Mercury Levels in Vegetation Growing on Contaminated Soils in Southwestern Montana

Thomas G. Waring, Environmental Engineering Department, Montana Tech of the University of Montana, Butte, MT 59701

Kristen M. Waring, School of Forestry, Northern Arizona University, P.O. Box 15018, Flagstaff, AZ 86011

Abstract

Contamination at former gold mine sites is common because mercury was used to extract gold by amalgamation of which some was lost to soils. Mobilization from soil to plants at these sites could result in high levels of mercury in plant tissues causing concern over spread of mercury through natural pathways such as grazing. We determined whether vegetation growing on three sites in southwestern Montana mobilized mercury from soil into roots or leaves. Two sites were known or suspected to have mercury contamination from past mining activity. The third site was an engineered repository for mining wastes. Soil mercury levels were highly elevated at the sites with past mining activity. Two grass species growing on the most contaminated site did not accumulate substantial amounts of mercury in either roots or leaves. Ponderosa pine (*Pinus ponderosa*) showed similar results (no accumulation) but we found Douglas-fir (*Pseudotsuga menziesii*) roots to have an accumulation of mercury. Repository soil had levels of mercury double the amount reported for U.S. topsoils, but levels in grass roots and leaves were not substantially elevated above soil levels. Hence, this repository is currently preventing movement of mercury from covered tailings into the vegetation on its surface. Species that were not accumulating mercury (thus not mobilizing mercury) could be utilized for vegetation rehabilitation on other mercury-contaminated sites.

Key Words: mercury, vegetation, soils, mining reclamation

Introduction

Mercury (Hg) has been used to amalgamate precious metals throughout history and was used extensively in Western U.S. gold fields including those in Montana. During 1850-1900, gold mining in the U.S. consumed an estimated 63 million kg of Hg (de Lacerda 1998). Efficiency of mercury utilization/recovery in gold processing was low and most estimates show a mass loss of mercury at least equivalent to the mass of gold recovered (de Lacerda 1998). Today, mercury is creating environmental concerns because there is potential for movement into food chains.

Many historical mining districts now have residual mercury in their environs – either from traditional milling and processing, or from placer mining operations. Placer mining operations often used mercury as an amalgam to remove gold from sand concentrates recovered during dredging operations (Lyden 1987). Mineral processing operations typically placed milled tailings into nearby drainages and floodplains. Some such tailings remain in place today. Flood events washed others down drainages and redeposited them. Some have been relocated into repositories.

Movement of mercury from soil into plants is a plausible scenario with variable pathways once in the plant. Mercury can be sequestered within plant tissues. In a broad study of a mine tailing field in Nova Scotia, Wong et al. (1999) found that several herbaceous plants accumulated mercury in addition to other heavy metals and suggested their use in phytoremediation. Alternatively, movement could occur through multiple pathways leading to wider mercury movement in the environment. Such pathways include consumption of vegetation by herbivorous or decomposer organisms that utilize dead plant components.

Patra and Sharma (2000) have discussed the wide variation in mercury uptake and movement within different plant species. Variation among plants followed by the uncertain pathways of mercury from plants into the environment provides a basis for research into these questions on a site-specific level. Few studies have documented plant mercury uptake. Without research specific to a site and vegetation present, it is difficult for land managers to provide restoration plans that utilize plants efficiently without causing further spread of mercury through the environment.

The objectives of this study were to determine whether different species (1) accumulated mercury when growing on contaminated soils, (2) varied in accumulation between roots and leaves, and (3) would be appropriate for revegetating contaminated sites.

Considerable research on the environmental movement and behavior of mercury has been published and summarized (U.S. Environmental Protection Agency 1997a, Nriagu 1994). Extensive research in aquatic environments has shown bioaccumulation of mercury in fish a widely recognized pollution problem (U.S. Environmental Protection Agency 1997b). Less research has been done regarding the movement of mercury in terrestrial ecosystems or uptake by plants. The bulk of the literature regarding mercury uptake by plants revolves around species of cultural or economic importance, such as garden vegetables or forest trees. Patra and Sharma (2000) reported that plant uptake through roots is correlated with the mercury level in the soil, i.e., plants exhibit higher mercury uptake at higher soil mercury levels. Comparatively, uptake for trees, especially in needles of conifers, seems as much related to atmospheric deposition as to soil concentrations (Patra and Sharma 2000).

