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Environmental mercury pollution by an abandoned chlor-alkali plant in Southwest China

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ABSTRACT

The chlor-alkali industry, which is one of the largest mercury (Hg) consumption and emission sectors in China, may lead to serious Hg pollution of the environment. In this study, we investigated Hg contamination in groundwater, stream water and sediment, the atmosphere, and soil around an abandoned chlor-alkali plant (CAP) in southwest China. The results indicated that the dissolved mercury (DHg) concentrations in groundwater within the CAP exceeded the national limit in 46.4% of the samples, and that this was a result of Hg leaching from upper contaminated salt slurry and soil. Moreover, THg concentrations of surface water and sediment were highly elevated, with maximum levels of 1940 ng/L and 74.6 mg/kg, respectively. Total gaseous mercury (TGM) levels inside the plant were also significantly elevated compared with those outside, which indicated the impact of Hg release from the salty slurry. The THg enrichment factors in surrounding soils ranged from 1.56 to 22.5 (with a mean of 7.18) compared with the regional background, while 28.6% exceeded the second-grade national limit of China. The spatial distribution of THg concentrations in the surrounding soils revealed a unique pattern, with a peak 1–1.25 km from the CAP. Overall, the results indicate that Hg release from the CAP has caused serious pollution of the surrounding environment.

1. Introduction

Mercury (Hg) is a global pollutant because of its high toxicity, global transport, persistence and bio-accumulation in the environment. Atmospheric mercury can be divided into three species based on its physicochemical characteristics, gaseous oxidized mercury (GOM), particulate-bound Hg (PBM) and gaseous elemental mercury (GEM). Moreover, the combination of GOM and GEM are considered as total gaseous mercury (TGM) (Fu et al., 2011). Gaseous oxidized mercury and PBM can be easily deposited and absorbed on a regional scale of the emission sources (Esbrí et al., 2015). Conversely, GEM, the dominant of atmospheric Hg, can remain in the atmosphere for a long time (0.5–2 a), during which it may be subjected to long-range transport across the world (Fu et al., 2015, 2016; Shah et al., 2016).

Atmospheric Hg originates from both natural processes (e.g., volcanoes and geothermal activity, emissions from water and soil interface, forest fires) and anthropogenic activities (e.g., artisanal small-scale gold mining, coal consumption, nonferrous metal smelting, cement production, the chlor-alkali industry) (Esdaile and Chalker, 2018; Streets et al., 2009; Pirrone et al., 2010; Driscoll et al., 2013). Anthropogenic sources account for ~30% of the total emissions to the global atmosphere each year (UNEP, 2013). In the past few decades, China has been the greatest contributor of global atmospheric Hg emissions (around 1/3), and has consumed nearly half of the Hg produced worldwide (UNEP, 2013). Anthropogenic Hg emissions in China were estimated to be 356 t in 2000 and 538 t in 2010 respectively, with an annual growth rate of 4.2% (Zhang et al., 2015). China also emitted 448 to 2151 t of Hg through exhaust gases, effluent and solid waste during 1980–2012 (Huang et al., 2017). Municipal sewage in China released 160 t of Hg to the environment in 2015, while total anthropogenic Hg released to aquatic environments in China reached 98 t in 2012 (Liu et al., 2016, 2018). As a result, China has received pressure from the rest of the world to reduce Hg emissions under the context of the Minamata Convention on Mercury (Wu et al., 2016; Zhang et al., 2016).

In the terrestrial environment, inorganic Hg (IHg) released from anthropogenic sources can be converted to methylmercury (MeHg) by sulphate-reducing bacterial (SRB) and iron-reducing bacterial (FeRB) under anoxic and sub-oxic conditions. Methylation primarily occurs along with oxidized/anoxic and hypolimnetic factors after entering

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aquatic ecosystems (Parks et al., 2013). Methylmercury, which is the most toxic species of Hg, can bioaccumulate through the aquatic food chain, after which it poses health risks to humans via seafood consumption (Driscoll et al., 2013). Recent studies have indicated that rice planted in Hg contaminated areas can bioaccumulate MeHg (Zhang et al., 2010), and that rice consumption is the main pathway of human MeHg exposure in inland China (Feng et al., 2008; Zhang et al., 2010; Li et al., 2012). Moreover, health risks of MeHg exposure were found to exist in Hg contaminated areas based on hair MeHg concentrations in specific populations exceeding the guidelines set by the United States Environmental Protection Agency (USEPA) of 1 μg/g and the World Health Organization (WHO) of 2.3 μg/g (Feng et al., 2008; Li et al., 2009, 2011, 2015). Accordingly, increased attention is needed in Hg contaminated sites to address this issue.

