Pollution and Probabilistic Human Health Risk Assessment of Potentially Toxic Elements in the Soil-water-plant System in the Bolkar Mining District, Niğde, South-central Turkey

Abdurrahman Lermi (✉ alermi@ohu.edu.tr)

Niğde Ömer Halisdemir University: Nigde Omer Halisdemir Universitesi

Emmanuel Daanoba Sunkari

Niğde Ömer Halisdemir Üniversitesi: Nigde Omer Halisdemir Universitesi

Research Article

Keywords: anthropogenic activities, human health risk assessment, ore slags, pollution assessment, potentially toxic elements, arsenic contamination

Posted Date: May 4th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-456493/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on July 21st, 2021. See the published version at <https://doi.org/10.1007/s11356-021-15398-w>.

**Pollution and probabilistic human health risk assessment of potentially toxic elements
in the soil-water-plant system in the Bolkar mining district, Niğde, south-central Turkey**

Abdurrahman Lermi^{1*} & Emmanuel Daanoba Sunkari^{1, 2}

¹Department of Geological Engineering, Niğde Ömer Halisdemir University, 51240, Niğde,
Main Campus, Turkey

²Department of Geological Engineering, University of Mines and Technology, Faculty of
Mineral Resources Technology, P.O. Box 237, Tarkwa, Ghana

*Corresponding author: alermi@ohu.edu.tr

*ORCID: <https://orcid.org/0000-0003-4117-689X>

Acknowledgement

Mr. Gökhan KELEBEK is sincerely acknowledged for his role in sample collection during the Part A section of this study. The second author is grateful to the Scientific and Technological Research Council of Turkey (TÜBİTAK) for the continuous financial support as a doctoral research fellow.

Ethics declarations

Funding: The geochemical analysis in this study was financially supported by the Scientific Research Office (BAP) of Niğde Ömer Halisdemir University, Turkey with the project No: FEB 2007/07.

Ethics approval: The authors declare that the submitted manuscript is original. Authors also acknowledge that the current research has been conducted ethically and the final shape of the research has been agreed by both authors. Authors declare that this manuscript does not involve researching about humans or animals.

Conflicts of interest/Competing interests: The authors declare no conflicts of interests/ competing interests.

Availability of data and material (data transparency): All data used in the study will be readily available to the public.

Code availability (software application or custom code): All software applications used in this study were the licensed software applications used by Niğde Ömer Halisdemir University, Turkey.

Consent to participate: The authors consent to participate in this research study.

Consent to publish: The authors consent to publish the current research in ESPR journal.

Authors' contributions: **Abdurrahman Lermi:** Conceptualization, Methodology, Investigation, Supervision, Writing-Original draft preparation, Validation, Writing- Reviewing and Editing. **Emmanuel Daanoba Sunkari:** Methodology, Software, Data curation, Writing-Original draft preparation, Visualization, Writing-Reviewing and Editing.

Highlights

- Pollution assessment reveals moderate to extremely high pollution of PTEs in the soil.
- Water hazard index values indicate that 100% of the samples are of extreme toxicity.
- Bioconcentration factors show high levels of element transfer from the soil and water to the plants.

- About 55.6% of the samples have high carcinogenic risk values of arsenic in drinking water.

Abstract

Globally, potentially toxic elements (PTEs) are regarded as an important group of pollutants for the wider environment because of their intrinsic toxicity and probable accumulation in the soil-water-plant system. In this regard, this study assessed the pollution levels and probable human health risks of PTEs in the soil-water-plant system in the Bolkar mining district of the Niğde Province in south-central Turkey. Pollution assessment using contamination factor, enrichment factor, index of geoaccumulation, and soil pollution index reveals moderate to extremely high pollution of PTEs in the soil, exposing the soils to extreme toxicity levels. The areas that fall under the toxic to extremely toxic categories are in proximity to the ore slags and agricultural lands towards the central and southern domains of the study area. The water hazard index (WHI) values indicate that 100% of the samples collected in both winter and fall seasons are of extreme toxicity ($WHI > 15$). Arsenic is the dominant contaminant among the PTEs in the soil and water samples. The bioconcentration factor values of the PTEs in most of the fruit plants are > 1 , indicating very high levels of element transfer from the soil and water to the plants. The probabilistic human health risk assessment involved exposure to arsenic in groundwater (a major pathway to humans) since it is the only carcinogenic element in this study. The estimated daily intake of arsenic-contaminated water exceeds the safe limit of 5×10^{-8} mg/kg/day. About 33.3% and 55.6% of the groundwater samples have higher hazard quotient and carcinogenic risk values of arsenic in the winter and fall seasons, respectively. This implies that the people are more exposed to the carcinogenic effects of drinking arsenic-contaminated water.

Keywords: anthropogenic activities; human health risk assessment; ore slags; pollution assessment; potentially toxic elements; arsenic contamination

1. Introduction

Potentially toxic elements (PTEs) are naturally dispersed through various environmental media with acceptable concentrations. However, due to the increasing rate of anthropogenic activities, the PTEs are being re-dispersed resulting in elevated concentrations (Elnazer and Salman 2020). Globally, it is well documented that the main anthropogenic sources of PTEs in the soil-water-plant system are mining activities, agricultural activities, sewage disposal, industrial and vehicular emissions (Lermi and Ertan 2019; Zango et al. 2019; Çiner et al. 2020; Kovacheva et al. 2020; Liu et al. 2020; Nganje et al. 2020). Among these, mining activities are the dominant routes of PTEs in the soil-water-plant system in metallogenic provinces. Ore slags left after mining can weather thereby releasing PTEs into the soil, which can in turn be leached into surface and groundwater resources and then become available for plant uptake. Excessive exposure to PTEs, especially Mn may lead to mental retardation and in extreme cases, Parkinson's disease (Li et al. 2018; Rahman et al. 2021). Over exposure to Cu through industrial and mining activities can lead to liver damage and impairment of the central nervous system, and in some cases, it can lead to lung cancer (Giri and Singh 2017). In addition, most of the non-essential PTEs like Pb, As, Hg, and Cd act as carcinogens and are the cause of many diseases, especially those involving the heart, nervous system, kidney, and bones (Järup 2003; Chiang et al. 2011; Zhan et al. 2014; Sunkari and Danladi 2016; Çiner et al. 2020).

A typical agricultural system involves the soil-water-plant nexus, which is essential for survival of the human race on earth. In this regard, the quality of the soil-water-plant system has become a global concern in the past decades. Although many published works were focused

on soil, water, and plant quality, there is paucity of research on assessment of the soil-water-plant system pollution as well as the associated human health risks. A few studies considered the pollution of potentially toxic elements (PTEs) in the soil-water-plant system in some countries like Morocco (El Azhari et al. 2017), Egypt (Salman et al. 2017; Elnazer and Salman 2020), Bangladesh (Alam et al. 2020), Bulgaria (Kovacheva et al. 2020), and Nigeria (Nganje et al. 2020). The significance of these studies in national development is the use of models such as pollution and human health risk assessment indices to understand the sustainability of the soil–water–plant system in food production, to determine the sources and dispersion mechanisms of PTEs.

