies in 1973, alligators were reported to be present in Hempstead, Miller, and Lafayette counties in Arkansas (Fig. 1). Within these three counties, it was estimated that an increasing population of 1,900 individuals inhabited 30.4 sq km of suitable habitat (Chabreck, 1973). A restocking effort was undertaken by the Arkansas Game and Fish Commission from 1972 to 1984. Approximately 2,800 alligators were released throughout the state in areas within its presumed historic range. About 80% of the alligators were stocked on private lands at the request of landowners. Alligators were initially transplanted from Grassy Lake, in Sevier County, Arkansas, but the majority was transplanted from Rockefeller and Sabine National Wildlife Refuges in Louisiana (Swaffar, 1993). Since the restocking effort, little information has been obtained concerning alligator populations in Arkansas. Growing evidence, such as increased sightings and interactions with humans, suggests that populations throughout Arkansas are increasing.

However, little empirical data exist to support this claim. To date, no published information concerning alligator populations or habitats is available for Arkansas.

In order to determine the current distribution of alligators within Arkansas, a telephone survey of AGFC personnel was incorporated in a geographical information system (GIS). Personnel from AGFC district offices and 24 AGFC wildlife officers were questioned about the occurrence of alligators in their respective areas. Responses typically provided information on known populations of alligators and also information about particular nuisance alligators. Potential alligator habitat identified in the Arkansas GAP project final report (USGS, 1998) was also included in the GIS. Additionally, ongoing research conducted by the authors, through the Arkansas Forest Resources Center (AFRC), provided information on several localities.

Information on potential habitat and alligator distributions from the Arkansas GAP project, the survey of AGFC personnel, and the authors' ongoing research were layered onto a county level map of Arkansas using ArcView 3.1. Layered data were then used to help identify areas, based on the combination of potential habitat and known localities, within the state that may have the highest concentrations of alligators. These areas were then delineated using heads-up digitizing in ArcView 3.1.

The Arkansas GAP data indicates that potential alligator habitat within Arkansas occurs largely in the Gulf Coastal Plain and Delta regions of the state (Fig. 2). Most of the habitat follows river and stream drainages such as the Arkansas, White, Ouachita, Saline, Red, and Sulphur rivers and Barholomew and Dorcheat Bayous. In addition, Millwood Lake, Grassy Lake, Lake Columbia and several other smaller lakes were also identified as containing alligators. Using information from the telephone surveys, a total of nine state wildlife management areas (WMA), three national wildlife refuges, three state parks, and one national memorial within Arkansas were identified as having alligator populations (Fig. 3). In addition to locations within protected areas such as WMAs, state parks, and national wildlife refuges, other specific alligator locations were also identified by AGFC personnel. Many localities occur on privately owned land or lakes within the state (Fig. 4). GIS analysis of the available data suggest five areas as potentially

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Fig. 1. Region containing the largest native population of alligators at the beginning of a restocking effort by the Arkansas Game and Fish Commission in 1973.
Fig. 2. Potential distribution of alligator habitat within Arkansas as identified by the Arkansas GAP project (USGS 1998).
Fig. 3. Selected public lands within Arkansas with reported locations of alligators or alligator populations.
Fig. 4. Reported locations of alligators or alligator populations occurring on private lands within Arkansas.
Concentrations of American Alligator Populations in Arkansas

Fig. 5. Areas within Arkansas believed to have the highest concentrations of alligators.
having the highest numbers of alligators within the state of Arkansas (Fig. 5).

Area 1: Lower Arkansas River / White River (Fig. 5) is located in the east central portion of the state. AGFC managed lands within this area include Dagmar, Wattensaw, Bayou Meto, and Trusten Holder WMA’s. Arkansas Post National Memorial and White River National Wildlife Refuge are also located within this area. Other locations that were identified within this area include Peckerwood Lake and Clear Lake.