Mercury, which is widely used as a catalyst in chlor-alkali plants (CAPs), may be discharged (mainly in the form of Hg^0) into wastewater, solid waste, and the atmosphere during the production process (Biester et al., 2002; Hissler and Probst, 2006). Mercury consumption by the polyvinyl chloride (PVC) sector accounts for over 60% of the annual consumption in China (Lin et al., 2016). Previous studies have indicated high Hg emissions from CAP in the southern United States (400–600 g day^{-1}, Southworth et al., 2004), as well as in Sweden and Italy (144–1296 g day^{-1}, Grönlund et al., 2005). Additionally, the rate of Hg emission from a PVC factory in China was found up to 4.9 g Hg per ton of PVC production (Ren et al., 2014). Even though China eliminated technologies employing Hg electrolytic caustic soda and acetic acid in the early 2000s, there are numerous abandoned CAPs, which may continuously release Hg to the surrounding environment (Zhao et al., 2009).

Therefore, this study was conducted to investigate Hg pollution in the groundwater, surface water, sediment, atmosphere, and surrounding soils impacted by an abandoned CAP. The results presented herein can provide basic data and scientific evidence for risk assessments and environmental remediation strategies for Hg contaminated areas around CAPs.

2. Materials and methods

2.1. Study area

The study site was an abandoned CAP in southwest China covering an area of about 40,000 m^2 (Fig. 1). The CAP, which was founded in 1958, was the largest chemical industry enterprise in southwest China. The CAP also contained a PVC factory and a pesticide factory. The production capacity reached 30,000 tons of caustic soda in response to the ion-exchange membrane process and 30,000 tons of PVC each year. Because of outmoded technology and environmental concerns, the CAP closed in April 2011. The production of Hg-cell caustic soda lasted from 1962 to 1991 and PVC production by calcium carbide continued from 1971 to 2011. The Salt Slurry covers the area of 11,000 m^2 and the total volume was estimated to be 100,000 m^3. It is now slated for conversion to a commercial and residential area because of urban expansion.

2.2. Sample collection

Drills were dug by piledriver and evenly distributed among the historic Electrolysis Workshop (EW), Salt Slurry (SS) site, Carbide Slag (CS) site, PVC Workshop (PVC), Pesticide Workshop (PW), Waste water Pipeline (PL), and Other (O) sites (Fig. 2). Groundwater samples were collected at each drill within the study area and from two wells northwest of the CAP (Fig. 3). The groundwater samples were filtered in situ using a 0.45 μm polyvinylidene fluoride filter (Millipore). Filtered and unfiltered river water and sediment samples were collected from seven sites along the Tanglangchuan River (nearby the CAP) and wastewater effluent channel (injected to the river) (Fig. 3). Prior to fieldwork, borosilicate glass bottles were strictly cleaned and then heated at 500 °C for 1 h to remove Hg. During collection, the sampling bottles were rinsed three times with water and the filtration equipment was only used once to avoid cross contamination. The groundwater was taken up from the drills by a PVC sampler and filled into the precleaned borosilicate glass bottles immediately. Water samples were preserved by adding 0.4% (v/v) ultra-pure HCl, after which they were placed into double plastic bags and stored in clean coolers (4 °C) until analysis. Sample collection, storage, and preservation were conducted in strict accordance with USEPA Method 1631E (USEPA, 2002).

The TGM concentrations inside and surrounding the CAP were measured in situ with a Lumex RA-915+ portable analyzer (Russia). Prior to measurement, this instrument was manually calibrated using its internal test cell. The limit of detection of the instrument is 1–2 ng/m^3 and it collects one datapoint per second; and the TGM data reported in this study had an average resolution of 10 min.

