Deposition Velocities of SO_2 and O_3 over Agricultural and Forest Ecosystems

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Abstract. The results of field studies that measured the flux and deposition velocity of SO_2 and O_3 are reported. Three of the studies were over agricultural crops (pasture, corn, and soybean), and two were over forest (a deciduous forest and a mixed coniferous - deciduous forest). In all cases the deposition velocity for SO_2 was higher than that for O_3. Diurnal cycles of SO_2 deposition velocity were similar in shape, but not magnitude for all surfaces; however those for O_3 showed some difference between forest sites where the peak was in the morning, and the agricultural sites where the peak occurred at mid-day. Seasonal cycles of SO_2 were affected by deposition to surfaces when leaves weren't active, yet surface conductance is significant, but not for O_3 where stomatal uptake is the primary pathway for deposition.

Keywords: deposition velocity, dry deposition, flux, ozone, sulfur dioxide

1. Introduction

Because of the high cost and complexity of direct flux measurements, national dry deposition networks measure concentrations of air pollutants and infer the flux of pollutants to the surface using a modeled deposition velocity. In the U. S., the 70+ site Castnet operational dry deposition network operated by the U. S. EPA, and the 10+ site Airmon research network operated by NOAA both use the multi-layer deposition velocity model (MLM) (Meyers *et al.*, 1998). In light of its importance, an evaluation of MLM was desirable.

There have been numerous field studies that measured deposition velocity, including work by Matt et al. (1987), Meyers and Baldocchi (1988), Erisman and Duyzer (1991), Padro et al. (1991, 1994), Fuentes et al. (1992), and Munger et al. (1996). While these studies collected valuable information, they did not necessarily collect the data needed to exercise the MLM, nor do they have a consistent set of measurements over varying ecosystems. To overcome these problems, a study was conducted that measured the deposition velocities of key pollutants and the associated meteorological and biological variables over a variety of agricultural and natural ecosystems, distributed about the eastern half of the United States. Studies were done over pastures in North Carolina and Alabama, soybeans in Kentucky and North Carolina, corn in Illinois, a salt-water estuary in New Jersey, and forests in North Carolina, Pennsylvania, and New York. Study duration ranged from six weeks to full growing seasons. Complete descriptions of the measurement systems and key sites may be found in Meyers *et al.* (1998), and Finkelstein *et al.* (2000). This paper is a synthesis of the observations from that program.

2. Data

Instruments at the various sites were mounted approximately 5 m above the top of the crop, or, in the case of the forest sites, on a 36 m guyed, walk-up, scaffold tower. Chemical analyzers were housed in an air conditioned box near the base of the tower, or in shelters built on the tower at the forest sites. Wind velocity and turbulence were measured with an ATI sonic anemometer. O_3 and SO_2 were sampled from a draft tube with the inlet immediately adjacent to the sonic. Fast response measurements of O_3 were made with a specially constructed analyzer that uses the chemiluminescent reaction of O_3 with eosin-y dye. Fast response SO_2 measurements were taken with a modified Meloy SA285-E total sulfur analyzer. Soil temperature and soil heat flux were measured near the base of the tower. Leaf area index (LAI) and stomatal resistance measurements were made at several locations throughout the canopy. Details on the instrumentation, data handling, quality assurance, and data acceptance criteria are in Meyers *et al.* (1998) and Finkelstein *et al.* (2000).

Data from five of the sites are discussed in this paper. The sites are a pasture in Sand Mountain, Alabama (SM), a corn field in Bondville, Illinois (BV), a soybean field near Nashville, Tennessee (NV), a deciduous forest near Kane, Pennsylvania (K), and a mixed deciduous-coniferous forest in the Sand-Flats Forest in the Adirondack Mountains of New York State (SF). The number of valid half-hour observations of deposition velocity varied considerably among sites and between SO_2 and O_3. The smaller number of SO_2 observations is a result of the lower ambient concentration and high minimum detectable limit (2 ppb) of our fast response SO_2 instrument. The number of half-hour observations for SO_2 and O_3 respectively are: BV-191, 704; SM-304, 1347; NV-374, 1852; K-1625, 2861; SF-191, 2494.

