Mercury concentration and isotopic composition of epiphytic tree lichens in the Alberta Oil Sands Region

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ABSTRACT

Mercury (Hg) is a toxic heavy metal that is found associated with fossil fuel deposits and that can be released to the atmosphere during fossil fuel combustion and/or processing. Hg emitted to the atmosphere can be deposited to aquatic and terrestrial ecosystems where it can be methylated by bacteria. Methylmercury is strongly biomagnified in food webs and this leads to toxic levels in high trophic level fish, the consumption of which is a major human exposure pathway. Epiphytic tree lichens have been widely used to investigate the relationship between atmospheric point sources of Hg and regional Hg deposition patterns. An intensive study of Hg concentration and stable isotopic composition of the epiphytic tree lichen Hypogymnia physodes was carried out in the area within 150 km of the Alberta oil sands region (AOSR) industrial developments. Concentrations of Hg were comparable to background values measured in previous studies from remote areas and were far below values observed near significant atmospheric industrial sources of Hg. Spatial patterns provide no evidence for a significant atmospheric point source of Hg from the oil sands developments and Hg accumulation actually decreases in lichens within 25 km of the AOSR development, presumably due to physiological responses of Hypogymnia physodes to enhanced SO2 deposition. Stable mercury isotope ratios show an increase in 199Hg and 201Hg within 25 km of the AOSR and we speculate that this is due to a change in the proportion of the various ligands to which Hg is bonded in the lichens, and a resulting change in the isotope fractionation during partial photochemical reduction and loss of Hg from lichen surfaces.

INTRODUCTION

Mercury (Hg) is a highly toxic and globally distributed atmospheric trace pollutant. It is released to the atmosphere from a range of industrial activities primarily as gaseous elemental mercury (Hg(0)) and reactive gaseous mercury (Hg(II)). Hg(0) has a long atmospheric residence time (~1 year) and can travel long distances before being oxidized to Hg(II) and deposited (Schroeder and Munthe 1998). Hg(II) has a much shorter residence time than Hg(0) and is rapidly deposited locally in precipitation and dry deposition downwind of atmospheric point sources (Keeler et al 2006; Sherman et al 2012). Once Hg(II) is deposited to aquatic and terrestrial ecosystems it can be methylated by sulfate and iron reducing bacteria producing highly toxic and bioaccumulative methylmercury. Biomagnification of atmospherically deposited mercury can result in the acquisition of high levels of methylmercury in high trophic position fish in remote lakes.
Consumption of fish is a major human exposure pathway for methyl mercury, especially for indigenous peoples (Chan and Receveur 2000).

Mercury bonds strongly to marine and terrestrial organic matter and is often associated with organic-rich geological deposits. The most important anthropogenic source of Hg to the atmosphere is through the burning of coal (Pirrone et al 2010). However, natural gas processing (Spiri and Mashyanov 2000) and oil refining (Wilhelm 2001) can also produce significant emissions of mercury. Although detailed studies have not been conducted previously, several studies have inferred that AOSR processing may result in enhanced atmospheric Hg emissions (Wilhelm 2000; Kelly et al 2010; Timony and Lee 2009) and that Hg is methylated and bioaccumulated resulting in elevated levels in fish in the region (Timony and Lee 2009). A study by Kelly et al. (2010) also reported that mercury, along with other trace metals, was elevated in snow near the AOSR developments.

There is a great need for monitoring of Hg deposition spatially near potential atmospheric point sources. Monitoring is particularly difficult in remote areas such as the Alberta oil sands region (AOSR) where atmospheric concentrations and deposition rates are difficult to measure due to lack of road access and electrical power needed to run atmospheric monitoring sites. The industrial development of the AOSR north of Fort McMurray, Alberta, Canada, has resulted in increases in some industrial atmospheric emissions in the region (Percy et al, this volume). The present study was designed to use a single species of naturally occurring tree lichens to evaluate if Hg deposition in the region close to the AOSR was enhanced relative to background values further from the AOSR developments.

Many different species of epiphytic tree lichen have been used previously as passive collectors of a variety of atmospheric pollutants (e.g., Purvis and Halls 1996), including mercury (e.g., Bargagli and Barghigiani 1991). Physiological differences between lichen species result in differing metal accumulation properties, and so we focused our study on a single species of epiphytic lichen, Hypogymnia physodes, that is widely distributed in the AOSR and that has been used extensively in previous studies of Hg deposition in other geographic regions (e.g., Makholm and Bennett 1998, Horvat et al 2000). Mercury was measured in the same lichen samples used for major and trace elements analyses (Edgerton et al, this volume) and Pb isotope studies (Graney et al, this volume). A gridded circular sampling pattern was used to allow the use of Hg and other major and trace elements in receptor modeling and impact assessment (Landis et al, this volume).