Surface soil samples in the cropland around the CAP were collected to evaluate possible Hg pollution (Fig. 3). The locations of all 28 samples were determined using a global positioning system (GPS). Soil samples were air dried at room temperature (~22 °C), then ground into powder to pass through a 200-mesh sieve. The salty slurry (SS) and soil pollution inside the CAP were investigated in companion papers (unpublished).

2.3. Analytical method

The THg (unfiltered) and dissolved Hg (DHg, filtered) in water samples were determined by BrCl oxidation, $SnCl_2$ reduction, and CVAAS detection (F732-S, Shanghai Huaguang Instrument Company). Water samples with low Hg levels (< 1 μg/L) were screened by cold vapor atomic fluorescence spectrometry (CVAFS, Tekran 2500). Particulate Hg (PHg) in water samples, defined as Hg bound to particulate matter, were calculated as the difference between THg and DHg concentrations.

The THg concentrations in soil and sediment samples were measured using a RA-915+ Hg analyzer coupled with a PYRO-915+ attachment (Lumex, Sholupov et al., 2004), which is based on thermal decomposition and subsequent Zeeman Atomic Absorption Spectrometry.

Quality control consisted of method blanks, certified reference materials (CRMs), and blind duplicates. The limits of detection (LODs) were 0.02 mg/kg for THg in solid samples, 0.05 μg/L water for Hg measured by CVAAS detection and 0.02 ng/L for CVAFS. The average THg concentrations obtained in Certificated Reference Material (GBW07405) were 0.30 ± 0.02 mg/kg (n = 5), which was consistent with the certified values of 0.29 ± 0.03 mg/kg. The average relative difference in percentage was < 10% for THg in duplicate samples.

2.4. Data analysis

All data were analyzed using the statistics software SPSS 21.0 for Windows. The data were tested for normal distribution by the Kolmogorov-Smirnov test. If data were not normally distributed, they were log transformed for further statistical analysis. The data are reported as the means ± standard deviation (SD) for normally distributed data and the geometric mean (geomean) for log transformed data. The correlation between THg in surface water and sediment was tested by spearman analysis.

3. Results and discussion

3.1. Groundwater

The DHg concentrations in the groundwater at different sites are shown in Table 1. Two well samples on the northwest side of the CAP showed relatively low DHg concentrations of 6.1 and 17.9 ng/L, respectively, which were taken as the background level. The DHg

