Tellus (1985) *37B*, 160–165

The chemistry and microphysics of intrastorm sequential precipitation samples

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(Manuscript received July 23, 1984; in final form April 1, 1985)

ABSTRACT

A slow moving cold front, which deposited over 40 mm of rain, was investigated for relationships between pH, ion concentrations and precipitation microphysics. For the first time, precipitation droplet size spectra were available using a Particle Measuring System's ground-based precipitation probe. The precipitation spectra allowed a preliminary analysis of below cloud rain scavenging: adsorption and impaction.

The cumulative rate of chemical precipitation versus cumulative water indicated two different slopes for the major ions contributing to the acidity of the precipitation. The slopes were consistent with a convective stage and a non-convective storm stage and this was consistent with rate of precipitation.

1. Introduction

A number of articles have recently appeared which describe the variation of pH (Anderson and Landsberg, 1979), elemental composition of aerosols and their size distribution (Tanaka, et al., 1980) and precipitation ion chemistry with storm meteorology (Wilson, et al., 1982; Hogan, 1983) or precipitation parameters (Seymour and Stout, 1983). While presenting results which are very valuable in relating precipitation parameters, e.g., precipitation intensity, scavenging of aerosols below cloud base to the ion concentrations measured in samples obtained over very short times, or to the salient meteorological parameters, none of the field work was able to mount an intensive enough program to introduce the microphysics of sequential precipitation and its variability.

This paper describes the chemical composition of precipitation, collected concurrently with the measurements of meteorological and microphysical parameters, during the passage of a slow-moving cold front at the observing site. These results were obtained to examine whether changes in identifiable physical parameters resulted in changes in the rate of magnitude of chemical precipitation, and to investigate the interrelationship between precipitation processes and the observed ion variation of concentrations in precipitation.

2. Instrumentation and observational technique

The data were obtained at the ASRC radiation fog site, adjacent to a runway at Albany Airport, Albany, NY, USA (Jiusto and Lala, 1983). A completely automated micrometeorological station was in operation with an MRI tipping bucket, Gill anemometers at 1 m, 4 m, 8 m and 16 m and temperature sensors at 0.1 m, 0.5 m, 1.0 m, 1.5 m, 2.0 m, 4.0 m, 8 m and 16 m.

Precipitation spectra were obtained by a Particle Measuring System's ground-based precipitation probe (GBPP-100). A laser beam is directed across a wide sampling gap and then downward to an array of photodetectors. A drop falling through this beam will cast a shadow on the photodetectors which is interpreted as its size from the number of detectors

blocked. The size discrimination ranges from 0.3 mm to 12 mm diameter with a 0.2 mm resolution. The probe was mounted 0.5 m above the grass surface and controlled so that the long axis could always be aligned with the prevailing wind direction. All micrometeorological and microphysical data were recorded on the ASRCs cloud physics data acquisition system.

A 27.5 cm diameter collecting funnel was placed about 1 m above the ground before the onset of precipitation. The funnel remained covered until the onset of precipitation. When a sufficient sample for 2 aliquots was obtained, the sample was removed for pH determination at the site and storage for ion chromatography analysis the next day. The ion chromatograph can facilitate the measurement of several ion concentrations: NH_4^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}. The estimated errors ($\pm\mu$Eq l^{-1}) are Na^+: 0.4, NH_4^+: 10.0, Cl^-: 1.0, NO_3^-: 5.0, SO_4^{2-}: 6.0.

The precipitation probe obtained raindrop spectra which were measured over a 2-minute interval and these data were then averaged over variable time periods which coincided with the duration of precipitation collection for ion analysis. Samples for ion analysis were taken on a 10–15 min time base for the first hour and then for each one-half hour over the next 4 hours. After the pH of precipitation was judged to have become constant by a steady rise from pH = 4.4 to pH = 5.0, the precipitation samples were collected over a 2-hour period for the next 6 hours.

