1.8

CHARACTERIZATION OF AIRBORNE PARTICULATE MATTER DURING THE LAND-LAKE BREEZE EFFECT STUDY IN CHICAGO, IL

Martina Schmeling*[#], Tinamarie Fosco[#] and Paul Doskey[†]
[#]Loyola University Chicago, Chicago IL, 60626
[†]Argonne National Laboratory, Argonne, IL 60439

1. INTRODUCTION

Particulate air pollution is a constantly growing problem in urban areas. The particulate matter present in pollution events contains often toxic or health impacting elements and is responsible for low visibility, might be triggering respiratory diseases like asthma, and can play an important role in formation or duration of smog events. Mortimer (2002). To characterize particulate pollution and pollution patterns in a highly industrialized coastal city like Chicago, the Land-lake Breeze Effects study was performed during July/August 2002 and June/July 2003. Aerosol filter samples for determination of trace elements, ionic compounds and organic species were collected before and during the lake breeze. Sampling took place at Loyola University Chicago Air Station (LUCAS, approx. 60m above ground and 200m west of Lake Michigan) with a temporal resolution of 1.5 hours and 1 hour for trace element aerosol samples, respectively. In addition to atmospheric aerosols, non-methane hydrocarbons (NMHCs) were collected and reactive trace gases monitored.

* *Corresponding author address*: Martina Schmeling, Loyola University Chicago, Department of Chemistry, Chicago, IL 60626; e-mail: mschmel@luc.edu

An automated weather station recorded the major meteorological parameter during the length of the study on a continuous basis. The particulate samples were analyzed by total reflection X-ray fluorescence after digestion of the filter matrix to quantify the elemental concentration.

Three different situations could be distinguished based on wind patterns recorded: a lake breeze occurs, characterized by a wind shift towards the east during the late morning; a constant wind direction was present throughout the collection period; and a change in wind directions not related to the lake breeze i.e. not from the east, was measured. In this study we will discuss a lake breeze event occurring on July 25, 2002 and a reference day, August 1, 2002.

2. EXPERIMENTAL

Atmospheric aerosols were collected on polycarbonate filter with open face filterholder for trace elemental determination. The collection was done at the Loyola University Chicago Air Station (LUCAS), a facility equipped with instrumentation to monitor photochemical reactive species, collect atmospheric particulates and record the local meteorology. The station is located on top of the tallest building on campus at about 60m height, 200m west of Lake Michigan and approximately 10 km north of downtown Chicago in a residential neighborhood. Sampling parameter and basic meteorological data for July 25, 2002 and August 1, 2002 are shown in table 1a and 1b. The differences in sampling length are associated with the lake breeze pattern and will be discussed in more detail in the results and discussion section.

After collection the filter samples were acid digested in a household microwave using special microwave acid digestion bombs. Gallium as internal standard was added to the solution before digestion to quantify the elemental concentrations.

The samples were then analyzed by total reflection X-ray fluorescence for trace elemental content. Schmeling (2001).

Time	**Temp. [°C]**	**WS [m/s]**	**WD**
7:00-8:30	20.5	4.8	S
8:30-10:00	21.3	3.6	S
11:00-12:00	22.0	5.5	SSE
12:00-13:00	21.8	5.4	SSE

Table 1a: Sampling parameter for *July 25, 2002*. *Time* refers to local time, *Temp*. corresponds to temperature in °C, *WS* refers to wind speed in m/s and *WD* to wind direction.

Time	**Temp. [°C]**	**WS [m/s]**	***WD***
7:00-8:30	25.9	6.7	*SW*
8:30-10:00	28.0	8.0	*SW*
11:00-12:00	29.7	8.9	*SW*
12:00-13:00	*31.1*	*7.6*	*SW*

Table 1b: Sampling parameter *for August 1, 2002*. The table headings are the same as in table 1a.

