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Demetra O. Salisbury University of Arkansas, Fayetteville

Ralph K. Davis University of Arkansas, Fayetteville

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A Hydrogeological and Hydrochemical Connection Between the Decatur City Spring and Crystal Lake, Benton County, Arkansas

Demetra O. Salisbury and Ralph K. Davis 118 Ozark Hall University of Arkansas at Fayetteville

Fayetteville, AR 72701

Abstract

Arkansas is ranked nationally in the production of broilers, laying hens, turkey, swine and beef cattle. These animals produce large volumes of waste, which are spread on pasture land as a method of disposal, as well as a source of fertilizer, resulting in nonpoint source contamination of surface water and ground water. One area of concern includes the Decatur City Spring, which provides municipal water for the city of Decatur. A total of eight sites in the surrounding area were monitored routinely for water quality parameters, including pH, specific conductance, and nitrate-nitrogen. Water temperature and spring and lake stage were also recorded. Crystal Lake (site 7), an impoundment of Wolf Creek (site 4) is south and upstream from the Decatur City Spring (site 3). It has been proposed that the city spring and lake are hydrogeologically connected. Additionally, there are two springs, (sites 5 and 6) both northwest and downstream of the lake, below the dam, that provide most of the flow to Wolf Creek. Spring site 1 is downstream from Decatur City Spring on Wolf Creek. Results indicate relatively low, but consistent nitrate concentrations for sites 7 (0.7-1.4 mg/L), 5 (0.4-1.0 mg/L) and 6 (0.2-0.6 mg/L), which are the lake and two springs below it, respectively. These consistent concentrations, as well as the similar periodicities, suggest an association between these three sites. Higher nitrate concentrations are exhibited for sites 3 (2.4-3.0 mg/L) and 1 (2.4-2.9 mg/L), which are the city spring and the spring north of it. There is also correlation in the periodicity of these two sites indicating a relationship between them. Based on similar fluctuations in the hydrochemical data, it can be concluded that Crystal Lake and Decatur Spring are hydrogeologically related. Water flows from Crystal Lake to the two springs below the dam. These springs feed Wolf Creek which is then connected to Decatur Spring via a losing segment just above the spring, hydrogeologically connecting Decatur Spring to Crystal Lake.

Introduction

Agriculture is considered the primary source of pollution for surface water and ground water (Novotny and Chesters, 1981), but it is necessary to provide food and sustain the economy. The degradation of ground water quality in agricultural areas is ubiquitous, but the problem becomes more severe where natural mechanisms to purify the contaminants are lacking. Karst regions are particularly susceptible to pollution problems because there is rapid infiltration of surface water to ground water through the highly permeable limestone. The surface water may contain contaminants such as agricultural byproducts, including animal wastes and fertilizers, which do not have sufficient time to chemically or biochemically degrade because there is less water to host rock contact (Novotny and Chesters, 1981). In these areas ground water may be the source of water for homes and rural communities.

Karst terrain comprises forty percent of the land area east of Tulsa, Oklahoma (White et. al., 1995), and fifteen percent of the United States (Robinson, 1982), including major agricultural states such as Alabama, Arkansas,

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Florida, Kentucky, Missouri and Virginia. Arkansas is ranked nationally in the production of broilers (#1), laying hens (#8), turkeys (#3), swine (#15), and beef cattle (#18) (Cooperative Extension Service, 1994; Arkansas Agricultural Statistics, 1994). These animals produce large volumes of waste which are spread on pasture land as a method of disposal and a source of nutrients for crops. Northwest Arkansas also has extensive carbonate terrain with a limestone that is readily soluble and extensively fractured, and includes many caves, sinkholes and solution channels that make the aquifer particularly susceptible to contamination (Leidy, 1989).

Nonpoint source contamination of surface and ground water in western Arkansas has resulted from the waste spreading operations (Adamski, 1987). The main contaminants associated with the wastes are nitrate-nitrogen, phosphorous and bacteria. Novotny and Chesters (1981) define nonpoint pollution as highly dynamic in random intermittent intervals with the most severe impact during or following a storm event, and the point of entry often cannot be identified or defined. In order to protect the ground water resources, it is necessary to identify the areas and mechanisms by which pollutants can enter the ground water flow system and to develop reliable diagrams of transport of contamination and flow paths within the system (Freeze and Cherry, 1979).

