Chemosphere 169 (2017) 333–341

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Risk assessment for the mercury polluted site near a pesticide plant in Changsha, Hunan, China

Haochen Dong [a], Zhijia Lin [b], Xiang Wan [a], Liu Feng [a, *]

[a] Department of Environmental Sciences and Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China
[b] Hunan Institute of Geological Survey, Changsha, Hunan 410116, PR China

HIGHLIGHTS

- Total concentration and fraction distribution of mercury were characterized.
- Soil physicochemical properties were built-up for fractionation analysis.
- DGH method and model were introduced for risk assessment.

ARTICLE INFO

Article history:
Received 22 July 2016
Received in revised form
3 November 2016
Accepted 15 November 2016
Available online 22 November 2016

Handling Editor: Martine Leermakers

Keywords:
Mercury
Delayed geochemical hazard
Risk assessment

ABSTRACT

The distribution characteristics of mercury fractions at the site near a pesticide plant was investigated, with the total mercury concentrations ranging from 0.0250 to 44.3 mg kg^{-1}. The mercury bound to organic matter and residual mercury were the main fractions, and the most mobile fractions accounted for only 5.9%–9.7%, indicating a relatively low degree of potential risk. The relationships between mercury fractions and soil physicochemical properties were analysed. The results demonstrated that organic matter was one of the most important factors in soil fraction distribution, and both OM and soil pH appeared to have a significant influence on the Fe/Mn oxides of mercury. Together with the methodology of partial correlation analysis, the concept and model of delayed geochemical hazard (DGH) was introduced to reveal the potential transformation paths and chain reactions among different mercury fractions and therefore to have a better understanding of risk development. The results showed that the site may be classified as a low-risk site of mercury DGH with a probability of 10.5%, but it had an easy trend in mercury DGH development due to low critical points of DGH burst. In summary, this study provides a methodology for site risk assessment in terms of static risk and risk development.

1. Introduction

Following the rapid social and economic development over the past several decades, soil pollution by mercury (Hg) has been observed worldwide (Van Straaten, 2000; Gochfeld, 2003; Gosar et al., 2006; Qiu et al., 2006; Cordy et al., 2011). For example, in the entire Lake Victoria Goldfields of Tanzania, Africa, approximately 3–4 t Hg was released annually into the atmosphere (Van Straaten, 2000). In the Amazon region, mercury has been released during gold mining operations, resulting in methylmercury exposure via the food chain (Gochfeld, 2003). Additionally, in the mining areas of Guizhou, China, mine wastes contain total Hg concentrations ranging from 79.0 to 710 mg kg^{-1}, with significant conversion of methyl-Hg in the study areas, causing potential health risks (Qiu et al., 2006).

Mercury is a persistent pollutant and the bioaccumulation and biomagnification of toxic pollutants has a significant impact on human health and ecological environment. The health and ecological risks associated with mercury-polluted sites have been widely recognized and studied. The data from the Wuchuan mercury mining area (one of the largest mercury mining areas in Guizhou province, China) showed that people living near a mercury mining site experienced adverse health effects caused by mercury exposure. Total concentration of Hg measured in the hair of the residents near the mercury mining area reached 210 mg kg^{-1}, far beyond the value of the control group (Li et al., 2008a, 2008b). In the USA, mercury contamination with the highest concentration reaching 2.10 mg kg^{-1} was discovered in Fort Totten by measuring

* Corresponding author.
E-mail address: fengliu-buct@vip.sina.com (L. Feng).

http://dx.doi.org/10.1016/j.chemosphere.2016.11.084
0045-6535/

the total concentration of Hg with a comprehensive evaluation process related to human health risk (Goldblum et al., 2006).

Risk assessment based on the total amount of pollutants is an intuitive and simple method that has been applied to heavy metal contaminated sites in early stages (Agusa et al., 2005; Goldblum et al., 2006; Mieiro et al., 2009). However, as with the development of a deeper understanding of environmental behaviour and ecological effect of pollutants, the inadequacy of this method has become increasingly apparent. Since the method does not take into consideration the differences in environmental effectiveness and biological availability between various chemical forms of metals, the method often overestimates the potential risk (Goldblum et al., 2006).

