Heavy Metal Content of Rainwater in Geneva, New York During Late 1982*

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Two topics of concern in atmospheric pollution are the acidity of rain and the possibility of heavy metal contamination. Acidity is caused by the reactions of oxides of nitrogen and of sulfur with water, leading to the ions H^+, NO_3^-, and SO_4^{2-} in rain (COWLING 1982). Heavy metal contamination may come from dust, ocean spray, combustion and industrial wastes. An effort to determine the natural background of such pollution has been reported in which cores of glaciers were examined for their ion content (JOSEPHSON 1982). Much work has been carried out to determine the origins and transport of man-made pollution (NATIONAL ACADEMY 1981).

Many previous studies of metal ions in the atmosphere have collected samples of particles by filtering air (BEGNOCHE and RISBY 1975, SUGIMAE 1975). Although these studies show what substances are suspended in the atmosphere, they do not show directly what falls out of the atmosphere at any particular place. Further, no correlation with the precipitation acidity is possible in such studies. Several networks of precipitation sampling stations have been developed which have measured ionic content of precipitation but not heavy metals (COWLING 1982, MUNGER and EISENREICH 1983).

We have tried to provide a more or less complete determination of the precipitation-borne pollution fallout in a rural setting that has not been included in the established networks. Rainwater samples were collected at a relatively isolated site near Geneva, New York from September through December 1982 and at another similar site starting in late November. The samples were analyzed for 19 metallic (or metalloid) elements, NO_3^-, SO_4^{2-}, pH, and conductance.

MATERIALS AND METHODS

Samples were collected by clamping a polyethylene funnel (26.0 cm internal diameter) at a height 2 meters above the ground to a fence post. The funnel tip was jammed tightly into a 500 mL polyethylene bottle. The collection bottles were rinsed with distilled water before use. Most samples were taken at a weather monitoring station maintained by the New York State Agricultural

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Experiment Station two miles west of Geneva. A few samples were taken one mile north of Dresden, New York, 14 miles south of Geneva. The sample collectors were left out continuously. However, if no rain fell for several days, the collector was rinsed with distilled water and a fresh bottle was put out.

Samples were weighed and stored at room temperature, approximately 20°C. The pH of each sample was measured.

The concentration of nitrate was determined by measuring the absorbance at 202 nm. Although chloride and sulfate ions have absorption bands nearby at shorter wavelengths, these are sharp and do not overlap the nitrate band appreciably. The absorbance at 202 nm is related to the concentrations of these ions by the equation: $A = k\ell c$ where values of k at 202 nm are 0.152, 4.6 x 10^{-4}, and 4.1 x 10^{-5} mLμg^{-1}cm^{-1} for NO_3^-, Cl^-, and SO_4^{2-}, respectively, and path length ℓcm and concentration c μg/mL.

The concentration of sulfate was determined by a nephelometric procedure (SOTERA 1979). A sample of 25 mL rainwater was mixed with 2 mL $BaCl_2$ reagent in a 50 mL beaker. The mixture was then poured into a 10 cm optical cell which was placed in the light beam of an atomic absorption spectrometer. The total scattering was measured at 422.7 nm (calcium lamp) for the five minutes between 5 and 10 minutes after mixing. The solutions were stable during this period and the turbidities were constant. The measurements were calibrated with Na_2SO_4 samples up to 14 μg SO_4/mL, which bracketed the rainwater samples. The $BaCl_2$ reagent contained 5% $BaCl_2 \cdot 2H_2O$, 1% gelatin, and was 0.006$\underline{M}$ in HCl.

Electrical conductivity was measured with a Chemtrix Type 70 Conductivity Meter. The meter was calibrated with a series of KCl solutions and standard reference data (KOLTHOFF and ELVING 1965, WEAST 1969).

The samples were analyzed for 19 elements with an inductively coupled plasma emission spectrometer (ICP), model Plasma-100 by Instrumentation Laboratory Inc. Samples were aspirated directly into the instrument with no chemical treatment. Each sample was analyzed twice; first within two weeks of collection, and second about six weeks after collection; no significant changes were found. The ICP was calibrated with a solution prepared from commercial standards (Fisher Scientific Co.).