Human beings can be exposed to PTEs through consumption of water and food, inhalation of soil particles, and ingestion of soil (geophagia) (Elnazer and Salman 2020). Among all these routes, dietary intake of polluted food happens to be the principal route of PTEs in the human system (Ji et al. 2013). Pollution of foodstuff with PTEs is mostly due to soil pollution, which is a major setback to agricultural productivity in many parts of the world (Chauhan et al. 2018). Therefore, considering the intrinsic toxicity of PTEs and their potential accumulation in the soil-water-plant system, they are globally regarded as an important group of pollutants for the wider environment and thus, the need for human health risk assessment (Ngole-Jeme 2016). The potential human health risks from PTEs are generally assessed by carcinogenic and non-carcinogenic risk assessment methods such as lifetime exposure level (ADD_{life}) and hazard quotient (HQ) (Chen et al. 2018). By the use of these methods, the level of pollution loading can be ascertained, which will provide useful constraints to scale and determine potential health risks. In terms of the effect of the PTEs on plants, the bioconcentration factor (BCF) also referred to as biological adsorption coefficient (BAC) is widely used to determine the accumulation levels of PTEs from soil to plants (Kabata-Pendias 2011; Jiang et al. 2020; Luo et al. 2020; Nganje et al. 2020). However, contamination factor

(CF), enrichment factor (EF), index of geoaccumulation (I_{geo}), and soil pollution index (PI) have been effectively used to estimate the extent of soil contamination by PTEs (e.g., Darwish and Pöllmann 2015; Kowalska et al. 2018; Dan-Badjo et al. 2019; Kabala et al. 2020; Lermi and Sunkari 2020; Nganje et al. 2020).

The Bolkar mining district is an ancient metallogenic province that has been under exploration since the 1880s. The ore deposits in this area are mostly chromite and Sb-W-Hg-Au deposits (Akçay et al. 1995), Mn deposits (Öztürk 1997; Lermi et al. 2016), MVT- and CRD-type Pb and Zn deposits (Hanilçi and Öztürk 2011; Hanilçi 2019), Fe-Zn skarn deposits (Kuşçu (2019), bauxite, Al and Fe-rich laterite deposits (Hanilçi 2013; Hanilçi 2019). Exploration and mining of these deposit types have left abundant ore slags (Fig. 1) in the area that are continuously being weathered and dispersed. Despite this threat to the soil-water-plant quality and human health, no study has documented the pollution levels and human health risks of PTEs derived from the ore slags to the soil-water-plant system. Therefore, this study is aimed at assessing the pollution levels of PTEs in the soil-water-plant system in the Bolkar mining district of the Niğde Province in south-central Turkey by using pollution indices like contamination factor, enrichment factor, index of geoaccumulation, soil pollution index, water hazard index, and bioconcentration factor. The current study, which is a follow-up (Part B) to the earlier study (Part A) on the geochemical dispersion of PTEs in the soil-water-plant system of the study area will also determine the probabilistic human health risks associated with the exposure of PTEs in the groundwater resources since they are the major pathways to humans residing in the study area.

2. Materials and methods

2.1. Study area and sample collection

The study area is located in the Niğde Province in the Gümüş village in the Central Anatolian Part of Turkey (Fig. 1). The climatic conditions prevailing in this area reflect that of continental climate where there is a period of dryness in the summer season and wetness in the winter season. The study area is bounded by high altitude mountains up to 3200 meters above sea level. The highest average precipitation is about 58 mm and mostly occurs in May, whereas the least average precipitation is about 5 mm and occurs in August. Temperatures are usually low to about -5°C in January, whereas relatively high temperatures up to 22°C are usually recorded in July. The main rocks in the area are metamorphic rocks such as marble and schist and volcano-sedimentary rocks like pyroclastics, pillow lavas, andesite, basalt, limestone, dolomite, which are intruded by granitoids in some places (Fig. 1; Clark and Robertson 2002; Alpaslan et al. 2006; Lermi and Sunkari 2020). There are abundant ore slags in most parts of the study area due to the ancient mining activities (Fig. 1).

Details of the sample collection and analysis are presented in the Part A of this research (under-review). In all, a total of 40 composite samples were collected from the soil profile in the area and sent to the ACME Analytical Laboratories, Vancouver, Canada for analysis of PTEs using ICP-MS method. A total of 20 groundwater samples were collected in 500 ml polyethylene bottles, acidified with nitric acid to a pH < 2 (Lermi and Ertan 2019) and then sent to the ACME Analytical Laboratories, Vancouver, Canada for analysis of PTEs using Ultra trace ICP-MS method. For the plants, leaves of fruit plants were collected in paper bags, washed, dried, ground in agate mortar, and filtered with a 100 mesh sieve (Dan-Badjo et al. 2019; Wang et al. 2019). About 1 g of the ground samples was acidified using HNO₃ and

analyzed in aqua regia by means of Ultra trace ICP-MS method at the ACME Analytical Laboratories, Vancouver, Canada.

2.2. Pollution assessment

2.2.1. Contamination factor (C_f)

Contamination factor (C_f) is mostly used to assess the extent of soil pollution by PTEs, especially the metallic PTEs. In this study, the C_f was calculated from the equation (1) after Hakanson (1980):

$$CF = \frac{C_{PTE}}{C_{BV}} \quad 1$$

where CF is the contamination factor, C_{PTE} is the concentration of each PTE, and C_{BV} is the background value of each PTE, which is the world average crustal value. The CF values calculated from the above equation were interpreted according to the four classes of contamination of Hakanson (1980); $CF < 1$ (low contamination), $1 \leq CF \leq 3$ (moderate contamination), $3 \leq CF \leq 6$ (considerable contamination) and $CF > 6$ (very high contamination).

2.2.2. Enrichment factor (EF)

The EF was calculated by comparing the concentrations of the individual PTEs in the soils against average crustal values or unpolluted soil using data from Bowen (1979). In this study, the EF was assessed based on the background values of the PTEs in the average shale (Turekian and Wedepohl 1961). Aluminium was used as the normalization element because of its conservative nature even under extreme pedogenic processes (Ettler et al. 2006). The EF values of the studied soils were calculated from equation 2:

$$EF = \frac{(C_i/C_{Al})_s}{(C_i/C_{Al})_b}$$

2

where $(C_i/C_{Al})_s$ is the PTE/Al ratio in the samples and $(C_i/C_{Al})_b$ is the PTE/Al ratio in the background sample (average shale). For assessing the enrichment levels of the individual PTEs, five classes have been suggested by Andrews and Sutherland (2004); $EF < 2$ (minimal pollution), $EF 2 - 5$ (moderate pollution), $EF 5 - 20$ (significant pollution), $EF 20 - 40$ (high pollution) and $EF > 40$ (extreme pollution).

2.2.3. Index of geoaccumulation (I_{geo})

The level of anthropogenic influence of each PTE on the soil was assessed using the index of geoaccumulation (I_{geo}) by Müller (1969), equation 3:

$$I_{geo} = \log_2 \left[\frac{C_n}{1.5B_n} \right]$$

3

where C_n is the PTE (n) concentration and B_n represents the background concentration of that PTE (n) in the average shale. The factor 1.5 permits assessment of the fluctuations of the natural content of the PTE in the environment (Wei et al. 2009). The interpretation of the calculated I_{geo} values was based on the classification scheme of (Müller 1981); $I_{geo} < 0$ (no pollution), $0 \leq I_{geo} \leq 1$ (no to moderate pollution), $1 \leq I_{geo} \leq 2$ (moderate pollution), $2 \leq I_{geo} \leq 3$ (moderate to heavy pollution), $3 \leq I_{geo} \leq 4$ (heavy pollution), $4 \leq I_{geo} \leq 5$ (heavy to extreme pollution), and $I_{geo} > 5$ (extreme pollution).

