

# Observations of $\text{NO}_y$ , $\text{CO}$ , and $\text{SO}_2$ and the origin of reactive nitrogen in the eastern United States

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**Abstract.** We have developed a technique to quantify better the relative significance of reactive nitrogen sources at a given site by measuring  $\text{NO}_y$ ,  $\text{SO}_2$ , and  $\text{CO}$ . Measurements taken on Maryland's eastern shore of the Chesapeake Bay indicate that, on average, a minimum of 20% of the  $\text{NO}_y$  is coming from coal-fired point sources. Measurements in Shenandoah National Park, Virginia, and near Arendtsville, Pennsylvania, indicate that these minimum fractions are 34% and 32%, respectively. The remainder is coming predominantly from mobile sources, though there are some  $\text{NO}_y$  sources whose influence cannot be determined with this technique. If the emissions inventories are taken to be correct, half the emitted  $\text{NO}_y$  has been lost (probably deposited as nitrate) by the time it reaches the site. Analysis of air parcel back trajectories reveals that the likely source of elevated  $\text{SO}_2$  levels, and therefore point source emissions of  $\text{NO}_y$ , is the industrialized midwest of the United States.

## 1. Introduction

Like many other large metropolitan areas, those in the eastern United States suffer from periodic ozone episodes in summertime. Since ozone is formed when hydrocarbons are oxidized in the presence of  $\text{NO}_x$  ( $\text{NO}_x$  = nitric oxide ( $\text{NO}$ ) + nitrogen dioxide ( $\text{NO}_2$ )), efforts at reducing ozone concentrations have centered on reducing these precursors. Until recently, it was thought that reducing hydrocarbon emissions would result in the most significant ozone reductions, because hydrocarbons fuel the ozone production cycle, and reductions in hydrocarbon levels produce consistent reductions in ozone levels. Owing to substantial biogenic hydrocarbon emissions [e.g., Jiang *et al.*, 1997; Fuentes *et al.*, 1995; Davis *et al.*, 1994] and the reactivity of those compounds, [e.g., Chameides *et al.*, 1992], the efficacy of controls on anthropogenic hydrocarbon emissions is reduced.  $\text{NO}_x$  reductions, in contrast, shift the ozone burden temporally and spatially, [e.g., National Research Council (NRC), 1991] and can actually result in an increase of ozone levels near source areas, and a decrease of ozone farther downwind. It appears that reductions of both  $\text{NO}_x$  and hydrocarbons will be necessary to substantially reduce ozone levels in the troposphere [Fiore *et al.*, 1998; Oltmans *et al.*, 1998]. Reductions in  $\text{NO}_x$  emissions would have the additional benefit of reducing acidification and nitrification of surface waters by reducing the amount of reactive nitrogen (nitric acid in particular) deposited to those waters. In any case, if  $\text{NO}_x$  emissions are to be reduced, the impact of various sources must be better quantified. Emissions inventories (such as those produced by the U. S. Environmental Protection Agency (EPA)) are currently the easiest way to do this. According to the EPA emissions inventories [EPA, 1997], in 1996, 41% of  $\text{NO}_x$

came from power plants and industrial combustion, 49% came from on- and off-road vehicles and engines, and 10% came from other sources. Unfortunately, emissions inventories offer little information on the relative local importance of  $\text{NO}_x$  sources in ozone formation and acid deposition at a given site and cannot offer any information as to the hourly, daily, or weekly variations in such emissions. Emissions inventories also do not account for the altitudes of sources, so an elevated source which readily distributes its pollutants over a wide area is treated the same as a low-lying source.

In this paper, we present new measurements of  $\text{NO}_y$  (total reactive oxides of nitrogen, defined as  $\text{NO}_y = \text{NO}_x +$  the nitrate radical ( $\text{NO}_3$ ) + 2  $\times$  dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) + nitric acid ( $\text{HNO}_3$ ) + nitrous acid ( $\text{HONO}$ ) + peroxyacetic acid ( $\text{CH}_3\text{C(O)OOH}$ ) + peroxyacetyl nitrates (PAN ( $\text{RC(O)OO NO}_2$ )) + organic nitrates ( $\text{RONO}_2$  and  $\text{ROONO}_2$ ) + particulate nitrate, ( $\text{pNO}_3^-$ )), sulfur dioxide ( $\text{SO}_2$ ), carbon monoxide ( $\text{CO}$ ), and ozone ( $\text{O}_3$ )) as well as a pair of complementary techniques for assessing the relative importance of stationary, coal-fired sources of  $\text{NO}_y$  and mobile sources, such as automobiles. One technique uses EPA emissions inventories and measurements of  $\text{SO}_2$  and  $\text{CO}$  to determine the relative importance of point and mobile sources of  $\text{NO}_y$ , while a second employs regression analysis to fit  $\text{NO}_y$  as a function of  $\text{SO}_2$  and  $\text{CO}$ . Finally, the spatial origins of air parcels reaching our site on the eastern shore of the Chesapeake Bay have been determined by using a back-trajectory model and segregating the trajectories according to  $\text{SO}_2$  and  $\text{CO}$  levels measured at the site.

## 2. Chemistry of $\text{NO}_y$ , $\text{SO}_2$ , and $\text{CO}$

Since the chemistry of  $\text{NO}_y$  is well documented [e.g., Seinfeld and Pandis, 1998], only a brief synopsis is given here. Reactive nitrogen is largely emitted as  $\text{NO}$  by anthropogenic sources and then oxidized quickly to  $\text{NO}_2$ . The lifetime for removal of  $\text{NO}_x$  in the boundary layer is thought to be of the order of 1-2 days [e.g., Munger *et al.*, 1998]. Deposition of the more soluble species created after reaction with  $\text{OH}$  may take somewhat longer, depending on the depth of the boundary layer (modulating dry deposition) and the amount of moisture available for wet deposition of  $\text{NO}_y$ .

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CO in the atmosphere may be emitted directly from combustion sources or formed as a by-product of the oxidation of hydrocarbons. It is primarily removed by reaction with OH in the troposphere and has a lifetime that varies from 1 to 4 months (or greater), depending on season, latitude, and available sunlight for photochemistry [e.g., NRC, 1991].

No natural sources of SO<sub>2</sub> in the eastern United States can approach the levels generated by coal-fired industrial facilities and paper mills, so SO<sub>2</sub> concentrations are good tracers for anthropogenic activity. Once released, SO<sub>2</sub> suffers a complex fate (see *Seinfeld and Pandis* [1998] for a detailed review). The net lifetime of gas-phase SO<sub>2</sub> is highly variable, being dictated by many factors, but is of the order of 1-2 days in the troposphere.

### 3. Methods

Measurements were conducted at the University of Maryland's Wye Research and Education Center on the eastern shore of the Chesapeake Bay (38.92°N, 76.15°W). Data were also obtained from Shenandoah National Park at Big Meadows (38.52°N, 78.44°W) and from Arendtsville, Pennsylvania (39.92°N, 77.30°W), through the North American Research Strategy for Tropospheric Ozone-Northeast (NARSTO-NE) program. The data for all three sites are summarized in Table 1.

