Atmospheric Mercury Measurements at Underhill Vermont

The Vermont Monitoring Cooperative, the University of Vermont, Ecosystems Research Group, Ltd., the University of Michigan, and the Vermont Department of Environmental Conservation, Air Quality Division are collaborating to measure atmospheric mercury pollution in Vermont.

Mercury as a pollutant

Mercury is used in industry, medicine and dentistry, and in commercial products such as fluorescent lights, thermostats, switches, and thermometers. Mercury is also present as a trace contaminant in coal and oil. Mercury is released into the atmosphere when metal ores are smelted or coal, oil or municipal and medical waste are combusted in facilities without proper pollution control technology, or even when we accidentally break a fluorescent light bulb. Large amounts of mercury have been released into the environment over the last several centuries by human activities, much of which is now stored in soils, vegetation, and lake sediments. Previously deposited anthropogenic mercury is re-emitted to the atmosphere by a process termed evasion and during forest fires.

Combustion processes emit mercury into the atmosphere in three major forms or "chemical species": gaseous elemental mercury (GEM), ionic mercury vapor (usually called reactive gaseous mercury, RGM), and ionic mercury that is bound to aerosol particles (HGP). The proportion of mercury emitted as GEM, RGM or HGP varies by combustion system, fuel source, and control technology. Uncontrolled coal-burning power plants emit approximately 50% RGM, 25% HGP and 25% GEM. Once released to the atmosphere, mercury cycles back and forth between the 3 major forms and the liquid phase. Ionic mercury may be photoreduced to the gaseous elemental form. The gaseous elemental form may be oxidized (primarily by reactions with ozone and the OH radical) to form ionic mercury. Ionic mercury (as either RGM or HGP) is readily soluble in water whereas GEM is not. Cloud and rain droplets scavenge RGM and HGP from the air resulting in dissolved ionic mercury in cloud water and rain water. Rainfall and cloud droplet capture by forests represent major pathways for transferring atmospheric mercury pollution to the landscape. Reactive gaseous mercury (RGM) and HGP dry-deposit directly to the surface of vegetation and to water. Because RGM is so "reactive" it is very sticky, has a high "deposition velocity" and therefore deposits rapidly, especially to moist or wet surfaces. HGP has a lower deposition velocity than RGM and represents a less efficient pathway for transferring atmospheric mercury to the landscape. Gaseous elemental mercury is assimilated into plant foliage through stomata in the same way a plant takes up carbon dioxide from the air. Once inside the leaf, GEM is thought to be oxidized by free radicals produced during photosynthesis and the resulting ionic mercury is likely bound by special molecules designed sequester harmful metals in the vacuole space. Due to atmospheric conversion reactions, dry-deposition, and washout of ionic mercury during transport, RGM and HGP concentrations in the atmosphere are typically just a few percent of the GEM concentration away from the immediate influence of emission sources. RGM and HGP concentrations are very dynamic, varying by as much as 2 orders of magnitude in 24 hours.

Rainfall washes off dry-surface deposited ionic mercury and carries it to the soil. When leaves fall from trees they transfer their internal accumulated mercury burden to the soil. Some of the soil, plant and water mercury burden is returned to the atmosphere when ionic mercury is photoreduced to the elemental form which is stable in the vapor phase at normal temperatures and is re-emitted in a process known as evasion. Mercury evasion rates and the biological and physical processes governing them remain poorly understood. Accurate quantification of mercury evasion rates is critical to understanding the lifetime of mercury the atmosphere and the time required to purge prior mercury pollution from the landscape once adequate anthropogenic emission controls are in place.

Once deposited to the land or water a small fraction of mercury pollution is converted to the organic methyl-mercury form by bacteria active in anaerobic conditions. While it was recently thought that this methylation activity was restricted to throughougly anoxic environments such as lake bottoms during summer stratification, recent research has shown the methylation process occurs widely in anerobic microsites in soils and sediments. Measurement of methyl mercury in forest tree leaves show that 1-3% of the total mercury in foliage is in the methyl-mercury form. At this time it is not clear if conditions within the plant lead to methylation or if this methyl-mercury represents atmospheric methyl-mercury that has been deposited to plants. Biologically significant levels of methyl mercury have been measured in precipitation (including at Underhill, VT). Possible mechanisms giving rise to the methyl mercury observed in the atmosphere are currently being investigated.