3. Results of a slow-moving cold frontal passage 4–5 November, 1982

3.1. Meteorological

A slow-moving cold front had been progressing across New York State from west to east for 2 days prior to arrival at the Albany County Airport, New York. Heavy precipitation of 25 to 50 mm in a 24-hour period had been associated with this system. The 00Z 5 November sounding for Albany indicates a constant, stable lapse rate to 200 mb and an average precipitable water of 38 mm to the 500 mb level. Cloud base was taken to be approximately 1 km above the sampling site. The limited fine mesh model trajectory for 1200 GMT Albany, New York on 4 November, 1982 indicates moisture advection from the Gulf of Mexico and along the Atlantic coast from the surface to 700 mb

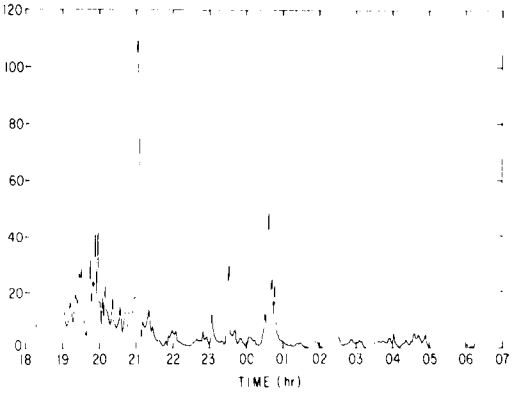

Fig. 1. Precipitation rate (mm h^{-1}) versus local time (EST) for the November 4–5, 1982 cold front passage.

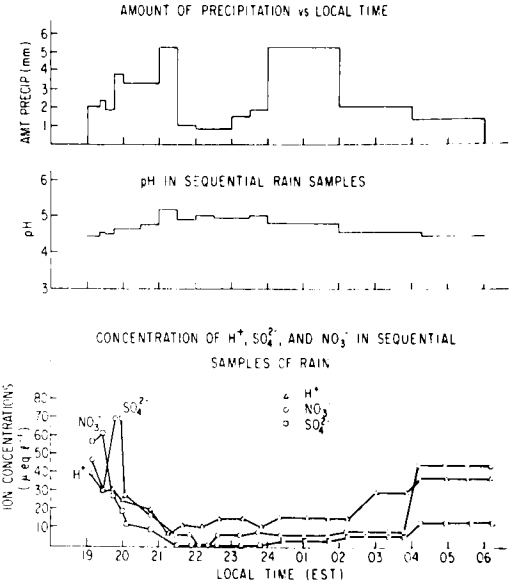

Fig. 2. Record of cold front passage November 4–5, 1982, depicting amount of precipitation, pH and selected ion concentrations.

level, which is consistent with this prefrontal situation.

Fig. 1 for the precipitation data at the site depicts the cold frontal passage at 1900 EST and precipitation ceasing at 0500 EST on 5 November, 1982. During this 10-hour period, there was a total of 44.4 mm of precipitation.

3.2. Chemical

Fig. 2 is a composite of precipitation amount, pH of precipitation and the concentration of the major

ions measured in the acid precipitation. The $[H^+]$ is correlated with $[SO_4^{-2}]$ and $[NO_3^-]$, 0.69 and 0.68, respectively. The major features are the rapid decrease of $[SO_4^{-2}]$, $[NO_3^{-1}]$ and $[H^+]$ during the second hour of the storm. During the first hour of the storm, $[SO_4^{-2}]$ and $[NO_3^-]$ show an oscillation in phase with the amount of precipitation while $[H^+]$ decreases during the period. All major ions remain at relatively low constant values over the majority of the precipitation duration (7 hours). During the last 2 hours of the storm, $[H^+]$, $[SO_4^{-2}]$ and $[NO_3^-]$ show an increase.

