



Mercury speciation and mobility in salt slurry and soils from an abandoned chlor-alkali plant, Southwest China

Chuan Wang^{a,b}, Zhengcheng Song^c, Zhonggen Li^a, Wei Zhu^a, Ping Li^{a,*}, Xinbin Feng^a

^a State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550081, China

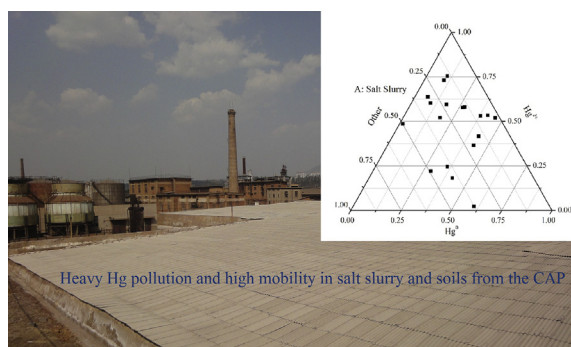
^b University of Chinese Academy of Sciences, Beijing, 100049, China

^c Key Laboratory of Karst Environment and Geohazard Prevention, Guizhou University, Guiyang, 550003, China

HIGHLIGHTS

- THg concentrations in salt slurry and soils from the abandoned CAP were highly elevated and varied widely.
- Hg^{2+} and Hg^0 were main speciation of Hg in the salt slurry and soils.
- The salt slurry were classed as hazardous wastes with an average TSHg concentration of 140 $\mu\text{g/L}$.
- The salt slurry and soils are significant Hg pollution sources to local environment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 August 2018

Received in revised form 18 October 2018

Accepted 22 October 2018

Available online 22 October 2018

Editor: Jay Gan

Keywords:

Chlor-alkali

Salt slurry

Soil

Mercury speciation

Mobility

ABSTRACT

Chlor-alkali plants (CAPs) are major consumers of mercury (Hg) and may be a source of severe Hg pollution to the environment. In this paper, the total mercury (THg) concentrations and the speciation and mobility of Hg were measured in salt slurry and soils collected from an abandoned CAP in Yunnan Province, China. THg concentrations in the salt slurry samples varied widely and ranged from 0.43 to 2640 mg/kg; THg concentrations varied vertically and were lower towards the surface than deeper in the profile. In the soils, a sample collected from electrolysis workshop had the highest THg concentration (3650 mg/kg). The main fractions of Hg in the salt slurry and soils were Hg^{2+} and Hg^0 , which accounted for 47.4% and 22.9% of THg in the salt slurry and 28.0% and 43.8% of THg in the soils on average, respectively. The Hg^0 concentrations decreased with depth in the soil profiles. The total soluble Hg (TSHg) concentrations in the salt slurry averaged at 140 $\mu\text{g/L}$ and ranged from 0.77 to 564 $\mu\text{g/L}$. The salt slurry and soils at the study site were seriously contaminated with Hg, which could potentially be released to the atmosphere or water bodies.

© 2018 Elsevier B.V. All rights reserved.

1. Introduction

Mercury (Hg) is considered as a global pollutant (Driscoll et al., 2013; Pacyna et al., 2016; Obrist et al., 2018). Gaseous elemental

mercury (GEM), the predominant form of atmospheric Hg, has long residence time (0.5–2 years) in the atmosphere (Fu et al., 2012, 2015), and can be transported for considerable distances from its source area (Pacyna et al., 2016; Obrist et al., 2014; Horowitz et al., 2014). Methylmercury (MeHg), the organic form of Hg, can bioaccumulate in the aquatic food chain, where it poses serious health risks to humans through consumption of seafood (Driscoll et al., 2013). Recent studies

* Corresponding author.

E-mail address: liping@mail.gyig.ac.cn (P. Li).

have confirmed that MeHg can be bioaccumulated in rice grain that grown in Hg-polluted sites, and rice consumption represents the main MeHg exposure pathway for inland population (Zhang et al., 2010a, 2010b; Feng et al., 2008; Li et al., 2015).

Atmospheric Hg originates from both natural (e.g., volcanoes, evaporation from soil and water, and wild fires) and anthropogenic sources (e.g., fossil fuel combustion, artisanal and small-scale gold mining, medical waste incineration, chlor-alkali plants and municipal waste) (Pirrone et al., 2010; Streets et al., 2017; Esbrí et al., 2015; UNEP, 2013). Anthropogenic Hg emission accounted for about 30% of the total amount of Hg release to the atmosphere worldwide; and China, the largest emitter of Hg, accounts for about 1/3 of global emissions (UNEP, 2013). In China, atmospheric Hg emission increased from 356 t in 2000 to approximately 530 t in 2014 (Zhang et al., 2015; Wu et al., 2016), and the amount of Hg released to aquatic environments in 2012 was estimated at 98 t (Liu et al., 2016). Because of the rapid economic development in China, the average concentration of GEM, at $2.86 \pm 0.95 \text{ ng/m}^3$, was significantly higher than the background concentration in the Northern Hemisphere ($1.5\text{--}1.7 \text{ ng/m}^3$) (Fu et al., 2015; Tang et al., 2018).

Chlor-alkali plants (CAPs) are the third largest industry user of Hg worldwide (Esbrí et al., 2015). In chlor-alkali industry, chlorine and caustic soda are produced in a reaction that is catalyzed by liquid Hg (Tang et al., 2018). About 28 t of Hg was discharged from CAPs worldwide in 2010 (UNEP, 2013). The Hg form emitted from chlor-alkali plants is mainly gaseous Hg (Hg^0 and Hg^{2+}), and soil is the main receptor (Gordeeva et al., 2017; Guédron et al., 2013). The net Hg deposition flux to soils in the vicinity of CAPs was estimated at between 2356 and $8952 \mu\text{g/m}^2$ per year (Biester et al., 2002).