Some previous studies have analyzed variations in the Hg content of naturally growing Hypogymnia physodes near atmospheric pollution sources (Makholm and Bennett 1998 and references therein, Horvat et al 2000, Sensen and Richardson 2002) and others have transplanted Hypogymnia physodes with low natural Hg concentrations to locations near atmospheric point sources and monitored changes in Hg concentration with time (Makholm and Bennett 1998 and references therein, Horvat et al 2000, Bialonska and Dayan 2005, Williamson et al 2008). Additionally, studies have been
carried out on the organic compounds produced by Hypogymnia physodes and their effect on metal binding in this species of lichen (Bialonska and Dayan 2005, Hauck and Huneck 2007, Hauck 2008). Collectively, these studies have shown that Hg concentrations in lichen increase near atmospheric point sources for Hg, and that Hypogymnia physodes, as well as other epiphytic lichens, can provide a useful semi-quantitative proxy for atmospheric Hg deposition.

In addition to the many studies that have measured Hg concentrations in epiphytic lichens, two previous studies explored variations in the stable isotopic composition of Hg in epiphytic lichens; but in species other than Hypogymnia physodes. Carignan et al (2009) and Estrade et al (2010) measured Hg concentrations and isotopic compositions of four tree lichen species (Usnea, Ramalinia, Evernia and Bryoria) from remote areas in Canada and Switzerland and rural and urban areas in France. They did not find a correlation between Hg concentration and that of other heavy metals (Cd and Pb) but they did document mass independent isotope anomalies in the odd mass Hg isotopes for all lichens sampled. Furthermore, these studies observed decreased mass independent Hg isotope anomalies near industrial atmospheric sources of Hg, and suggested that this was the result of additions of local anthropogenic Hg.

In this study, we measured total Hg concentrations (n=121) and stable isotopic composition (n=38) in Hypogymnia physodes collected in 2008 from trees at proximal and remote sites in a nested circular grid pattern distributed over 0.5 to 150 km from the AOSR industrial complex north of Fort McMurray, Alberta, Canada (see Edgerton et al., this volume). Spatial trends in Hg concentration and isotopic composition are used to evaluate the extent to which the AOSR developments have affected atmospheric Hg deposition. Hg concentrations and isotopic compositions are compared to values from the literature for measurements made in remote areas and near known point sources of Hg. Hg isotopic compositions are also compared to values measured from a variety of geological materials from the AOSR developments and nearby areas.

METHODS

Sample Collection and Preparation

A detailed field-sampling program was implemented during August-September 2008. Most sites were accessed by helicopter and others were visited by ground. At each site, composite samples of the lichen Hypogymnia physodes were collected from the branches of 6 trees within Jack Pine (Pinus banksiana) tree stands. Samples were stored in polyester sample bags and air dried in a laboratory at the University of Minnesota. Using Teflon coated tweezers, tissue samples were cleaned by removing all foreign materials (bark and other debris) and were then stored frozen until analysis. GPS location data for all sample collection sites were used to determine the distance from a midpoint located at the center of the AORS industrial operations (Edgerton et al., this volume). In 2009 bulk geological samples of oil sands, bitumen, processed tailing sand, overburden, and mine road material were acquired from active mining and energy processing operations in the
AOSR. Bulk samples of other undeveloped oil sand deposits exposed in outcrop in the Athabasca River valley north of the AOSR industrial developments were also obtained. All samples were shipped to the University of Michigan where they were freeze-dried, and ground to a powder. Lichen samples were ground in a ball mill (Spex 8000M) using a zirconium grinding vial and balls that were thoroughly cleaned between each sample. Geological materials were ground by hand in an agate mortar and pestle that was thoroughly cleaned between each sample. A n ~50 mg aliquot of each powdered sample was used for Hg concentration analysis and a 500 mg to 4 g aliquot of a sub-set of the samples was used for Hg stable isotope analysis.

Hg Concentration Analysis

Mercury concentrations were measured using quality control methods that included analysis of analytical standards, procedural blanks and replicate samples. Lichens and geologic samples were analyzed for total Hg concentration by combustion at 850°C and quantification by cold-vapor atomic absorption spectrometry (CVAAS; MA-2000, Nippon Instruments). Replicate analyses agreed within ±7% and the reporting limit was 0.5 ng Hg. The IRMM powdered lichen reference material BCR482 was run with each batch of eight samples and we obtained an average Hg concentration of 454±8 ng/g (1sd, n=19), which is within 5% of the certified value of 480±20 ng/g.