2.2.4. Soil pollution index (PI)

The contamination of PTEs in soil, especially in mining areas is usually a combination of several contaminants rather than a single element (Lee et al. 2006). In this regard, the concept of soil pollution index (PI) has become an effective way of assessing the combined influence of multi-elements on soils (Smouni et al. 2010; Dan-Badjo et al. 2013, 2019; Nganje et al. 2020). The PI is a criterion for assessing the overall toxicity of PTEs and its computation varies among different workers but the basic concept is the same. In this study, the PI of the soil was computed as the average ratio of metal concentration in the soil samples to background values of the metals (Bowen 1979) from equation 4:

$$PI = \left\{ \left(\frac{As}{5} \right) + \left(\frac{Cd}{0.06} \right) + \left(\frac{Co}{29} \right) + \left(\frac{Cu}{30} \right) + \left(\frac{Hg}{0.03} \right) + \left(\frac{Mo}{2} \right) + \left(\frac{Ni}{40} \right) + \left(\frac{Pb}{20} \right) + \left(\frac{Zn}{50} \right) \right\} / 9 \quad 4$$

where As, Cd, Co, Cu, Hg, Mo, Ni, Pb, and Zn are the concentrations of these PTEs in the soil samples whereas the denominators are their background values in unpolluted soil (Bowen 1979; Lindsay 1979). $PI > 1$ indicates that the soil is polluted by several PTEs owing to anthropogenic input. Generally, PI values < 5 indicate low toxicity, PI values between 5 and 10 indicate slight toxicity, PI values between 10 and 20 indicate moderate toxicity and PI values > 20 indicate extreme toxicity (Chon et al. 1996).

2.2.5. Water hazard index (WHI)

The water hazard index (WHI) was used in assessing the overall impact of the PTEs on water resources in the study area. It was computed as a ratio of the concentration of the individual PTEs to their maximum guideline values for drinking water in Turkey (TSE-266 2005). Equation 5 below was used for the computation of the WHI:

$$WHI = \left\{ \left(\frac{As}{0.01} \right) + \left(\frac{Cu}{3} \right) + \left(\frac{Sb}{0.01} \right) + \left(\frac{Pb}{0.05} \right) + \left(\frac{Zn}{5} \right) \right\} / 5 \quad 5$$

where As, Cu, Sb, Pb, and Zn are the concentrations of these PTEs in the water samples and the denominators are their standard guideline values in drinking water obtained from the Turkish Standards Institute (TSE-266 2005). The following categories of interpretation of the computed WHI values (Nganje et al. 2020) were used; $WHI < 5$ (low to minimal toxicity), $5 \leq WHI \leq 10$ (slightly toxic), $10 \leq WHI \leq 15$ (moderately toxic) and $WHI > 15$ (extremely toxic).

2.2.6. Bioconcentration factor (BCF)

The bioconcentration factor (BCF) is used to evaluate the accumulation levels of plants for the PTEs (Wang et al. 2019). It was calculated using equation 6:

$$BCF = \frac{CMIP}{CMIS} \quad 6$$

where CMIP is the concentration of the metal in the plants and CMIS is the concentration of the metal in the soil.

2.3. Probabilistic human health risk assessment

2.3.1. Exposure assessment

The exposure assessment reveals the routes and pathways through which humans are exposed to contaminants and estimates the amount, frequency and duration of exposure. In this study, the exposure assessment was limited to the water medium since the people largely depend on groundwater for drinking and irrigation purposes. The PTEs considered in this assessment include As, Cd, Ni, Pb, and Zn based on their elevated concentrations in groundwater. The

average daily dose (ADD) of the contaminant in the water was computed using the model of the United States Environmental Protection Agency (USEPA 1997, 2004).

$$ADD = \frac{C \times IR \times ED \times EF}{BW \times AT} \quad 7$$

where C is the concentration of the PTE in the water (mg/L), IR represents the ingestion rate (2 L/day) taken from (USEPA 2004), ED is the exposure duration (years) to the PTEs and according to the archives of the USEPA (USEPA 1997), 30 years is used, EF denotes the exposure frequency (days/year) taken as 365 days/year (USEPA 2004), BW is the average body weight (kg) (61.75) from Çiner et al. (2020), AT is the average time of exposure (d) and in this study, for the non-carcinogenic risk, $AT = ED \times 365$ and for carcinogenic risk, $AT = 77.434 \times 365$ since 77.434 is the average life expectancy of people living in Turkey (Karacan et al. 2020).

2.3.2. Non-carcinogenic risk assessment

Non-carcinogenic risk refers to toxic risks that are not up to the extent of causing cancers but cause harm to consumers due to exposure to PTEs. It is mostly computed in terms of hazard quotient (HQ):

$$HQ = \frac{ADD}{RfD} \quad 8$$

where RfD is the reference dose, which is taken from the United States Integrated Risk Information System for the individual PTEs (USEPA 2011). The RfD for As, Ni, Pb, Zn, and Sb are 3×10^{-4} , 2×10^{-2} , 3.5×10^{-3} , 3×10^{-1} , and 4×10^{-4} mg/kg/day, respectively. In assessing the non-carcinogenic risk, if the computed HQ exceeds 1, then it is interpreted that there is a potential health risk with respect to the particular element.

2.3.3. Carcinogenic risk assessment

Among the PTEs detected in the water samples in the study area, only arsenic is a carcinogen. Therefore, the carcinogenic risk (CR) associated with exposure to the intake of arsenic through the water samples collected from the study area was computed using the model of the USEPA (1989):

$$CR = ADD_{life} \times SF \quad 9$$

where ADD_{life} is the lifetime exposure level and is calculated by estimating the exposure suffered during the exposure duration over the life expectancy of the individual. SF (mg/kg/day) is the slope factor, which indicates the probability of having cancer due to exposure to arsenic. The SF for arsenic according to USEPA (2011) is 1.5 mg/kg/day. Computed CR values above 1×10^{-4} suggest that there is a carcinogenic risk with respect to exposure to arsenic for both children and adults (Zhang et al. 2019).

3. Results and discussion

3.1. Levels of pollution of PTEs in soil

Statistical summaries of concentrations of PTEs in the soil and the pollution assessment are given in Tables 1 and 2, respectively. The PTEs vary in the order $Au < Th < U < Co < Bi < Mo < Ag < V < Sr < Sb < Ni < Cu < Mn < Zn < Hg < Cd < Pb < As$ (Table 1), indicating that As is the most dominant potentially toxic element in the soil samples. In terms of contamination factors (CF), only Mn and Co are in the class of low ($CF < 1$) to moderate ($1 \leq CF \leq 3$) contamination, whereas As, Cd, Cu, Mo, Pb, Zn, and Sb fall in the class of low ($CF < 1$) to very high ($CF > 6$) contamination. However, Ni is in the class of moderate to very high contamination. The computed enrichment factor (EF) values also show that Mn is in the class

of moderate ($2 \leq EF \leq 5$) to significant ($5 \leq EF \leq 20$) pollution, Co in the class of moderate ($2 \leq EF \leq 5$) to high ($20 \leq EF \leq 40$) pollution, As, Cd, Cu, Mo, Pb, Zn, and Sb in the class of minimal ($EF < 2$) to extreme pollution ($EF > 40$). But the EF values of Ni show significant to extreme pollution. Accordingly, EF values of soil that ranges from 0.5 to 1.5 indicate that PTEs in the soil are mostly coming from crustal or geogenic sources whereas EF values higher than 1.5 reflect large input from anthropogenic sources (Zhang and Liu 2002; Lermi and Sunkari 2020). In the current study, the mean EF values for the investigated PTEs are all above 1.5, indicating that contribution from slag piles in the area and agricultural activities, which are the main anthropogenic sources of PTEs is intense. For the index of geoaccumulation (I_{geo}) values, Mn and Co fall in the class of no to moderate pollution ($0 \leq I_{geo} \leq 1$), Mo is in the class of no ($I_{geo} < 0$) to heavy ($3 \leq I_{geo} \leq 4$) pollution, whereas As, Cd, Cu, Pb, Zn, and Sb are in the class of no ($I_{geo} < 0$) to extreme ($I_{geo} > 5$) pollution. Nevertheless, Ni is distinctly within the moderate to heavy pollution class. This suggests that the results of the CF, EF and I_{geo} assessments corroborate with each other. Thus, it is clear that the soil samples have varied levels of pollution with regard to Mn, As, Cd, Co, Cu, Mo, Pb, Zn, and Sb.