Although the technique of chlor-alkali catalyzed by Hg was abandoned in the early 90s, Hg still can be released from Hg-contaminated salt slurry produced by the Hg-cell process (Fernández-Martínez et al., 2016). Hg pollution resulted from the production of CAPs has been studied extensively worldwide (Reis et al., 2010; Ullrich et al., 2007; Wängberg et al., 2003; Bravo et al., 2014). On average, the Hg consumption in alkali production in China was between 300 and 500 g/t. The carbide-based polyvinyl chloride (PVC) industry is the largest Hg user in China, and accounts for 60% of Hg consumption (Pirrone et al., 2010; Lin et al., 2016). A recent study estimated that 4.9 g of Hg was emitted from a PVC factory for every ton of PVC produced (Ren et al., 2014). However, few

studies considered the speciation and mobility of Hg in the salt slurry and surrounding soils at CAPs in China.

The aim of this study was to quantify Hg concentrations in the salt slurry and soils in an abandoned CAP and assess the potential environment impacts. The vertical distribution of THg concentrations and Hg speciation in the salt slurry and soils from the CAP were investigated. Leaching experiments were carried out to estimate the possible environmental impacts from the salt slurry and soils. The results from this study can be used to support remediation of this CAP. Information about Hg pollution to the atmosphere, groundwater, surface water, and soils surrounding the CAP has been reported in a companion paper (Song et al., 2018).

2. Materials and methods

2.1. Study site

The chemical plant covers an area of $40,000 \text{ m}^2$ (Fig. 1). As part of an urban development project, the chemical plant will be converted to commercial and residential area. The Local Environmental Protection Bureau has drafted “plan of heavy metal pollution prevention” and the land of the chemical plant will be remediated to reach the requirements of urban construction land.

The chemical plant, established in 1958, was the largest chlor-alkali and chemical operation in Yunnan province. It was also the only PVC and chlorothalonil pesticide operation in Yunnan Province. The annual production capacity is 30,000 tons of caustic soda with ion-exchange membrane process and 30,000 tons of PVC. The chemical plant closed in April 2011 because of environmental and safety concerns and the out-of-date technology.

2.2. Sample collection

The study area includes a salt slurry heap, a calcium carbide slag heap, chlor-alkali workshop, pesticide workshop, PVC workshop, and other auxiliary workshops.

The area of most interest for this study was the salt slurry heap, which extends over about $11,000 \text{ m}^2$. A total of 33 profiles of salt slurry were drilled and the drill sites were arranged at interval of 20 m (Fig. 2). Samples were collected from the upper (at the depth of 0–0.2 m), middle (0.8–1.5 m), and bottom (2.5–3.5 m) layer of the salt slurry profiles

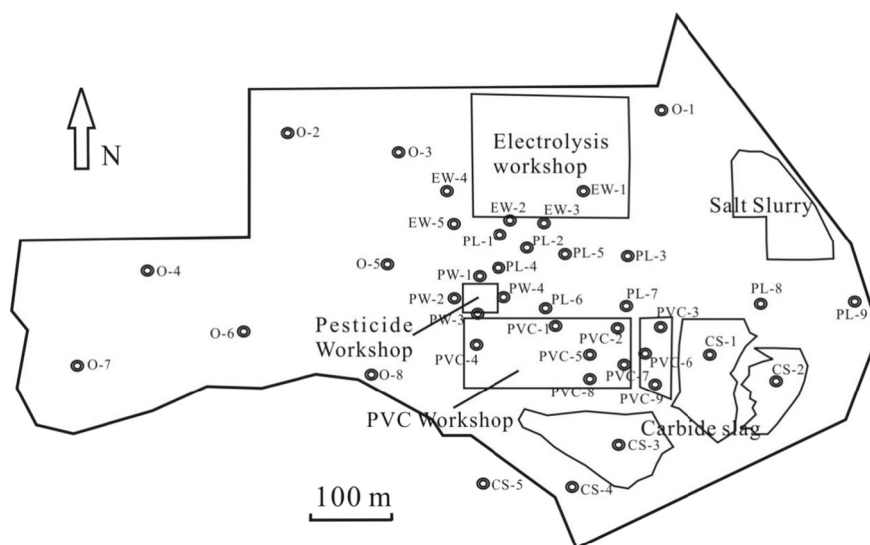


Fig. 1. Spatial distribution of sampling sites in the chemical plant.

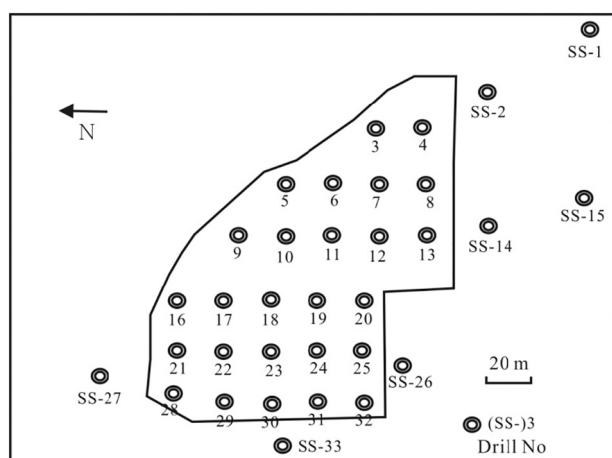


Fig. 2. Spatial distribution of sampling sites in the salt slurry heap.