Sample Preparation for Isotope Analysis

Hg was separated for isotopic analysis from lichens and geologic samples by combustion at 750°C, thermal decomposition at 1000°C, and inline trapping in a 1% KMnO₄ solution. To further purify Hg in the KMnO₄ solutions, the solutions were reduced with SnCl₂, purged with Hg-free air, and re-trapped in another 1% KMnO₄ solution. The Hg concentration of each of the KMnO₄ solutions was measured to determine recoveries, and to allow matching of standard and sample concentrations for isotope analysis. Details of the method are given in Biswas et al (2008) and Demers et al. (2012). Mean recovery following combustion for IRMM lichen reference material BCR 482 was 94% (± 4%, 1SD, n = 5), and mean recovery following both combustion and secondary purge and trap of BCR482 was 93% (± 3%, 1SD, n = 5).

Mass Spectrometry

Mercury in KMnO₄ solutions separated from lichens and bulk geologic samples was analyzed for isotopic composition with a multiple collector inductively coupled plasma mass spectrometer (MC-ICP-MS; Nu Instruments) using continuous flow cold vapor generation with SnCl₂ reduction. Instrumental mass bias was corrected using an internal Tl standard (NIST SRM 997, 205Tl/203Tl=2.38714) and sample-standard bracketing with the NIST SRM 3133 Hg standard. Analyses and standards were run at 5 ppb Hg. On-peak zero corrections were applied to all masses and isobaric interference from ²⁰⁴Pb was monitored using mass 206, but was always negligible.
We report isotopic compositions as permil (‰) deviations from the average of NIST SRM 3133 bracketing standards using delta notation following equation 1:

\[ \delta^{\text{Hg}} = \left[ \frac{{^{199}\text{Hg}} / {^{198}\text{Hg}}}{{^{199}\text{Hg}} / {^{198}\text{Hg}}_{\text{NIST SRM 3133}}} - 1 \right] \times 1000 \]  

where \( \delta^{\text{Hg}} \) is in units of permil (‰), and \( \delta^{\text{Hg}} \) is the mass of each mercury isotope between \(^{199}\text{Hg} \) and \(^{204}\text{Hg} \). We use \( \delta^{202}\text{Hg} \) to describe isotopic differences due to mass dependent fractionation (MDF). Mass independent fractionation (MIF) is defined as the deviation of the isotope ratios involving odd mass isotopes from the theoretically expected values determined by the kinetic mass-dependent fractionation law based on the measured \( \delta^{202}\text{Hg} \) (Blum and Bergquist 2007). MIF is reported in “capital delta” notation \( \delta^{\text{Hg}} \) in units of permil (‰), and is well approximated for small ranges in delta values (\( \Delta 10 \) ‰) by equation 2:

\[ \delta^{\text{Hg}} = \delta^{\text{Hg}} - (\delta^{202}\text{Hg} \times \ast) \]  

where \( \delta^{\text{Hg}} \) is the mass of each Hg isotope 199 and 201 and \( \ast \) is a constant (0.252 and 0.752, respectively; Blum and Bergquist 2007).

Analytical Uncertainty

The uncertainty of Hg isotope measurements was characterized using a secondary standard solution that is widely distributed (UM - Almaden) and an international lichen reference material (BCR482). The U M - Almaden standard solution is useful for inter-laboratory comparison and we obtained the following values for 10 replicate analyses carried out during the analyses of samples for this study: \( \delta^{202}\text{Hg} = 0.59 \pm 0.03\% \) (2sd), \( \delta^{199}\text{Hg} = 0.01 \pm 0.04\% \) (2sd), \( \delta^{201}\text{Hg} = 0.04 \pm 0.03\% \) (2sd). The lichen IRMM BCR482 is useful for assessment of the uncertainty of complete Hg separation and analyses and we obtained the following values for 6 replicate analyses carried out during the analyses of samples for this study: \( \delta^{202}\text{Hg} = 1.67 \pm 0.04\% \) (2sd), \( \delta^{199}\text{Hg} = 0.67 \pm 0.04\% \) (2sd) and \( \delta^{201}\text{Hg} = 0.68 \pm 0.03\% \) (2sd).