Location

The study area is located near the City of Decatur, Benton County, Arkansas (Fig. 1). The site was chosen because: (1) The area is underlain by carbonate rock which may be susceptible to contamination because of solution channels, secondary fractures, as well as the rapid underground movement of water. (2) The area is headquarters to a growing poultry industry which participates in poultry waste spreading operations in surrounding fields.

The City of Decatur obtains its municipal water supply from a spring about 1.5 miles north of town (Figure 2). The spring is approximately 1500 feet east of Wolf Creek and approximately 1 mile north of Crystal Lake, an impoundment of Wolf Creek. It has been reported that there is a positive correlation between spring level and water level at Crystal Lake (pers. comm., Rick McClain, Water Superintendent, City of Decatur, 1995).

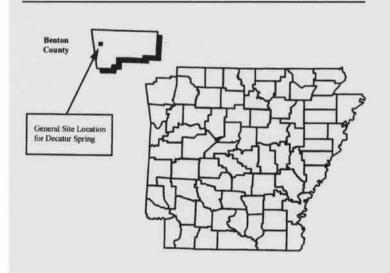


Fig. 1. Location of study area

Purpose and Objectives

The primary objective of this research was to determine if there is a hydrogeological and hydrochemical connection between the Decatur City Spring and Crystal Lake, Benton

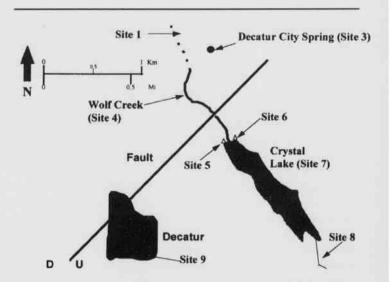


Fig. 2. Location of sites in the study area (modified from Monk, 1997)

Site Number	Site name
1	Spring north of the Decatur City Spring
2	Dried up before testing could occur
3	Decatur City Spring
4	Wolf Creek
5	Spring downstream from Crystal Lake
6	Spring downstream form Crystal Lake
5 6 7 8	Crystal Lake
8	Spring upstream from Crystal Lake
9	Corner Spring

County Arkansas. Secondary objectives were (1) to determine the quality of ground water in the area by analyzing samples from eight sites (Fig. 2) in the study area once a week for ten weeks, and (2) to identify current and potential nonpoint source contributors to contamination if pollution is detected.

Geology

The study area lies along the southern flank of the Ozark Dome and on the Springfield Plateau. Exposed rocks are primarily the St. Joe Formation overlain by the Boone Formation, both of the Mississippian system. In several areas the Upper Devonian Chattanooga Shale is exposed due to undercutting of streams, erosion and dissolution of limestone (Monk, 1997). Rocks are essentially undeformed with only one major mapped fault, Decatur Fault, trending northeast in the area. Decatur Spring is located on the downthrown block of the Decatur Fault and Crystal Lake is

on the upthrown block (Monk 1997). There is also an observed northwest trending lineament, that cuts through the location of Decatur Spring and continues southeast across and normal to the Decatur Fault, and through Crystal Lake. There are also many surface fractures and joints, which act as recharge mechanisms for precipitation entering the aquifer. All the above-mentioned structural features may control the movement of ground water, acting both as conduits and as barriers (Monk, 1997). Their identification is critical in identifying contamination sources and modeling ground water flow.

Upper Devonian Chattanooga Shale.--The Chattanooga is usually a black, carbonaceous, fissile shale, and acts as an effective regional confining unit. It is clayey and generally ranges from 10 to 75 feet thick, with joints trending northeast and northwest. There are areas of bright yellow pyrite present locally. The Chattanooga unconformably overlies Ordovician or Devonian Strata (Leidy, 1989).