to examine the vertical variation in the Hg concentration. Soil samples were collected at different depths and sampling continued until groundwater was encountered. A portable X-ray fluorescence spectrometer (Niton XL3t600, Thermo Fisher Scientific, Massachusetts, USA) was used to guide sampling by scanning the soil samples and soil samples did not collect until low Hg concentration (<6 mg/kg) which could not be measured. Five soil profiles at electrolysis workshop (EW), nine profiles at pipe line area (PL), nine profiles at PVC workshop, five profiles at carbide slag heap (CS), four profiles at pesticide workshop (PW) were drilled. A further eight profiles were collected from other areas as contrast. In one salt slurry/soil profile, there are several samples at different depths. The sampling sites were generally evenly distributed to ensure a representative picture of the Hg pollution in the study area obtained. The salt slurry and soil samples were dried at room temperature, and then ground to 200 mesh for further analysis.

2.3. Analytical method

Major elements in the samples were determined by chemical analysis, which conducted at State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The density of the soil and salt slurry samples was determined with cutting ring. The water contents were calculated based on the dry weight and the fresh weight. The organic matter (OM) contents were determined by the potassium dichromate volumetric method coupled with a water heating technique. The pH was measured using a pH electrode at a solid: water ratio of 1:2.5.

The total Hg (THg) concentrations in the salt slurry and soil samples were determined with an Hg analyzer (RA-915+) coupled with pyrolyzer (PYRO-915+) (Lumex, St. Petersburg, Russia). In this setup, the samples are decomposed thermally and the THg concentrations are detected by Zeeman atomic absorption spectrometry (Sholupov et al., 2004). Typical salt slurry and soil samples were selected for Hg speciation analysis and leaching experiments. The Hg^0 concentrations were taken as the difference between THg concentrations before and after heating for 24 h at 180 °C (Biester and Scholz, 1997; Wang et al., 2011). The samples were leached with 1 N HCl using a liquid to solid ratio of 10:1 at room temperature for 18 h. After filtration, the THg concentration were determined by cold vapor atomic absorption spectrometry (CVAAS). This process liberates most of the Hg that is not bound in HgS or Hg^0 and, in this study, was defined as the Hg^{2+} concentration. Concentrations of other Hg forms were obtained by subtracting the Hg^{2+} and Hg^0 concentrations from the THg concentrations.

Leaching experiments were carried out by shaking samples (20 g) for 18 h in 200 mL of a diluted solution of HNO_3 and H_2SO_4 ($pH\ 3.20 \pm 0.05$), as outlined in HJ/T299–2007 (SEPA, 2007a). The Hg concentrations in the filtered solution were determined using CVAAS and defined as total soluble Hg (TSHg) (Biester et al., 1999).

2.4. Quality control

Method blanks, blank spikes, matrix spikes, certified reference materials (CRMs), and blind duplicates were used to ensure the quality of the analysis. The limit of detection (LOD) for THg, Hg^{2+} , and Hg^0 in solid samples was 0.02 mg/kg and was 0.05 $\mu g/L$ for TSHg in the leachates from leaching experiments. The THg concentrations in GBW070009 and ERM-CC580 were 2.18 ± 0.08 and 130 ± 5.8 mg/kg, respectively, which were perfectly consistent with the certified values of 2.2 ± 0.4 and 132 ± 2 mg/kg. Recoveries for Hg^{2+} on blank and matrix spikes averaged at $98 \pm 3\%$ and ranged from 92% to 107%. The relative percentage difference for THg, Hg^0 , Hg^{2+} , and TSHg in the duplicate samples was, on average, $<7.7\%$.

2.5. Data analysis

For the statistical analysis, SPSS19.0 for windows was used. The THg concentration were described with the mean \pm SD (standard deviation) and descriptive statistics. The statistical tests were considered statistically significant if $p < 0.05$. The relationships between Hg^0 , Hg^{2+} and THg was evaluated with Pearson correlation analysis.

3. Results and discussion

3.1. Major elements

Major elements in the salt slurry are listed in Table 1. The salt slurry contained BaO, CaO, MgO, and K_2O . The main component was BaO, which accounted for as much as 79%. Barium chloride is added to precipitate sulfate during the chlor-alkali production process, leaving high BaO concentrations in the salt slurry.

The basic properties of samples from different areas of the site are listed in Table 2. The salt slurry and carbide slag were alkaline, reflecting the high concentrations of alkaline materials such as Ca, Mg, and K. The density of salt slurry is $1.20\ g/cm^3$, and the carbide slag is very light (with a density of $0.92\ g/cm^3$ on average).

Table 1
Concentrations of major element oxides in the salt slurry (%).

Major element oxide ($n = 12$)	Mean	SD	Min	Max
SiO ₂	3.32	1.80	1.15	7.46
Al ₂ O ₃	0.24	0.06	0.15	0.37
Fe ₂ O ₃	0.13	0.03	0.1	0.2
CaO	5.72	3.39	1.7	11.8
MgO	1.12	1.15	0.15	3.42
K ₂ O	0.57	0.57	0.1	2.28
Na ₂ O	0.17	0.13	0.021	0.54
MnO	0.02	0.01	0.01	0.03
TiO ₂	0.01	0.00	0.01	0.02
P ₂ O ₅	0.04	0.01	0.029	0.05
BaO	79.0	11.3	58.0	91.0
SrO	0.55	0.23	0.26	1.12
LOI	8.92	5.35	3.23	19.8
Total	99.9	0.13	99.7	100.2

Table 2
Properties of samples from different areas.