RESULTS AND DISCUSSION

Hg concentrations of Hypogymnia physodes

Total Hg concentrations for the 121 Hypogymnia physodes samples analyzed ranged from 71 to 268 ng/g with a mean value of 144 ± 33 ng/g (1sd) (Figure 1). These values are in the range typical for remote areas unaffected by point source Hg emissions. Makholm and Bennett (1998) reported background Hg concentrations for Hypogymnia physodes in northern Wisconsin of 110 to 155 ng/g and Bennett and Wetmore (1997) reported background values of 103 to 143 ng/g for northern Minnesota. Makholm and Bennett (1998, and references within) compiled background Hg concentration values for European studies as of 1998 and reported that most values (9 separate studies) ranged from 200 to 400 ng/g, whereas two studies in Scandanavia reported background values of 100 ng/g and 160 ng/g respectively. Since 1998 two additional studies measured
background Hg values in Hypogymnia physodes. Horvat (2000) measured a mean background value of 110±10 ng/g at a remote location in Slovenia and Sensen and Richardson (2002) measured a mean background Hg value of 148±46 ng/g at a remote location in New Brunswick, Canada. Altogether, comparison of the values reported here for Hg in Hypogymnia physodes in the AOSR are consistent with background values measured in a large number of studies of Hg in Hypogymnia physodes in both North America and Europe. This suggests that any Hg deposition associated with the AOSR development has not significantly elevated the Hg concentrations in lichens.

Previous studies have shown that Hg concentrations in natural Hypogymnia physodes collected near atmospheric Hg point sources, and Hg in Hypogymnia physodes transplanted to the vicinity of Hg point sources, have lichen tissue concentrations much higher than those we measured in the AOSR. Makholm and Bennett (1998) transplanted Hypogymnia physodes downwind of a chlor-alkali plant and after a year of exposure concentrations ranged up to 4418 ng/g at a distance of 250 m from the plant and up to 403 ng/g at a distance of 1250 m. Makholm and Bennett (1998, and references therein) also compiled the results of earlier studies of Hg in Hypogymnia physodes near point sources and found that in each of seven studies Hg concentrations were highly elevated near the source with values ranging from 770 to 36000 ng/g. In a more recent study, Horvat et al (2000) transplanted Hypogymnia physodes to locations around a natural gas treatment plant in Molve, Croatia and locations around a Hg mining area in Idrija, Slovenia, where measurements of the concentration of ambient total gaseous mercury (TGM) in air were also made. They found a strong correlation between the logarithm of the total Hg concentration in Hypogymnia physodes and the logarithm of the TGM concentration in air. Hg concentrations in Hypogymnia physodes were 110 ng/g at the time of transplant and ranged from 540 to 4430 ng/g after 6 months in the mining area. In another recent study Senson and Richardson (2002) analyzed Hg in naturally growing Hypogymnia physodes on spruce trees along transects near a Hg cell chlor-alkali plant in New Brunswick, Canada. They documented systematic increases in Hg concentration from a background value of 148 ng/g at a distance of 8 km from the plant to maximum value of 790 and 980 ng/g at a distance of 125 m along two different transects. In sum, these studies show that within about 1 to 8 km of atmospheric Hg point sources the Hg concentrations of Hypogymnia physodes are generally elevated far above background values. This reinforces our conclusion that the AOSR development is not a significant atmospheric Hg source that is detectable using lichen analysis and certainly does not generate atmospheric Hg levels near the magnitude of chlor-alkali plants, smelters, gas processing plants, or Hg mining areas that have been studied previously.

Hg concentrations of other species of epiphytic lichen

The literature is rich with investigations that have used epiphytic lichens other than Hypogymnia physodes to study Hg levels in the atmosphere. Because of physiological differences between species it is not advisable to directly compare metal concentrations between species. Nevertheless, these studies do confirm that for most species a concentration range of 100-200 ng/g total Hg is a common background concentration that is often observed in remote areas. Large increases in Hg
concentrations are often observed within about 8 km of large atmospheric Hg point sources, and lichen Hg concentrations generally correlate with TGM concentrations in air (Bargagli and Barghigiani 1991; Guevara et al 2004; Grangeon et al 2012; Tretiach et al 2011). Using four different lichen species (but not including Hypogymnia physodes) Landers et al (1995) observed increased Hg concentrations in Alaska with closer proximity to the marine coastline. Carignan and Sonke (2010) measured Hg in three lichen species (but again not in Hypogymnia physodes) in Canada (mostly in Quebec) and found that Hg concentrations were well correlated with Br concentrations, and that both elements increased in concentration with decreasing distance to Hudson Bay. These authors attributed the spatial trends to a marine source of Br to the atmosphere, which is known to oxidize background Hg(0) in the atmosphere, which then led to increased deposition of Hg(II). The Carignan and Sonke (2010) study documents lichen Hg concentrations as high as 2060 ng/g in the lichen species Bryoria, 20 km from Hudson Bay but far from anthropogenic point sources. Hg concentrations dropped below 250 ng/g at distances greater than 800 km from Hudson Bay. The AOSR is about 800 km from both the Pacific Ocean and Hudson Bay and appears to be unaffected by this Hg deposition mechanism.

