Geographic Patterns and Temporal Trends of trace Metal Deposition using the Lichen Xanthoparmelia in Maricopa County, Arizona, USA

Ken G. Sweat[1], Thomas H. Nash III[1], Panjai Prapaipong[2], Paul T. Gremillion[3]

[1] Arizona State University School of Life Sciences, PO Box 874601, Tempe AZ 85287 kengsweat@asu.edu.
[2] Arizona State University School of Earth and Space Exploration, PO Box 871404, Tempe, AZ 85287
[3] Northern Arizona University Department of Civil and Environmental Engineering, PO Box 5621, Building 21/Room 132, Flagstaff, Arizona 86011

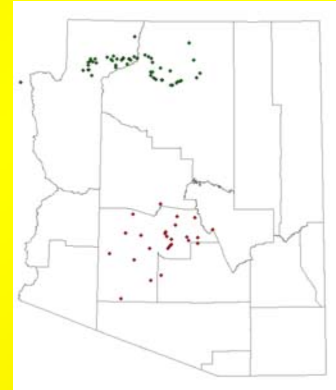

Figure 1. Sample locations

ABSTRACT

The epilithic lichen *Xanthoparmelia spp.* was used to assess atmospheric deposition of trace elements for Maricopa County, located in central Arizona, USA The study area consisted of 27 locations in Maricopa County corresponding to a previous study (Zschau et al., 2003) along with new locations added to increase spatial resolution. Long term temporal trends were assessed using additional lichens collected from the region in 1970-1973, focusing on decreases in Cu and Pb from the closing of copper smelters and the phase out of leaded gasoline and increases in Zn. Comparisons were also made to lichens collected from rural areas in and around Grand Canyon Park, Arizona and analyzed with the same techniques. Lichens were analyzed by both cold vapor technique for mercury (Hg) and wet digested in a high pressure microwave oven and analyzed by high resolution ICP-MS for a suite of trace elemental concentrations. Initial research suggests higher levels of almost all metals (anthropogenic and geologic) in Maricopa County. However, the highest locations for mercury were found in the northern areas, inside of the Navajo Nation. Initial multivariate analysis also suggests that lead in Maricopa County is now mainly from geologic sources, not anthropogenic as was concluded in the earlier work by Zschau et al (2003).

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 this study, the resurvey of Maricopa county is compared with sampling of 51 locations in the greater Grand Canyon region of northern Arizona. 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 the greater Grand Canyon region (see Figure 1), 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 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).

RESULTS

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

Element	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}
test of equal variances	0.79	2.0×10^{-53}	5.1×10^{-30}	3.9×10^{-11}	3.7×10^{-26}	0.012	0.18
Urban average (ppm)	271	51.0	1.06	0.463	30.0	0.778	100.0
Rural average (ppm)	213	12.0	0.447	0.405	14.9	0.552	62.50

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

Element	Chromium	Nickel	Scandium	Cobalt
T test	0.18	0.01	2.1×10^{-7}	8.0×10^{-11}
test of equal variances	0.43	4.6×10^{-56}	3.1×10^{-13}	0.40
Urban average (ppm)	17.3	13.3	3.43	3.14
Rural average (ppm)	15.5	6.16	2.02	1.94

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}
test of equal variances	2.8×10^{-70}	2.8×10^{-19}	8.3×10^{-21}	3.5×10^{-30}	5.4×10^{-20}
Urban average (ppm)	23.0	4.61	15.8	2.39	3.25
Rural average (ppm)	9.1	2.39	9.04	1.23	1.88

Table 2a. Comparison of 2006 and 1998 metal content of lichens in Maricopa county: Zschau et al's anthropogenic cluster

Element	Antimony	Palladium	Copper	Cadmium	Lead	Tin	Zinc
T-test	4.30×10^{-4}	n/a[1]	0.259	0.987	0.771	6.68×10^{-5}	1.88×10^{-6}
test of equal variances	4.07×10^{-4}	n/a[1]	1.10×10^{-7}	0.149	0.0592	2.62×10^{-9}	1.23×10^{-4}
2006 mean (ppm)	0.85	n/a[1]	31.51	0.46	27.77	1.01	82.53
1998 mean (ppm)	0.44	0.070	22.12	0.46	29.37	0.41	50.86

