Journal of Environmental Management 186 (2017) 192–200

Contents lists available at ScienceDirect

Journal of Environmental Management

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

Research article

# Bioavailability and risk assessment of potentially toxic elements in garden edible vegetables and soils around a highly contaminated former mining area in Germany

Vasileios Antoniadis [a,*], Sabry M. Shaheen [b,c], Judith Boersch [c], Tina Frohne [c,1], Gijs Du Laing [d], Jörg Rinklebe [c]

[a] School of Agriculture, University of Thessaly, Fytokou Street, GR-384 46, Greece
[b] University of Kafrelsheikh, Faculty of Agriculture, Department of Soil and Water Sciences, 33 516 Kafr El-Sheikh, Egypt
[c] University of Wuppertal, Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285 Wuppertal, Germany
[d] Laboratory of Analytical Chemistry and Applied Ecochemistry, Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, Ghent, Belgium

ARTICLE INFO

*Article history:*
Received 30 January 2016
Received in revised form
11 April 2016
Accepted 13 April 2016
Available online 23 April 2016

*Keywords:*
Toxic metal(loid)s
Transfer coefficient
Hazard quotient
Contamination pathways

ABSTRACT

Although soil contamination by potentially toxic elements (PTEs) in Europe has a history of many centuries, related problems are often considered as having been dealt with due to the enforcement of tight legislations. However, there are many unsolved issues. We aimed to assess PTE levels in highly contaminated soils and in garden edible vegetables using human health risk indices in order to evaluate the availability and mobilization of arsenic (As), copper (Cu), manganese (Mn), mercury (Hg), lead (Pb), and zinc (Zn). In four gardens in Germany, situated on, or in the vicinity of, a mine dump area, we planted beans (*Phaseolus vulgaris* ssp. *nanus*), carrots (*Daucus sativus*) and lettuce (*Lactuca sativa* ssp. *capitata*). We examined soil-to-plant mobilization of elements using transfer coefficient (*TC*), as well as soil contamination using contamination factor (*CF*), enrichment factor (*EF*), and bioaccumulation index ($I_{geo}$). In addition, we tested two human health risk assessment indices: Soil-induced hazard quotient ($HQ_S$) (representing the "direct soil ingestion" pathway), and vegetable-induced hazard quotient ($HQ_V$) (representing the "vegetable intake" pathway). The studied elements were highly elevated in the soils. The values in garden 2 were especially high (e.g., Pb: 13789.0 and Hg: 36.8 mg kg$^{-1}$) and largely exceeded the reported regulation limits of 50 (for As), 40 (Cu), 400 (Pb), 150 (Zn), and 5 (Hg) mg kg$^{-1}$. Similarly, element concentrations were very high in the grown vegetables. The indices of *CF*, *EF* and $I_{geo}$ were enhanced even to levels that are rarely reported in the literature. Specifically, garden 2 indicated severe contamination due to multi-element deposition. The contribution of each PTE to the total of measured $HQ_S$ revealed that Pb was the single most important element causing health risk (contributing up to 77% to total $HQ_S$). Lead also posed the highest risk concerning vegetable consumption, contributing up to 77% to total $HQ_V$. The presence of lead in both cases was followed by that of As, Mn and Hg. We conclude that in multi-element contamination cases, along with high-toxicity elements (here, Pb, As and Hg) other elements may also be responsible for increasing human health risks (i.e., Mn), due to the possibility of adverse synergism of the PTEs.



## 1. Introduction

Potentially toxic elements (PTEs), when in elevated concentrations, have detrimental effects on plants and humans (Kabata-Pendias, 2011; Cao et al., 2015). Although PTE origin in soils may be either lithogenic or anthropogenic, in most cases high PTE concentrations are associated with human-induced activities (Hooda, 2010). Potentially toxic elements are frequently

* Corresponding author.
*E-mail addresses:* antoniadis@uth.gr (V. Antoniadis), smshaheen@agr.kfs.edu.eg (S.M. Shaheen), t_frohne@yahoo.de (T. Frohne), rinklebe@uni-wuppertal.de (J. Rinklebe).
[1] Current address: Department I: Planning and Controlling, Universität Bielefeld, Germany, Universitätsstraße 25, 33615 Bielefeld, Germany.

http://dx.doi.org/10.1016/j.jenvman.2016.04.036
0301-4797/© 2016 Published by Elsevier Ltd.

concentrated around the geographical locality of certain industrial activities due to aerial deposition of industrial dust plumes or to the application of wastes to soil. For example, Li et al. (2015a) found decreasing PTE levels with increasing distance from a Pb/Zn smelter up to a distance of 10 km. In cases of slow PTE accumulation over several decades, the most probable metal transportation pathway is from the atmosphere to soil, soil to roots and roots to shoots. Xiong et al. (2014) tested two distinct metal application scenarios concerning vegetables and found that Cd and Pb transportation was more intense when vegetables were exposed to soil pollution compared to when exposed to direct aerial deposition. Thus, areas with a long history of industrial activity are expected to be highly contaminated (Massas et al., 2013; Kostarelos et al., 2015). Mines in particular (either active or abandoned) are mostly responsible for PTE contamination in soil, usually over a long period of time well exceeding the life-span of active excavation procedures (Kumar et al., 2015). Yet PTEs are the most troublesome contaminants due to their persistence and their ability to be transferred along the human food chain (Gall et al., 2015).

