Application of three methods for determining mercury speciation in mine waste

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ABSTRACT: Three methods, pyrolytic and chemical extractions (PCE), extended X-ray adsorption fine structure spectroscopy (EXAFS) and solid-phase-Hg-thermo-desorption (SPTD) were applied to determine mercury speciation in amended substrates and mine waste samples. Although these three methods determine Hg speciation by fundamentally different processes, comparison of the results are useful for validation of the three methods. PCE uses pyrolysis and weak leaches to determine relative percentages of volatile, 'soluble' and residual Hg in substrate. The results are operationally defined and specific species cannot be determined with this method. EXAFS is a nondestructive method which uses high energy synchrotron-sourced X-ray radiation to identify specific species based on scattering patterns. Least squares data analysis is done to link patterns to a database of model compounds. This method is most useful for identification of specific species, given that they are included in the model database. Identification of Hg^0 is difficult using EXAFS. SPTD identifies Hg species by incremental heating and comparison of thermal release patterns to a database of compounds. SPTD allows the identification of a more limited number of specific species than EXAFS, but is the best of the three methods for the identification of Hg^0. Overlapping release patterns make the identification of species, such as HgS and some forms of matrix-bound Hg, difficult.

Results of PCE analyses indicate that volatile and leachable forms of Hg in mine waste are low relative to the total Hg concentration. This was supported by EXAFS and SPTD analysis which identified HgS as the primary component of mine waste. In contrast, analysis of tailings from mills that utilized Hg to amalgamate Au and Ag from ores yielded conflicting results. The results of this study illustrate the importance of using multiple analytical methods for the evaluation of Hg in the substrate.

KEYWORDS: *mercury, mine waste, speciation, EXAFS, pyrolysis, selective extraction*

INTRODUCTION

Published methods for Hg speciation in a substrate include sequential extractions (Revis *et al.* 1990; Lechler *et al.* 1997; Wallschlager *et al.* 1998), solid-phase-Hg-thermo-desorption (SPTD) (Biester & Scholz 1997) and extended X-ray adsorption fine structure (EXAFS) spectroscopy (Kim *et al.* 2000). Sequential extraction methods, unless derived for specific substrates and carefully tested, may not be appropriate for determining Hg forms or binding sites in substrates (Sladek & Gustin 2002). Nirel & Morel (1990) stressed that results of sequential extractions for most trace elements have not been validated, and indiscriminate application of a method will produce meaningless results. Discrepancies of greater than 50% were noted in Hg analyses performed on samples from the Carson River Superfund Site, NV, by separate labs (Hogan & Smucker 1994). This degree of uncertainty indicates the need for critical evaluation of Hg speciation methods and their uses. Sladek & Gustin (2002) suggested that pyrolytic and chemical extractions (PCE) are best applied for determining the potential for Hg to be released from a substrate by volatilization or leaching. They found that pyrolysis at 80°C for 8 h efficiently removed elemental Hg (Hg^0) but small amounts (1–3%) of organic matter significantly reduced extraction efficiency. Pyrolysis was also found to remove a significant amount of amended $HgCl_2$.

The EXAFS spectroscopy method, which identifies Hg compounds by X-ray scattering patterns, represents the most recent advance in identification of specific Hg species. This method entails the bombardment of a sample with high energy X-rays generating photoelectrons from a specific element. The generation of photelectrons induces specific electronic scattering interactions between a central absorbing atom and

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Table 1. *Descriptions of samples used for assessment of speciation methods indicating rock type, type of mine and deposit type*

Sample and location or mining district	Description	Host rock	Mine and deposit type
Amended natural substratesr			
Pyramid Lake, NV (PLS)	Fine-grained sand amended with Hg^0, HgO, $HgCl_2$, and HgS	Igneous	None
Naturally enriched rock and soil			
McLaughlin Mine (Knoxville district, CA)	C horizon, partially reclaimed mine	Sedimentary	Hg–Au, silica-carbonate
Read Mine (Knoxville district, CA)	C horizon, partially reclaimed mine	Serpentinite	Hg, silica-carbonate
Silver Cloud Mine, NV	Waste rock	Volcaniclastic	Hg, hot spring
Clear Creek (New Idria district, CA)	C horizon, peripheral to mining	Serpentinite	Hg, silica-carbonate
San Carlos Mine, CA (New Idria district, CA)	C horizon, overburden from mine	Serpentinite	Hg, silica-carbonate
Calcines			
Aurora Mine (New Idria district, CA)	Dark red calcine	Serpentinite	Hg, silica-carbonate
New Idria Mine (New Idria district, CA)	Dark brownish red calcine	Sedimentary	Hg, silica-carbonate
Knoxville Mine (Knoxville district, CA)	Dark red calcine	Serpentinite	Hg, silica-carbonate
Turkey Run Mine (Knoxville district, CA)	Yellow brown calcine	Serpentinite	Hg, silica-carbonate
Tailings from amalgamation mills in the Carson River Superfund Site			
	Fine grained tailings	Igneous	
Park and Bowie Mill (Comstock district, NV)	Mill used for reprocessing tailings		Ag–Au, epithermal vein
Bessels Mill (Comstock district, NV)	Mill used to process local ores		

Silica-carbonate is an alteration by CO_2-rich fluids associated with serpentnite bodies (Rytuba 1993).

neighbouring atoms (Brown *et al.* 1988). The energy absorbed and the electron scattering can be used to derive molecular scale information. Kim *et al.* (2000) applied EXAFS methods for determining Hg speciation of Hg mine waste and found that specific Hg species were associated with different deposit types. In a comparison of EXAFS with a selective extraction method, Bloom & Katon (2000) found consistent results.