The Sand Mountain site was located about 1 km south of Crossville, AL, (34.29 N, 85.97 W). The measurement site was on a slight knoll with a downward slope of about 1% in all directions. Vegetation was pasture: 52% fescue, 20% blue grass, and 20% white clover. Small trees were located about 500 m to the SW and to the NW. The data collection period began April 15 and ended on June 13, 1995. Surface moisture was adequate for good growth throughout the period. Leaf area index (LAI) increased from about 1.0 on April 15 to about 2.3 by June 13.

The Bondville study took place at the University of Illinois Soil and Crop Experimental Station (40.05N, 88.37W). The fetch was uniform for several km. Data collection ran from August 18 until October 1, 1994. At the start of the experiment the corn was 1.8 to 2.4 m high. By September 2, the corn was starting to mature and by October 3 essentially all the leaves were brown. LAI was 3.0 on August 18, increasing to 3.3 by the end of August and then slowly decreasing to 2.5 by October 1. Soil moisture was adequate for the crop throughout the experiment.

The Nashville site was in a soybean field (36.65 N, 87.03 W), 60 km NNW of Nashville and 2 km west of Keysburg, KY. Gently rolling uniform fetch over the soybean crop extended to at least 1500 m through the SE and southern quadrants. A corn field was adjacent to the soybeans, 140 m to the west at the closest point. The soybeans were planted on June 13. Dry deposition sampling was initiated June 22 and ended October 11, 1995. The beans went through a rapid growth period from July 10 through August 5 with the LAI increasing from 1 to about 6. Precipitation was light after late July and by mid August the beans were drought stressed. The LAI gradually decreased to about 3 by the end of September.

The Kane Experimental Forest is located in northwestern Pennsylvania, (41.60°N, 78.77°W). The area has gently rolling topography and elevation changes of 15 to 30 m within 1500 m of the site. The tree canopy is nearly uniform in height, and tends to damp out variations in ground elevation. In the vicinity of the experiment, there is a mix of tree species: 38% Black Cherry (*Prunus serotina*), 34% Red Maple (*Acer rubrum*), 23% Sugar Maple (*Acer saccharinum*), and 5% others. The canopy is 22 to 23 meters high. The soil was moist throughout the year. Valid data were collected from April 29 to October 23, 1997. Leaf bud occurred approximately the second week of May. Leaves were senescent by the middle of October.

The Sand Flats State Forest is about 7 miles NE of Boonville, NY, (43.57° N, 75.24° W). Observations were taken from May 12 to October 20, 1998. Composition of the forest included 20% White Pine (*Pinus stròbus*), 20% Black Cherry (*Prunus serotina*), 17% Sugar Maple (*Acer saccharinum*), 15% Hemlock (*Tsuga canadensis*), 10% White Spruce (*Picea glauca*), 8% open space, and a scattering of others. The soil throughout the area is sandy and well drained. The topography of the area is quite flat within 1 km of the tower. Because of the mix of species, the vertical structure of the forest was quite different from that at Kane, with a much higher density of branches and needles at lower levels on the conifers mixing with the higher leaves of the deciduous trees.

3. Data Summary and Synthesis

Mean daytime and nighttime deposition velocities, ± one standard error, for SO_2 and O_3 at the five sites are shown in Figure 1(A and B). One of the most noteworthy things to observe is that the SO_2 deposition velocity is consistently higher, by 0.2 to 0.4 cm/s than that for O_3. Nighttime deposition velocity values are lower than they are during the day, but they are not insignificant, especially for SO_2.

A plot of daytime, growing season, mean deposition velocity vs. LAI (Figure 2) for all of the sites we studied shows how clearly deposition velocity depends on vegetation mass. The relationship is quite linear for O_3 and, with one curious exception, for SO_2 as well. The LAI for the forest sites are underestimated, due to the leaf clumping factor (Chason *et al.*, 1991). An appropriate increase in forest LAI would make the relationship even more linear. From the data displayed, except for the anomalous SO_2

value at BV, the best linear fits for daytime average deposition velocity during the growing season are: $SO_2DV = .2*LAI + .42$ $(R=.995)$; and $O_3DV = .15*LAI + .17$ $(R=.96)$.