Spatial Variation in Hg concentrations of Hypogymnia physodes

In order to explore whether the observed variability in the Hg concentration of Hypogymnia physodes in the vicinity of the AOSR is affected by the mining and energy production activities, we plotted the Hg concentrations of lichens as a function of the distance from the center of the production area (Figure 1). Regression of the data reveals a small (slope=0.33 ng/g per km) but significant (p=0.0002) decrease in the Hg concentration of lichens as the active mining and upgrading facilities are approached. The regression line drops from a Hg concentration of 171 ng/g at 155 km to 122 ng/g at 5 km. This behavior is the opposite of what has been documented in the literature near atmospheric point sources of Hg and is (as far as we are aware) the first documentation of decreasing Hg concentration in lichen as an industrial development is approached. We do note, however, that previous studies documenting increases in the Hg concentration of Hypogymnia physodes in the vicinity of atmospheric Hg sources, found elevated Hg in lichens only at distances of 8 km or less from the sources. The sampling distances in our study were generally much farther from the potential source than previous studies, and only 8 of the 121 Hypogymnia physodes samples were from 8 km or less distance from the center of the AOSR mining and energy production areas. However, even these samples within close proximity of the AOSR industrial development did not have elevated Hg concentrations.

Although a decrease in Hg in epiphytic lichens near industrial facilities has not been previously reported, a study comparing naturally growing and transplanted Hypogymnia physodes within a km of a chlor-alkali plant in Norway may provide some insight into this phenomenon. Steinnes and Krog (1977) found that Hg concentrations in naturally occurring Hypogymnia physodes reached a maximum of 950 ng/g in close proximity to a chlor-alkali plant. However, when they transplanted Hypogymnia physodes from a remote site to the industrial site they observed an increase in Hg content with time.
and found Hg concentrations in Hypogymnia physodes as high as 6000 to 8000 ng/g after 16 weeks of exposure. The authors suggested that the lower uptake of Hg by the naturally occurring lichens compared to the transplants may have been related to SO₂ exposure and resulting loss of vigor in the Hypogymnia physodes (Steinnes and Krog 1977). In the vicinity of the AOSR the sulfur content of Hypogymnia physodes is higher due to SO₂ deposition (Edgerton et al, Landis et al, this volume) and we suggest that this may have resulted in decreased Hg accumulation as suggested in the study of Steinnes and Krog (1977). Graney et al (this volume) observed a subtle decrease in Zn and Mn concentrations toward the center of the AOSR region in the same lichen samples we analyzed. They suggested that this trend may be related to canopy interactions or physiological processes in the lichens.

Hg Isotopic composition of Hypogymnia physodes

A subset of 38 Hypogymnia physodes samples that were analyzed for Hg concentration were also analyzed for their stable mercury isotopic composition. Variations in the isotopic composition related to mass dependent fractionation of Hg are reported as δ²⁰²Hg and samples ranged in values from -2.66 to -1.41‰ with an average value of -1.87 ±0.22‰ (1sd) (Figure 2). Mass independent fractionation (MIF) is reported here as •²⁰⁹Hg (but note that •²⁰¹Hg shows the same behavior) and samples ranged in values from -0.55 to +0.33‰ with an average value of -0.24 ±0.17‰ (1sd) (Figure 3). The ratio of •²⁰⁹Hg/•²⁰¹Hg is 0.997 (Figure 4), suggesting that the MIF results from photochemical reduction of Hg(II) to Hg(0) involving short-lived radical pair reactions and is caused by the magnetic isotope effect (Bergquist and Blum 2007; Blum 2011).

Two other investigations of Hg isotopic compositions of lichens have been published previously, but there have been no previous Hg isotopic studies of the lichen species Hypogymnia physodes. Carignan et al. (2009) and Estrade et al. (2010) measured Hg isotope values in remote areas in Canada and Switzerland and both urban and industrial areas in France in many different lichen species. These lichens ranged widely in δ²⁰²Hg values from 1.5 down to -2.2‰. The lichens analyzed in these previous studies also displayed negative values for •²⁰⁹Hg (and •²⁰¹Hg), with values ranging from -0.2 to -0.9‰. Lichens from remote areas showed the lowest •²⁰⁹Hg values (Carignan et al 2009) and values tended to become less negative in urban and industrial areas (Estrade et al 2010). At that time these authors interpreted the negative •²⁰⁹Hg values to be indicative of regional atmospheric Hg isotopic values and the increase in •²⁰⁹Hg near industrial areas as the impact of adding industrial point sources of Hg that had near-zero •²⁰⁹Hg values.

