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Calculation and application of Sb toxicity coefficient for potential ecological risk assessment

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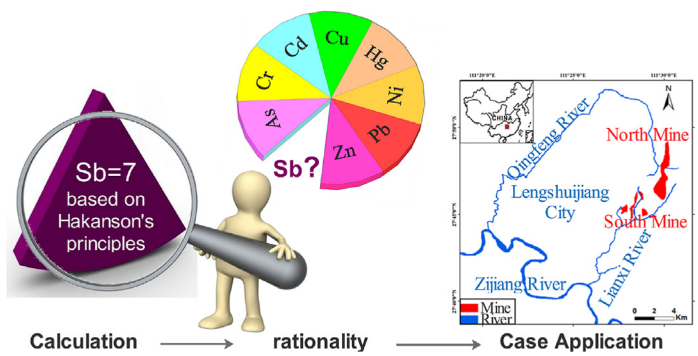
HIGHLIGHTS

- The no toxicity coefficient available limits its widespread use in RI for Sb.
- Sb′s toxicity coefficient was calculated based on Hakanson's principles.
- Sb′s toxicity coefficient (=7) was verified by different pollution indexes.
- E_r^i was a reliable and logical index for evaluating Sb pollution.
- Development of ecological risk index helps to broaden the serviceable range of RI.

GRAPHICAL ABSTRACT



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ABSTRACT

The potential ecological risk index (RI) is a diagnostic tool for pollution control which integrate the concentration of heavy metals with ecological effect, environmental effect and toxicity. However, the lack of toxicity coefficients for specific heavy metals limits its widespread use. In this study, we calculated the toxicity coefficient (=7) for antimony (Sb) based on Hakanson's principles, thus broadening the range of potential applications of this risk assessment tool. Taking the case of Xikuangshan (XKS), the largest Sb mine in the world, we predicted the potential ecological risk factor (E_r^i) of Sb for sediment and soil. This was then compared with the enrichment factor (EF) and index of geoaccumulation (I_{geo}). Results showed that Sb shared the similar pollution categories regardless of E_r^i, EF or I_{geo} indexes was used indicating the appropriateness of the determined toxicity coefficient. Regression analysis results further demonstrated that E_r^i was in agreement with bioavailable concentrations (Diffusive Gradient in Thin Films and Community Bureau of Reference extraction concentrations), particularly in sediments. This means that E_r^i is a reliable and logical index for evaluating Sb pollution in sediments within aquatic environments and in soils within terrestrial environments.

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1. Introduction

Various chemical, toxicological, and ecological approaches have been used to assess the impacts of heavy metals on the environment (Bonnail et al., 2016; He et al., 1998; Semenzin et al., 2008; Wang et al., 2013). The most direct approach to reveal the pollution status in the environment is chemical analysis of environmental concentrations of heavy metals. Several analytical methods for sequential extraction have been employed to investigate heavy metal fractionation (Nolan et al., 2003; Pueyo et al., 2008; Tessier et al., 1979). Ecological risk assessment is also necessary to evaluate environmental impacts resulting from exposure to one or more heavy metal stressors (Forbes and Galic, 2016). Several indices, such as the pollution index (PI) and the pollution

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load index (PLI) (Tomlinson et al., 1980), stress the importance of considering the ratio between concentration of heavy metals in the studied area and background values. Enriched factor (EF) was calculated by comparing the concentration of metal element with that of a reference element (Taylor, 1964), to identify mobilization or utilizability of examined metal (Buatmenard and Chesselet, 1979). The enrichment after regression analysis (ERA) method is used to analyze migration and transformation of three types of metals (Hilton et al., 1985). The geoaccumulation index (I_{geo}) estimates contamination by comparing preindustrial and recent metal concentrations (Loska et al., 2004; Müller, 1969). However, different toxic substance is intended to express the different levels of threat to the ecological system. It is thus not adequate to consider only total concentrations when evaluating potential ecological risk.

To quantitatively evaluate the potential ecological risk posed by metal pollutants in sediments, Lars Hakanson (National Sweden Environment Protection Board, Water Quality Laboratory Uppsala) developed a risk index (RI), which takes toxin concentrations, background values, and release coefficients into consideration (Hakanson, 1980). The RI focuses on the potential toxicological effects of a given contaminant (element), with evaluation of corresponding toxic effects using sedimentological, toxicological, and ecological ranking factors based on the “abundance principle”, “sink-effect” and “dimension-problem”. Since its development, the index has been widely applied in ecological risk assessment (Fernandes, 1997; Gao and Chen, 2012; Yi et al., 2011) and is still extensively used for evaluation of soils, sewage sludge, and road dust (but not for sediment) (Becouze-Lareure et al., 2016; Huang and Yuan, 2016; Huang et al., 2016; Wei et al., 2016; Xiao et al., 2016). Toxic coefficients of the corresponding metals are the primary requirement in this convenient and effective method for evaluating potential ecological risk. Hakanson calculated toxicity coefficients of the metal elements Cr, Zn, Cu, Pb, As, Cd, and Hg (Hakanson, 1980). Subsequent research led to identification of toxicity factors for Ti, Mn, V, Ni, and Co (Xu et al., 2008). However, potential ecological risk index exists a gap for Sb contaminated region due to its inexistence of toxicity coefficient for Sb.

