STATISTICAL ANALYSIS OF SPATIAL AND TEMPORAL VARIATIONS IN URBAN RAINWATER CHEMISTRY: CHANGES IN pH AND SULFATE ASSOCIATED WITH CLOSURE OF A COPPER SMELTER

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ABSTRACT

The influence of the sulfur dioxides emissions from a large copper smelter in Tacoma, Washington was studied by measuring the chemical composition of rainwater collected upwind and downwind of the source, both before and after the permanent closure of the smelter in 1985. Data analysis was based on a random effects analysis of variance model accounting for fixed effects of 25 sites nested within three geographic classes, a year effect, random effects for 10 storms observed over two years, and residual measurement variation. The test of a smelter closure effect is expressed as a test of an interaction between the class (e.g. upwind/downwind) and year factors in the model. After smelter closure, the upwind/downwind differences in pH and excess sulfate had decreased significantly compared to the pre-closure value. Statistical and substantive issues in the interpretation of these results are discussed.

Acknowledgements

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* Paper delivered by Paul D. Sampson at the International Acid Rain Conference, Lisbon, Portugal, September, 1987.
INTRODUCTION

In this paper, we examine the impact of a large SO$_2$ source on downwind rainwater composition. In general, measurement of this impact is confounded by many sources of variability: temporally and spatially varying emission sources, chemical reactions, background concentrations and meteorological processes, in addition to the inevitable variability due to experimental procedures (1-3). Thus many investigators have failed to demonstrate a significant impact of an individual point source on surrounding rainwater chemistry (4-8).

Measurement of many different events at multiple locations surrounding an individual source would appear to be the most straightforward approach to detecting a pollutant source's impact. Thus, on the basis of 113 rain events sampled within 50 km of the INCO smelter in Sudbury, Canada, Chan and coworkers demonstrated a highly significant (p < .0005) change in the aqueous concentration of hydrogen ion (H$^+$) and of sulfate ion (in excess of its seawater value, SO$_4$(xs)) downwind versus upwind of the source (9). However, in monthly samples taken near the same source, Chan and co-workers (10,11) did not observe a significant difference in H$^+$ or SO$_4$(xs) when the smelter closed for a strike, compared to samples collected during smelter operation. More encouraging are the results of Patrinos and coworkers (12), who observed a statistically significant (p < .05) increase in both H$^+$ and total sulfur species (SO$_4$ plus dissolved SO$_2$) downwind of a coal-fired power plant when using automated, covered collectors for three of five events sampled.

Unlike previous studies, we had the advantage of both time and place. Given a very clean background off the Pacific Ocean, consistent wintertime storm track and storm type, and very few SO$_2$ emission sources, the closure of the major SO$_2$ source, the ASARCO copper smelter, provided a unique opportunity. Our hypothesis was that with careful experimental design we could observe, with relatively few meteorologically pre-selected events, the impact of the smelter on downwind rainwater acid-base chemistry by measuring appropriate chemical species both upwind and downwind, before and after the permanent closure of the smelter on March 23, 1985.

Our experiment included several major steps: 1—careful screening of the raw data for internal consistency; 2—identification of an appropriate geographical subset of the data for testing the smelter impact; 3—examination of the spatial patterns of rainwater concentrations for consistency with emission source locations; 4—determination of the downwind-upwind differences in the concentration of the major acidic species, H$^+$, SO$_4$(xs), and NO$_3$, while the smelter was operating; 5—determination of the same downwind-upwind differences after the smelter closed; 6—calculation of the spatial, temporal, and experimental components of variance in the data; 7—testing of the significance of the change in steps 4–5; and 8—determination of the fraction of the smelter’s emissions which were deposited in the sampling area. Steps 4–7 are based on a random effects analysis of variance model for each of the chemical species. Analysis was complicated by a pair of problems which we discuss below: (a) unbalanced nesting of sites in the upwind and downwind classes, and (b) the fact that data analysis was most appropriately carried out on cube root transformed concentrations while the test of a smelter effect in step 7 is a test of interaction between the upwind/downwind and year factors in the original concentration units.

