Conf-9107104--17

PNL-SA--20055

DE92 002147

NOV 01 1991

SCAVENGING RATIOS BASED ON INFLOW AIR CONCENTRATIONS

W. E. Davis
R. N. Lee
J. M. Thorp
M. T. Dana
W. G. N. Slinn

July 1991

Presented at the
Fifth International Precipitation
Scavenging and Atmosphere-Surface
Exchange Processes
July 15-19, 1991
Richland, Washington

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

SCAVENGING RATIOS BASED ON INFLOW AIR CONCENTRATIONS

W. E. Davis, M. T. Dana, R. N. Lee, W. G. N. Slinn, and J. M. Thorp

Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, USA

ABSTRACT

Scavenging ratios were calculated from field measurements made during April 1985. Event precipitation samples were collected at the surface, but air chemistry measurements in the air mass feeding the precipitation were made from an aircraft. In contrast, ratios calculated in previous studies have used air concentration and precipitation chemistry data from only surface measurements. Average scavenging ratios were calculated for SO_4^{2-}, NO_3^-, NH_4^+, total sulfate, total nitrate, and total ammonium for 5 events; the geometric mean of these scavenging ratios were 8.5×10^5, 5.6×10^6, 4.3×10^5, 3.4×10^5, 2.4×10^6, and 9.7×10^4, respectively. These means are similar to but less variable than previous ratios formed using only surface data.

1. INTRODUCTION

An important aspect of the development, testing, and use of predictive acidic deposition models, such as RADM and ADOM (Chang *et al.*, 1987; Venkatram *et al.*, 1988), is the simulation of the chemical and physical processes in clouds and precipitation. These processes of precipitation scavenging are complicated, and the development of models to represent these processes requires supporting measurements. Ideally, the many chemical and physical variables would be measured in the storm and in the depositing precipitation. However, in practice, because of the difficult physical environment faced by experimenters, measurements must be limited in number and type.

The U. S. Department of Energy-sponsored field study, Processing of Emissions by Clouds and Precipitation (PRECP), provided supporting measurements for model comparisons. The first of the PRECP projects, PRECP-I, was conducted during the spring of 1985. One goal of PRECP-I was to make chemistry measurements of both the inflow air processed by frontal and convective storms and the deposited precipitation from these storms. Further, this field study was specifically designed to provide a direct meteorological link between inflow air measurements and ground precipitation chemistry measurements, thus allowing calculation of "improved" scavenging ratios (Barrie, 1985).

The scavenging ratio, k, is defined for a given pollutant species as k = concentration in precipitation / concentration in air. Consequently, this ratio represents the integral of all scavenging processes occurring in the storm. The integration is over space and time, as well as over a number of chemical and physical variables, such as pollutant and water fluxes, cloud microphysics, pollutant and precipitation particle-size distributions, and rates of chemical reactions in cloud and precipitation water (Slinn, 1984).

Scavenging ratios for various chemical species have been calculated by a number of authors (Barrie, 1985; Barrie and Neustadter, 1983; Engelmann, 1971; Gatz, 1974; Krey and Toonkel, 1974; Misra *et al.*, 1985; Niemann, 1982; Van der Westhuizen, 1969; Venkatram *et al.*, 1988). For all of these calculations, air concentrations were measured in surface air near the site of the precipitation measurements.

The large variations that exist in available scavenging ratios may be explained in several ways. One explanation is the use of the questionable assumption that air concentrations measured at the surface were the same as the air concentrations feeding the storm. In reality, this assumption may not be tenable in all cases, as will be illustrated below.

A second possible cause of large variations in scavenging ratios may be related to the method by which precipitation is sampled. If the sample is taken over a series of precipitation events, there can be several different sources of air feeding each precipitation event. Consequently, care must be exercised in selecting only those precipitation samples and air samples representing a single event. For example, multiple events can occur in a single 24-hour precipitation sample. During the 24 hours, a sample could contain precipitation from overrunning air ahead of a warm front, warm-sector rain, precipitation associated with the cold front, and precipitation from shower activity in the cold sector. The source regions of the air feeding each of these precipitation types can vary significantly. Therefore, with the ratios formed from different sources of air and the different sources of precipitation, variations in the ratios should be expected.

By designing a field program that both provides the chemical concentrations in an air mass before the scavenging process starts and limits the sampling of precipitation to a single event, "improved" scavenging ratios may be produced. These are expected to have less variance than existing ratios, if the removal process is similar for each event. The PRECP-I field study was designed to provide these measurements. The purpose of this paper is to report the calculated scavenging ratios from PRECP-I and to compare their variances with ratios calculated using only surface measurements. The paper presents a brief description of the PRECP-I cases selected and why they were selected for analysis, the computation of "improved" scavenging ratios for these cases, a comparison of the "improved" scavenging ratios with past scavenging ratios, and conclusions drawn from these comparisons.