Site	Matrix	n	Density (g/cm ³)	Water content (%)	OM (%)	pH
SS	Salt slurry	18	1.20 ± 0.29	16.3 ± 6.92	1.28 ± 0.95	9.05 ± 1.02
SS	Soil	23	1.14 ± 0.19	17.5 ± 5.94	1.36 ± 1.37	7.49 ± 0.98
PL	Soil	9	1.07 ± 0.21	13.9 ± 4.12	1.75 ± 1.86	8.45 ± 1.22
CS	Carbide slag	2	0.92 ± 0.01	21.4 ± 1.80	3.62 ± 0.21	10.5 ± 0.05
PVC	Soil	10	1.11 ± 0.25	13.1 ± 11.4	2.62 ± 5.54	8.49 ± 0.96
EW	Soil	9	1.15 ± 0.20	17.7 ± 4.27	3.22 ± 2.88	7.64 ± 1.03

3.2. THg concentrations

THg concentrations in the samples from different areas are listed in Table 3. The THg concentrations in the salt slurry samples were very high, and geometric mean of THg concentration reached 114 mg/kg. Overall, the THg concentrations in the salt slurry samples were uneven distributed, highly variable, and did not fit either a normal or lognormal distribution. The THg concentrations in the salt slurry samples ranged from 0.43 to 2640 mg/kg, and the THg concentrations in 75% (56/75) of the samples exceeded risk intervention values of soil contamination of development land (33 mg/kg) (MEEC, 2018). In Hg-cell chlor-alkali industry, liquid Hg is used as catalyst to produce chlorine and caustic soda, and most of the Hg is remained in solid waste.

The baseline THg concentration in soil in Yunnan Province is 0.058 mg/kg (EMSC, 1990). While THg concentrations in soil samples from underneath and around the salt slurry heap were high, with geometric mean of 1.63 and 2.83 mg/kg, respectively. The elevated THg concentrations in soil samples around the salt slurry heap may result from rainfall leaching and atmospheric deposition. The THg concentrations in 16% (14/87) of soil samples exceeded risk screening values of soil contamination of development land (8 mg/kg) (MEEC, 2018). The THg concentrations in soil samples from EW were high and had a geometric mean of 4.85 mg/kg. The sample with the highest THg concentration (3650 mg/kg) was from the EW, which shows massive Hg release during electrolysis process of chlor-alkali production. Other areas were also polluted with Hg, details of which are listed in Table 3. This indicated severe Hg pollution in the soils may cause the groundwater pollution and pose potential risks to human health.

The THg concentrations in the salt slurry varied with depth (Fig. 3). The lower THg concentrations in the upper layer (Table 4) may be related to improvements of the production process, which the ion-exchange membrane technique replaced the Hg electrolytic method in 1991. The salt slurry is, on average, 2.71 ± 0.67 m thick, and covers an area of about 11,000 m². Combining the basic information about the salt slurry, such as the density and the water content, and it estimated that the salt slurry contained about 3.41 ± 1.95 tons of Hg.

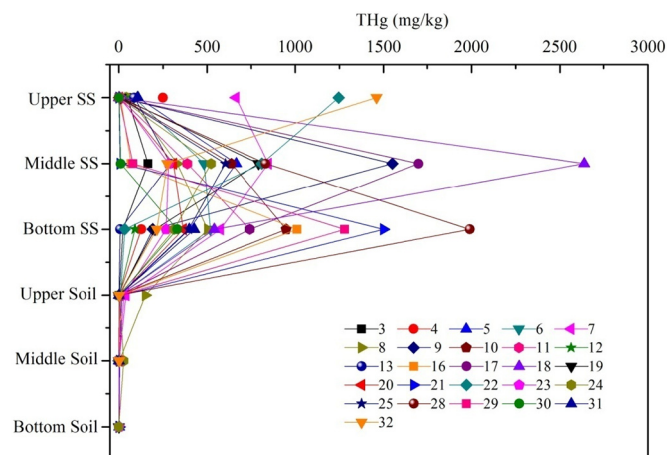
Table 3
THg concentrations in the samples from different areas of the study sites (mg/kg).

ID	Description	Matrix	n	Geomean	Mean	SD	Min	Max
SS	Salt slurry	Salt slurry	75	114	430	530	0.43	2640
SS	Soil under salt slurry	Soil	58	1.63	6.55	20.7	0.15	151
SS	Soil around salt slurry	Soil	29	2.83	22.5	62.6	0.21	289
EW	Electrolysis workshop	Soil	22	4.85	199	773	0.09	3650
PVC	PVC workshop	Soil	44	0.69	18.4	69.7	0.06	422
PL	Pipeline area	Soil	38	0.94	4.37	9.72	0.02	40.3
PW	Pesticide workshop	Soil	17	0.26	1.14	3.51	0.05	14.7
CS	Carbide slag	Carbide slag	20	1.07	11.3	32.9	0.09	145
O	Other area	Soil	36	0.66	5.50	18.1	0.02	107