The Wye site [*Civerolo and Dickerson*, 1998] is rural and located in the middle of a fertilized cornfield, 200 m from the nearest road. Nearby roads are only lightly used, though a well-traveled highway runs 6 km to the north of the site. The site is situated 50-60 km east of the urban centers of Baltimore, Maryland, and Washington, D. C., and often sees elevated ozone levels in the summer. There are five large power plants within 100 km of the site, with the closest being approximately 40 km away, just south of Baltimore. The land east of the site is largely rural farmland, so the site occasionally receives very clean air coming off the Atlantic Ocean from the east.

Instruments at the Wye site were kept in a climate-controlled shed, with Teflon tubing running from the instruments to sample inlets on towers. SO<sub>2</sub>, CO, and O<sub>3</sub> were sampled from 6 m above the ground, the air being filtered by Teflon filters (1- $\mu$ m-diameter pore size) before entering the instruments. The NO<sub>y</sub> inlet was a set of three heated (375°C) mo-

lybdenum wire mesh catalysts elevated 3 m off the ground. When fully grown, the corn canopy was approximately 2 m above the ground. Halfway through the experiment, the corn was harvested (on October 7 in the field north of the shed and a week later in the south field), leaving only the bottom ~30 cm of the cornstalks in the field. CO, ozone, and ultraviolet light intensity were measured from September through December of 1996, while SO<sub>2</sub> was measured from the end of September through the beginning of December. In addition, NO<sub>y</sub> was measured for three intensive periods in early October, late November, and mid-December.

Instruments at the other two sites were also kept in climate-controlled sheds with inlets mounted on 10-m towers. The Shenandoah site [*Doddridge et al.*, 1991; *Poulida et al.*, 1991] is located 200 m off of Skyline Drive in Shenandoah National Park. It is an elevated site (1100 m) in low wooded mountains and has only minimal local sources. We discuss measurements taken there from September 1 to December 31, 1996. The Arendtsville site is also rural, located in an orchard 55 km southwest of Harrisburg, Pennsylvania, amidst rolling hills at an elevation of 270 m; further details on the site are available through the NARSTO-NE program. We discuss measurements at Arendtsville taken from June 17, 1995, to September 25, 1995.

CO was measured by a nondispersive infrared monitor (Thermo Environmental Instruments Model 48, Franklin, Massachusetts), which was modified [*Dickerson and Delany*, 1988; *Doddridge et al.*, 1994] so it could be zeroed and operated at elevated pressures. The instrument was zeroed for 5 min. out of every half hour by passing the sample flow over a heated (150°C) catalyst of palladium on alumina. This effectively removes all CO from the inlet stream, while leaving other potential interferents, such as water vapor, intact. The instrument was calibrated monthly by direct measurement of a standard mixture of CO in air (Matheson Gas Products Inc., Baltimore, Maryland) which was compared directly with a National Institute of Standards and Technology (NIST) (Gaithersburg, Maryland) working standard reference material at NIST. Data were corrected accordingly, though the calibrations varied by only ~1% over the course of the experiment. The detection limit for this instrument, as configured, was 10 parts per billion by volume (ppbv) CO.

SO<sub>2</sub> was measured via a modified [*Luke*, 1997] commercial pulsed UV fluorescence instrument (Thermo Environmental Instruments, Model 43C) at the Wye site. The instrument was zeroed for 10 min. out of every half hour by passing the sample airstream through a potassium carbonate-impregnated paper filter. Prior to entering the instrument, the sample gas was dried using a Nafion tube dryer (Perma Pure, Inc., Toms River, New Jersey) to minimize quenching of excited SO<sub>2</sub> by water vapor. Calibrations were performed twice a day by dynamic dilution of an SO<sub>2</sub> standard in bottled air. The concentration of SO<sub>2</sub> in the standard (Scott-Marrin, Inc., Riverside, California) was determined at NIST by comparison with NIST working standard reference materials. The detection limit of this instrument is approximately 50 parts per trillion (ppt) of SO<sub>2</sub> in air. Unmodified pulsed fluorescence instruments were used at Shenandoah and Arendtsville and were subject to regular calibrations as per NARSTO-NE protocol.

NO was measured using a modified [*Dickerson et al.*, 1984] commercial ozone chemiluminescence detector (Thermo Environmental Instruments Model 14B at Wye, and Model 42 at

Table 1. Site Statistics

Site	CO	SO <sub>2</sub>	NO <sub>y</sub>	O <sub>3</sub>
Wye				
Mean, ppbv	219	2.8	8.1	23
RMS, ppbv	236	4.3	10.3	29
Standard deviation, ppbv	87	3.2	6.3	18
Hours	1739	1256	474	1563
Shenandoah				
Mean, ppbv	145	2.6	7.1	36
RMS, ppbv	150	3.7	8.7	38
Standard deviation, ppbv	37	2.6	5.1	12.5
Hours	2206	2716	2308	2714
Arendtsville				
Mean, ppbv	171	4.3	7.8	49
RMS, ppbv	180	7.0	9.0	53
Standard deviation, ppbv	58	5.5	4.5	21
Hours	2199	2242	2307	2342

Arendtsville and Shenandoah). The instrument was calibrated by dynamic dilution of a NO standard (Matheson Gas Products, Inc.) with zero air (Scott-Marrin, Inc.). NO concentration in the standard was determined at NIST by comparison with a NIST working standard reference material. NO<sub>y</sub> was measured by conversion of NO<sub>y</sub> to NO on a heated (375°C) molybdenum mesh surface [Fehsenfeld *et al.*, 1987; Williams *et al.*, 1998; Nunnermacker, 1990] and subsequent detection by the NO instrument mentioned previously. The efficiency of conversion was tested by gas phase titration of an NO standard with ozone to produce NO<sub>2</sub>, which was then drawn through the converter and NO detector described. The conversion efficiency at all times exceeded 90%. The conversion efficiency of other NO<sub>y</sub> compounds was not tested. This technique offers great precision, with a detection limit of approximately 50 ppt, but owing to possible interferences from conversion of non-NO<sub>y</sub> species on the molybdenum catalyst, its absolute accuracy is only ±30%.

Ozone was measured using a commercial detector (Thermo Environmental Instruments Model 49) that was not modified. The instruments at the Shenandoah and Wye sites agreed with standard ozone monitors at NIST to within 1%. Data were corrected for this small difference. The Arendtsville instrument was calibrated in accordance with NARSTO-NE protocol.

#### 4. Emissions Inventory Analysis

CO and SO<sub>2</sub> may be employed as tracers for mobile and point sources of NO<sub>x</sub>, respectively, since mobile sources emit high levels of CO and relatively little SO<sub>2</sub>, while the opposite is true for point sources. Our mobile source category is based on EPA's area sources of NO<sub>x</sub> and CO. Briefly, we refer to mobile sources as all vehicles powered by gasoline and diesel fuel, including on-road vehicles and off-road sources such as motorized lawn and garden equipment, light commercial vehicles, and recreational marine vessels, among others. Subtracted from this total is the small contribution from airplanes, because most of their emissions are at altitudes high in the troposphere and are unlikely to dramatically affect urban air pollution. Mobile sources account for most of the CO emitted (95 times that emitted by point sources) and likewise, most of the area sources of NO<sub>x</sub>. Our point source category is composed of emissions of NO<sub>x</sub> and SO<sub>2</sub> from power plants and industrial combustion. Point sources emit a substantial amount of SO<sub>2</sub>: 30 times that emitted by mobile sources [EPA, 1997]. Taken together, these mobile and point sources account for 90% of the NO<sub>x</sub> emissions in the United States. Therefore most NO<sub>x</sub> emissions should be well correlated with either SO<sub>2</sub> or CO emissions, leaving relatively little NO<sub>x</sub> uncounted.

