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Rapid Reduction of Nitrate Ion In Rain Water

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In the past 10 years, there have been numerous studies of the effect of delayed analysis or storage before analysis on the measured concentrations of several chemical species found in precipitation, with the major emphasis on the changes in free acidity (Galloway and Likens, 1976; Madsen, 1982; Keene and Galloway, 1984; de Pena et al., 1985; Mahendrappa, 1985; Sisterson et al., 1985; Chan et al., 1987; Tang et al., 1987; Bigelow et al., 1989). Only two of these reports identify the consumption of nitrogen (N) species as a significant problem associated with samples that had been stored for some time before nitrate [N(V)] analysis. Mahendrappa (1985) compared nitrate analyses of rainwater performed upon collection with those performed on samples after cold storage and on samples that were stored in the field. Storage time was as long as a month. Decreases in nitrate concentration as large as 50% were observed during storage. In a study comparing event samples with weekly samples, de Pena et al. (1985) found an average 14% decrease in nitrate in the time period between the event and the collection of weekly samples.

Alteration of pH has most often been attributed to dissolution and reaction of basic compounds contained in suspended solids or to the microbial oxidation of organic acid anions. It is possible that alteration of nitrate concentration may be attributable to microbial reduction also.

Michaelis-Menten (pseudo-zero order) kinetics are observed in most cases of the bacterial reduction of N(V) in soil. However, when concentrations of substrates are so low as not to saturate the enzyme, the reaction is first order in N(V) (Bowman and Focht, 1974).

The reduction of N(V) in rainwater may be connected to the reduction of N(V) in soils. The association of metal ions in rainwater with agricultural/soil sources has been confirmed by the PCA analysis of wet deposition (Hooper and Peters, 1989). Abnormally high concentrations of metal ions may be an indication of the inclusion of soil or soil water components into rainwater.

This laboratory studied 62 rainfalls that occurred in the 19 month period beginning in January, 1987. The original purpose of this study was to examine the dilution effect of rainout on the major ionic species found in rainfall and the relationships between these species. During this study, 7 samples were observed in which a significant reduction of nitrate ion occurred in a storage period of

days rather than weeks. Rates of loss were greater than those cited above by more than an order of magnitude. These rapid losses have implications for the interpretation of N(V) concentrations in rainwater. It is the purpose of this report to bring to the attention of investigators of within-event precipitation chemistry the possibility of nitrate loss in fractions taken early in a rainfall.

The sampling site was in a residential area of the central region of Jonesboro, Arkansas, a city of 48,000 surrounded by agricultural land. The collector was located at the center of a 12 m x 9 m area free of overhead obstacles. There was no problem with wind carried debris except when wind velocity exceeded 40 km h⁻¹, conditions that did not occur during any of the events described below. Nor was the problem of rainwater rebounding from trees or structures ever observed.

The rainwater was collected using a 25 cm diameter polyethylene funnel placed at a height of approximately 1 m above the ground. The rainwater was immediately transferred to a 250 mL polyethylene bottle. For each event described herein, the funnel was washed to remove dry precipitate usually immediately before the rain event began but no longer than 5 h before the onset of rainfall so that contamination from this source was minimized.

Rainwater was collected as sequential fractions within each event. A small aliquot was taken for pH measurement and the rest immediately refrigerated at 5°C. Generally, each fraction was equivalent to 2 - 6 mm of rainfall.

Within 24 h of collection all samples were filtered through a pre-weighed 0.45 µm membrane filter. For the 1988 samples, a fiberglass prefilter was used in addition to the membrane filter. Since there was, initially, no expectation of observing any reduction of N(V), the sample bottles were used as storage containers after being cursorily washed to remove any adhering solids, rinsed with distilled water, and drained. The filtrate was returned to that bottle and placed back in refrigeration at 5°C until the initial anion analysis was completed. This cursory washing of the sample bottles, without sterilization, may have led to the discovery of the effect described herein since trace catalysts adhering to the walls may have a part in this effect.