In Fig. 3a,b,c, the cumulative water precipitation versus cumulative ion precipitation is presented for the ions H^+, NO_3^-, SO_4^{2-}, Cl^- and Na^+. Examination of Fig. 3a shows 3 distinct rates of hydrogen ion concentration with respect to water precipitation. Initially, the onset of precipitation is governed by small drops of relatively high concentration. The break occurs at the first decrease in precipitation, and is averaged with the driving mechanism for the next increase in precipitation which is accounted for by the large drop sizes $\geqslant 3.1$ mm which results in a decreased slope due to dilution. Finally, with the onset of decreased precipitation at the end of the storm, again driven by the concentration of small drops, the slope increased because of a decrease in liquid water content. Cumulative $[SO_4^{-2}]$ and $[NO_3^-]$ show only 2 different slopes, with the sulfate initially being steeper than the nitrate. The dramatic change in slopes at ~13.0 mm H_2O reflects the end of the sharp decrease of the sulfate and nitrate ions at the beginning of the storm, or possibly another physical mechanism. Over the remainder of the storm, both slopes are the same indicative of the levelling off at low ion concentrations. The last point representative of the increase in ions at the storm's end is not included.

The last plots of $[Na^+]$ and $[Cl^-]$ show a structure that closely parallels that of $[H^+]$ and presumably are both related to the intensity of rainfall or liquid water content and more importantly, the raindrop size. Of interest is the cross-over at 16 mm of precipitation which is just before the sharp decrease in precipitation amount at 2130 EST.

In all cases, the cumulative ion concentrations pass through the origin which is indicative of cloud formative processes and minimal if no scavenging below cloud base. Also, the decrease in slope for all ions with respect to water precipitation after the

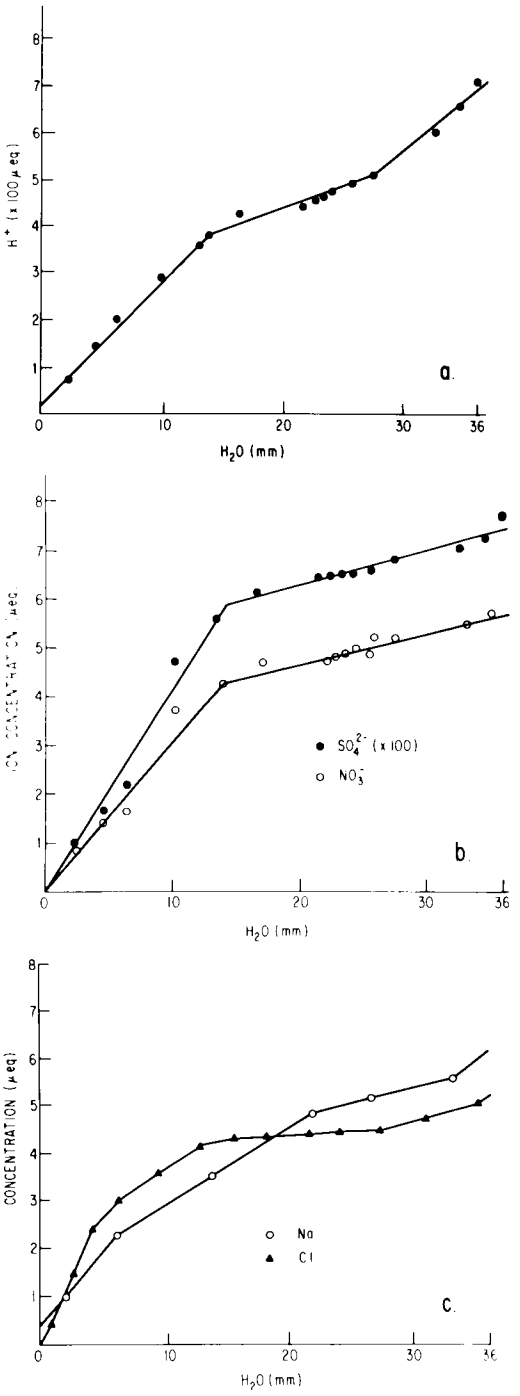

Fig. 3. Cumulative precipitated ion versus cumulative water precipitated during the November 4–5, 1982 cold front passage. (a) hydrogen. (b) Sulfate and nitrate. (c) Chlorine and sodium.