Northern Europe, especially Germany, has a long history of heavy industry. The mining industry, in particular, spans over many centuries. Consequently, tight regulations have been implemented in recent decades resulting in satisfactory law enforcement. For this reason, PTE-related concerns are often overlooked, although they do exist. Most of the recent works monitoring PTEs and employing related human health risk assessment derive from Asia (e.g., China: Wang et al., 2009; Chen et al., 2013; Zu et al., 2014), Africa (e.g., Tunisia: Boussen et al., 2013; Algeria: Cherfi et al., 2014; Swaziland: Cele and Maboeta, 2016), and elsewhere (e.g., Peru: Bech et al., 2012). As a result, there is a scarcity of recent data concerning studies of PTE availability using quantitative contamination indices and of PTE-related human health risk assessment scenarios associated with vegetable consumption or direct soil dust inhalation by local people in Northern Europe. This scarcity concerns mostly organized studies (not mere monitoring), assessing the levels of various PTEs in soil and in common garden vegetables in areas where PTEs have been deposited over very long periods (Tersic et al., 2009). In such areas, PTE mobility may be highly elevated, although it is believed that soil ageing processes lead to reduced acuteness in PTE toxicity (Bolan et al., 2013). Moreover, short-scale studies employing many PTEs simultaneously have revealed that trace elements, when in elevated concentrations, reveal an antagonistic behavior in plants. In a hydroponics test, e.g, Li et al. (2013) found that Cd and Zn concentrations were significantly reduced in plant tissues of the hyperaccumulator *Sedum plumbizincicola* in the presence of gradually elevated Cu concentrations. However, it is unknown what the combined effect of a multi-metal contamination situation would be in the case of slow PTE deposition over time, such as that attempted to be studied here. There are various studies which assess PTE absorption by plants in spiked soils (Al Chami et al., 2015) or in areas recently applied with PTE-loaded materials (e.g., sewage sludge) (Wierzbowska et al., 2016). However, those studies cannot adequately predict the long-term fate of PTE.

Thus, the aim of this work was to assess (a) the phytoavailability of As, Cu, Mn, Hg, Pb, and Zn in commonly grown garden vegetables in a heavily contaminated mine dump in Germany, where PTEs have reached very high levels and have been deposited over centuries, and (b) human health indices concerning the risk associated with PTE soil-to-plant mobility and with consumption of vegetables that contain PTEs.

## 2. Materials and methods

### 2.1. Site description, soil characterization, and experimental setup

The study sites were located approximately 32 km eastward of Cologne, close to the town of Engelskirchen-Ehreshoven. The area is located in the federal state of North Rhine-Westphalia, Germany. The geological parent material mainly consists of Devonian sandstone and silty claystone. The soils are loamy Cambisols according to IUSS Working Group WRB (2014). The climate is Atlantic and is mainly characterized by mild summers and winters. The long term annual precipitation is approximately 1212 mm and the average long-term daily air temperature ranges from 5.4 °C (minimum) to 12.2 °C (maximum). Further details about the study site are documented by Börsch (2014).

The sites were close to the former mining area "Kastor," which is known to be highly contaminated (Oberbergischer Kreis, 1993). Mainly, lead glance (PbS) and sphalerite (ZnS) have been mined over many centuries. These activities have been documented since A.D. 1122 (Börsch, 2014). Based on previous studies (Oberbergischer Kreis, 1993), we selected 4 sites in this area, named gardens No. 1, 2, 3, and 4 thereafter. Organic carbon (OC) was 3.62% in garden-1, 7.24% in garden-2, 2.43% in garden-3, and 3.40% in garden-4, while pH values were slightly acidic (6.7, 6.0, 6.2, and 6.2 for gardens-1, 2, 3, and 4, respectively). In those gardens, we established open-air growth experiments with three commonly grown vegetables: Beans (*Phaseolus vulgaris* ssp. *nanus*, in gardens 1, 2, 3, and 4), carrots (*Daucus sativus*, in gardens 1, 3, and 4) and lettuce (*Lactuca sativa* ssp. *capitata*, in gardens 1, 3, and 4). Plants where grown in $1 \times 1$ m$^2$ beds; we followed the common practices of irrigation and fertilization of the same garden vegetables in the area.

### 2.2. Sampling and analysis

Vegetables were cultivated for 60 days from April to May 2013. All plant parts were harvested and beans were separated into seed, leaf, shoot, and root, while carrots and lettuce were separated into leaf, shoot, and root (10 different plant parts from the 3 tested plants). Plant parts were acid-washed with 2% $HNO_3$, rinsed with $H_2O$, and air-dried. Roots were additionally treated with ultrasonic bath for 10 min to separate soil material from plants. The plant material was finely grounded in a metal-free rotary mill; thereafter 0.4 g of the material was extracted with 4 mL $HNO_3$ and 0.4 mL $H_2O_2$ in a microwave oven (MLS-ETHOS plus, MLS GmbH, Leutkirch, Germany).

From the same garden beds, soil samples were collected, air-dried, and passed through a 2-mm sieve. The samples were extracted with *aqua regia* (3 g soil in 21 mL HCl and 7 mL $HNO_3$) to determine the concentrations of As, Cu, Fe, Hg, Mn, Pb, and Zn. These concentrations will be considered as "total concentrations" in this study, ignoring the fact that certain parts may remain in the residuum. However, it is well established that the *aqua regia* extraction is the best available technique to determine the ecologically relevant fractions, although its pertinence is case- and site-specific. In particular, this procedure is standard in DIN ISO 11466 (1997) and therefore recommended for evaluating the "soil-to-human" pathway exposure in the German Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV, 1999). Ammonium nitrate extraction was used to assess the potential mobile fraction of As, Cu, Fe, Hg, Mn, Pb, and Zn (10 g soil extracted with 25 mL 1 M $NH_4NO_3$, and filtered through a syringe-forced 0.45-μm filter) (DIN ISO 19730, 2009). Each soil sample was extracted in duplicate. Concentrations of As, Cu, Fe, Mn, Pb, and Zn in plant and soil (*aqua regia* and ammonium nitrate extracts) were