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

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The lack of high quality measurements of Hg and trace elements in cloud and fog water led to the design of a new collector for clean sequential sampling of cloud and fog water. Cloud water was collected during nine non-precipitating cloud events on Mt. Mansfield, VT in the northeastern USA between August 1 and October 31, 1998. Sequential samples were collected during six of these events. Mercury cloud water concentrations ranged from 7.5 to 71.8 ng l^{-1}, with a mean of 24.8 ng l^{-1}. Liquid water content explained about 60% of the variability in Hg cloud concentrations. Highest Hg cloud water concentrations were found to be associated with transport from the Mid-Atlantic and Ohio River Valley, and lowest concentrations with transport from the north of Mt. Mansfield out of Canada. Twenty-nine event precipitation samples were collected during the ten-week cloud sampling period near the base of Mt. Mansfield as part of a long-term deposition study. The Hg concentrations of cloud water were similar to, but higher on average (median of 12.5 ng l^{-1}) than Hg precipitation concentrations (median of 10.5 ng l^{-1}). Cloud and precipitation samples were analyzed for fifteen trace elements including Mg, Cu, Zn, As, Cd and Pb by ICP-MS. Mean concentrations were higher in cloud water than precipitation for elements with predominately anthropogenic, but not crustal origin in samples from the same source region. One possible explanation is greater in-cloud scavenging of crustal elements in precipitating than non-precipitating clouds, and greater below-cloud scavenging of crustal than anthropogenic aerosols.

Introduction

Although often present in the environment in low concentrations, small quantities of many trace elements are of ecological interest due to their necessity as nutrients or their toxicity as pollutants. Nutrient trace elements include Mg, Mn, Cu and Zn, some of which become toxic at high concentrations. Others, including the heavy elements such as Hg, Cd, As, and Pb are of environmental concern due to their high toxicity and widespread industrial use. The atmosphere plays an important role in the transport and subsequent wet or dry deposition of trace elements. Although there are significant natural sources of trace elements in the atmosphere, all are at least somewhat enhanced by anthropogenic emissions. For several elements including As, Cd, Hg, Pb and Sb, anthropogenic atmospheric emissions are currently believed to be equal to or greater than natural atmospheric sources on a global scale.[1] With the exception of Hg, which has both a vapor and aerosol phase, trace elements are associated with aerosol particles in the ambient environment.

Atmospheric trace element measurements can also be used to identify the emission sources that have influenced a particular air sample. Recognizing source "signatures" is possible because different pollution sources emit particular elements or ratios of elements. Typical examples are V and Ni from oil combustion, As, Sb and Mo from coal combustion, As, Zn, Ni, Cu, Cd, and Pb from mining and smelting processes and Mg, Ti and Mn from soil and mineral dust.[2–4]

Mercury is a known toxin to humans, animals and plants with both natural and anthropogenic origins.[5–8] Hg is of special concern because of its prevalence and ability to bioaccumulate in aquatic food webs. One of the primary pathways by which Hg enters watersheds is through atmospheric deposition.[9,10] Understanding the sources, atmospheric transport, chemistry and deposition of Hg therefore is crucial to finding a solution to this problem.[11] Cloud and fog likely play an important role in the cycling of Hg, but little research has been devoted to this phenomenon.

Clouds affect the atmospheric transport of Hg by acting as a reaction vessel for aqueous chemistry, influencing the rates at which atmospheric Hg is incorporated into raindrops, and ultimately deposited *via* precipitation. With the exception of recent measurements during polar sunrise in the arctic,[12] gas phase reactions have been found to have little importance to atmospheric Hg chemistry,[13] while aqueous chemical reactions in clouds are the primary mechanism that determines atmospheric Hg speciation. Clouds provide the medium for conversion of Hg species between the elemental gas, divalent gas and particle adsorbed forms. These forms have very different reactivities and atmospheric removal rates that will ultimately affect the deposition and transport rates of Hg.[14,15]

Chemical species are often more concentrated in cloud droplets than in precipitation collected at the same location, and some major ions have been found to be up to two orders of magnitude greater than in corresponding precipitation events.[16–19] Consequently, cloud water deposition *via* impaction with surfaces such as trees, plants and man made structures is known to be a major source of pollutants to many watersheds.[20,21] Recently, Evans and Hutchinson[22] found evidence for the importance of cloud deposition to Hg cycling by using moss and lichens to measure high elevation Hg deposition in Quebec.