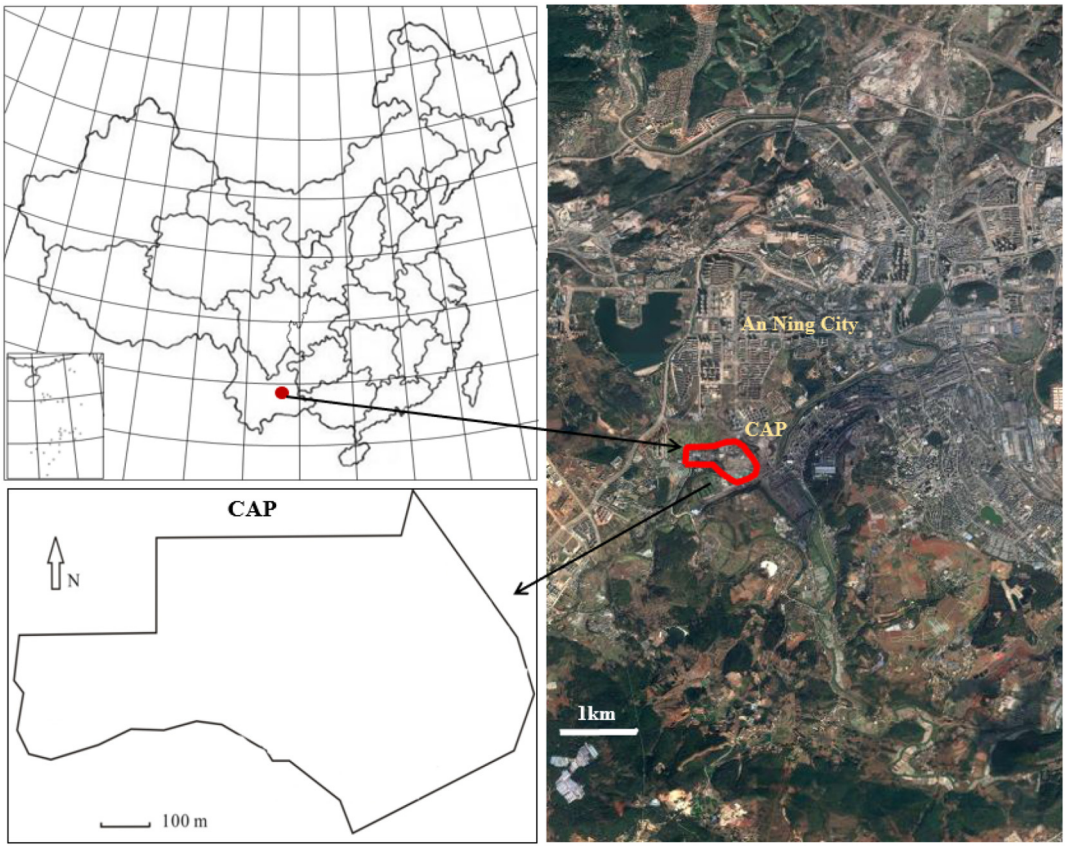

Fig. 1. Geographic location of the studied chlor-alkali plant.

concentrations in the groundwater at the SS sites ranged from 0.014–3600 μg/L with a geomean of 41.5 μg/L. Additionally, 88% (22/25) of the samples exceeded the national standard for groundwater quality (1 μg/L). The DHg concentrations in the groundwater at the carbide slag (CS) sites were 2.28, 42.5, and 28.0 μg/L, all of which exceeded the national standard. Moreover, the DHg concentrations in the groundwater at sites around SS and EW were relatively high (geomeans of 0.88 and 0.56 μg/L, respectively). Detailed information is listed in Table 1.

Overall, the DHg concentrations exceeded the national limit in

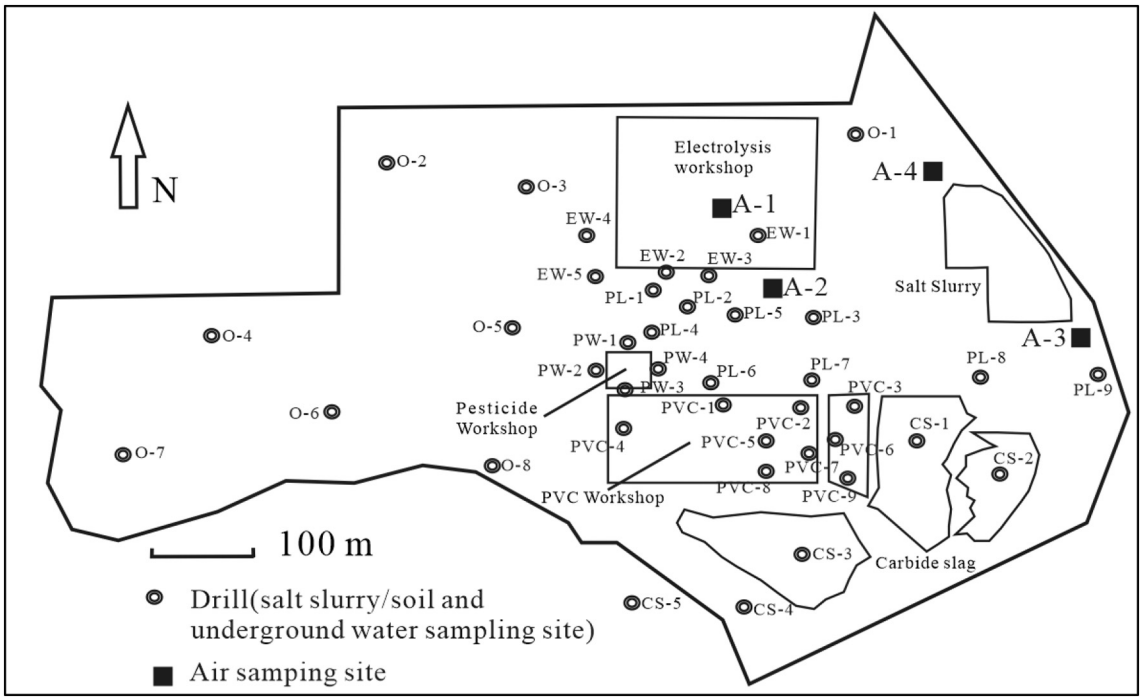

Fig. 2. Spatial distribution of groundwater and air sampling sites at the chlor-alkali plant.

