



Transportation and transformation of mercury in a calcine profile in the Wanshan Mercury Mine, SW China



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ARTICLE INFO

Article history:

Received 20 August 2016

Received in revised form

9 October 2016

Accepted 10 October 2016

Available online 4 November 2016

Keywords:

Mercury

Mobilization

Calcine pile

Speciation

XANES

ABSTRACT

Calcination of Hg ores has resulted in serious contamination of mercury (Hg) in the environment. To understand the mobilization of Hg in the calcine pile, the speciation of Hg in a profile of a large calcine pile in the Wanshan Mercury Mine, SW China was investigated using the X-ray absorption spectroscopy (XANES), to understand the mobilization of Hg in the calcine pile. Higher concentrations of Hg were observed at the 30–50 cm depth of the profile, corresponding to a cemented layer. This layer is observed in the entire pile, and was formed due to cementation of calcines. Hg species in calcines include cinnabar (α -HgS), metacinnabar (β -HgS), elemental Hg(0), and minor mercuric chloride (HgCl₂), but these Hg species show dramatic changes in the profile. Variations in Hg speciation suggest that extensive mobilization of Hg can occur during weathering processes. We show that the cemented layer can prevent the leaching of Hg and the emission of Hg(0) from the pile. High MeHg concentrations were found near the cemented layer, indicating Hg methylation occurs. This study provides important insights into the environmental risk of Hg in mining areas.

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1. Introduction

Mercury (Hg) mines are critical sites of Hg pollution since retorting of Hg ores results in release of large amount of waste materials to the environment (Kim et al., 2000; Jiang et al., 2006; Qiu et al., 2005). Hg retorting is conducted at high temperatures (600–800 °C), which leads to massive waste calcines. Although retorting process can recover over 90% of Hg during calcination of Hg ores, waste calcines are still rich in Hg (Gray et al., 2006). In the Wanshan Mercury Mine (WMM), which is China's largest and world's third largest Hg mine, long term Hg mining of Hg has resulted in $\sim 1.3 \times 10^8$ tons of calcines, and have caused serious contamination of Hg to the surrounding environment (Zhang et al., 2004; Qiu et al., 2005; Jiang et al., 2006; Zhang et al., 2010; Yin et al., 2013). Hg speciation in waste calcines are very variable (Stein et al., 1996; Kim et al., 2004; Gray et al., 2004; Yin et al., 2013).

Understanding the Hg speciation in calcines is an important step to evaluate its environmental risk, because the mobility, toxicity and bioavailability of Hg vary largely among different Hg species (Balogh et al., 2008; Yin et al., 2010).

Hg speciation has been determined by many techniques including sequential extraction (Liu et al., 2006), thermal release analysis (Biester et al., 1999), and X-ray absorption spectroscopy (XANES) (Kim et al., 2000; Skyllberg et al., 2005). The XANES has many advantages due to the direct and non-destructive measurement of samples (Kim et al., 2003, 2004; Gray et al., 2004; Jew et al., 2010; Yin et al., 2013; Rimondi et al., 2014). Mine wastes of the WMM and other Hg mines has been investigated by the XANES. Previous studies demonstrated that Hg ores mainly consisted of cinnabar (α -HgS), whereas calcines contain unroasted α -HgS, metacinnabar (β -HgS), elemental Hg(0), and minor secondary Hg salts (Kim et al., 2000, 2003, 2004; Gray et al., 2004; Jew et al., 2010; Yin et al., 2013; Rimondi et al., 2014). Changes in Hg speciation between Hg ores and calcines indicate significant Hg transformation occurs during the Hg retorting process. Different Hg species have completely different mobility and bioavailability (Stein et al., 1996). Soluble Hg species are more easily methylated

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via both biological and abiotic processes, which form methyl mercury (MeHg), the most toxic form of Hg in the environment (Li and Cai, 2013).

