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Atmospheric Acidity Measurements During the Lake Michigan Urban Air Toxics Study

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ABSTRACT

During the summer of 1991, as part of the Lake Michigan Urban Air Toxics Study (LMUATS), measurements of atmospheric reactive gases, fine fraction, and size fractionated acidic aerosol samples were taken at two sites (South Haven, MI and on the research vessel, *Laurentian*). The fine aerosol samples were collected using an annular denuder system (ADS) which allowed quantification of acidic and basic gases, as well as inorganic ions in the fine particle fraction (<2.5 μm). The size fractionated data was obtained using a six stage micro-orifice impactor (MOI) equipped with ammonia-scrubbing denuders.

The ADS aerosol results showed extreme episodic behavior which correlated well with air mass transport from the southwest. The maximum concentrations observed in South Haven after over lake transport from the southwest were 241 nmol/m^3 for aerosol strong acidity (H^+), and 3.8 ppb for nitric acid (HNO_3). These elevated acid levels were accompanied by hourly maximum O_3 concentrations of 128 and 153 ppb, respectively. Levels at South Haven and aboard the *Laurentian* were very similar for most of the species measured. Size fractionated particulate mass results also compared well for most species, and showed a typical size dependent behavior. Measurents of aerosol acidity are also compared to those taken in Ann Arbor, MI during the one month study.

INTRODUCTION

The Lake Michigan Urban Air Toxics Study (LMUATS) was jointly carried out by the University of Michigan and the U.S. Environmental Protection Agency during the summer of 1991. A primary goal of the study was to quantify the levels of toxic air pollutants in the southern Lake Michigan basin in order to determine how much of the airborne pollutants are being deposited to aquatic and terrestrial ecosystems. Measurements of atmospheric acidity, both gaseous and aerosol strong acidity, $H,^+$ were performed to

chracterize the chemical composition of the atmosphere and to investigate the behavior of the regional and urban plumes advecting across Lake Michigan.

EXPERIMENTAL

Annular denuder/filter pack measurements were performed at two of the four sites operated during the LMUATS. The first was South Haven, MI, located in a rural area approximately 5 miles from the lake. The inlet to the samplers was approximately 7 feet above the ground in an open field. Continuous monitoring equipment was also operated at this site as part of the Lake Michigan Ozone Study (LMOS) providing hourly ozone (O_3), NOx, and meteorological data.

The second site was the University of Michigan's research vessel, the *R/V Laurentian*. The ship was positioned in two areas during the study. The first station or on-lake monitoring position was about 20 miles west of Muskegon. The second station was about 4-10 miles E-NE of the Chicago-Gary urban/industrial area. The sampling inlets were roughly 5 feet above the deck but off the side of the bow area of the ship (which stood an additional 20' above the surface of the water). Sample collection took place only when the vessel was anchored which keeps the bow pointing into the prevailing wind at all times.

Acidic aerosol and gas measurements were taken at South Haven throughout the duration of the study while the size fractionated samples were collected occasionally. While the *Laurentian* was docked, two 12-hour samples were collected in South Haven from 8am-8pm and 8pm-8am CDT. While the ship was on station, 3 samples were taken daily at South Haven and on the R/V *Laurentian*: 8am-2pm, 2pm-8pm, 8pm-8am CDT. All size fractionated samples were 24-hours in duration starting at 8am CDT, and were operated at both South Haven and on the R/V *Laurentian*. ADS samples were also collected in Ann Arbor as part of an ongoing study of atmospheric acidity in Michigan.

The annular denuder sampling system was used for collection of acidic aerosols and gases and has been described previously (Koutrakis, *et al.* 1988, Keeler *et al.*, 1990). The ADS was utilized to quantify gaseous SO_2, HNO_3, HONO, NH_3, and fine fraction (<2.5 μm) particulate species SO_4^{2-}, NO_3^-, NH_4^+, and aerosol strong acidity (H^+). Additionally, the system removes the gaseous ammonia and protects the collected particulate matter from possible neutralization.