Figure 3 (A and B) shows the average diurnal curves for SO_2 and O_3 at the five sites. Because the number of observations is small, there is a fair degree of uncertainty in the SO_2 curves. Nonetheless, one can see the expected minimum shortly after sunset, with a slight increase in the predawn hours, probably caused by increased humidity and surface moisture, followed by a rapid increase after sunrise. The peak occurs between morning and mid-day. The values decrease quite rapidly in the late afternoon and evening. The O_3 curves are more regular because of the larger number of samples. The values are quite low at night, except for the Sand Flats forest. Deposition velocities at all sites rise rapidly in the early morning, and decrease rapidly in the late afternoon. The forest sites have a peak in deposition velocity in the morning, while the crop sites peak at mid-day. We speculate that this reduction at the forest sites after the early morning peak is caused by sunlight heating the leaf surface, and a significant vapor pressure deficit, which causes the stomata to partially close. The same effect does not seem to be present in crops. The reason for the higher nighttime deposition velocities observed at Sand Flats, which may also be seen in Figure 1B, is not obvious, but we speculate that it may be due to nocturnal stomatal conductance by some one or more species present at that site. Musselman and Minnick (2000) have listed over one hundred species of plants for which nocturnal stomatal conductance has been observed. And, while none of the dominant species at the site were in their list, they note that the list is far from inclusive, as tests have not been made on most types of plants.

Seasonal cycles of daytime deposition velocity, composed of weekly average values, are shown in Figure 4 (A and B). Again, because of the smaller number of observations, the SO_2 figures are less certain, and have more missing values. One point of note in comparing these cycles is that the O_3 cycles show a more pronounced minimum in the early spring and late fall than do the SO_2 cycles. This difference is especially evident in the Kane Forest data. We suspect that this difference is caused by the deposition of SO_2 to the surfaces of the branches and other structures in the forest, causing a significant deposition velocity of SO_2 even in the absence of leaves. Because O_3 deposition is more strictly a stomatal effect, the deposition of O_3 in the spring and fall is greatly diminished. The comparison of the deposition velocity for SO_2 between the Kane, Sand Mountain, and Nashville sites is instructive. At Kane, with significant surfaces, the deposition velocity is rather high even without leaves. At Sand Mountain, the grass covered pasture had some stomatal activity in the early spring, and some surfaces for deposition. At Nashville there were no plants above ground at the start of the experiment (week 24) and the deposition velocity was the smallest, only half the value of the deposition velocity at Kane. On the other hand, comparing these sites for O_3 shows quite similar values at the start of the respective growing seasons, again indicating that surfaces are much more important for SO_2 deposition.

4. Conclusion

In the field studies reported here, vegetation mass, as measured by LAI, is the dominant variable controlling deposition velocity. We noted significant differences between SO_2 and O_3 deposition velocity. SO_2 deposition velocity is larger at all sites. SO_2 deposition velocity has two important pathways, to the interior of leaves through the stomata, and to the surfaces of the plants and ground. O_3 deposition velocity is principally controlled by plant stomata. Differences are noted in the diurnal cycle of stomatal opening between forests and agricultural crops, with the peak time of day for deposition velocity occurring in the morning over forests, and at mid-day over crops.

Measurable amounts of deposition occur at night for both pollutants. Nocturnal deposition may be more significant than originally thought for plant damage (Musselman and Massman, 1999) and deserves more careful study. Deposition to surfaces, the effect of wetness, and the chemistry of that wetness, and deposition during the winter are also areas that have received too little attention and are important in understanding total loadings of pollutants to ecosystems and the relationship between dry deposition and plant damage.