At many Hg mining sites in the world, long term Hg mining has resulted in many large calcine piles. Although previous studies reported differences in Hg speciation between Hg ores and roasted calcines (Kim et al., 2003, 2004; Gray et al., 2004; Jew et al., 2010; Yin et al., 2013; Rimondi et al., 2014), the transportation and transformation of different Hg species within calcine piles are still not well understood. In this study, we reported dramatic changes in Hg speciation in a profile of the WMM calcine pile, which indicates mobilization of Hg occurs during weathering.

2. Methods

2.1. Study area and sampling

The WMM, which is located in the northeastern Guizhou Province, is known as the “mercury capital” of China (Fig. 1A). The WMM has a sub-tropical humid climate with abundant precipitation (1200–1400 mm per year) (Zhang et al., 2010). Large scale Hg mining activities in the WMM were completely ceased in 2004, however long-term Hg mining activities have resulted in several large piles, mainly consisting of roasted calcines (Qiu et al., 2005; Jiang et al., 2006). Most of these piles are located at the sources of major rivers of the WMM. Release of Hg from calcine piles have caused Hg contamination to the surrounding environment such as soils, sediments and waters (Zhang et al., 2004, 2010; Qiu et al., 2005; Yin et al., 2016).

In September 2011, a profile (70 cm depth) was excavated on the top of the WuKeng pile, which is one of the largest calcine piles in the WMM (Fig. 1B). The profile was pictured as shown in Fig. 2, and three layers can be identified: (1) from the surface to 30 cm depth, calcines are tan-colored and loosed; (2) a light tan layer is located at the 30–50 cm depth. Calcines of this layer are cemented and are difficult to excavate; (3) below 50 cm, there are fresh calcines which are loosed and gray-colored. Calcine samples were collected at 10 cm interval. At each sample site, about 1 kg of calcine samples was collected. Samples were packaged in plastic bags. The samples

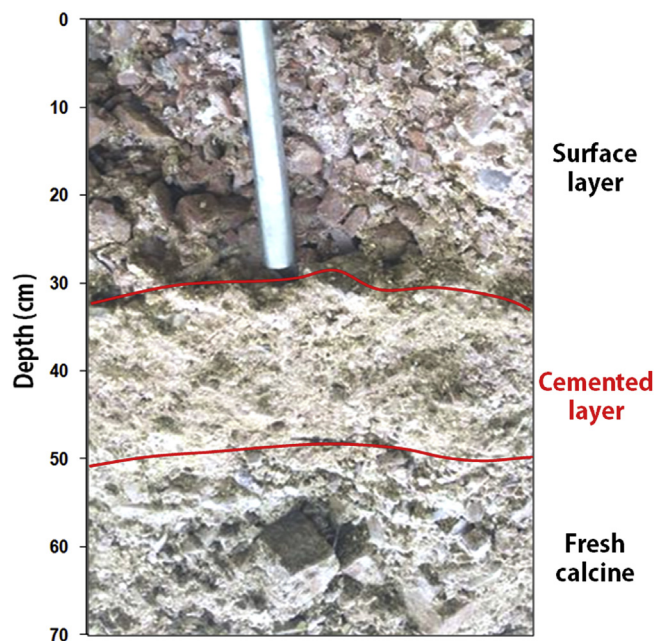


Fig. 2. Picture showing the profile excavated on the roof of the WuKeng pile.

were then air-dried, ground, and sieved to 100 mesh in the laboratory, prior to further analysis.

2.2. Total mercury and methyl mercury analysis

Total mercury (THg) concentration of the sample was measured by a Lumex RA 915+ Hg analyzer (detection limit: 0.5 ng/g) following the method by Sholupov et al. (2004). THg analysis of standard reference material (NIST SRM 2710, soil) yielded an average recovery of $98.0 \pm 1.4\%$ ($n = 5$, 2SD). Me-Hg concentrations were determined by a cold vapor atomic fluorescence spectrometry (CVAFS) following the method by US EPA (2001). Measurements of certified reference materials (ERM-CC580, sediment) yielded a