Methyl-mercury is a potent neurotoxin and is readily concentrated in animal tissues. Methyl-mercury accumulates in both aquatic and terrestrial food webs. Higher trophic level organisms with longer life-spans and slower growth rates exhibit the highest total and methyl-mercury burdens. Vermont and many other states have been forced to issue advisories against the consumption of popular fish species due their accumulated mercury levels. Emerging science is recognizing biologically significant mercury burdens in top-level consumer organisms in terrestrial food webs. There is particular concern about mercury impacts on insectivorous birds.

Atmospheric Mercury Observation Program

The atmospheric mercury observation program at Underhill, Vermont is designed to provide a comprehensive picture of atmospheric mercury pollution. The areas of investigation range from the temporal patterns of mercury concentration and speciation, to identification of sources of atmospheric mercury pollution arriving in Vermont, to direct measurements mercury deposition and evasion. The Underhill Air Quality Measurement site hosts a wide range of air pollution monitoring programs funded and operated by state and federal agencies. Other measurements include sulfur, nitrogen, and acid deposition, ground-level ozone, toxic substances, trace metals, fine particulate mass, UV-radiation, and meteorology. These additional measurements significantly enhance the ability to interpret the atmospheric mercury observations.

Atmospheric mercury research began at Underhill in 1992 when UVM and UMAQL began a long-term monitoring program for mercury in precipitation. Precipitation samples are collected by an automated collector which opens only during a precipitation event (figure). Samples are shipped by the site operator to UMAQL for analysis by the cold-vapor atomic fluorescence (CVAFS) method. The record of mercury concentrations and deposition in individual rain and snow events at Underhill is now the longest event-based record of mercury deposition in the world. During the 1990s pioneering studies of mercury accumulation in forest tree leaves, mercury in cloud water, and the wash-off of dry deposited material from tree leaves were conducted by UVM students in cooperation with UMAQL. In 2004 the Underhill site joined the international Mercury Deposition Network (MDN). In 2005 a study was initiated to compare the performance of the 3 primary samplers used to collect mercury in precipitation. This study will serve to inform the international mercury community about how to merge data collected with the different types of collectors for regional analyses as well as which collector is best suited for future mercury monitoring.

Figure. The University of Michigan (left) and Mercury Deposition Network (right) automated samplers for collecting mercury in precipitation. Moisture on a wetness-sensing element (on pole at upper right of the Michigan collector) causes the lid to automatically open, exposing a clean sample train for collection of rainfall. Site operators exchange sample trains following each rain or snow event.

Twenty-four hour integrated samples for total gaseous mercury (TGM = GEM+RGM) and HGP were collected every sixth day during the 1990s by UMAQL. Continuous measurements of speciated mercury (GEM, RGM, HGP) and periodic measurements of mercury vapor exchange fluxes (deposition and evasion) were initiated in 2004 through a partnership with Ecosystems Research Group, Ltd. Mercury speciation measurements are made with state-of-the-art Tekran® 1130, 1135, and 2537A analyzers using the atomic fluorescence method (figure). GEM is measured every 5 minutes, with average concentrations reported hourly. RGM is collected for a 2-hour period every 3 hours on a KCl-coated annular denuder which is then thermally desorbed, converting the ionic mercury to elemental form for analysis by the Tekran® 2537A.

Figure. Continuous mercury speciation sampling apparatus (Tekran® 1130 and 1135 sampling heads) deployed at the Underhill Air Quality Site (left). Tekran 1130 pump module (lower right) and 2537A continuous ambient mercury vapor analyzer (upper right).

Mercury flux measurements (deposition and evasion) above the forest canopy at Underhill are made using the modified Bowen-ratio method. This method involves measuring the total gaseous mercury (TGM = RGM + GEM) concentration at two heights above the canopy using a system of valves and a Tekran® 2537A to establish the concentration gradient. The mercury flux (deposition or evasion) is proportional to the concentration gradient. The constant of proportionality is a function of the atmospheric turbulence and is determined using micrometeorological methods. Carbon dioxide flux (related to plant photosynthetic activity) and water vapor flux (related to plant transpiration) are measured in the same manner using a

LI-COR 7000 infrared CO_2/H_2O analyzer. These additional flux measurements provide information allowing the investigation of plant physiological activity on mercury deposition and evasion rates. Inlets for mercury, CO_2, H_2O sampling as well as the micrometeorological instrumentation are mounted atop the VMC Canopy Research Tower located 0.2 miles from the Air Quality Monitoring Site (figure).