2. THE PRECP-I FIELD STUDY

The PRECP-I field study was carried out during April and early May 1985 in the upper Midwest and northeastern United States. Aircraft and ground operations were

based at Columbus, Ohio. Surface precipitation sampler locations used for calculating scavenging ratios are shown in Figure 1.

The aircraft operations used two aircraft, a DC-3 from the Pacific Northwest Laboratory (PNL) and a Queen Air from Brookhaven National Laboratory (BNL), to provide air chemistry measurements in inflow air. Both aircraft were equipped with air filter packs to collect NH_3, NH_4^+, SO_4^{2-}, NO_3^-, HNO_3, and SO_2 samples (Tanner *et al.*, 1985). A total of 16 aircraft missions were conducted during PRECP-I.

Precipitation samples collected in the surface network for the event were analyzed for the same species excluding dissolved SO_2. Surface precipitation sampling was performed using polyethylene funnel-and-bottle collectors. Three separate samples were collected at the network sites to provide quality control on chemistry and precipitation amount measurements. These samples were refrigerated and air shipped to the precipitation chemistry laboratory at PNL. Chemical analysis procedures were conducted in accordance with the MAP3S precipitation chemistry network procedures (Dana, 1988). Relevant event samples from the Oxford, Ohio, site of the MAP3S network and the Zanesville, Ohio, Utility Acid Precipitation Study Program network were also employed in some of the scavenging-ratio calculations.

Only five PRECP-I events met the two criteria: 1) that the air mass sampled by the aircraft provided inflow for the precipitation sampled, and 2) that the precipitation samples collected at the surface were single-event samples. To test the first criteria, 850-mb trajectories were used to determine if the boundary-layer air sampled by the aircraft was representative of the air feeding the collected precipitation. Next, synoptic surface charts and precipitation reports were examined to ensure that the surface precipitation was from a single event. The five events meeting these criteria were those for April 5, 7, 11, 19 and 20, and 24.

2.1 Event I. 5 April, 1985

At 1200 GMT the warm sector of a slowly moving frontal system was located over Ohio. A cold front extended from a low centered over southern Michigan across northern Indiana to northeastern Texas. Precipitation at the sampling sites was from showers and thunderstorms occurring just ahead of the cold front as it moved through Ohio. Figure 2 shows the sampling flight pattern in the boundary layer and the trajectory of the sampled air. The trajectory indicates that the air mass sampled moved over the samplers about 3 hours before precipitation was collected.

2.2 Event II. 7 April, 1985

A trough of low pressure was located over eastern Ohio at 1200 GMT. The trough moved eastward generating areas of rain and snow in the cold air pushing down from the northwest. The trough moved eastward into Pennsylvania by 1800 GMT but the showers of rain and snow continued in Ohio for the remainder of the day. Figure 3 shows the trajectory of the sampled air mass passing over the surface sampling site during the time when precipitation was occurring.

FIGURE 1. Surface precipitation sampler locations (•) used for calculating scavenging ratios.

