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Mercury concentrations in the lichen *Xanthoparmelia* spp. in the greater Grand Canyon region of Arizona, USA

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Abstract: The purpose of this study is to document the level and spatial distribution of mercury in the lichen, *Xanthoparmelia* spp., in the greater Grand Canyon region of northern Arizona, USA. Lichens were analyzed with a cold vapor technique and the resulting data were used to interpolate surface concentration maps. The results of this study suggest that mercury levels in the region are at or slightly elevated above background, although a clear source of mercury cannot be determined to be contributing to the levels found in the lichens.

Keywords: mercury, lichen, Grand Canyon, monitoring, *Xanthoparmelia*, coal power plants

Introduction

The Grand Canyon is a major canyon system located on the Colorado River in northern Arizona. The canyon is a national park, a major global tourist destination and an American icon (PYNE 1998). In the greater region, there are also several coal-fired power plants, including Coronado Generating Station (GS) at St. Johns, Arizona; Springerville GS in Springerville, Arizona; Navajo GS at Page, Arizona; Four Corners GS at Farmington, New Mexico; Craig GS at Craig, Colorado; and Hayden GS at Hayden, Colorado. Additionally, Mohave GS in Laughlin, Nevada ceased operation in 2005, and all interested parties have abandoned efforts to restart the plant (SRP 2010).

Recently, several research efforts have been conducted to determine the nature of air pollution and weather patterns that affect visibility at the Grand Canyon in northern Arizona. The studies included the Subregional Cooperative, Electric Utility, National Park Service, and Environmental Protection Agency Study (SCENES), the Winter Haze Intensive Tracer Experiment (WHITEX), the Winter Visibility Study (WVS), and the Measurement of Haze and Visual Effects (MOHAVE) experiment (MUELLER et al. 1986; MALM et al. 1988; RICHARDS et al.

1991; WATSON et al. 1993). Loss of visibility has been correlated with small secondary sulfate particles (LINAK & PETERSON 1981). Local sources of sulfate investigated with tracers included the Navajo Generating Station, a 2,250 MW coal power plant near Page, Arizona (CHEN & BORNSTEIN 1999), and the Mohave Generating Station, a 1,580 MW coal power plant near Laughlin, Nevada (WHITE et al. 1999). Regional sources considered included the Los Angeles and Las Vegas urban areas, and regions of New Mexico and Arizona. KUHNS et al. (1999) concluded that over half of the winter haze at Marble Canyon was attributable to the Navajo GS, and during the summer 7 % of the haze could be attributed to the Mohave GS. Other studies contribute a significant component of the haze to pollutants from the metropolitan Los Angeles area (ASBAUGH et al. 1985; WHITE et al. 1999; FARBER et al. 2000; LINDSEY et al. 1999). Although most of the work related to sulfur, some examination of metals was made. The SCENES project had among its objectives to characterize the aerosol composition in the area. Quantities of S, Pb, Cu, As and V significant enough for conditional frequency analysis were found at Hopi Point (VASCONCELOS 1999). Emissions from coal power plants are the source for many of these metals, including As, Co, Cr, Pb, and U (CHAUDHARY et al. 1984). Coal power plants are also major sources of mercury, and combined with waste incineration, "most likely bear the greatest responsibility for direct anthropogenic mercury deposition to the continental U.S. (U.S. ENVIRONMENTAL PROTECTION AGENCY 2000)." Three quarters of global emissions of mercury are attributed to the burning of fossil fuels, especially coal (PACYNA & PACYNA 2002). Metal accumulation has been also correlated with emissions from coal power plants in passerine birds (LLACUNA et al. 1995) and lichens (OLMEZ et al. 1985).

The weather patterns in the region that are responsible for the transport of air pollutants have also been extensively studied. Winter wind patterns have been modeled with cluster-analysis (KAUFMANN & WHITEMAN 1999). Airflow patterns were found to have a distinct diurnal cycle, produced by thermally induced winds near the ground. During the winter, a stable boundary layer can also form at or above the rim of the canyon (WHITEMAN et al. 1999). The boundary layer prevents mixing of air within the canyon and air aloft, and may keep air pollutants trapped in the canyon for several days.

Summer wind patterns have been described based on regional synoptic meteorology. FARBER et al. (2000) describe summer wind patterns as generally converging towards the lower Colorado River Valley, due to a semi-permanent thermal low produced by desert heating. A separate analysis of the entire year resulted in significantly different weather patterns during the fall not observed in other seasons (VASCONCELOS 1999).

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.

Lichens have been utilized extensively as biomonitors of metal deposition from air pollution (reviewed in GARTY 2001). The lichens concentrate metal pollutants actively when in solution and passively by particle impaction. Lichens have often been used in the assessment of mercury pollution in the local environment.