Because some fraction of the pollutants arriving at a particular site have likely been oxidized since their emission, it is more reasonable to use NO<sub>y</sub> than NO<sub>x</sub>, especially in light of the importance of HNO<sub>3</sub> to acidification and nitrification of lakes and streams [e.g., Valigura *et al.*, 1994]. Similarly, in place of SO<sub>2</sub>, one should use total oxidized sulfur (SO<sub>2</sub> + sulfate). CO concentrations are not useful tracers for anthropogenic NO<sub>x</sub> emissions unless one subtracts the background level of CO not associated with any anthropogenic NO<sub>y</sub>. That background level includes CO from oxidation of hydrocarbons and other large-scale CO sources in the troposphere, as well as CO emitted by anthropogenic sources so distant that any NO<sub>y</sub> associated with them has been removed. The background CO levels were deter-

mined by examining data from Niwot Ridge, Colorado (40°03'N, 105°35'W, 3475 m), and Wendover, Utah (39°54'N, 113°43'W, 1320 m), taken by the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) Carbon Cycle Group [Novelli *et al.*, 1998], and taking the average of all CO data flagged as background CO levels by NOAA/CMDL. Background CO levels vary with season, so the average background level was determined over the time covered by each data set. For the Wye River site and Shenandoah National Park (September-December data), that level was 112 ppbv, while 105 ppbv was used at Arendtsville, Pennsylvania (June-September). These numbers are in good agreement with earlier measurements [Goldan *et al.*, 1995] suggesting a CO background level of 110±20 ppbv for a site near Boulder, Colorado. The CO above background, indicated by ΔCO, is a reasonable tracer for CO emissions likely to be associated with NO<sub>y</sub>.

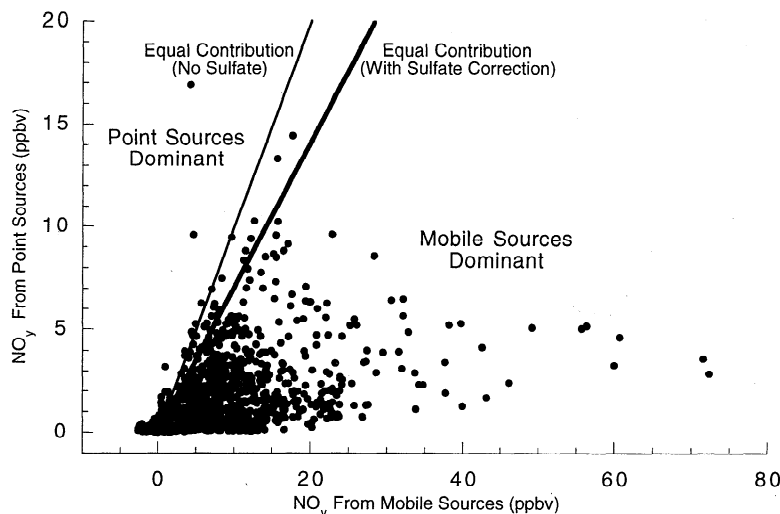
Let NO<sub>y|p</sub> represent the fraction of NO<sub>y</sub> from point sources, and let NO<sub>y|m</sub> represent the fraction of NO<sub>y</sub> due to mobile sources; then

$$\text{NO}_{y|p} = \frac{\text{NO}_y}{\text{SO}_2} \bigg|_p [\text{SO}_2]_p \quad (1)$$

$$\text{NO}_{y|m} = \frac{\text{NO}_y}{\text{CO}} \bigg|_m [\text{CO}]_m \quad (2)$$

where [SO<sub>2</sub>]<sub>p</sub> is the concentration of SO<sub>2</sub> due to point sources and [CO]<sub>m</sub> is the concentration of CO due to mobile sources. This analysis assumes that SO<sub>2</sub> and CO are conserved tracers for NO<sub>y</sub> emissions, an issue which will be addressed in the discussion of results. NO<sub>y</sub>/SO<sub>2|p</sub> and NO<sub>y</sub>/CO<sub>m</sub> represent the molar ratios of NO<sub>y</sub> to SO<sub>2</sub> from point sources and NO<sub>y</sub> to CO from mobile sources, respectively. Assuming that the EPA emissions inventories [EPA, 1997] are correct, one gets the molar ratios SO<sub>2</sub>/NO<sub>y|p</sub> = 1.75 and CO/NO<sub>y|m</sub> = 11.9. These ratios are in agreement with measurements of CO/NO<sub>y</sub> ratios for mobile sources [Buhr *et al.*, 1992; Goldan *et al.*, 1995] and point sources [Buhr *et al.*, 1992]. The ratio of SO<sub>2</sub> to NO<sub>y</sub> for point sources is derived from power plant data for Connecticut, Delaware, Kentucky, Maryland, Michigan, New Jersey, New York, North Carolina, Ohio, Pennsylvania, Rhode Island, South Carolina, Virginia, Washington, D. C., and West Virginia, in the United States. The extent of this region was determined by grouping 24-hour back trajectories into eight sectors and taking the average trajectory length for each sector; data from any state that fell substantially into this area were included in the ratio. The ratio of CO to NO<sub>y</sub> for automobile emissions was determined from national data. On a state-by-state basis this ratio was within 25% of the national average for every state above except North Carolina, where it was 37% high. If we take the worst-case scenario and assume that the ratio is 40% too high, then the fraction of NO<sub>y</sub> coming from automobiles is reduced by 15%. The possible effect of reformulated gasoline on this ratio is not clear, but likely rather small, since it reduces both NO<sub>x</sub> and CO emissions. A tunnel study [Kirchstetter *et al.*, 1999] found that the CO/NO<sub>x</sub> ratio dropped by 16% with use of reformulated gasoline.

