Science of the Total Environment 569–570 (2016) 191–200

Contents lists available at ScienceDirect

Science of the Total Environment

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

Modeling and mapping of critical loads for heavy metals in Kunshan soil

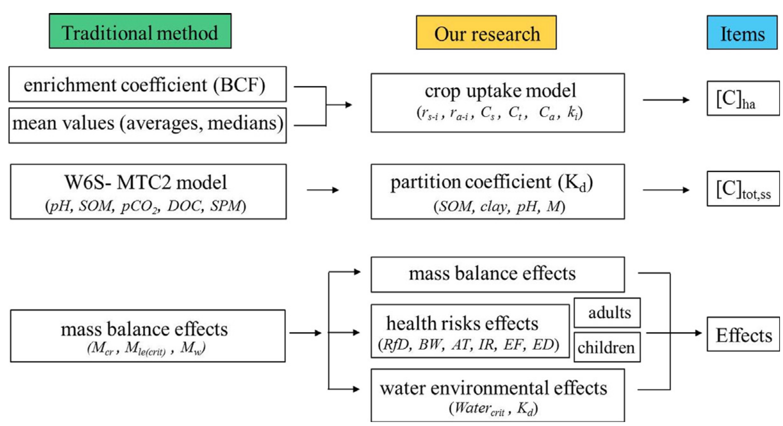
Shaohua Wu [a,b,*], Yaxing Shi [a], Shenglu Zhou [a,*], Chunhui Wang [a], Hao Chen [a]

[a] *School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 210023, China*
[b] *Key Laboratory of Watershed Geographic of Chinese Academy of Sciences, Nanjing 210008, China*

HIGHLIGHTS

- Spatially explicit methods are provided to calculate critical loads of heavy metal.
- The plant absorption of heavy metal model is used to improve critical load approach.
- Critical loads based on three different effects are compared.
- Exceedances of critical load are helpful to find high risk areas of soil pollution.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form 6 June 2016
Accepted 11 June 2016
Available online xxxx

Editor: F.M. Tack

Keywords:
Critical loads
Heavy metals
Mass balance model
Health risk
Water quality

ABSTRACT

The assessment of critical loads of metals in soil can be used as an important tool for evaluation and for risk precaution of future inputs of metal in order to avoid the occurrence of heavy metal pollution and its long-term risks for people. In this study, critical loads of Cd, Cu, and Pb in farming and non-farming areas of Kunshan were calculated based on three main effects. Two of these effects, limit value of daily metals dose and different environmental water quality criteria are new ways to calculate the critical content of heavy metals. The mean value of critical loads decreased in the order Cu > Pb > Cd when calculated using mass balance effects, child health risk effects, and adult health risk effects. Critical loads were highest in the areas near construction land, areas of low critical load were scattered throughout the city. The areal proportion of critical load exceedance is greatest for Pb based on mass balance effects, followed by Cu based on water quality effects, and Cd based on mass balance effects. Exceedances only occurred in 6% and 3% of farming areas for water quality effects for Cd and Pb when compared critical load values to the input fluxes in the Yangtze River delta. However, for these metals, values were up to 83% and 100%, respectively, based on mass balance effects. Exceedances completely covered non-farming areas for each effect for Pb. Most exceedances occurred in the north and south of the city in non-farming areas. Spatially explicit critical loads of heavy metals based on the different effects can serve as a reference for controlling the emissions of heavy metals effectively and meeting the demands of different management objectives.

* Corresponding author at: School of Geographic and Oceanographic Sciences, Nanjing University, Nanjing 2100, China.
E-mail addresses: wsh@nju.edu.cn, shaohuawu@126.com (S. Wu), zhousl@nju.edu.cn (S. Zhou).

http://dx.doi.org/10.1016/j.scitotenv.2016.06.072

1. Introduction

The rapid growth of the global population, global economy, and the high consumption of resources profoundly affect changes in the earth system, resulting in a series of global problems that include environmental pollution and land degradation. In recent years, the problem of soil contamination by heavy metals has increasingly become the focus of attention. The annual global metal production in 2000 for cadmium (Cd), copper (Cu), and lead (Pb) exceeds that of 100 years ago by 9, 17, and 3 times, respectively (Han et al., 2002). Annual emissions of Cd, Cu, Pb and other heavy metals will mostly enter the soil, causing soil heavy metal pollution that will change the composition, structure, and function of the soil and will also be transmitted to plants and animals and, ultimately, to humans via the food chain (Chen et al., 2015; Peralta-Videa et al., 2009; Ran et al., 2016). Soil heavy metal pollution has become a severe problem in many parts of the world (Facchinelli et al., 2001; Solgi et al., 2012), especially in developing countries. China's rapid development over the past several decades has led to massive industrialization and urbanization, causing soil pollution by heavy metals that has been both serious and widespread (Li et al., 2014; Wang et al., 2001).

With the change of economic growth mode, industrial transfer, and the enhancement of human control, the emissions of heavy metals have begun to decline in some developed countries. The heavy metal pollution in China is more severe than that of the developed countries because of the rapid social and economic development (Chen et al., 2015; Zhuang et al., 2009). Much soil heavy metal pollution and many high risk areas have resulted from heavily-polluting enterprises or industrially-intensive areas, mining exploration areas, and urban and suburban areas. In addition, the quality and safety problems of food affected by soil heavy metal pollution have increased year by year and have become an important factor affecting the health of humans and social stability (Ning et al., 2015; Tóth et al., 2016; Zhu et al., 2010). Therefore, under the scenario of China's rapid economic development, it is urgent to study the accumulation process of heavy metals in soil and determine the risk response mechanisms.

