

METHODS DEVELOPMENT FOR SAMPLING MERCURY IN SOIL WATER IN FORESTED WATERSHEDS

1996

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Health warnings about mercury (Hg) concentrations in Lake Champlain fish have prompted public concern and created an interest in studying the mechanisms of Hg transport in the environment. Results of previous studies have suggested that forest soils may play an important role in the loading of Hg into surface waters, but little is known about the rivers draining into Lake Champlain. A study comparing the chemistry of soil water with that of stream water on the western side of Mt. Mansfield is under way to test several hypotheses.

Work in 1996 was completed to identify a suitable device with which to collect soil water for the 1997 field season. For this study, two different soil water sampling devices were tested. Laboratory tests compared the amount of Hg in water poured through the devices with the amount of Hg in control samples. Soil water collectors of each kind were installed in the field, and the volumes of water collected during several rain storms were compared. Ultimately, the fiberglass wick device was chosen for our study over the zero-tension lysimeter.

INTRODUCTION

Currently there is concern about the level of mercury (Hg) in fish in Lake Champlain and in other, more remote lakes in the northeastern U.S. It is generally thought that most environmental Hg originates from industrial emission sources and is transported in the atmosphere. Studies in the U.S. and Sweden indicate that some of the Hg in lakes most likely comes from the watershed. The movement of Hg in forest soils may therefore play an important role in the loading of Hg into surface waters draining into Lake Champlain. We are conducting a study comparing the chemistry of soil water and stream water to test several hypotheses about Hg transport in an upland watershed.

Research activity is taking place in three areas along two streams on the western side of Mount Mansfield: one area (at approximately 850 m in elevation) along "Stream 10" near the intersection with the CCC Road, and two areas (at elevations of 520 and 550 m) along "Nettle Brook" near the Butler Lodge Trail. Both streams are currently being monitored as part of other VForEM work. Soil water and stream water samples will be collected during storm events in the spring and summer of 1997. Samples will be analyzed for total Hg, DOC, color, major ions, and pH.

Work in 1996 was completed to identify a suitable device with which to collect soil water for the 1997 field season. Although there are numerous methods for sampling soil water, only the methods that are believed to sample water moving through the soil horizons were considered. For example, the technique of extracting water from bulk soil samples or soil cores was not used because these methods yield water samples that represent the solute concentration in micropores and macropores (Boll et al., 1992) but not

necessarily the concentrations in bulk flow. Many methods that use bulk soil samples require air-drying and re-wetting soil, and this method alters the chemistry of the collected solution sample (Lawrence and David, 1996). Tension lysimeters also extract tightly-bound water contained in small soil pores (Swistock et al., 1990), and so tend to collect higher concentrations of soil constituents. In addition, strict requirements of ultra-clean laboratory methods for analyzing trace levels of Hg limited the possible materials usable for sampling to those known to be non-contaminating. For this study, two different soil water sampling devices were tested for use, and these devices are described in the following paragraphs.

Zero-tension Lysimeter (ZTL). ZTLs collect solution that moves downward through the soil by force of gravity, often through macropores. This method is therefore believed to be representative of soil water that is actually moving through the soil. ZTLs require that the soil above the samplers be saturated during collection (Boll et al., 1992). One drawback of lysimeters is that their installation can disturb the overlying soil and root structures, but the soil eventually (within several months) recovers to pre-installation conditions.

Fiberglass Wick Sampler. A new technique to sample water and solutes moving through the unsaturated layers in soil uses fiberglass wicks to collect water by capillary action (Holder et al., 1991; Poletika et al., 1992; Boll et al., 1992; Knutson and Selker, 1996; Brandi-Dohrn et al., 1996). The wick is self-priming and acts as a hanging water column, making it possible to draw samples from unsaturated soil without external application of suction (Boll et al., 1992). Based on a study by Brandi-Dohrn et al. (1996), there is evidence that the wick method collects solute concentrations representative of water in motion through the soil profile, whereas suction cup samplers collect concentrations of water adhering to soil particles.

