CUBS and Bondville GPIC Monitoring 2005 Progress Report

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Introduction

This report provides initial analysis of data from the Chicago urban background system (CUBS) and the Bondville monitoring system. The primary measurements discussed are from continuous particle ion chromatographic (gpic) systems operating at Bondville and at Northbrook. The Bondville system has been running since May, 2003. The Northbrook system operation began in February, 2005. The Northbrook data is being processed similarly to the data handling methods set up for the Bondville system and the current version of the data for both systems is in the attached CD. The analysis in this report focuses on an initial comparison of the simultaneous Northbrook and Bondville data for PM2.5 sulfate and nitrate. We plan to develop these ideas further in the near future and report the results in a journal article. The more complete analysis will extend over a longer simultaneous time period and include the other gpic species measured, namely PM2.5 ammonium, and gaseous ammonia, SO_2, and HNO_3, as well as incorporating auxiliary data such as temperature, wind speed and direction, and trajectory analysis.

At present the Northbrook data from 2/18/05 to 1/9/06 have been processed. In addition the Bondville data has been processed up to 9/26/05 giving an 8-month period for simultaneous comparison. In instances below where only Northbrook data is considered the longer time span is used while for comparisons of the two sites the 8-month record is used. The Bondville GPIC system (gpic1) reports concentrations of both gas and particulate constituents over a 30 minute cycle time while the Northbrook system (gpic2) has a cycle time of 40 minutes. In order to compare the measurement from the two systems the particulate sulfate and nitrate concentrations were interpolated to obtain average hourly concentrations. The analysis here focuses on the daily average and diurnal average concentrations of PM2.5 sulfate and nitrate.

Data Analysis

The statistical analysis of the data in Table I shows similar overall behavior of sulfate and nitrate at the two sites. As one might expect, the mean values at Northbrook are higher for both particulate sulfate and nitrate. Plots of the daily average of sulfate (Figure 1) and nitrate (Figure 2) at the two sites show that there are, however, periods when the Bondville concentrations are higher. In both locations the sulfate concentrations are higher in the summer than the winter. From a seasonal standpoint the nitrate at Bondville is higher during the winter and spring months and falls off to much lower values in the summer and fall, similar to the behavior seen in past Bondville data. At Northbrook the PM2.5 nitrate seasonal trend is higher in the warmer seasons.

The average diurnal behavior at the two sampling sites shows considerable differences. First, the particulate sulfate at Bondville (Figure 3) is low at nighttime and shows a peak during midday. The nighttime particulate sulfate values at Northbrook are as high at night as during the daytime.

These general trends are born out by SO_2 measurements from an entirely different source, the EPA Air Quality System (AQS) database (formerly AIRS). For example, the diurnal average of the 1995 AQS summer data from a Chicago site and a downstate site near Bondville are shown in Figure 4. The downstate SO_2 concentrations are low during the nighttime and evening hours and show a peak during the daytime, whereas the diurnal SO_2 concentration in Chicago is relatively flat.

The diurnal data for particulate nitrate in Figure 5 also shows a different pattern at the two sites. At Northbrook the nitrate behaves much like the downstate sulfate with a peak during the daytime, although occurring somewhat later during the day. The Bondville particulate nitrate tends to have higher values at night and to fall off during the daytime.

Figure 6 shows the diurnal averages of the molar nitrate to sulfate ratio at Bondville and Northbrook. They are comparable and slightly less than unity during the early morning hours at both locations indicating a slight preponderance of sulfate to nitrate. During the daytime the Bondville aerosol becomes dominated by sulfate. By contrast nitrate is the dominant species of in the urban aerosol during the daytime.

Discussion

The Bondville PM2.5 sulfate data generally follow patterns seen in the past with higher values during the summer compared to the winter and higher values during the daytime than at night. We have also found higher nitrate particulate levels in the winter than the summer at Bondville consistent with the present results. The less pronounced diurnal variation of sulfate in Chicago differs from the trend at Bondville, although it does appear to be consistent with SO_2 behavior from the AQS data. The Chicago diurnal variation of particulate nitrate with higher values during the daytime is completely unexpected based on past analysis of the Bondville data.