Biester & Scholtz (1997) applied pyrolysis, or incremental heating of a sample at a specific rate, to identify specific Hg species amended as pure dry compounds to quartz powder, and no difference in results was obtained when Hg compounds were added to soils uncontaminated by Hg. However, they found that pure Hg species added in solution to soils resulted in identification of additional matrix-bound Hg species. They suggested that this indicated a change in the oxidation state of the Hg added and/or binding to a variety of inorganic or organic soil components. They compared thermo-desorption results with results of a sequential extraction method and found that SPTD was able to discriminate specific Hg species, while the sequential extraction identified most of the Hg as being in the residual phase. This paper discusses the results of the application of PCE, EXAFS and SPTD for determining Hg speciation in substrate.

METHODS

Samples

Samples analysed consisted of sand from Pyramid Lake, NV, amended separately with Hg^0 (Fisher Scientific), $HgCl_2$ (Sigma Aldrich), HgO (Sigma Aldrich) and HgS (Sigma Aldrich), and substrates geologically and anthropogenically enriched in Hg (Table 1). Amended substrates were made by placing 1 kg of the Pyramid Lake sand (composed largely of quartz, feldspars, micas and minor clay minerals) and the Hg compound in a 2.5 l bottle, purging with argon and rolling on a bottle roller for 24 h to homogenize the mixture.

PCE analyses (Sladek & Gustin 2002) were performed at the University of Nevada (Reno, Nevada). Sample splits were distributed to Chris Kim at Stanford University, California, for EXAFS analysis (Kim *et al.* 2000) and Harald Biester at the Institute of Environmental Chemistry, Heidelberg, Germany, for SPTD analysis (Biester & Scholz 1997).

PCE method

The PCE extraction method applied in this paper was developed in the process of evaluating sequential extraction methods for the identification of Hg species in mine waste (Sladek & Gustin 2002). The PCE method removes volatile Hg from a substrate by heating a sample and collecting the evolved Hg on carbon traps. Soluble and residual Hg species are quantified by the use of chemical extractions. The amount of Hg extracted by these procedures is a function of the Hg species present and the substrate composition. For the pyrolytic extraction a 1 g sample aliquot is placed in a 25 ml Teflon® vessel and heated at 80°C for 8 h. Volatilized Hg is purged with N_2 carrier gas and collected on an iodated carbon trap. Mercury collected on the trap is then removed by placing the charcoal and 5 ml of 3 $HNO_3 : 1\ H_2SO_4$ in a 50 ml volumetric flask and digesting at 125°C. Bromine monochloride, which extracts a further fraction of the Hg, is added as a preservative after cooling. No significant breakthrough was found to occur for Hg loaded onto the charcoal traps and charcoal was found to release *c.* 97% of amended Hg.

The extraction to remove soluble species entails placing a 1 g sample in a 50 ml Teflon® vial to which 15 ml of 0.5M NH_4Cl are added. The vial is shaken and allowed to equilibrate overnight. The leachate and solids are separated by centrifuging and filtering through a 0.45 μm syringe filter. The leachate is then acidified with 3 ml of 16M HNO_3. After the pyrolytic and soluble species extractions, residual Hg is removed by hot aqua regia digestion. Extraction solutions are stored in 50 ml volumetric flasks and brought up to volume with 20% HCl before analysis. Mercury concentration is determined using a Varian SpectrAA model 220 Atomic Absorption Spectrometer (AAS). Sodium borohydride is used as the reductant and the closed cell analyser tube is heated to eliminate interference by water vapour (Sladek & Gustin 2002). This method can be used to quantitatively determine volatile, 'soluble' and total Hg fractions as low as 25 $ng\,g^{-1}$ for 1 g samples or 2.5 $ng\,g^{-1}$ for 10 g samples. Additional extractions can be used to determine other environmentally significant Hg fractions, such as methyl Hg or organically bound Hg (cf. Wallschlager *et al.* 1998).