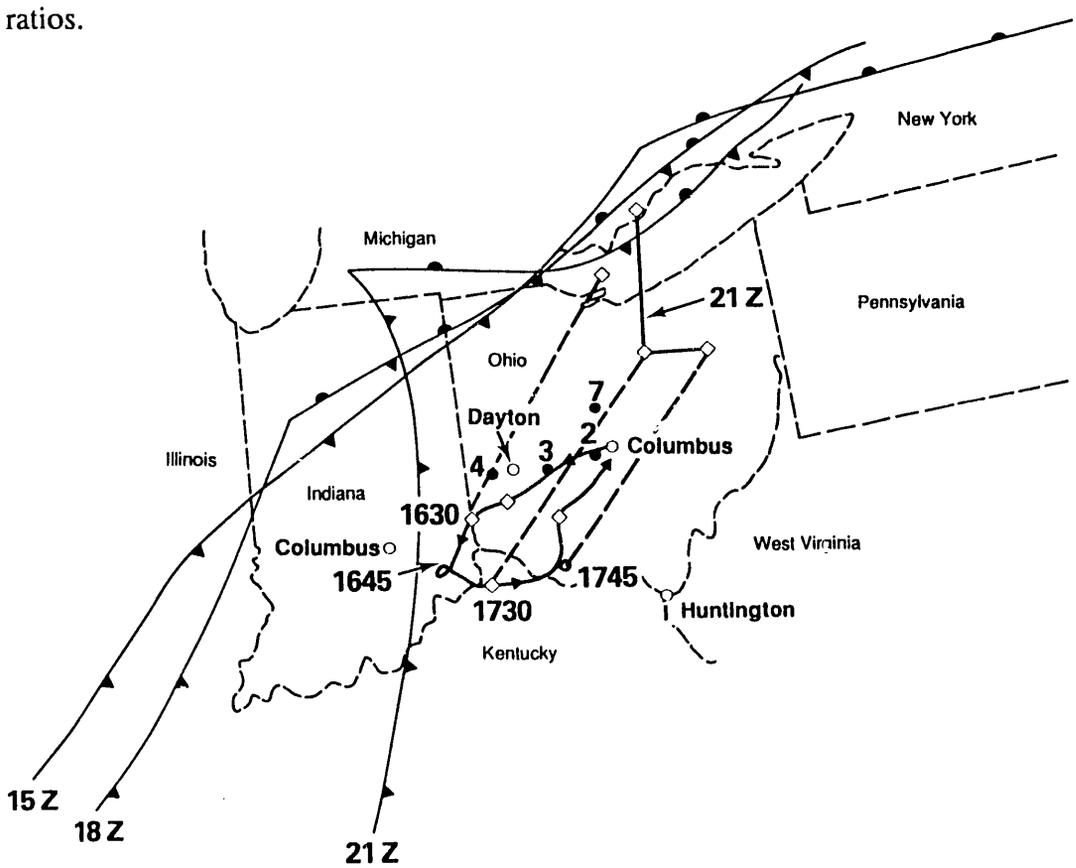

FIGURE 2. Aircraft sampling path (solid lines), frontal positions, and trajectories of air masses (dashed lines) for April 5, 1985.

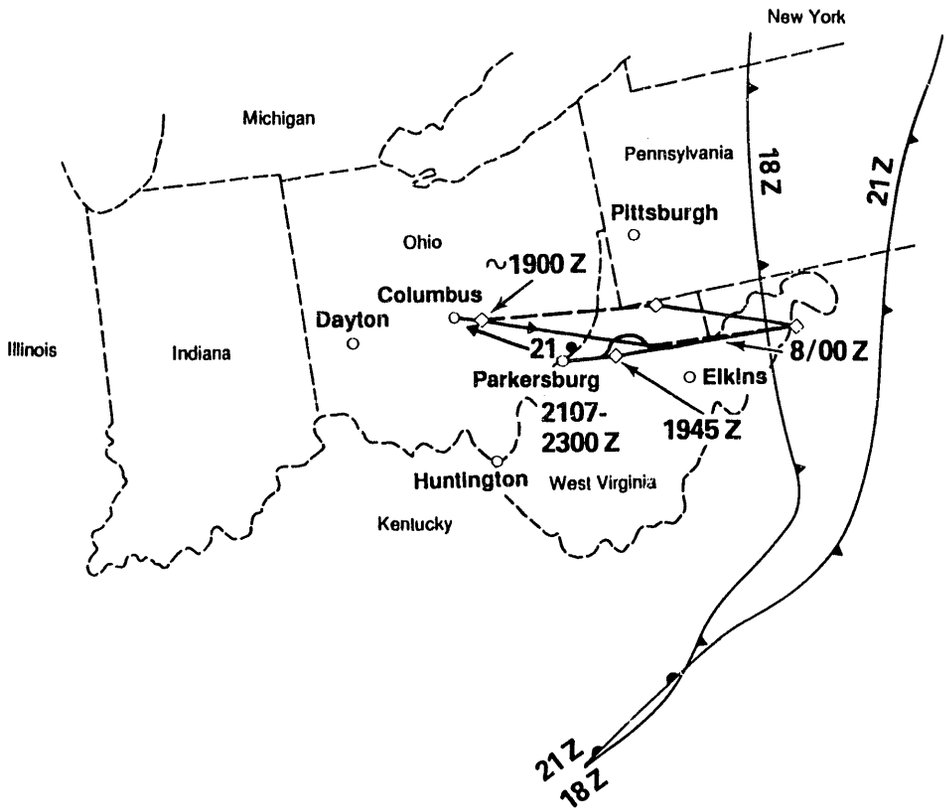

FIGURE 3. Aircraft sampling path (solid lines), frontal positions, and trajectories of air masses (dashed lines) for April 7, 1985.

2.3 Event III. 11 April 1985

Scattered light rain occurred in the trough ahead of a cold front moving slowly southward toward Ohio. Figure 4 shows the trajectory of the sampled air mass moving over the surface sampling sites during the period of precipitation.