The values computed from the soil pollution index (PI) assessment revealed that the PI values ranged from 2.51 (low toxicity potential) to 407 (extreme toxicity potential) (Table 1). All the samples have PI values > 1 (Table 1), suggesting that relatively high contents of PTEs are in the soils of the historical Bolkar mining area, exposing the soils to extreme toxicity levels. The lowest PI values are around the non-mine and non-agricultural areas without slag piles indicating low accumulation of the PTEs in these areas (Fig. 2). The areas that fall under the toxic to extremely toxic classes are in proximity to the slag piles and agricultural lands towards the central and southern domains of the study area (Fig. 2). Interestingly, the PI values in this study are higher than PI values in other studies elsewhere in the world (Smouni et al. 2010; Dan-Badjo et al. 2019; Nganje et al. 2020). For instance, in the mining areas of eastern

Morocco, Smouni et al. (2010) reported PI values in the range of 0.08 – 47.7, lower than those reported in this study. This confirms the fact that the proximity of the ore slags to the sampling sites is a contributory factor to the pollution of the PTEs in the soil.

3.2. Levels of pollution of PTEs in water

Statistical summary of the concentrations of PTEs in the water samples is given in Table 3. Among the PTEs, arsenic (As) has the highest concentration ranging from 0.80 – 287 µg/L with a median of 2.90 µg/L in the winter season, whereas the concentration varied from 1.20 to 373 µg/L with a median of 9 µg/L in the fall season (Table 3). The water hazard index (WHI) values indicate that 100% of the samples collected in both seasons are of extreme toxicity (WHI > 15) (Fig. 3). The combined effect of multi-PTEs is therefore very evident in the studied water samples. During the winter season, the WHI values varied in the range of 35.9 – 6334 (Fig. 3), whereas in the fall season the WHI values significantly increased from 42.6 to 8805 (Fig. 3). Certainly, the water in the vicinity of the ore slags is highly polluted and thus, detrimental to human health.

3.3. Bioaccumulation effect of PTEs in plants

Table 4 contains statistical summary of the concentrations of plant samples in this study. The average concentrations of the PTEs in the fruit plants vary in the order of Zn < As < Pb < Fe, implying that Fe is the most enriched element in the plants. Plants can only absorb some of the elements in the soil through cation exchange. Some authors state that the most suitable amount of elements for biological nutrition is equivalent to the amounts in groundwater (Nguyen et al., 2005). Therefore, to clearly understand the bioaccumulation capacities of the plants, the bioconcentration factors (BCF) were computed. The BCF is a factor that indicates the degree

of the plant to absorb PTEs from the surrounding water resources (Nguyen et al. 2005). The results indicate that the fruit plants in the region copiously absorb Fe, Pb, Zn, and As and act like bio-accumulators (Table 4). Moreover, the BCF for most of the fruit plants are > 1 (Table 4), indicating very high levels of element transfer from the soil and water to the plants. This is attributed to the high solubility of most secondary minerals in the area under alkaline conditions (Kabata-Pendias and Pendias 2000). Bioaccumulation of PTEs by plants is potentially detrimental to the organisms that feed on the leaves and fruits of these plants and may cause undesirable disorders in the long term. Essentially, the high BCF values suggest that human health and plant growth in the region are under jeopardy. Therefore, the stakeholders in the area should take necessary measures to curtail the menace.

3.4. Constraints from probabilistic human health risk assessment

In terms of the computed estimated daily intake (EDI) values for the various PTEs, arsenic (As) appears to be the element dominant in groundwater in both seasons and the people are more exposed to the intake of arsenic-contaminated groundwater than the other PTEs (Tables 5 and 6). The EDI values of As range from 0.00003 to 0.00929 mg/kg/day in the winter season (Table 5), whereas they range from 0.00011 to 0.01206 in the fall season (Table 6). All the samples in both seasons have EDI values exceeding the safe limit of 5×10^{-8} mg/kg/day indicating that the inhabitants of the study area are all exposed to the health implications emanating from the intake of As-contaminated water (Zhang et al. 2019). The results obtained in this study can be compared with that of Zhang et al. (2019) and Barzegar et al. (2019) who reported higher EDI values of As in groundwater in China and Iran, respectively.

The USEPA (1989) indicated that when the hazard quotient (HQ) values of groundwater in any environment exceeds the threshold of 1, then there is a potential health risk

associated with the consumption of water contaminated with PTEs. This study reports higher HQ values for As in the winter season (0.08637 - 30.97436; Table 5) and fall season (0.12955 - 40.21592; Table 6). About 33.3% of the water samples have higher HQ values of As in the winter season, whereas 55.6% of the water samples have higher HQ values of As in the fall season. Comparing this with the EDI values in both seasons, it can be concluded that the residents of the study area drink more water in the fall season due to the high temperature conditions and are thus, more exposed to the non-carcinogenic effects of drinking groundwater enriched in arsenic. Apart from As, in the winter season, one sample representing 11.1% of the total samples has HQ value with respect to Pb > 1 and 2 samples representing 22.2% of the total samples also have HQ values with respect to Sb > 1 (Table 5). However, in the fall season, only 2 samples have HQ values with respect to Sb exceeding the safe limit of 1 (Table 6).

The carcinogenic risk (CR) is expressed in terms of the probability that one is likely to have cancer owing to the intake of arsenic-contaminated water during a lifetime exposure of approximately 77 years, since that is the life expectancy age for people living in Turkey (Karacan et al. 2020). The CR of being exposed to As by the drinking water is in the range of 0.00002 to 0.00540 in the winter season (Table 5). This suggests that some of the samples have high CR values in view of the safe limit of 1×10^{-4} . Just like the HQ values for As, approximately 33.3% of the samples have CR values above the safe limit (Table 5). Moreover, the CR values are relatively higher in the fall season varying in the range of 0.00002 to 0.00701 (Table 6). It is also worth mentioning that the CR values exceed the safe limit of 1×10^{-4} in almost 55.6% of the samples in the fall season, similar to the trend shown by the HQ values with respect to As in the fall season (Table 6). Definitely, the As concentrations in the water samples are extremely high exposing the people to the risk of carcinogenesis or keratinization of the skin (Health and Environment 2016). This calls for a great deal of attention by the government and key stakeholders in the historical Bolkar mining area within the Nigde

Province. The results of this study have provided evidence for a nexus among soils, plants and water in the area.

