The Relationship between Particulate Chemistry and Air Masses in Southern Indiana

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(Manuscript received 26 March 1988, in final form 20 August 1988)

ABSTRACT

The particulate characteristics of the surface layer of the atmosphere over a region of southwest Indiana were determined for forty-two 24-hour periods between September 1985 and April 1986. The water-soluble sulfate, chloride and sodium content of particles classified into mass median diameters (MMD) of 7, 3.3, 2, 1.1 μm and less than 1.1 μm, was related to different air masses.

Atmospheric concentrations of chloride and sodium and the S/Cl and Na/Cl ratios in particles with MMD greater than or equal to 3.3 μm were used to differentiate between maritime and continental air masses. Maritime, compared to continental, air masses had higher concentrations of sulfate in all particle sizes. Both synoptic situations had high concentrations of sulfate-bearing particles with MMD < 1.1 μm and to a lesser degree with MMD 7 μm. It was concluded that the MMD > 3.3 μm particle chloride and sodium were primarily due to sea-salt particles and that the MMD < 1.1 μm and some of the MMD 7 μm sulfate particles in greater concentrations in the maritime air mass air were probably largely due to anthropogenic sources to the south of Indiana.

1. Introduction

Inherent in the development of air masses is the adaptation of the chemical environment as well as the thermal environment to the source regions. Maritime air masses can be expected to contain large particles with high chloride and sulfate content resulting from the incorporation of sea spray aerosol into the resident surface air (Duce et al. 1965, Johansson et al. 1974). On land, chloride particulates are produced from automobile exhaust, road salting, fertilization, soil dust entrainment, and industrial emissions (Hidy 1984). Typically, automobile exhaust and industrial emissions produce small (MMD of 1 μm or less) chloride particulates, whereas road salt, potassium chloride fertilizer, and locally entrained soil produce large particle chloride. As with chloride, large sulfate particulates derive from sea salt spray, fertilization, and soil-dust entrainment. In addition, some oxidized sulfur species may condense on preexisting large aerosols, but the small particulate sulfate is primarily a result of oxidation of sulfur dioxide released by industrial emissions (Cox 1974).

Junge (1963) stated that the chloride particles associated with maritime air are in the 1 to 10 μm diameter range, while particles associated with land-modified air are typically <1.0 μm diameter. Johansson and coworkers (1974) compared the aerosols over north Florida with the marine environment and found that while the nuclei > 4 μm of chloride were distinctly originating from sea spray, the >4 μm fraction of sulfate not only corresponded with marine air, but also with coastal and continental air.

Observation by Crozier and coworkers (1952) and Twomey (1955) indicate that the sea-salt particles can be carried hundreds of kilometers over the continental land mass at altitudes of 700 to 3000 m. Junge (1953) found particles of chloride ranging in size from 0.8 to 8.0 μm diameter increased in concentration in Central Europe with the advection of maritime air, while those 0.08 to 0.8 μm in diameter decreased in concentration. Giant particle sulfate in Hawaii was identified by Junge (1953) as being of sea-salt origin and consistent with the chloride concentration of the same fraction. As the air mass advects over land, the mixing at the boundary layer results in a relatively uniform distribution of sea-salt particles throughout the mixed layer with the exception of the lowest 200 meters where impaction and settling results in lower concentrations (Toba 1965).

Junge (1953) also noted that high concentrations of sulfate in the giant particles were found over industrialized Central Europe as well as over Hawaii. Hardy et al. (1976) studied the particulate environment over Miami, Florida and found that distance from the sea coast corresponded with reduction in large particle (>2 μm equivalent aerodynamic diameter) chloride concentrations and to a lesser extent sulfate concentrations. Patterson and Wagman (1977) found a trimodal distribution of chloride particulates with less than 0.5 μm particles associated with automobile emissions, particulates near 1 μm with sea salt, and larger particulates...
with dredging operations off Seacaucus, New Jersey. Gladney and coworkers (1974) found the chloride in Boston, Massachusetts predominantly due to marine aerosols. When the winds were from inland, the chloride and sodium particulates were in some measure evenly distributed across size classes, whereas they were concentrated in the larger size classes when the winds were from the ocean.