All analyses reported in this study, except those done by ion chromatography (IC), were performed according to standard methods (Franson, 1980). Analyses of the

concentrations of the nitrate and nitrite ions were performed by the cadmium reduction method and/or IC using Varian a 5000 liquid chromatograph equipped with a Wescan 269-001 anion column and using an elutant of 1 mM phthalic acid adjusted to a pH of 4.8 to 5.0. A UV detector at 250 μm was used. The pH was determined using a glass electrode. The metal ions were determined using atomic adsorption (AA).

The IC and the spectrometers were recalibrated after every 8 to 10 samples. Samples spiked with standard solution were regularly analyzed. The average percent recovery of the spike in N(V) samples was 96.8% for the samples described herein; for the metal ions, recovery averaged 98%.

In 1988 care was taken to examine samples of high solids content and high metal ion concentration for the presence of N(III) and/or significant decreases of N(V) with time from collection. Concentrations of the N species were determined within hours of collection and again 11 to 28 days later.

The rainwater samples discussed here constitute a subset of a total of 288 fractions collected from 62 rain events sampled between January, 1987 and July, 1988. In the period from February, 1987 to July, 1988, 94 fractions from 23 rainfalls were analyzed for N(V) at two different times. Five of the 23 rainfalls yielded 7 atypical samples, i.e. fractions which exhibited a rapid decrease in N(V) concentration (Table 1).

Table 1. Analyses of Precipitation Samples Exhibiting a Detectable Reduction of N(V) during Storage, 1987-1988, and the volume weighted average (VWA) for the first fraction of all rainfall samples. The concentration of all ions is given in $\mu\text{eq L}^{-1}$.

Sample	VWA	14-1	14-2	27-1	27-3	57-1	58-1	59-1
Date Collected		870503	870503	870910	870910	880417	880503	880513
Date, Analysis 1		870504	870505	870927	870927	880422	880516	880516
Date, Analysis 2		870505	870506	880105	880105	880503	880527	880527
Solids (mg/L)	20	103	37	9.2	25.2	<2.0	69	53
pH, Analysis 1	4.00	4.78	4.49	3.91	3.35	3.92	---	5.26
pH, Analysis 2		---	---	---	---	4.20	5.29	5.44
N(V), Analysis 1	80	110	26	64.3	38.9	36	61	200
N(V), Analysis 2		69	19	2.1	1.4	26	<1	169
NH ₄ ⁺	34	---	---	<3	59	103	53	96
K ⁺	30	223	394	37	2.8	7.3	330	46.3
Metal Cations	153	732	642	373	43.6	77.3	566	440
K ⁺ /Na ⁺	1.0	1.1	2.7	1.1	0.48	0.24	8.5	0.50
Estimated k (d ⁻¹) at 22°C		0.741**	0.32*	0.034	0.033	0.030	>0.45	0.015
* * at 5°C								

** at 5°C * = determined from five data points - = not determined

Five of the atypical samples were the first fractions collected from the rain event. In the 3 atypical samples in which the rate constant (k) for the reduction was greater

than 0.3 d⁻¹, the concentrations of solids, total metal cations (Na, K, Ca, and Mg), and K/Na, were significantly greater than the volume weighted average concentrations of those species in all 62 first fractions.

Of these atypical samples, the most notable and the most thoroughly studied was the first fraction from the fourteenth rainfall sampled (designated 14-1), collected on 5 May 1987 (designated here as 870505). For this sample, IC analyses for N(V) were performed on each of the four days subsequent to collection, revealing that the amount of nitrate ion was decreasing rapidly with time. The decrease in the concentration of N(V) with time since collection for sample 14-1 is illustrated in Fig. 1, along with the best fit line determined by regression analysis. The regression analysis of the data for fraction 14-1 indicates that the ln C plot provides the best fit ($R^2=95.0\%$), suggesting first order kinetics which is expected for the reduction of N(V). The rate constant is (0.741 ± 0.098) d⁻¹. The rate constant for sample 14-2 was estimated from two points to be 0.32 d⁻¹, smaller but still indicative of rapid reduction. These values are all the more striking since both samples were stored at 5°C from the time of collection.