Size fractionated samples were collected at South Haven and aboard the R/V *Laurentian* using a six-stage micro-orifice type impactor (Koutrakis *et al.*, 1989, Keeler *et al.*, 1990). The six stages have been characterized to separate atmospheric aerosols into the following size ranges when operated at 30 LPM: #1: > 5 μm #2: 5-2.5 μm #3: 2.5-1μm #4: 1-.6 μm #5: .6-.18 μm #6: <.18 μm (Marple and Rubow, 1984). The system is designed to operate with a minimal pressure drop so that vaporization of water and subsequent alteration of the aerodynamic diameter of the particles being collected is avoided (Biswas *et. al.*, 1987). The impactors were placed in a stand which forced incoming air to pass through 8-citric acid-coated honeycomb-style aluminum denuders to remove ambient ammonia (Koutrakis *et al.*, 1988). The aerosol material was collected onto Teflon filters (Teflo) and analyzed identically to the Teflon filters from the ADS.

Sulfate collected on ADS, MOI and on dichotomous filters (analyzed by XRF) were compared to assess the precision of the three techniques. Regression analysis of XRF S against ADS SO_4^{2-} shows quite good results with a slope of 0.33 ng/m^3 S / ng/m^3 SO_4^{2-} and a correlation coefficient of 0.994. Likewise, the regression of ADS SO_4^{2-} versus MOI SO_4^{2-} (fine fraction, stages 3, 4, 5 and 6) displays a slope of 0.93 and a correlation coefficient of 0.986. These results indicate that the collection and analytical techniques utilized were comparable and precise.

RESULTS

In all, 74 ADS samples were collected in South Haven, and 22 on the *Laurentian* and a total of 17 MOI samples at the two sites. The measured $H^+$and SO_4^{2-} concentrations at the two sites can be seen in Figures 1 and 2. A statistical summary of these values as well as concentrations measured in Ann Arbor during the same period are shown in Table 1. The values measured are typical of summertime values previously measured in the midwest U.S. (Pierson *et al.*, 1989). Concentrations of most species were slightly higher on the *Laurentian* (relatively close to Chicago) than in South Haven but in general levels were very similar.

Although most species measured showed their peak concentrations during an episode (see below) two species, HNO_3 and SO_2 showed significant deviations from this pattern. Peak values for HNO_3 were observed during the evening of July 11 and were measured to be 41.8 and 10.4 ppb on the *Laurentian* and at South Haven, respectively. SO_2 also showed its peak value during this overnight sample. Unfortunately, no sample was collected in South Haven due to power failure, but the Laurentian SO_2 level was 31.9 ppb. The concentration spike was not displayed in any of the other species measured. As the mixed layer trajectory switched from the NW on the 11th to the SW on the 12th, it appears that emissions from the Muskegon/Grand Haven area were transported to the ship (off Muskegon) and to South Haven. A similar brief event occurred during the evening of 6 August. The second highest value for SO_2 was observed during this period on the *Laurentian*, but without a similar peak in South Haven. This can be easily explained by examining the air mass trajectory during the period which carried emissions from the Gary/Michigan City area north to the *Laurentian* anchored off Chicago. The contact of this plume was confirmed by operators on the ship from the pronounced odor, visibility degradation, and ozone depletion with winds from the direction of the Fe-Steel plant.

A sustained episode of elevated pollutant levels was observed in South Haven from July 16-22. This episode resulted in peak concentrations of HNO_3, particulate SO_4^{2-}, and aerosol strong acidity (H^+) and SO_2 of 3.8 ppb, 241 nmole/m^3 and 9 ppb, respectively. Most of these species showed typical day/night variation (daytime values being higher). This episode was associated with sustained air mass transport from the SW bringing pollutants from the St. Louis/industrial areas in central Illinois through the Chicago/Gary area. High ozone concentrations were measured during this period in South Haven with maximum hourly values of 128 and 153 ppb being reported.