More recently, several studies of atmospheric Hg isotopes have shown that Hg(II) deposited from the atmosphere in precipitation has positive •²⁰⁹Hg (and •²⁰¹Hg) values, and that gaseous Hg(0) in the atmosphere has negative •²⁰⁹Hg (and •²⁰¹Hg) values. Furthermore, these studies have demonstrated that there are fractionation mechanisms that can cause Hg with more positive •²⁰⁹Hg to be released from surfaces following
photochemical reduction of Hg(II) to Hg(0) (Gratz et al 2010; Sherman et al 2010, 2012; Demers et al 2012). In a recent investigation of Hg isotope systematics in a forested ecosystem in northern Wisconsin (USA), Demers et al (2012) found that gaseous elemental Hg(0) with $^{199}$Hg of -0.2‰ is oxidized and deposited to tree leaf surfaces, and that subsequent photochemical reduction and loss of a portion of this Hg results in increasingly negative values for $^{199}$Hg in leaves, averaging about -0.3‰. This same Hg isotope fractionation process may occur on lichen surfaces as well as on leaves. We suggest that Hg(0) is deposited to lichen surfaces, becoming oxidized to Hg(II) as it binds with ligands in organic acids. Photochemical reactions then cause partial reduction and loss of some Hg(II) as Hg(0) with more positive $^{199}$Hg, and the Hg(II) that remains in the lichen acquires more negative $^{199}$Hg values.

Spatial Variation in Hg Isotopic Composition of Hypogymnia physodes

The $\delta^{202}$Hg values of the lichens from this study are plotted versus distance from the active mining and energy production activities on Figure 2. $\delta^{202}$Hg values do not vary significantly with distance ($p = 0.350$) from the active energy production areas and are similar to values for foliage from trees in northern Wisconsin (USA) measured by Demers et al (2012). Values are unaffected by proximity to the AOSR developments, as would be expected, because Hg concentrations show no evidence for addition of Hg from this source.

In contrast, $^{199}$Hg (and $^{201}$Hg) values shift dramatically with distance from the AOSR development (Figure 3). At distances of >25 km the average $^{199}$Hg value is -0.38±0.07‰ whereas at <25 km the average $^{199}$Hg value is -0.13±0.15‰ and reaches a maximum value of +0.33‰. The dramatic increase in $^{199}$Hg values combined with the decrease in Hg concentrations of Hypogymnia physodes near the AOSR development is somewhat puzzling. It appears that either i) the AOSR development is emitting Hg with very high $^{199}$Hg values, but accumulation of Hg in the lichens near the AOSR is suppressed to the point that Hg concentrations actually appear to decrease near the active energy production areas or ii) there are physiological effects in the lichens near the active energy production areas due to deposition of other pollutants (in particular SO$_2$) that both suppresses Hg accumulation and alters the mass independent fractionation of Hg on lichen surfaces resulting in an increase in $^{199}$Hg values. Each of these alternate explanations is discussed in more detail below.

Hg Isotopic Composition of Oil Sands Materials

To explore the possibility that the AOSR development is emitting Hg with highly elevated $^{199}$Hg values, and that this is responsible for the high $^{199}$Hg values in lichens in close proximity to the AOSR, we analyzed bulk samples of geological materials from the AOSR (see Landis et al, this volume). Oil sand, bitumen, processed tailings sand, overburden and road materials from mines between Ft M cM urray and Ft M cK ayy were analyzed. Weathered oil sand that naturally outcrops along the Athabasca River north of Fort M cK ayy (and has not been mined) was also analyzed. The concentration of Hg in the oil sands ranged from 4.1 to 38.8 ng/g, processed sands from tailings ranged from 1.9 to
10.6 ng/g, and the bitumen, overburden and road material were 14.3, 13.1 and 32.8 ng/g, respectively. In comparison, Hg concentrations are 3.5 ng/g in mean volume weighted US crude oil and 100 ng/g in mean volume weighted US coal (Wilhelm et al 2007; Toole-O’Neil et al 1999). The mean background Hg concentration for lake sediments in Alberta was recently reported as 36 ng/g (Nasr et al 2011), and indicates that the oil sands and associated materials do not have Hg concentrations that are far above background sediment concentrations.

- $^{199}$Hg and $^{202}$Hg values of the geologic materials analyzed are plotted along with values for the lichens on Figure 5. Oil sand, bitumen, processed sand and overburden from mines between Fort McMurray and Fort McKay fall in a narrow range of Hg isotope values that overlap with values for Hypogymnia physodes collected > 25 km from the mines, but have lower $^{199}$Hg and higher $^{202}$Hg than Hypogymnia physodes collected < 25 km from the mines. A single sample of road material from the mines has $^{199}$Hg ~ 0.3‰ higher than the other mine samples and could possibly represent addition of Hg from oil, brake pads or diesel fuel. The three samples of oil sand from the Athabasca River north of Fort McKay also have $^{199}$Hg values about ~ 0.3‰ higher than the mine samples. These samples have $^{199}$Hg closer to the values of the Hypogymnia physodes < 25 km from the mines, and $^{202}$Hg values about ~ 0.5‰ higher, but these deposits are not currently mined or processed.