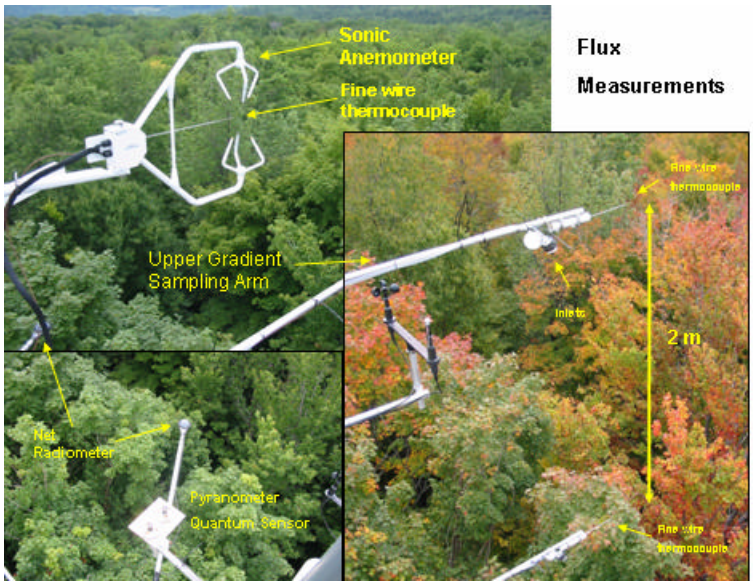

Figure. Elements of the flux measurement system deployed above the forest canopy at the VMC Canopy Research Tower in Underhill, VT.

Results

Several scientific papers have been published describing or using the information on atmospheric mercury collected at Underhill. Burke et al (1995) described the seasonal patterns in atmospheric mercury concentrations and deposition. Mercury concentrations and wet-deposition were highest in summer months and lowest in winter months, particularly when airflow associated with a precipitation event was from the south through west. Subsequent analyses using other wet deposition measurements throughout northeastern North America demonstrated that this seasonal pattern occurs throughout the region (Miller et al. 2005; VanArsdale et al. 2005). Rea et al. (1996) found that the volume-weighted mean concentration of mercury in throughfall (the water falling through the forest canopy) at Underhill was higher than the corresponding value in open-field precipitation during a 6-week summer period (12 ng L^{-1} vs. 6.5 ng L^{-1}). They attributed the increased concentrations below the canopy as due to the wash-off of dry deposited material (RGM and HGP) from the surface of leaves. Similar studies elsewhere have confirmed this finding. The authors estimated that mercury dry deposition to the surface of leaves amounted to 11.7 ug m^{-2} y^{-1}. Rea et al. (1996) also observed a 13 ug m^{-2} flux of mercury to the forest floor from mercury (GEM) accumulated internally in forest leaves. During this period the authors estimated wet-deposition of mercury to be 7.9 ug m^{-2} y^{-1}. This

study demonstrated that dry deposition was responsible for 75% of total mercury deposition at Underhill.

In the late 1990s Lawson et al. (2003) and Malcom et al. (2003) investigated the concentration mercury in cloud water near the summit of Mt. Mansfield adjacent to Underhill, Vermont. They found that mercury in cloud water was similar to but slightly higher (by a factor of 1.2) than the concentrations observed in precipitation. This difference can be explained by the generally smaller size (and lower water volume) of cloud droplets compared to rain droplets. Mercury does not appear to be as readily enriched in clouds droplets as are other pollutants such as sulfur and nitrogen. This is due to the exceedingly low concentrations of the soluble mercury forms (RGM and HGP) in the atmosphere and the very low water solubility of the dominant form (GEM). Similar to the earlier work of Rea et al (1996), Lawson et al. (2003) found that throughfall in the high-elevation balsam fir forests was substantially enriched in mercury with respect to precipitation, due to both dry deposition and cloud droplet interception. Similar to the earlier results for precipitation (Burke et al. 1995), the highest cloud water concentrations were observed when air flow was from the southwest.

