



Project Summary

A Study of the Formation and Transport of Acidic Species by Non-Precipitating Cumulus Clouds During VENTEX-84

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A field experiment was conducted by Pacific Northwest Laboratory (PNL) in Kentucky during the period July 8 to August 18, 1984 as part of the VENTEX-84 field study to investigate the formation of sulfate and nitrate aerosols and the vertical transport of pollutants by non-precipitating cumulus clouds. VENTEX is a research component of the National Acid Precipitation Assessment Program.

Analyses of data collected from DC-3 and Cessna 411 aircrafts and from ground sampling show ratios of sulfate concentration to the total sulfur concentration (the sum of sulfate and sulfur dioxide) to be larger at the top of clouds than at their bases. In-cloud oxidation rates were calculated to be in excess of 100%/hr. The ratio of the total nitrate concentration (the sum of nitric acid and nitrate aerosols) to the total sulfur concentration at cloud tops, was higher than that at cloud bases on many days. This result suggests that nitrate can form in the clouds but not as frequently as does sulfate. Ground concentrations of ammonia declined around midday followed by an increase in the afternoon. Sulfur dioxide concentrations exhibit an opposite trend. A case study of morning and afternoon soundings of ozone indicated vertical transport of pollutants from the mixed layer to the cloud layer.

This Project Summary was developed by EPA's Atmospheric Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Cumulus clouds form by convective activity that originate near the surface. These clouds ingest and chemically process polluted air from various altitudes within the mixed layer. Oxidation is enhanced, so that transformation rates over regional or continental scales are increased significantly when clouds are present even part of the time. Also, pollutants transferred to the cloud layer undergo horizontal transport and dispersion quite different from flow in the mixed layer. These cloud processes need to be investigated and parameterized for use in regional models that simulate the transport, transformation, and deposition of airborne acidifying agents. Currently under development is an Eulerian framework, Regional Scale Acid Deposition Model (RADM). This development work is a scientific response to the requirements of the Energy and Security Act of 1980, Title VII for a means by which proposed acid deposition mitigation strategies can be tested. RADM is designed to incorporate all known important processes dealing with emissions, transport and transformation of acidic chemical species and their deposition to the surface of the earth.

In keeping with the comprehensiveness of the model development effort, the modeling of the vertical exchanges and transformations that occur as a re-

sult of these convective clouds, so ubiquitous during the warm season, and so highly variable in space and time is an important component of the RADM. The processes associated with these clouds are many and complicated. Presently, knowledge about them is very limited. The program, VENTEX, (Venting Experiment), sponsored by the National Acid Precipitation Assessment Program, and administered by the United States Environmental Protection Agency is designed to provide an experimental basis for the development of parametric schemes and computer modules for treating these processes in the RADM. The principal objectives of VENTEX are to determine the production of sulfate and nitrate aerosol particles by non-precipitating cumulus clouds and to investigate the vertical transport of pollutants caused by cumulus convection. The field study effort was conducted near Lexington, Kentucky over a period of three summers from 1983 to 1985. This report covers the experiments conducted by Pacific Northwest Laboratory (PNL) during the summer period from July 8 - August 18, 1984, which is called VENTEX-84.

Cloud Chemistry

Samples of aerosols and trace gases were collected above the mixed layer in cloud-free air (background samples), generally above 3,000 m MSL, at the cloud inflow region (cloud bases) and cloud outflow region (cloud tops) using the instrumented DC-3 aircraft. At each level, the aircraft flight routes consisted of horizontal bow-tie paths with one leg of the flight path passing over the VENTEX ground sampling site. Several parameters were measured in real-time; these are: O_3 , SO_2 , NO_x , aerosol light scattering, aerosol size distribution, temperature, dew point temperature, altitude, turbulence in the inertial subrange, and aircraft position. The aircraft was equipped with two high-volume samplers. Each sampler used a filter pack that exposed 21.2 cm² of the filter area. One filter pack consisted of a Teflon filter for the collection of aerosols, followed by a cellulose filter impregnated with sodium chloride for nitric acid collections, followed by another cellulose filter impregnated with potassium carbonate and glycerine for sulfur dioxide collections. The second filter pack employed a Teflon filter, backed by a cellulose filter treated with oxalic acid for the collection of ammonia gas. As part of the surface-level

sampling, two filter packs were used to measure chemical composition of aerosols and to monitor the concentrations of sulfur dioxide and ammonia gas.