initial downpour indicates that the convective activity was immediately behind the slow-moving cold front and the non-convective part of the storm, which is similar to prefrontal rain in the classic cold front, occurs later during the storm. The convective part of the storm which is associated with the advection of moisture from the Gulf and Atlantic coastal area has a Cl^-/Na^+ mass ratio of 1.2 as compared to 1.8 for sea water. Rossby and Egnér (1955) documented the variation in the Cl^-/Na^+ ratio as dependent upon the prevailing circulation. The post convective ratio for $Cl^-/Na^+ = 0.83$ is possibly due to the loss of chlorine behind the cold front, since the slow-moving system had been precipitating for 2–3 days prior to its arrival in Albany, New York. Input of Na^+ from a local source, such as pulp mill, would also tend to produce a similar ratio.

3.3. *Microphysics of precipitation*

In order to try and establish the influence of precipitation spectra upon the ion concentrations obtained, 3 different size cuts were used: small; $r_g = 0.2$ mm; moderate range from 0.8 to 2.4 mm with an $r_g = 1.5$ mm and large drop $r_g = 3.9$ mm. The small size had a large number concentration but contributed less than 5% to the rainfall mass. The maximum contribution to rainfall is the moderate range, and the large class, although containing the random outliers, only contributes about 20% to the rainfall mass.

A comparison of cumulative plots of $N(\#/cm^3) \times r_g$; xr_g^2; and xr_g^3 with the cumulative plots of nitrate and sulfate versus cumulative mm of water indicates only one apparent graphical relationship for $r_g = 0.22$ mm as a gaseous absorber, Fig. 4.

This can be understood in a straightforward way. While nothing is known about in-cloud processes, scavenging of gases and of particles below cloud base can be related to $N \times \Pi r_g^2 \times t$ (time of fall) and $N \times \Pi r_g^2 \times V_T \times t$ (time of fall) where V_T is the terminal velocity. This reduces to two simple relationships for a constant 1 km cloud base; adsorption is $\propto Nr_g^2 \times t$ and volume swept out, i.e., impaction, is $\propto Nr_g^2$.

Since the cumulative plots indicated that below cloud scavenging by adsorption might be important for $r_g = 0.22$ mm, plots of discrete ion concentrations versus Nr_g^2 and Nr_g^3 for a 1 km cloud base were utilized to see if any relationship existed.

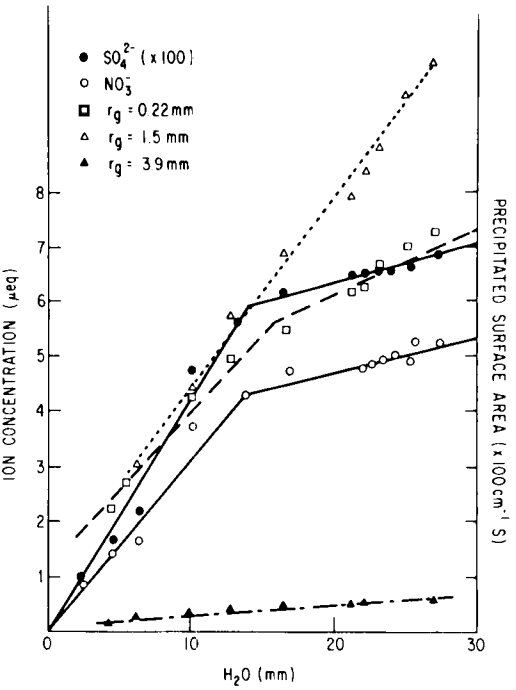

Fig. 4. Cumulative precipitated sulfate and nitrate ions, and cumulative precipitated raindrop surface areas versus cumulative water precipitated.

In two instances, for $r_g = 0.22$ mm and 1.5 mm, $[SO_4^{-2}]$ and $[H^+]$ were related to the time of fall. In both instances 3 outliers out of 14 data points had to be discarded. In only one instance did $[NO_3^-]$ show any indication of a relationship with time of fall for $r_g = 1.5$ mm. In this case, 4 outliers of 14 points had to be discarded.

