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Environmental Impact of Mn Mining Wastes on the Accumulation of Potential Hazardous Elements in Soil and Crop Grains in Western Drama Plain, Macedonia, Northern Greece

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Chronic exposure of humans to a contaminated terrestrial ecosystem is a matter of general health concern (Adriano, 2001). Potential hazardous elements (PHEs) represent a serious threat to the environment in general, and can have adverse effects on plants, animals and humans (Alloway, 2005; Kabata-Pendias and Mukherjee, 2007; Abreu *et al.*, 2014).

Active or abandoned mining areas can be significant sources of PHEs contamination for the surrounding areas, including agricultural land (*e.g.*, Navarro *et al*., 2008). Specifically, excessive accumulation of PHEs in cultivated topsoil (0-20cm) around mining areas, results in their elevated uptake by food crops, thus posing great concern because of potential human health risk, at least to local inhabitants, via the food chain (*e.g.*, Zhuang *et al.*, 2009). Therefore, in recent years increasing attention has been paid to the issue of excessively high levels of PHEs in agricultural soil, near mining areas (*e.g.*, Hua *et al.*, 2018), and the transfer and accumulation of PHEs in the soil-plant system became a popular research topic (*e.g.*, Wang *et al*., 2017).

The present study was conducted in the western part of Drama plain (WDP) of Macedonia, Northern Greece, at an effort to assess the potential human health risk via the dietary route, probably coming from toxic PHEs dispersed from an abandoned Mn mine. The results are expected to raise awareness among the public on the safety of consuming food products grown at particular sites of WDP. Mining and mineral processing activities at the well-known 25km Kato Nevrokopi Mn mine of Drama district (an abandoned mine since 1994), have generated enormous piles of mine wastes (tailings, low grade ore, ore concentrate) deposited within the Xiropotamos stream valley, without any safety measures for the environment. Their erosion and downstream transport by the Xiropotamos stream resulted in the dispersion of the mine wastes and their deposition on the land of WDP. Thus, around the stream, the alluvial soil has attained a black colour due to mixing with the mine wastes (Sofianska, 2013). WDP constitutes an agricultural area producing mainly cereals. The corn–wheat rotation system is the dominant cropping pattern. Therefore, information about the concentration of PHEs in agricultural soil and cultivated food crops in WDP is very important for assessing health risk on the local population. The purpose of the study was to assess the concentration of PHEs and their spatial distribution in the soil of WDP. A control site, unaffected from mine wastes, was selected for comparison. The contamination levels of soil and the ability of plants to accumulate PHEs were estimated by means of the pollution load index (*PLI*) and the bio-accumulation factor (*BAF*), respectively.

Paired soil and plant (corn–wheat) grain samples were collected and analysed for Mn, Pb, Zn, Cu, Cd and As by inductively coupled plasma mass spectrometry (ICP-MS), after leaching with hot aqua regia, at the certified ACME Analytical Laboratories of Canada. The results of the research (Table 1) were as follows: PHEs concentrations in the WDP soil samples exceed significantly the average composition of agricultural soil worldwide. Locally, the concentrations of all analysed PHEs exceed soil quality standards (Kabata-Pendias, 2011). The reported PHEs are hosted in the Mn mine ore minerals, and were also found in the WDP soil samples (Sofianska, 2013). Spatially, the higher PHEs concentrations were found on the agricultural land along both sides of the Xiropotamos stream, and their levels in soil generally decreased with distance from the stream. The concentration trend of PHEs (average values) in the studied soil samples is Mn>Pb>Zn>As>Cu>Cd. Average values of *PLI*, calculated on the basis of the maximum permissible limits for agricultural soil (Chiroma *et al*., 2014), follow the order Mn>As>Pb>Cd>Zn>Cu. Based on *PLI* values, soil in the study area is on average characterised as very strongly contaminated by Cu, slightly polluted by Zn and Cd and very strongly polluted by Mn, Pb and As.

The concentration of PHEs (average values) in the wheat and corn grains follow the trend Zn>Mn>Cu>Cd>As>Pb and Zn>Mn>Cu>Pb>As>Cd, respectively. Among the studied PHEs, Cd concentration in wheat grains (4 sites out of 11) and Pb in corn grains (2 sites out of 9) were found to exceed the permissible limits, whereas all other PHEs in both types of grain were within the acceptable levels for food consumption as suggested by the World Health Organization (WHO). The concentration of PHEs in grain samples were affected by their concentrations in the soil substrate, as well as by the plant species, as recorded in other investigations (*e.g.*, Wang *et al.*, 2017). Specifically, the concentration of Mn, Pb, Zn, Cu, and As in crop grains increased with increasing PHEs concentrations in soil, whereas those of Cd have the opposite trend.

BAF values of food crops for the considered PHEs were below 1. They displayed the order Pb<Mn<As<Cd<Cu<Zn for wheat, and Pb<As<Mn<Cd<Cu<Zn for corn, and they tend to decrease rapidly with increasing PHEs in soil, a finding consistent with previous studies (*e.g.*, Wang *et al*., 2017). It is worth noting that *BAF* values are the highest in the control site, where the *PLI* are the lowest for the PHEs.

Paired wheat and corn plants grown in the same soil substrate displayed different accumulation and translocation patterns. Wheat plants have a higher ability to transfer soil Mn, Zn, Cu, Cd and As in their grains than corn, while corn grains accumulate higher amounts of Pb.

In conclusion, the WDP agricultural soil is strongly affected by PHEs due to the dispersion of the mine wastes from the

25km Mn mine. The reported results for the crop grains for all PHEs were found on average to be within the standards set by WHO. Given that there are land sites where Cd or Pb accumulation in food crops may pose a health risk to the local population through the consumption of wheat or corn, it is proposed either to take necessary measures as, for example, remediation of contaminated soil or to avoid planting these cereals in the particularly contaminated land sites.

Table 1. Basic statistical data of PHEs measured in the soil–crop system of western Drama plain.

Sample type/Parameter	Mn (mg/kg) mean/range	Pb (mg/kg) mean/range	Zn (mg/kg) mean/range	Cu (mg/kg) mean/range	Cd (mg/kg) mean/range	As (mg/kg) mean/range
Surface soil	25,180 730–13,013	844 45–1996	486 59–2140	92 13–153	6 1.5–27.5	224 10–1077
World agricultural soil[1]	488	27	70	38.9	0.41	6.83
Max.permissible limit for soil[1]	2000	100	300	100	3	20
Pollution load index (PLI)	12.6 0.35–65.1	8.44 0.45–20	1.62 0.20–17.3	0.92 0.13–1.53	1.99 0.17–9.17	11.2 0.50–53.9
Wheat grain composition	37.7 28–46	0.071 0.01–0.15	37.6 22.7–67.9	5.14 3.81–6.98	0.18 0.03–0.39	0.13 <0.1–0.3
Corn grain composition	5.78 4.00–11.0	0.31 0.05–1.09	22.9 18.9–33.3	1.59 1.25–2.66	0.011 <0.01–0.03	0.014 0.1–0.3
Max.permissible limit for food[2]	500	0.30	100	73	0.20	–
BAF[3] corn ($x10^{-4}$)	29.6 0.88–85.4	9.69 1.37–10.8	1211 240–3305	298 44–985	136 2.76–938	27.4 3.21–100
BAF wheat ($x10^{-4}$)	125 4.81–283	4.01 0.16–12.8	1725 564–3847	1096 352–1626	709 19.9–1950	30.5 3.54–154

[1]Kabata-Pendias, (2011); [2]Chiroma*et al*., (2014); [3]Bio-accumulation factor

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