Science of the Total Environment 646 (2019) 19–28

Contents lists available at ScienceDirect

Science of the Total Environment

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

An integrated approach to identify quantitative sources and hazardous areas of heavy metals in soils

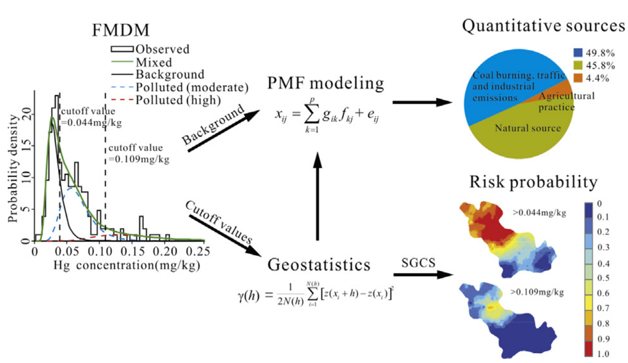
Jianshu Lv [a,b,*], Yang Liu [c]

[a] College of Geography and Environment, Shandong Normal University, Jinan 250014, China
[b] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China
[c] Business School, University of Jinan, Jinan 25002, China

HIGHLIGHTS

- An integrated approach was proposed to examine sources and hazardous areas of heavy metals.
- FMDM was employed to establish background standards and pollution thresholds.
- PMF with FMDM background was used to partition source contributions.
- SGCS with FMDM pollution thresholds was applied to determine hazardous areas.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 17 May 2018
Received in revised form 17 July 2018
Accepted 18 July 2018
Available online xxxx

Editor: F.M. Tack

Keywords:
Heavy metals
Source
Hazardous areas
Integrated approach
Uncertainty

ABSTRACT

Identifying quantitative sources and hazardous areas of heavy metals is a crucial issue for soil management. For this purpose, an integrated approach composed of finite mixture distribution modeling (FMDM), positive matrix factorization (PMF) and sequential Gaussian co-simulation (SGCS) was proposed. FMDM was used to establish background standards and pollution thresholds. PMF supported by FMDM background standards was applied to estimate the source apportionment. Hazardous areas of single metals were delineated using SGCS with FMDM pollution thresholds and uncertainty analysis, and overall hazardous areas were defined by the presence of multiple metals. This integrated approach was applied to a dataset of seven metals as a case study. FMDM indicated that the distributions of Cr, Cu, Ni, and Zn were fitted to two-dimensional mixture distributions, representing a background distribution and a moderately polluted distribution. The distributions of Cd, Hg, and Pb were composed of a three-component lognormal mixture distribution, corresponding to the background, moderate, and high pollution distributions. Three sources were apportioned. Cr, Cu, Ni, and Zn were dominated by parent materials. Parent materials contributed 52.6%, 45.8%, and 81.9% of Cd, Hg, and Pb concentrations, respectively. Human emissions from coal combustion, industrial work and traffic had significant influences on Hg, Cd, and Pb, with contributions of 49.8%, 26.9%, and 15.6%, respectively. Agricultural practices were exclusively associated with 20.5% of Cd. Overall, hazardous areas exceeding moderate pollution thresholds covered 17.4% of the total area, corresponding to urban areas and industrial sites, whereas overall hazardous areas above high pollution thresholds were limited to 0.01% of the total area.

* Corresponding author at: College of Geography and Environment, Shandong Normal University, Ji'nan 250014, China.
E-mail address: lvjianshu@126.com (J. Lv).

https://doi.org/10.1016/j.scitotenv.2018.07.257
0048-9697/

1. Introduction

Heavy metals are well known because of their ecotoxicity and persistence and are of great importance to soil environments (Alloway, 2013; Rodríguez Martin et al., 2015). Heavy metals in soils are controlled by natural background levels and human inputs with complex influencing mechanisms (Christensen et al., 2018). Natural background levels of heavy metals in soils are mainly inherited from parent rocks. Human activities that influence heavy metal contents include coal combustion, traffic emissions, industrial manufacturing, mining, and agricultural practices(Alloway, 2013), and the impact of anthropogenic inputs commonly exceeds natural background with enhanced urbanization and industrialization. Source apportionment is essential for successfully regulating pollutant inputs, and an adequate understanding of heavy metals background levels facilitates establishing an appropriate standard for soil remediation (Ha et al., 2014; Hu and Cheng, 2013; Li et al., 2015). This combination of natural factors and human activity also results in complex spatial variability (Lv et al., 2013). The areas where heavy metal contents exceed the given thresholds are defined as hazardous areas in this work. Delineating hazardous areas is more valuable for decision-makers for effective soil environment management than mapping spatial variability (Lin et al., 2016).