Sb has been categorized as a priority pollutant by the United States Environmental Protection Agency (US EPA) and by the European Union (EU, 1976; USEPA, 1979). It is the fourth member of Group VA of the Periodic Table of the Elements and is widely distributed in nature, including in the lithosphere, pedosphere, hydrosphere, atmosphere, and biosphere. The reserve of Sb is mainly concentrated in many types of mineral deposits, particularly those containing Sb_2S_3 (stibnite) and Sb_2O_3 (senarmontite, valentinite) (Boyle and Jonasson, 1984; Filella et al., 2002). As a fascinating element, Sb has been used by human since the Early Bronze Age (Smichowski, 2008). In modern times, Sb and its compounds are widely used for industrial production and in daily life. For example, the element is used in catalysts for production of polyethylene terephthalate (PET), as a flame retardant in production of paper, plastic, pigments, rubbers, paints, coatings, ceramics, adhesives, and textiles, as a component of brake linings and cable coverings, as well as in ammunitions and bearings (Reimann et al., 2010; Smichowski, 2008). Because of increased natural and anthropogenic emissions and related significant environmental hazards for plants, animals, microorganisms, and humans (Okkenhaug et al., 2011; Wei et al., 2015; Wu et al., 2011), Sb pollution is becoming a global issue that is raising increasing environmental concern (He et al., 2012; Li et al., 2015; Shotyk et al., 2005).

Considering the above, the objectives of this work were: (1) to calculate the toxicity coefficient of Sb based on Hakanson's principles; (2) to validate the developed toxicity coefficient via a case study; and (3) to assess the degree of contamination of Sb and As in soils collected from the Xikuangshan (XKS) Sb mine area using different indices. Calculating the toxicity coefficient of Sb and the development of ecological risk index will serve to broaden the serviceable scope of potential ecological risk assessment.

2. Calculation toxicity coefficient for Sb

Toxic coefficient of Sb was calculated based on Hakanson's principles, putting sedimentological, toxicological, and ecological ranking factors into consideration based on the abundance principle, while taking into consideration sink effects and dimension problems (Hakanson, 1980). The validity and rationality of the developed coefficient is also discussed.

2.1. Step 1: the abundance principle

The abundance principle states that the potential toxicological effect of an element is proportional to its abundance, consistent with well-established general theory (Hilton et al., 1985). Relevant methodology includes the following: (1) basic material for the evaluation lists in Table 1. It shows the abundance of various elements in different types of geological and biological media (igneous rock, soils, fresh water, land plants, and land animals); data from different types of media can be natural and beneficial to make a revision of the results. (2) Relative abundance data. Table 2 ranks the abundance of eight elements (As, Cd, Cr, Cu, Hg, Pb, Zn, Sb) in five media. Hakanson (1980) assigned a value of 1.0 to the element with the highest concentration in every medium. In igneous rocks, for example, Cr is given a value of 1.0 because of its highest concentration in this medium, with this being 500 times higher than that of Cd, which has a value of 500. We can see all the results of relative abundance in Table 2. (3) Abundance numbers. Abundance numbers for ten elements in five media are given in the lower part of Table 2. The sum of these five abundance numbers for every element is given in the column marked Σ_1^5. (4) Balancing of extreme abundance numbers. To avoid inappropriate weighting, the largest value of these five abundance numbers is discarded, with the remaining four abundance numbers summed in the column marked Σ_1^4. The abundance numbers in the last column are obtained by division by 4.4 (the value of Zn, the lowest Σ_1^4 value). The sequence of abundance numbers is as follows: Zn < Cu < Pb < Cr < Sb < As < Cd < Hg. According to Hakanson, abundance numbers are not equivalent to toxicity factors; sink effects and dimension problems also need to be taken into consideration.

2.2. Step 2: sink effects

Sink effects are related to the fact that different elements make different ‘fingerprints’ in sediment and have different tendencies to be deposited in the sediments. Following Hakanson's methodology, only lakes or their sub-basins are considered for calculation of sink factors. An element's sink factor is determined as follows:

$$\text{Sink factors} = \frac{\text{natural background values for fresh water}}{\text{preindustrial reference value for lake sediments}}$$

Table 1
Abundance of various elements in different media ($\times 10^{-6}$).

Element	Igneous rock	Soil	Fresh water	Land plants	Land animals
As[a]	1.8	6	4.00E-04	0.2	≤0.2
Cd[a]	0.2	0.06	<0.08	0.6	0.5
Cr[a]	100	100	1.80E-04	0.23	0.075
Cu[a]	55	20	1.00E-02	14	2.4
Hg[a]	0.08	0.03–0.8	8.00E-05	0.015	0.046
Pb[a]	12.5	10	5.00E-03	2.7	2
Zn[a]	70	50	1.00E-02	100	160
Sb[a,b,c]	0.2	1	1.00E-04	0.4	≤0.01

[a] Bowen (1966).
[b] Boyle and Jonasson (1984).
[c] Reimann et al. (2010).

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