Materials and Methods

Study Areas

We selected three field sites (Fig. 1): two sites with historical mining operations and a mine waste repository. The Silver Creek site, located approximately 24 km north of Helena, Montana, was extensively placer mined using hand and hydraulic methods from the mid 1860's until 1904 (Lyden 1987). Later in 1939-1940, a dragline dredge operation recovered gold from an estimated 1.1 million cubic meters of gravel in about a 3-km stretch of this stream bottom (Lyden 1987). The study site was located in this dredged area. Upstream about 6.5 km, mineral deposits were discovered near Marysville, Montana in 1875. The last mining activity in the drainage occurred from the mid 1970s thru 1986 in operations that reprocessed previously deposited tailings from the Marysville area. This site is contaminated with mercury. The U.S. Geological Survey reported in a survey paper that the mercury content of U.S. soils averages about 0.1 μg/g (U.S. Geological Survey 1970). It further reports that anomalies around the world's mercury deposits fall in a range of 10 to 100 μg/g. Studies by Sambathkumar (2002) and Nagulapaty (2001) found mercury concentrations from 0.06 to 30 μg/g in the Silver Creek Drainage.

The Ranch site was located ~1.6 km northwest of Silver Creek along Trinity Creek, an intermittent stream that had been placer mined as evidenced by gravel piles parallel to its path. This mining likely took place sometime from 1875 to 1921—the "period of greatest prosperity for the area" (Lyden 1987). We found no information to indicate whether mercury was used in the mining process along Trinity Creek.

The Comet site was a mine waste repository. The wastes came from the abandoned Comet Mine and mill near Basin, Montana. The last of its tailings and waste rock were moved in 2001 from the drainage below the mine into an engineered repository located near a ridge top about 1.6 km southeast of the mine.

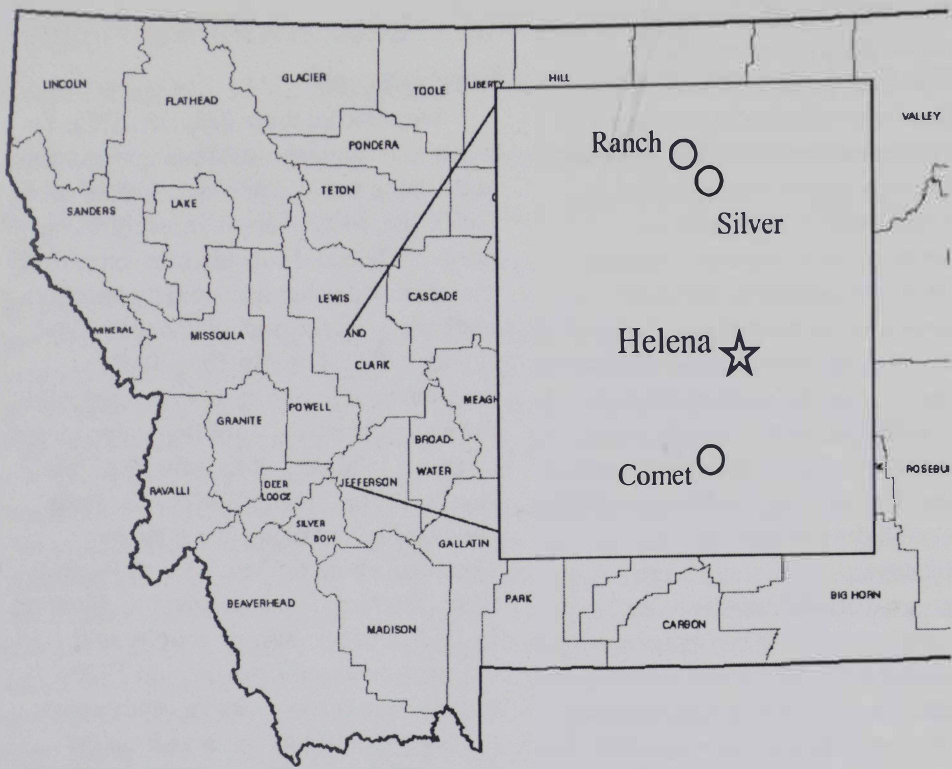

Fig 1. Location of three mercury contaminated mine sites in southwestern Montana. Helena is the state capital.