Mississippian St. Joe Formation .-- The St. Joe Formation is characterized mostly by lightgray to reddish brown, fossiliferous, chert-free limestone that rests unconformably over the Chattanooga Shale. The limestone shows occasional grading from fine to coarse grains, but it occurs in single beds that are local to a section and cannot be correlated from section to section (Shanks, 1976). According to Shelby (1986) the St. Joe carbonates can be divided into four facies: bioclastic lime mudstone, bioclastic lime wakestone, bioclastic lime grainstone, and bioclastic lime packstone. The St. Joe Formation shows variability in thickness in north Arkansas, ranging from 6 to 84 feet with an average thickness of 45 feet (Shanks, 1976). In Northwestern Arkansas, the St. Joe can be subdivided into four members. In ascending order these include the Bachelor, Compton, Northview, and Pierson. These subdivisions are often hard to differentiate in their lithic zones, but can all be identified in the section exposed below the dam at Crystal Lake. Sites 5 and 6, the springs below Crystal Lake discharge from the St. Joe Limestone and appear to be controlled by the Northview Shale, which acts as a local lower confining unit for these springs (Monk, 1997). There are many joints in this unit trending both northeast and northwest, which may act as structural controls to flow.

Boone Formation.--The Boone Formation lies conformably over the St. Joe Formation, and the boundary is marked by a thin calcareous shale unit (Manger and Shanks, 1977). The thickness of the Boone is variable due to active erosion (Shelby, 1986) and ranges from 50 feet to 375 feet (Leidy, 1989).

The Boone Formation is divided informally into two segments designated as upper and lower, primarily differentiated by the type of chert development with the contact being a conformable one (Shelby, 1986). Dark colored chert, formed at or near the time of deposition, comprises the Lower Boone, while the Upper Boone contains light-colored, later diagenetic chert formed by replacement processes (silica replacing carbonate sediment) after deposition (Shelby, 1986).

The Boone formation is important to this study because the Decatur City Spring flows out of the Upper Boone.

Materials and Methods

The following chemical parameters were evaluated for all water samples:

Temperature °C pH Conductivity µS/cm Nitrate-N mg/L Alkalinity mg/L Chloride mg/L Temperature, conductivity, pH and alkalinity analyses were done in situ.

Samples were collected in 500 mL plastic bottles, placed in coolers, and brought to the laboratory for chemical analyses. The sample bottles were cleaned in the laboratory prior to collection and were then rinsed three times at each site, before each sample was taken. The methods of analysis for each parameter are as follows:

- Temperature: Temperature was measured in the field with a digital conductivity meter, which contained an internal thermometer. The accuracy was $+/- 0.1^{\circ}$ C.
- pH: pH was measured in the field using an Orion digital pH meter with an accuracy of 0.01 pH units. The meter was calibrated with pH 4 and pH 10 buffer solutions prior to each day's use.
- Conductivity: Conductivity was measured in the field using a digital conductivity meter with an accuracy of +/- 5%. The meter was calibrated with a standard solution prior to each field visit.
- Nitrate-N concentrations were determined Nitrates: in the lab within the recommended 24 hour holding period (U.S. EPA, 1976). Samples were first filtered using 45 µm media pads. The samples were then analyzed using the Hach Company colorimetric cadmium reduction method utilizing NitraVer 5 nitrate reagent. Twenty-five milliliters of sample were pipetted into each of two 1/2 inch spectrophotometric cells. One cell, the sample blank, was placed into Hach DR/2000 direct reading spectrophotometer set at 500 nm. NitraVer 5 reagent powder was added to the second cell. The cell was shaken for one minute and allowed to stand for 5 to 14 minutes before inserting it into the spectrophotometer to determine the transmittance. The accuracy of the nitrate test is determined to be +/- 0.5 mg/L.

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Alkalinity: Alkalinity concentrations were determined in the field. Fifty milliliters of sample were pipetted into a beaker. The sample was brought to 100 mL by the addition of deionized water. Phenolphthalein was added to the solution. All samples remained colorless at this point indicating the phenolphthalein alkalinity was zero. One bromcresol greenmethyl red indicator powder pillow was added to the mixture, turning it green. The solution was titrated with 0.02 N standard sulfuric acid until the solution turned a light blue-gray. The accuracy of the alkalinity test is determined to be +/- 1 mg/L.

Chloride:

Chloride concentrations were determined utilizing the Hach Company mercuric nitrate methods (Hach Company, 1995) using mercuric nitrate standard solution (0.0141 N) and dipenylcarbazone reagent powder. The reagent powder was added to 100 mL of sample and mixed with a magnetic stirrer. The mixture was then titrated with 0.0141 N mercuric nitrate standard solution until the color changed from yellow to a light pink. The mL of titrant was multiplied by 0.10 to determine the chloride concentration in mg/L. The accuracy of the chloride test is determined to be +/- 1 mg/L.