Paciga and Jervis (1976) reported that the particulate sodium and chloride at several sites in Toronto, Canada had a MMD of 4.0 and 0.6 μm respectively during the summer and both had a MMD of 9 μm during the winter. They identified the predominant source of summer chloride as automobile, power, plant, and incinerator emissions. The high winter MMD was attributed to the use of road salt.

Particle size distributions of chloride measured by Lee and Patterson (1969) at sites in Philadelphia, Pennsylvania, Cincinnati, Ohio and Chicago, Illinois in the summer and fall showed all MMDs near 0.85 μm. They concluded that industrial and automobile emissions were the primary source of chloride.

Further evidence of aerosol origin can be gained by calculating the S/Cl and the Na/Cl ratios. Sea salt (as dissolved within sea water) has a S/Cl ratio of 0.05 (Miller et al. 1972), while aerosols derived from sea salt have a S/Cl ratio of 0.59 (Hidy 1984). Typically, soil materials have a S/Cl ratio near 2.0 (Johansson et al. 1974). Hardy and coworkers (1976) used these ratios to substantiate the origins of the measured chloride in Miami, Florida. Crecelsius and coworkers (1980) found a S/Cl ratio of soil crust in Colstrip, Montana of 4.0.

Another useful ratio is that of Na/Cl in sea salt which averages 0.55 (Miller et al. 1972); however, aerosols resulting from seawater entrainment have a lower average, 0.36 (Hidy 1984). Gladney and coworkers (1974) point out that the ratio over land invariably shows a deficiency of Cl relative to that of seawater.

It seems clear that ratios of Na/Cl from 0.36 to 0.55 and S/Cl from 0.05 to 0.59 and the presence of sulfate and chloride particles with MMD > 7 μm are generally accepted evidence of marine origin of particulate material. Low S/Cl can, however, occur in continental air masses when high chloride soils are entrained. Rasool (1973) identifies the soils of the west as likely sources of chloride. The coincidence of giant particulate sulfate with times of local field fertilization provides evidence of potentially contaminated samples. Likewise, high amounts of giant chloride particles collected soon after local use of road salt suggests contamination. Comparison of local surface soil sulfate and chloride content with the analysis of material collected on the sampler may be used to check for soil contamination. After removal of the potentially contaminated samples, the identification of maritime or continental air should be possible given the size distribution and composition of chloride and sulfate-bearing particulates in the atmosphere. This study identifies air masses over southwest Indiana and relates their chemical characteristics across particle sizes to their origin.

2. Methods

Two high volume (HIVOL) samplers and an Andersen five stage impactor located at a farm near Decker, Indiana were run for 24 hour periods at a flow rate of 21.24 cm³ s⁻¹ for the HIVOLs and 9.44 cm³ s⁻¹ for the Andersen sampler, resulting in a sample volumes of 1835.14 m³ and 815.62 m³ respectively. All samplers were mounted at a height of 7 m with a rectangular gabled roof over the intake. The upper size limit for both the Andersen and HIVOL samplers was approximately 30 μm, varying with wind speed (Hidy 1984). The lower limit of collection for the HIVOL sampler using a quartz filter was approximately 0.05 μm. The Andersen cascade impactor sampler had four stages of Whatman 41 filters which separated the aerosol into the size classes with effective cutoff diameters of 7, 3.3, 2, and 1.1 μm, and a last stage (a quartz filter) had with an effective cutoff diameter of approximately 0.05 μm.

Aerosol samples were collected every three and four days (alternating) from 11 September 1985 to 4 December 1985 and every seven days from then until 31 March 1986. All filters were quality-assured prior to and after exposure and cataloged by the Indiana State Board of Health. Quality assurance involved the repeated weighting of dessicated filters for constancy. No sample collections were used in the analysis if: 1) the sampler flow rate deviated by 7% from the previously defined rates, 2) the sample time was less than 1380 min or greater than 1540 min, or 3) the beginning to ending flow rate deviated by more than 10%. Latex gloves were worn during the handling of filters to reduce the risk of contamination by contact with perspiration.