Six soil samples were analyzed for cadmium by ICP. Three soil cores were taken at the weather monitoring station; two to depths of 25 cm and one to 15 cm. Three other soil cores had been taken from an orchard nearby; two in 1975 to depths of 10 cm, and another at one of the same sites in 1978 to 25 cm. The cores were in 5 cm segments, so these six cores comprised 22 separate samples. The soil was dried in air, ground with a mortar and pestle and sieved. Material that passed through a 100 mesh sieve (diameter less than 149 x 10^{-6}m) was used. Samples of one gram were boiled in 30 mL HNO_3 for 3 hours, diluted to 200 mL with

water, and allowed to settle. The clear supernatant solution was analyzed for cadmium at 214 and 226 nm.

A pond water sample was taken near the weather monitoring station. The cadmium concentration was measured in the same manner as rain water.

RESULTS AND DISCUSSION

The results for rainwater are shown in Tables 1 and 2. The data in Table 1 are cumulative values for various collection periods. For example, all of the results for September have been combined although 12 separate samples were obtained in that month. The periods used for November and December were chosen to allow a direct comparison between the two collection sites. The collections ended December 16 because of cold weather. Sulfate concentrations were not measured in the August and September samples. Table 2 is a list of 13 elements which were sought by ICP analysis but were generally not found. In the smallest samples, measurable but small concentrations of Mn and Ni were found but usually these and the other elements listed were not detectable. Table 3 shows weather conditions and cadmium concentrations for selected individual samples.

The specific conductance of each sample was measured. The values were in the range 8 to 120 μmho cm^{-1}. These are not listed but are discussed below.

The cadmium concentrations found in the soil samples showed no variation with depth to 25 cm. The 13 samples from the three cores taken at the weather monitoring station had an average concentration of 3.4 ± 0.4 μg Cd/g soil. Mean values for the two orchard sites were 4.0 ± 0.6 and 2.9 ± 0.5 μg Cd/g soil. The two cores taken at the same orchard site in 1975 and 1978 gave nearly identical values, 4.0 μg/g. The concentration of cadmium in the pondwater was 0.000 μg/mL ± 0.001 at each of the three wavelengths used for the ICP measurement.

The collection funnels used were as efficient as the official rain gauge at the principal collection site. During this experiment, a total rainfall of 8.85 inches was reported, while we collected a total mass of 11.92 kg rain. These numbers imply an effective inner diameter of 26.0 cm for the collection funnel; direct measurement gives an average value 26.1 cm. The effect of biological debris on ion concentrations in rainwater collected in open containers has been shown to be negligible (LEWIN and TORP 1982).

The analytical results for each sample may be tested for completeness or accuracy in two ways; the concentration-weighted ionic charges should add to zero, and the conductance calculated for the known ionic concentrations should equal the measured conductance. Both of these conditions were examined with the samples obtained after October 1. The total positive normality for H^+, Ca^{2+}, Mg^{2+}, Cd^{2+}, Zn^{2+} and Fe^{3+} was compared with the total negative normality

576

Table 1. Ionic content of rainwater.

Collection Interval	Mass (kg)	$<pH>$[3]	H^+[4]	Ca[5]	Mg[5]	Cd[5]	Zn[5]	Fe[5]	P[5]	NO_3^-[6]	SO_4^{2-}[6]
8/26-31[1]	0.36	4.02	6.5	118	33.6	22.3	1.9	1.4	43.3	0.81	---
9/1 -30[1]	2.80	4.30	26.3	374	88.1	24.7	7.2	5.0	90.3	2.31	---
10/1 -31[1]	1.82	4.56	9.4	359	76.4	17.6	13.3	2.4	33.0	1.01	1.63
11/1 -20[1]	4.22	4.30	39.8	234	46.2	28.7	18.0	2.9	11.2	2.04	2.66
11/21-30[1]	1.77	4.18	22.2	30	6.6	71.7	39.2	3.8	7.8	0.74	1.28
12/1 -16[1]	0.93	4.33	8.3	50	9.6	22.8	1.3	2.2	8.6	0.49	0.62
11/21-30[2]	1.66	4.20	19.7	33	7.2	18.1	2.9	5.0	0.0	0.52	0.95
12/1 -16[2]	0.70	4.34	6.0	73	13.8	4.5	0.5	3.8	2.7	0.39	0.51

[1] Collected at NYSAES weather station, Geneva, New York.
[2] Collected at Dresden, New York.
[3] $<pH>$ = - log (total moles H^+/total volume collected).
[4] Moles H^+/hectare.
[5] Grams of element/hectare.
[6] Kilograms of ion/hectare.

Table 2. Elements sought by ICP analysis but not found.

