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Chemical and biological methods to evaluate the availability of heavy metals in soils of the Siena urban area (Italy)

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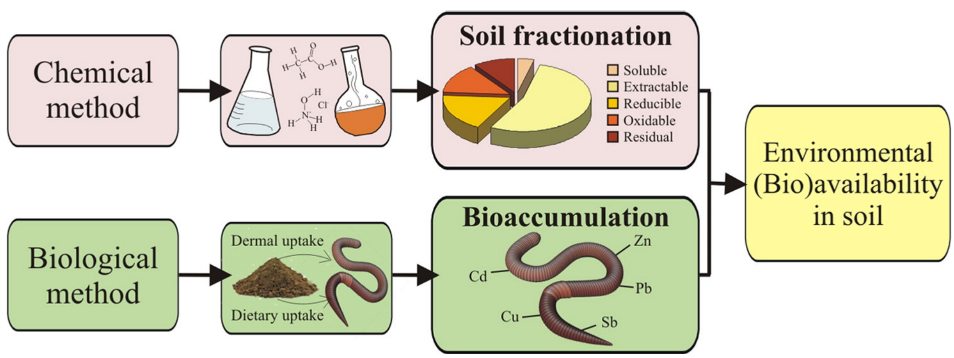
HIGHLIGHTS

- Heavy metal availability in soil was assessed by soil fractionation.
- Heavy metal bioavailability in soil was assessed by accumulation in earthworm tissue.
- Chemical methods do not consider the biological factors influencing availability.
- Bioavailability is influenced by physiology and ecological behaviour of earthworms.
- Chemical and biological methods should be merged to assess element availability.

GRAPHICAL ABSTRACT



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ABSTRACT

A biogeochemistry field study was conducted in the Siena urban area (Italy) with the main objective of establishing the relationship between available amounts of heavy metals in soil assessed by a chemical method (soil fractionation) and bioavailability assessed by a biological method (bioaccumulation in earthworm tissues). The total content of traffic-related (Cd, Cu, Pb, Sb, Zn) and geogenic (Co, Cr, Ni, U) heavy metals in uncontaminated and contaminated soils and their concentrations in soil fractions and earthworms were used for this purpose. The bioavailability of heavy metals assessed by earthworms did not always match the availability defined by soil fractionation. Earthworms were a good indicator to assess the bioavailability of Pb and Sb in soil, while due to physiological mechanisms of regulation and excretion, Cd, Cu and Zn tissue levels in these invertebrates gave misleading estimates of their bioavailable pool. No relationship was identified between chemical and biological availability for the geogenic heavy metals, characterized by a narrow range of total contents in soil. The study highlighted that chemical and biological methods should be combined to provide more complete information about heavy element bioavailability in soils.

1. Introduction

The distribution of heavy metals in soil fractions, so-called chemical fractionation, is an important aspect of soil geochemistry as it governs the behaviour of these elements in soil and plays a relevant rule in determining their availability for soil biota. Availability is considered an essential parameter for effective uptake and accumulation of heavy metals in soil organisms, and therefore an important tool in assessment of environmental risk. A number of physico-chemical and biological processes influence the bioavailability of heavy metals in soil, indicating that their transfer from soil to biota is as a very complex phenomenon.

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According to a general definition, "*The bioavailable fraction of a chemical is the fraction of its total amount present in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by (micro)organisms from either the direct surrounding of the organism or by ingestion of food*" (Peijnenburg et al., 2007). In this view, the available fraction of a chemical element in soil depends both on soil factors such as element distribution in soil fractions and physico-chemical processes occurring with time (e.g. ionic exchange, acid dissolution and redox reactions), and on biological factors such as the physiological activities of soil organisms, especially affecting ingested soil (Harmsen, 2007; Peijnenburg et al., 2007).

Considering the various factors influencing element availability in soil, more specific available pools may be defined (Harmsen, 2007; Peijnenburg et al., 2007; Maleri et al., 2008; Alvarenga et al., 2012): 1) the "effective available" pool consisting of water-soluble and extractable fractions, which are the most mobile and very active pool of a chemical element, mainly regulated by rapid reactions in soil such as water solubilization, ionic exchange and acid dissolution; 2) the "potentially available" pool, consisting of reducible and oxidable fractions, namely the leachable and partly active pool mainly mobilizable by redox reactions; 3) the "bioaccessible" pool, the amount of a chemical element that can be released through digestion by water and ingested soil; this is the fraction most available for intestinal uptake.

The availability of a chemical element for soil organisms may be assessed by two complementary ways: chemical and biological methods. The chemical methods are single or sequential extraction procedures to determine the amount of a chemical associated with a specific soil fraction, such as water-soluble, extractable, reducible, oxidable and residual. The partitioning of heavy metals in these fractions is mainly controlled by the physico-chemical properties and composition of soil (e.g. pH, cation exchange capacity and organic matter content) as well as reactions such as sorption, precipitation and coprecipitation. The element fractions determined by chemical extractions can therefore be defined operationally by the procedures used, as well as functionally as effective and potentially available pools (Gupta et al., 1996; Peijnenburg et al., 2007). As bioavailability is not merely a chemical concentration, the extraction procedures may only offer a snapshot of the different fractions of chemicals to which soil species may be exposed, but this does not consider the biological aspects, such as physiology, behaviour and exposure time. Therefore, assessment of the available fraction by chemical methods is empirical and highly dependent on the extraction procedure used.