METHODS

Two different tests were completed to identify which soil water collector would be more suitable for use in the field study. The tests were designed to answer the following two questions:

1. Does either device release or adsorb Hg or other heavy metals?
2. Which soil water collector collects more water?

Zero-tension lysimeters were constructed of 14.7 cm-diameter Pyrex funnels containing silica sand (170 cm² sampling area). Silica sand is assumed to be the least reactive media to use in the funnel but it has been demonstrated to adsorb metals. McGuire et al. (1992) tested the adsorption of cadmium, cobalt, chromium, and zinc at three different pH levels (4, 6, and 8) on silica sand that is typically packed around tension lysimeters to achieve good contact with the soil. At a pH of 4, up to 6% of these metals were lost from solution via adsorption, and adsorption increased at higher pH levels.

Fiberglass wick samplers consist of a length of 1.5-inch diameter wick encased in Pyrex glass tubing (30 cm x 4 cm) placed vertically within the soil. At the top end, the glass tubing is flared out to form a flat plate where the top portion of the wick is unraveled and pressed flat on the plate. This part of the wick is in contact with the soil, and the area of the plate is the sampling area. Our wick samplers were constructed with a plate diameter of 14.7 cm (170 cm² sampling area). Water flowing through the soil is intercepted by the sampler plate, drawn into the wick, and conducted down the glass column. The water ultimately drains into a sample bottle via Teflon tubing (based on Holder et al., 1991). Adsorbance of Hg by the wick fibers had not yet been reported in the literature, but was cause for concern because of the large number of possible exchange sites created by the fibers.

Laboratory Tests

In the laboratory, initial performance of the collectors was quantified using rain water to simulate field conditions. Rain water (250 ml) was slowly poured through three ZTLs and two fiberglass wick samplers. These samples were analyzed for Hg and compared against control samples of rain water.

It was hypothesized that ion exchange sites in the collectors (which might adsorb or desorb Hg) would become saturated with time in the field. A ZTL and fiberglass wick sampler were placed in the field for a period of one month (27 September 1996 to 27 October 1996). The sampling devices were removed from the field and tested again as above using rain water. These samples were analyzed for Hg and other trace metals.

Water Volume Tests

Soil water collectors were installed in the field by digging soil pits (approximately 3'x2' and 2½' deep) and tunneling laterally so that the soil water collectors could be placed under a given depth of undisturbed soil. After installation of the samplers, access holes were back-filled with moistened soil. Solutions drain from a Teflon tube into a large container where sample bottles are placed.

Two shallow (4-7 cm below ground surface) and two deep (22-28 cm below ground surface) collectors were installed of both the ZTL and fiberglass wick collectors (a total of 8 collectors) at the lower elevation site along Nettle Brook.

Soil water was collected after three substantial rain events in September and October, 1996 to determine the volume collection efficiency. Rainfall amount was crudely estimated using a single rain gauge placed under the tree canopy. Rainfall amounts were 2.7, 7.4, and 7.2 cm for storms before the dates of October 12, October 23, and November 10, 1996.

RESULTS

In the first laboratory experiment, both the ZTL and wick collector adsorbed approximately 20% of Hg compared to control samples (Figure 1). Although this adsorbance rate seems high, it was better than expected and was considered acceptable for use with trace mercury analysis.

After one month in the field, laboratory rinses (using rainwater, as above) from both the ZTL and wick collectors initially contained more Hg than control samples (Figure 2). Out of three rinses, only the third rinse showed a slight adsorption of Hg. Because there were some unremovable soil particles on both collectors following extraction from the field, some of the Hg in the first two rinses may be attributable to Hg that was flushed through the wick or sand. Therefore, this experiment was not conclusive regarding saturation of ion adsorption sites.

Trace metal concentrations were also analyzed in these samples (Figure 3). Because of small sample sizes, only qualitative comparisons can be made. Similar to the Hg results, concentrations were highest in rinse 1 and declined during rinses 2 and 3. Mg was leached by the ZTL, and Pb was adsorbed by both devices. These data also suggest that Cr, Mn, and Ni may be leached by the ZTL, and Cu, Cd, and Zn may be adsorbed by both the ZTL and the wick. Samples were also analyzed for Ce, La, Nd, Rb, Sr, and Ti, however the results are not summarized here.