3.3. Hg speciation

The portion of Hg speciation in salt slurry and soil samples are showed in Fig. 4. The Hg²⁺ concentrations in the selected salt slurry samples ranged from 0.57 to 1170 mg/kg and averaged 204 mg/kg. The Hg²⁺ was the main form of Hg in the salt slurry samples and accounted for 47.4% of THg on average. The Hg²⁺ and THg concentrations in the salt slurry samples were significantly correlated ($r = 0.99$, $p < 0.01$). The average of Hg²⁺ concentrations in selected soils was 9.23 mg/kg with a range of 0.01–383 mg/kg, and Hg²⁺ accounted for 22.9% of THg on average. Significant correlation ($r = 0.998$, $p < 0.01$) was also observed between the Hg²⁺ and THg concentrations in the soil samples. The percentages of Hg as Hg²⁺ was significantly higher in the salt slurry than in the soil samples ($p < 0.01$). Compared with Hg⁰, Hg²⁺ can leach by water or rainfall and it is easier to be utilized microorganism than Hg⁰. This shows that Hg in the salt slurry is more active than in the soils. The continuous release of Hg from salt slurry via leaching and erosion by rainwater resulted in Hg contamination in the groundwater and surrounding soils. In a companion paper, 46.4% (32/69) of dissolved Hg concentrations in groundwater within the CAP exceeded national limit (1 µg/L), and 28.6% (8/28) of THg concentrations in surrounding soils exceeded the second-grade national limit of China (0.5 mg/kg) (Song et al., 2018).

Comparison of the results from this study with those of other studies showed that the Hg²⁺ concentrations in the salt slurry samples were comparable with those in mine wastes from Hg mines in Texas, USA

**Fig. 3.** Vertical distribution of the THg concentrations in the salt slurry profiles.**Table 4**
THg concentrations at different depths in salt slurry (mg/kg).

Depth	n	Geomean	Mean	SD	Min	Max
Upper	25	14.8	164	384	0.43	1460
Middle	25	309	581	609	7.53	2640
Bottom	25	322	545	485	7.67	1990

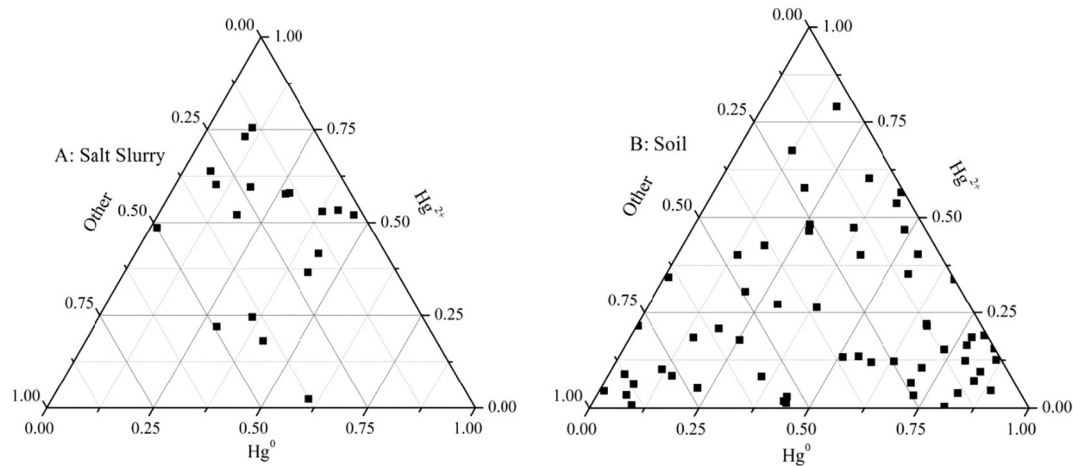


Fig. 4. Triangular chart showing portion of Hg speciation in salt slurry (A) and soils (B).

(1.5–2100 mg/kg, with a mean of 180 mg/kg) (Gray et al., 2006), mine-waste calcine and soil in Hg Mines, Southwest Alaska (0.01–483 mg/kg) (Gray et al., 2000) and much higher than those in calcines and waste rocks in China Hg mines (0.002–8.33 mg/kg) (Li et al., 2013).

The Hg^0 concentrations in selected salt slurry samples ranged from 0.02 to 196 mg/kg and averaged at 51.9 mg/kg. The Hg^0 concentrations in selected salt slurry samples accounted for 28.0% of the THg on average. The average of Hg^0 concentrations in selected soils was 55.6 mg/kg with a range of 0.01–2570 mg/kg, and the portion of Hg^0 as THg in soils was 43.8% on average. The Hg^0 concentrations in 14.0% (8/57) of the selected soils samples exceeded the screening level of Hg^0 in residential soil of 11 mg/kg set by US Environmental Protection Agency (2018); and the Hg^0 concentrations in 7.0% (4/57) of the soils exceeded that threshold for industrial soil of 46 mg/kg, also recommended by US Environmental Protection Agency (2018). The percentage of Hg as Hg^0 was significantly higher in soils than in salt slurry ($p < 0.01$). The Hg^0 concentrations in soil varied with depth (Fig. 5) and were highest in the upper layer and decreased as the depth increased. In the CAP, Hg contaminated wastes can be point sources of atmospheric Hg (Zhu et al., 2018). This shows that the Hg^0 in the soil samples originated from atmospheric deposition of emitting from production process or salt slurry. Soils can also re-emit Hg^0 to the atmosphere under certain environmental conditions as secondary

pollution source, posing a threat to the local environment and contributing to global atmospheric cycling of Hg.

The Hg^0 concentrations in the salt slurry and soil samples were comparable to those in soils from Wanshan Hg mines, where the concentrations ranged from 7.47 to 443.8 mg/kg (Wang et al., 2011). The average contributions of Hg^0 to THg in the salt slurry (28.0%) and soil samples (43.8%) in this study were also comparable to those in contaminated soils in Wanshan Hg mine (where the contributions ranged from 10.1% to 76.4%) (Wang et al., 2011), Oak Ridge in the USA (10–30%) (Liu et al., 2006), and sediments of Haihe River, China (23.7–65.8%) (Shi et al., 2005).