Results of the analysis of filters from the MOI were used to observe the size distribution of chemical species at the two sampling sites. SO_4^{2-}, NH_4^+ and H^+ consistently appeared on stages 4, 5 and 6 (primarily 4 and 5). The observation of these species in <1 μm

diameter particles is typical of other similar measurements (Pierson *et al.*, 1989). Mass mean diameters of H^+, SO_4^{2-} and NO_3^- were calculated from data from all 6 stages by determining the approximate diameter size at which 50% of the mass resided . The graph suggests that H^+ and SO_4^{2-} were on very small particles of mass mean diameter approximately 0.35 μm while NO_3^- appeared to reside on slightly larger sizes (1.5 μm).

Changes can be observed in the chemical profile of fine fraction aerosols measured during the LMUATS. The H^+ to SO_4^{2} ratios at different sites were 0.78, 0.44, and 0.16, on the R/V Laurentian, South Haven, and Ann Arbor, respectively. This indicates that the acidic SO_4^{2} aerosol measured over the lake is to a large extent unneutralized. However, as the aerosol is transported inland, even a short distance as at South Haven, an additional 25% of the acidity is neutralized. This is most likely due to rapid fumigation of the air mass after reaching the shoreline where relatively high levels of ammonia react rapidly with the acidic SO_4^{2}. However, compared to the average inland values measured in Ann Arbor during the study, both the over-lake and South Haven areas appear to be exposed to relatively unneutralized sulfate.

CONCLUSION

The acidic aerosol measurements during the LMUATS indicate that western Michigan is impacted by sulfate-containing air masses as is much of the region, and that the atmosphere can be quite acidic during certain episodic conditions. It appears that air masses transported long distances over large bodies of water, eg., Lake Michigan, can maintain the acidity of the aerosols until reaching the downwind shoreline, where rapid neutralization may occur. This over-water transport may provide relatively large exposures of atmospheric acidity to areas located near the shore.

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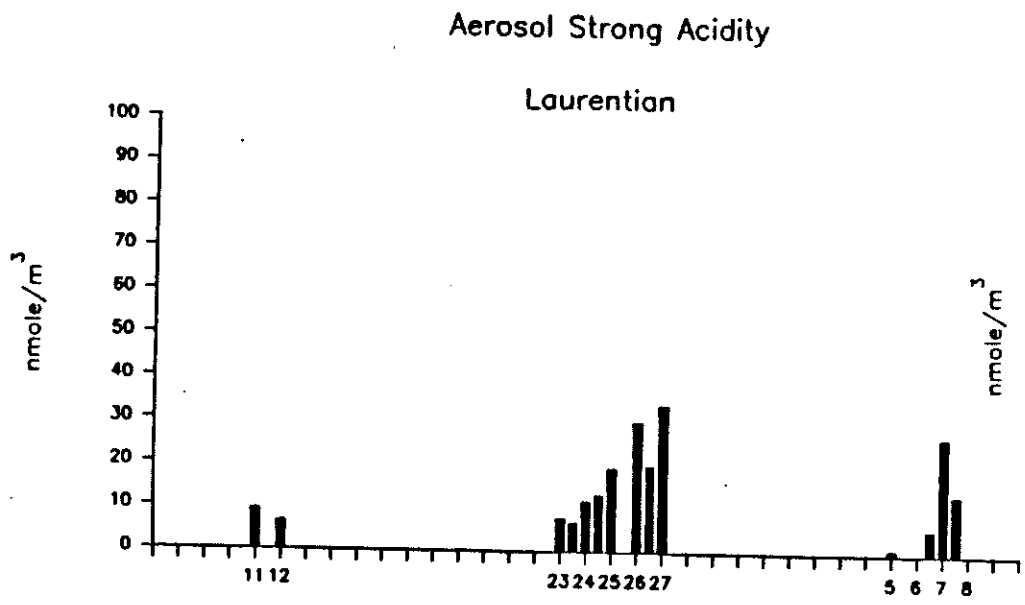
Table 1. Levels of atmospheric trace species measured during the LMUATS from 8 July - 9 August, 1992.