Results and Discussion

Nitrates.--Nitrate-N concentrations (Fig. 3) occur in ground water primarily due to agricultural processes such as waste spreading and application of fertilizers (Hem,1992). Where concentrations are elevated, adequate denitrification has not occurred. The background nitrate concentration in Northwest Arkansas is 1 mg/L or less (Adamski, 1996).

In the study area, Corner Spring (site 9) had the highest nitrate concentrations probably due to agricultural activity in the surrounding fields. The concentrations exhibited at this site are somewhat unique to the rest of the study area. Corner Spring discharges west of the Decatur Fault where the outflow passes across the Fault zone about two miles southwest of Wolf Creek. A portion of this higher nitrate water may be infiltrating into the ground water along the fault. It would then follow the regional gradient to the northeast and may represent one source of higher nitrate water entering Wolf Creek in the area below the Crystal Lake dam.

The spring (site 8) upstream from Crystal Lake is probably connected to the lake (site 7), as supported by the correlation coefficient of 0.76. The spring has a higher average

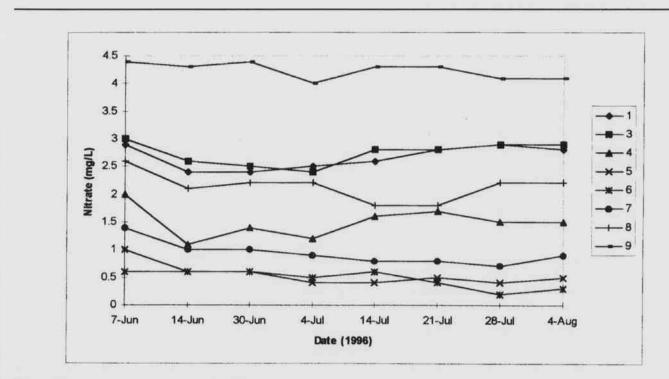


Fig. 3. Nitrate concentrations for the study area

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Sites Correlated	Nitrates	Conductivity	Temperature	рН	Chloride	Alkalinity
8-7	0.76	-0.63	0.97	-0.04	8E-04	0.074
7-5	0.95	-0.17	0.96	0.436	0.639	-0.075
7-6	0.58	-0.7	0.95	7E-04	0.687	0.236
5-4	0.56	0.96	0.95	0.459	0.353	-0.052
6-4	-0.032	0.57	0.93	0.177	0.447	-0.239
5-6	0.45	0.66	1	0.359	0.272	0.593
4-3	0.78	0.92	0.97	0.577	-0.11	0.498
3-1	0.88	0.42	0.99	0.769	0.051	-0.141
3-7	0.15	0.18	0.98	0.496	-0.34	0.278

nitrate concentration, 2.13 mg/L. than the lake, 0.938 mg/L, where denitrification presumably occurred primarily due to nitrate uptake by plants in the lake.

Correlation coefficients (Table 1) support the conclusion that water seeps from Crystal Lake to the two springs below it (sites 5 and 6), further denitrification occurs, due to uptake by plants and transport through the lake sediments. A significantly larger correlation between sites 7 and 5 (correlation coefficient: 0.95) and a smaller change in the average concentration of nitrate-N of 0.39 mg/L, suggest that there may be a shorter transport time between sites 7 and 5 than between sites 7 and 6. Spring temperature fluctuations also support this interpretation. The water from the two springs below the lake flows into Wolf Creek (site 4) where nitrate concentrations increase by approximately 1 mg/L. The increase is probably due to the agricultural activities occurring in the surrounding fields.

Wolf Creek is then connected to the Decatur City Spring (site 3) via the Decatur Fault running perpendicular to the creek, supported by the correlation coefficient of 0.78 and dye trace work conducted by Monk (1997). Average nitrate-N concentrations increase from 1.5 mg/L to 2.7 mg/L, from the creek to the spring. Site 3 also displays the second highest range in nitrate-N concentrations. This is probably due to agricultural activities in the surrounding fields. North of the Decatur City Spring is another spring (site 1) with the same average nitrate-N concentrations as the Decatur City Spring.