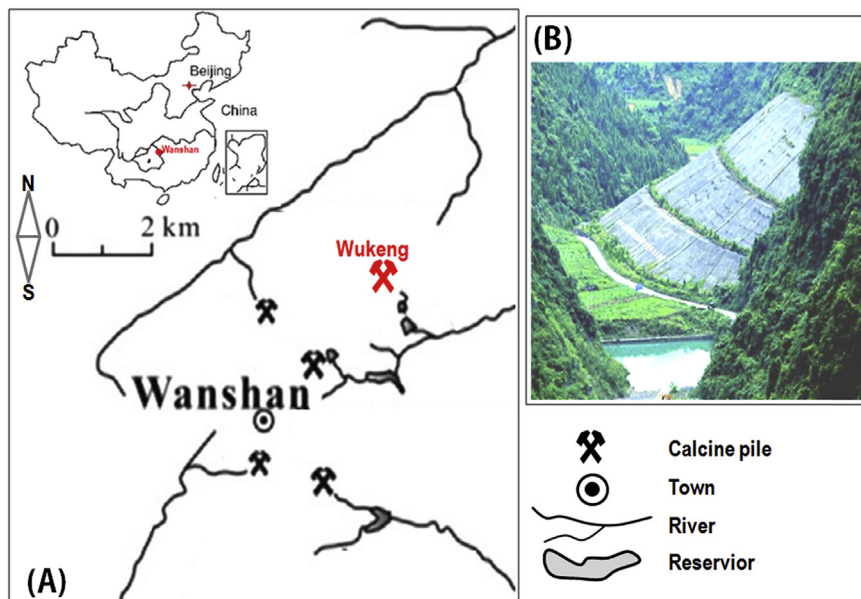


Fig. 1. Study area (A) and sampling site (B).

recovery of $89.9 \pm 5.4\%$ ($n = 5$, 2SD) for MeHg. The relative percentage difference of duplicate samples was $<3\%$.

2.3. Mercury speciation analysis

Hg L_{III} -edge X-ray absorption spectra for all the samples and references were collected by using a Si (111) double crystal monochromator (detuned approximately 30% to minimize higher order harmonics) at the 1W1B beamline station of the Beijing Synchrotron Radiation Facility (BSRF, Beijing, China). The storage ring was operated at 2.5 GeV with a beam current of approximately 200 mA. An energy range of -120 to 400 eV relative to the Hg absorption L_{III} -edge (12.284 keV) was used. Hg reference compounds included $HgCl_2$, $HgSe$, $HgSO_4$, α -HgS, β -HgS, HgO , $Hg(Ac)_2$, and $Hg(0)$. Reference compounds spectra were collected in transmission mode while the sample spectra were collected in fluorescence mode under ambient conditions and calibrated for each scan by collecting the spectra of HgO reference that were put after the samples. Multiply scans were conducted to get satisfactory spectra with an adequate signal to noise ratio. The beamline energy was stable with ± 0.1 eV within 24 h and the Hg spectra were continually collected, thus there was minor energy shift during the data collection. The reproducibility of the repeated measurements on the same spot and repeated scans over different spots for each sample is good, suggesting no radiation damage on the samples. Linear combination fits (LCF) were performed from -25 to 65 eV on all sample spectra by Athena program in the IFEFFIT package (Newville, 2001), during which, the e_0 was not allowed shift because the sample spectra were calibrated by HgO reference. The accuracy of the LCF is determined by many factors and cannot be calculated, however, the overall error of the Hg speciation determination was considered to be about 10% (Kim et al., 2004).

3. Results and discussion

3.1. Total Hg concentration profile

Calcines in the WMM show extremely high THg concentrations ranging from 20 to 133 $\mu\text{g/g}$. THg concentrations are largely variable among three layers (Fig. 4A). Specifically, in the upmost layer (depth: 0–30 cm) THg concentration ranged from 20 to 74 $\mu\text{g/g}$ and increased with depth. The cemented layer (depth: 30–50 cm) has a concentration THg of up to 133 $\mu\text{g/g}$. The fresh calcine layer (depth: 50–70 cm) has relatively lower THg (23–35 $\mu\text{g/g}$), according to previous results on fresh calcines in the WMM (Yin et al., 2013).

