Airborne measurements of the antarctic cloud water acidity

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Samples of cloud water were collected from antarctic coastal stratus during the 1982 – 1983 austral summer to assess the natural component of cloud-water acidity. The pH value ranged between 4.9 and 6.2, and the average value was below that expected for the Antarctic, so far from all anthropogenic sources of acidic and acidifying substances. Acidity was found to increase with height inside the cloud probably due to the entrainment of sulfate ($SO_4^=$) rich stratospheric air at the cloud top. Average levels of $SO_4^=$ were found to be of the same magnitude as those in more anthropogenic regions while nitrate (NO_3^-) levels were much lower in antarctic stratus clouds than elsewhere.

The observational platform used for this study was an instrumented, ski-equipped Hercules airplane described by Saxena (1983). The sampling site was chosen within 50-kilometers radius from the McMurdo Communication Center using the satellite photographs. Samples of cloud water were collected using teflon probes approximately 122 centimeters in length and 5 centimeters in diameter. The probe was exposed to supercooled cloud droplets through the sextant port in the fuselage of the LC-130 airplane. On the surface of the cylinder, there were little cups 0.63 centimeter in diameter at the rim. The probes were triply washed with deionized water before the deployment following the procedure of Hegg and Hobbs (1981). Being thermodynamically unstable, the supercooled droplets froze upon impinging on the probe, which was projected upward from the fuselage while the airplane made tracks within the antarctic coastal clouds. The cups on the surface of the probe provided preferential sites for the ice accumulation. The iced cylinder was then removed and stored in a clean plastic bag that had been sterilized following the standard procedures prescribed by the Environmental Protection Agency. Collected cloud water was immediately retrieved from the bag and stored in scrupulously cleaned and sterilized plastic vials which were kept frozen in dry ice.

The samples were analyzed at the Environmental Research Laboratories, National Oceanographic and Atmospheric Administration (NOAA), Boulder, Colorado. The samples were unfrozen before analysis and brought to room temperature. Approximately 1 milliliter of the sample was used to determine the pH and sodium concentration with selective electrodes. Another 1 milliliter was used to determine the chlorine (Cl^-), nitrate (NO_3^-), and sulfate ($SO_4^=$) ion concentrations using an ion chromatograph. There is a detection threshold of about 10^{-6} moles for the ion concentration, and the measured (Nagamoto et al. 1983) pH values are accurate to within 0.1. In addition to the cloud water samples collected during December 1982, precipitation samples were also collected on 6 January 1983 at McMurdo under calm winds. Using a portable buoy (Saxena and Curtin 1983), samples of the Ross Sea water were collected on 8 January 1983. These samples were also analyzed at the NOAA laboratory using identical procedures as mentioned above.

Results of the analysis of the cloud water samples are presented in the table. On 27 December 1982 clouds formed over the Ross Sea at 600 meters mean sea level (MSL) with a cloud thickness of about 100 meters. The winds measured by the McMurdo radiosonde at cloud level were from the northeast at 5 to 15 knots. The pH of cloud water samples ranged between 5.7 and 6.2

On 31 December 1982 clouds formed at 950 to 1,500 meters MSL over the Ross Sea. The winds at this level as indicated by the McMurdo sounding were from the southeast at 10 to 15 knots. There is a significant difference in the pH value for these clouds in comparison to those of 27 December. The range of pH measured on 31 December 1982 was from 4.9 to 5.6.

The graph in figure 1 shows the value of pH as a function of height inside the cloud. The straight line is the least squares best fit for the data with a calculated correlation coefficient of -0.85. Acidity increases with height in the cloud.

Because the samples were taken on two different days with low-level clouds being sampled on one day and higher level clouds on another, acidity may possibly have varied for some other reasons. It might be that the clouds from each day are associated with air masses that came from different source regions and followed different trajectories. This could be possible