One quarter of each filter was extracted in 40 cc of distilled water by ultrasound for 30 seconds and analyzed using an updated Dionex model 16 ion chromatograph that included a Spectrophysics 4270 integrator, autosampler, and controller. The anions were separated in a A54A separator after passing through MPIC neutral guard and AG1 guard columns. The eluent consisted of a solution of 0.00075 M NaHCO₃ and 0.0022 M Na₂CO₃. A solution of 0.0125 M H₂SO₄ gave baseline suppression. Detection of the anions was by conductivity. The integrator was calibrated after every ten samples with standards of 0.5 and 1.0 ppm Cl combined with 5.0 and 10.0 ppm SO₄ respectively. Integration assumed a linear relationship between the peak area and anion concentration.

Andersen and HIVOL filter blanks (¼ section) were analyzed using the same procedures as above. The average values for the unused filters is given in Table 1. All air concentrations discussed in the following sections have been corrected for the filter blanks. In some cases the filters used in the Andersen sampler lost mass.
Table 1. Concentrations (μg m⁻³)* of ions extracted from unexposed filters (blanks).

<table>
<thead>
<tr>
<th>Ion</th>
<th>7</th>
<th>3.3</th>
<th>2.0</th>
<th>1.1</th>
<th>&lt;1.1</th>
<th>Hi-vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>0.0837</td>
<td>0.0637</td>
<td>0.0837</td>
<td>0.0637</td>
<td>0.0539</td>
<td>0.0311</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.0355</td>
<td>0.0466</td>
<td>0.0355</td>
<td>0.0466</td>
<td>0.0366</td>
<td>0.0720</td>
</tr>
<tr>
<td>Na</td>
<td>0.0078</td>
<td>0.0114</td>
<td>0.0078</td>
<td>0.0114</td>
<td>0.0129</td>
<td>0.0131</td>
</tr>
</tbody>
</table>

* Conversions from ppm to μg m⁻³ based on the sample time for the appropriate filters.

during use resulting in a negative weight gain from exposure. The filter weight loss was apparently due to the loss of fibers during installation, removal and operation. Air concentration results are based only on soluble materials extracted from the filters and therefore not influenced by minor filter loss of mass. When an estimate of total, rather than soluble, particulate mass was needed the HIVOL filter weight was used for comparison. The preparation and chemical analysis procedures of the Andersen and the HIVOL filters were identical, permitting comparisons of sulfate, sodium, and chloride concentrations in the particles collected on the two types of samplers.

The median mass diameter (MMD) of the sulfate, sodium, and chloride bearing particulates was estimated using the Andersen sampler data. The MMD for each element was estimated by plotting the effective cutoff diameters of each collector stage versus the cumulative percent mass greater than or equal to that effective cutoff diameter on log probability paper (Lee and Goranson 1972).

The approximate influence of relative humidity on particle size was estimated using approximation formulas of Fitzgerald (1975) for both unsaturated and saturated atmospheres. It was assumed that: 1) the relative humidity at the earth’s surface was representative of the surface boundary layer and that the diurnal variation is approximately sinusoidal; 2) the chemical bearing particulate distribution is distributed uniformly within a size fraction; 3) the salt aerosol particle could be approximated by pure NaCl properties; and 4) that the first approximation of the influence of relative humidity on particle size could be made based on 20°C solubilities.

The errors associated with impactor sampling such as particle bounce, reentrainment, interstage losses, and overlap of particle size distributions for successive filter stages have not been evaluated in this study. Without knowledge of the relative proportion of dry and wet particles during each sampling period, efficiency of collection cannot be accurately estimated. In general, however, particle bounce and reentrainment may be expected to shift the particle size distribution towards smaller particles.

Surface soil within 100 m to the north, south, and west of the samplers was sampled to a depth of 2 cm. The concentration of soluble Na, Cl and SO₄ in the soil was determined on two samples from each bearing using bulk soil samples centrifuged with 20 ml of distilled water.

Relative humidity (screen) and precipitation estimates for the sampling days were based on the Vincennes, Indiana agricultural weather station operated by the NOAA Midwest Agricultural Weather Service Center. This station was approximately 20 kilometers north of the particulate sampling site. Precipitation days were defined as any day in which precipitation greater than a trace was recorded at the Vincennes site. While spatial variability of precipitation is expected, the precipitation at Vincennes provides an approximation for the potential washout of particulates at Decker, Indiana.