Miller et al. (2005) developed a spatial model for mercury deposition in Northeastern North America based on the observations at Underhill and elsewhere in the region. They estimated that dry deposition of RGM, HGP, and GEM was responsible for over two-thirds of deposition to forested landscapes in the region. Rimmer et al. (2005) showed that mercury in the blood of the high-elevation Bicknells Thrush was positively correlated with the dry mercury flux to foliage estimated by Miller et al. (2005), emphasizing the biological significance of the GEM deposition pathway and the potential risks of atmospheric mercury pollution to terrestrial food webs. The Miller et al. (2005) model also suggests that both wet and dry deposition of mercury is likely to be greater in southern Vermont than in northern Vermont where Underhill is located. Rimmer et al. (2005) found the mercury in blood of Bicknells Thrush was higher in birds nesting on Stratton Mountain in southern Vermont than in birds nesting on Mt. Mansfield in northern Vermont.

Keeler et al. (2005) described the long-term record of mercury concentration and deposition in precipitation at Underhill. This record (1993 – 2006) covers an important period of time when US mercury emissions were reduced by 45% (1990 – 1999; USEPA, www.epa.gov) and emissions in the Northeastern states and Eastern Canadian Provinces dropped by 54% during 1998-2003 (C. Mark Smith, NESCAUM 2004 Mercury Conference, Portland ME). Despite significant national and regional emissions reductions, there was no decline (no trend) in either mercury concentrations in or deposition from precipitation. Emissions from the utility sector were nearly constant during this period, while large emission reductions resulted from new controls on municipal and medical waste incinerators. Both Keeler et al. (2005) and VanArsdale et al. (2005) – who analyzed the Underhill data in conjunction with additional data from MDN sites in the region – determined that most of the annual mercury deposition is associated with a small number of "high-deposition" periods or events, typically occurring from spring through early fall, when air-masses had traveled from the south and southwest to reach Underhill (figure). These high deposition events appear to be associated with meteorological conditions that result in air-mass trajectories that bring air from

high emissions density regions to the northeast during periods of vigorous convective mixing resulting in moderate to heavy rainfall (figure).

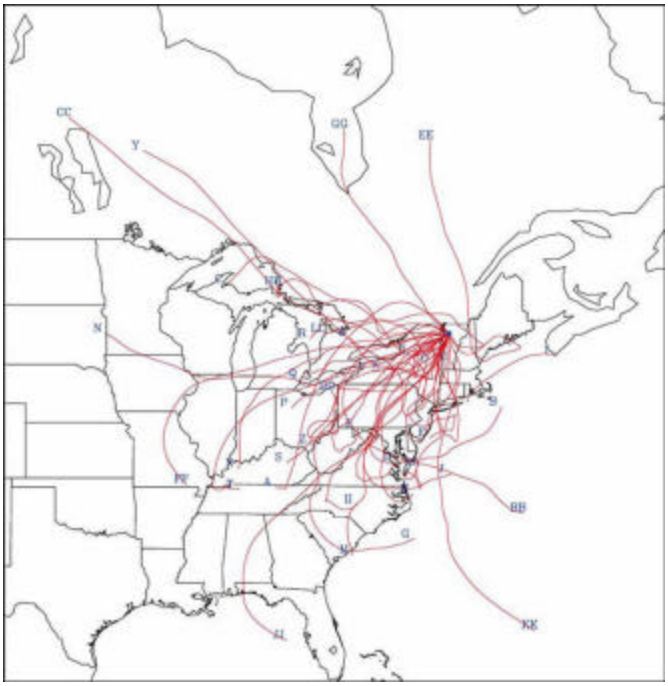

Figure. Air-mass backward trajectories calculated with the NOAA-HYSPLIT model for the highest mercury wet deposition events from 1993 to 2004 (from Keeler et al. 2005).