Despite the importance of clouds to chemical cycling, measurements of Hg in cloud water are lacking. This research aims to provide a more complete understanding of the Hg cycle

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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 Hg in cloud water, characterize cloud chemistry at a high-elevation site, and understand the factors that control measured concentrations. The second objective, which is presented in Lawson *et al.*,[27] is to estimate and determine the relative importance of direct water, Hg and pollutant deposition from clouds to a high elevation forest. Lawson *et al.* found that increases in rain amount due to orographic effects and cloud water deposition result in much higher wet deposition of Hg at high elevations.

Methods

Cloud collector design

The cloud collector designed for this study is modeled after the strand collectors utilized by many researchers and monitoring programs including the Atmospheric Science Research Center,[28] the US Mountain Cloud Chemistry Project,[29] and the Canadian Chemistry of High Elevation Fog Program.[30] Several modifications to the collector were necessitated for Hg and trace element sampling. Most collectors are constructed of either polypropylene, which is known to adsorb Hg, or out of metal, which cannot be acid cleaned. This collector is made entirely of Teflon, the material of choice for trace Hg sampling, with the exclusion of three Techtron PPS (Polyphenylene Sulfide) supporting rods. TFE Teflon rods were originally utilized but contracted more in cold than the PTFE Teflon strands causing the strands to become slack. The 960 Teflon strands have a diameter of 0.4 mm to give a 50% collection efficiency cutoff at 0.2 μm drops.[28] The Teflon funnel at the base of the collector attaches to a Teflon bottle by an adapter containing a glass vapor lock to prevent sample volatilization.[31] The adapter also includes a Teflon slide valve, allowing for easy bottle switching during sequential sampling without loss of liquid from the funnel.

Site description

Mt. Mansfield, with a summit elevation of 1204 m, is located about 35 km east of Burlington, VT and Lake Champlain in the northeastern USA. Our sampling site was selected just above the tree line near the summit of the mountain to allow for direct interception of ambient clouds. A red spruce–balsam fir forest covers the upper slopes of the mountain to an elevation of approximately 1200 m. At an elevation of 400 m on the western slope of the mountain, a Hg monitoring station located at Proctor Maple Research Center (PMRC) has been in operation since December 1992.[25] NRG Systems, INC provided wind data from a Maximum # 40 Anemometer operated at 15 m above the summit. The mean wind speed observed during cloud sampling periods was 10.3 m s^{-1} with a range of 1.6 to 17.3 m s^{-1}.

Sample collection, preparation and analysis

Non-precipitating regional cloud events were sampled from August 1–October 31, 1998. A maximum of three sequential samples was collected per event dependent on duration and sample volume collection rate. At the conclusion of field collection, samples were immediately transported to PMRC. A sub-sample was poured off from each sample in a portable HEPA filtered air chamber for major ion analysis at the University of Vermont Environmental Testing Lab. The remainder of the bulk samples were refrigerated (4 °C) and shipped overnight to the University of Michigan Air Quality Laboratory (UMAQL), where they were acidified with HNO_3 (to 0.2% v/v solutions) to prevent retention of trace elements on the bottle walls. Acidified cloud samples were allowed to equilibrate for a minimum of twenty-four hours after which a sub-sample was poured off into an acid cleaned polypropylene bottle for trace element analysis. The remaining sample, in the original Teflon bottle, was oxidized with BrCl (to 1% v/v solutions) for Hg analysis.

Clean techniques required for trace level Hg and elemental research were employed throughout sampling and analysis. All sample preparation and analysis was conducted in a class 100 clean room for Hg and a class 1000 clean room for trace elements, both at UMAQL. All bottles and glassware used for Hg or trace element samples were cleaned extensively using a modified version of a procedure developed by Rossmann and Barres.[32] The long acid soaks in the procedure were replaced by six-hour heatings, first in 3 M HCl and then 3.5% (by volume) HNO_3. All bottles and supplies were rinsed at least five times with MilliQ ultrapure water (18.2 MΩ·cm resistivity; Millipore Corp.) after acid cleaning. The collector was cleaned by soaking in HCl and then HNO_3 (each 10% by volume) for a minimum of twenty-four hours each. Within four hours of sampling, the collector was removed from the HNO_3 and rinsed thoroughly (10–15 min) with Milli-Q water.

