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# Heavy Metal Content of Rainwater in Geneva, New York, During 1983

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A survey of heavy metals in rainfall at this location was reported earlier (Aten et al. 1983). The salient features of the results of that study were that Ca and Mg were the most prevalent elements and were strongly correlated while the concentrations and absolute amounts of Zn, Fe, and P were small and not well correlated. The total amount of Cd found was surprisingly large but was poorly correlated with anything else. The present study is a partial repetition of the earlier one over the time interval March through October 1983, and included measurements of the pH and specific conductance of rainwater, as well as the concentrations of 19 elements. Special attention has been paid to detection limits in order to identify which elements were regularly below the detection limits. No measurements of anion concentrations were included in this study.

## MATERIALS AND METHODS

Samples were taken, as reported previously (Aten, et al. 1983), with an open polyethylene funnel attached to a polyethylene bottle and were collected immediately after rainfalls. During June two samples of dry deposition were taken by rinsing the collector with distilled water. For each sample the mass, pH, and specific conductance was measured and the concentrations of 19 elements were determined by inductively coupled plasma emission spectroscopy (ICP)(Plasma 100; Instrumentation Laboratory Inc.); element concentrations were determined by using three emission lines for Cd and one line for each other element. All water samples were analyzed directly by the ICP with no special preparation.

## RESULTS AND DISCUSSION

The ICP results for 79 samples were obtained in 13 analysis sessions with each sample being analyzed twice in different sessions. Thus, there were 158 determinations of each elementary emission line. A single determination by ICP consisted of six readings which was printed as an average concentration, C, and the standard deviation of the six readings, Q. Since it appeared that several elements were not present in measurable concentrations, it was desired to reduce the data in a way that would provide a systematic comparison with the noise level of the instrument in the measurements.

Accordingly, the following quantities were calculated for each element (except calcium and magnesium):

1. The average concentration
   $$\bar{C} = \Sigma C_i/(79 \times 2)$$
   and its standard deviation, $\sigma$.
2. Within each analysis session the average concentration and its standard deviation, $\sigma_s$, and the average of the standard deviations of the instrument, $Q_s$. The standard deviation of the concentration, $\sigma_s$ was divided by $Q_s$ to provide 13 values of this ratio, which were averaged to obtain $\langle\sigma_s/Q_s\rangle_{13}$.

   The quantities defined above are listed in Table 1.

These results may be interpreted as follows:

If an element were absent, the mean concentration should be zero, within $\pm Q$, and $\sigma$ should approximate $Q$. Thus, $\bar{C} \pm \sigma = 0 \pm Q$. If an element were present, then not only $\bar{C}>0$ but $\sigma>\bar{C}>Q$ should be true. Since the noise levels for some elements varied from one analysis session to another, the criteria above are somewhat crude. A more sensitive comparison of concentration with noise is provided by the quantity $\langle\sigma_s/Q_s\rangle_{13}$ so that the standard deviation in concentration is compared with the mean instrument noise within each session, and the ratios are averaged over the 13 analysis sessions. If an element were absent, $\sigma_s$ and $Q_s$ should be approximately equal and the lower limit to $\sigma_s/Q_s$ would be unity. To the extent that an element is present at variable concentrations, $\sigma_s$ will increase, and $\sigma_s/Q_s$ should become larger than unity. The size of $\sigma_s/Q_s$ may be taken as a measure of the probability that the element is present. As shown in Table 1, the lowest $\langle\sigma_s/Q_s\rangle_{13}$ observed is somewhat less than unity, near 0.4. It seems safe to claim that the elements Co, As, Cr, V, Sn, Pb, Sr, Cu, Al, Ba, Ti, and Ni were not present in our rain samples at concentrations greater than the instrumental uncertainties, $\bar{Q}$ (Table 1). For each of these elements, $\bar{C}$ is well within the interval $0 \pm Q$, and $\sigma \simeq Q$. Note that there is considerable variation in Q from element to element. The mean ratio $\langle\sigma_s/Q_s\rangle_{13}$ varies from 0.4 to 3.3 for this group, consistent with the previous comments. The elements Fe, P, Zn, Mn, and Cd have values of $\langle\sigma_s/Q_s\rangle_{13}$ greater than 5 and, therefore, are present in measurable concentrations. The treatment of the data given above has three obvious drawbacks:

(1) it suppresses a few individual concentrations which were obviously above the detection limit but which were rare occurrences, (2) it does not use effectively the correlation that should exist between the duplicate results, (For example, in eight samples, the determinations of Ni gave good agreement between duplicate runs and the concentrations were well above the noise level. However, in most samples it was clear that the Ni concentration was too low to measure, less than 0.01 mg/L.) and (3) it does not include possible correlation between the marginal elements and those obviously present. The latter item could have been included in our calculations, but was not, since the result