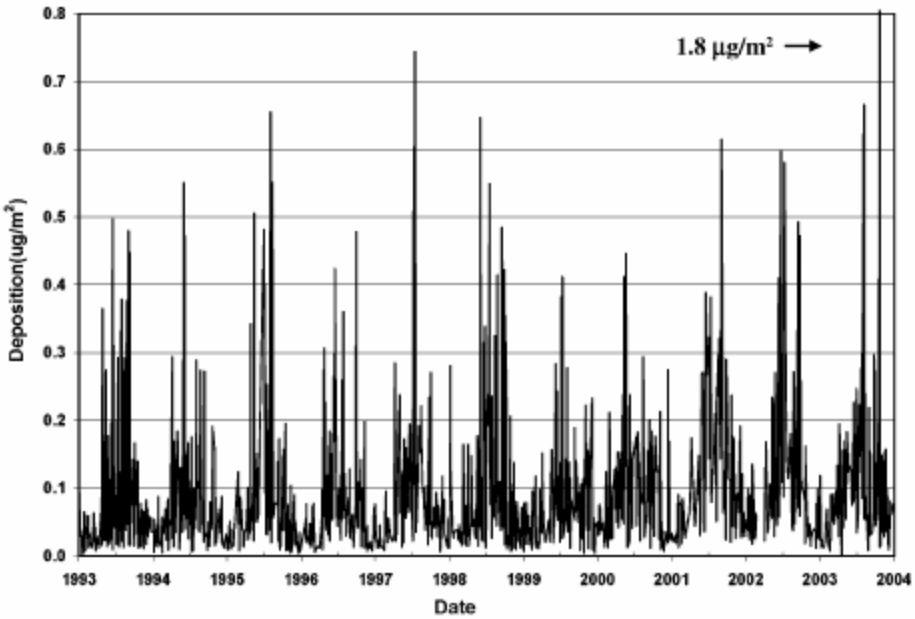

Figure. Wet Deposition of Mercury at Underhill, Vermont from 1993 to 2004 (from Keeler et al. 2005). There is a stong seasonality to deposition, with the highest deposition events tending to occur from late spring through early fall. There was no trend in wet-deposition over the period during a period of stable emissions from electric utility boilers and strongly declining emissions from municipal waste combustion and medical waste incinerators.

Preliminary results from the recently initiated mercury speciation sampling show a similar relationship between high air-concentrations of RGM and air-mass trajectories traveling over major emission sources in route to Underhill. RGM transport events occur in all seasons. Pennsylvania, OH, western NY, and NJ appear to be important source regions for significant RGM dry-deposition events based on NOAA HYSPLIT model air-mass back-trajectories (figure, Miller et al. manuscript in preparation). Ambient GEM concentrations range from 1.0 to 3.5 ng m^{-3} and average about 1.7 ng m^{-3}. RGM concentrations range from 0 to124 pg m^{-3}.

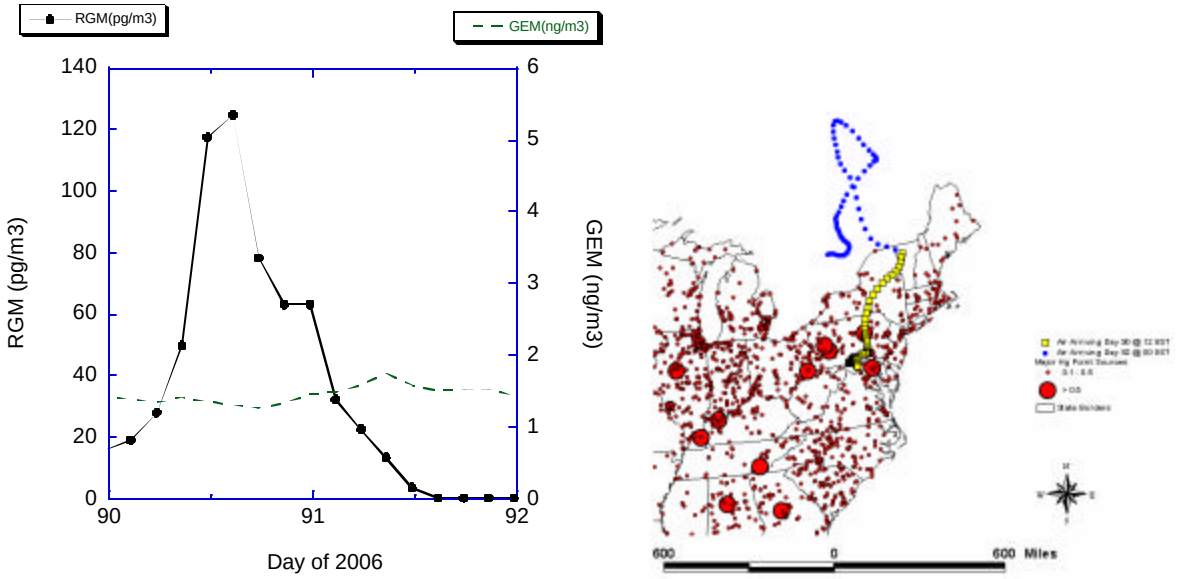

Figure. RGM and GEM concentrations over time during a major transport event during March 31/April 1 2006 (left). GEM was slightly depleted, while RGM reached the peak value observed at Underhill of 124 pg m^{-3} just after mid day on day 90 when NOAA-HYSPLIT model 72-hour air-mass backward trajectory calculations indicated air that had stagnated over major sources in PA and VA moved north to Underhill (yellow boxes, right). RGM concentrations dropped to near zero while GEM concentrations increased slightly as air-flow shifted to a trajectory from Canada after a frontal passage (blue circles, right).