The presence of the loosed layer overlying the cemented layer

followed by fresh calcines (as shown in Fig. 2) is almost found at the entire Wukeng pile, and other piles in the WMM. Weathering processes driven by factors such as rain, wind, sunlight and organism activities are thought to play important roles in forming the cemented layer. The WMM is a carbonate-hosted hydrothermal Hg deposit (Zhang et al., 2004). Retorting of Hg-bearing carbonate rocks at high temperatures (600–800 °C) resulted in calcines, which are mainly consisted of carbonate ($CaCO_3$) and lime (CaO) (Zhang et al., 2004). When calcines meet air and water at surface of the pile, calcium bicarbonate [$Ca(HCO_3)_2$] forms. $Ca(HCO_3)_2$ is soluble and easily transported to the underneath. However, $Ca(HCO_3)_2$ could again transform to the insoluble $CaCO_3$ when water is continuously lost at deep layers. This process results in the cementation of calcines. The WMM has a sub-tropical humid climate with an annual precipitation of 1200–1400 mm per year (Zhang et al., 2010), which may facilitate the formation of $Ca(HCO_3)_2$, especially at the surface layer (e.g., at the 0–30 cm depth). The consolidated layer at the depth of 30–50 cm may be a result of the cementation process. The cemented layer can prevent the underlying fresh calcines (below 50 cm depth) from cementation, due to its low water permeability. The reaction between calcine with air and water can be also revealed by the color of the calcine. Iron oxides such as FeO and Fe_2O_3 are associate components in calcines of the WMM (Zhang et al., 2004). When reacted with air, FeO is readily oxidized to Fe_2O_3 . The formation of Fe_2O_3 may explain the tan-colored calcines at the 0–30 cm layer. Colors of the cemented layer and underlying fresh calcines that change from light tan to light grayish, may reflect a decrease of Fe_2O_3 formation.

The variation of THg may be explained by the sample inhomogeneity for different batches of calcines. However, it may be the solely reason for THg variations in our profile, considering the fact that calcines in the WMM were produced from retorting of similar ore materials using the same retorting technique (~ 800 °C). The calcines were moved to the pile latterly, allowing the mixing of different calcine batches. The collected samples (1 kg for each) were crushed, ground, and sieved in the laboratory, so the samples inhomogeneity can be further reduced. In our study, mobilization of Hg in calcines seems to be another important reason to cause the changes of THg in the profile. Leaching of calcines has shown to result in high soluble Hg concentration in water (Navarro et al., 2009; Stetson et al., 2009). THg concentration in the 0–30 cm layer increases with increased depth can be explained by the leaching process (Fig. 4A). The cemented layer has the highest THg, indicating this layer could prevent the transport of leached Hg to the underneath. This can be proven by the relatively lower THg in the underlying fresh calcines.

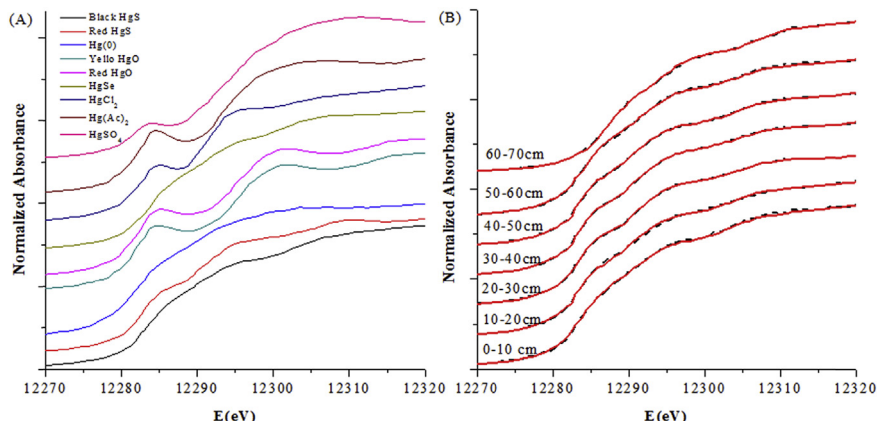


Fig. 3. EXAFS spectra of the reference materials (A) and samples (B).