EXPERIMENTAL DESIGN

Each rain event which we sampled was pre-selected according to criteria that specified winter rains from cyclonic frontal systems with south-southwesterly winds, no convergence, and relatively uniform precipitation over the mesoscale extent of our network. Winter sampling was chosen to minimize variability associated with temperature and cloud type. If a morning forecast (based on 950-500 mb weather maps, NOAA’s aloft soundings at Quillayute on the Washington coast, satellite imagery, and local weather observations) predicted these conditions, the samplers were deployed at noon that same day. Based on our forecasts, fourteen events were sampled during February and March of 1985 and 1986, seven in 1985 during smelter operation and seven in 1986 after the smelter closed. Of these 14 events, 10 were meteorologically consistent with our forecast criteria, with precipitation accumulations of 0.35 to 1.0 cm, and are reported here.
The sampling network consisted of 38 sites located in grassy areas away from overhanging objects, local combustion sources, automobile traffic, and sources of windblown dust. Figure 1 displays a map of the Puget Sound indicating the location of the copper smelter, the urban areas of Seattle, Tacoma, and Olympia, and the sampling sites which are labeled according to a classification discussed below. The sites were operated by University of Washington personnel and trained volunteers from the Seattle Water Department, community colleges, and nearby high schools. Experimental procedures are presented elsewhere (13).

![Map of Western Washington State, USA, with rainwater sampling sites coded by meteorological/source class (see text).](image)

For four storms, 10 collectors were co-located at a site in the center of the network surrounded by a large grassy field in order to generate more detailed information on the magnitude and distribution of the experimental errors (14). This "ten-sampler" experiment was used to identify outliers and screen the paired samples from each site (15,16). An ion measurement was rejected only if the measurement compared poorly with the corresponding value in the co-located pair and it showed a discrepant charge balance. Overall, fifteen percent of the H⁺, SO₄²⁻(xs), and NO₃⁻ data were missing due to failure to collect a sample or as a result of the screening procedures. These were filled by estimation from other samples based on regression for pairs over the data set and the other measurements at the same site, or the measurement at a nearby, correlated (0.6<r<0.95) site (15).

We investigated whether the 38 sampling sites could be organized into classes which were homogeneous with respect to spatial variability in measured ion concentrations. The sampling design included a large number of sites to insure our finding the smelter plume and to gain information about spatial patterns. The grouping of stations in classes represents a simple statistical model of the dominant spatial structure and provides a
convenient (more powerful) basis for significance testing. The sites were classified according to a priori information as to wind direction and the location of the major SO$_2$ emission sources. The site classes were consistent with a multivariate classification based upon smelter related trace metal concentrations determined for two storms during smelter operation (16).

RESULTS

Site Classification

The a priori site classes are labeled on Figure 1 as: 1—upwind of the smelter (Olympia and Tacoma); 2—immediately downwind of the smelter (Vashon Island and South Seattle); 3—downwind of both the smelter and South Seattle (North Seattle and eastward); 9—east of the smelter; and 0—near specific local sources. Samples from classes 0 and 9 had higher values for Ca$^{++}$, V, and/or NO$_3^-$ than the other classes and were deemed distinct ($p<.05$) from samples in the other classes by the multivariate analysis. Class 9 samples may have been smelter influenced (high SO$_4^{2-}(xs)$) but were not considered for further analysis because spatial patterns suggested that an unidentified source may have influenced the results for two storms in 1985. The exclusion of class 9 samples is conservative in the sense that including them in further analysis increases the perceived smelter influence (15).

Table 1. Five-storm unweighted mean concentrations (µeq t$^{-1}$) by year and class$^*$

<table>
<thead>
<tr>
<th>Year/Class</th>
<th>H$^+$</th>
<th>SO$_4^{2-}(xs)$</th>
<th>NO$_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1985/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>14.6</td>
<td>12.1</td>
<td>6.1</td>
</tr>
<tr>
<td>2</td>
<td>28.7</td>
<td>24.3</td>
<td>7.9</td>
</tr>
<tr>
<td>3</td>
<td>22.6</td>
<td>19.0</td>
<td>12.9</td>
</tr>
<tr>
<td>9</td>
<td>24.6</td>
<td>23.2</td>
<td>16.1</td>
</tr>
<tr>
<td>1986/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>7.5</td>
<td>5.9</td>
<td>3.9</td>
</tr>
<tr>
<td>2</td>
<td>10.6</td>
<td>11.3</td>
<td>4.3</td>
</tr>
<tr>
<td>3</td>
<td>12.0</td>
<td>13.5</td>
<td>6.0</td>
</tr>
<tr>
<td>9</td>
<td>8.8</td>
<td>5.4</td>
<td>4.5</td>
</tr>
</tbody>
</table>

$^*$ The overall charge balance for 338 samples, expressed as the arithmetic mean ratio of cation to anion equivalents per sample was 1.24 (median = 1.11).