Vertical Transport

The study of vertical transport utilized two instrumented aircraft, the PNL DC-3 and Cessna 411. The Cessna 411 aircraft was instrumented to measure temperature, dewpoint temperature, ozone, light scattering, altitude, and aircraft position. The aircraft flew two missions each experiment day and obtained at least two to three vertical profiles of these species per mission. The aircraft also made several in-cloud passes near the tops of the clouds between vertical transects. Wind speed and direction, temperature, and relative humidity were measured at midday by means of radiosonde.

Results and Discussion

Cloud Chemistry

The in-cloud formation of sulfate and nitrate were examined by comparing the concentrations at cloud tops against the concentrations measured at cloud bases. In Table 1 the concentrations of sulfate and total nitrate at cloud bases were divided by the total sulfur (the sum of sulfate and sulfur dioxide), and the values at cloud tops were first corrected for background values and then divided by the total sulfur at that altitude. The background samples were needed because when clouds penetrate into the free atmosphere above, they mix with dry air and evaporate; thus, the samples taken at the cloud outflow must be cor-

rected for the background concentrations. The nitric acid and the nitrate aerosols were combined because when ammonium nitrate and sulfuric acid dissolved in the droplet evaporates, an exchange of ions takes place resulting in the formation of nitric acid and ammonium sulfate. The letters B and T refer to the measurement location, at cloud base and cloud top respectively.

The table shows that the ratio of sulfate to the total sulfur at cloud tops is higher than that at cloud bases in all five days, and the changes in the ratio is much larger than the estimated combined errors in the measurements. In the case of total nitrate, three days (August 4, 8, and 12) show in-cloud nitrate formation. On the other two days, no production was detected. This is the first time that nitrate formation in natural clouds has been observed. The oxidation rate of sulfur dioxide in the cloud system was estimated using the following procedures. Let the concentrations of sulfur dioxide and sulfate be represented by X and Y, respectively. Therefore, the time rate of changes in X and Y are:

$$dX/dt = -kX - KX \quad (1)$$

$$dY/dt = kX - KY \quad (2)$$

where k is the oxidation rate of SO_2 and K is the reduction rate due to dilution and diffusion. Define a descriptor R such that:

$$R = X/(X+Y) \quad (3)$$

TABLE 1. Ratios N/S and SO_4/S at cloud bases, B, and cloud tops, T, where N is the concentration sum of nitric acid and nitrate aerosols, and S is the sum of sulfate and sulfur dioxide concentrations. K is the first order oxidation rate of SO_2 in clouds in %/minute. The ammonia and ozone concentrations are in nanomoles/m³ and ppb respectively, and the temperature, T is in °C.

Date	Height	N/S	SO_4/S	K	NH_3	O_3	T
7/30	B	$0.53 \pm .07$	$0.80 \pm .02$	15.0	4.6	60	19.1
	T	$0.27 \pm .04$	$0.99 \pm .01$	1.0		56	16.3
7/31	B	$0.46 \pm .01$	$0.72 \pm .03$	9.9	11.7	40	20.3
	T	$1.77 \pm .12$	$0.92 \pm .01$	6.5		27	14.3
8/04	B	$0.52 \pm .07$	$0.005 \pm .00$	10.9	15.2	57	22.6
	T	$2.39 \pm .31$	$1.00 \pm .00$	3.3		48	14.4
8/08	B	$0.62 \pm .08$	$0.24 \pm .03$	6.7	52.3	81	24.9
	T	$0.90 \pm .11$	$0.71 \pm .03$	20.4		66	19.6
8/12	B	$0.27 \pm .03$	$0.18 \pm .02$	8.0	5.0	78	20.2
	T	$0.24 \pm .30$	$0.71 \pm .03$		--	68	16.8

Differentiating both sides of equation (3) with respect to t , and substituting for the time derivatives from equations (1) and (2) results in the following equation:

$$dR/dt = -kR \quad (4)$$

k is influenced by many processes. It includes the reaction rate between SO_2 and the oxidizers, functions that take into account the transfer of the gases from the air to the cloud droplets, and the concentrations of the oxidizers. Temperature changes as droplets rise from cloud bases to cloud tops will affect the value of k . For diagnostic analysis, it is assumed that k is constant with respect to t , X , and Y . Integrating equation (4) yields the following:

$$kt = \ln R_0 - \ln R \quad (5)$$

where R_0 is the descriptor value at $t = 0$, at cloud bases.