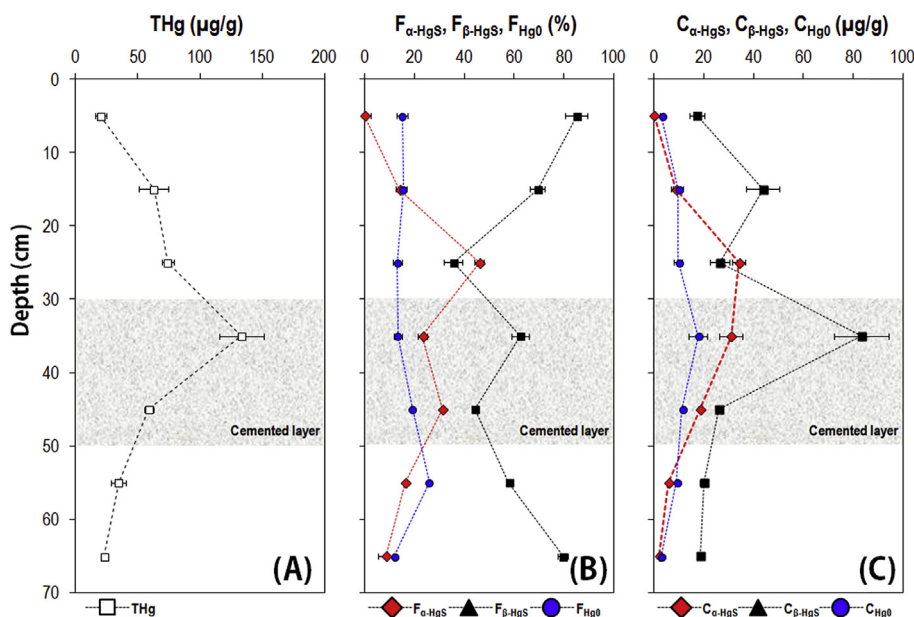


Fig. 4. THg concentrations (A), $F_{\alpha\text{-HgS}}$, $F_{\beta\text{-HgS}}$, F_{Hg0} (B), and $C_{\alpha\text{-HgS}}$, $C_{\beta\text{-HgS}}$, C_{Hg0} (C) in the profile of the WuKeng pile. (A) uncertainties are present as the 2SD value of duplicate samples; (B) uncertainties are present the Athena reported LCF error; (C) uncertainties are estimated as errors propagation of A and B.

3.2. Hg speciation profile

Previous studies have shown that Hg in calcines mainly exists as $\alpha\text{-HgS}$, $\beta\text{-HgS}$, elemental Hg(0), and minor Hg salts (Kim et al., 2000, 2003, 2004; Gray et al., 2004; Jew et al., 2010; Yin et al., 2013; Rimondi et al., 2014). In this study, principal component analysis (PCA) was firstly performed to estimate the number of components in a series of spectra, and LCF analysis was further used to determine the fraction of each component. Our PCA analysis indicated that Hg in the WMM calcines could be described by at least three components, which likely represent $\alpha\text{-HgS}$, $\beta\text{-HgS}$ and elemental Hg(0). However, a fourth component was also considered for the Hg salt component during our LCF analysis. R-factors (Table 1) were used to judge the LCF quality. Our LCF analysis successfully estimated the fractions of four components as shown in Table 1, and Fig. 3B indicates the LCF fitting is good.