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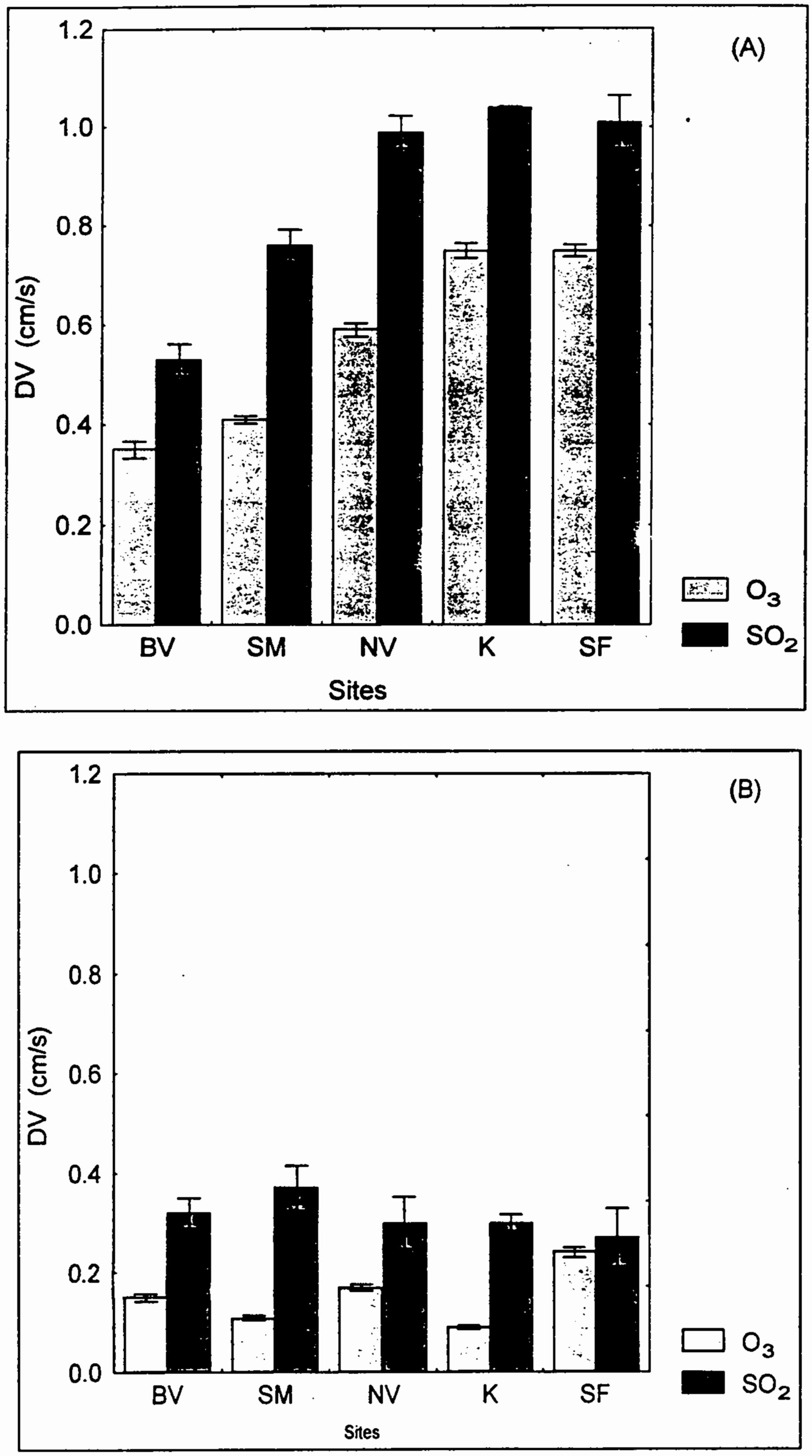

Figure 1. Average deposition velocity, ± 1 standard error, for O_3 and SO_2 during the day (A) and at night (B) at five sites; Bondville (BV), Sand Mountain (SM), Nashville (NV), Kane (K) and Sand Flats (SF).