Major ion analyses were performed at the University of Vermont Environmental Testing Laboratory. Cations were analyzed by inductively coupled plasma-atomic emission spectrometry on a Perkin Elmer Optima 3000 DV. Anions were analyzed by ion chromatography using a Dionex IC 2010i. Trace element samples were analyzed in a clean room at the UMAQL by inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer ELAN 5000). Mercury concentrations were determined using a Tekran 2537 (Tekran, Inc.) which utilizes cold vapor atomic fluorescence and gold trap amalgamation following a wet analysis protocol.[33]

Results and discussion

Atmospheric Hg monitoring has been ongoing at PMRC since 1993, and follows the US Environmental Protection Agency method IO-5. Concentrations measured at this location are comparable to those measured at rural and remote sites in the Great Lakes Region of North America[34,35] and Sweden.[36] From January 1993 through December 1997, the mean concentration of Hg measured at PMRC was 8.0 ng l^{-1} in event precipitation (σ = 8.5 ng l^{-1}, n = 538), 1.6 ng m^{-3} vapor phase Hg (σ = 0.3 ng m^{-3}, n = 305) and 9.3 pg m^{-3} total particulate phase Hg (σ = 6.6 pg m^{-3}, n = 346).

Liquid water content

Cloud liquid water content (LWC) was calculated based on the collector size, overall collection efficiency and wind speed.[37] Since wind speed was measured about 15 m above the summit, LWC may be overestimated, and should be considered as an upper limit. The estimated LWC ranged from 0.005 to 0.24 g m^{-3} with an event mean of 0.11 g m^{-3}. The clouds sampled on Mt. Mansfield had LWC lower than those typically sampled at 1620 m at Whiteface Mountain, approximately 75 km to the west, across Lake Champlain.[28] Based on visual observations, the sampling location was usually near cloud base (within 100 m), which is typically a region of low LWC.[38] In addition, non-precipitating clouds, which were measured in this study, typically have a lower LWC than precipitating clouds.[28]

Cloud chemistry

Ten cloud events were sampled on Mount Mansfield from August 1–October 31, 1998. Each of these ten episodes was on a separate day. Six of the cloud events were sequentially sampled into two or three fractions. One cloud event included

Table 1 Arithmetic mean, median, minimum and maximum concentrations of trace elements measured in cloud water and precipitation, Mt. Mansfield, VT

		Hg	Mg	Ti	V	Mn	Ni	Cu	Zn	As	Sr	Mo	Cd	Sb	La	Ce	Pb
Cloud (n = 9)	Mean	24.8	203	1.32	4.15	7.51	1.84	3.42	34.31	1.11	2.33	0.12	0.28	0.43	0.108	0.167	5.45
	Med.	12.5	26	0.55	1.52	1.98	0.59	0.98	14.25	0.66	0.63	0.05	0.18	0.14	0.025	0.037	2.26
	Min.	7.5	11	<.22	0.43	1.29	<.12	0.25	3.40	0.10	0.24	0.01	0.03	0.06	0.010	0.015	0.21
	Max.	71.8	1441	6.13	23.27	39.98	11.07	15.62	156.38	4.20	14.00	0.56	0.88	2.12	0.676	0.984	27.23
Rain (n = 30)	Mean	11.9	22	0.62	0.35	1.53	0.44	0.67	4.01	0.11	0.40	0.03	0.05	0.05	0.025	0.041	0.54
	Med.	10.5	15	0.27	0.24	1.12	0.15	0.42	2.52	0.10	0.26	0.03	0.03	0.05	0.020	0.034	0.46
	Min.	2.0	3	<.22	0.01	0.09	<.12	0.04	0.31	<.02	0.03	<.01	<.01	<.03	<.002	<.001	0.03
	Max.	35.4	95	5.84	1.19	5.69	4.01	4.50	16.33	0.26	1.30	0.10	0.31	0.12	0.077	0.154	1.45

Hg concentrations are expressed in ng l^{-1}, all other elements are expressed in µg l^{-1}.

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[39] and Dutkiewicz and Husain[37] sampled in summer and fall seasons while Khwaja *et al.*[40] and Siefert *et al.*[41] sampled during summer only. Concentrations measured in this study were quite similar to those measured within the previous 11 years, especially considering the small number of events sampled in all. Before the 1990's clean sampling techniques were not routine so the possibility of contamination should be considered when reviewing values in the literature.[43] Recent measurements of Pb in cloud water agree quite well, with means of 5.4 µg l^{-1} of Miller and Friedland[42] for a summertime Whiteface Mountain study, 7.7 µg l^{-1} of Khwaja *et al.*,[40] and 5.5 µg l^{-1} of this study. In 1982, the mean Pb concentration of cloud water on Mt. Mansfield was measured as 51 µg l^{-1}, a level that is much higher than recent measurements.[18] The higher concentrations are possibly due to emissions from motor vehicles using leaded gasoline at a time when Pb had not yet been completely phased out as a fuel additive. The only elements for which concentrations during previous studies differ from this one are Zn and Sb, which were higher in this study. The approximately 2 × higher mean concentrations for these two elements in this study can be attributed to a few cloud events with higher concentrations than were measured by others. With the small number of samples described here, or reported by all researchers, it is not possible to describe spatial, seasonal or long-term trends in cloud water concentrations.