3. RESULTS AND DISCUSSION

3.1 July 25, 2002 – Lake Breeze Day

During the land-lake breeze study 2002, four atmospheric aerosol collections were performed each day over a period of four weeks. The first two collections (7:00-8:30 and 8:30-10:00) were carried out before occurrence of a possible lake breeze and the second two collections during a possible lake breeze event. The shorter sampling duration for the last two collections was intended to be able to follow changes in elemental concentrations more closely during a lake breeze event. Four lake breeze days occurred out of 20 collection days in total. From these days July 25, 2002 was selected for discussion here. A shift in wind direction from south towards the south east indicated the appearance of a lake breeze on this day (Table 1a). Figure 1 shows the elemental concentrations determined for the four collection periods covered on July 25. Some of the elements detected have been omitted for illustration purposes as they are not relevant for the discussion.

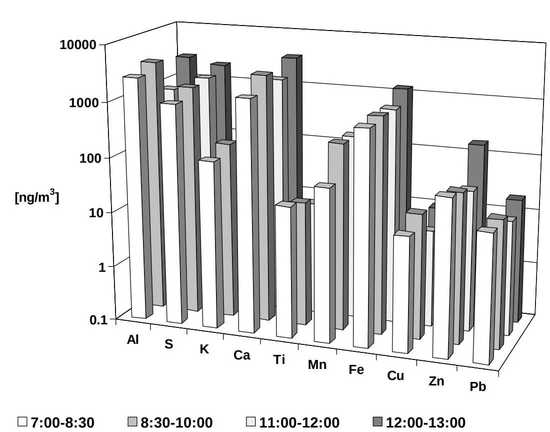

Figure 1: Concentrations for selected elemental species on July 25, 2002 shown in ng/m^3.

On July 25, the last collection, which occurred during the lake breeze, showed noticeably higher concentrations for several elements. This could be an indication that either the wind speed increased or a new air mass did pass through the sampling station with a change in wind direction. The wind speed readings are shown in table 1a and indicate essentially the same average wind speed for collection 3 and 4. This finding is consistent with other lake breeze days, where the last collection shows increased elemental concentrations, but no significant change in wind speed. Also in table 1a the wind direction is shown which changed from S to SSE between 10:00 and 11:00 local time. It is very likely that a new air mass was brought to the sampling station by this change, which passed through the station during the last collection period.

Further evidence for an air mass change for the second set of samplings can be found when the elements shown in figure 1 are summarized in two sets. Set A refers to the collections before lake breeze (collection 1 and 2) and Set B to the two collections during lake breeze (collection 3 and 4). Table 2 highlights the concentrations and displays in the last column the percentage change between these two sets. A "+" is marking an increase and "-" is marking a decrease in concentration. As can be seen, several elements increased in concentration whereas others decreased. The decrease in elemental concentration was found on other occasions as well and is associated to boundary layer mixing occurring during the day. On July 25, major decreases were observed for some earth curst elements like aluminum and titanium. A significant increase of 49%, however, was registered for sulfur. Sulfur in the particulate form is present as sulfate and is considered as a secondary pollutant. Thus it needs to be formed in the atmosphere and the concentration will increase during the day based on its formation rate. Other elements like Mn, Fe and Zn also increased significantly for the second collection set. This could be an indication that the air mass did originate or at least passed through Gary, IN, with its industrial area. Gary is located SSE of the sampling station.

Element	**Set A [ng/m^3]**	**Set B [ng/m^3]**	**% change**
Al	6316	3550	-44
S	2467	3666	+49
K	267	195	-27
Ca	4605	5284	+15
Ti	41.8	24.8	-41
Mn	302	398	+32
Fe	1553	2058	+32
Cu	30.4	15.3	-50
Zn	118	200	+70
Pb	40	30.7	-23

Table 2: Elemental concentrations for July 25, 2002 summarized in Set A (collection 1 and 2) before the onset of a lake breeze and Set B (collection 3 and 4), during a lake breeze. The last column indicates the percentage change between Set A and Set B.