4. Conclusion

This study was conducted to assess the pollution levels and probable human health risks associated with the dispersion of potentially toxic elements (PTEs) into the soil-water-plant system of the Bolkar mining district in south-central Turkey. The soil samples have soil pollution index values > 1 , suggesting that relatively high contents of PTEs are in the soils of the historical Bolkar mining area, exposing the soils to extreme toxicity levels. Other pollution assessment indexes such as contamination factor, enrichment factor, and index of geoaccumulation reveal that the soils are moderately to extremely polluted with respect to the PTEs. For the water samples, 100% of the samples collected in both winter and fall seasons show extreme toxicity ($WHI > 15$) for the PTEs. The fruit plants also show high levels of bioaccumulation in terms of their Fe, Pb, Zn, and As concentrations. The human health risk assessment indicates that the water poses significant cancer risks due to the high arsenic content. The carcinogenic risk is associated with 55.6% of groundwater in the area, raising an alarm for the vulnerable population. In all, this study has provided significant data for the monitoring and management of mine waste in the historical Bolkar mining district.

References

- Akçay M (1995) Fluid inclusions and chemistry of tourmalines from the Gümüşler Sb-Hg±W deposits of the Niğde Massif (Central Turkey). *Chemie der Erde* 55:225-236.
- Alpaslan M, Boztuğ D, Frei R, Temel A, Kurt MA (2006) Geochemical and Pb–Sr–Nd isotopic composition of the ultrapotassic volcanic rocks from the extension-related Çamardı-Ulukışla basin, Niğde Province, Central Anatolia, Turkey. *Journal of Asian Earth Sciences* 27(5):613-627.
- Andrews S, Sutherland RA (2004) Cu, Pb and Zn contamination in Nuuanu watershed, Oahu, Hawaii. *Science of the Total Environment* 324(1-3):173-182.
- Barzegar R, Moghaddam AA, Adamowski J, Nazemi AH (2019) Assessing the potential origins and human health risks of trace elements in groundwater: a case study in the Khoy plain, Iran. *Environ Geochem Health* 41(2):981–1002.
- Bowen HJM (1979) *Environmental Chemistry of Elements*. Academic Press, London, 333 p.
- Chauhan PS, Mishra SK, Misra S, Dixit VK, Pandey S, Khare P, Khan MH, Dwivedi S, Lehri A (2018) Evaluation of fertility indicators associated with arsenic contaminated paddy fields soil. *Int J Environ Sci Technol* 15:2447–2458.
- Chen T, Lei C, Yan B, Li LL, Xu DM, Ying GG (2018) Spatial distribution and environmental implications of heavy metals in typical lead (Pb)-zinc (Zn) mine tailings impoundments in Guangdong Province, South China. *Environ. Sci. Pollut. Res* 25:36702–36711.
- Chiang CT, Chang CK, Hwang YH, Yuan TH, Su CC, Tsai KY, Lian L (2011) A critical exploration of blood and environmental Chromium concentration among oral cancer

patients in an oral cancer prevalent area of Taiwan. *Environ. Geochem. Health* 33:469–476.

Chon HT, Cho CH, Kim KW, Moon HS (1996) The occurrence and dispersion of potentially toxic elements in areas covered with black shales and slates in Korea. *Appl. Geochem* 11:69-76.

Çiner F, Sunkari ED, Şenbaş BA (2020) Geochemical and Multivariate Statistical Evaluation of Trace Elements in Groundwater of Niğde Municipality, South-Central Turkey: Implications for Arsenic Contamination and Human Health Risks Assessment. *Archives of Environmental Contamination and Toxicology* 1-19. <https://doi.org/10.1007/s00244-020-00759-2>.

Clark M, Robertson A (2002) The role of the Early Tertiary Ulukisla Basin, southern Turkey, in suturing of the Mesozoic Tethys Ocean. *Journal of the Geological Society* 159(6):673-690.

Dan-Badjo AT, Guero Y, Dan Lamso N, Tidjani AD, Ambouta KJM, Feidt C, Sterckeman T, Echevarria G (2013) Evaluation de la contamination des sols par les éléments traces métalliques dans les zones urbaines et périurbaines de la ville de Niamey (Niger). *Revue des BioRessources* 2(2):82–95.

Dan-Badjo AT, Ibrahim OZ, Guéro Y, Morel JL, Feidt C, Echevarria G (2019) Impacts of artisanal gold mining on soil, water and plant contamination by trace elements at Komabangou, Western Niger. *Journal of Geochemical Exploration* 205:106328.

Darwish MAG, Pöllmann H (2015) Trace elements assessment in agricultural and desert soils of Aswan area, south Egypt: Geochemical characteristics and environmental impacts. *Journal of African Earth Sciences* 112:358-373.

466 El Azhari A, Rhoujjati A, El Hachimi ML, Ambrosi JP (2017) Pollution and ecological risk
 467 assessment of heavy metals in the soil-plant system and the sediment-water column
 468 around a former Pb/Zn-mining area in NE Morocco. *Ecotoxicol Environ Saf* 144:464–
 469 474.

470 Elnazer AA, Salman SA (2020) Critical load model and pollution indices application for water–
 471 soil–plant system assessment around El-Hammam canal, East El-Alamein, Egypt.
 472 *International Journal of Environmental Science and Technology* 3:1-2.

473 Ettler V, Mihaljevič M, Šebek O, Molek M, Grygar T, Zeman J (2006) Geochemical and Pb
 474 isotopic evidence for sources and dispersal of metal contamination in stream sediments
 475 from the mining and smelting district of Příbram, Czech Republic. *Environmental*
 476 *pollution* 142(3):409-417.

477 Giri S, Singh AK (2017). Human health risk assessment due to dietary intake of heavy metals
 478 through rice in the mining areas of Singhbhum Copper Belt, India. *Environmental*
 479 *Science and Pollution Research* 24(17):14945-14956.

480 Hakanson L (1980) An ecological risk index for aquatic pollution control. A sedimentological
 481 approach. *Water research* 14(8):975-1001.

482 Haniłçi N (2013) Geological and geochemical evolution of the Bolkardağı bauxite deposits,
 483 Karaman, Turkey: transformation from shale to bauxite. *Journal of Geochemical*
 484 *Exploration* 133:118-137.

485 Haniłçi N (2019) Bauxite deposits of Turkey. In: Pirajno F, Dönmez C Şahin MB (ed) *Mineral*
 486 *Resources of Turkey. Modern Approaches in Solid Earth Sciences*. Springer Nature
 487 Switzerland 16(15):681-730.

488 Hanilçi N, Öztürk H (2011) Geochemical/isotopic evolution of Pb–Zn deposits in the Central
 489 and Eastern Taurides, Turkey. *International Geology Review* 53(13):1478-1507.

490 Health and Environment (2016) Chemical environment: Arsenic.
 491 <https://www.healthandenvironment.org/environmental-health/environmental>
 492 [risks/chemical environment-overview/arsenic](https://www.healthandenvironment.org/environmental-health/environmental). Accessed Aug 2016.

493 Järup L (2003) Hazards of heavy metal contamination. *Br. Med. Bull* 68:167–182.

494 Ji K, Kim J, Lee M, Park S, Kwon HJ, Cheong HK, Jang JY, Kim DS, Yu S, Kim YW (2013)
 495 Assessment of exposure to heavy metals and health risks among residents near
 496 abandoned metal mines in Goseong, Korea. *Environ Pollut* 178C:322–328.

497 Jiang F, Ren B, Hursthouse A, Deng R (2020) Evaluating health risk indicators for PTE
 498 exposure in the food chain: evidence from a thallium mine area. *Environmental Science*
 499 *and Pollution Research* 1-9.

500 Kabala C, Galka B, Jezierski P (2020) Assessment and monitoring of soil and plant
 501 contamination with trace elements around Europe's largest copper ore tailings
 502 impoundment. *Science of the Total Environment* 738: 139918.
 503 <https://doi.org/10.1016/j.scitotenv.2020.139918>.