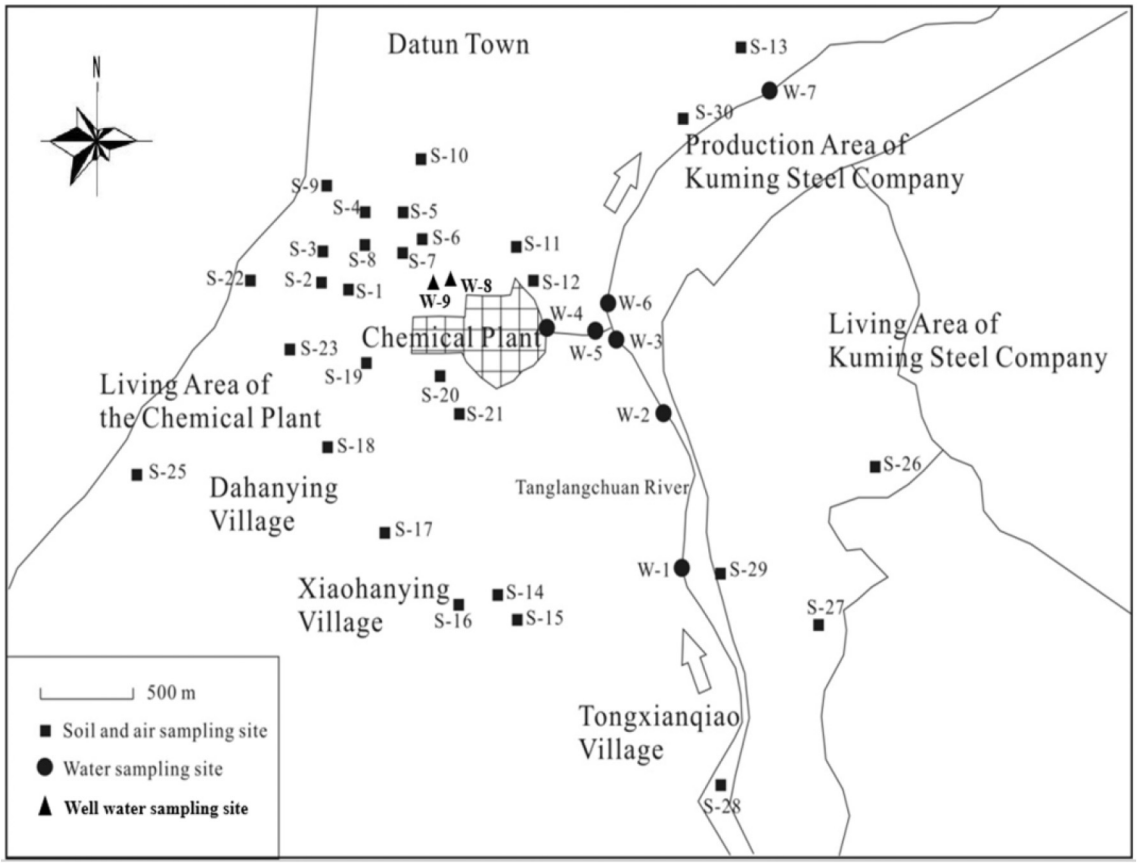

Fig. 3. Spatial distribution of soil and water sampling sites around the chlor-alkali plant.

Table 1
DHg concentrations in the groundwater at different sites (μg/L).

Site	n	Geomean	Mean	STD	Min	Max	Exceeding rate (Ratio of > 1 μg/L)
SS	25	41.5	396	853	0.014	3600	88%
Around SS	7	0.88	2.65	2.70	0.01	7.26	71.4%
EW	5	0.56	10.2	22.1	0.012	49.8	20%
PVC	9	0.02	0.10	0.18	0.003	0.52	0
PL	9	0.04	0.45	1.12	0.003	3.42	11.1%
PW	4	0.01	0.01	0.002	0.005	0.009	0
CS	3	14.0	24.3	20.4	2.28	42.5	100%
O	7	0.02	0.15	0.31	0.005	0.83	0
Total	69	0.82	146	542	0.003	3600	46.4%

SS, Salt Slurry; EW, Electrolysis Workshop; PVC, PVC Workshop; PL, Waste water Pipeline; PW, Pesticide Workshop; CS, Carbide Slag; O, other sites.