Speciation analysis in a bioavailability study could provide a different perspective for risk assessment. In this approach, the different chemical forms of heavy metals such as mercury are identified in order to characterize their mobility and toxicity (Issaro et al., 2009). Sequential extraction procedure (SEP) has been widely applied as a tool in the speciation analysis for metal extraction in soils, especially the Tessier SEP (Tessier et al., 1979; Issaro et al., 2009). There are five defined fractions in the order of extraction difficulty with different occurrence of forms. In 1993, European Community Bureau of Reference (BCR) certified the extractable contents of a trace metal in sediments following a three-step extraction procedure (Quevauviller et al., 1997) that has recently become a commonly used tool for soil (sediment) studies (Mäkelä et al., 2011; Chakraborty et al., 2014; Kerolli–Mustafa et al., 2015). Compared with Tessier SEP, BCR extraction has fewer steps and a weaker phenomenon of redistribution/re-adsorption that gives rise to better reproducibility. Both Tessier and BCR SEP have been widely used in previous studies of Hg in many mining areas in China, showing that the Hg concentrations in mining areas range from 0.100 to 790 mg kg^{-1} with 60%–80% HgS as the main existing form (Horvat et al., 2003; Li et al., 2007; Qiu et al., 2013; Yang et al., 2014). Both methods have shortcomings in the extraction of mercury (Issaro et al., 2009) for example, a Hg redistribution/re-adsorption pattern may occur and cause incomplete extraction. According to recent studies, a new approach proposed by the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT) has been used for a fractionation study at the Almadén mercury mine area in Spain. The comparison between the addition of Hg concentration to each fraction and the measured total Hg, ranged between 92% and 99%, and proved the feasibility of the new method (Fernández-Martínez and Rucandio, 2013; Fernández-Martínez et al., 2014; Fernández-Martínez and Rucandio, 2014). The implemented SEP can also be useful in providing information about the amount of mercury available in different contaminated areas for risk assessment. A study of the plants in the Almadén mining area found very low available mercury, including water-soluble and exchangeable fractions in all samples (Millán et al., 2006). Even so, Tessier SEP is still valid and favourable for risk assessment of heavy metal pollution (Islam et al., 2015; Rosado et al., 2016).

From another point of view, soil physical and chemical properties are also an integral part of the assessment. A previous study has shown that pH provides the most useful information for estimating an element's migration that can be an important parameter for the assessment of the available mercury. Furthermore, Cation Exchange Capacity (CEC) does not improve the ability to predict the movement of ions through these natural soils (Korte et al., 1976). Nordén (1994) studied pH and organic matter (OM) content of forest topsoil and found that the differences in soil organic matter content between the plants were small. However, these studies focus on either the chemical forms or the total concentration of mercury statically and unilaterally, and therefore, the resultant static risk assessment of the sites overlooks the transformation between these forms in the soil.

Ming et al. (2005) proposed the concept of delayed geochemical hazard (DGH) that revealed the dynamic transformation among different forms and became a tool for risk assessment. "Total releasable content of the pollutant" (TRCP) and "total concentration of active species" (TCAS) are two important concepts related to DGH. TRCP focuses on the releasable content that is equal to the total content of the pollutants in the soil (sediment) minus the content of some compounds that are quite stable with respect to activation and release in the soil (sediment) even under extreme conditions (Ming et al., 2004). TCAS is the active characteristic of the pollutant and indicates the concentration of some species in TRCP involved in much more activity under certain environmental conditions (Ming et al., 2004).

Our previous study (Zheng et al., 2015) demonstrated the nonlinearity changes among different chemical fractions that occur when geochemical conditions are altered in soil by soil column tests. The results provided a possibility to establish a mathematical model to quantify the potential development of DGH. The structure and characteristics of the original model are shown in Fig. 1. The X axis indicates TRCP (C) in the soil system and the Y axis indicates TCAS (Q). The fitting curve L_0 represents the trend in TCAS with the increase in TRCP; continuous input of pollutants into the soil system altered the increasing trend in TCAS. At first, an increase of TRCP (ΔC) resulted in a little increase in TCAS (ΔQ_1); however, when continuous accumulation of TRCP reached a certain degree, the same increase in TRCP, ΔC, would give rise to a greater increase in ΔQ, TCAS (ΔQ_2). This was in accordance with the non-linear mutational rising of TCAS.

The previously fitted results depending on the Tessier method showed a dynamic evolution process that could be quantitatively expressed with a nonlinear polynomial and the highest degree of these polynomials are 3. Combined with the preceding digital model of DGH, we could characterize two special points: critical point of burst and burst point as follows:

Critical point of burst, where the first and second derivatives are zero and convexity and concavity of the curve are altered, represents the beginning of DGH.

When the first derivative reaches the maximum value and the second derivative is zero, the critical point that can be calculated and related to maximum slope, represents the most active stage of DGH (Ming et al., 2005).

In a recent study (Zheng et al., 2015), a DGH model expressed with nonlinear polynomials was successfully used to assess the risk of a mercury polluted site.

The mercury polluted area that is the focus of this study is located in Hunan, Changsha, near an abandoned pesticide factory (PF). Among other compounds, the main products of the factory were arsenic agents (such as calcium arsenate used in pesticides and other arsenate herbicides, bactericides, etc.), organochlorine, organophosphorus, organ nitrogen, and chlorothalonil. Due to managerial negligence during the early phases of the factory, massive discharge of pollutants to the surrounding soil caused different degrees of heavy metal pollution, including mercury and arsenic. To accurately assess the potential environmental risk of mercury pollution, total concentration of Hg and distributions based on the Tessier method were measured for a preliminary static risk assessment of the site. Meanwhile, statistical analysis techniques were used to analyse the effect of soil physical and chemical properties on mercury accumulation of various forms and elucidate the interactions among different mercury forms. Then, A DGH model was imported to characterize the dynamic evolution process of risk and provide basic data for site management and remediation. The methods used in this study provide a new concept for risk