Table 2 Arithmetic mean, median, minimum and maximum concentrations of major ions measured in cloud water (n = 7), Mt. Mansfield, VT

	Ca^{2+}	K^{+}	Mg^{2+}	Na^{+}	SO_4^{2-}
Mean	0.28	0.32	0.15	0.14	2.19
Med.	0.18	0.37	0.03	0.10	0.94
Min.	0.02	0.04	0.01	0.02	0.39
Max.	0.80	0.52	0.95	0.51	8.44

Concentrations are expressed in mg l^{-1}.

Table 3 Comparison of range and mean concentrations (µg l^{-1}) of trace elements measured in cloud water in this study at Mt. Mansfield and by others on additional mountains in the northeastern US

	Mansfield	Whiteface			Washington
	1998 $n = 9^a$	1987 $n = 3^b$	1993/1994 $n = 7^c$	1993/1995 $n = 14^d$	1987 $n = 7^e$
V	0.4–23 4.2	—	—	—	0.3–27 5.0
Mn	1.3–40 7.5	5.5–29 13	0.3–30 5.7	—	0.4–19 4.4
Cu	0.3–16 3.4	<2.0–7.7 3.9	<0.07–24 4.1	—	—
Zn	3.4–156 34	<10–43 18	—	—	4.3–31 17
As	0.1–4.2 1.1	—	—	0.29–3.4 0.72	0.5–1.9 0.9
Sb	0.06–2.1 0.4	—	—	—	0.07–0.5 0.2
Pb	0.2–27 5.5	4.3–13 7.7	—	—	—

[a]This study. [b]Khwaja *et al.*[40] [c]Siefert *et al.*[41] [d]Dutkiewicz and Husain.[37] [e]Olmez.[39]

In this study, all trace elements measured in cloud water, including Hg, were moderately correlated with each other typically at $r^2 > 0.6$ and $p < 0.001$. Unlike Hg, other trace elements are primarily associated with particles and are not typically present as gases in the ambient atmosphere. Consequently, these elements are only incorporated into cloud water by scavenging of aerosol particles. The moderate and highly statistically significant correlation between elements in cloud water suggests that the aerosol incorporated into the cloud water reaching Mt. Mansfield is an aged aerosol emitted by multiple regional anthropogenic and natural sources. As aerosols age during transport and are processed by clouds in the atmosphere, their composition will become more homogenized. Aerosols scavenged by clouds that subsequently evaporate likely result in a more uniform aerosol population.[44] The high variability observed in Hg and trace element concentrations between samples, despite correlation between different trace elements, indicates that meteorological factors are influencing cloud concentrations. These factors likely include changes in LWC and cloud microphysics that will affect concentrations without changing the relative ratios of one element to another. Despite the general consistency of trace elements ratios measured in Mt. Mansfield cloud water, individual source "signatures" can be identified for particular events and are discussed below.

LWC was inversely related to Hg concentrations of sequential cloud water samples (Fig. 1). Inverse relationships have been observed in studies of major ion cloud chemistry[28] and would be expected if LWC differences result from droplet growth or evaporation. One study in particular related total ionic content and LWC by a power function (r^2 = 0.27, n = 570).[45] The fit improved when only sequential samples from

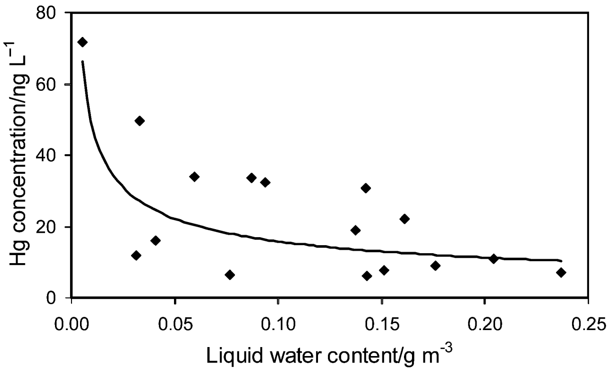

Fig. 1 Liquid water content *versus* Hg cloud concentration for 16 cloud water samples from 9 events.