504 Kabata-Pendias A (2011) Trace elements in soils and plants/fourth editions. CRC Taylor and
 505 Francis Group, Boca Raton, p.505.

506 Kabata-Pendias A, Pendias H (2000) Trace Elements in Soil and Plants. CRC Press, Boca
 507 Raton, Florida.

508 Karacan I, Sennaroglu B, Vayvay O (2020) Analysis of life expectancy across countries using
 509 a decision tree. *Eastern Mediterranean Health J* 26(2):143–151.

510 Kovacheva A, Vladov I, Gabrashanska M, Rabadjieva D, Tepavitcharova S, Naney V,
 511 Dassenakis M, Karavoltsos S (2020) Dynamics of trace metals in the system water–
 512 soil–plant–wild rats–tapeworms (*Hymenolepis diminuta*) in Maglizh area, Bulgaria. J
 513 Trace Elem Med Biol 58:126440. <https://doi.org/10.1016/j.jtemb.2019.126440>.
 514 Kowalska JB, Mazurek R, Gąsiorek M, Zaleski T (2018) Pollution indices as useful tools for
 515 the comprehensive evaluation of the degree of soil contamination—A
 516 review. Environmental Geochemistry and Health 40(6):2395-2420.
 517 Kuşcu İ (2019) Skarns and Skarn Deposits of Turkey. In Mineral Resources of Turkey. Cham,
 518 Switzerland: Springer, pp. 283- 336.
 519 Lee CS, Li X, Shi W, Cheung SC, Thornton I (2006) Metal contamination in urban, suburban,
 520 and country park soils of Hong Kong: a study based on GIS and multivariate statistics.
 521 Sci. Total Environ 356 (1):45–61.
 522 Lermi A, Ertan G (2019) Hydrochemical and isotopic studies to understand quality problems
 523 in groundwater of the Niğde Province, Central Turkey. Environmental Earth
 524 Sciences 78(12):365.
 525 Lermi A, Sönmez M, Aydın F (2016) Mineralogy and Geochemistry of the Kiziltepe (Çamardı-
 526 Niğde) Mn Prospect in Central Anatolia, Turkey. International Multidisciplinary
 527 Scientific GeoConference: SGEM: Surveying Geology & Mining Ecology
 528 Management 1:421-428.
 529 Lermi A, Sunkari ED (2020) Geochemistry, risk assessment, and Pb isotopic evidence for
 530 sources of heavy metals in stream sediments around the Ulukışla Basin, Niğde, southern
 531 Turkey. Turkish Journal of Earth Sciences 29(7):1167-1188.
 532 <https://doi.org/10.3906/yer-2001-9>.

533 Li L, Yang X (2018) The essential element manganese, oxidative stress, and metabolic
 534 diseases: links and interactions. *Oxidative medicine and cellular longevity*.

535 Lindsay WL (1979) *Chemical Equilibria in Soils*. John Wiley and Sons, New York.

536 Liu G, Shi Y, Guo G, Zhao L, Niu J, Zhang C (2020) Soil pollution characteristics and systemic
 537 environmental risk assessment of a large-scale arsenic slag contaminated site. *Journal*
 538 *of Cleaner Production* 251:119721.

539 Luo X, Ren B, Hursthouse AS, Jiang F, Deng RJ (2020) Potentially toxic elements (PTEs) in
 540 crops, soil, and water near Xiangtan manganese mine, China: potential risk to health in
 541 the foodchain. *Environmental Geochemistry and Health* 1-12.

542 Müller G (1969) Index of geoaccumulation in sediments of the Rhine River. *Geojournal*, 2:
 543 108-118.

544 Nganje TN, Edet A, Cuthbert S, Adamu CI, Hursthouse AS (2020) The concentration,
 545 distribution and health risk from potentially toxic elements in the soil-plant-water
 546 system developed on black shales in SE Nigeria. *Journal of African Earth Sciences*
 547 103806. <https://doi.org/10.1016/j.jafrearsci.2020.103806>.

548 Ngole-Jeme VM (2016) Heavy metal in soils along unpaved roads in South West Cameroon:
 549 contamination levels and health risks/. *Ambio* 45(2):374–386.

550 Nguyen HL, Leermakers M, Elskens M, Ridder FD, Doan TH, Baeyens W (2005) Correlations,
 551 partitioning and bioaccumulation of heavy metals between different compartments of
 552 Lake Balaton. *Sci. Total Environ.* 341:211-226.

553 Öztürk H (1997) Manganese deposits in Turkey: distribution, types and tectonic setting. *Ore*
 554 *Geology Reviews* 12(3):187-203.

555 Rahman MA, Hashem MA, Rana MS, Islam MR (2021) Manganese in potable water of nine
 556 districts, Bangladesh: Human health risk. Environ Sci Pollut Res.
 557 <https://doi.org/10.1007/s11356-021-14016-z>.

558 Salman SA, Elnazer AA, El Nazer HA (2017) Integrated mass balance of some heavy metals
 559 fluxes in Yaakob village, south Sohag, Egypt. Int J Environ Sci Technol 14:1011–1018.

560 Smouni A, Ater M, Auguy F, Laplaze L, El Mzibri M, Berhada F, Doumas P (2010) Évaluation
 561 de la contamination par les éléments-traces métalliques dans une zone minière du
 562 Maroc oriental. Cahiers Agricultures 19(4):273–279.

563 Sunkari ED, Danladi IB (2016) Assessment of trace elements in selected bottled drinking water
 564 in Ghana: a case study of Accra metropolis. Int. J. Water Resour. Environ. Eng
 565 8(10):137–142. <https://doi.org/10.5897/IJWREE2016.0685>.

566 TSE-266 (2005) İçme Suları Standardı. Türk Standartları Enstitüsü, Baskı TSE, TS, Ankara
 567 266:1–25.

568 Turekian KK, Wedepohl KH (1961) Distribution of the elements in some major units of the
 569 earth's crust. Geological Society of America Bulletin 72(2):175-192.

570 US EPA (1997) Exposure Factor Handbook (EPA/600/p-95/002Fa) (Update to Exposure
 571 Factors Handbook EPA/600/8-89/043). Environmental Protection Agency Region I,
 572 Washington DC.

573 USEPA (1989) Risk Assessment Guidance for Superfund. Volume I: Human Health
 574 Evaluation Manual (Part A). US Environmental Protection Agency EPA/540/1-89/002.

575 USEPA (2004) US EPA Office of Water. Office of Science and Technology (EPA-822-R-00-
 576 001). Environmental Protection Agency Region I, Washington DC 20460.
 577 www.epa.gov/safewater.

578 USEPA IRIS (2011) US Environmental Protection Agency's Integrated Risk Information
 579 System. Environmental Protection Agency Region I, Washington DC, pp. 20460.
 580 <http://www.epa.gov/iris>.

581 Wang Z, Liu X, Qin H (2019) Bioconcentration and translocation of heavy metals in the soil-
 582 plants system in Machangqing copper mine, Yunnan Province, China. Journal of
 583 Geochemical Exploration 200:159-166. <https://doi.org/10.1016/j.gexplo.2019.02.005>.

584 Wei B, Jiang F, Li X, Mu S (2009) Spatial distribution and contamination assessment of heavy
 585 metals in urban road dusts from Urumqi, NW China. Microchemical Journal 93(2):147-
 586 152.

587 Zango MS, Sunkari ED, Abu M, Lermi A (2019) Hydrogeochemical controls and human health
 588 risk assessment of groundwater fluoride and boron in the semi-arid North East region
 589 of Ghana. Journal of Geochemical Exploration 207:106363.