In order to calculate k , the transport time t between cloud bases and cloud tops is needed. Assuming an average updraft velocity, w , of 1.0 m/s for the cloud t is determined by dividing the thickness of the cloud field by w . The calculated values of k are shown in Table 1. The result shows very fast conversion rates. It should be noted that even if the updraft velocity is off by a factor of two or three, the rate is still very high. Furthermore, the calculated rate varies from one day to the next and does not seem to correlate with any of the parameters listed in the table. Of course what is missing from the data is a measurement of H_2O_2 . This measurement was not taken during VENTEX-84 but was made during VENTEX-85. Although the VENTEX-85 data have not been thoroughly processed and analyzed, preliminary examination show that the measured concentration of H_2O_2 is in the range of 1.0 to 6.0 ppb, certainly large enough to oxidize dissolved SO_2 in the cloud droplets. Furthermore, there is a strong indication that H_2O_2 formed in the clouds. This was evident from vertical profiles which show peaks in the concentrations within the cloud layer.

Results of the ground measurements of ammonia concentration show a decline around midday followed by an increase in the afternoon. On the other hand, the sulfur dioxide concentration peaks around noontime. At night and early morning the ammonia is emitted at the surface into and confined within a

shallow layer that is capped by the nocturnal temperature inversion. By mid-morning the inversion height rises and the ammonia is mixed and distributed over a deeper layer. In the late afternoon, mixing is suppressed and therefore the concentration rises. The sulfur dioxide data suggests that the main sources of SO_2 are elevated plumes. The weak (or absent) vertical mixing during the late afternoon, nighttime, and early morning keep the concentration at the surface low. However, at midday, when vertical mixing is most vigorous, the plumes are mixed to the ground and a rise in the SO_2 concentration is expected.

Vertical Transport

Vertical sounding and horizontal transect data collected by the instrumented Cessna-411 aircraft were analyzed to investigate the pollutant transport into the cloud layer. The data indicated ozone concentrations and aerosol light scattering inside the clouds are higher than those outside at the same elevation. The difference in the ozone concentration between the cloud and its environment is in the range of 5 to 15 ppb, which is comparable to the difference between concentration of the mixed layer and the layer above the mixed layer. This shows that the in-cloud concentrations are of mixed layer origin. During the morning, the baseline ozone concentration values above the mixed layer varied from about 49 to 53 ppb

while in the afternoon the range was 52 to 60 ppb. Since these measurements were taken above the mixed layer, the results suggest an accumulation of ozone, and by inference other pollutants, in the cloud layer (including the entrainment layer), due to cloud activity during the intervening period.

Summary

Preliminary results show that the ratio of sulfate concentration to the total sulfur concentration (the sum of sulfate and sulfur dioxide) at top of clouds is much higher than the measured at their bases. As a result, cloud oxidation rates were calculated to be in excess of 100%/hr. The calculation assumed an average updraft velocity of 1.0 m/sec. The ratio of the total nitrate concentration (the sum of nitric acid and nitrate aerosols) to the total sulfur concentration at cloud top, was higher than that at cloud base on many days. This result suggests that nitrate can form in the clouds but not as frequently as sulfate. The ammonia concentrations measured on the ground show a decline around midday followed by recovery in the afternoon. On the other hand, the sulfur dioxide concentrations show an opposite trend for the one day that was examined. The vertical profiles of ozone measured between the morning and afternoon sounding indicated that pollutants from the mixed layer have been transported vertically to the cloud layer, and accumulation occurred.

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The complete report, entitled "A Study of the Formation and Transport of Acidic Species by Non-Precipitating Cumulus Clouds During VENTEX-84," (Order No. PB 86-220 357 / AS; Cost: \$9.95, subject to change) will be available only from:

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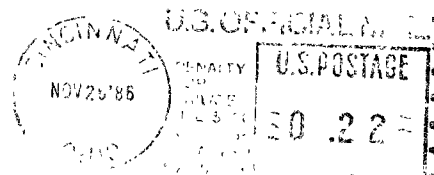
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