2.4 Event IV. 19-20 April 1985

Showers and thundershowers occurred in a frontal zone over northern Pennsylvania, western New York, and southern Ontario. Figure 5 shows the sampling flight pattern and the trajectory of the sampled air when precipitation was occurring. A similar supportive sampling flight on April 21 was made but is not shown in the figure.

2.5 Event V. 24 April 1985

A cold front moved slowly through Ohio on April 24. Scattered showers occurred in the warm sector ahead of the front with the Zanesville site receiving precipitation at 1300 GMT before the aircraft sampling. The trajectories indicated passage of the sampled air, shown in Figure 6, within 3 hours of precipitation at the surface sites.

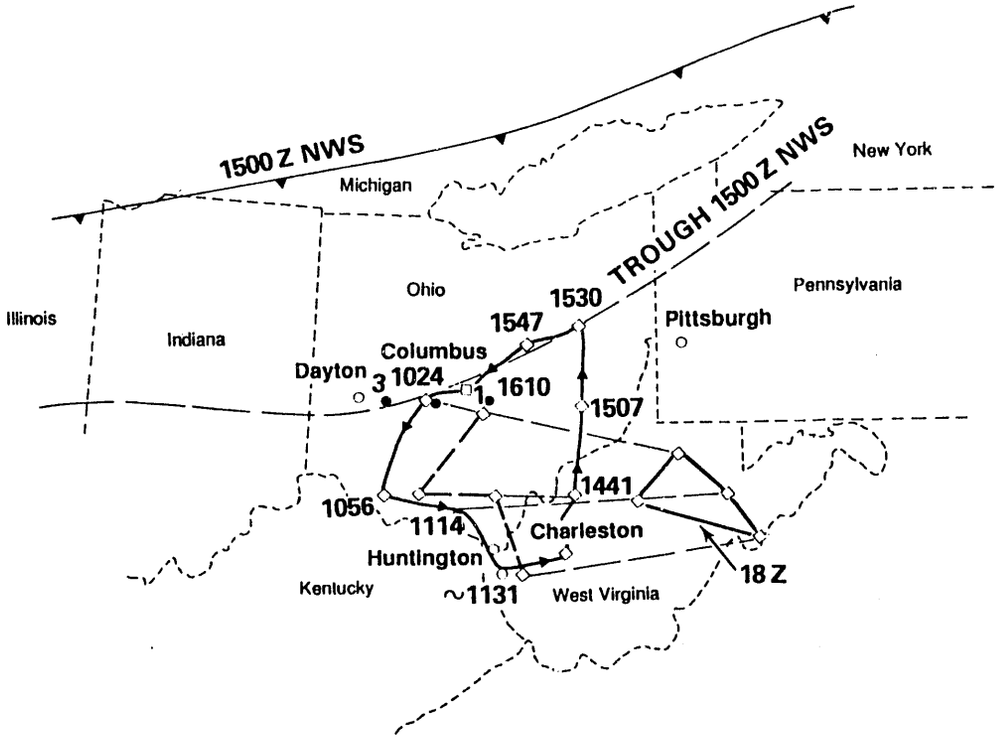

FIGURE 4. Aircraft sampling path (solid lines), frontal positions, and trajectories of air masses (dashed lines) for April 11, 1985.