Significant differences have been shown in levels of mercury accumulation in lichens in an urban environment as opposed to lichens in a pristine rural environment in Argentina (GUEVARA et al. 2004). Lichens have been used to monitor mercury from point sources such as a chlor-alkali plant (SENSEN & RICHARDSON 2002), a mercury thermometer factory (KRISHNA et al. 2003), and geothermal power plants (LOPPI et al. 2006). Analysis of lichens near past producing mercury mines (PLOUFFE et al. 2003; LOPPI 2001) as well as active small scale gold mines (IKINGURA et al. 2006; IKINGURA & AKAGI 2002) have recorded elevated mercury levels correlated to mining activities. Lichens have also been used to assess air quality around a reservoir (MUNTEANU & MUNTEANU 2007), as part of the biotic data of anthropogenic contamination of Greenland (RIGET et al. 2004), and to assist in the estimation of potential mercury release from a crown forest fire (FRIEDLI et al. 2007).

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 & 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).

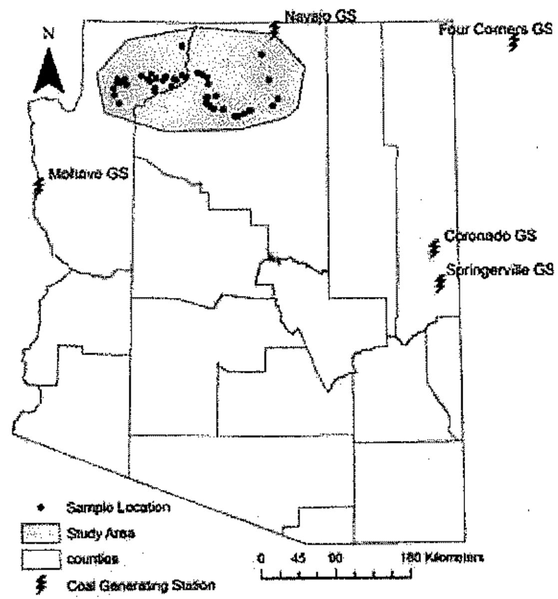

Fig. 1. Study area within northern Arizona.

Methods

The overall objective of this study was to document the spatial pattern of mercury deposition as reflected in lichens (*Xanthoparmelia* spp.) as of 2006 within the area encompassing the greater Grand Canyon region. The genus *Xanthoparmelia* was selected as the most suitable biomonitor of metal deposition in the region, because it is one of the few macrolichens (readily obtaining enough material for analysis is critical) in arid areas (NASH et al. 1977). It 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 mercury are assessed using lichens sampled from 46 locations both north and south of the Grand Canyon (see Fig. 1) collected in the summer of 2006.

Five separate rocks with *ca.* 25 cm^2 of lichen thalli on each were gathered at each sample location within a *ca.* 100 m^2 area for analysis. Once back in the laboratory, three lichens from each location of *ca.* 6–8 cm in diameter were removed from the rock substrate with plastic forceps and cleaned thoroughly using nano pure water under a laminar flow hood. The cleaned thalli were stored in high-density polyethylene bottles until air dry. The lichen material was then homogenized in a ball mill to prepare for mercury analysis. Forceps, bottles and all other lab ware were soaked for at least 72 hours in 10 % nitric acid and then triple rinsed in nano pure water before use. Mercury content was measured using a Leco AMA 254 Mercury Analyzer cold vapor mercury analyzer. Accuracy of the analyzer was confirmed every five samples with the use of IAEA-336 lichen reference material (HELLER-ZEISLER et al. 1999). The means of the three separate thalli from each location were used then to generate the interpolated mercury concentration map. Surface maps were interpolated among the 43 locations using ArcGIS Geostatistics and Spatial Analyst packages. Inverse distance weighting was used for the interpolation of surfaces.

Results

Mercury readings in the lichens averaged 209 ppb, with a standard deviation of 69.7 ppb. The highest reading was 408 ppb, and the lowest was 98.9 ppb. The means and standard deviations for each sample locations are listed in Tab. 1. The interpolated concentrations of mercury across the study area are depicted in Fig. 2.

Correlation analysis of the amount of mercury and the elevation of the sample location reveals a significant negative correlation ($r = -0.380$, $p = 0.0093$).

Discussion

The range of mercury concentrations found in this study is similar to mercury levels in lichens in other pristine areas. Mercury concentrations in Nahuel Huapi National Park, Patagonia, Argentina ranged from 55.8 to 1,380 ppb (GUEVARA 2004), which is about three times the concentrations found in this study at the high end. Analysis of *Hypogymnia physodes* estimated background mercury levels averaging 88 to 148 ppb, with significant differences found in lichens on different tree substrates (SENSEN & RICHARDSON 2002). Mercury levels found in unidentified lichens in Prince Albert National Park, Saskatchewan, Canada ranged from 30–227.1 ppb (FRIEDLI et al. 2007). Samples of *Parmelia* sp. and *Usnea* sp. were found to have mercury levels of 50–100 ppb in pristine areas used as a control, while areas near small scale gold mines recorded concentrations up to 3100 ppb (IKINGURA & AKAGI 2002). A background range of 100–200 ppb mercury in lichens of the genera *Parmelia* and *Xanthoria* has been reported for Italy (LOPPI 2001). Some care must be used in comparing these values, as most previous work has used epiphytic or corticulous lichen species, where this study used a saxicolous genus. Levels of mercury in this study do generally agree with background levels of other studies, although the high end of the concentration does suggest that some enrichment has occurred, most likely through anthro-pogenic sources. One factor complicating a straightforward interpretation of patterns is the relative amount of snow that each location has.