After relocation, the waste materials were covered sequentially with a geotextile cushion, a geosynthetic clay liner, a Geonoet filter fabric geocomposite, an organically amended cover soil and then with about 15-25 cm of topsoil salvaged earlier from the site (M. Browne, personal communication, April 2003). The cover soil was planted with a grass and forb seed mixture in fall 2001, and the area was fenced to prevent grazing. We chose this site to determine whether the repository was working as intended to prevent movement of mercury into the cover vegetation.

The climate of southwestern Montana is a cool and dry continental type. Wide seasonal and daily variations characterize temperatures. Daytime temperatures in winter average from 4 to 10 °C but may be as low as -20 °C. Daytime temperatures in summer typically range from 15 to 25 °C. The frost-free period averages ~ 70 days—mid-June to late August. Precipitation varies with location and altitude. There is a distinct spring/summer rainy season in May/June with an average of 89 mm of precipitation/month. Approximately half of annual precipitation falls as snow (U.S. Department of Commerce, NOAA.1988). The closest weather stations to the study sites were 6.4 km from Boulder, Montana (~ 240 m lower than the repository site) and at Austin, Montana (~ 6 km south of the Silver Creek site). Highest average monthly temperatures occur in July at both sites with temperatures of 17 °C at Austin and 18°C near Boulder. Lowest monthly temperatures occur in January with average temperatures of -7°C at Austin and -6°C at Boulder (U.S. Department of Commerce, NOAA. 1997). Precipitation isopleths indicate that the Silver and Ranch sites lie in the 41- to 46-cm precipitation zone, whereas the Comet repository site is in the 46- to 51-cm precipitation zone (U.S. Department of Agriculture 1977).

Field Procedures

Soil samples were obtained at 10- to 20-m intervals along transects crossing the approximately 20-ha sample areas. Each sample was collected at a depth of 10 to 20 cm using a spade to first lift the soil and then obtaining the sample with a plastic spoon. To avoid cross-contamination among samples, care was taken to only sample soil that had not contacted the shovel surface.

For each soil sample, we obtained a composite by combining eight sub-samples, which were collected by sampling at 1 and 2 m away from the center point in each cardinal direction. After obtaining all the sub-samples, we discarded the spoon and placed the sample on ice in the cooler for transport to the laboratory where it was frozen for later analysis. Samples were cooled and frozen to preserve mercury concentrations as collected.

We obtained vegetation samples at the same locations as the soil samples. Samples of leaves/needles were clipped directly into plastic sampling bags taking care to clip only leaves and avoid stems. New growth and one-year needles were separately sampled from ponderosa pine (*Pinus ponderosa*) and Douglas-fir (*Pseudotsuga menziesii*) trees. Scientific names of all plant species sampled appear in Table 2. We distinguished new growth needles from older needles by their lighter color. For root samples, the soil around selected plants was lifted as in the soil sampling above. We grasped roots with forceps and clipped with scissors into sampling bags. To avoid cross contamination among samples, the forceps and scissors were rinsed with acidified water and then with deionized water between each vegetative sample. Samples were placed on ice for transport to the laboratory and freezing.

All vegetative samples were composites taken from three to five plants of each species at each sample location. The number of plants composited into each sample varied because each sample location included variable numbers of plants and species. Sometimes there were no plants of some species. In such cases, we added sampling locations in which selected species occurred within the study area. Soils were also obtained at these added locations.