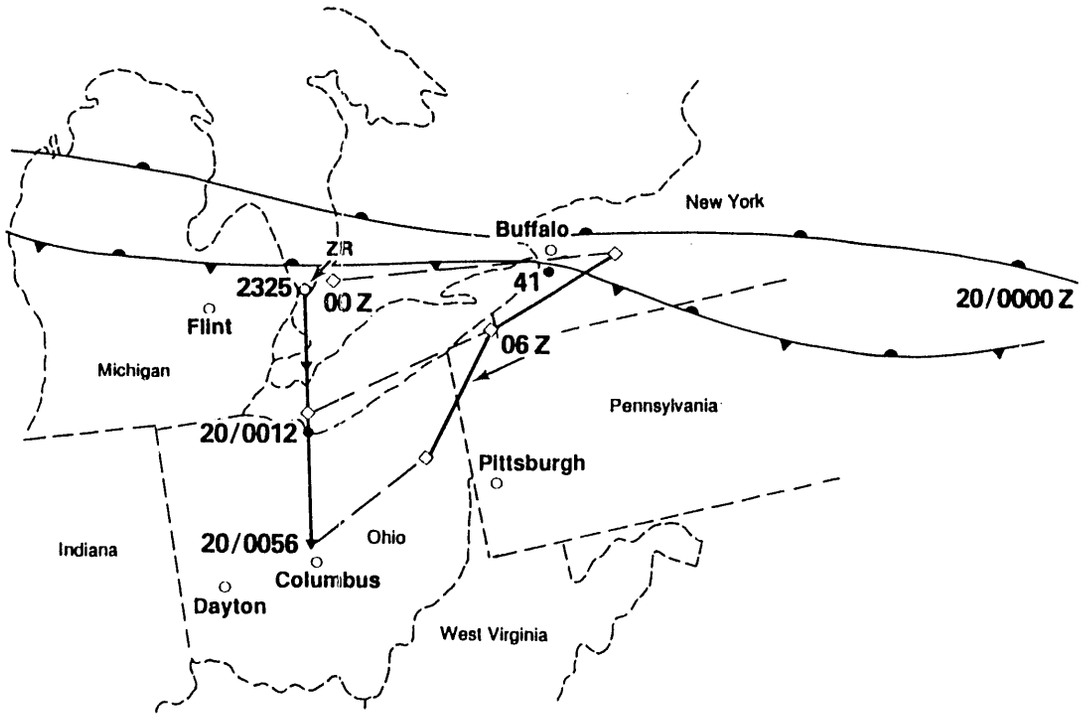

FIGURE 5. Aircraft sampling path (solid lines), frontal positions, and trajectories of air masses (dashed lines) for April 19-20, 1985.

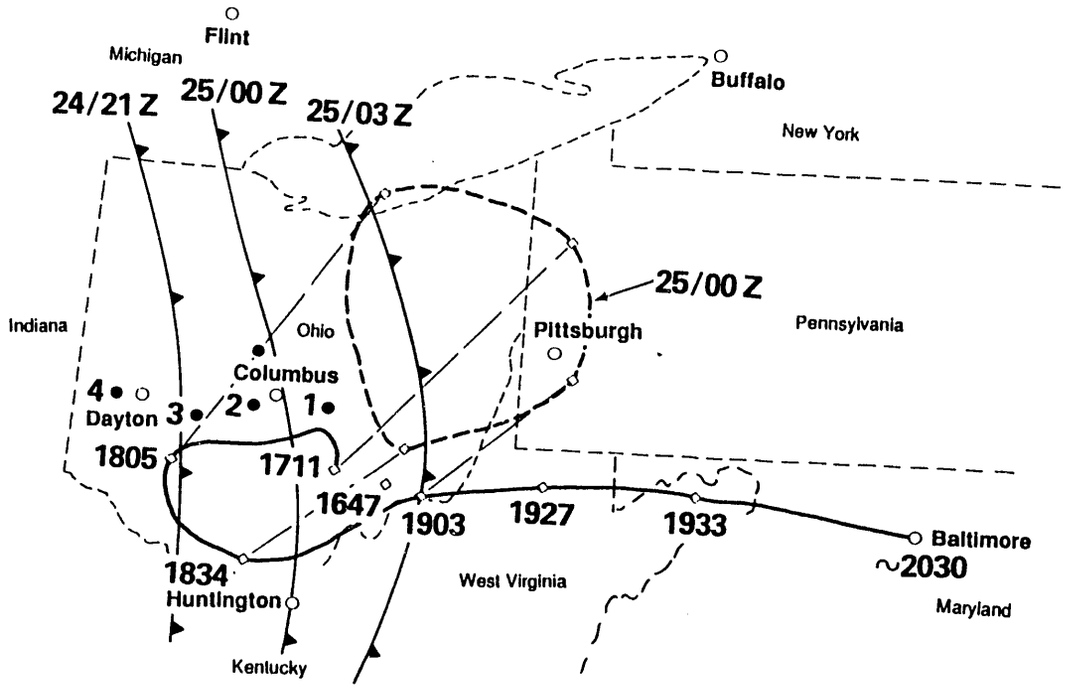

FIGURE 6. Aircraft sampling path (solid lines), frontal positions, and trajectories of air masses (dashed lines) for April 24, 1985.

3. RESULTS

Calculated scavenging ratios are shown in Table 1. The units chosen for calculating the scavenging ratio were μM/l in air and μM/l in water; although the scavenging ratio is a dimensionless quantity, its magnitude is different if other units are used. The total sulfate ratios were formed by combining the concentrations of SO_4^{2-} aerosol with gaseous SO_2. The total nitrate ratios were formed by combining the air concentrations of NO_3^- aerosol with gaseous HNO_3. And total ammonium ratios were formed by combining the concentrations of NH_4^+ aerosol with gaseous NH_3. Where more than one aircraft air sample was available, the average air concentration was used to form the ratio. Table 1 shows the algebraic mean of the scavenging ratios for individual events and all events in PRECP-I; also included are the geometric mean and the geometric standard deviation of all scavenging ratios.