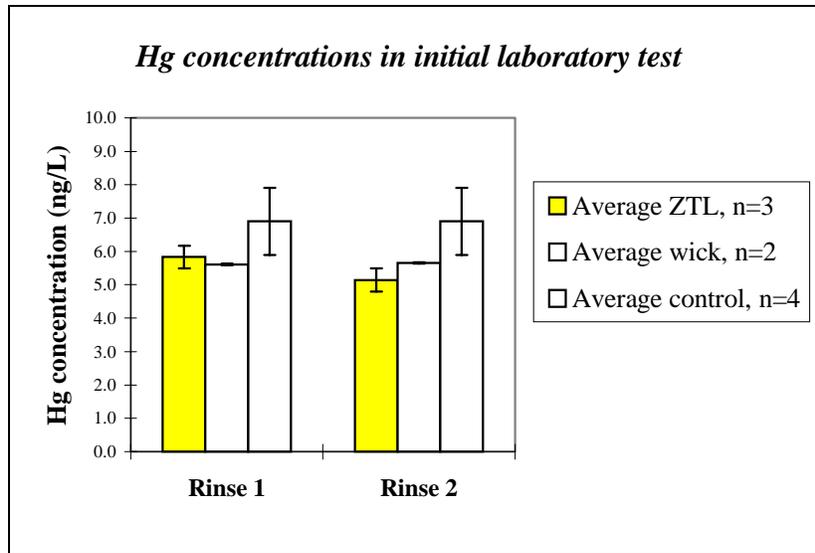


Figure 1. Results from the first laboratory test comparing Hg concentrations in rain water (control) vs. water poured through ZTL and wick devices. Error bars represent one standard error of the mean (not visible for wick because of small sample size and consistent results).

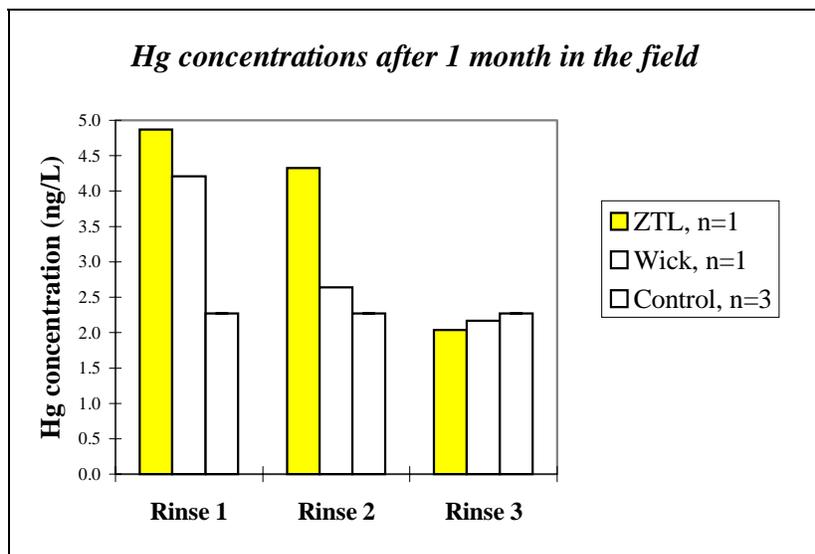
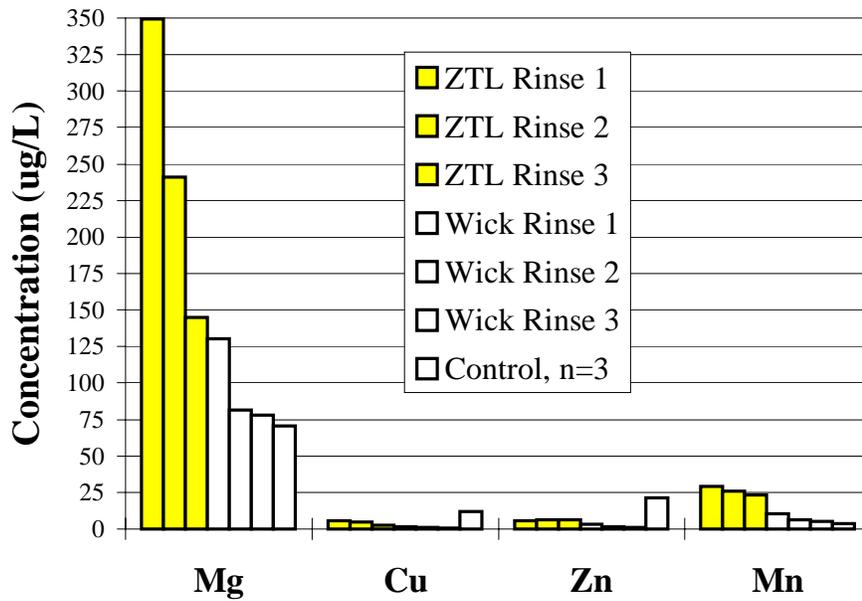