Laboratory Procedures

We analyzed samples for total mercury according to U.S. Environmental Protection Agency method 245.5 (U.S. Environmental Protection Agency 1991) using Cold Vapor Atomic Absorption Spectroscopy (CVAAS). The matrix for the CVAAS calibration standard was the same as used for sample preparation. We removed soil samples from the sampling bag, mixed, and placed in beakers to air dry. Upon reaching constant air-dry weight, the sample was mixed again. We placed samples of 0.2 g into a digestion bottle with 5.0 ml Aqua regia (3:1 conc. HCl:conc. HNO3) and heated for 2 min in a water bath of 95 °C. After cooling, 50 ml of de-ionized water and 15 ml of 5-percent w/v potassium permanganate solution were added, and the sample was mixed and placed into a 95 °C water bath for 30 min. After cooling, 6.0 ml of 35-percent w/v sodium chloride-hydroxylamine-hydrochloride solution and 55 ml of de-ionized water was added before filtering and measuring the final sample volume. The sample was then analyzed for total Hg using CVAAS.

Leaves and roots were rinsed with de-ionized water and dried. Upon reaching constant air-dry weight, the sample was fully mixed. Samples of 0.2 g were weighed and placed into a digestion bottle with 6 ml 35-percent hydrogen peroxide in a 95 °C water bath for 5 min. We then added 1.0 ml of 1:1 v/v concentrated nitric acid and the bottle returned to the water bath for ten min. After cooling, 50 ml of de-ionized water, 15 ml 5-percent w/v of potassium permanganate,

Table 1. Soil mercury concentrations at each study site.

Site	Hg (µg/g) Mean	Std. Dev	Range
Silver Creek	22.357	28.56	0.366-79.949
Comet Mine			
Soil cap	0.192	0.029	0.167-0.231
Tailings	0.924	0.084	0.820-1.02
Ranch	1.155	1.546	0.073-5.809

Table 2. Mercury concentrations by species and site, southwestern Montana.

Species	Site		Root Hg (µg/g)	Leaf Hg (µg/g)	Root/shoot ratio
Slender wheatgrass	Comet	N	5	5	
(Elymus trachycaulus)		Mean	0.01	0.013	0.8
		Std. Dev.	0.007	0.005	
	Ranch	N	5	5	
		Mean	0.003	0.005	0.6
		Std. Dev.	0.002	0.002	
	Silver	N	5	5	
		Mean	0.008	0.004	2.0
		Std. Dev.	0.011	0.003	
Needleandthread grass	Silver	N	5	5	
(Stipa comata var. comata)		Mean	0.027	0.006	4.5
		Std. Dev.	0.042	0.001	
Canada bluegrass	Comet	N	5	5	
(Poa compressa)		Mean	0.005	0.006	0.8
		Std. Dev.	0.005	0.003	
Big sagebrush	Ranch	N	5	3	
(Artemisia tridentata)		Mean	0.017	0.002	8.5
		Std. Dev.	0.021	0.002	
	Silver[1]	N	5	2	
		Mean	0.229	0.008	28.6
		Std. Dev.	0.375	0.011	
Skunkbrush	Ranch	N	4	5	
(Rhus trilobata)		Mean	0.003	0.001	3.0
		Std. Dev.	0.001	0.001	
	Silver[2]	N	4	4	
		Mean	0.104	0.001	104.0
		Std. Dev.	0.201	0.001	
Spotted knapweed	Ranch	N	4	6	
(Centaurea biebersteinii)		Mean	0.007	0.001	7.0
		Std. Dev.	0.007	0.001	
	Silver	N	5	4	
		Mean	0.012	0.075	0.2
		Std. Dev.	0.024	0.145	
Common yarrow	Comet	N	5	5	
(Achillea millefolium)		Mean	0.005	0.005	1.0
		Std. Dev.	0.003	0.004	
Ponderosa pine	Ranch	N	5	10	
(Pinus ponderosa)		Mean	0.003	0.001	3.0
		Std. Dev.	0.001	0.001	
	Silver	N	5	10	
		Mean	0.003	0.003	1.0
		Std. Dev.	0.002	0.002	
Douglas-fir	Ranch	N	4	9	
(Pseudotsuga menzeisii)		Mean	0.002	0.002	1.0
		Std. Dev.	0.001	0.001	
	Silver	N	9	10	
		Mean	0.061	0.002	30.5
		Std. Dev.	0.062	0.002	

[1].One outlier removed from root sample = 4.078 µg/g
[2].One outlier removed from root sample = 2.108 µg/g

5 ml of 0.25 M sulfuric acid, and 8 ml of 5-percent w/v potassium persulfate were added, the solution was then mixed and placed in the water bath at 95 °C for two hours. After cooling 50 ml of de-ionized water was added before filtering, volume measurement, and analysis for total Hg using CVAAS.