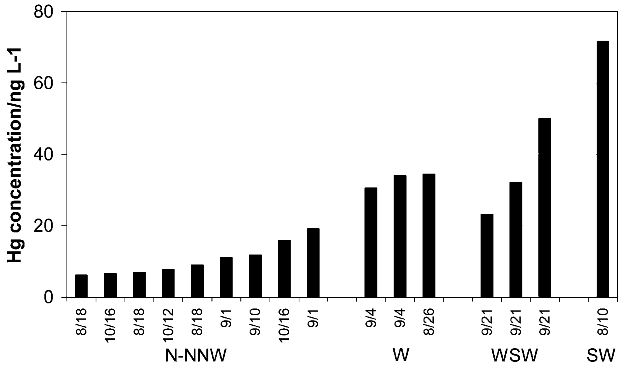

Fig. 2 Mercury cloud water concentration categorized by air mass source region. N-NNW = north through north-northwest sector; W = west; WSW = west-southwest; SW = southwest.

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 Trajectory) model for the samples from the nine cloud events.[46] This model predicts the most probable trajectory of an air mass reaching the sampling location based on input of Eta Data Assimilation System (EDAS) or when not available FNL (National Center for Environmental Protection) meteorological data. The meteorological input data is produced by the National Weather Service and archived by the National Oceanic and Atmospheric Administration. The EDAS data set consists of a 79 by 59 conformal grid with 80 km resolution and 23 vertical levels, output at three-hour intervals. The FNL data set consists of a 129 by 129 polar stereographic grid with 190.5 km resolution, 14 vertical levels and is updated every six hours.

A clear trend is evident when sequential samples are clustered by their probable source region. Fig. 2 illustrates that cloud water associated with air masses which originated from the north and northwest of Mt. Mansfield were lower in concentration than with those from the west and southwest of the site. It should be noted that the liquid water content does not explain this pattern, as there was no dependence of LWC on air mass history for the clouds sampled in this study. The Hg concentrations measured in cloud water reveal a relationship with upwind transport direction in which higher cloud water Hg concentrations were associated with transport from the high Hg emission regions of the Mid-Atlantic and Ohio Valley.[47] The major source types in these areas include medical and municipal waste incineration, coal fired power plants and trace element processing such as smelting. In addition, these source areas encompass several large urban areas with large Hg emissions densities. Consequently, levels of ambient Hg in urban areas are typically 2-fold higher than Hg levels in the surrounding rural areas.[14] Similar transport relationships were obtained for most of the trace elements quantified with one notable exception (September 1) that is discussed as a case study below.

Cloud chemistry *versus* precipitation chemistry

Few studies have compared concentrations of trace elements in precipitation and cloud water. In a tropical montane forest in Venezuela, non-precipitating cloud water concentrations often exceeded that of precipitation for Al, B, Fe, Mn, Zn and Pb.[50] Olmez[39] collected seven pairs of precipitation and cloud samples from Mt. Washington in the summer of 1987, and analyzed the samples for several trace elements using instrumental neutron activation analysis. Cloud concentrations were typically higher than precipitation concentrations, with an average ratio of cloud to precipitation concentration greater than one for all elements (V, Cr, Mn, Fe, Zn, As, Se, Br, Sb, La, Ce, Sm).

Precipitation was collected during the study period from the site located at 400 m elevation on the western aspect of Mt. Mansfield. During the two months of cloud water collection, only non-precipitating cloud events were sampled, thus preventing simultaneous collection of precipitation samples. Nevertheless, comparing the small number of cloud events and precipitation samples collected during the same time-period is informative. Hg and trace element cloud water concentrations often exceed those typically found in precipitation. Meteorological analysis revealed that the majority of cloud samples were associated with transport from north, while only 30% of precipitation events were associated with northerly transport. Transport history has been shown to play an important role in the levels of aerosol trace elements[48] and likely influences the average levels in cloud water as well. This difference may have an effect on measured concentrations due to meteorological conditions and emissions sources associated with transport from particular regions. To eliminate these effects on concentration, cloud and rain samples from northern trajectories only were compared ($n = 5$ cloud events and 7 precipitation events) (Fig. 3).