Element	Detection Limit[1]	Element	Detection Limit[1]
Ba	.002	Ni	.01
Sr	.02	Cu	.005
Ti	.002	Al	.05
V	.002	As	.05
Cr	.004	Sn	.05
Mn	.003	Pb	.04
Co	.005		

[1] Detection limit in µg/mL in rainwater. A concentration of
0.01 µg/mL is equivalent to a total fallout of 23.4 g/hectare
in this sampling period, or 6.3 g/hectare/month.

for NO_3^-, SO_4^{2-}, and $H_2PO_4^-$. The negative normality is systemati-
cally larger by $(4 \pm 2) \times 10^{-5}$ N, which is 20% of the average sum
of the positive and negative normalities. This difference is
equivalent to 1 µg/mL of doubly charged ions of atomic weight 50
and may occur in several ways. The sulfate or nitrate measure-
ments may be systematically too large, or the elements listed in

Table 3. Selected weather data and cadmium concentrations.

		Geneva			Wind			Dresden	
Date	Mean Vector[1]	Distance[2]	Direction[3]	Rain[4]	Mass[5]	Cd[6]		Mass[5]	Cd[6]
8/25	0.76	58	300	10	135	0.721[7]			
8/26	8.34	146	250	2	100	0.003[7]			
8/27	4.98	81	210	0					
8/28	7.07	120	240	4	43	1.52[8]			
9/3	5.43	86	220	19	305	0.093			
9/4	8.30	128	230	2					
9/5[9]	5.30	81	230	0	25	0.261			
9/11[9]	2.81	43	150	0					
9/14	8.84	98	130	0	115	0.003[7]			
9/15[9]	2.61	76	130	69	970	0.070			
10/1[9]	3.82	73	170	2					
10/4[9]	3.54	89	220	0	20	0.884			
10/9[9]	6.08	92	220	0					
10/12[9]	10.97	123	130	45	463	0.004			
11/25[9]	6.41	---	225	9					
11/29	15.18	---	140	33	511	0.673		570	0.049
11/30	6.87	---	230	3	112	0.009			
12/14	8.50	---	140	0					
12/15	5.91	---	150	0	150	0.013			
12/16	7.81	---	140	25	390	0.248		512	0.020

[1] Miles per hour.
[2] Time integral of wind speed measured 1.5 feet above ground.
[3] Degrees from north.
[4] Hundredths of inch measured in rain gauge.
[5] Grams of water in our collectors.
[6] Cadmium concentration in rain in μg/mL.
[7] No rain; collector was rinsed with distilled water.
[8] Maximum Cd concentration observed.
[9] Average conditions from this date to the next collection date.

Table 4. Linear Correlation Coefficients.

	H^+	Ca	Mg	Cd	Zn	Fe	P	NO_3^-	SO_4^{2-}
H^+	1.000								
Ca	0.064	1.000							
Mg	0.004	0.979	1.000						
Cd	0.241	0.431	0.428	1.000					
Zn	0.067	0.102	0.061	0.055	1.000				
Fe	0.401	0.002	0.078	0.073	0.134	1.000			
P	-0.074	0.395	0.504	0.013	-0.049	0.449	1.000		
NO_3^-	0.511	0.748	0.739	0.365	0.078	0.365	0.546	1.000	
SO_4^{2-}	0.082	0.840	0.852	0.067	0.259	0.302	0.672	0.771	1.000

Table 5. Relative Concentrations of Metal Ions in Atmospheric
          Precipitation and Particles, and in Fly Ash (Fe = 1).

Ca	Mg	Al	Fe	Zn	Cd	Sample and Ref.
65.	15.0	0	1	4.5	10	Rain. This work.
1.5	0.2	0.9	1	0.13	.002	NBS SRM 1648; Urban Particles (GREENBERG 1979).
...	...	...	1	0.12	.001	Atmos. particles in Rio de Janeiro (TRINIDADE et al. 1981).
2.4	0.3	...	1	0.29	0	Atmos. particles in central Pennsylvania (BEGNOCHE and RISBY 1975).
...	...	...	1	0.10	.003	Atmos. particles in Japan (SUGIMAE 1975).
1.6	1.0	3.1	1	0.006	0	Coal fly ash (CAMPBELL et al. 1978).
0.8	0.2	2.1	1	0.004	2×10^{-5}	NBS SRM 1633; Coal Fly Ash (FAILEY et al. 1979).

Table 2 may add to some significant concentration even though each
is small, or the ICP results may be systematically low, or the pH
determination may be systematically high, or other ions that were
not looked for may be present. In connection with the last point,
three samples were tested for sodium emission but none was
detected. The samples were not tested for ammonium ion, and
chloride was assumed to be unimportant since it has been shown to
be absent from Adirondack snow (GALVIN and CLINE 1978).

