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

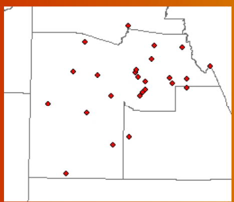


Figure 1. Sample locations in Maricopa County

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

Typical thallus collected for study

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 at the sites closest to the Navajo Power Plant. Multivariate and spatial analyses are used to further explore trends in metal deposition.

INTRODUCTION

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). 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. 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 with the software PCORD 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).

Table 1a. 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	1.85×10^{-3}	n/a	0.119	0.240	0.805	3.16×10^{-8}	1.43×10^{-6}
test of equal variances	2.43×10^{-4}	n/a	4.18×10^{-13}	0.712	0.292	5.20×10^{-10}	3.34×10^{-4}
2006 mean (ppm)	0.866	Below detection limits	51.26	0.476	30.07	1.11	81.47
1998 mean (ppm)	0.5	0.0702	22.32	0.457	28.51	0.419	50.94

Table 1b. 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	4.92×10^{-6}	6.81×10^{-6}	1.17×10^{-4}	2.61×10^{-6}
test of equal variances	7.93×10^{-10}	0.593	0.326	0.443
2006 mean (ppm)	19.53	3.19	9.03	3.03
1998 mean (ppm)	5.86	1.94	18.25	4.78

Table 1c. Comparison of 2006 and 1998 metal content of lichens in Maricopa county: Zschau et al's rare earth element cluster

Element	Neodymium	Praseodymium	Yttrium	Dysprosium	Gadolinium
T-test	3.70×10^{-4}	9.31×10^{-6}	8.06×10^{-5}	2.52×10^{-3}	0.0908
test of equal variances	4.09×10^{-8}	4.44×10^{-5}	1.02×10^{-6}	4.08×10^{-7}	7.21×10^{-4}
2006 mean (ppm)	17.77	4.02	14.93	2.14	3.03
1998 mean (ppm)	8.28	2.22	5.30	5.02	4.40

RESULTS

Table 2a. 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	0.00978	5.15×10^{-5}	0.114	0.406	0.00344	0.166	0.0425
test of equal variances	0.507	2.08×10^{-11}	0.111	0.565	2.53×10^{-7}	3.81×10^{-8}	0.152
Urban average (ppm)	0.256	22.3	0.419	0.457	30.1	0.500	50.9
Rural average (ppm)	0.210	9.94	0.483	0.499	15.2	0.679	45.7

Table 2b. Comparison of rural and urban areas for select metals- Zschau et al's mafic rock cluster

Element	Chromium	Nickel	Scandium	Cobalt
T test	7.02×10^{-8}	1.50×10^{-9}	2.58×10^{-12}	0.391
test of equal variances	1.51×10^{-7}	3.89×10^{-6}	0.934	0.459
Urban average (ppm)	5.86	18.25	4.78	1.94
Rural average (ppm)	13.63	4.23	1.94	2.15

Table 2c. 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	0.302	0.179	1.14×10^{-4}	1.61×10^{-4}	0.00163
test of equal variances	0.015	0.227	0.168	2.46×10^{-14}	2.54×10^{-10}
Urban average (ppm)	8.28	2.22	5.3	5.02	4.40
Rural average (ppm)	9.19	2.55	8.76	1.31	1.88

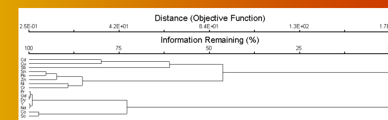


Figure 1a. Cluster analysis of 15 elements used by Zschau et al. (2003)

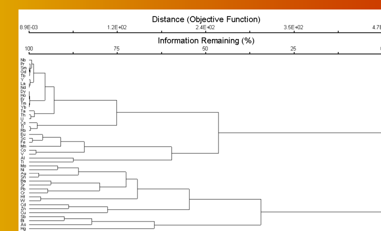
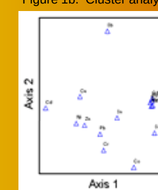


Figure 1b. Cluster analysis of 44 elements used in this study.



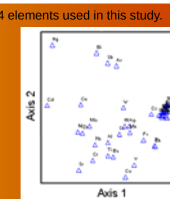


Figure 2a & 2b. The first two principle components axes of 15 elements used by Zschau et al. (2003), containing ca. 63% of the variation (left) and the first two principle components axes of 44 elements examined in this study, containing ca. 45% of the variation.

PRELIMINARY RESULTS, DISCUSSION AND FUTURE DIRECTIONS

Differences in metal content of the lichens in Maricopa county from the Zschau study to this one are listed in tables 1a, 1b, and 1c. A nonsignificant increase in lead is noted, as well as significant changes in some metals in each of the three clusters. Preliminary results suggest that for certain metals associated with anthropogenic sources (lead, mercury, copper and zinc) levels were significantly higher in Maricopa county than in the Grand Canyon region (see table 2a). Comparisons of metals in Zschau's rare earth cluster and mafic rock cluster demonstrate mixed results, with some metals (dysprosium, gadolinium, nickel and scandium) significantly higher in the urban area, other metals (yttrium and chromium) significantly higher in the rural areas and other metals (neodymium, praseodymium and cobalt) not significantly different between the two areas (tables 2b and 2c).

Cluster analysis using fifteen of the elements that Zschau analyzed demonstrates two clusters that together account for approximately 60% of the variation explained (figure 1). The first cluster includes cadmium, copper, tin, antimony lead, zinc, nickel and chromium, which is here interpreted as anthropogenic in nature. The second cluster contains praseodymium, gadolinium, dysprosium, ytterbium, neodymium, cobalt and scandium, and is here interpreted as widely distributed rare earth elements. In contrast to Zschau's work (2003), no separate cluster for mafic rocks appears in the cluster analysis. Instead, cobalt and scandium form a separate subcluster in the rare earth element cluster, and nickel and chromium pair together as a tertiary subcluster in the anthropogenic cluster (figure 1a). Principal components analysis yields similar groupings. The first three principal components were deemed to be signifcant since the broken stick eigen value was greater than the eigenvalue, and the three components account for almost 75% of the total variation. A plot of the first two axes is shown in figure 2a. Analysis of the larger set of elements (44) examined in this study shows similar results for both cluster and principal components analysis (see figures 1b and 2b). 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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