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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