Rain Chemistry

Table 1 summarizes the observed mean concentrations of H$^+$, SO$_4^{2-}(xs)$, and NO$_3^-$ for all 10 storms. The mean values are not volume weighted and are presented by class and year. Based on contributions to the sample charge balance, H$^+$ and SO$_4^{2-}(xs)$ are the most important ionic species. Three species not shown, Na$^+$, Mg$^{++}$, and Cl$^-$, are present in ionic ratios comparable to seasalt; they also form a single principal component which varies independently from the other major ionic species and therefore can be ignored in an analysis of the smelter's contribution to downwind acid rain. Calcium ion in excess of that in seasalt appears to be the most important base followed by NH$_4^+$. The total base cations (sum of Ca$^{++}(xs)$ and NH$_4^+$) were about 70-90% of H$^+$ in both years. Class 3 had the highest average Ca$^{++}$ concentrations, possibly due to the local influence of a cement plant.

Figure 2 charts the spatial variation in the average concentrations of SO$_4^{2-}(xs)$ before and after smelter closure. The high SO$_4^{2-}(xs)$ concentrations to the northeast and immediately downwind of the smelter during its operation
are not evident in the period after closure. However, note also that there are apparent changes from one year to the next in the region upwind of the smelter. For this reason, assessments of smelter effects cannot be based only on 1985-1986 mean differences for downwind sites; rather, we must test for year×site interaction effects; that is, larger year effects for the downwind class than for the upwind class. A figure for H⁺ concentrations is similar to that for SO₂(xs), but the figure for NO₃ shows no apparent differences in the spatial pattern before versus after the smelter closure.

Figure 3(a) presents boxplots (displaying group medians, quartiles, and range) for the sample distributions of SO₂(xs) by class and year, demonstrating skewness that is most pronounced in class 2 (immediately downwind) samples during smelter operation. To fulfill the basic assumptions of an analysis of variance, i.e., that the residuals have constant variance and be approximately normally distributed, it was necessary to transform the data. A cube root transformation was most appropriate for all three species of interest. Figure 3(b) presents boxplots for SO₂(xs) on the cube root scale.

![SO₂(xs) boxplots](image)

Figure 2. Map of five storm unweighted mean SO₂(xs) concentrations, (a) 1985—before smelter closure; (b) 1986—after smelter closure.

**Variance Components**

We first applied a traditional balanced, mixed effects analysis of variance model (17) to determine variance components associated with storm-to-storm variability, storm×site interaction, and measurement error for rainwater ion concentrations. The measurement variability, estimated from the replicate pairs of samples at each site, includes both sampling and analysis errors. Year, site, and year×site fixed effects terms were also included. The results of this analysis showed that the experimental measurement component was small compared to the other components and could be ignored (15).

This variance components analysis also revealed large random effects for storms. Separate analyses for the different classes of sites suggested different storm-to-storm variability in the different classes, indicating perhaps different storm dependent physical/chemical processes in or below the plume. Ad-hoc tests of the significance of upwind/downwind mean differences could not easily be carried out using means computing from the separate analyses because the estimated upwind and downwind means are correlated by virtue of the random storm effects common to all classes. Such tests could be carried out in terms of an ANOVA model with fixed site effects nested within classes, but the unbalanced nesting pattern (different numbers of sites in the three classes) cannot be accommodated by most traditional ANOVA packages. Fortunately, because the variance component associated with the replicate measurements at sites was small, we could eliminate it from the model by
averaging the replicates. Our model then fit in the framework of a flexible family of random effects models commonly applied to longitudinal (rather than spatial) studies (18). Software available from the Harvard School of Public Health was available to fit the full random effects model, including terms for unbalanced nesting of sites within classes and different storm-to-storm variance components within classes, and to test for year×class interaction effects.

Figure 3. Boxplots for the sample distributions of SO\textsubscript{2}(xx) by class and year, (a) in the original units, µeq t\textsuperscript{-1}, (b) for the cube root transformed data.