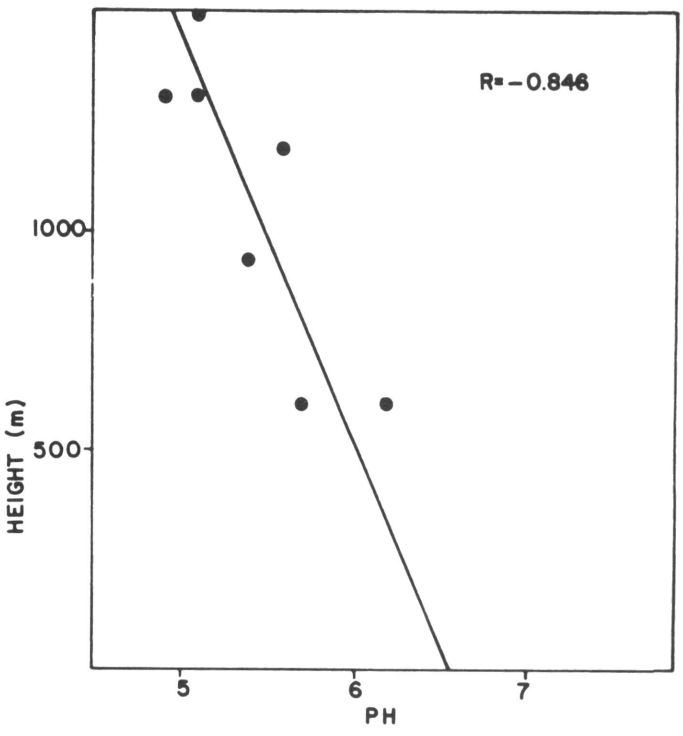

Figure 1. Plot of the pH values measured in cloud water samples as a function of height (mean sea level). ("m" denotes "meter.")

Ion concentration in the samples of cloud water, snow, and sea water collected at McMurdo, Antarctica

Sample	Date	Sample height (in meters above sea level)	pH	Ion Concentration (equivalent/liter)					Ratio			
				Hydrogen	Sodium	Chlorine	Sulfate	Nitrate	Hydrogen/ sodium	Chlorine/ sodium	Sulfate/ sodium	Nitrate/ sodium
1. Cloud	27 Dec. 1982	600	5.7	2×10^{-6}	2.1×10^{-3}	3.3×10^{-3}	3.3×10^{-4}	4.0×10^{-5}	1×10^{-3}	1.7	0.16	2×10^{-2}
2. Cloud	27 Dec. 1982	600	6.2	6×10^{-7}	—	—	—	—	—	0	—	—
3. Cloud	27 Dec. 1982	935	5.4	4×10^{-6}	5.2×10^{-4}	3.3×10^{-4}	1.0×10^{-4}	1.6×10^{-6}	8×10^{-3}	0.6	0.19	3×10^{-3}
4. Cloud	31 Dec. 1982	1,490	5.1	8×10^{-6}	4.3×10^{-4}	5.5×10^{-4}	1.0×10^{-4}	1.6×10^{-6}	2×10^{-2}	1.4	0.23	4×10^{-3}
5. Cloud	31 Dec. 1982	1,306	5.1	8×10^{-6}	1.0×10^{-4}	2.0×10^{-5}	3.3×10^{-5}	0	8×10^{-2}	0.2	0.33	0
6. Cloud	31 Dec. 1982	1,306	4.9	1×10^{-5}	1.1×10^{-4}	1.0×10^{-4}	3.1×10^{-5}	0	10^{-1}	0.1	0.28	0
7. Cloud	31 Dec. 1982	1,186	5.6	3×10^{-6}	5.2×10^{-4}	7.4×10^{-4}	1.0×10^{-4}	1.6×10^{-6}	6×10^{-3}	1.4	0.19	3×10^{-3}
8. Snow	6 Jan. 1983	Ground	5.3	5×10^{-6}	2.0×10^{-3}	2.2×10^{-3}	2.7×10^{-5}	3.2×10^{-6}	3×10^{-3}	1.1	0.14	2×10^{-3}
9. Sea water	8 Jan. 1982	Sea level	8.0	1×10^{-8}	5.6×10^{-1}	5.9×10^{-1}	5.4×10^{-2}	4.8×10^{-5}	2×10^{-8}	1.1	0.10	9×10^{-3}

since wind directions observed on these 2 days were 90° apart. However, even if the air masses followed different trajectories, it is unlikely that it should make a difference in the cloud-water acidity given the lack of anthropogenic sources in the region. The only potential site that could alter the pH of the clouds is the active volcano, Mount Erebus. The impact of Mount Erebus on the atmospheric chemistry of the region has been recently documented by Radke (1982). However, on both days the flow was coming from a direction opposite to that which could induce the involvement of the Mount Erebus plume. One explanation may be that lower clouds on 27 December 1982 contained more sea-salt particles which neutralized the acidity and yielded higher values of pH.