Mercury flux measurements were initiated in August of 2004. An extreme wind storm in December of 2004 toppled the VMC Forest Canopy Tower. Delays associated with insurance claims, engineering studies, and tower reconstruction caused the loss of a full season of mercury flux measurements. Flux measurements resumed in May 2006. Therefore, flux measurements are just now being made during the early and middle part of the growing season and can not be reported here. During the late growing season of 2004, periods of both mercury vapor deposition and emission were observed. Preliminary flux calculations suggest the forest was a net source of mercury vapor with a median net emission of 60 ng m^{-2} h^{-1} during late summer and fall of 2004 (Miller, 2004). A full year of measurements in 2006-2007 should reveal whether the forest at Underhill is a net source or sink from GEM on annual basis. These measurements will provide the information necessary to properly incorporate GEM dry deposition and GEM evasion into next-generation emissions transport models.

Gao et al. (2006) recently completed and published a steady-state mass balance model for total mercury in Lake Champlain. This effort included new estimates of atmospheric deposition to Lake Champlain using the recent model developed by Miller et al. (2005), ambient atmospheric mercury measurements from Underhill, and meteorological measurements made by the Vermont Monitoring Cooperative at Colchester Reef and Diamond Island. The mass-balance study identified atmospheric deposition as a major input of mercury to Lake Champlain and the emission of GEM (evasion of dissolved gaseous mercury DGM) from the lake surface as a critical process limiting the accumulation of mercury in lake water. However, the model-based quantifications of both the deposition and emissions fluxes are subject to considerable uncertainty due the lack of direct measurements of key model parameters such as DGM concentrations in lake water. NOAA-funded studies conducted by the research team this year will begin to provide some of the required measurements. An expansion of this study has been proposed that would allow tracking of mercury accumulation in plankton in response to chronic and episodic loading of mercury from atmospheric deposition. Initial measurements of methyl-mercury in precipitation at Underhill during 2005 provide evidence of significant atmospheric deposition of methyl mercury to Lake Champlain and other water bodies in Vermont. Also, both wet and dry deposition of mercury are highest from late spring through summer and early fall when > 50% of annual wet (VanArsdale et al. 2005, Keeler et al. 2005) and dry (Miller et al., in preparation) mercury deposition may occur in a small number of high deposition weeks or single events. Accordingly, Lake Champlain and other Vermont water bodies may be subject to significant episodic loading of methyl and ionic mercury during the period of peak biological activity.

Implications for air-pollution management

Observations of atmospheric mercury at Underhill Vermont have advanced the understanding of long-range transport, mercury speciation, deposition, and cycling and the exposure of biota to mercury pollution. The comprehensive suite of atmospheric mercury measurements at Underhill, Vermont paint a different picture of atmospheric mercury pollution than recent emissions-transport modeling studies. Emissions-transport modeling studies done in support of the Clean Air Mercury Rule (CAMR) suggested that deposition should be very low in northern Vermont and not highly influenced by the emissions of older electrical utility coal boilers in PA, OH, and elsewhere. In contrast, the observations at Underhill show significantly higher wet and dry deposition rates than predicted by emissions-transport models. Air-mass back-trajectory studies clearly show the highest air concentrations and the majority of wet and dry deposition is associated with air arriving from the vicinity of major utility coal boilers lacking mercury emissions controls. Furthermore, the lack of any trend in the long-term wet-deposition record at Underhill is consistent with steady emissions from the utility sector over the period of record, despite very large reductions in emissions from municipal waste combustors and medical waste incinerators. The contrasts between observations at Underhill and model predictions and the implications for air pollution control strategies have been conveyed to scientists and policy makers at regional and national meetings.

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Site Operators

The atmospheric mercury observation program at Underhill, Vermont would not be possible without the dedicated efforts of VMC staff members Mim Pendleton, Carl Waite, and Judy Rosvosky. These individuals maintain and operate the monitoring equipment and their hard work in all kinds of weather has been responsible for the high quality of the extensive observational record.

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