Table 1. Average values from ICP analyses used to estimate the mean detection limit for each element, and to estimate the likelihood that the element is not present at concentrations above the detection limit. Units mg/L

| Element | $\langle \bar{C}$ | $\pm\ \sigma\rangle_{158}^{a}$ | $\sigma_s^{b}$ max. | min. | $Q^{c}$ | $\langle \sigma_s/Q_s \rangle_{13}^{d}$ |
|---|---|---|---|---|---|---|
| Co | -0.0005 | 0.0086 | 0.0134 | 0.0013 | 0.0126 | 0.411 |
| As | 0.0296 | 0.293 | 0.2066 | 0.0136 | 0.2162 | 0.456 |
| Cr | 0.0026 | 0.0135 | 0.0208 | 0.0009 | 0.0168 | 0.520 |
| V | -0.0008 | 0.0030 | 0.0030 | 0.0017 | 0.0017 | 0.532 |
| Sn | -0.0194 | 0.102 | 0.1837 | 0.0084 | 0.1241 | 0.539 |
| Pb | 0.0009 | 0.0515 | 0.1495 | 0.0169 | 0.0607 | 0.592 |
| Sr | -0.0022 | 0.0159 | 0.0257 | 0.0038 | 0.0054 | 0.618 |
| Cu | -0.0065 | 0.0077 | 0.0101 | 0.0024 | 0.0020 | 1.345 |
| Al | 0.0200 | 0.0629 | 0.0783 | 0.0112 | 0.0309 | 1.516 |
| Ba | 0.0009 | 0.0026 | 0.0040 | 0.0007 | 0.0012 | 2.401 |
| Ti | -0.0004 | 0.0104 | 0.0107 | 0.0005 | 0.0019 | 2.835 |
| Ni | 0.0125 | 0.0343 | 0.0556 | 0.0030 | 0.0122 | 3.26 |
| Fe | 0.0138 | 0.0303 | 0.0667 | 0.0028 | 0.0061 | 5.04 |
| P | 0.301 | 0.549 | 0.7040 | 0.0150 | 0.1689 | 5.06 |
| Zn | 0.0168 | 0.0262 | 0.0952 | 0.0083 | 0.0064 | 7.84 |
| Mn | 0.0081 | 0.0102 | 0.0168 | 0.0025 | 0.0009 | 10.96 |
| Cd | 0.0395 | 0.0839 | 0.201 | 0.012 | 0.0068 | 18.8 |

[a] Arithmetic average concentration over 158 determinations of 79 samples with two analyses per sample. The standard deviation of the 158 results is σ.

[b] For each of the 13 analysis sessions the average concentration and its standard deviation was calculated. The maximum and minimum values for these 13 standard deviations are listed.

[c] Average instrument standard deviation over 158 determinations. This may be taken as an approximate detection limit.

[d] Within each analysis session, S, the standard deviation of the average concentration, $\sigma_s$, was divided by the mean instrument standard deviation, $Q_s$. These 13 ratios were averaged to obtain $\langle \sigma_s/Q_s \rangle_{13}$.

would have been ambiguous at best. The monthly cumulative results for the elements that were found ($H^+$, Ca, Mg, Cd, Fe, Zn, Mn, and P) are shown in Table 2. The overall average pH, 4.3, agrees well with the previous years' value 4.2. The samples for July were unusual since during most of the month there was no rain but the collector was left out and was not rinsed. At the end of the month two heavy rainfalls occurred on successive days and were collected separately. The first sample contained the dry deposition for the month plus whatever the rain carried, while the second was a routine rain sample. The first sample was obviously dirty and contained very high concentrations of Ca and Mg. Both samples were virtually neutral, but neither contained an exceptional concentration of any other element.

The internal consistency of the results was estimated by comparing

Table 2. Ionic Content of Rainwater(1983)

| Time(n) | Mass (kg) | $\langle pH\rangle^{a}$ | $(H^+)^{b}$ | $Ca^{c}$ | $Mg^{c}$ | $Cd^{c}$ | $Zn^{c}$ | $Fe^{c}$ | $Mn^{c}$ | $P^{c}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Mar(11) | 2.85 | 4.26 | 29.8 | 345 | 65.3 | 64.3 | 6.1 | 10.7 | 1.75 | 11.7 |
| Apr(12) | 5.13 | 4.37 | 41.0 | 976 | 126.9 | 18.5 | 7.8 | 5.9 | 0.86 | 372.0 |
| May(13) | 4.65 | 4.44 | 31.9 | 988 | 255.8 | 3.5 | 8.8 | 5.7 | 6.71 | 353.0 |
| Jun(10) | 4.34 | 4.09 | 66.6 | 1248 | 307.8 | 17.8 | 27.1 | 24.1 | 10.53 | 65.4 |
| Jul(2) | 0.71 | -- | 0.0 | 1530 | 429.4 | 2.9 | 1.0 | 0.0 | 2.54 | 54.1 |
| Aug(10) | 3.93 | 4.43 | 27.5 | 915 | 220.0 | 15.8 | 23.0 | 11.7 | 5.43 | 336.1 |
| Sep(8) | 2.79 | 4.25 | 29.4 | 536 | 120.7 | 21.4 | 4.0 | 4.2 | 3.68 | 59.6 |
| Oct(9) | 3.52 | 4.44 | 24.1 | 736 | 147.2 | 4.2 | 11.2 | 0.5 | 3.45 | 281.8 |
| $C_v^{d}$ | | | | 1.19 | 0.242 | 0.028 | 0.017 | 0.012 | 0.0063 | 0.288 |