Area 2: Bayou Bartholomew (Fig. 5) is located in the southeast corner of the state. AGFC managed lands within this area include Cut-Off Creek and Seven Devils WMA’s. Lake Chicot State Park also occurs within this area. Several other alligator locations were also identified. These include Lake Grampus, Bayou Bartholomew, McCones Brake, and Perkins Slough. Complaints about nuisance alligators are fairly common within this area. Alligators are known to invade aquaculture ponds found throughout this region.

Area 3: Ouachita River (Fig. 5) is located in the south central portion of the state. AGFC managed areas with alligator populations within this area include Sulphur River and Bois D’Arc WMA’s. One state park, Millwood State park, also occurs within this area. During the 1970’s this area contained the only known population of alligators in the state. Because of this and an abundance of suitable habitat, the number of alligators within this area is potentially higher than the other four areas.

Area 4: Red River / Sulphur River (Fig. 5) is located in the southwest corner of the state. AGFC managed areas with alligator populations within this area include Sulphur River and Bois D’Arc WMA’s. One state park, Millwood State park, also occurs within this area. During the 1970’s this area contained the only known population of alligators in the state. Because of this and an abundance of suitable habitat, the number of alligators within this area is potentially higher than the other four areas.

Area 5: Upper Arkansas River Valley (Fig. 5) is the northern most area identified in this study and is the smallest. Two AGFC managed areas, Gallia Creek WMA and Petit Jean WMA, occur in this area. Holla Bend National Wildlife Refuge also contains an alligator population. This population is a result of AGFC stocking. Two bodies of water within Petit Jean WMA, Fullen Pond and Kingfisher Lake, are also known to contain alligators.

Based on the Arkansas GAP data, 47 of the 75 counties in Arkansas contain potential alligator habitat. The majority of this potential habitat is located in the southern half of the state and is found in and along the major river drainages. Information compiled during this study conforms to the Arkansas GAP data. Much of the existing land that is considered to be alligator habitat is located on public land. The majority of these areas are WMA’s that are controlled by AGFC. There are many other areas within the state that do contain alligators. A large male was found dead in Craighead County, which is located in the northeastern corner of the state (Trauth and McCallum 2001). This animal was found at the northwestern extreme of the species range in the United States. Although alligators do occur in many localities within the state, we believe the five areas identified probably harbor the largest populations within the state. Continued management and research should probably focus on these five areas due to their relatively high concentrations of alligators and the resulting potential for alligator-human interactions.

Acknowledgments.—We would like to thank the Arkansas Game and Fish Commission personnel who participated in the telephone interviews. Without this important information, this project would not have been possible. Funding was provided by the Arkansas Forest Resources Center.

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Journal of the Arkansas Academy of Science, Vol. 56 [2002], Art. 1

Christopher L. Watt, Mark F. Roth, and Philip A. Tappe
Abnormalities in the Ozark Hellbender,
*Cryptobranchus alleganiensis bishopi*

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Declines in eastern hellbender, *Cryptobranchus alleganiensis alleganiensis*, populations have been reported in the scientific literature for over 50 years (Swanson, 1948). Nickerson and Mays (1973) provided state-by-state status reviews of the hellbender across its range. These state-level status reviews were updated by Williams et al. (1981). Since then, further reports of declining hellbender populations have occurred throughout the range of the species (Gates et al, 1985; Pfingsten, 1990). Only recently, have population declines in the Ozark hellbender, *C. a. bishopi*, been reported (Trauth et al., 1992; Wheeler et al., 2003).

There have been many putative reasons suggested for the decline of Ozark hellbender populations; among these are over-collection, habitat alteration, fishing, chemical spills, a 100-year flood, lowered dissolved oxygen levels, eutrophication, and water pollution due to industrial, municipal and recreational discharge (Federal Registry, 2001; Trauth et al., 1992; Wheeler et al., 2003). These and other similar studies combined with the limited range of this species have led to the Ozark hellbender being listed as a Federal Endangered Species Candidate (Federal Registry, 2001).

During the data collection for the initial status survey by Trauth et al. (1992) and subsequent studies (Wheeler and Trauth, unpubl. data), occasional notes were recorded regarding the body condition of individual salamanders. A review of these field notes indicated that many of these salamanders had abnormalities (e.g., missing toes, feet, limbs; Fig.1A). Some individuals possessed exposed bones in these regions (Fig. 1B), indicating recent injuries.