Potential Hg sources from the mining operations are similar to the background isotopic values in lichens > 25 km from the mining areas. Therefore, addition of this potential source of Hg would not shift the lichen Hg isotopic values appreciably. Even if all of the Hg in the lichens near the AOSR had the maximum observed $^{199}$Hg from the undeveloped Athabasca River oil sand, this could only explain the lichens with intermediate values and could not explain the highest lichen $^{199}$Hg values. Therefore, we can rule out addition of oil sand-derived Hg as the sole cause for the increase in $^{199}$Hg values of Hypogymnia physodes within 25 km of the AOSR area.

Proposed mechanism to explain Hg isotopic variability

We have argued above that the addition of Hg from the active mining and energy production activities does not adequately explain the changes in Hg isotopic composition observed in lichens within 25 km of the AOSR. Furthermore, the observed lower Hg concentrations in lichens near the AOSR are not consistent with addition of Hg from a point source to the regional background. We suggest that the increase in $^{199}$Hg values of Hypogymnia physodes within 25 km of the AOSR is caused by a change in the processes by which Hypogymnia physodes binds Hg(II) species onto ligands present in the lichens. Following deposition of Hg to the lichens, there appears to be a change in the reaction pathway and degree of photochemical reduction of Hg(II) from the lichen surfaces. This reduction in the loss of Hg(0) from the lichen surfaces appears to result in a change in the lichen $^{199}$Hg values.
Experimental studies of Hg isotope fractionation have shown that large magnitude mass independent fractionation (>0.2‰) is generally the result of photochemical reactions involving short-lived radical pairs (Blum 2011). The ratio of •\(^{199}\)Hg to •\(^{201}\)Hg and the observation of either the preferential loss or gain of odd isotopes of Hg in volatilized Hg(0) during reduction, has been shown to be related to the ligands to which Hg is bonded (Zheng andHintelmann 2010). Regression of •\(^{199}\)Hg versus •\(^{201}\)Hg for lichens from this study yield a slope of 0.997 (r\(^2\) = 0.947; Figure 4) and values are negative (meaning odd isotopes were preferentially lost). Hg (II) is known to be photochemically reduced to Hg(0) and emitted from leaf surfaces (Mowat et al 2011). Zheng and Hintelmann (2010) showed that when Hg (II) is bonded to a sulfur-containing ligand photochemical reduction and loss of Hg(0) from aqueous solutions results in residual Hg(II) with negative •\(^{199}\)Hg and •\(^{201}\)Hg. When the binding ligand is sulfurless, residual Hg(II) is observed to have positive •\(^{199}\)Hg and •\(^{201}\)Hg.

Lichens are known to produce a wide range of organic ligands, both containing and not containing sulfur, that play an important role in metal binding. Both intracellular binding of metals to sulfur-containing peptides (metallothioneins) and extracellular binding to sulfur-less organic acids is known to occur in lichens (Sarret et al, 1998). Although experiments exploring Hg isotope fractionation in the presence of these ligands have not yet been performed, we would expect that both positive and negative MIF could be produced by photochemical reduction of Hg(II) complexed with these various compounds. It seems likely that the net isotopic composition of lichen is the result of simultaneous negative and positive mass independent fractionation of Hg associated with different bonding environments in the lichen. Given this assumption, we suggest that Hypogymnia physodes collected >25 km from the active mining and energy production facilities have negative •\(^{199}\)Hg and •\(^{201}\)Hg that resulted from the dominance of photochemical reduction of Hg(II) from sulfur-bearing ligands compared to sulfur-less ligands. The increase in •\(^{199}\)Hg and •\(^{201}\)Hg that is observed closer to the active mining and energy production facilities could then be interpreted as a shift in the balance toward reduction of Hg(II) from sulfur-less ligands.