46.4% (32/69) of the groundwater samples collected from the plant. These results indicate serious Hg pollution of the groundwater in the CAP, especially at sites of SS and CS, which were highly impacted by the production activities. The salt slurry samples are classified as hazardous wastes with highly elevated THg concentrations and soluble Hg^{2+} concentrations (HW 29; MEP, 2016). Moreover, high DHg concentrations of the groundwater in the CAP suggested the continuous release of soluble Hg from upper contaminated salt slurry and soils. Overall, these findings indicate that leaching of Hg by rainwater has resulted in serious Hg pollution of the groundwater.

3.2. Surface water and sediment

The THg concentrations in surface water samples ranged from 8.4 to 1940 ng/L (Fig. 5). The levels at sites W-2 and W-3 in Tanglangchuan River were 8.4 and 11.2 ng/L, respectively, which can be considered the regional background. These background concentrations were comparable with THg concentrations observed in the Wujiangdu Reservoir (8.5–25.8 ng/L; Feng et al., 2009) in Guizhou, which has not been obviously impacted by human activities. As expected, the highest THg concentrations in surface water were observed in the channel (W-4, 1630 ng/L; W-5, 1940 ng/L), which exceeded the national standard of surface water quality (1 μg/L) of China. The THg concentrations in the stream water at W-6 increased slightly to 22.0 ng/L after mixing with waste water. The DHg concentrations ranged from 6.7 to 1100 ng/L, and this constituted the dominant portion (56.7–88.6%) of the THg concentrations in the stream water.

Similar to the THg concentrations in surface water, the highest THg concentrations in bottom sediment samples were detected at sites W-4 and W-5 (61.5 and 74.6 mg/kg, respectively). The lowest value (0.35 mg/kg) was found at site W-1, which was located in the upstream portion of the studied river (Fig. 3). Comparison of the THg concentrations in the sediments with the results of similar contaminated sites worldwide (Table 2) revealed that they were significantly higher than those from the Wuli River in China (0.15–15.4 mg/kg; Zheng et al., 2011), the coast of eastern Canada (0.04–0.28 mg/kg; Tony, 2016) and the Thur River in France (0.108–0.639 mg/kg; Hissler and Probst, 2006), but were comparable to the levels in the Sagua River of Cuba (0.165–97 mg/kg; Bolaños-Álvarez et al., 2016). However, highly elevated THg concentrations in sediments were observed in Balkydak Lake in Kazakhstan (0.36–617 mg/kg; Ullrich et al., 2007a, 2007b).

The PHg concentrations in the river water at site W-4 and W-5 were as high as 600 and 840 ng/L, respectively, indicating that the high Hg pollution in the wastewater channels may result both from leaching of soluble Hg and transport of particulate Hg from the salt slurry and contaminated soils. Significant correlation between THg concentrations in sediments and corresponding waters was observed ($r = 0.786$, $p < 0.05$, Fig. 4), indicating possible circulation of Hg between

Table 2
Comparison of THg concentrations in sediment and soil impacted by chlor-alkali plant worldwide.

Study site	Dominant industry	Soil (mg/kg)	Sediment (mg/kg)	Reference
Thur River, France	Chlor-alkali plant	0.016–0.339	0.108–0.639	Hissler and Probst, 2006
Lake Balkyldak, Kazakhstan	Hg-cell Chlor-alkali plant	0.10–3.30	0.36–617	Ullrich et al., 2007a, 2007b
Wuli river, China	Chlor-alkali Industry and Zn smelting	/	0.15–15.4	Zheng et al., 2011
Sagua River, Cuba	Chlor-alkali plant	/	0.165–97	Bolaños-Álvarez et al., 2016
Coastal marine, Canada	Chlor-alkali plant	/	0.04–0.28	Tony, 2016
Netherlands	Chlor-alkali plant	0.0043–1.150	/	Bernaus et al., 2006
Grenoble, France	Chlor-alkali plant	0.05–10	/	Grangeon et al., 2012
North-western Portugal	Chlor-alkali plant	0.010–90.8	/	Reis et al., 2009
Tanglangchuan river, Southwest China	Chlor-alkali plant	0.09–1.30	0.35–74.6	This study