Data were compiled by species and site and graphically compared. Small and variable sample sizes precluded use of direct statistical comparisons between the three sites; however, correlations between mercury levels among plant components and soil were done across sites. We removed two extreme outliers from the data set prior to analysis. Both samples were from roots and likely contaminated by soil particles not removed during the lab cleansing procedure.

RESULTS

Mercury in field soils

We found highly elevated concentrations of mercury at the Silver Creek site, lower but still elevated levels at the Ranch Site, and the lowest levels in the cover soils at the Comet repository site (Table 1). Estimated worldwide concentrations of surface crustal mercury average 0.07 µg/g (Lindberg et al 1979) and 0.1 µg/g for US topsoil (U.S Geological Survey 1970). The average levels found at the three sites were 22.36 µg/g at Silver Creek, 1.16 µg/g at the Ranch Site and 0.19 µg/g at the Comet Repository. These respective levels were approximately 225, 12, and 2 times greater than the average U.S. topsoil levels (Fig. 2). Tailings beneath the Comet Repository soil cap and liner averaged 0.85 µg/g or approximately eight times greater than the U.S. topsoil level.

Mercury in vegetation

The vegetative species growing at the Silver Creek and nearby Ranch site were similar (Table 2); hence, it was possible to sample two in-common tree species and one in-common grass species at each site. The Comet repository had no trees and one in-common grass species, i.e., slender wheatgrass, with the other two sites.

The concentrations of mercury found in the leaves of the species sampled were highest at the Comet site and similar at the Silver and Ranch sites (Fig. 2). Root mercury concentrations were similar at the Comet and Ranch sites but much higher with more variation at the Silver site (Fig. 2). The only species common to the three areas was slender wheatgrass (*Elymus trachycaulus).* The higher soil concentrations at the Silver Creek and Ranch sites did not result in increased mercury concentrations in leaves or roots of slender wheatgrass (Table 2). Similarly, needleandthread (*Stipa comata*) at the ranch site and Canada bluegrass (*Poa compressa)* at the comet site did not have elevated mercury concentrations even though growing in soils with elevated mercury content.

The two species of trees studied were ponderosa pine and Douglas-fir. Like the grasses, ponderosa pine did not show elevated mercury levels in either roots or leaves (needles) even though the trees grew in the Silver Creek soils with mercury levels averaging > 22 µg/g (Table 2, Fig. 2). However, Douglas-fir trees had slightly elevated root and needle mercury levels. Ponderosa pine growing in the heavily contaminated Silver Creek site soils accumulated very low levels of mercury in their roots and even less in first and second year needles. Comparatively, Douglas-fir trees accumulated some mercury in their roots and far lesser amounts in their needles. Our results indicated that ponderosa pine could likely grow on mercury-contaminated soils without causing mercury accumulation in roots or shoots. However, Douglas-fir trees had a high (25 to 1) root to needle ratio of mercury showing that this species has the potential to mobilize mercury into roots.

One objective was to determine the root to shoot mercury levels of plants growing on these sites. Some research has found root/shoot ratios of mercury of approximately 10:1 (Lindberg et. al. 1979). At the Silver Creek site, we found high root/shoot ratios for the shrub species and Douglas-fir but