Table 2b. Comparison of 2006 and 1998 metal content of lichens in Maricopa county: Zschau et al's mafic rock cluster

Element	Chromium	Cobalt	Nickel	Scandium
T-test	$1.6\ 1 \times 10^{-7}$	8.01×10^{-6}	1.61×10^{-5}	8.93×10^{-9}
test of equal variances	2.11×10^{-7}	0.499	0.171	0.603
2006 mean (ppm)	15.90	3.06	8.89	4.79
1998 mean (ppm)	5.79	1.93	18.13	2.80

Table 2c. Comparison of 2006 and 1998 metal content of lichens in Maricopa county: Zschau et al's rare earth element cluster

Element	Cerium	Neodymium	Praseodymium	Yttrium	Dysprosium	Gadolinium
T-test	n/a[1]	7.24×10^{-5}	9.31×10^{-6}	1.42×10^{-7}	1.01×10^{-3}	4.30×10^{-2}
test of equal variances	n/a[1]	1.29×10^{-3}	2.71×10^{-3}	0.0170	4.83×10^{-11}	3.09×10^{-6}
2006 mean (ppm)	n/a[1]	13.89	3.75	11.48	1.99	4.37
1998 mean (ppm)	18.24	8.44	2.24	5.33	5.00	2.86

PRELIMINARY RESULTS, DISCUSSION AND FUTURE DIRECTIONS

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. Differences in metal content of the lichens in Maricopa county from the Zschau study to this one are listed in tables 2a, 2b, and 2c. A nonsignificant decrease in lead is noted, as well as significant increases in some metals in each of the three clusters. Cluster analysis of data (not shown) suggests that lead is no longer part of the anthropogenic cluster, interpreted as the result of declining lead levels in the atmosphere from the cessation of using lead additives in gasoline. Statistical and geospatial techniques will next be applied to determine underlying patterns of metal deposition to relate them to their potential sources.