The artificial quantities [CO]<sub>m</sub> and [SO<sub>2</sub>]<sub>p</sub> may be expressed in terms of measured quantities if one makes the approximation that most of the CO and SO<sub>2</sub> emissions stem from point and mobile sources as outlined earlier. Mathematically, denot-



**Figure 1.** Relative source strengths at the Wye River site for fall of 1996.  $\text{NO}_y$  from point sources was determined by dividing the  $\text{SO}_2$  level by 1.75, the appropriate emissions ratio for  $\text{SO}_2$  to  $\text{NO}_x$ .  $\text{NO}_y$  from mobile sources was obtained by first subtracting 112 parts per billion by volume from the CO level and then dividing the remainder by the emissions ratio ( $\text{CO}/\text{NO}_x$ ) of 11.9. Therefore a 1:1 ratio (thin line) represents equal contributions from both point and mobile sources. The bold line shows where the 1:1 line lies if  $\text{SO}_2$  levels are multiplied by 1.4 to account for sulfate. Points to the right of these lines indicate conditions where mobile sources are the dominant sources of  $\text{NO}_y$ , and those lying to the left reflect the dominance of point sources.

ing  $[\Delta\text{CO}]$  as the CO above the natural background level,

$$[\Delta\text{CO}] \approx [\text{CO}]_p + [\text{CO}]_m \quad (3)$$

$$[\text{SO}_2] \approx [\text{SO}_2]_p + [\text{SO}_2]_m \quad (4)$$

The  $[\text{CO}]_p$  and  $[\text{SO}_2]_m$  terms are small and may be written in terms of the product of an emissions ratio and  $[\text{CO}]_m$  and  $[\text{SO}_2]_p$ , respectively, to give

$$[\Delta\text{CO}] = [\text{CO}]_m \left( 1 + \frac{[\text{CO}]_p}{[\text{CO}]_m} \right) \quad (5)$$

$$[\text{SO}_2] = [\text{SO}_2]_p \left( 1 + \frac{[\text{SO}_2]_m}{[\text{SO}_2]_p} \right) \quad (6)$$

These can be rearranged to give the relations between the measured quantities,  $[\text{SO}_2]$  and  $[\Delta\text{CO}]$ , and the desired quantities,  $[\text{CO}]_m$  and  $[\text{SO}_2]_p$ . Using these equations, one may obtain the ratio of  $\text{NO}_{y,p}$  to  $\text{NO}_{y,m}$  as the product of three factors:

$$\begin{aligned} \frac{\text{NO}_{y,p}}{\text{NO}_{y,m}} &= \frac{\frac{\text{NO}_y}{\text{SO}_2} \Big|_p [\text{SO}_2]_p}{\frac{\text{NO}_y}{\text{CO}} \Big|_m [\text{CO}]_m} \\ &= \left( \frac{\text{NO}_y}{\text{SO}_2} \Big|_p \right) \left( \frac{\text{SO}_2}{\Delta\text{CO}} \right) \left( \frac{1 + \frac{[\text{CO}]_p}{[\text{CO}]_m}}{1 + \frac{[\text{SO}_2]_m}{[\text{SO}_2]_p}} \right) \end{aligned} \quad (7)$$

The first factor comes from emissions ratios, and the second is obtained from measurement. The third factor, also determined

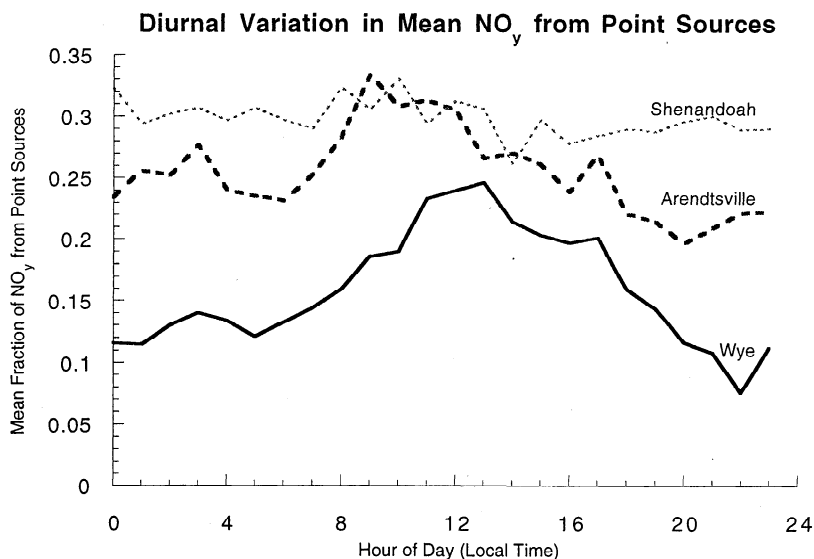
from emissions ratios, is 0.978 [EPA, 1997]; it is close to 1.0 because emissions of CO from point sources and  $\text{SO}_2$  from mobile sources are minimal. Denoting  $\text{NO}_{y,p}/\text{NO}_{y,m}$  as  $x$ , one may write the following:

$$\text{Fraction of } \text{NO}_y \text{ attributed to mobile sources} \quad 1/(1+x)$$

$$\text{Fraction of } \text{NO}_y \text{ attributed to point sources} \quad 1/(1+1/x)$$

A graphical representation of the results of this technique (Figure 1) shows the relative amounts of  $\text{NO}_y$  from point and mobile sources. In using this technique, one sees (Figure 2) that the fraction of  $\text{NO}_y$  due to point sources depends on time and the location of the site. Though on average it is 16% at Wye, 25% at Arendtsville, and 30% at Shenandoah National Park, this fraction varies from 0% to nearly 100% at all three sites. When these averages are weighted by the  $\text{NO}_y$  mixing ratio, they become 18%, 27%, and 32% for Wye, Arendtsville, and Shenandoah, respectively.

Since approximately a third of atmospheric sulfur may already be in the form of sulfate aerosol [e.g., Husain *et al.*, 1998], the measured  $\text{SO}_2$  term (the numerator of the second factor) in (7) should really be sulfate +  $\text{SO}_2$ . An estimate of the size of this correction should be made by increasing the  $\text{SO}_2$  concentration to account for the  $\text{SO}_2$  that has already been converted to sulfate. Measurements of sulfate were obtained from the National Park Service's Interagency Monitoring of Protected Visual Environments (IMPROVE) program for Washington, D. C., Shenandoah National Park (colocated with our site), Dolly Sods, West Virginia (in Monongahela National Forest), and Brigantine National Wildlife Refuge in New Jersey. These filter packs were exposed twice a week for one day and later analyzed by an off-site laboratory. To determine an approximate correction, we examined the average ratio of sulfate to  $\text{SO}_2$  as a function of time of year and site location. This suggests that  $\text{SO}_2$  mixing ratios should be multiplied by 1.4 at the Wye site, 1.3 at Shenandoah, and 1.5 at Arendtsville. After



**Figure 2.** Mean fraction of  $\text{NO}_y$  from point sources as a function of time of day at the Wye, Arendtsville, and Shenandoah sites. When corrected for sulfate, the values on the curves increase by factors of roughly 1.2 (Shenandoah), 1.3 (Wye), and 1.4 (Arendtsville), but the shape remains the same. Note that the strength of the diurnal variation is much less at the elevated Shenandoah site than at the low-altitude Wye and Arendtsville sites.

applying this correction, the average contribution to  $\text{NO}_y$  from point sources becomes  $20 \pm 5\%$  at the Wye site,  $32 \pm 8\%$  at Arendtsville, and  $34 \pm 8\%$  (95% confidence intervals) at Shenandoah. At Wye, the lower quartile (25th percentile) was 8% and the upper quartile was 29% of  $\text{NO}_y$  coming from power plants, while at Shenandoah the lower and upper quartiles were 14% and 50%, respectively. At Arendtsville, those quartiles were at 13% and 47%. Uncertainties in the emissions inventories dictate the uncertainties in these quantities, which are more likely to be systematic than random. The uncertainties calculated above were calculated from an assumption of 10% uncertainty in the emissions inventories.