The model fitted includes fixed effects for year, class, sites within classes, and year×class interactions. Different random effects were fitted for storms (nested within years) for each of the three classes of sites; this is equivalent to fitting random effects for storms and storm×class interactions. The model can be written down as
\[ X_{ivjk} = m + c_v + s_j(v) + y_i + y_c iv + B_{kv(i)} + E_{ivjk} \]

where

- \( X_{ivjk} \) = the concentration for a given ion expressed on a cube root scale,
- \( m \) = overall fixed mean,
- \( c_v \) = fixed class effect for classes, \( v=1,2,3, \)
- \( s_j(v) \) = fixed effect for site \( j \) within class \( v, j=1,2, \ldots, n_v \),
- \( y_i \) = fixed year effect, \( i=1,2, \ldots \),
- \( y_c iv \) = fixed year-class interaction,
- \( B_{kv(i)} \) = random storm effect for storm \( k \), class \( v \), within year \( i, k=1,2, \ldots, 5 \),
- \( E_{ivjk} \) = residual.

This model assumes that the effects of storms are uniform within classes, but allows them to vary randomly between classes. The residual term effectively includes random storm-site interactions within classes (which is appropriate assuming homogeneous effects within classes) as well as sampling and measurement error.

Table 2 presents the year-class interactions computed by transforming the means on the cube root scale back to original concentration units. It is important to note that there are upwind/downwind differences apparent in both years, presumably due to local urban sources not associated with smelter closure. As explained above, greatest interest lies in the year-class interaction effects for smelter related species, \( H^+ \) and \( SO_4^{2-}(xs) \). These are the "smelter effects," i.e., the change in upwind/downwind difference with year. We would not expect a significant interaction with \( NO_3^- \) because this is not a smelter-emission by-product.

Table 2 also presents the significance level for tests of these interaction effects for each ion. As shown, both the \( H^+ \) and \( SO_4^{2-}(xs) \) interaction effects are significant, whereas the \( NO_3^- \) effect is not. We have chosen to present one-tailed \( p \) values for both \( SO_4^{2-}(xs) \) and \( H^+ \) because these species were expected to decrease in the absence of smelter emissions. The direction of the change in \( NO_3^- \) was not presumed and thus a two-tailed \( p \) value is given.

It is important to note that these tests of interaction were carried out on the cube root transformed concentrations because this was the most appropriate scale of measurement for a normal, random effects ANOVA model. However, the definition of interaction depends on such transformations (19), while our real interest lies in interaction effects defined in original concentration units as expressed in Table 2. (Data displaying perfect additivity in means, i.e. no interaction, on one scale of measurement, would display some degree of interaction on any other nonlinearly transformed scale of measurement.) The interaction (i.e. smelter) effects are greater in magnitude in the original concentration units. \( P \) values for the null hypothesis of no interaction in original concentration units can reasonably be inferred to be smaller (i.e. more significant) than those presented in Table 2. An approach to approximating appropriate \( p \) values for tests of interaction effects on the original scale will be presented elsewhere (20).

The estimated components of variance are given in Table 3. For \( SO_4^{2-}(xs) \) the storm-to-storm variance components are quite comparable across classes, but drop slightly in the year following smelter closure. For \( H^+ \) ion we again find lesser storm-to-storm variance components in year 2, and a residual variance component which is generally larger than the storm-to-storm component (and of comparable magnitude to the residual component for \( SO_4^{2-}(xs) \)). However, the storm-to-storm variability appears to increase across the three classes in year 1. We cannot easily explain this phenomenon; it may be largely a reflection of the large uncertainty in these variance estimates which are, after all, estimated only on the basis of 5 storms.
Table 2. Year by class interaction (i.e. smelter) effects and approximate p-values for tests derived from the random effects model.

<table>
<thead>
<tr>
<th>Ionic Specie</th>
<th>H⁺</th>
<th>SO₄²⁻(xs)</th>
<th>NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1/Class 2</td>
<td>-10.4 (.02)</td>
<td>-7.9 (.05)</td>
<td>-1.1 (.51)</td>
</tr>
<tr>
<td>Class 1/Class 3</td>
<td>-1.3 (.47)</td>
<td>-1.5 (.37)</td>
<td>-3.5 (.26)</td>
</tr>
</tbody>
</table>

* A class 1/class 2 interaction with year is computed, for example, as \((\bar{X}_{11} - \bar{X}_{12}) - (\bar{X}_{21} - \bar{X}_{22})\) where \(\bar{X}_{vi}\) denotes the mean observation for class \(v\) in year \(i\). Means are in original concentration units (μeq l⁻¹) transformed back from the cube root scale.