590 Zhan HY, Jiang YF, Yuan J, Hu XF, Nartey OB, Wang BL (2014). Trace metal pollution in
 591 soil and wild plants from lead–zinc smelting areas in Huixian County, Northwest China.
 592 Journal of Geochemical Exploration 147: 182–188.
 593 <http://dx.doi.org/10.1016/j.gexplo.2014.10.007>.

594 Zhang J, Liu CL (2002) Riverine composition and estuarine geochemistry of particulate metals
 595 in China—weathering features, anthropogenic impact and chemical fluxes. Estuarine,
 596 Coastal and Shelf Science 54(6):1051-1070.

Zhang Y, Xu B, Guo Z, Han J, Li H, Jin L, Chen F, Xiong Y (2019) Human health risk assessment of groundwater arsenic contamination in Jinghui irrigation district, China. Journal of environmental management 237:163-169.

List of Tables

Table 1. Statistical summary of concentrations of PTEs in soil samples in the study area (all PTEs are measured in ppm; Al, Fe, Mg, and Ti are measured in wt.%; PI = Soil Pollution Index; NSAS = Number of Samples Above Standard; Standard values taken from Bowen 1979)

Table 2. Soil pollution assessment using contamination factor (CF), enrichment factor (EF), and index of geoaccumulation (I_{geo})

Table 3. Statistical summary of concentrations of PTEs in water samples in the study area (all ions are measured in mg/L, whereas PTEs are measured in $\mu\text{g/L}$)

Table 4. Statistical summary of the concentrations of PTEs in fruit plant samples in the study area (Au and Hg are measured in ppb, whereas the other elements are measured in ppm)

Table 5. Health risk assessment of groundwater in the winter season

Table 6. Health risk assessment of groundwater in the fall season

Figure Captions

Figure 1. Location and geology map of the study area (after Lermi and Sunkari 2020)

619 **Figure 2.** Spatial distribution of soil pollution index values

620 **Figure 3.** Water hazard index (WHI) for (a) winter season and (b) fall season

621

622

623

624

625

626

Table 1.

Parameter	Al	Fe	Mg	Ti	Mn	U	Th	V	Sr	As	Cd	Co	Cu	Hg	Mo	Ni	Pb	Zn	Ag	Au	Sb	Bi	PI
Min.	0.77	2.28	1.17	0.02	466	0.20	0.40	28.0	63.6	4.00	0.06	21.6	17.2	0.00	0.08	186	9.85	23.8	0.00	0.00	0.18	0.04	2.51
Max.	3.46	12.2	9.72	0.18	2030	10.0	4.70	122	397	10000	27.5	60.0	1094	0.33	80.2	750	9998	7939	86.5	0.25	560	63.4	407
Mean	2.45	4.44	3.26	0.08	959	1.06	2.06	68.9	180	770	3.47	42.1	122	0.02	7.01	467	3056	632	7.88	0.01	36.8	6.14	50.7
Median	2.59	4.28	2.96	0.07	977	0.50	2.00	69.5	164	162	1.19	42.9	55.0	0.00	3.15	470	807	149	1.58	0.00	6.44	1.09	12.4
STD	0.62	1.61	1.63	0.04	275	1.66	1.00	17.9	68.3	1724	5.22	8.91	185	0.06	13.4	128	3807	1343	15.1	0.05	93.1	11.3	77.8
Standard	8.80	4.70		0.50	850					5.0	0.06	20.0	30.00	0.03	6.20	40.0	20.0	50.0	90.0	90.0	1.50		
NSAS	None	11.00		None	30.0					39.0	39.0	40.0	37.0	4.00	10.00	40.0	36.0	32.0			28.0		

627

Element	Statistic	CF	EF	I _{geo}
Mn	Minimum	0.55	2.16	-1.45
	Maximum	2.40	13.5	0.67
	Mean	1.13	4.39	-0.47
As	Minimum	0.31	1.00	-2.29
	Maximum	769	4339	9.00
	Mean	59.2	262	2.96
Cd	Minimum	0.20	0.65	-2.91
	Maximum	91.8	518	5.93
	Mean	11.6	48.8	1.53
Co	Minimum	1.08	4.31	-0.47
	Maximum	3.00	23.5	1.00
	Mean	2.10	8.08	0.45
Cu	Minimum	0.38	1.25	-1.97
	Maximum	24.3	137	4.02
	Mean	2.71	11.4	0.14
Mo	Minimum	0.01	0.05	-6.86
	Maximum	12.9	73.0	3.11
	Mean	1.13	4.92	-1.95
Ni	Minimum	2.73	13.2	0.87
	Maximum	11.0	69.8	2.88
	Mean	6.86	26.4	2.14
Pb	Minimum	0.49	2.15	-1.61
	Maximum	500	2819	8.38
	Mean	153	604	4.72
Zn	Minimum	0.26	0.86	-2.50
	Maximum	88.2	498	5.88
	Mean	7.02	30.9	0.61
Sb	Minimum	0.12	0.42	-3.64
	Maximum	373	2105	7.96
	Mean	24.5	111	1.48

629

630

631

632

633 **Table 3.**

Parameters	Winter Season						Fall Season					
	Min.	Max.	Mean	Median	STD.	CV	Min.	Max.	Mean	Median	STD.	CV
Al	2.00	332	43.6	10.0	102	233	8.00	7101	1030	43.0	2243	218
Fe	10.0	324	84.3	24.5	123	146	10.0	1075	258	30.0	418	162
Mn	1.00	55.1	11.6	2.00	19.5	168	1.30	291	44.7	5.70	90.8	203
Cr	2.90	9.50	4.80	4.20	2.10	43.5	2.00	15.5	5.00	3.60	4.20	82.4
Co	0.00	1.00	0.20	0.10	0.30	181	0.00	3.30	0.70	0.10	1.10	163
Ba	7.70	65.6	33.4	37.2	20.2	60.5	15.2	112	45.2	41.2	27.2	60.3
Ni	2.40	9.30	4.90	4.30	2.30	47.2	0.20	47.0	10.7	3.60	15.1	142
Cu	1.40	5.30	3.30	3.20	1.50	45.5	1.40	40.4	8.60	4.30	11.7	136
Pb	1.70	135	17.7	3.10	41.3	234	2.80	65.4	15.7	7.10	19.2	122
Zn	6.50	182	53.4	33.1	60.5	113	3.90	342	85.5	9.50	124	145
Mo	0.10	13.5	2.00	0.50	4.10	211	0.30	14.4	2.30	0.60	4.30	187
Sb	0.20	29.2	5.80	0.70	10.5	181	0.30	64.3	10.5	1.70	20.4	194
As	0.80	287	56.2	2.90	107	191	1.20	373	66.4	9.00	122	184
V	0.80	5.40	2.20	1.80	1.50	65.2	0.80	6.50	2.80	2.80	1.80	64.0