The largest range in event-average values for scavenging ratios was for total ammonium, with a factor of 80 from the minimum to the maximum. The scavenging ratios having the smallest range were for total sulfate with a factor of 2.5 from minimum to the maximum average. Figure 7 shows the variations of the scavenging ratios with total precipitation; most variability occurs with the least precipitation.

4. DISCUSSION

Misra *et al.* (1985) reported more than 800 scavenging ratios for three surface sites and for all seasons in Ontario and Minnesota. Their calculations are based on daily

TABLE 1. Scavenging Ratios for PRECP-I

Date	NH_4^+	SO_4^{2-}	NO_3^-	Total Nitrate	Total Sulfate	Total Ammonium
Events						
April 5	1.3e05	3.0e05	2.2e06	2.2e06	2.5e05	5.5e04
April 7	7.3e05	6.2e05	2.6e06	2.4e06	2.9e05	5.0e05
April 11	1.3e06	1.0e07	2.6e06		1.7e05	
April 19-20	5.1e06	6.6e05	8.4e06	1.4e06	4.7e05	4.5e06
April 24	1.7e06	1.6e06	1.3e07	2.9e06	6.2e05	
Averages						
Algebraic Mean	1.6e06	6.1e05	5.6e06	7.5e05	2.3e05	6.9e05
Geometric Mean	4.3e05	8.5e05	5.6e06	2.4e06	3.4e05	9.7e04
Geometric Standard Deviation	4.2	2.0	2.3	1.4	1.8	4.9

(24-hour) air concentrations and daily precipitation concentrations. The results of their calculations are summarized in Table 2. The geometric means of their results for total sulfate and total nitrate are comparable with results presented for PRECP-I; however, the PRECP-I data have smaller variation, as shown by the standard deviations in Table 2.

For the PRECP-I ratios, the variability appeared to increase with decreasing total precipitation. The cause of this variation could represent a number of different processes, such as evaporation of the rain, the sampler's position with respect to a rain shaft, or variations in the removal process. Additional data will be required to resolve this variability.

TABLE 2. Scavenging Ratios from PRECP-I and from Misra *et al.* (1985)

	SO_4^{2-} Geom. Mean (STD)	NO_3^- Geom. Mean (STD)	Total Sulfate Geom. Mean (STD)	Total Nitrate Geom. Mean (STD)
PRECP-I	8.5×10^5 (2.0)	5.6×10^6 (2.3)	3.4×10^5 (1.8)	2.4×10^6 (1.4)
Misra *et al.*, 1985	$3.4\text{-}7.6 \times 10^5$ (3.9-4.8)	$2.4\text{-}19 \times 10^6$ (4.2-5.7)	$2.2\text{-}3.7 \times 10^5$ (3.2-3.7)	$0.74\text{-}2.1 \times 10^6$ (2.6-3.4)