A study by Bialonska and Dayan (2005) measured changes in the production of organic acids by samples of Hypogymnia physodes when they were transplanted to four different sites where they were exposed to industrial emissions of metals and SO\(_2\). Site-specific changes in production of various organic acids was observed, with some increasing and others decreasing with exposure. For example, an increase in the content of physodic acid was observed in all transplanted lichens and the authors suggested a possible role for this compound in defense against stress caused by exposure to pollutants (Bialonska and Dayan 2005). Although highly speculative, we suggest that exposure of Hypogymnia physodes in the AOSR near active mining and energy production facilities to SO\(_2\) and other metals could have changed the balance of the various organic acids produced in the lichens. Increased complexation of Hg(II) to these sulfur-less compounds, with resulting enhanced photochemical reduction of Hg and loss back to the atmosphere, is a possible explanation for both the increase in •\(^{199}\)Hg and •\(^{201}\)Hg and decrease in total Hg concentration observed in the lichens <25 km from the mining and energy production facilities.
CONCLUSIONS

A single species of epiphytic tree lichen (Hypogymnia physodes) was sampled in 2008 at remote sites in a nested, circular grid pattern 0.5 to 150 km from the center of industrial development in the Alberta Oil Sands Region north of Fort McMurray, Alberta, Canada. Total Hg concentrations in epiphytic lichens have been used in previous studies as a measure of spatial variations in atmospheric Hg deposition and to delineate the near field influence of atmospheric point sources of Hg. The stable Hg isotopic composition has also recently been used as a monitor of additions of local anthropogenic Hg to regional background deposition. Hg concentrations in Hypogymnia physodes in the AOSR ranged from 71 to 268 ng/g, which is similar to that measured by others for remote sites in other regions. Based on concentration alone there is no evidence for anomalously high atmospheric Hg deposition near the AOSR mining and energy production facilities. In fact, small variations with distance show that Hg concentrations decrease with proximity to the facilities. This conclusion is in contrast with the finding of Kelly et al (2010) who observed increased Hg concentrations in snow near the AOSR energy development facilities.

The stable Hg isotope composition of the lichens does, however, change systematically with distance from the potential industrial sources. Most notably the lichens display varying levels of mass independent fractionation with both *\(^{199}\)Hg and *\(^{201}\)Hg ranging from near 0.0‰ close to the oil sands developments and systematically falling to -0.4‰ about 25 km away. The *\(^{199}\)Hg*/\(^{201}\)Hg slope is close to one, suggesting that the mass independent fractionation results from photochemical reduction of Hg(II) to Hg(0). Mass dependent fractionation does not change systematically with distance from the oil sands developments, and *\(^{202}\)Hg* averages -1.9‰. The spatial trends show that the energy production activities influence the *\(^{199}\)Hg* and *\(^{201}\)Hg values without significantly affecting the *\(^{202}\)Hg* values and have the effect of lowering the Hg concentrations of the lichens. Measurements of the Hg isotopic composition of the oils sands themselves show that they cannot explain the variation in Hg isotopic composition of Hypogymnia physodes near the energy production facilities. It is possible that other atmospheric pollutants, such as SO\(_2\) (which is known to affect the vitality of lichens), are influencing Hg retention in the lichens. Hypogymnia physodes is also known to respond to SO\(_2\) by changing its production of organic acids. This may affect the proportions of different ligands to which Hg is bonded, thus influencing the photochemical reduction of Hg on lichen surfaces, which we suggest is the cause of the observed mass independent fractionation.

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FIGURE CAPTIONS

Figure 1. The concentration of Hg in lichens (in ng/g) versus the distance of the sample collection point from the center of the energy production activities (in km).

Figure 2. The $\delta^{202}\text{Hg}$ value of Hg in lichens (in permil) versus the distance of the sample collection point from the center of the energy production activities (in km).

Figure 3. The $\Delta^{199}\text{Hg}$ value of Hg in lichens (in permil) versus the distance of the sample collection point from the center of the energy production activities (in km).

Figure 4. The $\Delta^{199}\text{Hg}$ value of Hg in lichens (in permil) versus the $\Delta^{201}\text{Hg}$ value of Hg in lichens (in permil).

Figure 5. The $\Delta^{199}\text{Hg}$ value of Hg (in permil) versus the $\delta^{202}\text{Hg}$ value of Hg (in permil) in lichens as well as in a variety of geological materials from the AOSR region.
Figure 1.

![Graph showing the relationship between Total Hg (ng/L) and Distance from Center of Energy Production Activities (Km). The graph includes a trend line with the equation $y = 0.323x + 120$, and $R^2 = 0.190$, $p=0.0002$. Additionally, there is an analytical uncertainty band.]
Figure 2.

\[ y = -0.0007x + 1.84 \]

\[ R^2 = 0.0244 \]

\[ p = 0.350 \]
Figure 3.
Figure 4.

\[
\begin{align*}
\Delta^{\text{201}}\text{Hg (per mil)} & = 0.997x + 0.109 \\
R^2 & = 0.947 \\
p & < 0.0001
\end{align*}
\]
Figure 5.