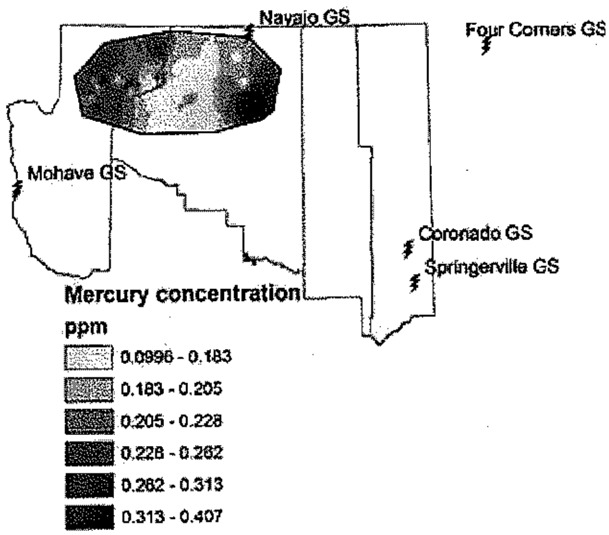

Fig. 2. Mercury concentrations across the study area.

The duration of snow cover over the lichen may lower the amount of mercury it absorbs. To test this, a correlation between elevation and mercury concentration was run, yielding an r value of -0.380, with a P value of 0.0093. This negative correlation between altitude and concentration suggests that the snow cover does reduce mercury absorption, though other explanations such as an increased amount of precipitation at higher elevations causing those lichens to grow faster and thus absorb less mercury are possible.

Analysis of spatial patterns reveals little influence on mercury concentrations (see Fig. 2). Elevated levels in the western end of the study area are probably the result of emissions from the now decommissioned Mohave Generating Plant and the urban area of Las Vegas, since previous research on sulfur determined signatures from both sources were detectable at the Grand Canyon (LINDSEY 1999). Elevated levels in the southeastern part of the study area are more difficult to interpret. Although a nearby source of mercury is the Navajo Power Plant, mercury from this source should have also elevated levels in the northeastern section of the study area, where levels are quite lower than the points in the southeastern section. Other power plants east (Four Corners GS) and southeast (Coronado GS and Springerville GS) of the study area would have contributed as well. Other research has suggested that mercury signatures in lichens are back to

Tab. 1. Means and standard deviations of three thalli for each sample location.

Latitude	Longitude	Average Mercury concentration (ppb)	Standard deviation (ppb)
36.17400	-111.41219	408	172
36.37503	-113.47372	372	202
36.35594	-113.13469	361	56
36.09908	-111.48242	345	51
36.38669	-113.05403	314	46
36.10864	-113.54025	297	41
36.74206	-112.70756	285	38
36.26889	-113.61494	278	39
36.42497	-112.70636	276	65
36.04856	-111.77961	262	37
36.36678	-112.96119	250	23
36.33747	-113.57222	242	16
36.40917	-112.92306	232	28
36.31397	-113.45050	222	37
36.20181	-112.25169	216	77
36.43100	-113.12144	215	50
36.12889	-112.37550	212	28
36.18806	-112.34950	209	48
36.03969	-111.80597	205	21
36.24697	-113.07064	200	87
36.37022	-113.56325	199	18
36.19731	-113.60964	198	16
36.19731	-113.60964	198	16
36.19903	-113.60178	191	25
36.45792	-112.49661	188	58
36.38478	-112.81344	185	21
36.40442	-112.65160	184	58
36.28356	-113.06469	182	24
36.01186	-111.86625	179	11
36.65722	-111.63169	177	16
36.37578	-113.16681	174	23
36.38303	-111.53283	171	49
36.09519	-112.32706	170	48
36.41258	-113.24428	169	61
36.40572	-112.37139	163	10
36.3320	-113.52697	159	11
36.06578	-112.27156	159	43
35.98142	-111.94844	157	16
36.43472	-112.43128	152	23
36.05672	-112.14947	151	18
35.98158	-111.98567	149	27
36.37417	-112.78339	148	45
36.38539	-112.80378	147	32
36.33583	-112.35000	141	16
36.18428	-112.38022	128	18
36.39944	-112.92700	117	17
36.30475	-112.83900	99	11

background levels at *ca.* 3.4 km away from a chlor-alkali plant (SENSEN & RICHARDSON 2002). Also, using a smaller cell size in generating an interpolated surface yields quite chaotic patterns (maps not shown), due to the inherent variability in mercury concentrations and haphazard locations of the sample sites. Given the low levels of mercury throughout the study area, and relative lack of pattern in the spatial analysis, mercury concentrations are here interpreted to be a combination of both geologic and anthropogenic sources, although the data are not sufficient to determine relative contributions of each.

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