$\alpha\text{-HgS}$ is dominant Hg form in ores of the WMM and other Hg deposits in the world (Rytuba, 2003; Hintelmann and Lu, 2003; Smith et al., 2008; Yin et al., 2013). The observation of unroasted $\alpha\text{-HgS}$ in calcines indicates that the retorting process is inefficient in recovering Hg from ores. $\beta\text{-HgS}$, Hg(0) and HgCl_2 found in calcines have been explained by Hg transformation during the roasting process (Kim et al., 2000, 2003, 2004; Gray et al., 2004; Jew et al., 2010; Yin et al., 2013). Fractions of $\alpha\text{-HgS}$ ($F_{\alpha\text{-HgS}}$), $\beta\text{-HgS}$

($F_{\beta\text{-HgS}}$), Hg(0) (F_{Hg0}) and HgCl_2 (F_{HgCl_2}) are shown in Fig. 4B $\alpha\text{-HgS}$, $\beta\text{-HgS}$ and Hg(0) are the major species of Hg in calcines. The F_{HgCl_2} is generally <10%, lower than the error associated with the LCF procedure, so it will not be discussed. $F_{\alpha\text{-HgS}}$ increases with increased depth at the 0–30 cm layer, and gradually decreases at the 30–70 cm depth. $F_{\beta\text{-HgS}}$ shows an inverse distribution pattern with $F_{\alpha\text{-HgS}}$. Leaching of calcines by rain may be the cause of the vertical difference between $F_{\alpha\text{-HgS}}$ and $F_{\beta\text{-HgS}}$. Under low temperature and oxygenated conditions, the solubility of $\alpha\text{-HgS}$ is about three times higher than that of $\beta\text{-HgS}$ (Holley et al., 2007), and therefore $\alpha\text{-HgS}$ is more easily leached by water. The cemented layer prevents the transport of water to the underneath, which may explain the higher $F_{\alpha\text{-HgS}}$ above the cemented layer. Relatively consistent F_{Hg0} , except a slightly higher value right below the cemented layer, was observed. During the retorting process, although most Hg is recovered as Hg(0) at high temperatures, a substantial amount of Hg(0) is still adsorbed in calcine matrices. Calcine piles have been shown to be an important Hg(0) emission source to the atmosphere in the WMM (Wang et al., 2007). Theoretically, release of Hg(0) should eventually result in decreased F_{Hg0} at surface calcine layers, however this is in disagreement with the relatively constant F_{Hg0} of the profile. The lack of decreased F_{Hg0} in surface calcines may be explained by contribution of Hg(0) from deep layers. Higher F_{Hg0} values found below the cemented layer

Table 1
THg and MeHg concentrations, and fractions of major Hg species in the Wukeng calcine pile. R-factors were used to judge the LCF quality.

Depth (cm)	^a THg (µg/g)	^a MeHg (ng/g)	^b $F_{\alpha\text{-HgS}}$ (%)	^b $F_{\beta\text{-HgS}}$ (%)	^b F_{Hg0} (%)	^b F_{HgCl_2} (%)	R factor
0–10	20 ± 4.4	0.4 ± 0.0	<5	85.0 ± 4.6	15.0 ± 2.2	<5	0.00001
10–20	73 ± 11.7	1.2 ± 0.1	13.8 ± 1.4	69.5 ± 3.0	15.4 ± 1.4	<5	0.00005
20–30	74 ± 4.9	9.6 ± 0.6	45.9 ± 1.8	35.6 ± 3.7	13.1 ± 1.8	5.4 ± 0.9	0.00002
30–40	133 ± 17.7	11.3 ± 0.7	23.1 ± 1.8	62.5 ± 3.6	13.3 ± 1.7	<5	0.00003
40–50	59 ± 3.5	1.4 ± 0.1	31.1 ± 0	44.3 ± 0.0	19.1 ± 0.0	5.5 ± 0.0	0.00003
50–60	35 ± 5.9	1.0 ± 0.1	16.3 ± 0	57.8 ± 0.0	25.8 ± 0.0	<5	0.00009
60–70	23 ± 1.3	0.5 ± 0.0	8.3 ± 3.1	79.7 ± 2.1	12 ± 0.0	<5	0.00004

^a Uncertainties are present as the 2SD value of duplicate samples (n = 3).
^b Uncertainties are present as the Athena reported LCF error.

(depth: 50–60 cm) supports our hypothesis because the cemented layer can prevent the transport of Hg(0) emitted from the underlying layers.