Previous measurements in a rural area of the Adirondack Mountains of New York have always indicated that the cloud water ion concentrations were the major contributor to precipitation ion concentrations and not below cloud scavenging (Castillo, et al., 1983; Castillo, 1984). It is important to remember that this below cloud scavenging analysis was in part initiated by a similarity of $\sum N \times r_g^2$ and ion concentrations versus cumulative mm of water. However, a plot of total rain versus local time shows two distinct slopes that look similar in form to the ion concentrations slopes. The break occurs where a change in rate of precipitation takes place from 15 to 20 mm h^{-1} to a lesser rate. Rogers (1983) indicates that rainfall rates in excess of ~25 mm h^{-1}

are associated with convective activity. It seems reasonable to accept the implication of convective and non-convective precipitation influencing the storm microphysics and precipitation influencing the storm microphysics and precipitation ion chemistry.

4. Discussion

Hogan's (1983) results can be interpreted to show an inverse relationship between $[H^+]$ and $[SO_4^{-2}]$ and $[NO_3^-]$. This does not seem to be the case in the results presented for this slow-moving cold front. Also, Seymour and Stout (1983) indicate a similar inverse phenomena, as Hogan, during the onset of precipitation between $[H^+]$ and $[SO_4^-]$ and $[NO_3^-]$. Rather than this inverse relationship, our results indicate an in-phase oscillation of the 3 ions which results in a rapid decrease of all ion deposition. 50% of the total SO_4^{-2} and NO_3^- ion deposition is accounted for within the first 10–15% of the total rainfall. This is in agreement with the previously mentioned work of Seymour and Stout. Our major finding is that within experimental analysis error and sample error, the major changes in ion concentrations can be accounted for by changes in convective versus non-convective precipitation.

Anderson and Landsberg (1979) could find no relationship between pH and precipitation rate as was borne out in this study. In the beginning of the storm when the drop size distribution is essentially constant, i.e., large drops average >3.0 mm and high concentration of 0.1 to 0.5 mm drops, we would expect efficient below cloud scavenging. However, there are at least two possible mechanisms why the pH decreased. First, is there maritime advection of air, as indicated by a 1.2 Cl/Na ratio by mass. This would allow for an input of urban pollutants from the Atlantic seaboard which are possibly more acidic than local calcareous surface aerosols. Secondly, the slow-moving cold front had been precipitating heavily for 2–3 days prior to arriving at Albany, New York and all large soil aerosols quite possibly had been scavenged and precipitated out. The local area is composed of calcareous soil which would have a neutralizing effect. While Anderson and Landsberg cite the fact that raindrop size tends to decrease as precipitation rate decreases, it is also evident that a more important factor is the decrease in total number concentration of droplets with 0.1 to 0.5 mm diameter—a decrease by a factor of 4.

It is noted that our plots of cumulative ion deposition versus precipitated water agree with Hogan's (1983) work: a very steep slope during advective or non-convective activity. The exact processes responsible for this dichotomy are not easily identifiable from the limited data at this time. In part, important gas concentration measurements, soluble and insoluble aerosol fractions and basic cloud microphysics need to be obtained to fill missing gaps.

5. Conclusion

The ability to compare precipitation droplet spectra with changing ion concentrations and precipitation rates was invaluable. The research needs to be extended to other seasons and types of storm to investigate precipitation rate and its relationship to the observed changes of ion concentrations during sequential precipitation sampling.

The limited data also indicated an apparent below cloud scavenging by adsorption. Future research should be directed at verifying this technique by the inclusion of gas monitoring equipment during a precipitation event. Also, the analysis would substantially benefit in the future from aircraft sampling of cloud micro-physical parameters.

6. Acknowledgements

This research was carried out under grants NOAA NA82RAC00074, DAAG 2981 K0019, and NSF 320-1243A. The ion chromatography analysis was carried out by Anne Marie Pitaniello. We also wish to thank Austin Hogan for his thoughtful discussions and comments concerning this research.

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