3.2 Reference Day

In figure 2 the elemental concentrations for the same species as in figure 1 are shown for August 1, 2002. This day was considered as a reference day with no change in wind direction therefore only locally produced or injected species are expected to be found in the air mass.

As expected, a decrease in concentration was detected over the four collection periods for most elemental species on August 1, 2002. As already mentioned this is related to boundary layer mixing during the day. Only very few elements, including sulfur, showed some increase in concentrations for the last two sampling periods. The increase in sulfur concentration (here in form of sulfate) was much less than during the lake breeze day and is most likely due to local photochemical production. In table 3 the same elements are summarized as Set A and Set B like in table 2. Also here in the last column the changes between set A and set B in percent are shown. Interestingly aluminum and titanium, which showed the larges decrease on a lake breeze day, are among the elements with increasing concentrations. This might be due to local sources, but has to be further investigated.

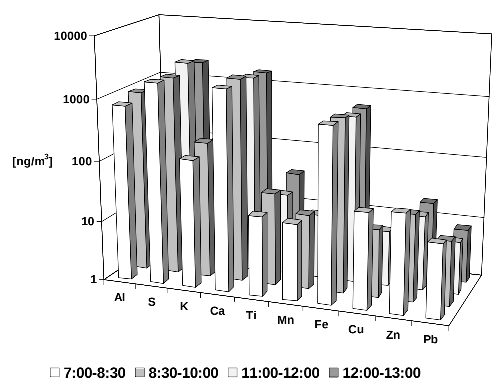

Figure 2: Concentrations of the same elemental species as selected in figure 1 for August 1, 2002.

Element	**Set A [ng/m^3]**	**Set B [ng/m^3]**	**% change**
Al	1720	1947	+13
S	3785	4515	+19
K	306	291	-5
Ca	4025	3290	-18
Ti	53.2	56.3	+6
Mn	34.6	29.6	-15
Fe	1403	1091	-22
Cu	48.9	11.9	-76
Zn	66.9	34.9	-48
Pb	27.2	14.8	-46

Table 3: Elemental concentrations summarized as Set A (collection 1 and 2) and Set B (collection 3 and 4) as well as the change between them shown as percent.

3.3. Comparison July 25, 2002 and August 1, 2002

When comparing July 25, 2002 (lake breeze day) and August 1, 2002 (reference day) the results indicate that some elements, notably sulfur, experience a significant difference in concentration before and during the lake breeze but not as pronounced on reference days. For sulfur the increase is 49% on a lake breeze day, but only 19% on a reference day. We think that this is related to photochemical reactions happening inside the air parcel residing above Lake Michigan, transported by westerly wind (land breeze) in the morning or during the night onto the lake. Musk (1988). Pollutants trapped in this parcel are exposed to intense sunlight in summer and are able to react with each other to form secondary species such as sulfate. This parcel enriched with secondary pollutants will be transported back towards the shore during the lake breeze and added to the pollutants already produced locally. This might explain the dramatic increase in sulfate during the lake breeze compared to a reference day. Such behavior was found on other lake breeze days as well and the study carried out in summer 2003 should provide additional data with respect to this event.

These results, however, suggest that a lake breeze pattern like occurring in Chicago could have major implications for coastal environments with respect to human health. It might also alter local radiative properties of the aerosol since the processed particulates are often smaller in size, differently composed and more reactive as the non-processed ones. In order to solidify our findings, future investigations will include the characterization of secondary organic compounds besides the trace elements before and during the lake breeze as well as size classified sampling.

4. REFERENCES

Mortimer, K.M.; Neas, L.M.; Dockery, D.W.; Redline, S.; Tager, I.B., 2002: “The effect of air pollution on inner-city children with asthma”. Eur. Respir. J. **19**, 699-705.

Musk, L.F. 1988: *Weather Systems*, Cambridge University Press, 160pp.

Schmeling, M., 2001: Total reflection X-ray fluorescence – a tool to obtain information about different air masses and air pollution. *Spectrochim. Acta.*, **B56(11)**, 2127-2136.