From 1990 to 2002, we recorded abnormalities on 8% (17 of 215) of the hellbenders examined. Because we made no consistent effort to record all abnormalities during this time period, this frequency reflects the minimum rate of abnormalities for the Ozark hellbenders examined. This rate exceeds the expected background abnormality rate of >2% (Johnson et al., 1999; Kaiser, 1999). Missing toes, feet, and limbs account for 60% (10 of 17) of the abnormalities we observed. This is comparable to an eastern hellbender population studied in Ohio (Pfingsten, 1990) that reported a 25% overall abnormality rate, in which 80% were related to missing toes, feet, or limbs.

Three peculiar abnormalities were found during our field studies: a hellbender with multiple tumors, a hellbender with a bifurcated hind limb, and a blind hellbender. The hellbender with tumors was found in the Spring River, Arkansas during a 1992 survey (see Trauth et al., 1992). This animal was collected and examined histologically (see Trauth et al., 2002; Harshbarger and Trauth, 2002).

The Ozark hellbender (472 mm total length, TL) with a bifurcated hind limb (Fig. 1C) was found in the North Fork of the White River, Missouri, during our ongoing demographic study. Examination of the field notes revealed this animal was probably the same animal captured at that location during a previous survey (Wheeler, 1999). Split limbs are normally thought to occur during embryonic development, as a result of parasites, chemical contaminants, and resulting interactions between the two (Kiesecker, 2002). Although split limb abnormalities reduce activity in some amphibians (McCallum, 1999), this hellbender appeared unaffected, as it was observed using the anteriorly-positioned leg segment (see Fig. 1C) during normal movements.

A large Ozark hellbender (467 mm TL, 416 g) from the Eleven Point River was determined to be blind. The orbit of the left eye lacked an eyeball, and skin had grown into the empty socket (Fig. 1D). In addition, the right socket was partially covered by skin-covered tissue, and no eyeball was evident. There was no evidence of scar tissue or other markings around either socket to suggest a possible cause of this abnormality. The eyes of the hellbender are small, and little is known about their utility during activity. They presumably have a limited role in foraging (Reese, 1905); however, Beck (1965) and Green (1933) reported hellbenders being caught on artificial lures, and Smith (1907) and Nickerson and Mays (1973) found that food items were taken if moved along the side of the head in front of the eyes. The size of this blind hellbender and the lack of evidence indicating recent injury supported the idea of the lateral line system playing a major role in foraging (Oliver, 1955 cited in Nickerson and Mays, 1973).

Investigation of amphibian abnormalities may elicit hypotheses regarding population declines (McCallum and Trauth, in press); however, distinguishing between unnatural and natural abnormalities can be problematic.
Abnormalities in the Ozark Hellbender, *Cryptobranchus alleganiensis bishopi*

Fig. 1. Photographs of the Ozark hellbender showing abnormalities. A. Feet missing—specimen from the Spring River. B. Exposed bone within digit—specimen from the Eleven Point River. C. Bifurcated limb—specimen from the North Fork of the White River. D. Empty eye socket (see arrow)—specimen from the Eleven Point River.

Intraspecific aggression (Nickerson and Mays, 1973) may account for a high rate of limb abnormalities we observed. One can only assume the limb bifurcation and lack of eyes are two abnormalities that occurred during development.

ACKNOWLEDGMENTS.—We are grateful to the Departments of Biological Sciences and Environmental Sciences, Arkansas State University; Arkansas Game and Fish Commission (AG&FC); United States Fish and Wildlife Service; United States Geological Survey; and Missouri Department of Conservation for permits and financial support. We also thank Charles McDowell, Vernon Hoffman, and Kelly Irwin (AG&FC) for field assistance.
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Federal Registry. 2001. Endangered and threatened wildlife and plants; Review of plant and animal species that are candidates or proposed for listing as endangered or threatened, annual notice of findings on recycled petitions, and annual description of progress on listing actions; Proposed rule. October 30, 2001.