Species	Site	N	Mean	Median	SD	Min	Max
NH_3	South Haven	69	1.3 ppb	1.2	1.2	0	9.7
	Laurentian	18	1.8	1.5	1.4	0	5.1
	Ann Arbor	22	3.1	3.0	.8	1.8	4.4
HNO_3	South Haven	70	.7 ppb	.4	.8	0	3.2
	Laurentian	19	1.3	1.2	1.0	0	3.7
	Ann Arbor	22	.8	.5	.7	0	2.6
SO_2	South Haven	70	1.7 ppb	.9	1.9	.2	8.9
	Laurentian	19	2.6	1.4	3.6	0	15.8
	Ann Arbor	22	2.8	2.2	2.0	.7	8.7
Acidity	South Haven	70	22.1 nmole/m^3	9.2	41.3	0	240.5
	Laurentian	19	15.6	15.2	11.9	0	35.1
	Ann Arbor	22	24.2	6.7	41.4	0	129.7
NH_4^+	South Haven	70	72.1 nmole/m^3	36.5	91.9	0	397.6
	Laurentian	10	35.0	33.8	26.8	0	98.4
	Ann Arbor	22	131.3	37.5	171.4	13.2	544.1
NO_3^-	South Haven	70	6.3 nmole/m^3	5.0	6.0	0	29.2
	Laurentian	19	1.2	0	3.1	0	13.0
	Ann Arbor	22	10.7	7.0	12.3	0	59.4
SO_4^{2-}	South Haven	70	46.3 nmole/m^3	22.1	61.0	0	281.3
	Laurentian	19	30.7	18.6	26.1	8.7	96.9
	Ann Arbor	22	79.0	23.1	102.3	5.2	329.3


Aerosol Strong Acidity
Laurentian
nmole/m3
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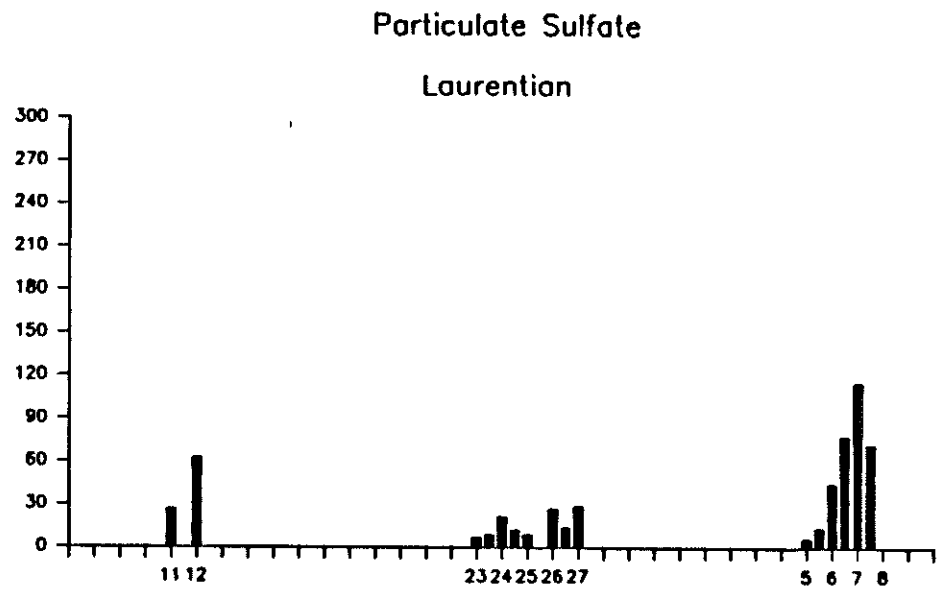
10
20
30
40
50
60
70
80
90
100
11 12
23 24 25 26 27
5 6 7 8


Particulate Sulfate
Laurentian
nmole/m3
0
30
60
90
120
150
180
210
240
270
300
11 12
23 24 25 26 27
5 6 7 8

