Multiple Environmental Monitoring Techniques for Assessing Spatial Patterns of Airborne Tungsten

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This paper describes the application of the chemistry of total suspended particulates, lichens/mosses, and surface dust for assessing spatial patterns of airborne tungsten and other metals. These techniques were used recently in Fallon, NV, where distinctive spatial patterns of airborne tungsten were demonstrated. However, doubt has been raised about the extent of airborne tungsten in Fallon. Therefore, these techniques were tested specifically for W in another town that has a small industry known to emit tungsten particles. Airborne particulates were collected in Sweet Home, OR, as well as in nearby comparison towns to provide baseline data. Lichens/mosses were collected in Sweet Home near the known source of W as well as outside of Sweet Home. Surface dust was collected throughout Sweet Home to map concentrations of metals. All three of these environmental monitoring techniques confirm that W is elevated right near the known source of airborne W in Sweet Home but not elsewhere in Sweet Home. This test should allay doubts about the multiple findings of elevated airborne W in Fallon, NV, and this should also instill confidence in these techniques generally for assessing W and other metals in urban environments.

Introduction

This paper describes the testing of three environmental monitoring techniques for assessing spatial patterns of airborne tungsten. One, the chemistry of total suspended particulates filtered directly from outdoor air reflects spatial patterns of airborne metals (1). Two, lichen/moss chemistry also reflects spatial patterns of airborne metals (2). Three, surface dust chemistry fine-tunes spatial patterns of airborne particles that settle onto outdoor surfaces, thereby potentially identifying source areas of particular metals (3).

These three techniques were used recently to assess spatial patterns of airborne metals in Fallon, NV (39°25′ N, 118°44′ W), a small town located 100 km east-southeast of Reno. Total suspended particulates showed that airborne tungsten and cobalt are elevated in Fallon relative to comparison towns (4). Lichens confirmed high W and Co in Fallon relative to outlying desert areas (5), and surface dust fine-tuned spatial patterns of deposition of W and Co within Fallon and isolated a source area for these metals (6).

Doubt has been expressed about the extent of the situation of elevated airborne W and Co in Fallon (7, 8), due in part to the source of airborne W and Co not being conclusively identified and to the environmental monitoring techniques not being proven accurate specifically for W and/or Co. The objective of this study was to demonstrate the accuracy of these environmental techniques for W in an urban setting with a known source of airborne W. A town similar in population size to Fallon but with a known source of airborne W was tested using the same three environmental monitoring techniques used in Fallon. The results from these environmental monitoring techniques were evaluated with respect to the known source of W to demonstrate their accuracy for assessing airborne W.

Experimental Section

Study Site. Sweet Home, OR, was the town used for this test (Figure 1a). Located in the Willamette Valley, Sweet Home is similar to Fallon in population size and in being a discrete, rural community (Table 1). Sweet Home is much wetter than Fallon climatically, and Sweet Home is within a forested ecoregion while Fallon is in the intermountain semidesert (9). These differences in total rainfall and in ecoregions undoubtedly affect the absolute amount of total suspended particulates across these broad regions, but relative compositions of airborne metals of individual towns within each region should not be affected by differences in regional climate or ecosystem type.

Sweet Home has a small industry that mills W and other metals and consequently emits airborne W and the other metals. This industry has been operating in Sweet Home since November, 2000. Although emissions from the facility have not been monitored directly, dust clearly emanates from the facility to the outdoor environment. Consequently, Sweet Home is ideal for testing environmental monitoring techniques for assessing spatial patterns of airborne W and other metals.

Total Suspended Particulates. Total suspended particulate (dust) chemistry is the measurement and interpretation
of element loadings in dust filtered directly from the air. Regulated vacuum blowers (10) draw known volumes of air through glass fiber filters (11, 12). Upon quantifying masses of trace elements collected, values are standardized to the volume of air sampled and expressed on a mass per volume basis (13). Mass per volume values can be compared with one another spatially and temporally as well as with standards established by regulatory agencies (14).

Airborne particulates were collected in Sweet Home as well as in Brownsville-Crawfordsville and Lebanon to provide comparison data (Figure 1b). The comparison towns are located within 20 km of Sweet Home and are similar to Sweet Home in terms of population, climate, and ecosystems (Table 1), but the comparison towns do not have industrial sources of fine W powders. Within each community, outdoor airborne dust was collected at homes of volunteer participants. Airborne dust samples were collected using portable, high-volume particulate air samplers with brushless motors to avoid possible contamination by copper (10). Filters were 510 μm thick and had up to 99.99% retention for particles down to sub-μm in size (15). Filters did not contain binders or waterproof coatings, thereby minimizing element backgrounds (12). Individual sampling sessions were 1 day in length, long enough to collect enough dust to measure but short enough to avoid saturating the filters. The sampling sessions were done in consecutive days during 1 week in May 2005.