The Decatur City Spring and Crystal Lake have a wide variation in nitrate-N concentrations over the summer. While the two sites may be connected, the differences in chemistry and low correlation coefficient may be indicative of the indirect flow path from the lake to the spring, and the increasing agricultural activity downstream. As water flows from the lake to the spring, it first travels to the two springs below it (sites 5 and 6), which then feed Wolf Creek (site 4). As the water moves from Wolf Creek to the Decatur City Spring, it picks up nitrates as base flow from the adjacent aquifer. Thus, the hydrochemistry of the lake is different from the hydrochemistry of Wolf Creek below Crystal Lake.

Conductivity.—Conductivity (Fig. 4) is the ability of a substance to conduct an electric current (Hem, 1992). Conductivity is caused by the presence of ions (charged particles) in solution and is dependent upon temperature. An increase in ion concentration causes an increase in conductivity; pure water has a very low electric conductance.

Conductivity values decrease an average of 111 μ S/cm as water flows from the spring upstream (site 8) from Crystal Lake to the lake. The decrease at the lake probably occurs because it has a greater input from surface water sources which have had less water/rock interaction. From other chemical analyses, such as nitrate-N, it appears that water seeps from the lake to the two springs (sites 5 and 6) below it, where the conductivity values are elevated, consistent with water/rock interaction, as the water moves through the lake sediments and the limestone aquifer to the two springs.

Correlation statistics (Table 1) support the observation that water flows from sites 5 and 6 into Wolf Creek (site 4). Conductivity values decline at Wolf Creek although not as significantly as observed at the lake. This reduction in conductivity in Wolf Creek is another indication that water is entering the creek from another source, probably the adjacent aquifer.

From Wolf Creek to the Decatur City Spring (site 3), there is an average increase in conductivity values. of 38 μ S/cm. The short rise can be attributed to increased agricultural activities, a short transport time, and water/rock interaction. The connection between these two sites is supported by the correlation coefficient of 0.9.

The conductivity values at site 5 increase over the course of the summer. This may be due to increased iron which can be seen as a precipitate in the water emanating from the spring. The source of the iron precipitate is probably the pyrite (FeS_2) present in the Pierson Shale Member of the St. Joe Formation. The reason for the anomalous temporal increase is unknown.

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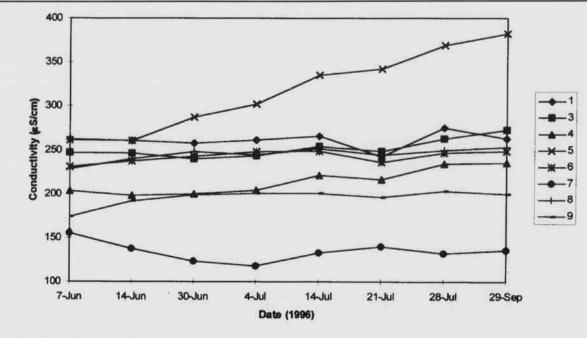


Fig. 4. Conductivity values for the study area.

Temperature.--Water temperature (Fig. 5) is lowest at the spring upstream (site 8) from Crystal Lake (average: 13.9° C) and highest in the lake. Crystal Lake (site 7) had the highest temperature range (average: 25.4° C) over the testing period due to solar heating.

From the lake to the first spring below it (site 6), the temperature range of the water decreases (average 15° C), although not to the level observed at site 8, suggesting less time for thermal equilibration and more surface water contribution. The temperature also decreased at the second

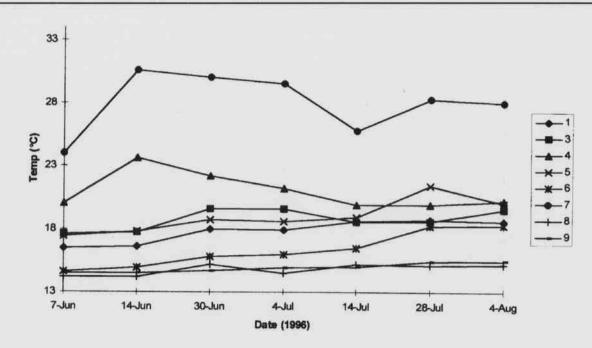


Fig. 5. Temperature values for the study area.

spring below the lake (site 5), suggesting more surface water contribution, or shorter residence time, than occurs at site 6. The high variance at site 5 may also reflect the increased surface water contribution, which if it is the lake, as hypothesized, was erratic as observed in Fig. 5. The correlation coefficient between the lake and sites 5 and 6 are 0.96 and 0.95, respectively.