Although these samples of northerly origin are generally the lowest in Hg of all cloud samples collected, the same result was evident in which cloud concentrations were generally greater than that of precipitation. Concentrations in cloud samples were also higher than in precipitation only for Pb, Cd, As, Zn, V, Cu, Mo, and Sb. This finding is consistent with previous research on major ions in which cloud water was found to be more concentrated than precipitation in major ions.[16,17,19] Concentrations were similar however between cloud and precipitation for Mn, Ni, Ce, Mg, Ti, La, and Sr (shown for Mg and Ce in Fig. 3). This group includes elements that are predominately crustal in origin, while elements in the previous group containing Pb, are typically of anthropogenic origin.

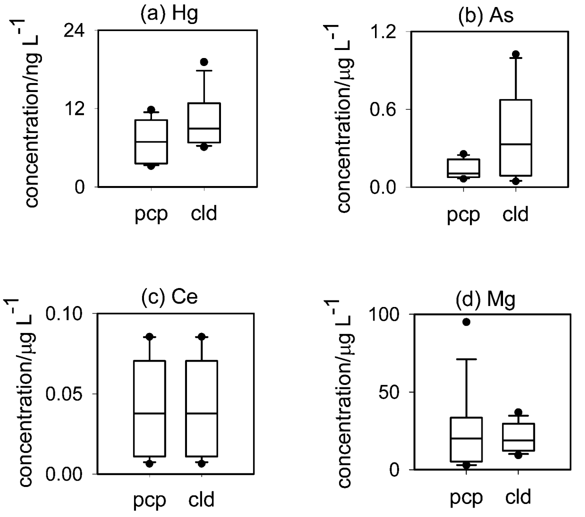

Fig. 3 Distribution of concentrations of (a) Hg, (b) As, (c) Ce and (d) Mg in precipitation and cloud water, including only those samples associated with back trajectories from north of Mt. Mansfield. Box delineates median, 25th and 75th percentiles. Bar extends to 10th and 90th percentiles. Maximum and minimum represented by points.

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 µm) 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 µm) 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.

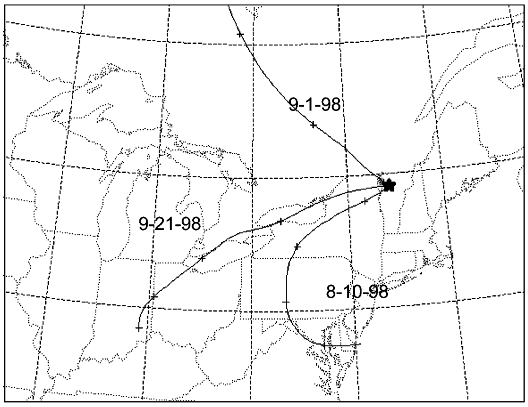

Fig. 4 HYSPLIT back trajectory for cloud events on August 10, 1998 (Hg concentration = 71.8 ng l^{-1}), September 1, 1998 (Hg concentration = 12.5 ng l^{-1}), and September 21, 1998 (Hg concentration = 36.4 ng l^{-1}). Tick marks delineate twelve hour increments in the back trajectory from the sampling site at Mt. Mansfield, represented by a star.

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 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. Prior to the event, haze greatly reduced visibility. The three sequential samples collected (Fig. 2) were high in Hg with concentrations decreasing from 50 to 23 ng l^{-1} over the sampling period. Several ions were highest on this day, including Ca^{2+}, Na^{+} and $SO_4{}^{2}$. Highest concentrations (with the exception of August 10) were measured on this day for Pb, V, Ni, As, Mg and Sr. This event was associated with west-southwest transport (Fig. 4) and high concentrations are likely the result of the influence of the industrial regions of Lake Erie and Ontario. Although transport remained constant from the west-southwest, LWC increased over the event from 0.05 to 0.14 to 0.24 g m^{-3}, resulting from a nearly 10 °F drop in temperature accompanied by a much smaller drop in the dew point. Concentrations of most ions and all trace elements decreased steadily over the event. Ratios of trace element concentrations (*i.e.* Hg/Pb, Zn/Cd), however, were constant over the three sequential samples. This suggests that the change in concentrations over the course of the event resulted from changing LWC and not varying source influence or aerosol composition of the feeder air. Some of the elements that were enhanced (As, Cd, Sb, and Mo) and the trajectory path of the event are characteristic of what Olmez *et al.*[53] identify as a "US regional source," the major Hg and trace element contribution of which they attribute to Midwestern coal combustion sources.