Considering the nitrate data in more detail, notice from Figure 2 that the magnitude of many of the peaks in daily average nitrate concentrations at Northbrook are larger than the peak in the diurnal average at Northbrook shown in Figure 5. Since the daily average includes those lower values that occur during the day, the diurnal average for those days with the large spikes occur must be considerably larger than the overall diurnal average. Figure 7 shows the nitrate diurnal averages at Northbrook for those days selected according to the arbitrary condition that the daily average particulate nitrate was greater than 1.4 $\mu g/m^3$. The results show that on those 47 out of 282 days, when the these spikes in the PM2.5 nitrate concentrations occurred, the peak values were over twice the average value, and the peak value occurs during the afternoon. The figure also shows that the diurnal average for those days when the daily average is less than 1.4 $\mu g/m^3$ is similar in shape to both the overall diurnal average and the diurnal average of the high values.

In Figures 8 and 9 the simultaneous data from both sites have been partitioned according to what time of day the peak occurs – whether before or after 11:00 am. The diurnal patterns when partitioned in this way show characteristics of both the overall diurnal average at Bondville in which the concentrations fall from a peak value before dawn to lower values during the day (identified here as the "early mode") and the characteristic pattern of the average diurnal behavior at Northbrook with concentrations rising after dawn and peaking in the afternoon (defined as the "late mode"). The early mode behavior at Northbrook has differences from that at Bondville in that a clear peak is not observed but rather a more uniform decrease to the daytime low value, actually similar in appearance to the Northbrook sulfate diurnal pattern (Figure 3). Also, the peak values in the late mode behavior at Bondville do not persist as long as the late mode behavior at Northbrook.

The characteristics of the behavior of the two diurnal modes at Northbrook and Bondville are summarized in Table II. The two modes occur with about equal frequency at Bondville while the late mode occurred about 70 % of the time at Northbrook. The early mode concentrations were almost the same at both sites. The late mode concentration at Northbrook was 2.2 times that at Bondville and 1.5 times the early mode concentration at Northbrook. Considering simultaneous behavior at the two sites, when the early mode occurred at Bondville it also occurred at Northbrook 74% of the time, and when the late mode occurred at Northbrook it also occurred at Bondville 82% of the time. The high likelihood of the occurrence of the same mode at both sites on a given day suggests that the underlying mechanism has a synoptic or regional character. The high concentration at Northbrook under the late mode behavior indicates that processes leading to particulate nitrate formation at Northbrook are somehow magnified.

In accordance with our previous analysis of the Bondville PM2.5 data, the early mode nitrate behavior is consistent with mixing of sulfate rich and nitrate poor aerosol to the surface as the mixing layer increases during the early daylight hours. Because of the irreversible chemical behavior of SO_2, as an atmospheric aerosol ages ammonium nitrate will basically react with ammonium that is left over after the available sulfate has been neutralized. This can lead to a sulfate rich-nitrate poor aerosol aloft which, after mixing to the ground during early daylight hours, would produce low nitrate concentrations. We believe this behavior is at least partially responsible for the decrease in nitrate during early daylight hours consistent with the early mode behavior. Another affect that would cause similar behavior, and between which we have been unable to distinguish, is a simple volatility effect where as the temperature warms after sunrise ammonium nitrate decomposes to ammonia and nitric acid which are volatile. Our earlier observations from the Bondville data, that under northerly winds the PM2.5 nitrate concentrations are higher and that nitrate is higher in proportion to sulfate, are consistent with both explanations. With northerly winds at Bondville there is less sulfate, since the SO_2 sources are more concentrated in the southerly directions. Also, the temperatures tend to lower values with northerly winds favoring more particulate nitrate. This general question of nitrate, in a sense, taking the place of sulfate is an important issue because it is a measure of the diminishing returns of reductions in SO_2 emissions and provides a basis to estimate future PM2.5 and visibility levels.