# One-tailed tests are used, except for NO₃⁻ for which two-tailed tests are used. See text.

Table 3. Estimated Variance Components for Random Effects*

<table>
<thead>
<tr>
<th>Ionic Specie</th>
<th>H⁺</th>
<th>SO₄²⁻(xs)</th>
<th>NO₃⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Storm-to-Storm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1985/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>(.116)²</td>
<td>(.242)²</td>
<td>(.269)²</td>
</tr>
<tr>
<td>2</td>
<td>(.283)²</td>
<td>(.258)²</td>
<td>(.297)²</td>
</tr>
<tr>
<td>3</td>
<td>(.510)²</td>
<td>(.246)²</td>
<td>(.443)²</td>
</tr>
<tr>
<td>1986/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>(.107)²</td>
<td>(.120)²</td>
<td>(.089)²</td>
</tr>
<tr>
<td>2</td>
<td>(.139)²</td>
<td>(.160)²</td>
<td>(.087)²</td>
</tr>
<tr>
<td>3</td>
<td>(.062)²</td>
<td>(.200)²</td>
<td>(.092)²</td>
</tr>
</tbody>
</table>

*Values inside parentheses are standard deviations in the cube root concentration units.

DISCUSSION AND CONCLUSIONS

The influence of the smelter on downwind rainwater acidity during the winter has been demonstrated by this experiment with relatively few events. In contrast to previous studies, we were able to discern the influence of other sources in the downwind field that might have easily been attributed to the smelter had we not made measurements after smelter closure. Interestingly, the influence of local urban sources on rainwater acidity in the Seattle urban area is substantial, its magnitude being such that no smelter influence was observed in this particular region. This same Seattle region had elevated vanadium levels in the three storms we have analyzed to date for this element, thus implicating fuel oil burning as a source of sulfates. We attribute the relative importance of the Seattle sources to the fact that these sources are low-level, resulting in higher concentration level SO₂ concentrations (and thus higher SO₄²⁻(xs) concentrations in rainwater) per unit mass of SO₂ emitted than the elevated smelter source. This hypothesis is consistent with the relatively small fraction of smelter SO₂ emissions deposited within the network. Estimates of smelter deposition (13), computed in the spirit of Chan et al. (9) indicate that from 40 to 80 percent of the deposited excess sulfate up to 60 km downwind during the
winter was from the smelter. Given that the local urban sources, presumably predominantly fuel oil burning, represent a relatively small fraction of the total SO$_2$ emissions within the sampling network, their observed influence on urban rainwater acidity deserves further investigation.

As noted earlier, the residual variance component is an important part of the overall variance of acidic species, being slightly larger than the storm-to-storm variance components. Before transformation to the cube root scale this residual storm-site variability was heterogeneous. We believe that this important, heterogeneous component of the variance of acidic concentrations in rainwater reflects substantial variation in the paths of the plume and in the in-cloud and below cloud SO$_2$ scavenging efficiencies from storm-to-storm, and hence considerable variability in storm effects from site to site. Properly accounting for this variability allows conclusions about the significance of the smelter's effect on rainwater chemistry to be made with relatively few rain events.

The type of random effects statistical analysis carried out here should be relevant for many other studies of environmental monitoring data. The fact that analysis was most appropriately carried out on a transformed scale, while inferences about interaction effects are desired in original units of measurement, is a problem which generally receives little attention. A paper in progress proposes an approximate solution to this problem (20).

The random effects model also provides a basis for computing "residuals" which are appropriate for the investigation of the spatial covariance structure in such mesoscale data. These residuals are the residuals from the estimated fixed effects components in the model (i.e., the random storm effects, and random storm x class interaction effects are not subtracted out). We are currently exploring the hypothesis that covariances between observations at different sites will reflect the predominant meteorological and consequent short-range transportation patterns for the storms sampled. This analysis is being carried out using a new nonparametric approach to spatial covariance estimation (21).

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