634

Fruit plant type	Walnut				Cherry				Pear				Plum				Grape						
PTEs	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Acceptable limit	Toxic level	BCF
Fe	150	3380	752	240	150	2780	480	530	160	11270	1432	245	180	890	378	290	250	380	325	335		200	3.80 - 4.50
Mn	48.0	205	124	113	19.0	90.0	37.1	38.0	27.0	205	69.1	48.0	26.0	54.0	39.0	36.0	16.0	95.0	41.3	27.0		300	2.40 - 3.20
Ni	0.70	7.10	2.80	2.25	1.20	4.60	2.61	2.10	1.50	15.7	6.09	5.50	1.60	6.50	2.93	2.60	1.00	4.80	2.35	1.80	0.10 - 3.70	10.0	2.20 -2.70
Co	0.10	0.30	0.20	0.13	0.07	0.26	0.14	0.20	0.07	1.71	0.57	0.43	0.08	0.31	0.17	0.15	0.07	0.28	0.15	0.13			
Mo	0.20	2.30	1.00	0.64	0.02	2.46	0.37	0.23	0.12	6.16	0.97	0.24	0.14	1.17	0.50	0.41	0.09	1.31	0.54	0.39	0.07 - 1.75		0.07 - 1.75
Cu	3.30	31.6	8.90	4.65	6.14	33.6	10.1	11.0	6.00	106	19.4	9.97	3.07	10.2	7.42	7.65	4.77	8.98	6.70	6.53	5.00 - 30.0	20.0	2.80 - 3.30
Pb	1.70	1185	221	28.9	2.68	1150	135	65.1	1.61	4443	490	21.62	2.98	195	48.6	32.9	2.76	62.8	32.7	32.6	5.00 - 10.0	30.0	3.30 - 4.50
Zn	9.40	257	66.1	27.0	8.50	206	37.1	32.4	11.7	846	119	37.7	8.60	62.5	25.3	23.4	13.2	35.3	25.1	25.9	27.0 - 150	100	2.50 - 3.10
Ag	0.00	0.29	0.05	0.01	0.00	0.29	0.03	1E-05	0.00	0.96	0.10	0.00	0.00	0.03	0.01	0.01	0.00	0.02	0.01	0.01			
As	0.60	192	37.2	7.00	0.70	181	21.2	17.0	0.30	527	59.7	3.70	0.50	27.4	7.08	6.00	0.40	8.70	4.60	4.65	0.009 - 1.50	5.00	1.80 - 3.00
Cd	0.01	0.07	0.03	0.02	0.01	0.07	0.02	0.02	0.01	0.46	0.14	0.08	0.01	0.05	0.02	0.02	0.01	0.03	0.02	0.02	0.05 - 0.20	5.00	1.50 - 2.50
Sb	0.05	21.7	4.09	0.48	0.07	22.1	2.41	1.25	0.04	60.6	6.71	0.29	0.05	2.76	0.67	0.47	0.05	0.87	0.46	0.45			2.60 - 3.80
Cr	0.90	2.90	1.42	1.15	1.00	2.30	1.41	1.80	1.00	7.10	1.94	1.30	1.00	1.70	1.32	1.30	1.10	2.20	1.50	1.35			
Ti	9.00	19.0	12.3	11.5	9.00	17.0	11.1	12.0	10.0	37.0	15.5	13.0	11.0	41.0	16.7	14.0	11.0	19.0	13.8	12.5			
Se	0.20	0.50	0.32	0.30	0.10	0.50	0.28	0.30	0.10	0.50	0.32	0.30	0.20	0.40	0.31	0.30	0.10	0.40	0.28	0.30			
Au	3.30	91.5	29.4	16.1	3.70	31.8	12.7	15.0	3.40	115	30.2	10.2	4.10	54.6	18.7	12.6	4.00	9.70	6.85	6.85			
B	95.0	277	179	176	29.0	91.0	54.9	29.0	23.0	83.0	37.5	34.5	30.0	67.0	42.7	42.0	28.0	54.0	39.8	38.5			
Hg	13.0	28.0	20.2	20.5	9.0	32.0	19.8	32.0	9.00	41.0	21.2	21.0	12.0	19.0	15.9	15.0	6.00	20.0	13.0	13.0	0.002 - 0.086		

637 **Table 5.**

Winter Season											
Estimated Daily Intake (EDI)						Hazard Quotient (HQ)					Carcinogenic Risk (CR)
Sample	As	Ni	Pb	Zn	Sb	As	Ni	Pb	Zn	Sb	As
GS1a	0.00003	0.00020	0.0001	0.0059	0.00001	0.08637	0.00130	0.02128	0.01965	0.01296	0.00002
GS1b	0.00006	0.00011	0.0002	0.0025	0.00002	0.21592	0.00324	0.06570	0.00837	0.03887	0.00004
GS2	0.00011	0.00008	0.0005	0.0003	0.00001	0.37787	0.00567	0.15639	0.00111	0.01457	0.00007
GS3	0.00929	0.00009	0.0001	0.0010	0.00095	30.97436	0.46462	0.02313	0.00342	2.36761	0.00540
GS4	0.00736	0.00030	0.0044	0.0044	0.00069	24.52901	0.36794	1.24558	0.01460	1.71903	0.00428
GS5	0.00003	0.00027	0.0001	0.0011	0.00001	0.09717	0.00146	0.03054	0.00371	0.02753	0.00002
GS6	0.00004	0.00018	0.0001	0.0013	0.00001	0.12955	0.00194	0.02684	0.00425	0.01700	0.00002
GS7	0.00105	0.00013	0.0001	0.0003	0.00014	3.50877	0.05263	0.01573	0.00108	0.34494	0.00061
GS8	0.00015	0.00015	0.0001	0.0002	0.00003	0.49663	0.00745	0.02961	0.00079	0.07126	0.00009
GS9	0.00007	0.00010	0.0001	0.0002	0.00003	0.24831	0.00372	0.01943	0.00070	0.06802	0.00004
Safe limits	5×10^{-8}	2×10^{-2}	2.5×10^{-2}	7×10^{-3}	6×10^{-3}	1	1	1	1	1	1×10^{-4}

Table 6.

Fall Season											
Estimated Daily Intake (EDI)						Hazard Quotient (HQ)					Carcinogenic Risk (CR)
Sample	As	Ni	Pb	Zn	Sb	As	Ni	Pb	Zn	Sb	As
GS1a	0.00036	0.00013	0.0008	0.0035	0.00006	1.20918	0.00063	0.24153	0.01171	0.13927	0.00021
GS1b	0.00088	0.00085	0.0021	0.0111	0.00011	2.94737	0.00423	0.60521	0.03696	0.26397	0.00051
GS2	0.00022	0.00002	0.0001	0.0001	0.00003	0.72335	0.00010	0.03609	0.00042	0.07773	0.00013
GS3	0.01206	0.00002	0.0006	0.0003	0.00208	40.21592	0.00010	0.15824	0.00108	5.20729	0.00701
GS4	0.00617	0.00001	0.0006	0.0030	0.00085	20.56680	0.00003	0.17490	0.01001	2.12308	0.00359
GS5	0.00004	0.00023	0.0001	0.0002	0.00001	0.12955	0.00113	0.02591	0.00079	0.02753	0.00002
GS6	0.00015	0.00010	0.0002	0.0087	0.00005	0.50742	0.00049	0.06015	0.02910	0.13036	0.00009
GS7	0.00135	0.00011	0.0001	0.0002	0.00017	4.50202	0.00053	0.02961	0.00055	0.43320	0.00078
GS8	0.00011	0.00152	0.0002	0.0002	0.00002	0.35628	0.00761	0.07033	0.00070	0.04130	0.00006
GS9	0.00014	0.00048	0.0002	0.0003	0.00003	0.47503	0.00240	0.05367	0.00097	0.07611	0.00008
Safe limits	5×10^{-8}	2×10^{-2}	2.5×10^{-2}	7×10^{-3}	6×10^{-3}	1	1	1	1	1	1×10^{-4}

Figure 1.

Figure 2.

Figure 3.

Figures

Figure 1

Location and geology map of the study area (after Lermi and Sunkari 2020) Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 2

Spatial distribution of soil pollution index values Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

Figure 3

Water hazard index (WHI) for (a) winter season and (b) fall season