Two sequential samples were obtained from an orographically enhanced cloud event on September 1 from 07:35 to 09:45. The Hg concentration increased from 10.8 to 18.9 ng l^{-1} from the first to second sample, which was the highest Hg concentration of any sample associated with flow from the north or northwest of Mt. Mansfield. Air transport remained

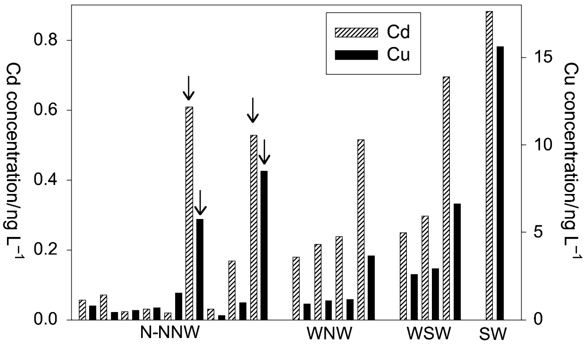

Fig. 5 Concentrations of Cd and Cu in cloud water samples, categorized by air mass source region, presented in the same order as in Fig 2. Arrows denote the high concentrations in the two sequential samples collected September 1.

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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References

1 J. E. Fergusson, *The Heavy Elements: Chemistry, Environmental Impact and Health Effects*, Pergamon Press, Oxford, 1990.
2 M. D. Cheng and P. K. Hopke, *Atmos. Environ.*, 1989, **23**, 1373.
3 T. G. Dzubay, R. K. Stevens, W. D. Balfour, H. J. Williamson, J. A. Cooper, J. E. Core, R. T. DeCesar, E. R. Crutcher, S. L. Dattner, B. L. Davis, S. L. Heisler, J. J. Shah, P. K. Hopke and D. L. Johnson, *Atmos. Environ.*, 1984, **18**, 1555.
4 J. M. Skeaff and A. A. Dubreuil, *Atmos. Environ.*, 1997, **31**, 1449.
5 T. W. Clarkson, *Environ. Health Perspect.*, 1993, **100**, 31.
6 M. W. Meyer, D. C. Evers, T. Daulton and W. E. Braselton, *Water, Air Soil Pollut*, 1995, **80**, 871.
7 C. Facemire, T. Augspurger, D. Bateman, M. Brim, P. Conzelmann, S. Delchamps, E. Douglas, L. Inmon, K. Looney, F. Lopez, G. Masson, D. Morrison, N. Morse and A. Robison, *Water, Air Soil Pollut*, 1995, **80**, 923.
8 K. K. Panda, M. Lenka and B. B. Panda, *Environ. Pollut.*, 1992, **76**, 33.
9 W. F. Fitzgerald, D. R. Engstrom, R. P. Mason and E. A. Nater, *Environ. Sci. Technol.*, 1998, **32**, 1.
10 M. S. Landis and G. J. Keeler, *Environ. Sci. Technol.*, 2002, **36**, 4518.
11 Expert Panel on Mercury Atmospheric Processes, *Mercury Atmospheric Processes: A Synthesis Report*, EPRI Report No. TR-104214, Tampa, USA, 1994.
12 W. H. Schroeder, K. G. Anlauf, L. A. Barrie, J. Y. Lu, A. Steffen, D. R. Schneeberger and T. Berg, *Nature*, 1998, **394**, 331.
13 G. Petersen, A. Iverfeldt and J. Munthe, *Atmos. Environ.*, 1995, **29**, 47.
14 G. Keeler, G. Glinsorn and N. Pirrone, *Water, Air Soil Pollut*, 1995, **80**, 159.
15 C. J. Lin and S. O. Pehkonen, *Atmos. Environ.*, 1999, **33**, 2067.
16 K. C. Weathers, G. E. Likens, F. H. Bormann, S. H. Bicknell, B. T. Bormann, B. C. Daube, Jr., J. S. Eaton, J. N. Galloway, W. C. Keene, K. D. Kimball, W. H. McDowell, T. G. Siccama, D. Smiley and R. A. Tarrant, *Environ. Sci. Technol.*, 1988, **22**, 1018.
17 D. W. Zhao, H. M. Seip, D. W. Zhao and D. B. Zhang, *Water, Air Soil Pollut*, 1994, **77**, 27.
18 T. Scherbatskoy and M. Bliss, in *The Meteorology of Acid Deposition*, ed. P. J. Samson, Air Pollution Control Association, Pittsburgh, 1984, pp. 449–456.
19 M. Igawa, Y. Tsutsumi, T. Mori and H. Okochi, *Environ. Sci. Technol.*, 1998, **32**, 1566.
20 K. C. Weathers, G. M. Lovett and G. E. Likens, *Atmos. Environ.*, 1995, **29**, 665.
21 E. K. Miller and A. J. Friedland, *J. Environ. Qual.*, 1999, **28**, 270.
22 C. A. Evans and T. C. Hutchinson, *Water, Air Soil Pollut*, 1996, **90**, 475.
23 T. Scherbatskoy, J. B. Shanley and G. J. Keeler, *Water, Air Soil Pollut*, 1998, **105**, 427.
24 A. W. Rea, G. J. Keeler and T. Scherbatskoy, *Atmos. Environ.*, 1996, **30**, 3257.
25 J. Burke, M. Hoyer, G. Keeler and T. Scherbatskoy, *Water, Air Soil Pollut*, 1995, **80**, 353.
26 A. McIntosh, *Lake Champlain Sediments Toxics Assessment Program, an assessment of sediment associated contaminants in Lake Champlain-Phase 1*, UVM School of Natural Resources, 1994.