3.4. Leaching experiment

The TSHg concentrations in leachates of selected salt slurry and soils samples were variable (Fig. 6). The mean of TSHg concentrations was as high as 140 $\mu\text{g/L}$ (with a range of 0.77–564 $\mu\text{g/L}$). About 88.2% (15/17) of the samples had TSHg concentrations that exceeded Grade V (1 $\mu\text{g/L}$), outlined in the National Surface Water Quality Standard of China (GB3838–2002) (SEPA, 2002). Of the 17 samples, 5 (or 29.4%) had TSHg concentrations that exceeded 100 $\mu\text{g/L}$ and met the criteria for hazardous solid wastes outlined in GB5085.3–2007 (SEPA, 2007b). The highly elevated TSHg concentrations indicated that large amounts of water-soluble Hg compounds were produced during the electrolysis process and were retained in the solid waste. These solid wastes are a significant source of Hg to the groundwater.

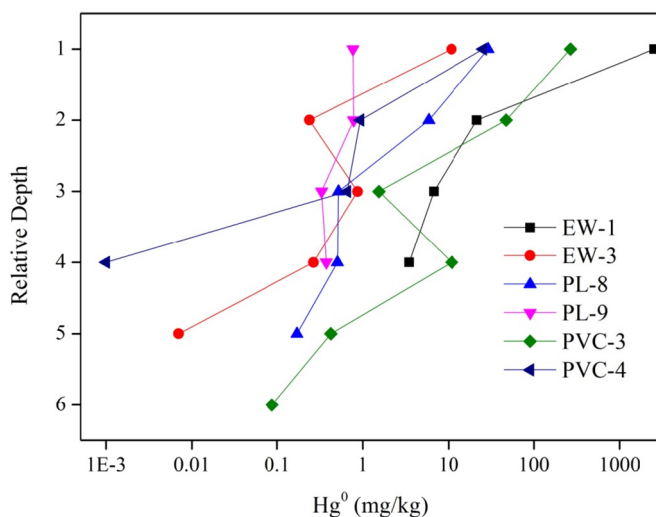


Fig. 5. Vertical distribution of the Hg^0 concentrations in the soil profiles.

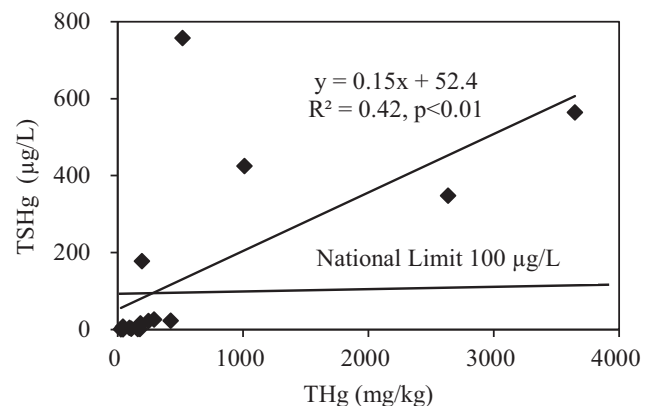


Fig. 6. The relationship between the TSHg in leachates and THg in corresponding samples.

Total soluble Hg accounted for only a small portion (0.01–1.46%) of THg in the selected samples. The TSHg in the leachates was significantly correlated with the THg in the solid samples ($r = 0.42$; $p < 0.01$) (Fig. 6). Based on the results, nearly 50% of the salt slurry samples could be classified as hazardous solid waste. The salt slurry in the study site must be appropriately treated to reduce the potential risks to the environmental and human health.

4. Conclusions

Salt slurry and soils collected from an abandoned CAP had high THg concentrations. Because of usage of liquid Hg as catalyst for chlor-alkali production, THg concentrations in salt slurry and soils at SS and EW were significantly elevated. The THg concentrations were highest in the middle of the salt slurry profiles (and were lower in the upper layer), reflecting a change in the manufacturing process. The Hg⁰ concentrations were highest in the upper layer of salt slurry and soil profiles, which indicated atmospheric Hg deposition. The high Hg²⁺ concentrations in the salt slurry may cause serious Hg contamination of surface water and groundwater. Because of the high TSHg concentrations, the salt slurry and soils could be classified as hazardous wastes. The Hg contaminated salt slurry and soils are needed to be properly treated to reduce the potential environmental and human health risks.

Acknowledgements

This study was funded by the National Natural Science Foundation of China (U1612442-3, 41622208, and 41573132), the Bureau of Frontier Sciences and Education, Chinese Academy of Sciences (QYZDJ-SSW-DQC005-03), CAS "Light of West China" Program, and the Youth Innovation Promotion Association, Chinese Academy of Sciences (2017442).