One may also calculate the amount of  $\text{NO}_y$  that one would predict if no  $\text{NO}_y$  were removed and  $\text{SO}_2$  and CO were perfect tracers. If that is the case, then (1) and (2) may be added to give total  $\text{NO}_y$ . In all cases, more  $\text{NO}_y$  is predicted than is actually measured, indicating that either a fair portion of the  $\text{NO}_y$  at each site has already been deposited or otherwise removed or that the emissions inventories are in error. On average, the ratio of  $\text{NO}_y$  observed to  $\text{NO}_y$  predicted is 49% at Wye, 52% at Shenandoah, and 48% at Arendtsville.

## 5. Regression Analysis

Regression analysis has been used before [e.g., Parrish *et al.*, 1991; Goldan *et al.*, 1995] along with principal component analysis [Buhr *et al.*, 1992] to examine the relationships between  $\text{NO}_y$ , CO, and  $\text{SO}_2$ . Since the major sources of  $\text{NO}_y$  also emit CO and  $\text{SO}_2$ ,  $\text{NO}_y$  should be well correlated with CO and  $\text{SO}_2$ . Regression analysis, fitting  $\text{NO}_y$  mixing ratios as a function of both  $\text{SO}_2$  and CO, bears this out. No emissions inventories are necessary for this approach, and multiplicative corrections for sulfate do not change the final result. The analysis here is similar to that commonly used to link aerosol loadings to their sources [e.g., Henry, 1992].

To examine possible day/night differences, two subsets of the data were analyzed with the regression technique (midnight (2300-0500 LT) and midday (1000-1500 LT) data) in addition to the analysis of the entire data set. No significant differences between daytime and nighttime regressions were found. Table 2 shows the results of the regressions and 95% confidence intervals for each parameter. The statistical uncertainty in each parameter depends on the number of degrees of freedom, the

**Table 2.** Regressions

Site	Time Period	Regression*	$r^2$
Wye	all data	$[\text{NO}_y] = 0.39 \pm 0.17[\text{SO}_2] + 0.091 \pm 0.010[\text{CO}] - 8.9 \pm 1.8$	0.80
	midday	$[\text{NO}_y] = 0.18 \pm 0.27[\text{SO}_2] + 0.096 \pm 0.026[\text{CO}] - 8.6 \pm 3.9$	0.88
	midnight	$[\text{NO}_y] = 0.48 \pm 0.59[\text{SO}_2] + 0.073 \pm 0.021[\text{CO}] - 6.7 \pm 3.3$	0.76
Shenandoah	all data	$[\text{NO}_y] = 0.79 \pm 0.07[\text{SO}_2] + 0.071 \pm 0.005[\text{CO}] - 5.1 \pm 0.7$	0.58
	midday	$[\text{NO}_y] = 0.88 \pm 0.13[\text{SO}_2] + 0.080 \pm 0.010[\text{CO}] - 5.6 \pm 1.3$	0.66
	midnight	$[\text{NO}_y] = 0.75 \pm 0.16[\text{SO}_2] + 0.073 \pm 0.011[\text{CO}] - 5.9 \pm 1.5$	0.51
Arendtsville	all data	$[\text{NO}_y] = 0.39 \pm 0.02[\text{SO}_2] + 0.041 \pm 0.002[\text{CO}] - 0.7 \pm 0.4$	0.60
	midday	$[\text{NO}_y] = 0.41 \pm 0.04[\text{SO}_2] + 0.041 \pm 0.004[\text{CO}] - 0.3 \pm 0.7$	0.70
	midnight	$[\text{NO}_y] = 0.36 \pm 0.04[\text{SO}_2] + 0.036 \pm 0.004[\text{CO}] - 0.2 \pm 0.7$	0.51

\*All values in brackets are parts per billion by volume of  $\text{SO}_2$ ,  $\text{NO}_y$ , or CO in air.

**Table 3.** Minimum Fractions of  $\text{NO}_y$  from Point Sources

Site	Emissions Inventory Analysis*	Emissions Inventory Analysis†	Regression Analysis
Wye	16±4%	20±5%	11±5%
Shenandoah	30±8%	34±8%	29±5%
Arendtsville	26±6%	32±8%	21±3%

\*No sulfate correction used.

†Corrected for sulfate.

number of distinct air masses sampled over the period of data used in the regression analysis, which is readily determined by an autocorrelation test. The maximum time for this to happen was 30 hours at Wye (for  $\text{SO}_2$ ), 29 hours at Shenandoah (for all three), and 64 hours at Arendtsville (for  $\text{NO}_y$ ). We have calculated the uncertainties in each regression using the number of statistically independent conditions encountered (8.7 at Wye, 33 at Arendtsville, and 65 at Shenandoah) while  $\text{NO}_y$ ,  $\text{SO}_2$ , and CO were being measured at each site. Spectral analysis of CO and  $\text{SO}_2$  time series showed that 96% of the variance in CO and 95% of that in  $\text{SO}_2$  (from the unpadding series) occur on timescales longer than 1 hour, so the use of hour averages is justified.

The suitability of the regression technique to analysis of these data sets (and their suitability to the distributions of CO and  $\text{SO}_2$  in these data sets) was examined by applying this technique to a simulated data set that used the real CO and  $\text{SO}_2$  measurements from each site and a simulated  $\text{NO}_y$  level, which was calculated as follows:

$$\text{NO}_y \text{ (simulated)} = ([\text{CO}] - 50)/10 + [\text{SO}_2]/2. \quad (8)$$

This technique generates a realistic distribution of  $\text{NO}_y$  values with known parameters. The divisors of 10 and 2 are the (arbitrary) simulated  $\text{SO}_2/\text{NO}_y$  and  $\text{CO}/\text{NO}_y$  emissions ratios, while the 50-ppbv offset of CO simulates the natural background level. In every case, the regression technique faithfully returned exactly the simulated emissions ratios and background CO level, and, of course, 100% of the variance was explained.

Once the regression equation is obtained, the contributions of mobile and point sources may be evaluated over a specific period by plugging the values of CO and  $\text{SO}_2$  into the appropriate regression equation. The intercept is incorporated into the CO term, as the contribution from the natural CO background, and evaluated to determine the contribution of mobile sources to  $\text{NO}_y$ . The  $\text{SO}_2$  term is likewise evaluated, but without the intercept. The results, given in Table 3, agree within experimental uncertainty with those obtained from the emissions inventory analysis.