How can we explain the late mode behavior observed here, in which the nitrate increases starting at daybreak to an early afternoon peak? Since the late mode behavior occurs at both locations on the same days, it is plausible the underlying cause involves regional transport that affects both sites or possibly similar photochemical conditions that promote the same chemical reactions at both sites. The late mode behavior is inconsistent with a volatility effect which posits a decrease in particulate nitrate at daybreak not an increase as in the late mode behavior. The notion of mixing upper air into the surface layer, a regional transport effect, cannot be totally discounted. Except under southerly transport, the upper air in Chicago should have less sulfate than at Bondville based on the distance from the heavily polluting Ohio Valley. If sulfate does not dominate the upper air PM2.5 concentration, then there is opportunity for higher PM2.5 ammonium nitrate concentrations which could mix to the ground and yield high nitrate as observed in the late mode behavior. This does not explain, however, why the late mode nitrate concentrations at Northbrook are so high: they are higher than the Northbrook early mode concentrations and higher than the both modes at Bondville where in contrast to Northbrook the early mode concentrations are higher than those of the late mode.

There is a well known process of ozone formation in Chicago that is consistent with the high late mode particulate levels of nitrate. Briefly, on days with a strong lake breeze effect, pollution from Chicago is carried out to Lake Michigan where, constrained to a shallow mixing layer and under clear conditions, photochemical reactions effectively produce ozone. The return lake breeze, which peaks at about 3-4 pm corresponds, to the peak ozone levels. The photochemical conditions responsible for the efficient ozone formation during the lake breeze cycle could also produce high PM2.5 nitrate. The Bondville late mode nitrate are not directly influenced by lake breezes. However, on days with a strong lake breeze cycle, favorable photochemical conditions should prevail regionally leading to the subdued late mode behavior at Bondville.

Conclusions

The composition of the PM2.5 measured at Northbrook shows some interesting features that distinguish it from the corresponding measurements at Bondville. In particular, the diurnal average PM2.5 nitrate at Northbrook builds from daybreak to reach a peak in the afternoon while the corresponding nitrate at Bondville goes from a peak at just before daybreak to lower values during the day. Also the Northbrook concentrations show a significant number of days when the particulate nitrate concentrations are especially high. A numerical partitioning of the diurnal data shows that, in fact, both sites appear to have a similar behavior consisting primarily of two modes, the early mode where the particulate nitrate peaks before 11 am and a late mode where it peaks after 11 am. The overall diurnal averages appear different at the two sites because at Bondville the early mode dominates while at Northbrook the late mode dominates. On a given day generally the same single mode is seen at both sites. A preliminary hypothesis that appears consistent with the observations is that the late mode is caused by photochemical effects promoting the formation of particulate nitrate and that the process is amplified at

Northbrook by the lake breezes. More generally, the approach is a step toward relating PM2.5 composition and loading to synoptic weather conditions.

Future Plans

We should be able to refine and improve the hypothesis with more complete meteorological data, for example, by directly correlating Northbrook late mode concentrations with strong lake breeze cycles. Further analysis of the more extensive Bondville data set in light of the postulated occurrence of the 2-mode behavior is a reasonable direction. The particulate ammonium, gaseous SO_2 and HNO_3 gpic data should help in further analysis.

Statistics

		gpic1_so4	gpic1_no3	gpic2_so4	gpic2_no3
N	Valid	3429	2695	3429	2695
	Missing	0	734	0	734
Mean		3.0143	.7314	3.3228	.9943
Median		1.7852	.3459	1.6576	.7103
Std. Deviation		3.81664	1.09799	4.71240	.92904
Percentiles	25	.6615	.1207	.7884	.4195
	50	1.7852	.3459	1.6576	.7103
	75	3.9277	.8287	3.9238	1.2387

Table I. Mean, median, standard deviation, and quartiles of PM2.5 sulfate at Bondville (gpic1_so4), nitrate at Bondville (gpic1_no3), sulfate at Northbrook (gpic2_so4), and nitrate at Northbrook (gpic2_no3) from 2/18/05 to 9/26/05.

		Bondville	Northbrook
Early mode	# days	76	46
	% of days	51%	31%
	avg daily conc (μg/m^3)	0.78	0.77
Late mode	# days	74	104
	% of days	49%	69%
	avg daily conc (μg/m^3)	0.52	1.14

Table II. Comparison of the number and percent of days and average daily PM2.5 nitrate concentrations (μg/m3) characterizing the late and early mode behaviors (see text) at Northbrook and Bondville.