In Memoriam

Harvey E. Barton, 1936 - 2002

Harvey Eugene “Gene” Barton passed away on November 19, 2002, at his home in Doniphan, Missouri. He is survived by his wife, Margaret, of Doniphan, and five children: Richard Barton of Dallas/Ft. Worth, Texas, Jeffrey Barton of Memphis, Tennessee, Larry Barton of Jonesboro, Arkansas, Peggy Wafford of Memphis, and Susan Dryer of Jonesboro. His brother, Berry Stafford of San Francisco, California, and 14 grandchildren also survive him. Funeral services were held November 22, 2003, in Doniphan with burial in Couch, Missouri.

The son of Harvey M. Barton and Ruth H. Wheeler Barton, he was born August 26, 1936, in Couch, Missouri. He married Margaret Clark in December 1954 and served in the U.S. Army until he was honorably discharged in 1958 as a Staff Sergeant.

Harvey attended the then Arkansas State College (ASC) where he received his B.S. in Biology in 1962 and his M.S. in Biology from ASC in 1963. He continued his graduate education at Iowa State University where he received a Ph.D. in Entomology in 1969. As a student of Dr. Don C. Peters, his dissertation research focused on the development of artificial diets for the corn rootworm.

Prior to accepting a faculty position at Arkansas State, Harvey worked for a brief period for the U.S. Food and Drug Administration. He joined the Arkansas State University (ASU) Biological Sciences Department as an Assistant Professor of Zoology in 1967. Shortly thereafter, he recruited a former Iowa State classmate, Dr. Larry A. Olson, to join him as a member of the biological sciences faculty. He retired in 1991 as a full professor after 24 years of service. During this time, Harvey served ASU as a devoted teacher and scholar. His primary teaching responsibilities included general zoology, general entomology and graduate level entomology courses in insect morphology and taxonomy. Those of us, whom he taught and mentored, remember him not only for his high standards and vast knowledge but also for his passion for entomology. This passion was contagious leading several of us into entomological careers.

As a professional entomologist, Dr. Barton’s strengths and research efforts focused on insect taxonomy with a fond interest in the Hemiptera. He published articles in various scientific journals including the Arkansas Academy of Science Proceedings, Journals of the Entomological Society of America, Tennessee Entomological Society and other entomological publications. His avid collecting and curatorial work greatly expanded the ASU Insect Museum. He built an extensive collection of hemipterans, particularly pentatomids, from Arkansas, Missouri and other regions of the southern United States.

Dr. Barton served as the Editor for the Arkansas Academy of Science Proceedings from 1989 - 1992, an onerous but much enjoyed task. In addition to the Arkansas Academy of Science, he held membership in the Entomological Society of America, American Registry of Professional Entomologists, The Coleopterists' Society, Tennessee Entomological Society, The Lepidopterists’ Society, New York Entomological Society, Southwestern Association of Naturalists, and Society of Sigma Xi.

Known as Harvey by his colleagues and former students, and Gene by his family and Missourian friends, we have all been privileged by having known him. He has touched our lives, and we will miss him.

--Lynita M. Cooksey and Larry A. Olson (Professor Emeritus), Department of Biological Sciences, Arkansas State University, State University, AR 72467-0599
John D. Rickett, 1944 - 2002

John Delbert Rickett, a full professor of the University of Arkansas at Little Rock, Biology Department, passed away on 6 April, 2002, the last day of the annual Arkansas Academy of Science meeting where he was to have presided as President. The loss of Dr. Rickett has saddened our department, students, and alumni and the membership of the Academy.

John was born on 12 December 1944 near Ludlow, Missouri. He attended Harding College, Searcy, Arkansas (B.A. Biology, 1966), Southern Illinois University Carbondale, Illinois (M.S. Zoology, 1969), and University of Kansas, Lawrence, Kansas (Ph. D. Systematics & Ecology, 1973). In 1973 John took a position at the University of Arkansas at Little Rock as an aquatic biologist, where he remained for his academic career to be tenured and promoted from assistant to associate rank in 1977 and to full professor status in 1993. He was a talented professor with strong accomplishments in teaching, research, and service. It is fitting to review some of the accomplishments of this remarkable colleague to point out how replacing him will be difficult and why he will never leave our memories.