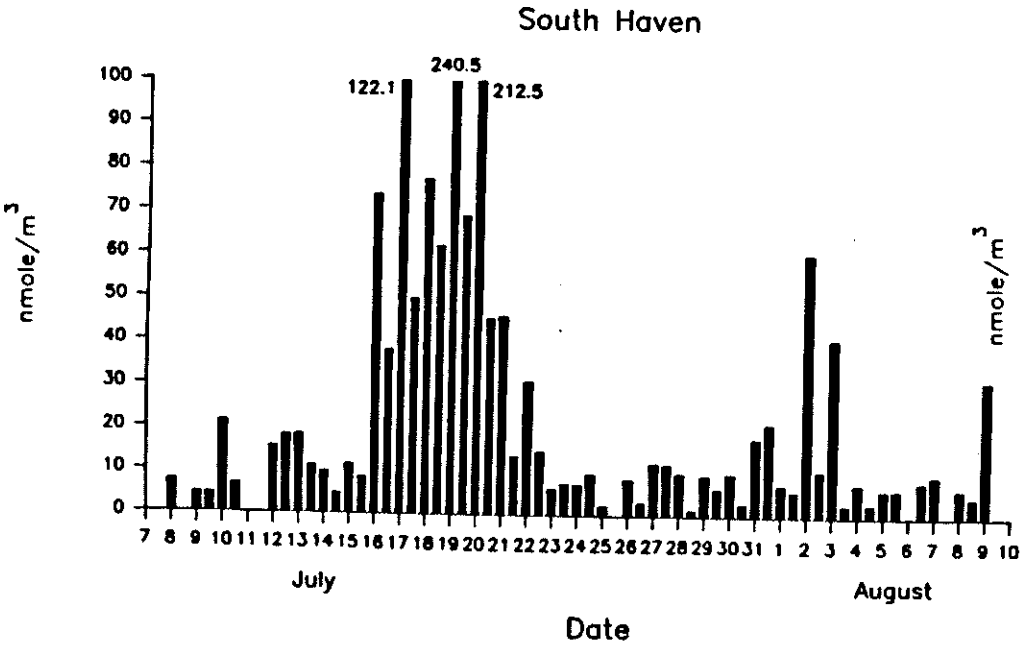
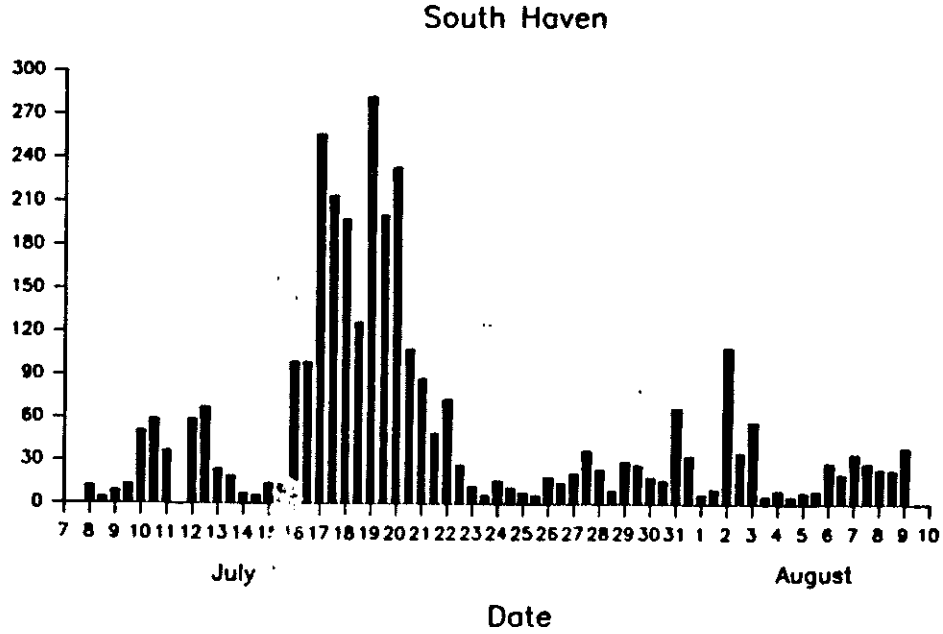

South Haven
nmole/m3
122.1
240.5
212.5
0
10
20
30
40
50
60
70
80
90
100
7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
July
August
Date

Fig. 1


South Haven
nmole/m3
0
30
60
90
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150
180
210
240
270
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7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1 2 3 4 5 6 7 8 9 10
July
August
Date

Fig. 2