Quality control for PCE analysis included analysis of the NIST San Joaquin standard ($1.4 \pm 0.08\ \mu g\,g^{-1}$Hg) with an error of <6% ($n = 15$). Reagent blanks were <0.2 ng. Reporting

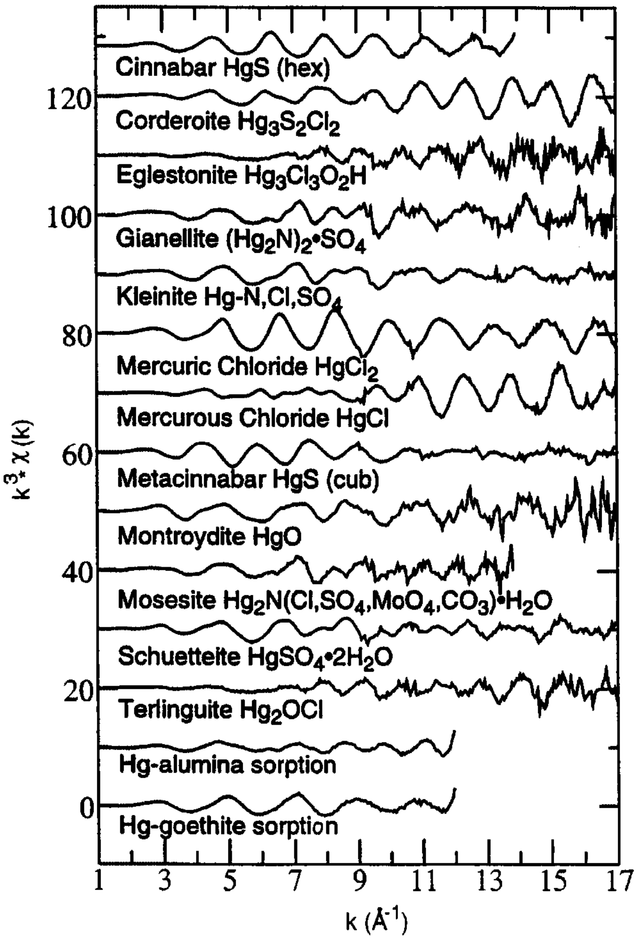

Fig. 1. EXAFS spectra for Hg minerals and adsorbed phases. The horizontal axis represents the conversion of energy to momentum space. The vertical axis is a *k*-cubed weighted expression of the EXAFS function (adapted from Kim *et al.* 2000).

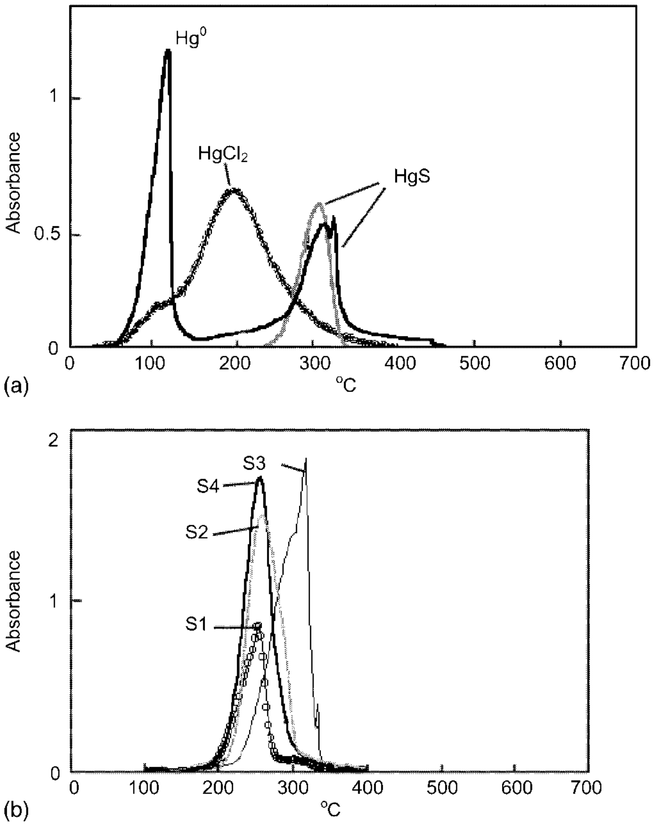

Fig. 2. SPTD release patterns for (**a**) inorganic Hg species. Patterns show the amount of Hg released versus temperature ramped at 0.5 °C s^{-1}. In (a) Combined Hg^0 and HgS pattern is for Hg^0–HgS sample from Almaden, Spain. HgS pattern (grey) is for synthetic HgS, (Merck) and (**b**) for Hg in humic acids (S1), synthetic red cinnabar (S2), red cinnabar from Almaden (S3) and metacinnabar (S4). ((a) adapted from Biester & Scholz 1997; (b) from Biester & Scholz 2000).

limit was 0.5 ng ml^{-1} and analytical precision for replicate analysis was ± 1.8% ($n = 18$).