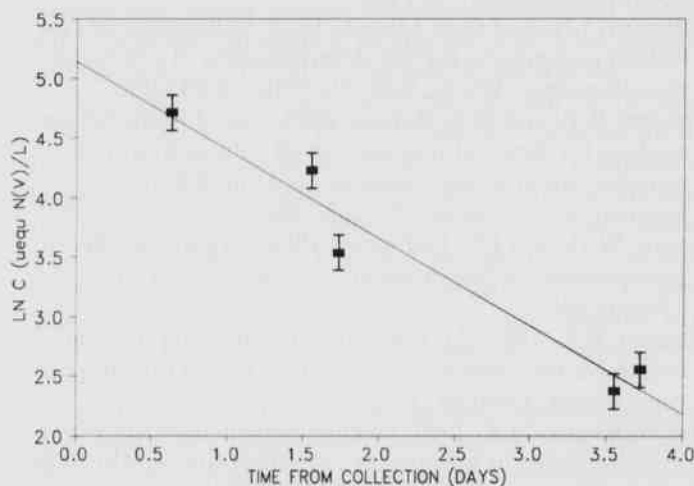


Fig. 1. Concentration of N(V) as a Function of Time from the Collection of Sample 14.1.

The other five samples were stored at 22°C between analyses. Their first order rate constants for disappearance of N(V) were also estimated from just two time separated concentration measurements. The rate constants ranged between 0.015 and >0.45 d⁻¹. In contrast, the mean rate constants for typical samples was 0.004 d⁻¹.

A study of the conditions under which nitrate ion

becomes an oxidizing agent in rainwater is warranted by these findings.

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Literature Cited

- Bigelow, D.S., D.L. Sisterson and L.J. Schroder.** 1989. An interpretation of differences between field and laboratory pH Program/National Trends Network Monitoring Program. *Environ. Sci. Technol.* 23:881-887.
- Bowman, R.A. and D.D. Focht.** 1974. The influence of glucose and nitrate concentrations upon denitrification rates in sandy soils. *Soil Biol. Biochem.* 6:297-301.
- Chan, W.H., A.J.S. Tang, D.H.S. Chung and N.W. Reid.** 1987. An analysis of precipitation chemistry measurements in Ontario. *Environ. Sci. Technol.* 21:1219-1224.
- de Pena, R.G., K.C. Walker, L. Lebowitz and J.G. Micka.** 1985. Wet deposition monitoring - effect of sampling period. *Atmos. Environ.* 19:151-156.
- Franson, M.A.H.,** managing editor: 1980, *Standard Methods for the Examination of Water and Wastewater*, 15th ed., APHA-AWWA-WPCF, Washington, D.C., 1134 pp.
- Galloway, J.N. and G.E. Likens.** 1976. Calibration of collection procedures for the determination of precipitation chemistry. *Water, Soil, Air Pollut.* 6:241-258.
- Hooper, R.P. and N.E. Peters.** 1989. Use of multivariate analysis for determining sources of solutes found in wet atmospheric deposition in the United States. *Environ. Sci. Technol.* 23:1263-1268.
- Keene, W.C. and J.N. Galloway.** 1984. Organic acidity in precipitation of North America. *Atmos. Environ.* 18:2491-2497.
- Madsen, B.C.** 1982. An evaluation of sampling interval length on the chemical composition of wet-only deposition. *Atmos. Environ.* 16:2515-2519.
- Mahendrappa, M.K.** 1985. Precipitation chemistry affected by differences in location of collection sites and storage methods. *Atmos. Environ.* 19:1681-1684.
- Sisterson, D.L., B.E. Wurfel and B.N. Lesht.** 1985. Chemical differences between event and weekly precipitation samples in northeastern Illinois. *Atmos. Environ.* 19:1453-1469.
- Tang, A.J.S., W.H. Chan, D.B. Orr, W.S. Bardswick and M.A. Lusic.** 1987. An evaluation of the precision, and various sources of error, in daily and cumulative precipitation chemistry sampling. *Water, Soil, Air Pollut.* 36:91-102.