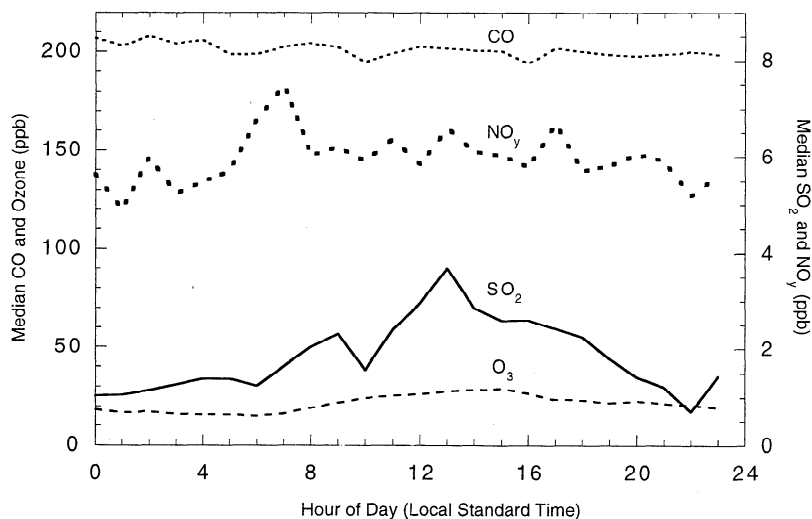
## 6. Back-Trajectory Analysis

A series of 48-hour back trajectories initialized at 1700 UTC and elevations of 500, 1000, and 1500 m above the Wye River site were obtained using the HYSPLIT4 model [Draxler, 1988, 1991] (see also the HYSPLIT4 Web site at <http://www.arl.noaa.gov/ready/hysplit4.html>). The model was run on the NOAA Air Resources Laboratory (NOAA/ARL) READY Web site, using 180-km 2-hourly output from the Nested Grid Model (NGM) for both horizontal and vertical winds. NGM data were archived and processed by NOAA/ARL from 91-km hourly data to 180-km 2-hourly data on a 33 x 28 polar stereographic grid covering the United States and Canada and their immediate coastal waters. The trajectories were subsequently clustered according to CO and  $\text{SO}_2$  concentrations to determine common source regions.

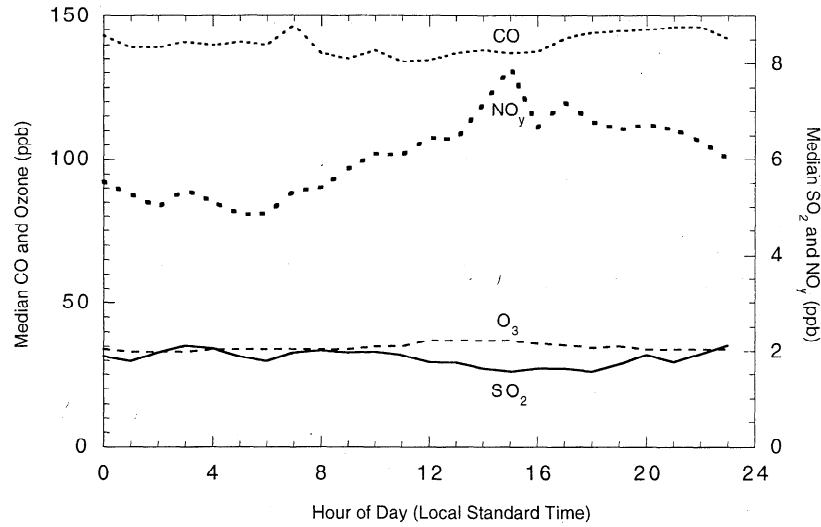
## 7. Discussion

### 7.1. Emissions Inventory Partitioning

The diurnal cycle (Figure 2) in the fraction of  $\text{NO}_y$  from point sources at each site is indicative of conditions at the site. At Shenandoah National Park, there is little if any diurnal variation in the fraction of  $\text{NO}_y$  from point sources, while Arendtsville and the Wye River site both show significant diurnal variations. Since the Shenandoah site is 1100 m above sea level, it is almost always above the planetary boundary layer [Poulida *et al.*, 1991; Doddridge *et al.*, 1992] except in the late afternoon, when the boundary layer is well mixed any-



**Figure 3.** Diurnal variations in CO,  $\text{NO}_y$ ,  $\text{SO}_2$ , and ozone at Wye River for fall of 1996. All values are parts per billion by volume; all times are local.

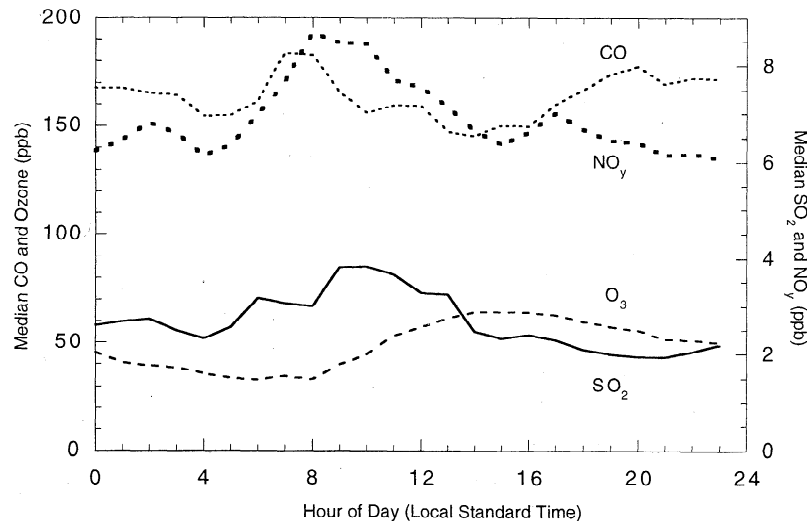


**Figure 4.** Diurnal variations in CO, NO<sub>y</sub>, SO<sub>2</sub>, and ozone at Shenandoah National Park for fall of 1996. All values are parts per billion by volume; all times are local.

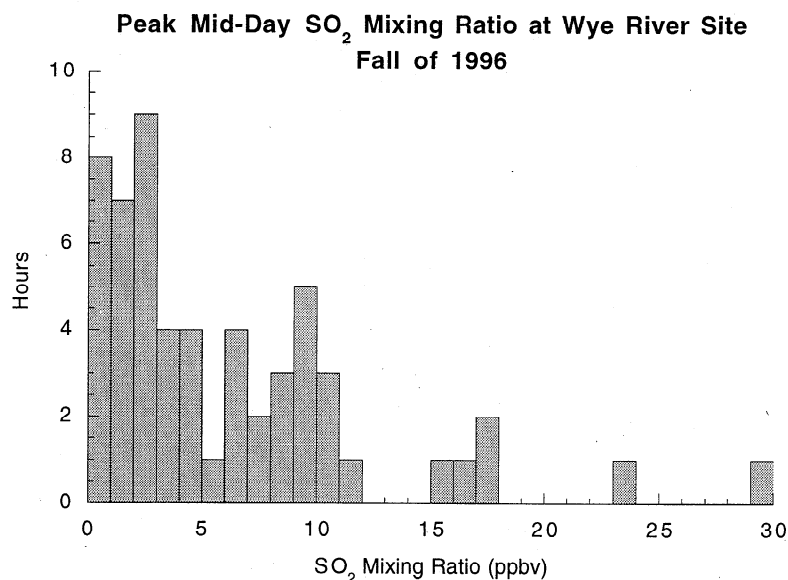
way, and its composition is therefore closer to that of the free troposphere. Both of the other sites are near sea level, so trace gas concentrations are significantly influenced by boundary layer dynamics and mixing. It appears that at the two low-elevation sites, pollution from distant point sources is being transported in the free troposphere and then mixed down to the surface as the boundary layer increases its depth [e. g. Ryan *et al.*, 1998].