EXAFS method

The EXAFS spectroscopy method (Kim *et al.* 2000) is a direct method of identifying specific Hg compounds in substrates with concentrations greater than 100 μg g^{-1}. Analysis by EXAFS involves using high-energy X-ray radiation from synchrotron sources to collect X-ray absorption spectra that detail the specific scattering interactions between the central absorbing Hg atoms and their first- and second-shell neighbouring atoms. An EXAFS spectrum from a homogeneous Hg species is used as a unique ‘fingerprint’ for that species which will enable its identification in unknown samples. Mercury species in natural substrates are determined by deconvoluting the EXAFS spectrum collected for the heterogeneous natural sample into the sum of its individual component species. This is done using linear least squares fitting of the patterns for the sample being analysed to a spectral database of pure Hg compounds and Hg sorbed onto synthetic oxides (Fig. 1). Multiple species are identified by an iterative process until no significant contributors remain (Kim *et al.* 2000). Quantitative determination of species concentrations is made by scaling the results to the total Hg content determined by a method such as aqua regia digestion and cold vapour atomic fluorescence spectroscopy (Kim *et al.* 2000). Limitations of this method include: a minimum Hg concentration of 100 μg g^{-1}; specific Hg species must be in the EXAFS spectral database for correct identification; and quantitative accuracy of the proportions of individual species present may vary by ± 15%, making identification of minor phases difficult. Sample size is limited to 200 mg and samples must be powdered for homogeneity.

SPTD method

SPTD (Biester & Scholz 1997) is an indirect method in which Hg species are determined by thermal desorption or decomposition temperatures. This method has a detection limit of 0.2 μg g^{-1}Hg and a maximum sample size of 200 mg. In SPTD analysis, the sample is placed in a quartz furnace and heated at a rate of 0.5°C s^{-1}. Volatilized Hg compounds are carried from the furnace with N_2 and reduced to Hg^0 by thermal reduction in a quartz tube heated to 800°C and subsequently analysed by flameless AAS. This method produces temperature-dependent Hg release curves that are species- and matrix-specific (Fig. 2). These release curves enable identification of species such as Hg^0, $HgCl_2$, HgO, HgS and matrix-bound Hg by comparison to pure Hg phases and reference materials. A quantitative determination of specific species can be made by peak integration (Biester *et al.* 2000). This method does not allow for the identification of as wide a variety of specific Hg species as EXAFS. It is also very difficult to distinguish between HgS and organically bound phases. Because of this, Biester *et al.*

Table 2. *Results of PCE, EXAFS and SPTD analysis of substrates amended, naturally enriched or anthropogenically contaminated with Hg*

Sample	PCE			EXAFS	SPTD
	Volatile %	Soluble %	Total μg g^{-1}		
Pyramid Lake sand amended with Hg compounds					
Hg^0	27.5 ± 1.3	38.0	127 ± 5	Concentrations too low for EXAFS analysis.	Hg^0 and matrix-bound Hg
$HgCl_2$	6.00 ± 0.29	73.9 ± 0.3	142 ± 1		Mostly $HgCl_2$, some elemental
HgO	0.51 ± 0.18	66.1 ± 5.4	93.2 ± 11.1		HgO
HgS	0.002	0.49 ± 0.03	81		HgS, some appears to be m-HgS
Soil and rock naturally enriched in Hg from CA and NV Hg mining areas					
McLaughlin Knoxville dist.	0.08 ± 0.02	0.12 ± 0.04	99.1 ± 1.9	48% HgS, 25% m-HgS 28% HgO	Most matrix + HgS
Reed Mine Knoxville dist.	0.71	<0.02	112 ± 22	61% HgS, 25% m-HgS 19% $Hg_3O_2SO_4$	HgS and smaller amounts of matrix-bound Hg
Silver Cloud	0.44 ± .05	0.0066	4560 ± 392	84% HgS 16% $HgCl_2$	HgS
San Carlos New Idria dist.	0.07 ± 0.03	0.33 ± 0.13	455 ± 58	74% HgS 26% $HgCl_2$	—
Clear Creek New Idria dist.	0.26 ± 0.03	0.07 ± 0.01	154 ± 14	89% HgS 11% $HgCl_2$	HgS
Calcine samples from CA mercury mines					
Aurora New Idria dist.	0.68 ± 0.07	2.45 ± 0.05	512 ± 39	18% HgS, 56% m-HgS 26% HgO	—
New Idria New Idria dist.	0.06 ± 0.01	4.12 ± 0.47	313 ± 43	62% HgS 38% $Hg_3O_2SO_4$	—
Knoxville Knoxville dist.	<0.1	<0.01	208 ± 41	54% HgS, 34% m-HgS 12% $HgCl_2$	Matrix-bound organic or FeOx Mostly HgS
Turkey run Knoxville dist.	0.005 ± 0.002	0.01	613 ± 1	58% HgS 42% m HgS	—
Tailings contaminated with Hg from mill sites in the Comstock district, NV					
Parke and Bowie Mill	0.04	0.16 ± 0.01	245 ± 10	70% HgS 30% m HgS	Matrix-bound Hg
Bessels Mill	0.2	2.72 ± 0.08	1070 ± 60	—	Matrix-bound Hg

Values for pyrolitic and leach extractions are percent of total Hg extracted. HgS indicates hexagonal or red cinnabar and m-HgS, cubic or metacinnabar. Samples that were not analysed are indicated by '—'

(2000) combined selective extractions to assess the presence of organically bound Hg with SPTD analysis.

