Geographic Patterns of Mercury Deposition using the Lichen *Xanthoparmelia* in Maricopa County, Arizona, USA

K. Sweat, T. Zambo, and T. Nash III
School of Life Sciences, Arizona State University, PO Box 874501, Tempe AZ 85287-4501

A typical specimen of *Xanthoparmelia sp.* used for air pollution biomonitoring.

ABSTRACT

Geographical patterns of atmospheric metal deposition in Maricopa County, Arizona, were assessed using 2006 collections of the epilithic lichen Xanthoparmelia spp. This study is a re-sampling of the 28 locations used in an earlier investigation by Zschau and Nash in 1998, along with two new locations sampled to increase spatial resolution. Lichens were removed from the rock substrate, cleaned and homogenized. Initially the homogenized samples were analyzed for mercury [Hg] with a mercury analyzer and will be wet digested and analyzed by high resolution ICP-MS for a suite of up to 40 elements. Spatial Hg patterns are plotted with ArcGIS software to identify potential "hot spots". Potential sources of these high Hg levels, such as power generation facilities, were sought at or in the vicinity of these hot spots.

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 (Bruteig 1993, Loppi and Bargagli 1996, Muir et al. 1993, Nash 1996), although care must be taken in the assessment of baseline levels (Gough et al. 1988; 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).

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, where possible, to determine historical trends in comparison to previous work. The genus *Xanthoparmelia* is selected as the most suitable biomonitor of metal deposition in metropolitan Phoenix region, 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 added to this research.

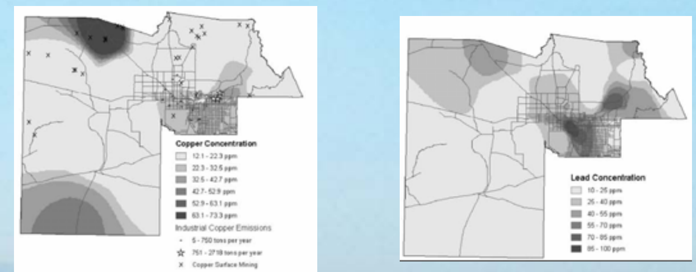
The lichen material will be cleaned and homogenized to prepare for metal analysis. Mercury content has been measured using a cold vapor mercury analyzer. The samples are to then be wet digested and analyzed by HP-ICP-MS for a suite of elemental concentrations (antimony [Sb], cadmium [Cd], cerium [Ce], 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).

PROGRESS TO DATE

During the 2006 summer, the Mr. Sweat collected samples at or near all of the locations used in the Zschau et al. (2003) study, as well as two new locations. During the fall 2006 semester, the student has prepared the samples for digestion and collaborated with Dr. Paul Gremillion at NAU to run mercury analysis on the samples. Mercury levels will need to be analyzed relative to the rare earth metal contents of the lichens to generate enrichment factors. These enrichment factors will then be used to generate surface maps similar to the ones presented by Zschau et al. (1999), examples of which (for lead and copper) are depicted below.



From Fig. 3. Spatial distribution of metal concentration as measured in Xanthoparmelia spp. in 1998. Zschau et al., 1999.

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View of the Phoenix skyline from South Mountain Park.