References

- Biester, H., Scholz, C., 1997. Determination of mercury binding forms in contaminated soils: mercury pyrolysis versus sequential extractions. *Environ. Sci. Technol.* 31 (1), 233–239.
- Biester, H., Gosar, M., Müller, G., 1999. Mercury speciation in tailings of the Idrija mercury mine. *J. Geochem. Explor.* 65 (3), 195–204.
- Biester, H., Müller, G., Schöler, H.F., 2002. Binding and mobility of mercury in soils contaminated by emissions from chlor-alkali plants. *Sci. Total Environ.* 284 (1–3), 191–203.
- Bravo, A.G., Cosio, C., Amouroux, D., Zopfi, J., Chevalley, P.A., Spangenberg, J.E., Ungureanu, V.G., Dominik, J., 2014. Extremely elevated methyl mercury levels in water, sediment and organisms in a Romanian reservoir affected by release of mercury from a chlor-alkali plant. *Water Res.* 49, 391–405.
- Driscoll, C., Mason, R., Chan, H.M., Jacob, D., Pirrone, N., 2013. Mercury as a global pollutant: source, pathways, and effects. *Environ. Sci. Technol.* 47 (10), 4967–4983.
- Environment Monitoring Station of China (EMSC), 1990. Background Value of Soil Elements in China. China Environmental Science Press, Beijing.
- Esbrí, J.M., López-Berdonces, M.A., Fernández-Calderón, S., Higuera, P., Díez, S., 2015. Atmospheric mercury pollution around a chlor-alkali plant in Flix (NE Spain): an integrated analysis. *Environ. Sci. Pollut. Res.* 22 (7), 4842–4850.
- Feng, X., Li, P., Qiu, G., Wang, S., Li, G., Shang, L., Meng, B., Jiang, H., Bai, W., Li, Z., Fu, X., 2008. Human exposure to methylmercury through rice intake in mercury mining areas, Guizhou province, China. *Environ. Sci. Technol.* 42 (1), 326–332.
- Fernández-Martínez, R., Gómez-Mancebo, B., Peña, E.J., Galán, P., Matsuyama, A., García, F., Rucandio, I., 2016. Monitoring of mercury and other metals mobility by sequential fractionation in soils nearby an abandoned chlor-alkali plant in Managua (Nicaragua). *Environ. Earth Sci.* 75 (6), 538.
- Fu, X., Feng, X., Sommar, J., Wang, S., 2012. A review of studies on atmospheric mercury in China. *Sci. Total Environ.* 421, 73–81.
- Fu, X., Zhang, H., Yu, B., Wang, X., Lin, C.-J., Feng, X.B., 2015. Observations of atmospheric mercury in China: a critical review. *Atmos. Chem. Phys.* 15 (16), 9455–9476.
- Gordeeva, O.N., Belogolova, G.A., Pastukhov, M.V., 2017. Mercury speciation and mobility in soils of industrial areas in the Baikal region, southern Siberia, Russia. *Environ. Earth Sci.* 76 (16), 558.
- Gray, J.E., Peter, U., Theodorakos, M., Bailey, E.A., Turner, R.R., 2000. Distribution, speciation, and transport of mercury in stream-sediment, streamwater, and fish collected near abandoned mercury mines in southwestern Alaska, USA. *Sci. Total Environ.* 260 (1–3), 21–33.
- Gray, J.E., Hines, M., Biester, H., 2006. Mercury methylation influenced by areas of past mercury mining in the Terlingua district, Southwest Texas, USA. *Appl. Geochem.* 21 (11), 1940–1954.
- Guédron, S., Grangeon, S., Jouravel, G., Charlet, L., Sarret, G., 2013. Atmospheric mercury incorporation in soils of an area impacted by a chlor-alkali plant (Grenoble, France): contribution of canopy uptake. *Sci. Total Environ.* 445, 356–364.
- Horowitz, H.M., Jacob, D.J., Amos, H.M., Streets, D.G., Sunderland, E.M., 2014. Historical mercury releases from commercial products: global environmental implications. *Environ. Sci. Technol.* 48 (17), 10242–10250.
- Li, P., Feng, X., Qiu, G., Zhang, J., Meng, B., Wang, J., 2013. Mercury speciation and mobility in mine wastes from mercury mines in China. *Environ. Sci. Pollut. Res.* 20, 8374–8381.
- Li, P., Feng, X., Chan, H.M., Zhang, X., Du, B., 2015. Human body burden and dietary methylmercury intake: the relationship in a rice-consuming population. *Environ. Sci. Technol.* 49 (16), 9682–9689.
- Lin, Y., Wang, S., Wu, Q., Larssen, T., 2016. Material flow for the intentional use of mercury in China. *Environ. Sci. Technol.* 50 (5), 2337–2344.
- Liu, G., Cabrera, J., Allen, M., Cai, Y., 2006. Mercury characterization in a soil sample collected nearby the DOE Oak Ridge Reservation utilizing sequential extraction and thermal desorption method. *Sci. Total Environ.* 369 (1–3), 384–392.
- Liu, M., Zhang, W., Wang, X., Chen, L., Wang, H., Luo, Y., Zhang, H., Shen, H., Tong, Y., Ou, L., Xie, H., Ye, X., Deng, C., 2016. Mercury release to aquatic environments from anthropogenic sources in China from 2001 to 2012. *Environ. Sci. Technol.* 50 (15), 8169–8177.
- Ministry of Ecology and Environment of China (MEEC), 2018. Soil Environmental Quality-risk Control Standard for Soil Contamination of Development Land (GB3600–2018). Environmental Science Press of China, Beijing.
- Obrist, D., Pokharel, A.K., Moore, C., 2014. Vertical profile measurements of soil air suggest immobilization of gaseous elemental mercury in mineral soil. *Environ. Sci. Technol.* 48 (4), 2242–2252.
- Obrist, D., Kirk, J.L., Zhang, L., Sunderland, E.M., Jiskra, M., Selin, N.E., 2018. A review of global environmental mercury processes in response to human and natural perturbations: changes of emissions, climate, and land use. *Ambio* 47 (2), 116–140.