Good teaching was everything to Professor Rickett. He taught lectures and laboratories in biology, zoology, ecology, limnology, fisheries, and ichthyology. He taught special summer field courses in Tropical Marine Biology at St. Ann's Bay, Jamaica, and a Barrier Island ecology and geology course as an adjunct associate professor of Lamar University, Beaumont, Texas. He taught numerous short courses for gifted high school students at the UALR Summer Science Institute and short courses for teachers on the environment and energy for the UALR College of Education. John never stopped learning, having taken 13 short courses to add new skills and techniques to his very full toolbox. In order to better document his many trips and short courses around the country, and to add material for seminars and his UALR courses, John took several photography courses at UALR and became a professional grade outdoor photographer. This was typical of John as he never did anything that he did not do it well.

Research was also important to Professor Rickett. While at UALR, Dr. Rickett received $258,000 in grants and contract monies. He wrote or co-wrote 16 contract reports, published 22 refereed publications, 21 technical reports, and an additional eight reviews. He authored or co-authored numerous oral presentations at meetings of the Arkansas Academy of Science, Southwestern Association of Naturalists, Arkansas Chapter of American Fisheries Society and American Society of Limnology and Oceanography. Ten of his independent study students presented papers at the Arkansas Academy meetings.

Service was equally important to John. He was a member of the Technical Advisory Board, Arkansas Water Resources Research Center, University of Arkansas from 1989 to present; New Perspectives Committee (renamed Ecosystem Management Advisory Committee) U. S. Forest Service, Ouachita National Forest from 1990 to 1997; Governing Board of Ouachita Mountains Biological Station, established in 1999; and Executive Board of Mississippi basin Interstate Cooperative Research Association (MICRA) from 1998 to present. At UALR, John recently was the Vice President of the Assembly of the College of Science and Mathematics, the Chair of the Humane Animal Care Committee, and the Biology Department Graduate Student Coordinator since its inception.

Complimenting his hectic professional schedule, John was an accomplished musician (serenading students for hours around a field trip campfire), master furniture craftsman, house builder, Sunday school teacher, and philosopher. John loved and spent many hiking and camping trips with his five sons - Paul, Mark, Daniel, James, and Steven. He also adored his wife Shannon and looked forward to spending many years with her.

Most importantly, Professor Rickett was a life member of the Arkansas Academy of Science, the editor of the Academy Newsletter from 1982 – 1988, Academy Secretary from 1989 to 1999, Vice President from 1999-2000, and President at the time of his death. His unbroken string of 20 years of leadership and hard work was surely the glue that helped keep the Academy focused as a state-wide scientific society during these past years. He served as judge of student presentations, chaired numerous sessions, and participated in the business and committee meetings that made things run seamlessly for the rest of us. Dr. Rickett will be missed but will never be replaced.
Publications of John D. Rickett:


Rickett, J. D. 1974. Trophic relationships involving crayfish of the genus Orconectes in experimental ponds. Prog. Fish Culturist 36:207-211.


—James H. Peck and Gary A. Heidt, Department of Biology, University of Arkansas at Little Rock, Little Rock, AR 72204.
List of Associate Editors and Reviewers for the Journal of the Arkansas Academy of Science, 2002

The Arkansas Academy of Science acknowledges the following individuals who served as outside reviewers of manuscripts submitted to the Journal during 2002. The editorial staff extends our heartfelt appreciation for the expertise and assistance provided by our colleagues. Only through your diligent efforts can we continue to produce a high quality publication.

