Comparison of Trace Metal Deposition in northern and central Arizona

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Typical lichen and moss encrusted rock from field sampling.

Abstract

Atmospheric deposition of trace elements to an epilithic lichen was assessed for an urban and rural area in Arizona, USA. The urban area consisted of 27 locations throughout Maricopa County corresponding to a previous study (Zschau et al., 2003); the rural area was 51 locations throughout the combined lands of the Grand Canyon National Park, Grand Canyon Parashant National Monument and areas of the Navajo Nation. Additional samples of *Xanthoparmelia spp.* were obtained from Arizona State University lichen herbarium material (1970-1973) sampled from the region to explore temporal trends, with an emphasis on decreases in Pb and Cu from the phase out of leaded gasoline and closing of copper smelters and increases in Zn from agriculture. Lichens were cleaned, homogenized and then samples were split to be analyzed by both cold vapor technique for mercury (Hg) and wet digested in a high pressure microwave oven to analyze by high resolution ICP-MS for a suite of trace elemental concentrations [Aluminum (Al), Antimony (Sb), Arsenic (As), Barium (Ba), Bismuth (Bi), Cadmium (Cd), Caesium (Cs), Chromium (Cr), Cobalt (Co), Copper (Cu), Dysprosium (Dy), Erbium (Er), Europium (Eu), Gadolinium (Gd), Hafnium (Hf), Holmium (Ho), Iron (Fe), Lanthanum (La), Lead (Pb), Manganese (Mn), Molybdenum (Mo), Neodymium (Nd), Nickel (Ni), Niobium (Nb), Platinum (Pt), Praseodymium (Pr), Rhenium (Re), Rubidium (Rb), Samarium (Sm), Scandium (Sc), Selenium (Se), Silver (Ag), Strontium (Sr), Tantalum (Ta), Terbium (Tb), Thallium (Tl) Thorium (Th), Thulium (Tm), Tin (Sn), Titanium (Ti), Tungsten (W), Uranium (U), Vanadium (V), Ytterbium (Yb), Yttrium (Y), and Zinc (Zn)]. Replicate measurements of International Atomic Energy Agency 336 lichen standard reference material are in close agreement with the certified elemental compositions. Cluster analysis and principal components analysis are used to compare patterns of deposition from anthropogenic and geologic sources. Initial research suggests higher levels of anthropogenic metals in the urban areas, including a significantly higher average mercury level in the urban lichens, although Hg is also emitted by power plants within 100 mile radius of the Grand Canyon area.

INTRODUCTION

Assessment of long-term air pollution patterns can often be difficult. Monitoring of pollutants over time can be resource intensive, and data collection with sampling devices needs to start years before analysis can begin. The use of living organisms as biomonitors is one method to overcome some of the drawbacks of monitoring air pollution over extended time periods.

As long-lived, slow-growing organisms, lichens are useful as surrogate receptors in atmospheric deposition monitoring investigations, where the integration of long-term signals requires monitoring (Nash 1989, Garty 2001). Because they do not possess nutrient absorbing roots, as found in vascular plants, they have a major dependence on atmospheric sources of nutrients (Nieboer et al. 1978, Nieboer and Richardson 1980). Compared to soil nutrient pools, atmospheric concentrations of nutrients are quite low, and consequently nutrient concentrating mechanisms, such as particulate trapping (Garty et al. 1979), uptake to cell wall exchange sites or transport intracellularly (Beckett and Brown 1984; Brown and Beckett 1985), sequestering in complexes formed with lichen secondary metabolites (Purvis et al. 1987), or impaction of aerosols (Knops et al. 1996) are characteristic of lichens. As a consequence, lichens have often been used to document atmospheric deposition of radionuclides (e.g. Palmer et al. 1965, Seaward et al. 1988, Biazrov 1994) and various other atmospheric pollutants (Puckett 1988, Nash and Gries 1995). When an appropriate stratified sampling design (e.g. with respect to lichen species choice, microhabitat characteristics, atmospheric exposure, etc.) is employed, then both local and regional deposition patterns are readily discerned (Loppi and Bargagli 1996, Muir et al. 1993, Nash 1996), although care must be taken in the assessment of baseline levels (Bennett 2000).

In an earlier investigation (Zschau et al. 2003), we determined past spatial patterns of atmospheric deposition across Maricopa County, Arizona, in 1998, based on samples from 28 sites, as analyzed by ICP-MS. The county is approximately L-shaped, extending over 200 km along its two longer axes, and contains the Phoenix metropolitan area, one of the fastest growing urban regions in the world. Although heavy industry is minimal within the Phoenix area, Arizona has historically been an important source of copper. Major sources of spatial elemental variation included copper mining and smelting (in an adjacent county), anthropogenic sources associated with the urban center (e.g. lead,) and location of special geological features, such as mafic rocks with elevated concentrations of Co, Cr, Ni, and Sc relative to average abundances in the Earth's crust. In addition, temporal comparisons for six of the same sites within the county were possible, based on collections made in the mid-1970's (Nash et al. 2003), where sufficient lichen material was available for analysis. Decreases in copper (cessation of smelting) and lead (switch to unleaded gasoline) were demonstrable and increases in zinc were found. Other research has demonstrated that trace metals are detected in lichens near a coal power plant (Olmez et al., 1985) and in lichens transplanted to the region of a coal power plant (Garty & Hagemeyer, 1988). For this investigation, we are also comparing our results in Maricopa County with samples taken from 51 locations in and around the greater Grand Canyon region of Northern Arizona.