The critical load is defined as the acceptable total load of anthropogenic heavy metal inputs, including deposition, fertilizer, and other anthropogenic sources (J-P et al., 2007). Knowledge of the critical load of heavy metal is an important management tool that can be used to prevent heavy metal pollution (Wu, 2009). The critical load of soil was originally used for studying surface water acidification. With the increased research into the effects of heavy metals and persistent organic pollutants (POPs), the critical load approach began to be used for trying to prevent and control human practices leading to excess heavy metals and POPs in soil (Boekhold and Zee, 1991; Schulin, 1993; Vries et al., 1998). The effect-based approach and the stand-still approach are the two main methods used to compute the critical load of heavy metals in terrestrial ecosystems. Maps of critical loads for heavy metals and their exceedances have been published for Europe and Canada (J-P et al., 2007; Patrick et al., 2003), using various approaches, but there have been few attempts to study the critical loads with respect to different environmental effects.

Our research has improved the critical load calculation model and we considered different effects on the basis of the traditional methods: (i) using the model of crop uptake of heavy metals to estimate the heavy metals removal by harvest of plants; (ii) using a transfer function of heavy metals to estimate the total metal concentration in soil solution and calculate critical leaching of heavy metals from the soil; (iii) taking into account different effects when calculating: mass balance effects, child health risk effects, adult health risk effects, and water quality effects. Critical loads of heavy metals for the different effects considered in this study can serve as a reference for policies for controlling the emissions of heavy metals effectively and providing a scientific basis for the input control of heavy metals under different management objectives.

2. Material and methods

2.1. Study site and sampling

For the study site, we chose the city of Kunshan, which is one of the most developed regions in China and close to Shanghai. Kunshan, located in eastern China, has a total area of 927.68 km^2 – the water area accounts for 23.1%. Kunshan has a subtropical monsoon climate, with an annual average temperature of 17.6 °C, and an annual average precipitation of 1200.4 mm. The population of Kunshan is about 1.65 million and the rate of urbanization is up to 75.1%. The soil consists of four types: Hydragric Anthrosols, Humic Gleysols, Gleyic Fluvisols, and Eutric Planosols. Hydragric Anthrosols was the main soil type and accounted for 93.8% of the soil in our study. Because of the rapid growth of industrial production, traffic, and population, Kunshan is faced with serious environmental problems caused by human activities.

126 soil samples (0–15 cm and 15–40 cm depth) were collected in five different functional areas: 26 in chemical industry areas, 15 in metallurgy industry areas, 18 in textile industry areas, 29 in farming areas, and 38 in livestock areas (Fig. 1). We recorded the location with a GPS, and all the samples were air-dried at room temperature for one week, sieved to 20-mesh and 100-mesh and stored in wide mouth bottles until analysis.

2.2. Soil analysis

The pH was determined in distilled water with a 1:2.5 soil-solution ratio with pH glass electrodes. The particle size distribution was determined using a laser particle size analyzer (Malvern Instruments Inc., Worcestershire, UK). The percentage of organic matter in the soil was measured by the titration method, which is based on the oxidation of organic matter by $K_2Cr_2O_7$. Elemental concentrations of Cu and Pb were determined using inductively coupled plasma optical emission spectrometry (Optima 3300DV, Perkin-Elmer, USA), and concentrations of Cd were determined by graphite furnace atomic absorption spectrometry after digesting soil samples with analytically pure nitric (HNO_3), perchloric ($HClO_4$),and hydrofluoric (HF) acids.

2.3. Calculation of mass balance effects (steady-state mass balance model)

The critical load for the considered system equals the sum of its tolerable outputs from agricultural products and leaching minus the natural inputs by weathering release (J-P et al., 2007; Vries et al., 2012). Steady-state model was used to calculate critical loads for mass balance effects. This method take into account all relevant metal fluxes in or out of the system that are required to reach a steady state situation. The formulae for farming and non-farming areas are as follows:

$$CL_a(M) = M_{cr} + M_{le(crit)} - M_w \tag{1}$$

$$CL_b(M) = M_{le(crit)} - M_w \tag{2}$$

where $CL_a(M)$ is the critical load of heavy metal M in the farming areas ($g \cdot ha^{-1} \cdot a^{-1}$) and $CL_b(M)$ is the critical load of heavy metal M in the non-farming areas. M_{cr} is net metal uptake in harvestable parts of plants ($g \cdot ha^{-1} \cdot a^{-1}$), $M_{le(crit)}$ is the critical leaching flux of heavy metals ($g \cdot ha^{-1} \cdot a^{-1}$) and M_w is the weathering release of heavy metals ($g \cdot ha^{-1} \cdot a^{-1}$). The weathering release of heavy metals can be neglected outside volcanic or ore-rich areas. Additional formulae used are:

$$M_{cr} = f_{cr} \cdot Y_{ha} \cdot [C]_{ha} \tag{3}$$

$$M_{le(crit)} = c_{le} \cdot Q_{le} \cdot [C]_{tot,ss} \tag{4}$$

$$Q_{le} = P - f_{cr} \cdot \left({P_m}^{-2} + \left(e^{(0.063 \cdot T_m)} \cdot E_m \right)^{-2} \right)^{-0.5} \tag{5}$$