- Pacyna, J.M., Travníkov, O., Simone, F.D., Hedgecock, I.M., Sundseth, K., Pacyna, E.G., Steenhuisen, F., Pirrone, N., Munthe, J., Kindbom, K., 2016. Current and future levels of mercury atmospheric pollution on global scale. *Atmos. Chem. Phys.* 16 (19), 12495–12511.
- Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R.B., Friedli, H.R., Leaner, J., Mason, R., Mukherjee, A.B., Stracher, G.B., Streets, D.G., Telmer, K., 2010. Global mercury emissions to the atmosphere from anthropogenic and natural sources. *Atmos. Chem. Phys.* 10 (13), 5951–5964.
- Reis, A.T., Rodrigues, S.M., Davidson, C.M., Pereira, E., Duarte, A.C., 2010. Extractability and mobility of mercury from agricultural soils surrounding industrial and mining contaminated areas. *Chemosphere* 81 (11), 1369–1377.
- Ren, W., Duan, L., Zhu, Z., Du, W., An, Z., Xu, L., Zhang, C., Zhuo, Y., Chen, C., 2014. Mercury transformation and distribution across a polyvinyl chloride (PVC) production line in China. *Environ. Sci. Technol.* 48 (4), 2321–2327.
- Shi, J., Liang, L., Jiang, G., Jin, X., 2005. The speciation and bioavailability of mercury in sediments of Haihe River, China. *Environ. Int.* 31 (3), 357–365.
- Sholupov, S., Pogarev, S., Ryzhov, V., Mashyanov, N., Stroganov, A., 2004. Zeeman atomic absorption spectrometer RA-915⁺ for direct determination of mercury in air and complex matrix samples. *Fuel Process. Technol.* 85 (6–7), 473–485.
- Song, Z.C., Li, P., Ding, L., Li, Z., Zhu, W., He, T., Feng, X., 2018. Environmental mercury pollution by an abandoned chlor-alkali plant in Southwest China. *J. Geochem. Explor.* 194, 81–87.
- State Environmental Protection Administration of China (SEPA), 2002. Environmental Quality Standards for Surface Water (GB3838–2002). Environmental Science Press of China, Beijing.
- State Environmental Protection Administration of China (SEPA), 2007a. Solid Waste-extraction Procedure for Leaching Toxicity-sulphuric Acid and Nitric Acid Method (HJ/T299–2007). Environmental Science Press of China, Beijing.
- State Environmental Protection Administration of China (SEPA), 2007b. Identification Standards for Hazardous Wastes-identification for Extraction Toxicity (GB5085.3–2007). Environmental Science Press of China, Beijing.
- Streets, D.G., Horowitz, H.M., Jacob, D.J., Lu, Z., Levin, L., Schure, A.F.H., Sunderland, E.M., 2017. Total mercury released to the environment by human activities. *Environ. Sci. Technol.* 51 (11), 5969–5977.
- Tang, Y., Wang, S., Wu, Q., Liu, K., Wang, L., Li, S., Gao, W., Zhang, L., Zheng, H., Li, Z., Hao, J., 2018. Recent decrease trend of atmospheric mercury concentrations in East China: the influence of anthropogenic emissions. *Atmos. Chem. Phys.* 18 (11), 8279–8291.
- Ullrich, S.M., Ilyushchenko, M.A., Kamberov, I.M., Tanton, T.W., 2007. Mercury contamination in the vicinity of a derelict chlor-alkali plant part I: sediment and water contamination of Lake Balyldak and the River Irtys. *Sci. Total Environ.* 381 (1–3), 1–16.
- United Nations Environment Programme (UNEP), 2013. Technical Background Report for the Global Mercury Assessment 2013. Geneva, Switzerland.
- US Environmental Protection Agency (USEPA), 2018. Regional Screening Levels of Risk Assessment. <https://www.epa.gov/risk/regional-screening-levels-rsls-generic-tables>, Accessed date: 30 July 2018.
- Wang, J., Feng, X., Anderson, C.W.N., Zhu, W., Yin, R., Wang, H., 2011. Mercury distribution in the soil-plant-air system at the Wanshan mercury mining district in Guizhou, Southwest China. *Environ. Toxicol. Chem.* 30 (12), 2725–2731.
- Wängberg, I., Edner, H., Ferrara, R., Lanzillotta, E., Munthe, J., Sommar, J., Sjöholm, M., Svaneberg, S., Weibring, P., 2003. Atmospheric mercury near a chlor-alkali plant in Sweden. *Sci. Total Environ.* 304 (1–3), 29–41.
- Wu, Q., Wang, S., Li, G., Liang, S., Lin, C., Wang, Y., Cai, S., Liu, K., Hao, J., 2016. Temporal trend and spatial distribution of speciated atmospheric mercury emissions in China during 1978–2014. *Environ. Sci. Technol.* 50 (24), 13428–13435.

- Zhang, H., Feng, X., Larssen, T., Shang, L., Li, P., 2010a. Bioaccumulation of Methylmercury versus Inorganic Mercury in Rice (*Oryza sativa* L.) Grain. *Environ. Sci. Technol.* 44 (12), 4499–4504.
- Zhang, H., Feng, X., Larssen, T., Qiu, G., Vogt, R.D., 2010b. In inland China, rice, rather than fish, is the major pathway for methylmercury exposure. *Environ. Health. Prospect.* 118 (9), 1183–1188.
- Zhang, L., Wang, S., Wang, L., Wu, Y., Duan, L., Wu, Q., Wang, F., Yang, M., Yang, H., Hao, J., Liu, X., 2015. Updated emission inventories for speciated atmospheric mercury from anthropogenic sources in China. *Environ. Sci. Technol.* 49 (5), 3185–3194.
- Zhu, W., Li, Z.G., Li, P., Yu, B., Lin, C.-J., Sommar, J., Feng, X.B., 2018. Re-emission of legacy mercury from soil adjacent to closed point sources of Hg emission. *Environ. Pollut.* 242, 718–727.