METHODS AND GOALS

The overall objective is to document the spatial pattern of past elemental deposition as reflected in lichens (*Xanthoparmelia* spp.) as of 2006 within the region encompassing the greater metropolitan Phoenix area (Maricopa county) and the greater Grand Canyon region, as well as, where possible, to determine historical trends in comparison to previous work. In the process we anticipate being able to accomplish the following:

1. Determine patterns of elemental deposition patterns (Cu, Ag, As, etc.) associated with the various pollution sources that impact the area.
2. Determine existing vanadium deposition patterns (associated with vehicles).
3. Determine lead deposition patterns (associated with historic uses with vehicles).
4. Determine any changes in deposition patterns from previous research in Maricopa county (Zschau et al., 2003).

The genus *Xanthoparmelia* is selected as the most suitable biomonitor of metal deposition in both regions, because it is one of the few macrolichens (readily obtaining enough material for analysis is critical) in arid areas (Nash et al. 1977), is easily recognizable in the field, and has already been used for similar investigations (Zschau et al. 2003; Nash et al. 2003). Spatial patterns of atmospheric deposition of trace elements to these epilithic lichens will be assessed using the locations of the Zschau et al. (2003) study with two additional sites in Maricopa county and 51 sites in northern Arizona (Figure 1) added to this research.

The lichen material was cleaned and homogenized to prepare for metal analysis. Mercury content has been measured using a cold vapor mercury analyzer. The samples have been wet digested and analyzed by HP-ICP-MS for a suite of elemental concentrations (antimony [Sb], cadmium [Cd], cerium [Ce], chromium [Cr], cobalt [Co], copper [Cu], dysprosium [Dy], europium [Eu], gadolinium [Gd], gold [Au], holmium [Ho], lead [Pb], lutetium [Lu], neodymium [Nd], nickel [Ni], palladium [Pd], platinum [Pt], praseodymium [Pr], samarium [Sm], scandium [Sc], silver [Ag], terbium [Tb], thulium [Tm], tin [Sn], uranium [U], vanadium [V], ytterbium [Yb], yttrium [Y], and zinc [Zn]).

Surface maps for concentrations of at least mercury, cadmium, lead, copper, nickel, and zinc will be interpolated among the 30 locations using ArcGIS Geostatistics and Spatial Analyst packages. Multivariate statistical analysis will be used to analyze and correlate deposition patterns of the various metals.

Because the *Xanthoparmelia* grows on rocks, part of the elemental variation observed in the area will doubtlessly be related to underlying variation in geology and associated blowing dust. Accordingly, it will be necessary to interpret the results in terms of basic knowledge of geochemistry (e.g. Levinson 1974; Taylor and McLennan 1985) as well as specific knowledge of the geochemistry in the region (e.g. Reynolds 1988; Titley and Anthony 1989). Because known pollution sources are present in the region, the results will also have to be interpreted in light of known emission data (e.g. U.S. Environmental Protection Agency 1997).

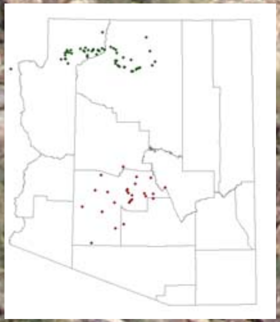

Figure 1. Sample locations

PRELIMINARY RESULTS

Comparisons of metal amounts across the entire dataset were made and the resulting p values listed in tables 1a, 1b, and 1c.

Table 1a. Comparison of rural and urban areas for select metals-Zschau et al's anthropogenic cluster

Metal	Mercury	Copper	Tin	Cadmium	Lead	Antimony	Zinc
T test	4.1×10^{-7}	5.0×10^{-4}	1.7×10^{-8}	0.018	4.4×10^{-6}	0.077	5.9×10^{-5}
F test	0.79	2.0×10^{-53}	5.1×10^{-30}	3.9×10^{-11}	3.7×10^{-26}	0.012	0.18
Urban average (ppb)	271	51,000	1060	463	30,000	778	100,000
Rural average (ppb)	213	12,000	447	405	14,900	552	62,500

Table 1b. Comparison of rural and urban areas for select metals-Zschau et al's mafic rock cluster

Metal	Chromium	Nickel	Scandium	Cobalt
T test	0.18	0.01	2.1×10^{-7}	8.0×10^{-11}
F test	0.43	4.6×10^{-56}	3.1×10^{-13}	0.40
Urban average (ppb)	17,300	13,300	3430	3140
Rural average (ppb)	15,500	6160	2020	1940

Table 1c. Comparison of rural and urban areas for select metals-Zschau et al's rare earth elements cluster

Metal	Neodymium	Praseodymium	Yttrium	Dysprosium	Gadolinium
T test	6.1×10^{-4}	2.0×10^{-8}	3.9×10^{-7}	6.4×10^{-7}	1.6×10^{-6}
F test	2.8×10^{-70}	2.8×10^{-19}	8.3×10^{-21}	3.5×10^{-30}	5.4×10^{-20}
Urban average (ppb)	23,000	4610	15,800	2390	3250
Rural average (ppb)	9100	2390	9040	1230	1880

Progress and future directions

In the summer of 2006 all samples were collected. Since then, mercury analysis was completed in the fall of 2006, and the final wet digests and ICP-MS analysis completed by November 2007. Preliminary results suggest that for almost all metals, the lichens had significantly higher amounts in the southern, urban areas than in the more rural northern regions of Arizona (see tables 1a, 1b and 1c). Anthropogenic activities are suspected to be directly related to the increased amounts of metals in the anthropogenic cluster; the increased levels of rare earth and mafic rock minerals in the lichens are potentially the result of construction activities related to the development of virgin desert lands, with increased dust released from blading and clearing. Statistical and geospatial techniques will next be applied to determine underlying patterns of metal deposition to relate them to their potential sources.

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