Additional analysis

Backscatter and energy dispersive X-ray analyses (EDS) using a Jeol 840 scanning electron microscope (SEM) were conducted on polished thin sections and grain mounts of sieved and panned concentrates of amalgamation mill tailings from the Carson River Superfund Site. Since EDS analyses are qualitative, HgS and Ag_2S standards, and an unprocessed ore sample were used for comparative analyses. Water-soluble chloride analysis for naturally enriched substrates and mine waste were performed by the Nevada Bureau of Mines and Geology. The process consisted of leaching a 1 g sample in 10 ml of distilled water at 100°C for 1 h and analysis by ion chromatography using a Dionex Model 2000i/SP.

RESULTS AND DISCUSSION

Table 2 lists the results of speciation analysis by the three methods. The amounts of Hg extracted by the PCE method and Hg species identified by EXAFS and SPTD are shown as a percentage of total Hg. Total Hg values are the mean of triplicate analyses determined by the PCE method (sum of 'soluble' and residual Hg).

Amended samples

Analysis of Hg-amended Pyramid lake sand by PCE indicated that volatility decreases in the manner $Hg^0 > HgCl_2 > HgO > HgS$, and solubility decreases with $HgCl_2 > HgO > Hg^0 > HgS$. Mercury concentrations of these samples were too low for EXAFS analysis. Results of analysis of these amended samples by SPTD were generally consistent with respect to the species added with minor amounts of additional Hg phases reported for a few samples (Fig. 3). Some of the Hg in the HgS-amended sample was released at the temperature range of metacinnabar (m-HgS) decomposition, and for the Hg^0-amended sample, analysis indicated that most of the amended Hg^0 was elemental but some of it had become matrix bound. The amount of Hg removed in the pyrolytic extraction of the Hg^0-amended sample was very low (27.5%), with an additional (31.2%) extracted as 'soluble' Hg. These observations indicate that a change in the oxidation state of some of the Hg^0 occurred during amendment or storage. Bloom & Katon (2000) found that Hg species amended to natural samples equilibrated according to the physiochemical characteristics of the substrate.

Geologically-enriched samples

The PCE extractions of geologically-enriched samples yielded less than 1% of the Hg as volatile and 'soluble' Hg (Table 2). Analysis by EXAFS and SPTD methods indicated that the