This boundary layer activity can most easily be seen in the diurnal variation of SO<sub>2</sub> levels (Figures 3-5). SO<sub>2</sub> levels at the Wye and Arendtsville sites peak in the daytime, when SO<sub>2</sub> is mixed down to the surface from distant sources, and are nearly constant at night. Constant nighttime levels at the Arendtsville and Wye sites reflect a balance between occasional nighttime transport to the site (when the surface is not isolated by a boundary layer cap) and deposition to the surface. In contrast, the Shenandoah site shows no such diurnal variation in SO<sub>2</sub>. Higher levels of daytime SO<sub>2</sub> at the Arendtsville

and Wye sites dictate that the point-source contribution to NO<sub>y</sub> is appreciably higher in the daytime than at night. Since the daytime is also the time of peak ozone production, this is the time period that must be considered when tailoring ozone abatement strategies. Point sources therefore are responsible for a significant fraction of the total NO<sub>y</sub> observed at all three sites but are not responsible for the majority of NO<sub>y</sub>. It should be remembered that these are lower limits, since some of the atmospheric sulfur has already been deposited. One must also be careful in extending the conclusions from the Wye and Shenandoah sites to summertime ozone problems, since these measurements were taken in the fall, and not in the summer, when ozone is at its peak. The median fraction of NO<sub>y</sub> from point sources is also higher at both Shenandoah and Arendtsville, likely the result of their location upwind of the Baltimore-Washington urban corridor, which has a higher fraction of its NO<sub>x</sub> emissions from mobile sources than the areas upwind of Shenandoah and Arendtsville.



**Figure 5.** Diurnal variations in CO, NO<sub>y</sub>, SO<sub>2</sub>, and ozone at Arendtsville, Pennsylvania, for summer of 1995. All values are parts per billion by volume; all times are local.



**Figure 6.** Histogram of peak daytime daily SO<sub>2</sub> mixing ratio at the Wye River site for fall of 1996. The data fall into four modes: 0-1.25 ppbv (not resolved in this graph), 1.25-5 ppbv, 5-15 ppbv, and over 15 ppbv.

## 7.2. Regression Analysis

Examining the regression formulae reveals some interesting features. The value of the zero-[NO<sub>y</sub>] intercept that comes from regression analysis is mostly governed by the background CO concentration at the Wye and Shenandoah sites (98 and 71 ppbv, respectively). This estimate of background CO levels differs from our previous estimate not only because of the sizable statistical uncertainties in these quantities (Table 2), but also because natural NO<sub>y</sub> and SO<sub>2</sub> sources contribute to the NO<sub>y</sub> intercept. The Arendtsville site in particular appears to have been affected by a high background level of NO<sub>y</sub>; interpreting the zero-[NO<sub>y</sub>] intercept as only due to background CO levels gives a CO background of 18 ppbv. The coefficient of the CO concentration (slope) is in agreement with the EPA emissions ratio of [NO<sub>x</sub>]/[CO] = 0.084 [from EPA, 1997] at Wye (0.091) and only slightly lower (0.071) at Shenandoah. In contrast, the Arendtsville data are consistently lower (0.041) than the emissions ratio. These ratios compare favorably with the estimates of Buhr *et al.* [1992] of 0.075±0.027 for area sources and Goldan *et al.* [1995] of 0.069 and are lower than the National Acid Precipitation Assessment Program (NAPAP) inventory [Saeger *et al.*, 1989] estimate of 0.12 for the eastern United States.

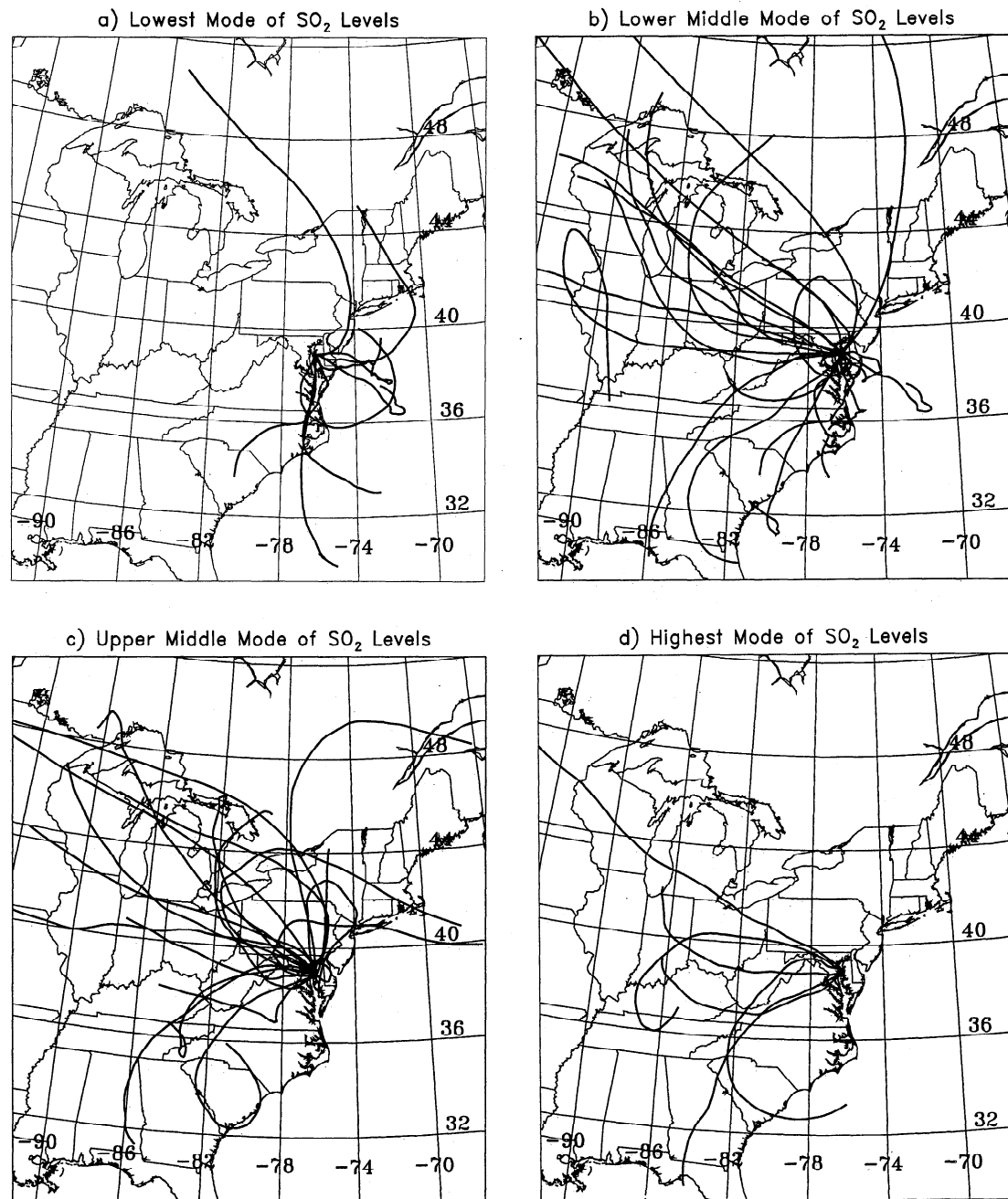
The coefficient of [SO<sub>2</sub>] for all data is 0.4 at the Wye and Arendtsville sites and 0.8 at Shenandoah, while the EPA [NO<sub>x</sub>]/[SO<sub>2</sub>] emissions ratio (the 12-state average) is 0.57 (the national average is 0.64). Pennsylvania emissions, however, are characterized by a high sulfur content, so the lower coefficients at Wye (frequently downwind of Pennsylvania) and Arendtsville may be a reflection of that fact. However, Buhr *et al.* [1992] obtain 0.71 for point sources from their analysis of data from Scotia, in western central Pennsylvania. Since point sources are fewer in number and their emissions will vary depending on the fuel and the emissions control technology used, one does not necessarily expect close agreement with measurements conducted at other sites at different times.