The temperature at Wolf Creek (site 4, average: 18.8° C) decreased over the testing period, due to a greater ground water contribution, probably from sites 5 and 6, and the adjacent aquifer. The correlation coefficient between Wolf Creek and Crystal Lake, the surface water components of this study is 0.8. This high correlation value is probably due to analogous solar heating at both sites.

There is a decrease in temperature from Wolf Creek to the Decatur City Spring, due to underground transport and equilibration with the aquifer, with an average temperature of 16.7° C. The range in temperature at the Decatur City Spring was the highest observed, (17.6 - 19.6° C), suggesting significant connection between surface water in Wolf Creek and the spring. The water temperature also decreased at site 1.

pH.--The pH (Fig. 6) of a solution is the measure of the hydrogen ion activity. The activity is controlled by interrelated chemical reactions that produce or consume hydrogen ions (Hem, 1992).

The pH at spring (site 8) upstream from Crystal Lake is neutral to slightly basic (average: 7.7). Downstream from site 8 at Crystal Lake (site 7), the pH increases (average: 8.5) to the most alkaline solution in the area. The increase can be attributed to decaying organic matter in the lake and to agricultural pollution. The anomalous decrease on 14-Jun may be attributed to experimental error. The correlation coeffficient between these two sites is insignificant. This may be because there is not a steady rate of decay of the organic matter.

There is an average decrease in pH of 1.25 from Crystal Lake to site 5, one of the springs below the lake. There is also a decrease in pH of 1.28 from Crystal Lake to site 6, the other spring below the lake. There is no pH correlation between either spring and the lake, or between the springs themselves.

The pH values at sites 5 and 6, which have been observed to flow into Wolf Creek is more acidic than those at Wolf Creek. This is anomalous because spring water, which reacts with carbonate bedrock should be more alkaline. Iron oxides were observed to be precipitating from both springs 5 and 6 over the course of the project. In addition, a strong hydrogen sulfide odor was noted at site 6. The water at both springs was undergoing reduction-oxidation changes. As the water passes through the lake sediments it becomes anoxic and iron, probably from pyrite weathering, goes into solution. When the water discharges from the springs it is oxygenated and the iron precipitates. The water at both springs is in disequilibrium which may account for the lower pH at these sites. Compared to Wolf Creek, there is a decrease in pH at the Decatur City Spring (site 3). The correlation coefficient between the Decatur City Spring

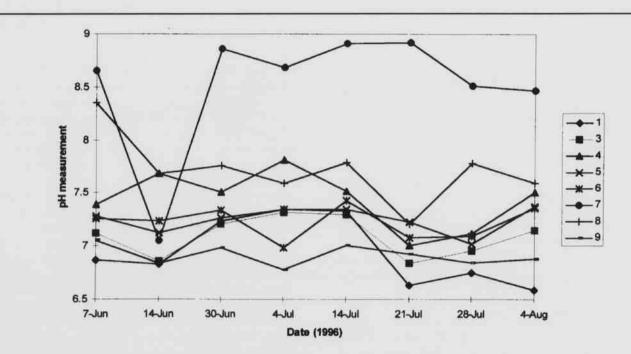


Fig. 6. pH values for the study area.

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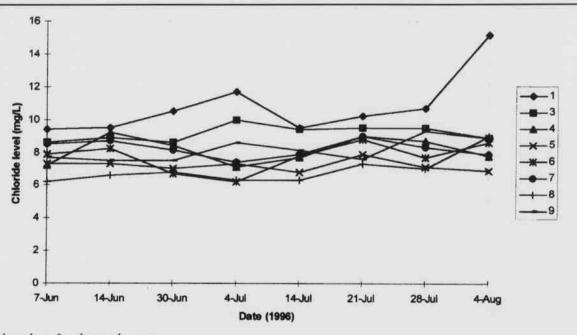


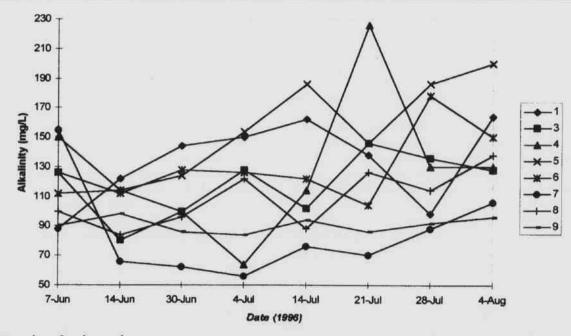
Fig. 7. Chloride values for the study area.