The Daily Weather Maps of the NOAA-National Weather Service were used to classify the air masses prevalent during the times of filter exposure. Checks on the identification of maritime or continental air masses were made using the NOAA-National Meteorological Center FTJ FOUS 24 h trajectory forecasts for 0000 and 1200 UTC on the two days prior to sampling. While errors in trajectory forecasts based on the Reap (1972) model are expected, the broad expanse of the source regions of interest was assumed to reduce the influence of spatial errors on the utility of the results in defining the air masses involved. To account for horizontal displacement, all trajectory forecasts for the Vincennes area were based on interpolation of the trajectory forecasts for Louisville, Kentucky, Peoria, Illinois, and Indianapolis, Indiana. The trajectory forecasts for both the surface and 850 mb were evaluated to determine the air mass classification. Continental air masses were defined as air masses located west and/or north of Indiana during the prior two days. These air masses would therefore include modified maritime air masses from the Pacific Ocean. Maritime air masses were defined as air masses located in the vicinity of the coastline of the Atlantic Ocean or the Gulf of Mexico within the prior two days.

3. Particulate chemistry

The average water-soluble chloride, sulfate and sodium levels of the atmosphere found in particulates collected at a height of 7 meters for the 42 measurement days are found in Table 2. The 0.66 μg m⁻³ average
Table 2. Distribution of chloride, sodium, and sulfate among the five size classes.

<table>
<thead>
<tr>
<th>MMD (μm)</th>
<th>Cl Mean (µg m⁻³)</th>
<th>Cl SD (µg m⁻³)</th>
<th>Na Mean (µg m⁻³)</th>
<th>Na SD (µg m⁻³)</th>
<th>SO₄ Mean (µg m⁻³)</th>
<th>SO₄ SD (µg m⁻³)</th>
<th>Na/Cl Mean</th>
<th>S/Cl Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>0.173</td>
<td>0.180</td>
<td>0.160</td>
<td>0.071</td>
<td>0.517</td>
<td>0.396</td>
<td>2.77</td>
<td>2.22</td>
</tr>
<tr>
<td>3.3</td>
<td>0.153</td>
<td>0.116</td>
<td>0.129</td>
<td>0.062</td>
<td>0.339</td>
<td>0.321</td>
<td>1.01</td>
<td>0.95</td>
</tr>
<tr>
<td>2.0</td>
<td>0.067</td>
<td>0.099</td>
<td>0.143</td>
<td>0.057</td>
<td>0.425</td>
<td>0.456</td>
<td>4.34</td>
<td>4.23</td>
</tr>
<tr>
<td>1.1</td>
<td>0.165</td>
<td>0.111</td>
<td>0.137</td>
<td>0.072</td>
<td>0.875</td>
<td>0.796</td>
<td>1.01</td>
<td>2.31</td>
</tr>
<tr>
<td>&lt;1.1</td>
<td>0.099</td>
<td>0.062</td>
<td>0.130</td>
<td>0.037</td>
<td>2.839</td>
<td>1.384</td>
<td>2.75</td>
<td>22.65</td>
</tr>
<tr>
<td>Total</td>
<td>0.657</td>
<td>0.699</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

concentration of particulate chloride compares favorably with the results of Laird and Miksad (1978) and Paciga and Jervis (1976). The particulate distribution of chloride and sulfate in MMD of 7, 3.3, 2, 1.1 and less than 1.1 μm varied widely throughout the sampling period. No significant seasonal trend in the total particulate or MMD greater than 3.3 μm particle chloride concentrations was evident (Fig. 1). Of the six sample dates with total chloride particulate concentrations greater than 1 µg m⁻³, all but 24 November 1985 and 29 January 1986 occurred prior to the first freeze and first snowfall.