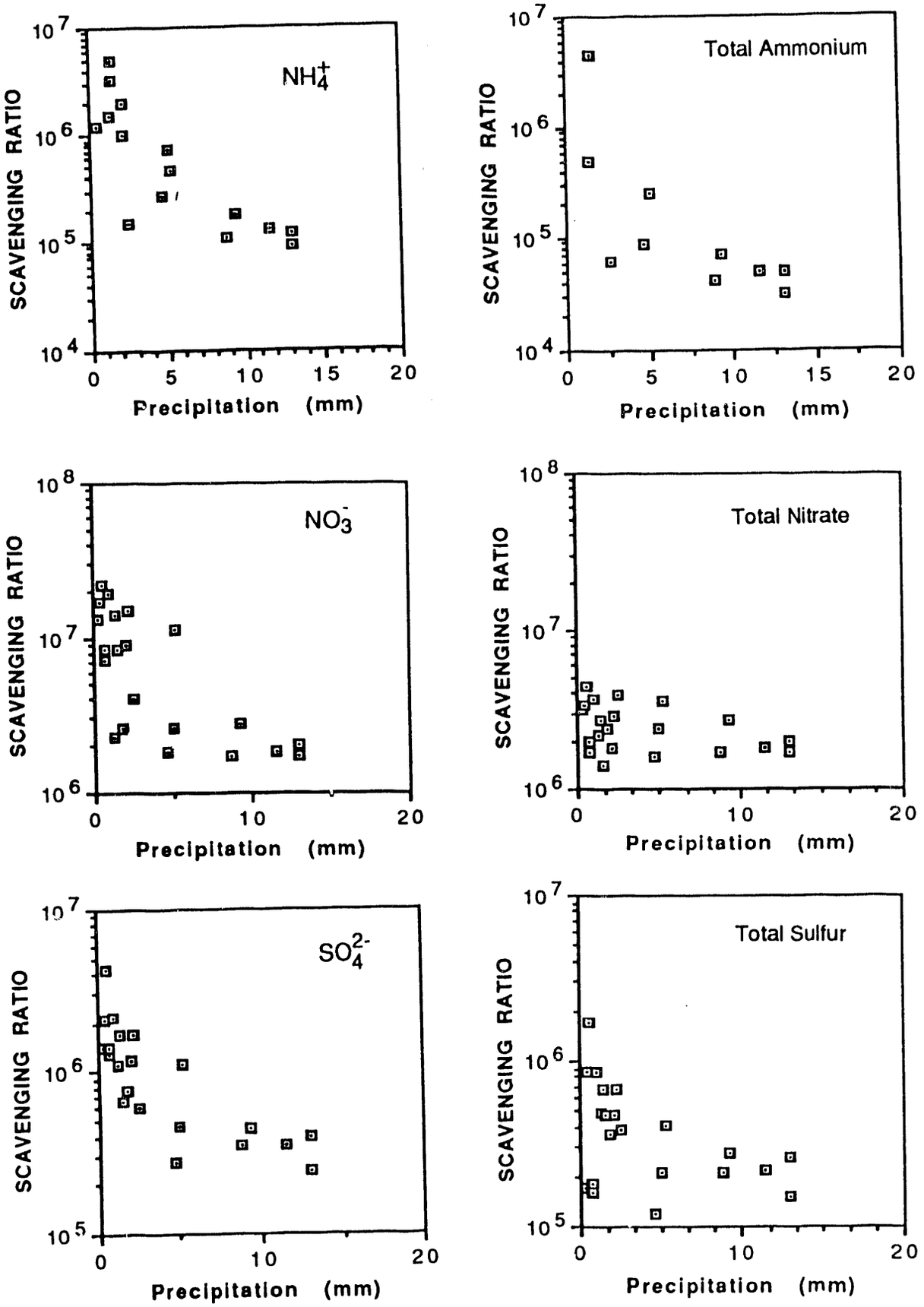

FIGURE 7. Scavenging Ratios from PRECP-I Events

5. CONCLUSIONS

Air chemistry and precipitation measurements from PRECP-I were used to compute an "improved" scavenging ratio. Air chemistry and surface precipitation samples were from the same event. When ratios calculated from these measurements were compared to previously published ratios, the averages of the ratios were similar, but significantly, the "improved" ratios were found to have a smaller geometric standard deviation. In the case of total sulfate, the geometric standard deviation computed by Misra *et al.* (1985) was between 3.2 and 3.7, whereas the geometric standard deviation of ratios formed from the PRECP-I data was 1.8.

Based on these results, the scavenging ratios formed by separating the precipitation samples into event samples and using only aircraft samples of the air mass involved in the precipitation process appear to be an improvement because they produce averages comparable with past measurements but with less variability. The small variability could be partly a result of the smaller number of samples made within a single month; the ratios reported by Misra *et al.* (1985) were calculated for all seasons.

6. ACKNOWLEDGMENTS

These results represent the effort of a substantial number of people without whose support this work would not have been possible. Support was provided by the PNL group: G. W. Dennis, R. V. Hannigan, J. L. Gregory, K. M. Busness, G. L. Laws; and the BNL group: P. H. Daum, R. L. Tanner, R. M. Brown, J. Tichler, and M. Leach. This research was sponsored by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

7. REFERENCES

Barrie, L. (1985) Scavenging ratios, wet deposition, and in-cloud oxidation: an application to the oxides of sulfur and nitrogen. *J. Geophys. Res.* **90,** 5789-5799.

Barrie L. and Neustadter J. (1983) The dependence of sulphate scavenging ratios on meteorological variables. In *Precipitation Scavenging, Dry Deposition and Resuspension* (R. G. Semonin and R. W. Beadle Coord.), Elsevier, New York, NY.

Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R. and Walcek, C. J. (1987) A three-dimensional eulerian acid deposition model: physical concepts and formulation. *J. Geophys. Res.* **92,** 14,681-14,700.

Dana, M. T. (1988) *The MAP3S Network Data and Quality Control Summary for 1985.* PNL-6461, Pacific Northwest Laboratory, Richland, WA.