(site 3) and the spring north (site 1) of it is 0.8 and there is only a 0.1 variance in values, indicating these two sites are probably connected.

Chloride.--The chloride (Fig. 7) form of chlorine is the only oxidation state of significance in water exposed to the atmosphere. Chloride is present in all natural waters, but generally the concentrations are low. Chloride can be

accounted for by rain, snowfall or leaching of sediments, although the third reason is less significant than the previous two (Hem ,1992). The chloride ion is also a conservative ion, which means it does not readily react with any other molecules present in the water sample.

Chloride concentrations for the spring (site 8) upstream from Crystal Lake are the lowest in the study area (average:





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6.9 mg/L). As the water moves downstream to Crystal Lake (site 7) there is an average 1.3 mg/L rise in chloride concentrations. The chloride ions may be introduced from surrounding fields as the water is transported from site 8 to site 7. The correlation coefficient between Crystal Lake and the two springs below it are 0.6 and 0.7 respectively, while the average change is 1 and 0.4 mg/L. The change in chloride concentrations from sites 5 and 6 to Wolf Creek is 0.9 and 0.4 mg/L, respectively.

There is an increase of chloride concentration of approximately 1 mg/L from Wolf Creek to the Decatur City Spring (site 3). The source of these chloride ions is probably the surrounding pasture land. As the water flows to the spring (site 1) north of the Decatur City Spring, the chloride concentrations remain about the same until the end of the testing period when there is a 2 mg/L differential. The increase may be indicative of an increase in agricultural activity, such as the use of animal waste as fertilizer (Adamski, 1987).

Alkalinity.--The alkalinity (Fig. 8) of a solution is defined as the capacity for solutes it contains to react with and neutralize acid. In most natural waters the alkalinity is produced by the dissolved carbon dioxide species, bicarbonate and carbonate (Hem, 1992). On examination of the alkalinity data, no definite trends could be established.

Summary and Conclusions

Based on hydrochemical and hydrogeologic data, it can be concluded that Crystal Lake, Wolf Creek, and the Decatur City Spring are hydrogeologically connected. Water flows from the lake to the two springs below it, often providing the only outflow from the lake. From the springs, the water flows into Wolf Creek, which is then connected to the Decatur City Spring via a losing segment, on the downthrown side of the Decatur Fault.

The data collected in this research also displays the impact of agriculture, specifically animals, on the ground water in the area. Five sites (sites 1,3,4,8,9) have concentrations of nitrate-N, greater than the observed background concentrations for non-agricultural areas of the Ozark Dome. Ground water flows out of the spring (site 8) upstream from Crystal Lake with an elevated nitrate-N concentration. The presence of pollutants is also indicated by the high conductivity values for this site. Water/rock interaction may be an additional source of high conductivity values. Denitrification occurs in the creek flowing out of site 8 and in the lake, resulting in lower nitrate-N concentrations at Crystal Lake.

Further denitrification occurs as the water passes through the lake and lake bottom sediments to the two springs (sites 5 and 6) below the lake. Increased conductivity values due to water/rock interaction, further substantiate that water flows from the lake to the springs. The temperature also dropped significantly in the transport system suggesting a relatively long residence time between the lake and the two springs. This may represent the time needed for the water to flow through the fine grained lake bottom sediments.

As the water flows from sites 5 and 6 into Wolf Creek (site 4), nitrate-N concentrations increase significantly, probably due to an observed increase in the agricultural activities in the surrounding pastures, where aerial photographs show more that twenty poultry houses within a one mile radius.

Wolf Creek is then connected to the Decatur City Spring via a losing segment just above the spring. Nitrate-N concentrations are further elevated. This is in correlation to an increase in agricultural activities in the vicinity of the spring. A slight increase in conductivity values can be attributed to water/rock interaction.

Agriculture is having an impact on the quality of ground water that supplies the City of Decatur. This becomes apparent with the rise of nitrate-N concentrations in ground water in the areas with surrounding pasture lands. To protect the ground water resources in this area, it was necessary to identify the areas and mechanisms by which pollutants enter the ground water flow system, and the ways the contamination spread.

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