Both the emissions inventory and regression analyses should be considered estimates of the minimum contribution to NO<sub>y</sub> from point sources. To be ideal tracers, CO and SO<sub>2</sub> would have the same lifetime as NO<sub>y</sub>. However, since SO<sub>2</sub> is removed from the atmosphere more rapidly than CO, point-source emissions are necessarily underestimated. To estimate the size of this correction, one may consider a simple model in which each of the species is removed with its own lifetime. This can substantially affect the emissions inventory analysis, since the amount of SO<sub>2</sub> relative to CO is clearly affected. If SO<sub>2</sub> and NO<sub>y</sub> are assumed to have the same lifetime (so half of the atmospheric sulfur, like NO<sub>y</sub>, has been removed), then the contribution from point sources roughly doubles. However, a simple multiplicative correction does not alter the partitioning between mobile and point sources in the regression analysis. Because both the average amounts of each compound and the slopes of CO versus NO<sub>y</sub> and SO<sub>2</sub> versus NO<sub>y</sub> are affected by such a correction, there is no net change in the analysis. However, an event which affects one species but not another would tend to destroy the correlation between NO<sub>y</sub> and both CO and SO<sub>2</sub>. A concrete example would be a rainstorm occurring in an area with fresh CO, SO<sub>2</sub>, and NO<sub>x</sub> emissions, which would wash out a considerable fraction of the SO<sub>2</sub> but relatively little NO<sub>x</sub> or CO. The signal from SO<sub>2</sub> could then be lost by mixing from other air parcels, and the reactive nitrogen would be incorrectly labeled as having come from mobile sources. The data from both techniques therefore are to be taken as lower limits for the point source contribution to NO<sub>y</sub>, since some of the atmospheric sulfur has certainly been deposited to the surface.

## 7.3. Back-Trajectory Analysis

To examine the locations of distant sources, we grouped back trajectories by trace gas mixing ratio. For the Wye site, this kind of analysis only makes sense for SO<sub>2</sub>, since it has no substantial sources less than 40 km away. Since a tight nighttime boundary layer usually forms over the Wye site, night-





**Figure 7.** Back trajectories for each of the four modes illustrated in Figure 6: (a) 0-1.25 parts per billion by volume (ppbv), (b) 1.25-5 ppbv, (c) 5-15 ppbv, and (d) over 15 ppbv. Note that as the SO<sub>2</sub> level increases, the trajectories point away from the Atlantic Ocean and toward the industrialized midwestern United States.

time SO<sub>2</sub> levels have more to do with the amount of SO<sub>2</sub> present during the day and the rate of dry deposition than nighttime transport. The SO<sub>2</sub> data were therefore segregated by peak daytime level of SO<sub>2</sub> (see histogram, Figure 6), with SO<sub>2</sub> levels falling into four categories: 0-1.25 ppbv (10 days), 1.25-5 ppbv (22 days), 5-15 ppbv (19 days), and over 15 ppbv (6 days). The back trajectories were divided accordingly and are presented in Figure 7. The influence of clean air from off the Atlantic Ocean is clear; the only trajectory which originates deep inside the continent spent most of its time at relatively high altitudes before descending only when it got near the Wye

site. The others originate either over the Atlantic or near its western edge. As one moves from the cleaner trajectories to the dirtier ones, the influence of the Ohio River Valley as well as the nearby stacks south of Baltimore and south of Washington, D. C., become clear: Trajectories become more westerly with increasing SO<sub>2</sub> levels. As one might expect, a similar pattern is seen in the fraction of NO<sub>y</sub> attributed to point sources at Wye. On days when back trajectories come from the south and east over the Atlantic Ocean, the average fraction of NO<sub>y</sub> from point sources in the middle of the day (with sulfate correction) is 22%, while that from all other directions is 29%.

A similar analysis using CO revealed no significant differences between trajectories when CO concentrations were low and those when CO was high.

## 8. Conclusions

Measurements taken at the University of Maryland's Wye Research and Education Center on Maryland's eastern shore of the Chesapeake Bay, at Big Meadows in Shenandoah National Park in Virginia, and at a site near Arendtsville, Pennsylvania, have been used to partition  $\text{NO}_y$  between sources that emit CO and  $\text{NO}_y$  and sources that emit  $\text{SO}_2$  and  $\text{NO}_y$ . These correspond to mobile sources (such as automobiles) and point sources (such as coal-fired power plants), respectively. On the basis of emissions inventories and observed concentrations of CO,  $\text{SO}_2$ , and  $\text{NO}_y$ , we estimate a minimum of 20% of  $\text{NO}_y$  at Wye, 34% of  $\text{NO}_y$  at Shenandoah, and 32% of  $\text{NO}_y$  at Arendtsville to be coming from point sources. Since  $\text{SO}_2$  has a substantially shorter lifetime than CO, these fractions are to be taken as lower limits of the point source contribution to  $\text{NO}_y$ . Furthermore, if the emissions inventories are correct, approximately half of the  $\text{NO}_y$  has been deposited as nitrate by the time the air reaches all three sites. This suggests a lifetime for  $\text{NO}_y$  of the order of 1-2 days, since that is the time required for transport from the industrialized midwestern United States.

Results from a regression analysis, a technique independent of emissions inventories, are consistent with those from the emissions inventory approach without sulfate corrections, giving minimum contributions of 11%, 29%, and 21% of  $\text{NO}_y$  from power plants at the Wye, Shenandoah, and Arendtsville sites. This is significant, since regression analysis depends on variations in CO,  $\text{SO}_2$ , and  $\text{NO}_y$ , and is therefore not as vulnerable to differences in their lifetimes. The  $\text{CO}/\text{NO}_y$  ratios determined from these analyses agree with emissions inventories and past measurements at the Wye and Shenandoah sites, but differ somewhat from emissions inventories at the Arendtsville site.  $\text{SO}_2/\text{NO}_y$  ratios agree more loosely with emissions inventories, as might be expected, given the variable nature of point sources.

At the Wye site, back-trajectory analyses suggest the industrialized midwest as the direction from which the highest levels of  $\text{SO}_2$ , and therefore the highest levels of emissions from industrial point sources, came. In contrast, CO measurements showed no such simple pattern.

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