During sampling sessions, five samplers were deployed in Sweet Home, while five other samplers were deployed in a comparison town. Concurrent sampling can account for changing regional weather through time, though the weather wound up being consistently dry and mild during the entire week of sampling. Between sampling sessions, filters of all samplers were changed and comparison-town samplers were moved to the next town, while Sweet Home samplers were left in place. For one sampling session, all ten samplers were deployed in Sweet Home in order to maximize spatial coverage there.

At participant houses, air samplers were placed several meters from buildings and as far as possible from potentially confounding issues such as trees, pet areas, and barbeques. The 102-mm diameter, vertically oriented, open-face intake orifices were positioned at a height of 1.5 m above the ground (16) and pointed in random directions. Samplers and intakes were sheltered from dew and settling dust by umbrellas that were attached to the samplers. Air flow rate was initialized to 0.45 m³ min⁻¹ (16 ft³ min⁻¹), the highest rate attainable by the brushless motors. Flow rate at the end of each sampling session was recorded, and duration of each sampling session was measured to ±0.1 h. Total volume of air sampled was calculated as the product of average flow rate by duration of sampling (11).

Prior to deployment in the field, clean filters were weighed at room temperature and humidity to ±0.0001 g. Upon completion of each sampling session, dusty filters were folded dust side inward and stored in paper envelopes (10). Dusty filters were reweighed after stabilizing to the same room temperature and humidity as during preweighing (17). Filters were touched only while wearing dust-free, latex gloves (10).

See the Supporting Information for details on inductively coupled plasma, mass spectroscopy (ICP–MS) measurement of air filters for contents of metals.

Lichens and Mosses. Lichen/moss chemistry is the measurement and interpretation of element concentrations in lichens, which are symbiotic associations of fungi and algae (18), or mosses, which are nonflowering plants. Lichens and mosses are ideal biomonitors of atmospheric chemical composition, including heavy metals. They lack true roots, thereby diminishing the influence of growth substrates on their chemical composition, and they lack a cuticle, allowing easy incorporation of atmospheric constituents directly into their tissues (19). Although they are fundamentally different organisms from one another, lichens and mosses have shown similar results as biomonitors of atmospheric metals in paired research (20).

Lichens and mosses are abundant on trees in the Pacific lowland mixed forest (21, 22). The strategy for lichen/moss chemistry in Sweet Home was to compare contents of metals in lichens or mosses near the known source of W versus well outside of Sweet Home (23). Ten distinct mosses were collected from a stand of Douglas-fir (Pseudotsuga menziesii) located 70 m south–southeast of the known source of W, and seven more mosses were collected from a stand of cottonwood (Populus sp.) located 160 m northeast of the known source of W (Figure 1c). These mosses were Isotomium stoloniferum. For comparison, a stand of Douglas-fir with the same type of moss as well as a type of lichen (Usnea sp.) was located about 10 km away from Sweet Home, just outside of Crawfordsville (Figure 1b). To assess the interchangeability of these moss and lichen types, a mixture of both was sampled at the Crawfordsville site, with six lichens and four mosses collected. All sampling sites were at least 50 m from principal highways, minimizing effects of automobile traffic on their chemical composition.

Sampled lichens and mosses were growing on trees located meters apart from one another. Several grams of lichen or moss tissue were collected by pulling it from the tree while wearing clean gloves. Tissues were placed in clean, air-permeable envelopes and stored in a dust-free box. Prior to chemical measurement, lichen and moss tissues were rinsed lightly for just a few seconds in deionized water to remove surface dust (24), and extraneous material was removed manually. After air-drying, tissues were ground to a size class of ~0.1 mm using a ceramic, nonmetallic mortar and pestle.

See the Supporting Information for details on ICP–MS measurements of lichen and moss tissues for contents of metals.

Surface Dust. Surface dust chemistry is the measurement and interpretation of element concentrations in fine sediments that accumulate on outdoor surfaces. Surface dust is an ideal indicator of atmospheric deposition, including heavy metals. By collecting surface dust in a systematic grid pattern, concentrations of airborne metals can be mapped to pinpoint sources of elevated airborne metals (25). Paired analysis of
surface dust and total suspended particulates can be particularly fruitful for confirming airborne metals and their spatial patterns (26).

The strategy for surface dust chemistry was to map concentrations of elements in outdoor dust within Sweet Home. Twenty-two surface dust samples were collected along a semigrid pattern throughout Sweet Home. Grid cell length was somewhat variable due to the road system of Sweet Home being irregular, but it averaged approximately 0.5 km with slightly higher spatial density near the known source of W. Geographic coordinates were recorded for each sample to facilitate mapping of contents of metals.