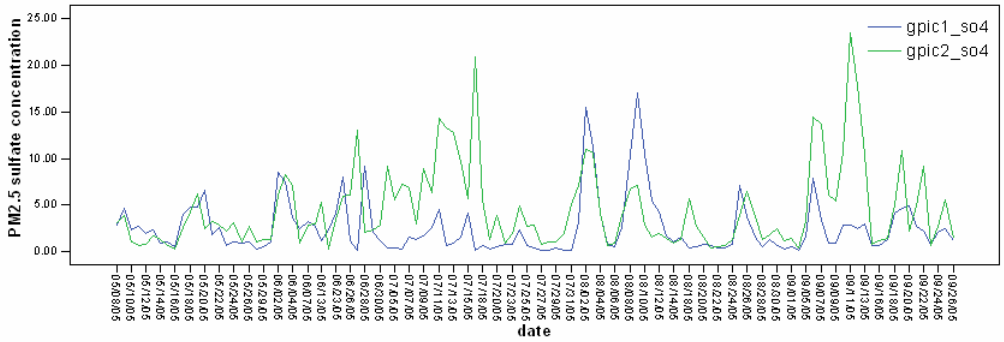

Figure 1. Average daily PM2.5 sulfate concentration (ug/m^3) at Bondville (gpic1_so4) and Northbrook (gpic2_so4) from 2/18/05 to 9/26/05.

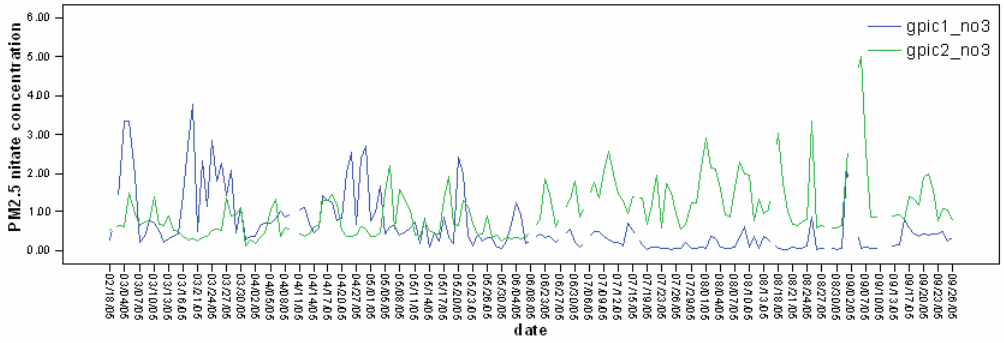

Figure 2. Average daily PM2.5 nitrate concentration (ug/m^3) at Bondville (gpic1_no3) and Northbrook (gpic2_no3) from 2/18/05 to 9/26/05.

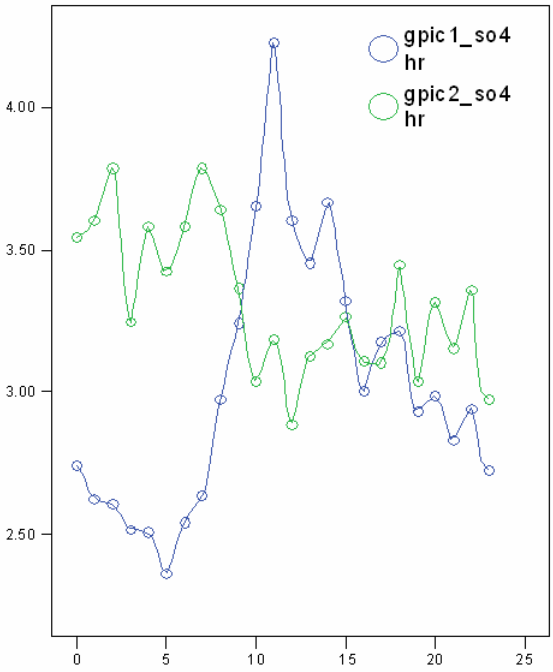

Figure 3. Diurnal hourly PM2.5 sulfate concentrations at Bondville (gpic1_so4) and Northbrook (gpic2_so4) (ug/m^3)