Concentrations of α -HgS ($C_{\alpha\text{-HgS}}$, $\text{THg} \times F_{\alpha\text{-HgS}}$), β -HgS ($C_{\beta\text{-HgS}}$, $\text{THg} \times F_{\beta\text{-HgS}}$) and Hg^0 (C_{Hg^0} , $\text{THg} \times F_{\text{Hg}^0}$) were calculated as shown in Fig. 4C. Similar to the THg profile, high $C_{\alpha\text{-HgS}}$ and $C_{\beta\text{-HgS}}$ values are mainly in the cemented layer. The cemented layer therefore absorbs the α -HgS and β -HgS leached from surface layers, and prevents Hg leaching from underlying layers. High C_{Hg^0} values also occurs in the cemented layer, and it gradually decreases from upper to deeper layers. This indicates that the cemented layer may prevent also Hg(0) emission from the underneath layers.

3.3. Me-Hg concentration profile

Me-Hg concentrations in the profile ranged from 0.3 to 11.3 ng/g (Table 1 and Fig. 5). The presence of MeHg indicates that Hg methylation occurs in mine wastes (Gray et al., 2003). The fraction of MeHg (F_{MeHg} , MeHg/THg) ranged from 0.002 to 0.013% (Fig. 5). High MeHg concentrations and F_{MeHg} values were observed at the interface between the surface layer and the cemented layer. This interface is thought to have high moisture and anoxic conditions due to accumulation of water above the cemented layer and less contact to air, thereby favorable for microbial methylation activities (Raposo et al., 2008). Previous studies have shown higher rates for Hg methylation than MeHg demethylation at anoxic conditions. Leaching of calcines results in more soluble Hg near the cemented layer, and soluble Hg species are more easily methylated via both biological and abiotic processes (Stein et al., 1996). MeHg may also leach from surface layers, and the cemented layer prevents the transport of MeHg to the underneath. The low MeHg and F_{MeHg} in the uppermost calcines may be a result of low Hg methylation,

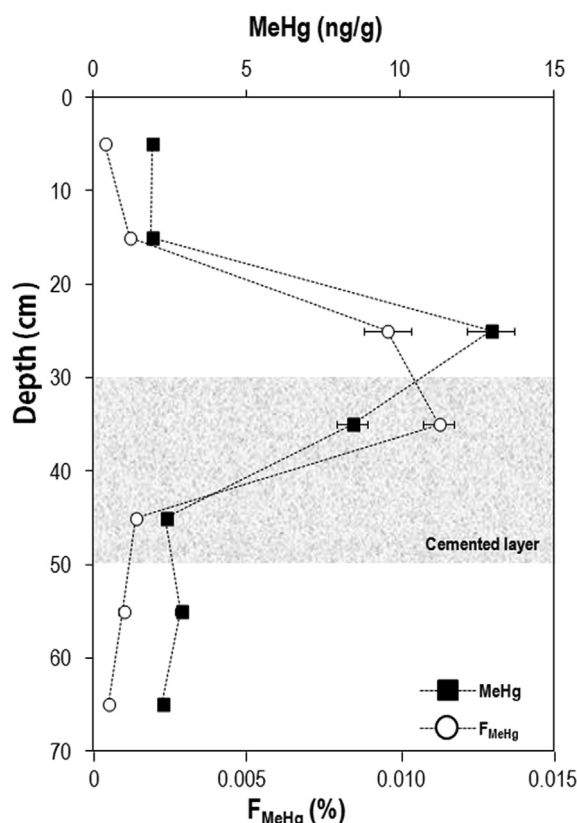


Fig. 5. MeHg concentrations and F_{MeHg} in the profile of the WuKeng pile.

higher demethylation (such as photodemethylation), and loss of MeHg by leaching. The low MeHg and F_{MeHg} content in fresh calcines at deep layers may be explained by the presence of low soluble Hg species and low microbial activities due to low moisture and high pH and reduced leaching of MeHg from the upper layers due to the barrier constituted by the cemented layer.