Samples were collected mostly from paved surfaces using a clean brush and clean paper as a dustpan (3). Samples were stored in clean polyethylene vials. All samples were sieved to isolate the fine fraction (<0.150 mm) for analysis. Sieved samples were transferred to clean, glass, screw-cap vials and oven-dried at 100 °C for 24 h. Coarse and fine fractions from each sample were archived in the event that future analyses are necessary.

See the Supporting Information for details of instrumental neutron activation analysis of surface dust for contents of metals.

Results

Total Suspended Particulates. From the session with all ten air samplers located in Sweet Home, several metals measured in total suspended particulates show acute peaks of elevated loadings at the known source of W. In particular, W shows a peak at the known source with a loading 4 orders of magnitude higher than the background levels of more distant locations (Figure 2). Tungsten loading follows a steep power function of distance from the known source with an R² of 0.93. Similarly, Sn, Ni, Cu, Mn, Co, Mo, Cr, and Pb show peaks with high loadings at the known source compared to low background levels throughout Sweet Home (see the Supporting Information, Figure 1). These other metals also follow steep power functions of distance from the known source, with R² values ranging from 0.79 to 0.96. This pattern of a power function decrease with distance is typical of airborne contaminants from a point source (27).

The metals that show peaks at the known source of W are elevated in Sweet Home relative to comparison towns. In particular, median loadings of W are higher in Sweet Home than in Brownsville-Crawfordsville or Lebanon separately as well as when grouped together to maximize sample size (Figure 3). Similarly, median loadings of Sn, Ni, Cu, Mn, Co, Mo, Cr, and Pb are mostly higher in Sweet Home than in Crawfordsville or Lebanon (see the Supporting Information, Figure 2). These differences are not always statistically significant as determined by the Mann–Whitney test of medians (28), but it is generally evident that airborne metals are elevated in Sweet Home relative to comparison towns.

Lichens and Mosses. Almost all metals are higher in content in mosses of Sweet Home than in lichens/mosses of Crawfordsville. In particular, W shows the greatest difference, with over 1400 times more W near the known source of W in Sweet Home than outside of Sweet Home (Table 2). Similarly, Ni and Sn contents are hundreds of times higher in Sweet Home mosses than outside, and several other metals are also at least ten times higher in content in Sweet Home (see the Supporting Information, Table 1). Relative to Sweet Home, Crawfordsville is more pristine environmentally, with no obvious point sources of airborne metals. As an urban environment, Sweet Home has more air pollution generally, conforming to the pattern of relatively higher air pollution for urban areas compared to the rural countryside (29).

This large difference in content of metals between Sweet Home and Crawfordsville is not due to comparing different organisms such as lichens and mosses. Within the Crawfordsville site, W is only slightly more concentrated in mosses than in lichens, but this difference is much smaller than between Sweet Home and Crawfordsville, which differ by 4 orders of magnitude (Table 2). With such a large environmental signal between sites, minor differences between mosses and lichens within a site are of no consequence. Most other elements measured in lichens and mosses also show this pattern (see the Supporting Information, Table 1). In other research, comparisons of lichens and mosses as biomonitor of airborne metals also show differences between these two data types that are usually small (30).

Furthermore, W is orders of magnitude more concentrated in Sweet Home mosses over typical crustal abundance (Table 2). By contrast, W is not higher than typical crustal abundance in Crawfordsville lichens or mosses. Indeed, no element measured in Crawfordsville lichens or mosses is higher than typical crustal abundance (see the Supporting Information,
of W in Sweet Home, again indicated by all three environ-
ments. Some of these metals are not used by the current industrial source of W, but they might have been used by earlier metalworking industries that operated in the area. Accordingly, these three environmental monitoring techniques accurately depict other airborne metals besides W.

These three environmental monitoring techniques are not equal to one another operationally. Surface dust chemistry can have high spatial resolution because it involves merely sweeping up surface dust, which is easy and inexpensive. In a multidisciplinary study of airborne metals of urban areas, surface dust chemistry might be done first in order to map depositions of metals with fine spatial resolution. If any metals were found to be elevated, then total suspended particulate sampling, which is more limited spatially due to needing expensive equipment, and lichen/moss sampling, which might be limited due to the mere presence or absence of lichens or mosses, could be used in targeted sampling to confirm spatial patterns of those metals.

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**Supporting Information Available**

Details of the chemical analytical procedures for measuring air filters, lichen and moss tissues, and surface dust and extended results for all three data types showing full suites of metals. This material is available free of charge via the Internet at http://pubs.acs.org.

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