Engelmann, R. J. (1971) Scavenging prediction using ratios of concentrations in air and precipitation. *J. Appl. Meteor.* **10,** 493-497.

Gatz, D. F. (1974) Scavenging ratio measurements in METROMEX. In *Precipitation Scavenging (1974)* (R. G. Semonin and R. W.Beadle Coordinators), pp 71-87. CONF-74 1003, Tech. Inf. Center, Proc. of symp. Champaign, IL 14-18 Oct. 1974.

Krey, P. and Toonkel, L. E. (1974) Scavenging ratios. In Precipitation Scavenging (1974) (R. G. Semonin and R. W.Beadle Coordinators), pp 61-70, CONF-74 1003, Tech. Inf. Center, Proc. of symp. Champaign, IL 14-18 Oct. 1974.

Misra, P. K., Chan, W. H., Chung, D., and Tang, A. J. S. (1985) Scavenging ratios of acidic pollutants and their use in long-range transport models. *Atmos. Env.* **19,** 1471-1475.

Niemann, B. L. (1982) Scavenging ratios for exceptional wet sulfate episodes in eastern north america from three event networks. In *Precipitation Scavenging, Dry Deposition and Resuspension* (R. G. Semonin and R.W. Beadle, Coord.), Elsevier, New York, NY.

Slinn, W. G. N. (1984) Precipitation scavenging. Chapter 11 in *Atmospheric Science and Power Production* (edited by Randerson D.), pp. 466-532. DOE/TIC-27601, U.S. Dept. Energy, Tech. Info. Center, available from NTIS, Springfield, VA.

Tanner, R. L., Tichler, J., Brown, R., Davis, W. E., Johnson, S., Patrinos, A. A. N., Sisterson, D., and Slinn, W. G. N. (1985) *PRECP - The Department of Energy's Program on the Nonlininearity of Acid Precipitation Processes.* BNL-38776, PRECP-85-1, Brookhaven National Laboratory, Upton, NY.

Van der Westhuizen, M. (1969) Radioactive nuclear bomb fallout - a relationship between deposition, air concentration, and rainfall. *Atmos. Env.* **3,** 241-249.

Venkatram, A., Karamchandani, P. K., and Misra, P. K. (1988) Testing a comprehensive acid deposition model. *Atmos Env.* **22,** 737-747.

DISCUSSION

J. I. SHEN. Could you tell us what the difference is between the air chemistry of air mass sampled by an aircraft and the surface air near a precipitation collector for a single precipitation event?

W. E. DAVIS. Since we were attempting to provide the average air mass air concentrations, no attempt was made to provide air concentrations near the surface. It would have been very interesting to have used 24 hour air

concentrations and precipitation samples to see how they would have compared to these "improved" ratios.

W. A. H. ASMAN. You showed that scavenging ratios for SO_4^{2-} concentration in precipitation is partly derived from oxidation of SO_2. If you define that the scavenging rate is the ratio SO_4^{2-} in precipitation/SO_4^{2-} in air, this does not reflect the uptake of SO_4^{2-} aerosol only as would be suggested by your graphs. Can you comment on this.

W. E. DAVIS. In the presentation, figures were shown of scavenging ratios for both sulfate and total sulfur. The scavenging ratios for sulfate does not reflect the oxidation of SO_2 but the ratios for total sulfur reflect complete oxidation of the SO_2.

L. A. BARRIE. This paper clearly demonstrates the care that should be taken in experimental design and data screening before a relationship between air and precipitation concentrations can be drawn. I point out in my paper that scavenging ratios assume a linear relationship between air and precipitation concentration. Do you feel this assumption justified for your data or in general?

W. E. DAVIS. I think that it would be very interesting to look for such a relationship. However, our data set from PRECP-I is somewhat limited for determining such a relationship. When the more extensive data set from the FBS field study is available, we will examine the combination of both sets to see if we can determine whether our data reflect such a relationship.

M. MURAKAMI. Scavenging ratio may strongly depend on the growth mode of precipitation particles. Can you comment on this point for your observational results?

W. E. DAVIS. I cannot comment on this because there were no aircraft measurements taken that could reflect on the growth mode of the precipitation. Modeling of the process and comparing the model results with the surface samples would be of interest.

M. MURAKAMI. Evaporation of rain drops between cloud base and ground surface sometimes causes a serious enrichment of chemical constituents. Did you take this effect into consideration?

W. E. DAVIS. This process was not explicitly taken into account. We see its effect in the scatter plots associated with low rainfall rates (which have relatively more scatter). This scatter could reflect increased evaporation in the falling raindrops.

END

DATE FILMED

2/28/92