The second overall constraint on the results is provided by the
conductance measurements. The specific conductance of each sample
was calculated with the experimental concentrations and published
single-ion equivalent conductivities at 20°C (KOLTHOFF and ELVING
1965). The average difference between calculated and observed
specific conductance values is 0.64 ± 2.1 μmho cm^{-1}. The sign of
this error implies that our concentration measurements were too
large by approximately 10^{-5} $\underline{N}$, assuming ions of equivalent conduc-
tivity 64. This error is about one fourth that found in the
charge balance above, but of opposite sign.

The method of collecting and of storing samples which we used may
have led to small losses of some metal ions by adsorption.
SUBRAMANIAN et al. (1978) reported losses of Al^{3+}, Fe^{3+}, Mn^{2+} and
Pb^{2+} comparable to our detection limits (Table 2), while Cu^{2+},
Cd^{2+}, Cr^{3+}, Ni^{2+}, and Sr^{2+} were stable at pH < 4.

The acidity of the rainwater varied from pH 3.6 to 7.3 with over-
all average 4.2 in agreement with COWLING (1982) for this region.
A value of pH 4.02 has been reported for Geneva, NY (LIKENS and
BORMANN 1974). Particulate matter which was obtained a few times
by rinsing the collector with distilled water was somewhat basic.

This usually acted to raise the pH of light rainfalls. However, the two most acidic rains were among the lightest. In heavy rains, the water collected later was generally less acidic and freer of other ions than the first to fall. This effect has been noted by DAWSON (1978) and by GASCOYNE and PATRICK (1981) in samples taken during rain storms. The extra acidity in the average rain at pH 4.2, compared with that in distilled water at pH 5.6, would require 2.9 kg $CaCO_3$/hectare/month to be neutralized in soil.

The concentration of cadmium is surprisingly large, especially in a few samples where values up to 1.52 μg/mL were found. To be more certain of these concentrations, three emission lines for cadmium were used in the ICP program; 214.4, 226.5, and 228.8 nm. The results from these lines agreed within $\pm$ 0.005 μg/mL. The graph of rainfall as a function of wind direction during our sampling period shows two maxima, a large one at $135^\circ \pm 10$ and a lesser one at $295^\circ \pm 10$. The wind directions and distances for samples with high cadmium concentrations are shown in Table 3. There is a coal-fired electric generating station and a processor of transition metals at Dresden, NY, 15 miles southeast of our collector. To see if one of these facilities might be the source of cadmium, we placed a second collector one mile north of Dresden in late November (Table 1). There is no correlation between cadmium concentrations in the Geneva and Dresden samples, and further, in the samples taken on 11/29 and 12/16, the Geneva concentrations were much higher than those in Dresden (Table 3). Apparently cadmium did not fall into our collector without rain (8/26 and 9/14 in Table 3), so it must be associated with very fine particles. The four highest concentrations of cadmium (8/28, 10/4, 11/29, and 12/16) are associated with approximate directions and distances of 200° and 140°, and 100 to 200 miles. These correspond to the Buffalo, Erie, Cleveland industrial corridor to the west and to northern New Jersey and New York City to the southeast. The correlation matrix (Table 4) shows no correlation between cadmium and any other ionic species.

The cadmium concentrations and distribution found in our soil samples and pond water imply that the apparent cadmium fallout in rain is either a very recent development or simply a fluctuation. The total cadmium fallout we observed, 188 g/hectare for 114 days, is equivalent to an annual accumulation of 0.6 μg Cd/g soil in the top 5 cm horizon. Although this is approximately our detection limit, if this rate of accumulation were maintained for many years a vertical gradient in the cadmium concentration would be expected (ATEN et al. 1980). However, the total cadmium concentrations found in these soils is only about six times this annual fallout and no gradient was detected. Finally, the absence of cadmium from the pond water, when compared with the average concentration in rain of 0.083 μg/mL, again supports the conclusion above.

The relative concentrations of principal metal ions found in rainwater, atmospheric particulates, and fly ash are compared in Table 5. Two large differences are apparent between our results

and the others. First, our samples contained much higher ratios of both calcium/iron and magnesium/iron than has been found in urban particles or in fly ash. Probably this is due to our rural environment and came from dust blown from agricultural fields. Second, the cadmium/iron ratios in our samples are abnormally high. We do not know the source of cadmium. We plan to continue collecting samples through the spring and summer of 1983 to see if the high cadmium fallout continues.

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