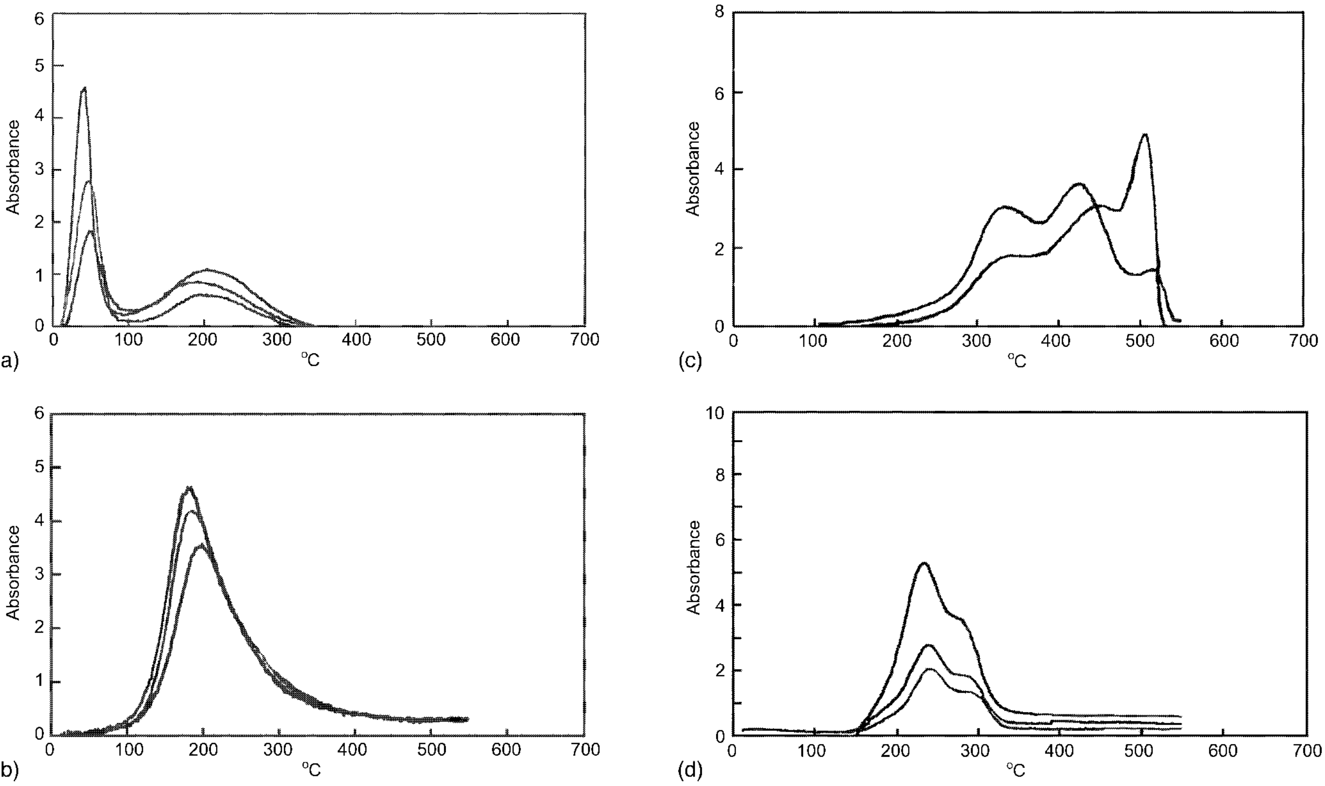

Fig. 3. SPTD release curve for (**a**) Hg^0 amended Pyramid Lake sand, (the peak at 200 °C indicates some of the Hg is matrix-bound); (**b**) $HgCl_2$-amended Pyramid Lake sand; (**c**) HgO-amended Pyramid lake sand; (**d**) HgS-amended Pyramid Lake sand, (release character is suggestive of m-HgS).

geologically-enriched samples were dominantly HgS and m-HgS. Results of EXAFS analysis also identified HgO, $HgSO_4 \cdot 2HgO$ and $HgCl_2$ in some of these samples.

Analysis by SPTD indicated that the Reed Mine and McLaughlin samples contained matrix-bound (organic compounds or iron oxides) Hg. Volatile Hg was highest for the Reed Mine relative to the other samples. EXAFS analysis identified $HgCl_2$ in the Silver Cloud, San Carlos and Clear Creek samples and 19% $HgSO_4 \cdot 2HgO$ in the Reed Mine sample. The San Carlos sample with 26% $HgCl_2$ (EXAFS) had the highest 'soluble' Hg. However, PCE extractions removed less Hg than expected given the percent of $HgCl_2$ identified by EXAFS analysis. Mercury chloride was not identified in either the Silver Cloud or Clear Creek samples by SPTD analysis. This, together with the low PCE 'soluble' Hg results, suggests that the $HgCl_2$ identification is likely due to current limitations in the EXAFS data library, but does not preclude some form of Hg-Cl being present. Cinnabar from the Silver Cloud mine has been demonstrated to contain Cl (McCormack 2000), and may have resulted in identification of $HgCl_2$ by EXAFS. Lower than expected PCE 'soluble' extractions in samples for which SPTD identified matrix-bound species may be due to strong matrix binding, Hg encapsulation within the sample, or insufficient strength of the NH_4Cl leach to liberate tightly bound Hg-Cl species. An additional factor that may have influenced comparison of results is that samples analysed by EXAFS and SPTD were crushed. All samples analysed by PCE, except for the Silver Cloud sample were not crushed. This may have resulted in PCE extractions removing Hg associated only with grain surfaces, and EXAFS and SPTD determining Hg speciation reflecting the bulk composition.

Calcine samples

Volatile Hg determined using PCE for all calcines was less than 1%, and 'soluble' Hg ranged from below detection limit (25 ng g^{-1}) to over 4% of total Hg. Similar to the naturally enriched samples, EXAFS and SPTD analysis indicated that Hg in the calcines is dominantly HgS and m-HgS. Again, PCE 'soluble' Hg was lower than expected for samples identified by EXAFS to contain Hg phases with higher solubility. The Aurora and New Idria samples had the highest 'soluble' Hg and were found to contain HgO and $HgSO_4 \cdot 2HgO$ by EXAFS analysis. The Knoxville sample which contains 12% $HgCl_2$ (EXAFS) had very low 'soluble' Hg and was found to contain matrix-bound Hg by SPTD analysis. Rytuba (2000) indicated that 'soluble' Hg in water impacted by mining in the New Idria mining district is sequestered by the precipitation of carbonate and silicate minerals. Such a process could result in masking soluble or exchangeable Hg species from weak leaches such as NH_4Cl.