The particulate chloride concentration within each particulate size class tends to be linearly correlated with the sum of the chloride contained in all particulate fractions (correlation coefficients of 0.84, 0.70, 0.82, 0.70, and 0.54 for the 7.0, 3.3, 2.0, 1.1 μm and less than 1.1 μm fractions respectively). The correlation between the chloride contained in the particulate fraction with diameters greater than or equal to 3.3 μm

Fig. 1. Temporal distribution of the total and MMD > 3.3 μm particulate chloride concentration.
and the sum of the chloride in all fractions is illustrated in Fig. 2. This linear relationship suggests that any sources of chloride-bearing particles greater than or equal to $3.3\,\mu m$, whether natural or man-made, is distant from the sampling location. Linear correlations between the sodium contained in the particulate fractions and the total sodium in all particulates were also strong [correlation coefficients of 0.84, 0.70, 0.67, 0.67, and 0.69 for the 7.0, 3.3, 2.0, 1.1 $\mu m$ and less than 1.1 $\mu m$ fractions respectively, (Fig. 2)].

The particulate sulfate concentrations in each size class except the MMD $7\,\mu m$ fraction, show linear correlations with the total sulfate in all fractions (correlation coefficients of $-0.004$, $0.59$, $0.34$, $0.73$, and $0.85$ for the 7.0, 3.3, 2.0, 1.1 $\mu m$ and less than 1.1 $\mu m$ fractions respectively). Evidence of discontinuity is seen in the relationship between the sulfate contained in the particulate fraction with diameters greater than $3.3\,\mu m$ and the total sulfate shown in Fig. 3. The $7\,\mu m$ fraction shows a nonlinear relationship resulting from a large increase in the fraction for periods in which the total sulfate concentration was greater than $5.6\,\mu g\,m^{-3}$. This increase in the large fraction when the total is high suggests a local source of giant particle sulfate.

4. Soil dust aerosol

Analysis of the bulk soil and soil dust aerosol for the fields immediately surrounding the samplers was conducted on 28 August 1986 (Table 3). Combining the soil concentrations of sulfate and chloride with the average mass impacted on the HIVOL (0.063 g d$^{-1}$) and $\geq 3.3\,\mu m$ MMD Andersen sampler filters (0.054 g d$^{-1}$) results in the potential concentrations shown in Table 3. When these are compared to the actual aerosol concentrations, it is clear that the local soils can only contribute $<1\%$ of the sulfate and chloride collected on the average aerosol sample. The bulk soil in the fields west and south of the sampler had an average S/Cl mass ratio of 0.52, while soils in the field east of the samplers had an average ratio of 1.02 (Table 3). While the S/Cl ratio on the filters approximates that for the fields east of the sampler, the absolute concentration of sulfate and chloride due to local soil dust impaction appears to be negligible.

5. Chemistry distribution

Averaged over the 42 sample periods, the atmospheric aerosol size distribution of soluble chloride was variable (Table 2). The lowest levels occurred in the MMD $2.0\,\mu m$ and $<1.1\,\mu m$ size classes. The MMD $7\,\mu m$ Cl accounted for 26% of the total concentration.

<table>
<thead>
<tr>
<th>Table 3. Concentration of SO$_4$ and Cl in local soils and their potential contribution to aerosols collected.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SO$_4$</strong></td>
</tr>
<tr>
<td>-------------------------------------</td>
</tr>
<tr>
<td>Average concentration in soils ($\mu g,g^{-1}$)</td>
</tr>
<tr>
<td>East of sampler</td>
</tr>
<tr>
<td>Southwest of sampler</td>
</tr>
<tr>
<td>Potential soil ($\mu g,m^{-3}$) contribution to aerosols*</td>
</tr>
<tr>
<td>From the east</td>
</tr>
<tr>
<td>From the south and west</td>
</tr>
<tr>
<td>Actual aerosol $dp \geq 3.3,\mu m$</td>
</tr>
</tbody>
</table>

* Soil concentration SO$_4$ and Cl multiplied by average collected mass of particulates $\geq 3.3\,\mu m$ MMD.
The distribution of soluble sulfate was skewed to the small particle sizes (Table 2), with the 1.1 μm and smaller MMD size classes accounting for 74% of the total concentration. The distribution of soluble sodium was relatively even (Table 2) with the 7 μm MMD size class containing 23% of the total concentration. This even distribution across particle size classes was also found by Gladney and coworkers (1974) and suggests both natural and anthropogenic sources of Na.