The increase of acidity with height was found even though the concentrations of $Na^{=}$, Cl^{-}, $SO_4^{=}$, and NO_3^{-} ions generally decreased with height. This can be explained if we consider that hygroscopic particles serve as CCN at the cloud base. During their lifetimes in the cloud, the droplets grow; consequently, the concentrations of the ions could be expected to be diluted and decreased. The ratios would remain constant with height in the cloud if no chemical processes were occurring. However, this is not the case; all the ion ratios vary with height with H^{+}/Na^{+} ratio varying two orders of magnitude. Of all the ratios, the only one that has a good correlation with height is $SO_4^{=}/Na^{+}$ (figure 2). The NO_3^{-}/Na^{+} ratios for four of the samples are lower than that of the sea water. The ratio of Cl^{-}/Na^{+} is probably not a significant contributor to the increase of acidity. This leads to an inference that the increase of acidity with height is due to an increase in the $SO_4^{=}$ concentration.

The mechanism by which $SO_4^{=}$ is introduced into the cloud is probably entrainment from the cloud top. As reported by Saxena and Ruggiero (1984), cloud droplet spectrum broadening is evident in the antarctic coastal stratus clouds and is believed to be due to entrainment of dry air at the cloud tops. It is quite likely that this process also entrains $SO_4^{=}$ into the cloud. The source for $SO_4^{=}$ is most likely a stratospheric-tropospheric exchange process that results in the sulfate transport (Hogan 1975) from the Stratospheric Junge sulfate layer. Another possibility is that the sulfur may be of biogenic origin as has been discussed by Saxena, Curtin, and Parungo (in press).

When we examine the results obtained from the precipitation sample, we realize that no simple conclusions can be drawn. The level of acidity in the cloud water and precipitation samples is the result of a series of complicated, complex processes occurring in the hydrologic cycle. Because of such complexity, further investigations should be made to determine the contribution of natural sources to the acidity of antarctic precipitation.

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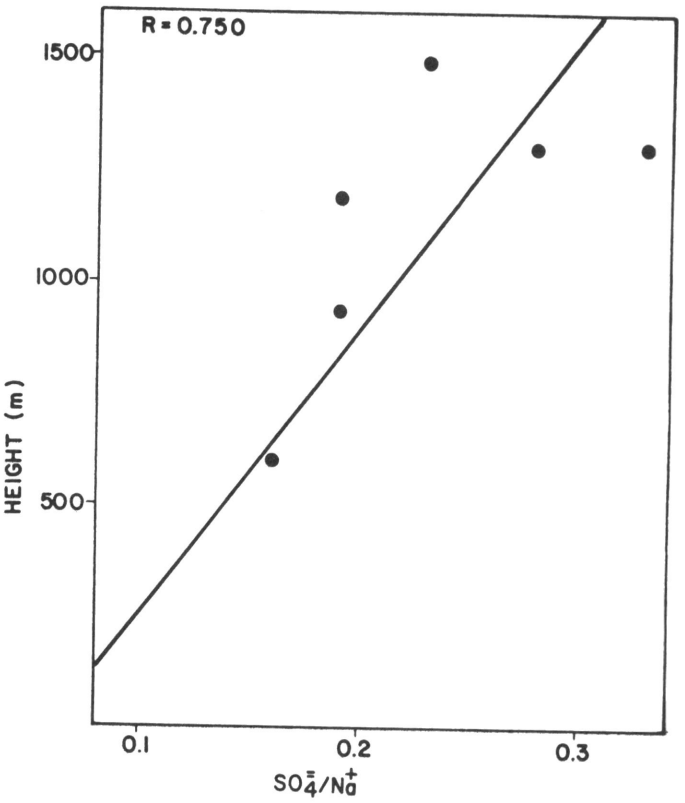

Figure 2. Plot of the ion ratio sulfate/sodium ($SO_4^{=}/Na^{+}$) of cloud water as a function of the sample height.

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