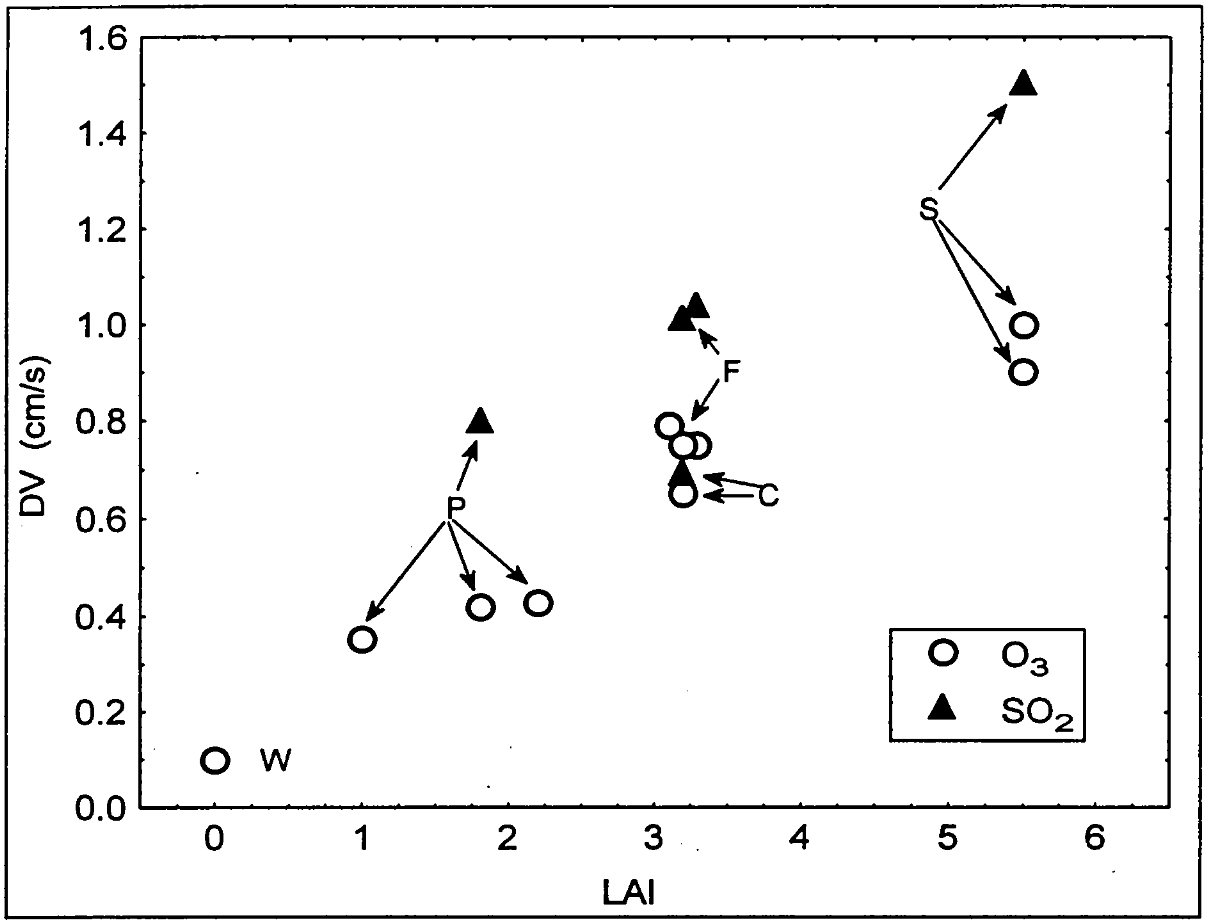

Figure 2. Average daytime deposition velocity (DV) for O_3 and SO_2 vs. leaf area index (LAI) at soybean (S), Forest (F), corn (C), pasture (P) and estuary (W) sites.