The average median mass diameter for soluble chloride, sodium, and sulfate was 3.0, 2.3 and 0.7 μm respectively. The average median mass diameter of chloride and sodium particulates places them in the range usually attributed to marine origin (Junge 1953; Lee and Patterson 1969; Gladney et al. 1974). The small size of the sulfate particulate suggests an anthropogenic source (Junge 1953).

Based on the average S/Cl mass ratios (Table 2), the particulates with MMD of 7, 2, 1.1 and less than 1.1 μm may be of land origin, while those with MMD of 3.3 μm may be of ocean origin. Such separation in size ranges for oceanic origin materials is unlikely, however. Assuming that there is a more rapid decrease in Cl than Na and SO$_4$ over land due to the anthropogenic sources of sodium particulates (Gladney et al. 1974), the high 7 μm S/Cl ratio should correspond with a high Na/Cl ratio. This is indeed the case. The correlation between these two ratios for the 7, 2, and <1.1 μm MMD size classes is due to two samples with high S/Cl and Na/Cl ratios in all three size classes (greater than 15 and 25 respectively). The high ratios are a result of low chloride concentrations. These low chloride concentrations may be a result of deliquescence of the <1.1 μm MMD size class particles (Andreae et al. 1986) and/or reaction of the chloride salt with HNO$_3$ resulting in HCl gas. The Na/Cl mass ratios (Table 2) show a magnitude variation with size class similar to the S/Cl ratio.

6. Sample date classification

Classification of the samples was made on the basis of the predominant air mass type as indicated from weather maps for the day of and the day prior to sampling. Trajectory forecasts were used to verify the classification of continental or maritime air masses. Winds in maritime type air mass sample days were predominantly southerly and corresponded with the presence of modified maritime air from the Gulf of Mexico or the Atlantic Ocean (Fig. 4). On the typical maritime day, trajectories showed a cold front north of Vincennes and a high pressure cell over the northeastern or southeastern United States. Winds in continental type air mass sample days came from the northwest and corresponded with the presence of continental air from Canada or the Great Plains which may or may not have crossed the Great Lakes region (Fig. 5). This classification also includes the greatly modified maritime air masses from the Pacific Ocean. Forty-two sample days were classified, fourteen as maritime-type air mass days and twenty-eight as continental-type air mass days.

The concentration of Cl, Na, and SO$_4$ in the particulate samples from maritime air masses was statistically higher than those from continental air masses (based

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**Fig. 4.** Representative maritime type air mass sampling day. The strong southerly winds characteristic of this type sampling day is present for several days prior to sampling, indicating strong maritime air mass character in Indiana. Conditions for 9 October 1985. Twenty-four h, 850 mb trajectory (dotted line) covers 0000 UTC to 1200 UTC 9 October.

**Fig. 5.** Representative continental type air mass sampling day. The strong westerly winds characteristic of this type sampling day is present for several days prior to sampling, indicating strong continental air mass character in Indiana. Conditions for 9 April 1986. Twenty-four h, 850 mb trajectory (dotted line) covers 0000 UTC to 1200 UTC 9 April.
on t-tests) at the 0.10 level for chloride and sulfate and at the 0.15 level for sodium. The maritime type days had average Cl, Na, and SO₄ concentrations of 0.80, 0.80, and 6.29 µg m⁻³ respectively, whereas the continental type days had average Cl, Na, and SO₄ concentrations of 0.59, 0.65, and 4.35 µg m⁻³ respectively (Table 4).

The mean distribution of the ions in particulate size classes are shown in Figs. 6 through 8. For all size classes of particulates the average concentration of sodium and sulfate in maritime type days was greater than that in continental type days. This was also true for chloride with the exception of the 1.1 µm size class. Significant differences in the concentrations of sodium between maritime and continental type days were found for the 7.7, 3.3, and <1.1 µm size classes at the 0.05 level. Significant differences in the concentrations of chloride between maritime and continental type days was found for the 7.7 and 3.3 µm size classes at the 0.10 level.