Figure 2: Results from the second laboratory test (after field installation) comparing Hg concentrations in rain water (control) vs. water poured through ZTL and wick devices.

Volumes of water collected by both devices in the field varied by amount of antecedent rainfall and by depth. The rain gauge measured 2.7 cm, 7.4 cm, and 7.2 cm for the three storms after which collection occurred. Generally, the shallow devices collected more water than deep ones, and the wick collected greater volumes than the ZTL. Our hope was to collect at least 50 ml in a sample to be able to analyze for Hg. After the first storm, no collectors in one of the pits collected enough water, but otherwise sample volumes exceeded 50 ml and commonly reached the bottle capacity of 500 ml.

Metal concentrations after 1 month in the field



Metal concentrations after 1 month in the field

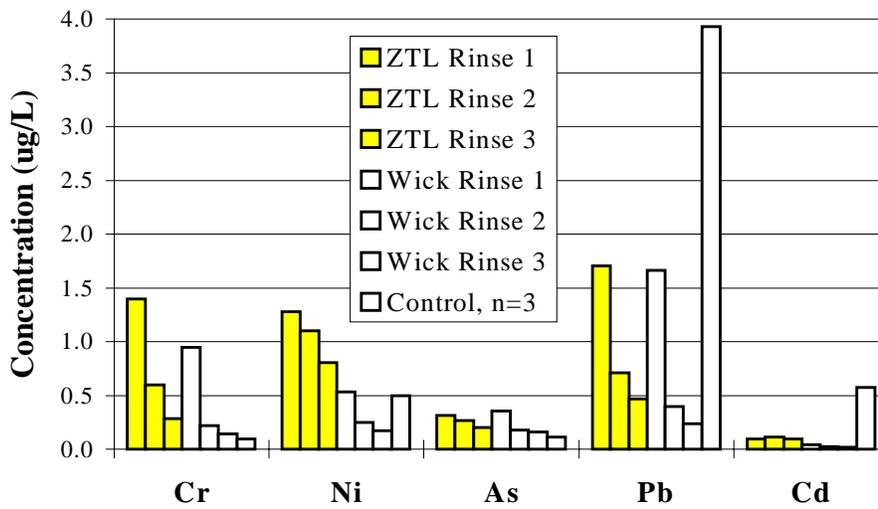


Figure 3. Results from the second laboratory test comparing trace metal concentrations. Rinses 1, 2, and 3 are shown left to right on graph (n=1 for each rinse).

Because the fiberglass wick sampler tended to collect more water and also had less effect on metal concentrations, the wick was chosen for use in the field study. At each of the three sampling sites, two sets of paired wick soil water collectors have been installed (four collectors at each site, two shallow and

two deep). Soil water will be collected from these sites during snowmelt and precipitation events beginning in 1997. These samples and streamwater samples collected during events will be analyzed for Hg, dissolved organic carbon (DOC), major ions, and other characteristics. The goal of this research will be to clarify relationships between soil water and stream water, and to understand mechanisms involved in Hg transport from forested watersheds to streams.

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