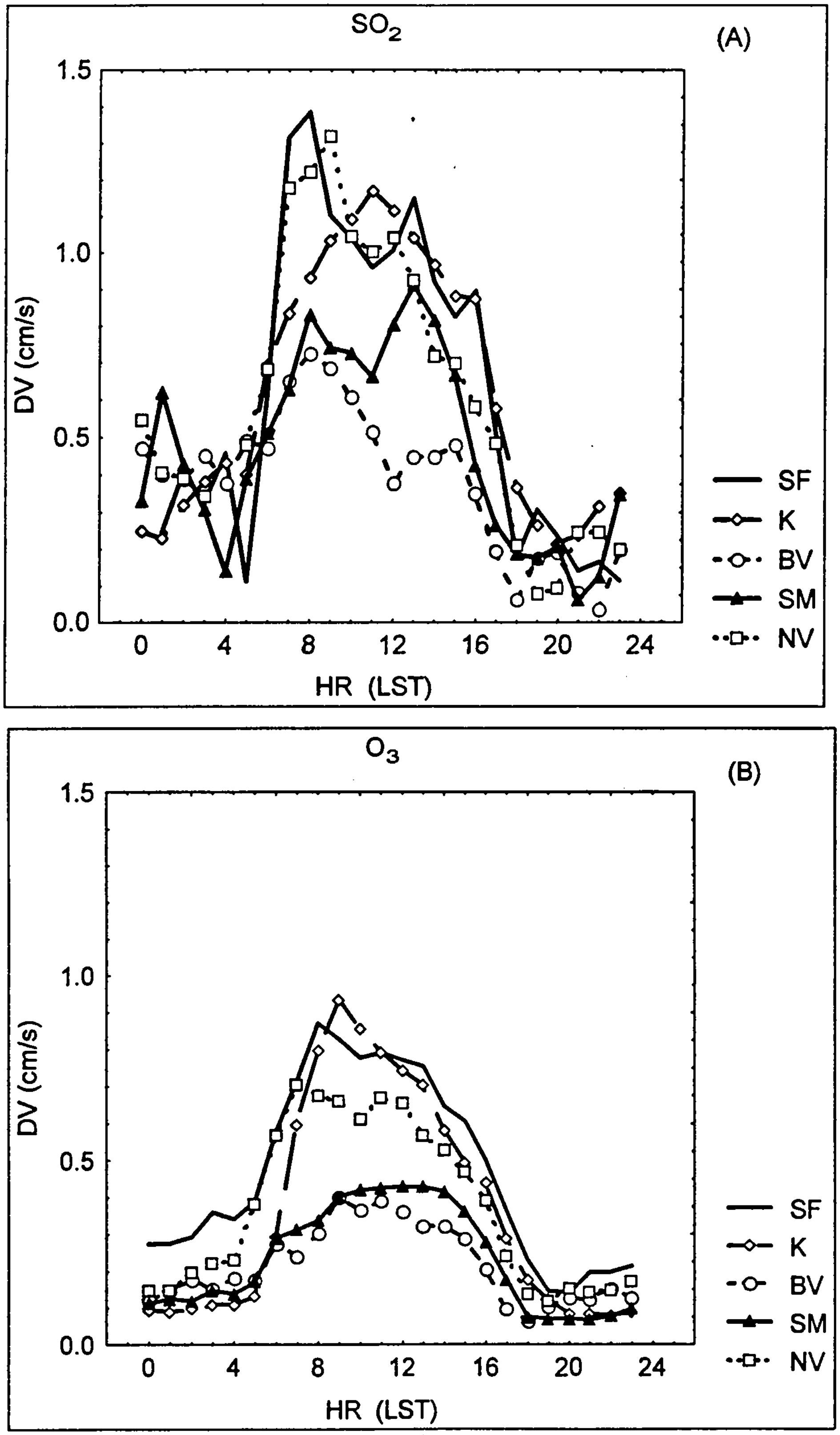

Figure 3. Average diurnal cycles of deposition velocity at five sites for SO_2 (A) and O_3 (B).