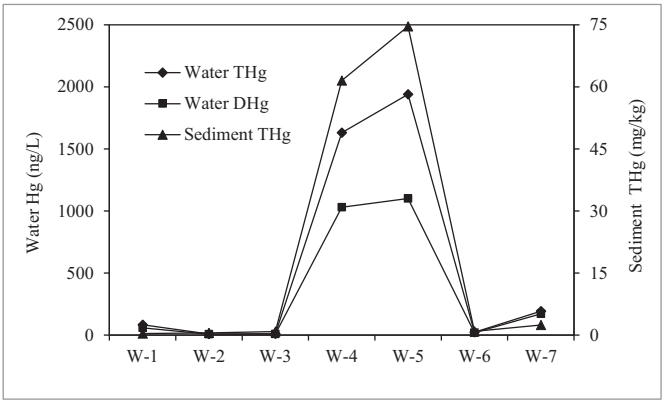

Fig. 4. Hg concentrations in surface water and sediments.

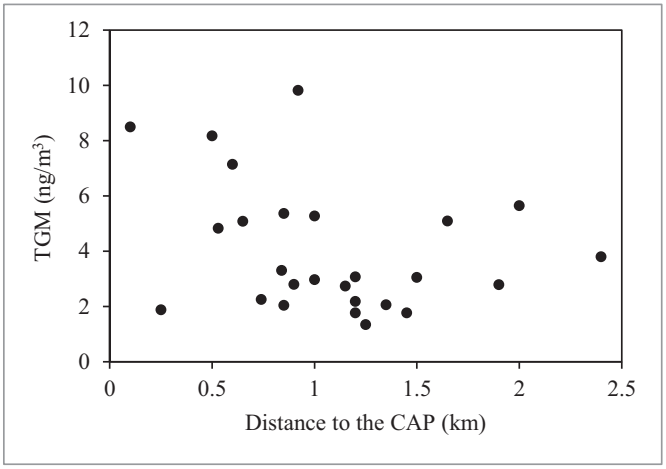

Fig. 5. Total gaseous Hg concentrations at different sites with distance to the CAP.

sediment and water compartments. The serious Hg pollution in surface water and sediment indicated that CAP was a significant Hg source to the surrounding aquatic system. Moreover, discharged IHg can be transformed into MeHg under anoxic environments, which can pose potential risks to aquatic systems and human beings (Bravo et al., 2014).

3.3. Atmospheric Hg

The TGM concentrations inside and outside of the CAP are shown in Table 3. The geomean of the TGM concentrations outside the CAP was 3.53 ng/m^3 (1.35–9.8 ng/m^3, n = 26), which was close to the global background (1.5–1.7 ng/m^3, Lindberg et al., 2007). The TGM concentrations inside the plant ranged from 1.40 to 1670 ng/m^3, which were significantly elevated when compared with those outside of the plant, with a geomean of 12.8 ng/m^3 (n = 52). In a companion paper (Zhu et al., 2018), the TGM concentrations in four sites around the SS were found to have been seriously impacted by production activities, as indicated by mean levels of 222, 35.4, 293, and 822 ng/m^3, respectively. All values exceeded the national standard for ambient air quality (50 ng/m^3) of China (MEP, 2012), and one exceeded the USEPA Reference Concentration (RfC) for chronic Hg exposure (300 ng/m^3) (US EPA, 1999). These findings confirmed that the SS and Hg contaminated soil in the plant were significant Hg emission sources to atmosphere.

The TGM concentrations outside the CAP decreased gradually with increasing distances from the CAP (Fig. 5). Elevated TGM concentrations were found in the region close to the CAP, and the TGM concentrations reached approximately 2 ng/m^3 at 2 km from the plant, indicating that the CAP was a significant point source of Hg emissions to the ambient atmosphere. Similar trends were obtained by previous studies conducted around the CAP (Southworth et al., 2004; Barregard et al., 2006; Gibicar et al., 2009). The TGM concentrations observed in this study were comparable to the results reported for CAPs from Spain (3.5–229 ng/m^3; Esbrí et al., 2015), Sweden (1.5–540 ng/m^3; Wängberg et al., 2005), and Italy (2.8–100 ng/m^3; Gibicar et al., 2009).