27 S. T. Lawson, T. D. Scherbatskoy, E. G. Malcolm and G. J. Keeler, *J. Environ. Monit.*, 2003, 10.1039/b210125d.

28 V. A. Mohnen and J. A. Kadlecek, *Tellus*, 1989, **41B**, 79.

29 V. A. Mohnen and R. J. Vong, *Environ. Rev.*, 1993, **1**, 38.

30 R. S. Schemenauer, *Atmos.-Ocean*, 1986, **24**, 303.

31 M. S. Landis and G. J. Keeler, *Environ. Sci. Technol.*, 1997, **31**, 2610.

32 R. Rossmann and J. A. Barres, *Sci. Total Environ.*, 1992, **125**, 405.

33 A. T. Vette, *PhD Thesis*, University of Michigan, USA, 1998.

34 M. Hoyer, J. Burke and G. Keeler, *Water, Air Soil Pollut*, 1995, **80**, 199.

35 N. Pirrone, G. Glinsorn and G. J. Keeler, *Water, Air, Soil Pollut.*, 1995, **80**, 179.

36 A. Iverfeldt, J. Munthe, C. Brosset and J. Pacyna, *Water, Air Soil Pollut*, 1995, **80**, 227.

37 V. A. Dutkiewicz and L. Husain, *Atmos. Environ.*, 1998, **32**, 2793.

38 H. R. Pruppacher and J. D. Klett, *Microphysics of Clouds and Precipitation*, Kluwer, Dordrecht, 2nd edn., 1997.

39 I. Olmez, personal communication.

40 H. A. Khwaja, S. Brudnoy and L. Husain, *Chemosphere*, 1995, **31**, 3357.

41 R. L. Siefert, A. M. Johansen, M. R. Hoffmann and S. O. Pehkonen, *J. Air Waste Manage. Assoc.*, 1998, **48**, 128.

42 E. K. Miller and A. J. Friedland, in *Proceedings of the Eighth International Conference on Heavy Metals in the Environment*, ed. J. G. Farmer, CEP Consultants Ltd., Edinburgh, 1991, pp. 86–89.

43 W. F. Fitzgerald and C. J. Watras, *Sci. Total Environ.*, 1989, **87**(88), 223.

44 J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics*, John Wiley & Sons, New York, 1998.

45 D. Moller, K. Acker and W. Wieprecht, *Atmos. Res*, 1996, **41**, 321.

46 R. R. Draxier and G. D. Hess, *Australian Meteorological Magazine*, 1998, **47**, 295.

47 US Environmental Protection Agency, *Mercury Study Report to Congress*, EPA 452/R-97-0003, Washington DC, 1998.

48 G. J. Keeler and W. R. Pierson, *Atmos. Environ.*, 1994, **28**, 1535.

49 M. Hoyer, *PhD Thesis*, University of Michigan, USA, 1995.

50 C. A. Gordon, R. Herrera and T. Hutchinson, *Atmos. Environ.*, 1994, **28**, 323.

51 V. A. Dutkiewicz, E. G. Burkhard, M. M. Hussain and L. Husain, *Atmos. Res.*, 1996, **41**, 337.

52 B. G. Martinsson, E. Swietlicki, H. C. Hansson, A. Wiedensohler, K. J. Noone, J. A. Ogren and A. Hallberg, *Tellus*, 1992, **44B**, 593.

53 I. Olmez, M. R. Ames and G. Gullu, *Environ. Sci. Technol.*, 1998, **32**, 3048.