



Mercury and trace elements in cloud water and precipitation collected on Mt. Mansfield, Vermont

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through direct atmospheric measurements. Mt. Mansfield, VT, in the Lake Champlain watershed, was chosen as the cloud sampling site. Atmospheric Hg concentrations and deposition have been extensively studied in this watershed which is known to contain fish and sediment contaminated by Hg.²³⁻²⁶ The first objective, addressed in this paper, is to quantify the amount of

precipitation and is treated separately in all statistical descriptions and analysis. Concentrations of Hg varied by an order of magnitude among the non-precipitating cloud events from 7.5 to 71.8 ng l⁻¹ with an arithmetic mean concentration of 24.8 ng l⁻¹.

Table 1 summarizes trace element concentrations and Table 2 summarizes major ion concentrations measured in non-precipitating cloud events sampled from August 1 through October 31, 1998. The events on August 10 and October 16 were not analyzed for major ions due to insufficient sample volume. The range of measured trace element concentrations was quite large with maximum concentrations approximately 30 to 100 times higher than minimums of most elements. The maximum to minimum ratios were greatest for Mg (130) and Pb (130).

Concentrations of selected trace elements in clouds in the northeastern US have previously been measured at Whiteface Mountain, NY and Mt. Washington, NH (Table 3). Olmez

individual events were plotted, each having a slightly different regression equation. This suggests that factors in addition to LWC influencing concentration vary more between events than during an event, as emission sources and meteorological parameters would. In our research on Mt. Mansfield, LWC was found on average to account for 60% of the variability in Hg cloud water concentrations ($r^2 = 0.6$, $p < 0.001$). Similar inverse relationships exist between LWC and measured concentrations of Ni, Mg, Sr, V, Mn, Rb, Sb, Mn, As and K^+ ($0.3 < r^2 < 0.6$). Correlations of LWC with Mo, Pb, Ti, Zn, Cd, Cu, Ca^{2+} , Mg^{2+} , Na^+ and SO_4^{2-} were not as strong ($r^2 < 0.25$) indicating that other factors influencing these concentrations overshadowed effects of LWC for the cloud events characterized in our study.

Meteorological analysis

Forty-eight hour back trajectories were calculated using the HYSPLIT4 (HYbrid Single-Particle Lagrangian Integrated

Differences in concentration between cloud and rain may result from the type of aerosol particle that an element is associated with. Anthropogenic aerosols tend to be small ($<1.0\ \mu\text{m}$) accumulation mode aerosols.¹ These anthropogenic elements are expected to be primarily associated with hygroscopic sulfate particles since they are often emitted from the same sources. Particles containing As were demonstrated to be hygroscopic for this reason.⁵¹ Alternately, aerosol particles with a crustal origin tend to be larger ($>2.5\ \mu\text{m}$) and are expected to be predominantly hydrophobic as was found for Mn.⁵² Size and hydrophobicity will affect the in- and below-cloud scavenging of particles since hygroscopic particles are good cloud condensation nuclei and large particles are most efficiently scavenged below cloud.⁴⁴ Precipitating clouds generally have a higher LWC and greater in-cloud convection than non-precipitating clouds, which may enhance concentrations of crustal elements in precipitating cloud drops. This is possible because the higher deliquescence point of crustal aerosol will only be reached in high LWC clouds. Additionally, high in-cloud convection should cause more collisions and impaction scavenging of interstitial hydrophobic crustal aerosols by cloud droplets. Below cloud scavenging of rain droplets should more effectively capture larger particles, thereby favoring scavenging of crustal over anthropogenic aerosols. We hypothesize that these factors can explain why crustal elements are relatively high in rain from Mt. Mansfield compared to non-precipitating cloud water.

The cloud event sampled on October 1 included rain in the first, and snow and ice pellets in the second and third sequential samples. The three sequential samples collected during this storm were less concentrated in Hg and other trace elements than all non-precipitating cloud samples collected during this study. One explanation for the low concentration is inclusion of precipitation, which was generally lower in Hg concentration than cloud water. Snow in particular was found during our previous research to be significantly lower in Hg than rain.^{49,10} Further research on the Hg chemistry of clouds that produce snow will be necessary to fully understand causes of lower snow Hg concentrations. The low concentration of this mixed snow/cloud event also suggests that clouds that produce frozen precipitation may typically be lower in Hg than clouds that produce rain.

Case studies

One sequential, non-precipitating cloud sample was collected on August 10, 1998 from 13:15 to 19:15 local time, preceding a precipitation event. This sample had the greatest concentrations of Hg and all trace elements investigated. The cloud event was intermittent with our lowest LWC ($0.005\ \text{g m}^{-3}$), resulting in insufficient sample volume for major ion analysis. This was the only sample associated with transport from the southwest and south of the site (Fig. 4), an area with many industrial and urban sources of Hg and other trace elements.⁴⁷ The particularly high Hg concentrations in this cloud event are likely the combined result of low LWC and Hg source influence.

On September 21 from 12:10 to 21:00, three sequential samples were collected during an orographically enhanced cloud event, produced as a cold front passed by the mountain.

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constant from the northwest during this event (Fig. 4). Relative to events associated with west and southwest flow, the Hg concentration was not particularly high, but Cu, Zn, As, Cd and Pb were noticeably elevated (Fig. 5). Trajectory analysis and trace metal data suggest that this event was strongly influenced by emissions from Canadian smelters, which emit Cu, Zn, As, Cd, and Pb.⁴ Liquid water content in this event was relatively high compared to other events sampled, and decreased from 0.20 to 0.14 g m⁻³ from the first to second sample. This corresponds to a 10–20% increase in concentration of most elements including Hg, Mn, Cu, As, Sb, and Pb during the event.

Conclusions

Non-precipitating cloud events sampled on Mt. Mansfield, VT were found to have Hg concentrations that varied by an order of magnitude. Sequential sampling revealed that concentrations changed by as much as a factor of two from the start to the end of the event. Meteorological analysis and trace metal data indicated that cloud water concentrations were highly influenced by exposure to anthropogenic sources in the Great Lakes, Ohio Valley and Mid-Atlantic regions. The other major factor responsible for variations in Hg and trace element concentrations identified was cloud liquid water content, which accounted for about 60% of the Hg variability.

Very low concentrations were measured in a snow producing cloud event. Consequently further investigations are warranted on whether low Hg levels in cloud water may be the cause of the low Hg concentrations typically observed in snow. These lower cloud concentrations may result from differences in scavenging and nucleation for frozen versus liquid clouds.

Cloud Hg concentrations were similar to, but slightly higher than those measured in rain at a nearby location. Higher concentrations were found for anthropogenic trace elements in the cloud versus precipitation, but crustal elements had equal concentrations clouds and precipitation. This is hypothesized to result from the association of crustal elements with less hygroscopic particles, which are not good cloud condensation nuclei, but are scavenged by impaction with drops in turbulent precipitating clouds and by falling rain below cloud. The relative importance of aerosol and gas phase Hg scavenging in and below-cloud, as well as in-cloud chemistry all appear to be necessary for predicting wet deposition and transport of Hg. The added input of trace elements and mercury from cloud water on Mt. Mansfield found in this study is further examined in Lawson et al.,²⁷ and determined to be a major source of pollutant deposition.

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