Biological methods identify the aliquot of the element available fraction that a soil organism can absorb and accumulate. These methods evaluate the bioavailability of a chemical element in soil through its bioaccumulation in soil organisms (mainly invertebrates), used as bioindicators exposed to a single or several chemicals. Biological methods also consider the physiological capacity of a soil organism to uptake chemical elements by dermal absorption and digestion in the gut, and to accumulate them in tissues.

An organism frequently used to assess bioavailability of heavy metals in soil is the earthworm (Peijnenburg et al., 1999; Conder et al., 2002; Maddocks et al., 2005; Nahmani et al., 2007). Earthworms are relatively efficient accumulators of essential and non-essential metals such as Cd, Cu, Pb and Zn (Morgan and Morgan, 1999; Lanno et al., 2004; Suthar et al., 2008). Several environmental and ecotoxicological studies have used these invertebrates as bioindicators of heavy metal levels in soil in contaminated areas, providing data for the assessment of environmental risk (e.g. Kennette et al., 2002; Nahmani et al., 2007; Suthar et al., 2008; Goix et al., 2015). Furthermore, chemical analysis of earthworms may provide an indication of bioavailable amounts of heavy metals (Maleri et al., 2008; Ruiz et al., 2011).

Uptake of heavy metals by earthworms is mainly from pore water, food and ingested soil particles (Oste et al., 2001; Lanno et al., 2004; Hobbelen et al., 2006). The storage, accumulation and excretion of these chemicals seem to be controlled by ecological and physiological factors (Spurgeon and Hopkin, 1996; Morgan and Morgan, 1999; Kamitani and Kaneko, 2007; Suthar et al., 2008; Nannoni et al., 2014). Field and laboratory studies have demonstrated that uptake and bioaccumulation of heavy metals by earthworms are not related to the total content of these contaminants in soil, as these organisms only respond to the biologically available and accessible fractions (Alexander, 2000; Dai et al., 2004; Harmsen, 2007).

An important target of biogeochemistry studies is to define the relationships between the chemical fractionation of heavy metals in soil and their uptake and bioaccumulation by soil organisms, that is, the relationships between the available (effective and potentially) and bioaccessible pools of heavy metals and the amounts accumulating in tissues.

The question is of particular concern in areas contaminated by heavy metals, such as urban areas. Urban areas are affected by several human activities such as vehicle traffic, industries, domestic heating and municipal waste incinerator, which are point and diffuse sources of toxic and potentially toxic heavy metals such as Cd, Cu, Pb, Sb and Zn. In urban settings, soil plays a key role in the environmental pathway of heavy metals, as it controls their accumulation and release to natural waters and soil biota. Soil is therefore a good indicator of human disturbance (contamination) and potential risk for the surface environment, especially the urban ecological system.

A number of studies have dealt with heavy metal contamination in urban areas, assessing the influence of human sources, mainly vehicle traffic, on the total contents of these contaminants in surface soils (e.g. Imperato et al., 2003; Acosta et al., 2011; Sun et al., 2010). To our knowledge, few studies have focused on the fractionation and mobility of heavy metals in contaminated urban soils (Burt et al., 2014; Acosta et al., 2015; Gu et al., 2016), and even less their availability in soil and transfer to earthworms (Pizl and Josens, 1995; Kennette et al., 2002; Nannoni et al., 2011).

In this context, a biogeochemistry field study was conducted in the urban area of Siena (central Italy) with the following aims: i) to determine the influence of contamination, mainly related to vehicle traffic, on the partitioning of heavy metals in soil fractions; ii) to establish the main soil fractions involved in uptake of heavy metals by earthworms; iii) to define the relationships between available and bioaccessible amounts of heavy metals in soil, evaluated by chemical extraction, and bioavailability assessed by bioaccumulation in earthworm tissues.

The present research is a prosecution of a previous study of Nannoni et al. (2014) focused on the relationships between the total soil contents of heavy metals in Siena urban soils and their accumulation in earthworm tissues, as well as the evaluation of the main soil properties as possible factor influencing metal uptake by these invertebrates.

2. Materials and methods

2.1. Study area

The present study was realized in the territory of Siena municipality including both the urban centre and the peri-urban, green-urban and non-urban zones. The resident population in the Siena city is of about 55,000 inhabitants, and the main human sources of heavy metals in the surface environment are the vehicle traffic and domestic heating in wintertime (Nannoni et al., 2014). About 50,000 vehicles move daily mostly along the ring road extending in the peri-urban sector of the Siena city. Since 1965, a limited traffic zone (LTZ) limits the vehicle traffic in the historic centre of Siena.

The study area is located in the northern part of the Siena basin. This basin is a NW-SE graben-type tectonic depression in which clayey-silty-marly to sandy-marly marine sediments of the Neogene-Quaternary succession deposited during Pliocene. These sediments represent the lithological substratum from which soils of the study area were formed.