Significantly positive correlations were observed between F_{MeHg} and $F_{\alpha\text{-HgS}}$ ($p = 0.02$), but F_{MeHg} is negatively correlated to $F_{\beta\text{-HgS}}$ ($p = 0.03$) (Fig. 6). This indicates that α -HgS is more responsible for Hg methylation than β -HgS and Hg(0). In the profile, high F_{MeHg} and $F_{\alpha\text{-HgS}}$ values are overlapped near the roof the cemented layer with higher moisture and anoxic conditions. Compared to β -HgS, the relatively high solubility of α -HgS would result in more soluble Hg. Soluble Hg species is more bioavailable and more easily methylated via biological and abiotic processes. High $F_{\beta\text{-HgS}}$ values were observed in both the uppermost layer and the fresh calcine layer, and these layers are in general associated with low F_{MeHg} . This can explain the negative correlation between F_{MeHg} and $F_{\beta\text{-HgS}}$. Previous studies have shown that Hg(0) is readily oxidized to soluble Hg^{2+} , which is liable to be converted into Me-Hg via microorganism methylation (Hu et al., 2013). However, no clear correlation between F_{MeHg} and F_{Hg^0} ($p = 0.35$) was observed in our study (Fig. 6), suggesting Hg(0) is not necessarily methylated at certain conditions. In our study, high F_{Hg^0} is found in fresh calcines right below the cemented layer, where microbial methylation may be low due to low moisture and high pH.

4. Conclusions

This study reported major species of Hg (e.g., α -HgS, β -HgS, Hg(0), etc.) in calcine piles of the WMM. Dramatic changes in Hg speciation in the calcine profile indicate that weathering could result in the mobilization of different Hg species, which strongly affects the mobility and bioavailability of Hg in calcine piles. Weathering also results in a cemented layer in the calcine pile. The cemented layer can prevent the leaching of Hg and the emission of Hg(0) from the pile. High MeHg concentrations were found near the cemented layer, indicating Hg methylation occurs at that spot.

As a result of long term Hg mining in the history, hundreds to thousands of calcine piles were left on Earth. These piles, containing various Hg compounds, would be subject to extensive weathering, because new calcines are not added to cover the piles any

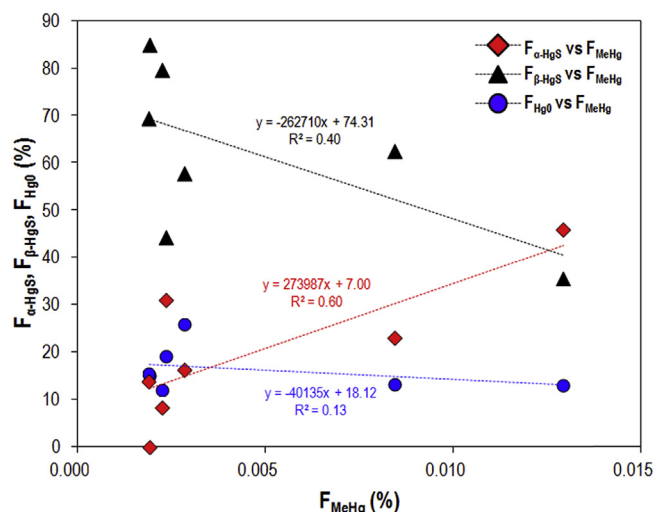


Fig. 6. Correlations of F_{MeHg} and $F_{\alpha\text{-HgS}}$, $F_{\beta\text{-HgS}}$, and F_{Hg^0} in the profile of the WuKeng pile.

more. Our results showed that cementation of the calcine piles occurs near the piles' surface. Therefore, the release of Hg from calcine piles in humid area may be decreased in the near future, due to cementation of the calcines. However, there is an increased risk in MeHg production from calcine piles, due to the accumulation of soluble Hg, high moisture and anoxic conditions near the cemented layers. Overall, our study provides important insights into environmental risk of Hg in calcine piles. This study also provides knowledge in remediation and prediction of Hg pollution from calcine piles.

Acknowledgments

The present study was financially supported by the National Natural Science Foundation of China (41303014), and the National Key Basic Research Program of China (2013CB430004).

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