Significant differences in the concentrations of sulfate between maritime and continental type days was found for the 7.7, 3.3, and <1.1 µm size classes at the 0.15 or lower level. The two largest fractions contributed 53% of the sodium, 57% of the chloride, and 18% of the sulfate in the maritime type air mass days and 48% of the sodium, 44% of the chloride, and 17% of the sulfate in the continental type air mass days. The higher concentrations of all three ion species in the two largest size classes of maritime compared to the continental air mass sampling days indicate different origins of the aerosols.

7. Local atmospheric influences

The size distribution of particulates is influenced by both washout of material by precipitation and near-saturation relative humidities. Measurable precipitation occurred during the sample days classified as maritime type air mass days more frequently than during sample days classified as continental type air mass days (57 versus 29%). The difference between the frequency of precipitation during the two days of air masses was statistically significant at the 0.1 level. However, there was no significant difference between the quantity of precipitation deposited during continental type air mass days and maritime type air mass days. In addition no significant linear correlation was found between the amount of precipitation or the occurrence of precipitation and the concentration of any of the three ions. Thus washout does not appear to influence significantly the results.

The average relative humidity during the sample days classified as maritime type air mass days was significantly higher than during continental type air mass days (α < 0.15). Using the approximations of Fitzgerald (1975) described above, the dry particle size distribution
was estimated as a function of the relative humidity of the surface air layer and the ambient particle size distribution. Adjusting the MMD by the above method showed that drying of the equilibrium droplets reduced the mass in all but the <1.1 μm size class by an average of 56, 42, 27 and 23% for the 7, 3.3, 2.0, and 1.1 μm size classes respectively. The <1.1 μm size class increased by 110%. Whereas the ambient distributions showed differences in all size classes, the higher levels of sodium, sulfate and chloride in the <1.1 μm size class was the only significant difference between air mass types when the distributions were normalized to dry air. This was expected since the net effect of estimating the dry aerosol was to shift the chemical content to the smaller size classes and the air masses were already differentiated by total chemical content. The model used to adjust the particulate distribution assumed a maximum particle diameter of 10 μm. If larger initial particles existed, the model overestimated the shift to finer particle size classes.

8. Source determinations

The average median mass diameters for chloride-bearing particles were 3.9 and 2.8 μm for the maritime-and continental-type days respectively, 2.8 μm for sodium for both type days, and 0.7 μm for sulfate for both type days.

Since the major sources of large particle Cl, SO₄, and Na are either soil dust, fertilizer, road salt, or sea spray, (Hidy 1984) and there is a negligible amount of Cl and SO₄ in the local soil dust, no local use or evidence of road salt aerosols, and no evidence for fertilizer fugitive sources, a maritime origin of the chloride large particle fraction is indicated.

The distribution of sodium and sulfate in both continental and maritime type days fit a power law distribution in agreement with Junge (1953). The distribution of chloride for maritime type days also fit a power law, while that for continental type days did not. Deviation from the fit was due to the 1.1 μm size class (Fig. 7). The source of this fraction is unknown.

The S/Cl ratio of the maritime type air mass samples (Table 4) was significantly higher than those from the continental type air mass samples for the 1.1 and <1.1 μm fractions at the 0.10 level. The Na/Cl ratio of the maritime type airmass samples (Table 4) was also significantly higher than the continental type air mass samples for the 1.1 and <1.1 μm fractions at the 0.15 level. The S/Cl ratios were lower for the maritime type air mass samples for all fractions larger than 2.0 μm however the S/Cl ratio is much higher in the maritime type air mass samples than the 0.02 ratio of seawater. The mean Na/Cl ratios were also lower for the maritime than the continental type air mass samples in all fractions larger than 2.0 μm. In all cases the Na/Cl ratios were greater than the 0.37 of sea spray. The significant differences in the S/Cl and Na/Cl ratios, combined with the magnitudes of the ratios associated with maritime type air masses indicate modification of the air mass chemistry due to anthropogenic source emissions as the air mass traveled northward over land.