Receptor models such as absolute principal component score/multiple linear regression (APCS/MLR), positive matrix factorization (PMF), and UNMIX do not depend on prior knowledge of source profiles and have been primarily applied for the identification and apportionment of heavy metal sources (Chen and Lu, 2018; Guan et al., 2018; Perrone et al., 2018; Sofowote et al., 2008). However, the receptor model, as pure multivariate statistical model, may produce biases and uncertainties in the source apportionment. Moreover, the factors from receptor model were identified as different sources by factor loadings of various variables based on the previous knowledge of researchers, which may result in the subjectivity of factor interpretation. The limitations of receptor model could be conducted by comparing the results from multiple models. Finite mixture distribution modeling (FMDM) can build a mixture distribution consisting of several component distributions of heavy metals, and each component represents natural background or human activity distributions (Lin et al., 2010; Portier, 2001; Yang and Chang, 2005). A baseline approach and multivariate analysis are typically used to identify the soil background levels (Albanese et al., 2007; Reimann and de Caritat, 2017; Reimann et al., 2005; Yang and Chang, 2006; Yotova et al., 2018). However, due to current human disturbances of the soil environment, it is difficult to acquire sampling sites that truly represent background soil levels (Yang and Chang, 2006). FMDM can effectively overcome the difficulties associated with defining background sites and has been successfully used to establish background standards and pollution thresholds of heavy metals (Hao et al., 2016; Hu and Cheng, 2013; Lin et al., 2010; Zhi et al., 2016; Zhong et al., 2014). The background standards derived from FMDM can be used to compare to the factor profiles from receptor models; this process facilitates demarcation of the source represented by natural factors and verifies the receptor model results. Zhi et al. (2016) first used FMDM and PMF to apportion the sources of soil Cd in croplands of Eastern China, but PMF failed to obtain a successful source apportionment. In this study, with the support of FMDM, we attempted to apply PMF to estimate source apportionment of heavy metals in soils.

Geostatistical methods including kriging and stochastic simulation provide effective tools to estimate or simulate spatial distributions of heavy metals (Juang et al., 2004; Lv et al., 2013; Rodríguez Martin and Nanos, 2016) and to determine hazardous areas (Chu et al., 2010; Juang and Lee, 1998). Lin et al. (2010), Zhong et al. (2014), and Hao et al. (2016) combined indicator kriging and FMDM to map the spatial patterns of heavy metal pollution in soil. Conditional simulation techniques such as sequential Gaussian simulation (SGS) and sequential indicator simulation (SIS) can be used to avoid the smooth effect of kriged estimation and examine the uncertainty of simulated concentrations (Goovaerts, 1997; Mueller and Ferreira, 2012; Webster and Oliver, 2007). However, conditional simulation requires more random access memory (RAM) and a faster processor than kriging (Emery and Silva, 2009; Yao et al., 2013). With the rapid development of computer hardware, conditional simulation has more potential in environmental studies. The univariate geostatistical simulation tends to ignore spatial interrelation among various variables and may be unsuitable for generating spatial distributions. Multivariate geostatistical simulations with a linear model of coregionalization fitting (LMC) could lead to a better understanding of spatial variability than univariate geostatistical simulation (Boluwade and Madramootoo, 2015; Franco et al., 2006; Liu et al., 2013; Suhrabian and Tercan, 2014). In this study, the spatial probability of pollution was mapped using sequential Gaussian co-simulation (SGCS) with pollution thresholds derived from FMDM, and hazardous areas were determined through minimizing spatial uncertainty.

Together, an integrated approach was proposed to identify quantitative sources and hazardous areas of heavy metals in soils and contains three steps: (1) to explore background standards and pollution thresholds using FMDM, (2) to estimate quantitative source apportionment using PMF supported by FMDM background standards, and (3) to determine hazardous areas using SGCS with the FMDM pollution thresholds and uncertainty analysis. The integrated approach was applied to a heavy metals dataset (Cd, Cr, Cu, Hg, Ni, Pb, and Zn concentrations of 209 surface soil samples) as a case study.

2. Materials and methods

2.1. Sampling and chemical analysis

Boshan, a typical industrial city in eastern China with a total area of 698.2 km^2, was selected as the case study area (Fig. S1). There are three industries in this area, ceramics, coal-fired power, and metal casting; most of this activity is distributed in and around the urban area (Fig. S2). Boshan is one of the most important ceramics production bases in China and contains significant reserves of coal. The intensive industries inevitably result in the accumulation of heavy metals in soils. Furthermore, the rapid industrialization and urbanization in future decades will aggravate this accumulation trend. The elevation ranges from 130 to 1100 m, decreasing in elevation from the south to the north (Fig. S2). The soil parent materials consist of dolomite, limestone, mudstone, sandstone, granite, and hornblendite as well as alluvium and proluvium (Fig. S2).

The study area was divided into 2 km × 2 km cells, and a total of 209 sampling sites were designated at the center of each cell. During field sampling, an alternative location close to predesigned sites was selected to obtain a natural soil in case the soils were unavailable at the original location. The coordinates of the sampling sites were recorded using a hand-held GPS. At each sampling site, four to six subsamples of topsoils (0–20 cm deep) within a 100 m radius were collected and mixed thoroughly in a polyethylene bag. The locations of the sampling sites are indicated in Fig. S1. Soil samples were air-dried and ground to <0.2 mm powder. After digestion of the samples, Cr, Ni, Pb and Zn concentrations were analyzed using a flame atomic absorption spectrophotometer (240 AA Agilent, USA), Cd contents were determined using a graphite furnace atomic absorption spectrophotometer (AA-7000 Shimadzu, Japan), and Hg concentrations were determined with an atomic fluorescence spectrometer (AFS230E Haiguang Analytical Instrument Co., Beijing, China). For details on the measurements, please refer to the related literature (Lu, 2000; Lv et al., 2014; Lv et al., 2013). A standard reference material, GSS-1 soil, obtained from the Center for National Standard Reference Material of China, was used for quality control. The recoveries of all seven metals were 100 ± 10%. Analytical reagent blanks were used in the sample preparation and analytical processes. All measurements were conducted in triplicate, and standard deviations were within ±5% of the mean.