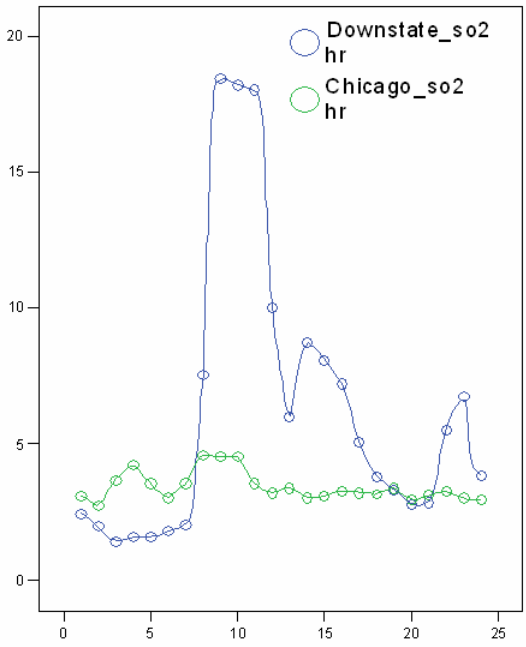

Figure 4. Diurnal average SO_2 concentrations (ppb) for a downstate monitoring station and a Chicago monitoring station.

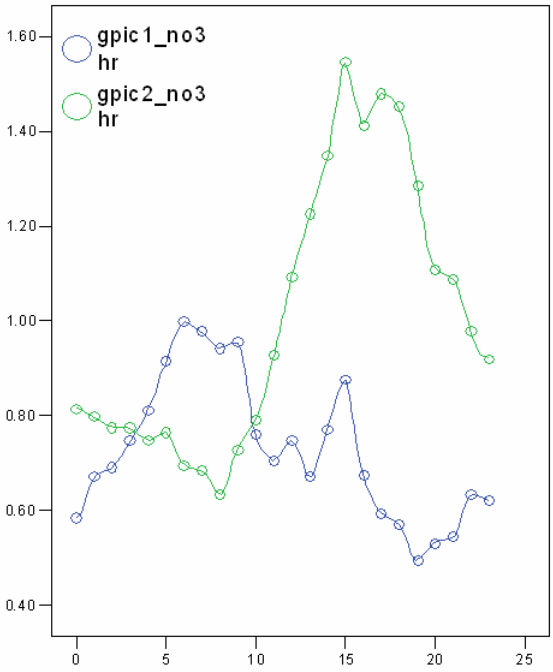

Figure 5. Diurnal hourly PM2.5 nitrate concentrations at Bondville (gpic1_no3) and Northbrook (gpic2_no3) in ug/m3

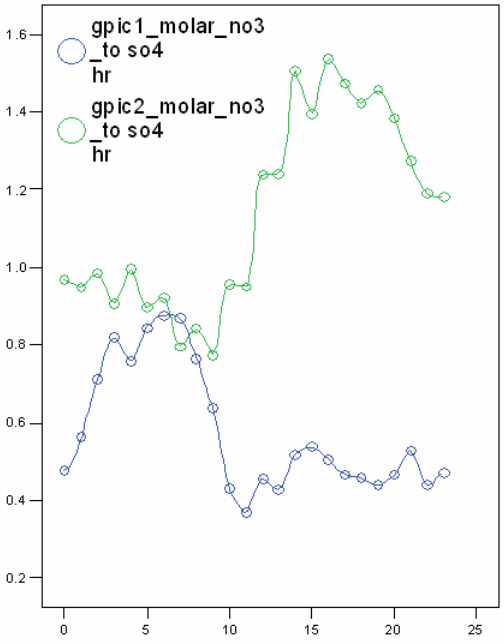

Figure 6. Diurnal average of molar ratios of PM2.5 nitrate to sulfate for Bondville (gpic1_molar_no3_to so4) and Northbrook (gpic2_molar_no3_to so4).