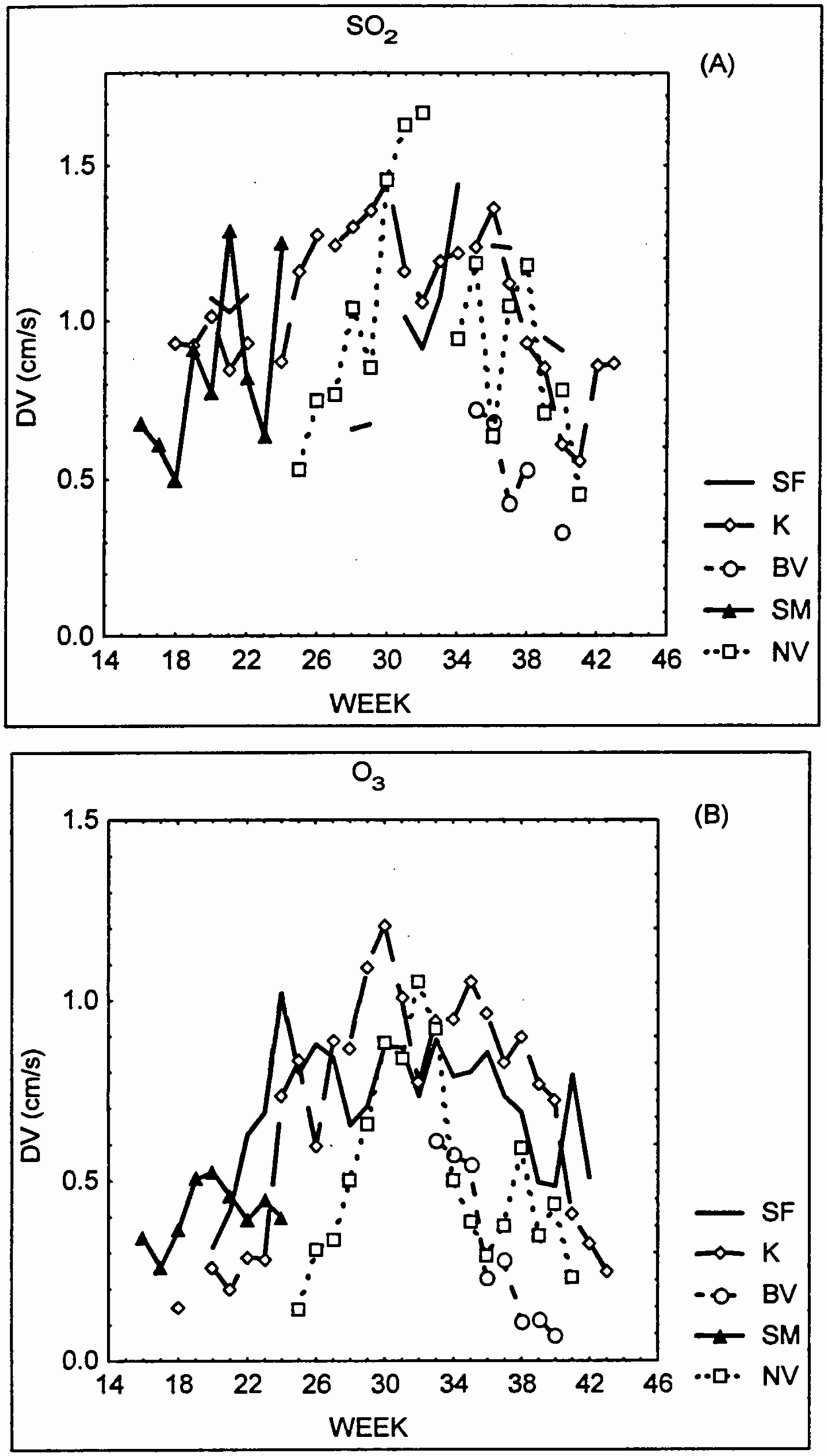

Figure 4. Weekly average daytime values of deposition velocity, showing the seasonal cycles, for SO_2 (A) and O_3 (B) at five sites.

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16. ABSTRACT

The results of field studies that measured the flux and deposition velocity of SO_2 and O_3 are reported. Three of the studies were over agricultural crops (pasture, corn, and soybean), and two were over forest (a deciduous forest and a mixed coniferous-deciduous forest). In all cases the deposition velocity for SO_2 was higher than that for O_3. Diurnal cycles of SO_2 deposition velocity were similar in shape, but not magnitude for all surfaces; however those for O_3 showed some difference between forest sites where the peak was in the morning, and the agricultural sites where the peak ocurred at midday. Seasonal cycles of SO_2 were affected by deposition to surfaces when leaves weren't active, yet surface conductance is significant, but not for O_3 where stomatal uptake is the primary pathway for deposition.

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