Typical thallus collected for study

Literature Cited

Beckett, R.P., Brown, D.H., 1984. The relationship between cadmium uptake and heavy metal tolerance in the lichen genus Peltigera. New Phytologist 97, 301-311.
Bennett, J.P., 2000. Statistical baseline values for chemical elements in the lichen Hypogymnia physodes. In: Agrawal, S.B., Agrawal, M. (Eds.), Environmental Pollution and Plant Responses. Lewis, Boca Raton, pp. 343-353.
Biazrov, L.G., 1994. The radionuclides in lichen thalli in Chernobyl and east Urals areas after nuclear accidents. Phyton [Austria] 34, 85-94.
Brown, D.H., Beckett, R.P., 1985, Minerals and lichens: localisation and effect. In: Vicente, C. Brown, D.H., Legaz, M.E. (Eds.), Surface Physiology of Lichens. Universidad Complutense de Madrid, Madrid, pp. 127-149.
Garty, J., 2001. Biomonitoring atmospheric heavy metals with lichens: theory and application. Critical Review in Plant Sciences 20, 309-371.
Garty, J., Galun, M., Kessel, M., 1979. Localization of heavy metals and other elements accumulated in the lichen thallus. New Phytologist 82, 159-168.
Garty, J. 1988. Heavy Metals in the Lichen Ramalina duriaei Transplanted at Biomonitorring Stations in the Region of a Coal-Fired Power Plant in Israel After 3 Years of Operation. Water, Air and Soil Pollution. 38,311-323.
Knops, J.M.H., Nash, III, T.H., Schlesinger, W.H., 1996. The influence of epiphytic lichens on the nutrient cycling of an oak woodland. Ecological Monographs 66, 159-179.
Levinson, A.A., 1974. Introduction to Exploration Geochemistry. Applied Publishing Ltd., Calgary, Canada.
Loppi, S. and Bargagli, R., 1996. Lichen biomonitoring of trace elements in a geothermal area (central Italy). Water, Air and Soil Pollution 88, l177-187.
Muir, D.C.G., Segstro, M.D., Wellbourn, P.M., Toom, D., Eisenreich, S.J., Macdonald, C.R., Welpdale, D.M., 1993. Patterns of accumulation of airborne organochlorine contaminants in lichens from the Upper Great Lakes Region of Ontario. Environmental Science and Technology 27, 1201-1210.
Nash, III, T. H., 1989. Metal tolerance in lichens. In: J. Shaw (ed.) Metal Tolerance in Plants: Evolutionary Aspects. CRC Press, Boca Raton, Florida, pp. 119-131.
Nash, III, T.H., 1996. Nutrient, elemental accumulation and mineral cycling. In Nash III, T.H. (Ed.), Lichen Biology. Cambridge University Press, Cambridge, pp. 136- 153.
Nash, III, T.H., Gries, C., 1995. The use of lichens in atmospheric deposition studies with an emphasis on the Arctic. Science for the Total Environment 160/161, 729-736.
Nash, III, T.H., Gries, C., Zschau, T., Getty, S., Ameron, Y., Zambrano, A. 2003. Historical patterns of metal atmospheric deposition to the epilithic lichen Xanthoparmelia in Maricopa County, Arizona, U.S.A. Journal of Physics IV (France) 107: 921-924.
Nash, III, T.H., White, S.L, Marsh, J.E., 1977. Lichen and moss distribution and biomass in hot desert ecosystems. Bryologist 80, 470-479.
Nieboer, E., Richardson, D.H.S., 1980. Lichens as monitors of atmospheric deposition. In: Eisenreich, S.J. (Ed.), Atmospheric Pollutants in Natural Waters. Ann Arbor Science, Ann Arbor, pp. 339-388.
Nieboer, E., Richardson, D.H.S., Tomassini, F.D., 1978. Mineral uptake and release by lichens: an overview. Bryologist 81, 226-246.
Olmez, I., Gulovali, M.C., Gordon, G.E., 1985, Trace Element Concentrations in Lichens Near a Coal-Fired Power Plant. Atmospheric Environment. 19, 1663-1669Pacyna, E., Pacyna, J. 2002. Global Emission of Mercury from Anthropogenic Sources in 1995. Water, Air and Soil Pollution 137, 149-165.
Palmer, H.E., Hanson, W.C., Griffin, B.I., Braby, L.A., 1965. Radioactivity measured in Alaskan natives, 1962-1964. Science 147, 620-621.
Puckett, K.J., 1988, Bryophytes and lichens as monitors of metal deposition. Bibliotheca Lichenologica 30, 231-267.
Purvis, O.W., Elix, J.A., Broomhead, J.A., Jones, G.C., 1987. The occurrence of copper-norstictic acid in lichens from cupriferous substrata. Lichenologist 19, 193-203.
Reynolds, S.J., 1988. Geologic Map of Arizona. Arizona Geological Survey Map 26, scale 1:1,000,000.
Seaward, M.R.D., Heslop, J.A., Green, D., Bylinska, E.A., 1988. Recent levels of radionuclides in lichens from southwest Poland with particular reference to 134Cs and 137Cs. Journal of Environmental Radioactivity 7, 123-129.
Taylor, S.R., McLennan, S.M., 1985 The Continental Crust: Its Composition and Evolution. Blackwell Scientific Publications, London.
Titley, S.R., Anthony, E.Y., 1989. Laramide mineral deposits in Arizona. In: Jenny, J.P., Reynolds, S.J. (Eds.) Geologic Evolution of Arizona. Arizona Geological Society Digest 17, Tucson, pp. 485-514.
U.S. Environmental Protection Agency 1997. Toxic Release Inventory 1987-1995. Pollution Prevention and Toxics (7407), EPA 749-C-97-003.
Zschau, T., Getty, S., Gries, C, Ameron, Y., Zambrano, A., Nash III, T.H. 2003. Historical and current atmospheric deposition to the epilithic lichen Xanthoparmelia in Maricopa County, Arizona. Environmental Pollution 125: 21-30.

Arizona State University

Central Arizona – Phoenix Long-Term Ecological Research CAP LTER