Table 3
TGM concentrations inside and outside of the chlor-alkali plant (ng/m^3).

ID	n	Geomean	Mean	STD	Min	Max
Inside	52	12.8	48.3	230	1.40	1670
Outside	26	3.53	4.07	2.28	1.35	9.80

3.4. Surrounding soils

The THg concentrations in 28 surface soil samples collected within 2.5 km from the CAP ranged from 0.09 to 1.30 mg/kg (with a mean of 0.40 mg/kg). The regional background of soil THg was 0.058 mg/kg (CNEMC, 1990). The enrichment factors in the studied soil samples ranged from 1.56 to 22.5 (with a mean of 7.18), which indicated obvious Hg pollution resulted from the CAP. Overall, 28.6% (8/28) of studied soil samples had THg concentrations exceeding the second-grade of the Environmental Quality Standard for Soils (SEPAC, 1995, 0.5 mg/kg). Local populations were found to be at risks of Hg exposure by consumption of Hg polluted agricultural crops.

Comparison of the results of the present study with those observed at CAP worldwide (Table 2) revealed that the levels in the soils investigated for this study were comparable to those found around CAPs in the Netherlands (0.0043–1.15 mg/kg; Bernaus et al., 2006), France (0.016–0.399 mg/kg; Hissler and Probst, 2006), and Kazakhstan (0.10–3.30 mg/kg; Ullrich et al., 2007a, 2007b). However, highly elevated soil THg levels were found in Grenoble, France (0.05–10 mg/kg, Grangeon et al., 2012) and northwestern Portugal (0.010–91 mg/kg; Reis et al., 2009).

Chlor-alkali plants were confirmed to be significant sources of pollution to the surrounding soils (Biester et al., 2002). In the present study, the THg concentrations increased with distance from the CAP

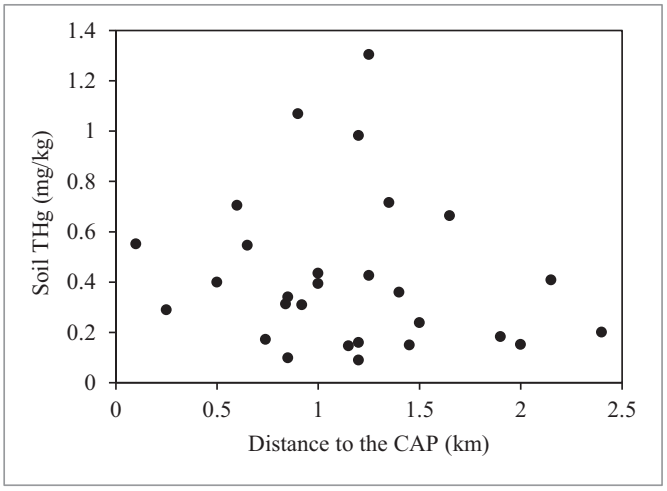

Fig. 6. THg concentrations in surrounding soils with distance to the CAP.

until peaking at 1–1.25 km from the site, after which they decreased (Fig. 6). These results reflect a pattern of atmospheric Hg release from the CAP and atmospheric Hg deposition in the surrounding soils, which was comparable to that observed for other studies of CAPs (Biester et al., 2002; Southworth et al., 2004; Tack et al., 2005).

4. Conclusion

The results of this study revealed that Hg released from the CAP caused serious pollution of the surrounding environment. Almost half of the groundwater samples were seriously contaminated with Hg. Moreover, stream water and sediment were contaminated with Hg by wastewater emitted from the CAP, and TGM concentrations inside the plant were highly elevated compared with the background levels. However, the peak Hg pollution in the surrounding soils occurred at 1–1.25 km from the CAP. Even if production activities ceased, the SS and Hg contaminated soils would likely continuously release Hg to the surrounding environment. Therefore, appropriate remediation practices are urgently needed to restore Hg pollution in the CAP to reduce health risks associated with Hg exposure to local residences. The Salt Slurry and heavily Hg contaminated soil should be properly disposed (such as thermal desorption) to remove the pollution source.

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