Mill tailings

Mercury in the Carson River mill tailings samples was initially assumed to be Hg^0 in the form of amalgams based on the high percentage of Hg^0 determined to be in Carson River sediments downstream of the sample sites for this study by Lechler *et al.* (1997). However, a lower percentage of volatile Hg in the tailings analysed in this study relative to that determined by Lechler *et al.* (1997) may be due to the lower pyrolytic extraction temperature (80°C verses 180°C) and shorter extraction duration (8 h verses 48 h), and/or the fact that the tailings analysed for the two studies are from different sites. PCE extractions of Parke and Bowie mill tailings indicated a volatile fraction of

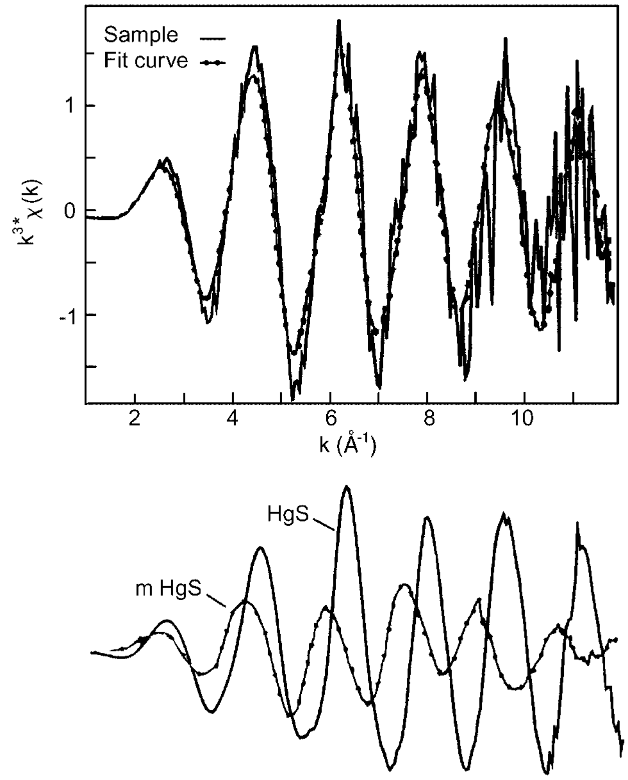

Fig. 4. EXAFS pattern for Parke and Bowie tailings showing fitting of metacinnabar (m-HgS) and cinnabar. The horizontal axis represents the conversion of energy to momentum space. The vertical axis is a *k*-cubed weighted expression of the EXAFS function.

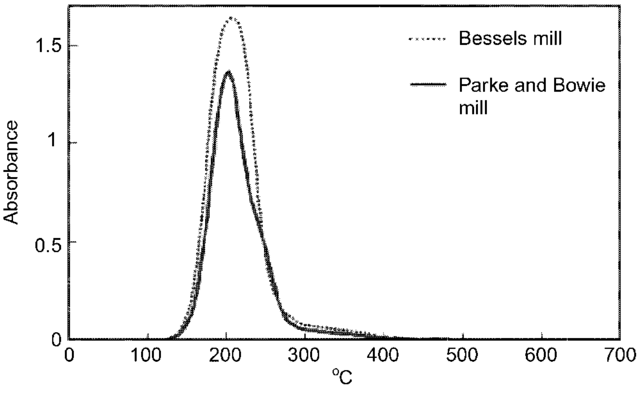

Fig. 5. SPTD release patterns for Bessels, and Parke and Bowie mill tailings.

0.04% and a 'soluble' fraction of 0.16%. EXAFS analysis identified HgS and m-HgS (Fig. 4) and SPTD analysis identified a form of matrix-bound Hg; however, release curves were not typical of Hg bound to organic compounds or iron oxides (Fig. 5). The EXAFS pattern in Figure 4 is shown for illustration only, for the phases cannot be identified graphically but by least squares fitting of the sample pattern to the model database.

Elemental Hg was the form amended to the ore at the Carson River Superfund site. However, little Hg was removed in the pyrolitic extraction, and HgS was identified by EXAFS and matrix-bound Hg by SPTD, suggesting that Hg now present in the tailings is not dominantly elemental Hg. To further investigate the form of Hg in the tailings, polished thin sections and grain mounts were anlayzed using petrographic and SEM-EDS methods.

The primary ore minerals of the Comstock mining district (part of the Carson River Superfund Site) are the silver sulphide, acanthite (Ag_2S), and electrum (an Au–Ag alloy). Pyrite (FeS_2) and other sulphides are also common (Lincoln 1923). The Washoe amalgamation process was the most widely used by mills that were located in the Comstock mining district (Smith 1943). The chemistry for the Washoe Process is similar to that of the Patio Process as described by Thompson (1991). In the Washoe Process, crushed ore, Hg^0, NaCl and $CuSO_4$ were mixed in large heated iron pans. The primary reactions involved the conversion of Ag_2S to AgCl. Large quantities of NaCl would maintain Ag as a soluble chloride complex ($AgCl_x^{-(x-1)}$). The $AgCl_x^{-(x-1)}$ was then reduced by Fe from the pans to form Ag^0 which was amalgamated by Hg^0. Silver and Au were then recovered by retorting the Hg from the amalgam product.