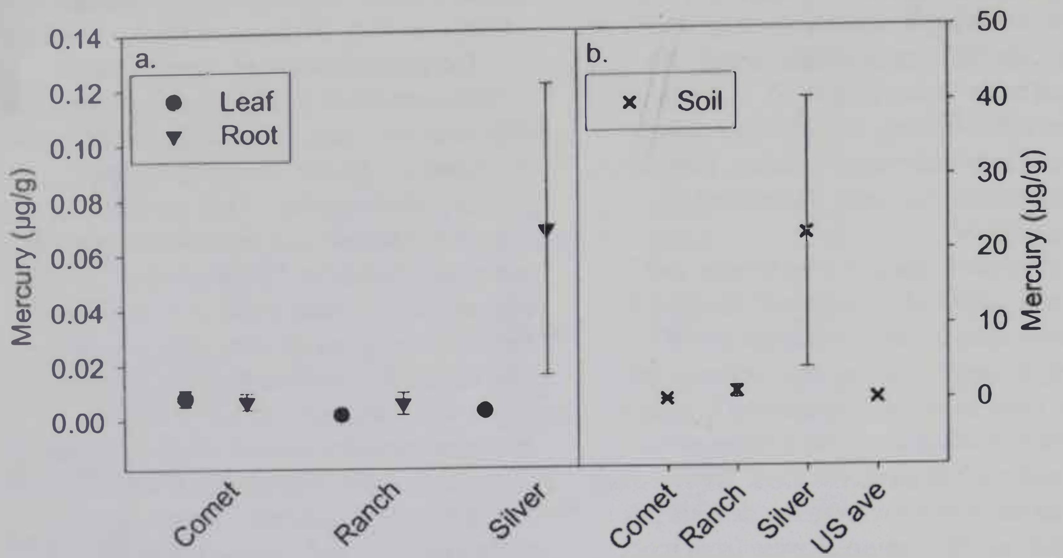

Figure 2. Mean mercury concentrations in roots and leaves at three contaminated sites in southwestern Montana; and b. comparative soil mercury concentrations at the same three sites and U.S. average topsoil (USGS, 1970). Points represent means; lines represent 95% confidence intervals.

not for the other species (Table 2). These results indicated that the three species with high root/shoot mercury ratios take up mercury into their roots but have a barrier that prevents transport of mercury from root to shoot. Correlations between root and soil mercury levels were significant (Pearson's = 0.408, $P = 0.002$) whereas the correlation between leaf and soil levels was only mildly so (Pearson's = 0.227, $P = 0.069$). The correlation between root and leaf mercury levels was quite low and not significant (Pearson's = 0.049, $P = 0.685$).

Discussion

Slender wheatgrass and needleandthread grass from the contaminated Silver Creek site did not accumulate large amounts of mercury in either roots or shoots. Likewise slender wheatgrass at the Comet site had low levels of mercury. Our findings indicated that these species could be used in revegetation of mercury-contaminated soils without danger of causing increased mercury mobilization.

We recommend that slender wheatgrass, needleandthread grass, and Canada bluegrass all be considered as acceptable grass species to be used in revegetating sites that might be contaminated with mercury. None of these species selectively accumulated mercury even though grown or growing on soils with elevated mercury concentrations. Similarly, ponderosa pine did not selectively accumulate mercury and could potentially be used to revegetate wastes containing mercury without the likelihood of mercury mobilization via roots or needles.

Vegetation type may impact movement of mercury throughout the plant. For example, Ellis and Eslick (1997) found correlations between root and leaf levels of mercury in shrubs and herbaceous species to soil mercury difficult to predict and highly variable on an abandoned mine site in Idaho. Barghigiani and Bauleo (1992) found levels of mercury in older leaves of silver fir (*Abies alba*) correlated with soil mercury. Overall correlations between root and soil and leaf and soil mercury were low in our study; however, we did not conduct species-specific correlations.

The techniques for reclaiming mining wastes used at the Comet Mine Repository appear to currently be preventing the movement of mercury from the covered wastes into vegetation. The long-term success of repositories in preventing the environmental movement of mercury or other metals could be demonstrated using the periodic assessment of on-site biomonitors like vegetation.

Rehabilitation of mine sites may include phytoremediation using plants known to accumulate toxic metals. The potential continued movement of accumulated metals through herbivory or decomposition may hinder such efforts. In non-woody plants, the root apparently provides a barrier to the movement of mercury throughout the plant since root levels of mercury are often on the order of 10 to 20 times levels in the leaves or shoot (Lindberg et al 1979). The root/shoot ratio of mercury could be important in the selection of species used in reclaiming mine wastes or revegetation of repositories as mercury that remains in the root is far less susceptible to movement through grazing, wind or water. Further study of the levels of mercury in vegetation growing on mercury contaminated soils is warranted to find other species that do not accumulate the metal and that could be used as restoration species on contaminated sites.