Adnan Al-Shariah, University of Arkansas – Fayetteville
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Renn Tumlinson, Henderson State University
Steven S. Vickner, University of Kentucky
Steve Watkins, University of Missouri - Rolla
Edmond W. Wilson, Harding University
Theo Witsell, Arkansas Natural Heritage Commission
Bin Zhang, Arkansas State University
Correction.—In the article, “Status of Three Plethodontid Salamanders (Genus Plethodon) from the Ouachita National Forest of Southwestern Arkansas” by Stanley E. Trauth and J. D. Wilhide which appeared in Vol. 53, 1999, of the Journal of the Arkansas Academy of Science, there were several errors in Tables 1 - 3 (in the County and the Section, Township, Range columns). In Table 1 (under County), in Locality 8 and 9 - Howard should be Polk; in 20 - 22, 24, 28 - 30 - Montgomery should be Polk, and in 23 and 25 - 27 - Montgomery should be Scott. In Table 2 (under Section, Township, Rang), row 8-S10 should be S23. In Table 3 (under Section, Township, Range), in Locality 12 and 13-R29 should be R28; in Locality 16 and 17-R30 should be R28; in Locality 19.
PUBLICATION POLICIES AND SUGGESTIONS FOR AUTHORS

The JOURNAL OF THE ARKANSAS ACADEMY OF SCIENCE appears annually. It is the policy of the Arkansas Academy of Science that 1) at least one of the authors of a paper submitted for publication in the JOURNAL must be a member of the Arkansas Academy of Science, 2) that only papers presented at the annual meeting are eligible for publication, and 3) that the manuscript is due at the time of presentation. In accordance with this policy, manuscripts submitted for publication should be given to the section chairman at the time the paper is being presented. Correspondence after this time should be directed to David A. Saugey, Managing Editor, U.S. Forest Service, P.O. Box 189, 8607 North Highway 7, Jessville, AR 71949.

Each submitted paper should contain results of original research, embody sound principles of scientific investigation, and present data in a concise and clear manner. The COUNCIL OF BIOLOGY EDITORS STYLE MANUAL, published by the American Institute of Biological Sciences, is an example of a convenient and widely consulted guide for scientific writers. Authors should strive for directness and lucidity, achieved by use of the active voice. Special attention should be given to consistency in tense, unambiguous reference of pronouns, and to logically placed modifiers. It is strongly recommended that all authors 1) inspect the existing format for feature articles and general notes in the JOURNAL OF THE ARKANSAS ACADEMY OF SCIENCE and follow that format while drafting their submission, and 2) submit their manuscript to another qualified person for a friendly review to appraise it for clarity, brevity, grammar, and typographical errors.

Preparation of Manuscript

The author should submit three copies of the manuscript, tables, and figures. A diskette containing manuscript, table and figure files MUST also accompany submitted materials. If at all possible save the document as a Microsoft Word 6.0 document. The figures should be saved as .tif, .jpg, or .eps files. Manuscripts must be double spaced on 8-1/2 x 11 inch bond paper with at least one inch margins on all sides. Do not staple pages together. Do not hyphenate words on the right-hand margin; do not submit word processed copy printed with justified right-hand margins. Set words in italics that are to be in italics (e.g., scientific names). If the manuscript istentatively designated, the author, which author is to receive correspondence and at what address. Correspondence author should also include e-mail address, daytime telephone number and fax number. Minimum font size is 12 for text.

An abstract summarizing in concrete terms the methods, findings and implications discussed in the body of the paper must accompany a feature article. The abstract should be completely self-explanatory.

A feature article comprises approximately six or more typed-written pages. A JOURNAL printed page is equal to approximately three and one-half typewritten pages and the author is assessed a PAGE CHARGE (see Procedure section). A separate title page, including authors names and addresses should be included with the manuscript. Feature articles are divided into the following sections: abstract, introduction, materials and methods, results, discussion, conclusions, acknowledgments, and literature cited. These sections should be centered. Subheadings should begin at the left-hand margin, but more than one subheading should be avoided.

A general note is usually one to five typewritten pages and rarely utilizes subheadings. A note should have the title at the top of the first page with the body of the paper following. Abstracts are not used for general notes.

Abbreviations: Use of abbreviations and symbols can be ascertained by inspection of recent issues of the JOURNAL. Suggestions for uniformity include the use of numerals before units of measurements (5 m), but nine animals (10 or numbers above, such as 13 animals). Abbreviations must be defined the first time they are used. The metric system of measurements and weights must be employed.

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