EDS analysis of two polished thin sections and five grain mount slides indicated that Hg was primarily associated with altered acanthite or altered acanthite containing Au inclusions. Acanthite in the tailings was found to be depleted in Ag when compared to acanthite identified in an unprocessed ore sample and an Ag_2S standard. Fourteen phases containing Ag, Hg and S ± Au were identified with varying ratios of Ag to the Hg + S peak. Since the Hg M α and β peaks overlap the S Kα1 peak, the occurrence of Hg in association with Ag_2S was confirmed by the presence of the Hg L α and β peaks between 9.5 keV and 12 keV. Other phases that were identified include Hg associated with pyrite ($n = 5$), amalgams of Ag and/or Au ($n = 3$) and HgS with no detectable Ag ($n = 3$). Trace amounts of Cl were found in some of the mineral phases where Hg was observed. The Hg-containing phases ranged in size from 3 μm to 40 μm. Most of the Hg phases were attached to much larger quartz particles but several were free of matrix.

Inefficient conversion of acanthite to $AgCl_x^{-(x-1)}$ by mills using the Washoe process could result in the Ag-depleted acanthite identified by EDS analysis. Excess S, resulting from the Ag depletion, may have provided sites for Hg to bind, resulting in the Hg–Ag–S association identified by EDS analysis.

The absence of Ag and Fe sulphide phases in the EXAFS database, along with the association of Hg with S phases and/or sulphide minerals, may have resulted in the identification of HgS as the dominant species in tailings by EXAFS analysis. The matrix-bound Hg identified by SPTD analysis may reflect the release curves for amalgams or Hg associated with Ag sulphides.

The differences in results of PCE analysis for the two tailings samples (Table 2) is probably a result of different milling processes or grain size differences. Reprocessing of tailings by the Parke and Bowie (Ansari 1989) mill may have resulted in removal of the more volatile and soluble Hg. This mill may have been more efficient than other mills since it was extracting the precious metals from ore that had previously been processed (tailings). Alternatively the finer-grain-size of the Bessels mill tailings may have provided greater surface area for retention of volatile and 'soluble' phases (Sladek & Gustin 2002).

The PCE extractions used in this study have the potential to provide valuable information about the volatility and solubility of Hg in a substrate, but further evaluation should be conducted to determine how the results relate to natural releases. A comparison of the pyrolytic extraction of Hg from samples collected at a site where *in situ* Hg emissions were measured indicate that the pyrolytic extraction removed Hg at a rate *c.* 250-fold that of the measured *in situ* vapour flux (Sladek &

Gustin 2002). In addition, comparison of the NH_4Cl leach results of calcine from New Idria to concentrations of Hg in surface water (Rytuba 2000) indicates the NH_4Cl leach may over-estimate the Hg removed by natural leaching by as much as 20-fold.

CONCLUSIONS

Each of the methods applied in this study gives valuable information regarding Hg speciation in mine waste. If determination of the Hg species and binding forms is the primary intent, EXAFS and SPTD are the most appropriate. The EXAFS method determines individual Hg species; however, the detection limit is high ($> 100\,\mu g\,g^{-1}$) and identification of individual species in samples which contain a great number of Hg compounds may be difficult. At present, SPTD appears to be the best method for identifying Hg^0. Elemental Hg can be identified by EXAFS, but if other crystalline Hg phases are present their contribution to the EXAFS spectrum will tend to mask the spectral contribution of Hg^0. Pyrolytic extractions of Hg^0 are highly influenced by sample matrix.

If the environmental mobility of Hg in a substrate is the most crucial information needed, PCE or similar extraction methods should be applied. Data obtained by EXAFS and SPTD provide insight as to whether Hg is in a stable form such as HgS or is in a soluble form such as $HgCl_2$. Determining the bioavailability or mobility of Hg in a substrate using EXAFS or SPTD analysis must take into account how the specific species and the substrate matrix will react under various environmental conditions. EXAFS and SPTD analysis generally showed agreement in identification of HgS. However, when EXAFS analysis identified m-HgS, SPTD analysis identified matrix-bound Hg. Since the SPTD patterns of m-HgS and matrix-bound Hg overlap, additional methods, such as extractions to identify organically-bound Hg, may be needed.

Conflicting results for samples such as those found to contain $HgCl_2$ by EXAFS and the Carson River tailings indicate that refinements in the speciation methods are needed. Mercury species data libraries for EXAFS and SPTD need to be expanded to better identify amalgams and other unique Hg associations. Conflicting identification of some species by the three methods supports the benefit of applying more than one technique. The PCE extraction can potentially prove useful for determining the relative percent or potential to release 'volatile' and 'soluble' Hg but this requires further investigation.

The authors wish to thank the US Environmental Protection Star Grant program for funding for this project. We are also grateful for assistance provided by the staff at the Stanford Synchrotron Radiation Laboratory in EXAFS experimentation, the Nevada Bureau of Mines and Geology for their assistance and the use of their AA during the early phases of these experiments, and the Mackay School of Mines Micro Beam Lab for assistance and use of their SEM. James Rytuba, US Geological Survey, collected and provided many of the samples from Californian mercury districts.

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