Conclusions

1. Slender wheatgrass, needle-and-thread, and Canada bluegrass should be considered for revegetation on mercury contaminated soils because they did not accumulate mercury when growing on sites with elevated mercury concentrations.
2. Ponderosa pine did not accumulate mercury when growing on a contaminated site and could also be used to revegetate wastes containing mercury without the likelihood of mercury mobilization via roots or needles.
3. The techniques for reclaiming mining wastes used at the Comet Mine Repository are currently preventing movement of mercury from covered wastes into vegetation.
4. Further study of mercury concentrations in vegetation growing on mercury contaminated soils is warranted to find other species that do not accumulate the metal and which could be used as restoration species on contaminated sites.

Acknowledgements

This study was funded by the U.S. Environmental Protection Agency through its Office of Research and Development under IAG DW89938870-01-0 through the U.S. Department of Energy (DOE) National Energy Technology Laboratory under Contract DE-AC22-96EW96405 and implemented by MSE Technology Applications, Inc. The authors thank Trisha Smith for field and laboratory assistance.

Literature Cited

Barghigiani, C., and R. Bauleo. 1992. Mining area environmental mercury assessment using *Abies alba*. Bulletin of Environmental Contamination and Toxicology 49:31-36.

de Lacerda, L. D. 1998. Mercury from gold and silver mining: a chemical time bomb? Springer-Verlag. Heidelberg, Germany. 146 pp.

Ellis, R. W., and L. Eslick. 1997. Variation and range of mercury uptake into plants at a mercury-contaminated abandoned mine site. Bulletin of Environmental Contamination and Toxicology 59: 763-769.

Lindberg, S. E., D. R. Jackson, J. W. Huckabee, S. A. Jansen, M. J. Levin, and J. R. Lund. 1979. Atmospheric emission and plant uptake of mercury from agricultural soils near the Almaden mercury mine. Journal of Environmental Quality 8:572-578.

Lyden, C. H. 1987. Gold placers of Montana. Montana Bureau of Mines and Geology, Reprint 6. 120 pp.

Nagulapaty, S. 2001. Methyl mercury: analytical methods and evaluation in aged gold mine tailings. MS Thesis, Montana Tech of the University of Montana. 99 pp.

Nriagu, J. O. 1994. Mercury pollution from past mining of silver and gold in the Americas. Science of theTotal Environment. 149:167-181.

Patra, M., and A. Sharma, 2000. Mercury toxicity in plants. The Botanical Review. 66:379-422.

Sambathkumar, S. 2002. Estimation of mercury flux from abandoned gold mine tailings in Montana. MS Thesis, Montana Tech of the University of Montana. 86 pp.

USDA Soil Conservation Service and the Montana Department of Natural Resources and Conservation. 1977. Average Annual Precipitation – Montana. Sheet 8 of 13.

U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA) 1988. Local climatological data, annual summary with comparative data, Helena, MT.

U.S. Department of Commerce, National Oceanic and Atmospheric Administration (NOAA) 1997. Local climatological data, annual summary with comparative data, Helena, MT.

U.S. Environmental Protection Agency. 1991. Methods for the Determination of Metals in Environmental Samples. EPA-600/4-91-010.

U.S. Environmental Protection Agency. 1997a. Mercury Study Report to Congress. EPA- 452/R-97-0003.

U.S. Environmental Protection Agency. 1997b. Mercury Study Report to Congress. Vol. IV. An Assessment of Exposure to Mercury in the United States. EPA-452/R-97-006.

U.S. Geological Survey. 1970. Mercury in the environment. USGS Professional Paper 713.

Wong, H. K. T., A. Gauthier, and J. O. Nriagu. 1999. Dispersion and toxicity of metals from abandoned gold mine tailings at Goldenville, Nova Scotia, Canada. Science of the Total Environment. 228: 35-47.

Received 1 March 2006
Accepted 24 July 2006