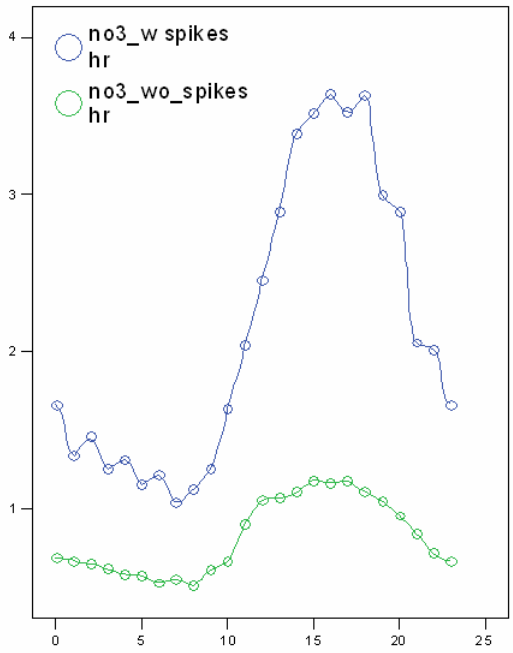

Figure 7. Diurnal average of PM2.5 nitrate at Northbrook for days when the daily average was above 1.4 (ug/m3) average peak

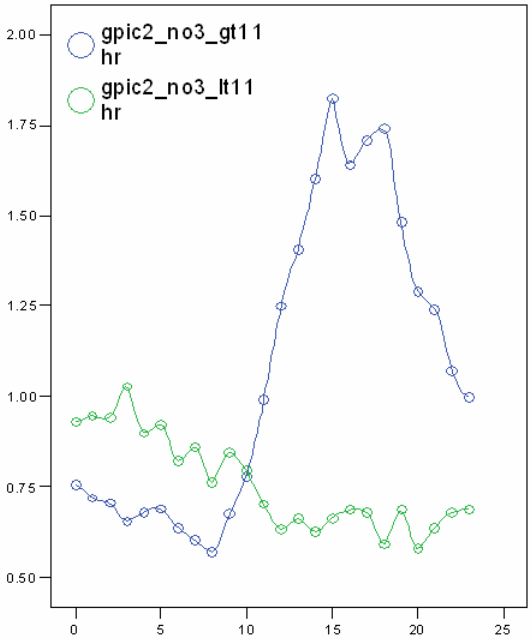

Figure 8. Diurnal average of PM2.5 nitrate concentrations (ug/m^3) at Northbrook for days when the time of occurrence of the daily peak concentration was less than 11 am (gpic2_no3_lt11) and greater than 11 am (gpic2_no3_gt11).

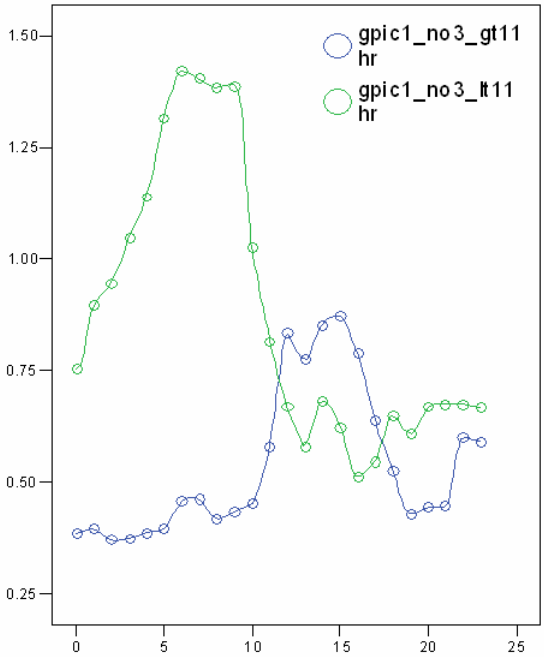

Figure 9. Diurnal average of PM2.5 nitrate concentrations (ug/m^3) at Bondville for days when the time of occurrence of the daily peak concentration was less than 11 am (gpic2_no3_lt11) and greater than 11 am (gpic2_no3_gt11).