[a] The volume-average pH. For all samples except July, the overall volume-average pH was 4.31.
[b] Mole $H^+$/hectare.
[c] Grams element/hectare.
[d] Volume-weighted average concentration, mg/L. July omitted.

the observed specific conductance with the theoretical value expected assuming that the positive ions were $H^+$, $Ca^{2+}$, $Mg^{2+}$, and $Cd^{2+}$ as determined by the pH and ICP readings, and that the negative ions were $NO_3^-$ and $SO_4^{2-}$ in equivalent concentrations (the mean equivalent conductance was used) and present in concentrations equivalent to the positive ions listed above. The concentrations of Fe, Zn, and P were omitted because their concentrations were usually small and their chemical forms were less certain than the others. Thus, the principal observed positive ion concentrations were used to estimate both the cation and the anion contributions to the specific conductance. The result of this calculation may be represented by the ratio:

(calc'd specific conductance/obs'd sp. cond.) = 0.9 ± 0.2

which implies that there were no large concentrations of other ions overlooked. Obviously, inclusion of Fe and Zn concentrations in the calculation would have raised the ratio slightly.

The linear correlation matrix for the concentrations of Ca, Mg, Mn, Cd, Fe, Zn, P, and $H^+$ is presented in Table 3. The significance of such correlations has been argued recently in an exchange of comments and caution in their use was urged (Charlson et al. 1985). However, several features are interesting and suggestive: (1) Ca and Mg are closely correlated, r=0.95, which implies a common source for these elements, probably agricultural lime. (2) P is somewhat correlated with Ca and Mg but not to anything else. This is consistent with the interpretation that the source of P is agriculture (phosphate fertilizers) but that it is handled independently of lime. (3) Cd, Fe, and Mn are loosely correlated suggesting a common metallurgical origin. (4) Zn and $H^+$ are rather independent with a negative correlation between both Zn and $H^+$ with Ca, Mg, and P.

The mean concentrations of Zn, Mn, and Cd are compared in Table 4

Table 3. Linear Correlation Coefficients.

| | Ca | Mg | P | Mn | Cd | Fe | Zn | $H^+$ |
|---|---|---|---|---|---|---|---|---|
| Ca | 1 | | | | | | | |
| Mg | 0.95 | 1 | | | | | | |
| P | 0.42 | 0.45 | 1 | | | | | |
| Mn | 0.27 | 0.27 | 0.12 | 1 | | | | |
| Cd | 0.15 | 0.07 | -0.11 | 0.28 | 1 | | | |
| Fe | 0.03 | -0.02 | -0.08 | 0.32 | 0.58 | 1 | | |
| Zn | -0.39 | -0.51 | -0.22 | -0.07 | 0.18 | 0.19 | 1 | |
| $H^+$ | -0.23 | -0.23 | -0.28 | 0.02 | -0.02 | 0.15 | 0.08 | 1 |

with values reported in other studies of rainwater. The concentrations of Zn and Mn which we observed, 0.017 and 0.008 mg/L respectively, are comparable to values reported previously. However, our mean cadmium concentration is 50 to 100 times greater than the other values in Table 4. As noted above, the first sample collected in July contained a large amount of soil dust and whatever other dry deposition was available but yielded only a moderate concentration of Cd, 0.025 mg/L. The range of Cd concentrations observed extended to a maximum of 0.53 mg/L, and of the 78 samples taken 24 had Cd concentrations between 0.025 and 0.53 mg/L. Since some local soil samples had been found to contain about 4 µg Cd/g soil, the cadmium concentration of only 0.025 mg /L in the first July sample must mean that the cadmium in soil is not soluble in rainwater but requires an acid digestion; apparently the local soil is not the source of the high cadmium concentrations found in some samples. Further, there must not be an industrial source of cadmium-containing dust or ash nearby because this sample would have contained an appreciable amount of it and could not have given such a low result. In addition, two samples of dry deposition, each collected for one week in June, had cadmium concentrations below the detection limit. The source of cadmium is unknown, appears not to be local, but did not affect samples from the central and southern U.S. which were collected before 1980 (Table 4).

Table 4. Mean Concentrations of Zn, Mn, and Cd in Rain from Different Locations.

| | Concentration (mg/L), volume-weighted mean. | | | | |
|---|---|---|---|---|---|
| Element | a | b | c | d | e |
| Zn | 17 | 10 | 147 | 5.6 | -- |
| Mn | 6.3 | 5 | 22 | 3.6 | 2.5 |
| Cd | 28. | 0.3 | 0.7 | 0.4 | 0.57 |

[a] This work. Geneva, NY, samples taken in 1983.
[b] Struempler (1979). Nebraska, 1973-4. Arithmetic mean.
[c] Thornton and Eisenreich (1982). Minnesota, 1978-9.
[d] Lindberg (1982). Tennessee, 1976-7.
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