Specifically the concentrations of small fraction sulfate and/or chloride is probably due to air mass modification by local anthropogenic sources rather than inherent in the residual maritime or continental air masses. The large particle chloride is a result of sea salt spray indicating that the transport of sea salt at least 1200 km inland from the Gulf of Mexico or the Atlantic Ocean is very efficient. If the long range transport of

<table>
<thead>
<tr>
<th>MMD (μm)</th>
<th>Cl (μg m⁻³) Mean</th>
<th>SD (μg m⁻³)</th>
<th>Na (μg m⁻³) Mean</th>
<th>SD (μg m⁻³)</th>
<th>SO₄ (μg m⁻³) Mean</th>
<th>SD (μg m⁻³)</th>
<th>Na/Cl</th>
<th>S/Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maritime</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.255 (0.238)</td>
<td></td>
<td>0.193 (0.091)</td>
<td></td>
<td>0.649 (0.415)</td>
<td></td>
<td>1.2</td>
<td>1.4</td>
</tr>
<tr>
<td>3.3</td>
<td>0.204 (0.152)</td>
<td></td>
<td>0.156 (0.077)</td>
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<td>0.459 (0.312)</td>
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<td>0.154 (0.069)</td>
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<td>0.499 (0.256)</td>
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<td>1.1</td>
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<td>0.152 (0.063)</td>
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<td>1.091 (0.498)</td>
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<td>1.2</td>
<td>3.4</td>
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<td>0.113 (0.075)</td>
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<td>0.150 (0.044)</td>
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<td>3.587 (1.575)</td>
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<td>46.9</td>
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<tr>
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<td></td>
<td>0.805 (0.805)</td>
<td></td>
<td>6.285 (6.285)</td>
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<tr>
<td>7</td>
<td>0.133 (0.130)</td>
<td></td>
<td>0.143 (0.052)</td>
<td></td>
<td>0.451 (0.377)</td>
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<tr>
<td>3.3</td>
<td>0.127 (0.086)</td>
<td></td>
<td>0.115 (0.049)</td>
<td></td>
<td>0.280 (0.313)</td>
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<tr>
<td>2.0</td>
<td>0.061 (0.109)</td>
<td></td>
<td>0.138 (0.050)</td>
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<td>0.389 (0.529)</td>
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<td>0.131 (0.075)</td>
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<td>0.768 (0.898)</td>
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<td>&lt;1.1</td>
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<td>0.119 (0.028)</td>
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<td>2.465 (1.130)</td>
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<tr>
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<td>4.353 (4.353)</td>
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soil dust from high chloride western soils (such as described by Crecelius and coworkers 1980) contributed to the sample chloride levels, the results would be expected to be reversed with highest Cl levels when the winds were westerly.

9. Summary and conclusions

A classification of particulate sample days was made based on trajectory and surface weather map analysis. Two classes of air masses were identified—modified maritime and continental—and their particulate chemistry compared. The maritime air mass type sample days had greater concentrations of soluble Cl, Na, and SO$_4$ than the continental air mass type sample days with size distributions fitting a power law. Ratios of S/Cl and Na/Cl for $dp \geq 3.3$ $\mu$m were lower in the maritime type samples than in the continental type samples. Enrichment of the $\leq 1.1$ $\mu$m size classes of Cl and SO$_4$ are direction dependent, not air mass dependent. Source, maritime versus continental, would not explain high concentration in small fractions; therefore, the maritime air mass appears to be gaining more anthropogenic SO$_4$.

While the maritime type air mass sample days had higher average relative humidity, resulting in enhanced particle diameter, such ambient conditions are typical or maritime air masses. Precipitation on the day of collection was not correlated to the total chemical deposited over the course of the study.

In southwestern Indiana the maritime type air mass is approximately 1200 km out of the source region and still contains a characteristic chloride and sodium signature. This extends the distance in which maritime air can be identified by its aerosol chemistry from the results of Junge (1953) in Central Europe.

While maritime or continental type air masses were identified by trajectories and synoptic weather maps, the large standard deviation variations in the results are partially due to differing amounts of air mass modification as a function of the history of the individual air masses as they moved out of their source regions. More definitive results may be attainable by historical trajectory analysis of each sample date and further classifying the sample day according to air mass history.

Acknowledgments. The authors wish to thank the Indiana Energy Association for providing manpower and equipment for the aerosol sampling, Indiana State Board of Health for the quality assurance of filters, and Michael Szumski and Michelle Patterson for chemical analyses.

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