Determination of Soluble/Exchangeable Metals in Peri-urban Farmland (*Ribeira dos Covões*) of Central Portugal

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Abstract - Heavy metal contamination of soil is widespread, and there is a potential risk of transferring toxic metals to agricultural crops, animals and humans. The total heavy metals content can indicate the extent of contamination, but this measure is not usually an accurate indication of the phyto-toxicity; therefore, a number of recent studies have investigated the bioavailable heavy metal fractions in soils and evaluated the phyto-toxic risks for humans. Soluble and exchangeable forms of metals in the soil are the fractions available for plants. The main purpose of the present study is to quantify the total and soluble/exchangeable fractions of heavy metals (Pb, Cr, Cu and Zn) in soils of peri-urban farmland in Portugal (*Ribeira dos Covões*). The results show that the total heavy metals content is greater than the soluble/exchangeable content, but no clear correlations were recorded: Pb – 70.8 mg/kg vs. 16.7 mg/kg, Cr – 25.0 mg/kg vs. 0.0 mg/kg, Zn – 383.3 mg/kg vs. 0.0 mg/kg, Cu – 183.3 mg/kg vs. 0.0 mg/kg in a horticultural garden (site 10), and; Pb – 270.8 mg/kg vs. 79.0 mg/kg, Cr – 25.0 mg/kg vs. 0.0 mg/kg, Zn – 12.5 mg/kg vs. 0.0 mg/kg, Cu – 33.3 mg/kg vs. 29.2 mg/kg in a backyard (site 18). It is possible that the use of a single extraction procedure, in the laboratory, may not provide a proper assessment of heavy metal forms, and it is therefore advisable to combine different extraction methods in order to correctly perform a risk-based evaluation.

Keywords: Bioavailable Fraction, Farmland, Heavy Metal, Peri-Urban, Portugal.

1. Introduction

Heavy metal contamination of soils is widespread and there is a risk of transfer of toxic and available metals to agricultural crops, animals and humans [1]. Heavy metals can induce toxicity in wildlife if the level in the soil reaches critical concentrations; accumulation in above-ground tissues of plants can also result in an increase of metal accumulation in top-soil, via leaf deposition, or can create an exposure pathway for metal introduction into the food chain [2]. Two main sources of heavy metals in soils can be considered: the natural pedo-geochemical background, which represents the heavy metal concentration inherited from the parent rock [3] and anthropogenic contamination, which can be directed via wastes [4], compost [5], or sewage sludge [6] or may diffuse via aerosol deposition [7].

The total heavy metal contents can indicate the extent of contamination, but is not usually an accurate indication of the phyto-toxicity [8 & 9]. Many recent studies investigated the bioavailable heavy metal fractions of mine soils [8 & 9] and evaluated the phyto-toxic risk for human receptors. Bioavailability is the proportion of total metals that are available for incorporation into biota (bioaccumulation). Total metal concentrations do not necessarily correspond with metal bioavailability [10]. However, the determination of heavy metal fractions is a more complex task than the determination of the total contents of heavy metals [11].

Several analytical methods have been used to quantify heavy metals in the soil; for example, the soil extraction with strong acids is commonly carried out to assess total heavy metals, and X-ray fluorescence spectrometry is used to determine the content of total elements (review in [12]). Soluble and exchangeable forms of metals in the soil are the fractions available

for plants, and it is known that extraction with ammonium acetate ($NH_4CH_3CO_2$) is one method for estimating the soluble and rapidly exchangeable pools of elements in the soil (cf. [12 & 13]).

The main purpose of the present study is to quantify the soluble/exchangeable portion of metals in peri-urban Portuguese farmland (*Ribeira dos Covões*) by means of the ammonium acetate extraction.

2. Peri-Urban Areas

Peri-urban areas are defined by the structure resulting from the process of pre-urbanisation [14], and comprise the landscape interface between urban and rural areas. A peri-urban area attracts new types of housing, transport infrastructures and multifunctional agriculture, with a wide range of recreation sites and ecosystem services. Urban development, by far the most rapidly expanding land use type in Europe (see Fig. 1 right), puts peri-urban areas under particular pressure: the growth of built development in peri-urban areas is likely to be up to four times as fast as in urban areas [15]. European-wide projections of built development in peri-urban areas estimate 1.4-2.5% per annum, and the total built development in peri-urban areas will double between 2040-2060 [15].

Fig. 1: Distribution of peri-urban areas in Europe (redrawn form [15]) (right) and study site (*Ribeira dos Covões*) in Portugal (left).

3. Study Site

The study was carried out in the peri-urban Ribeira dos Covões catchment (8°27'W and 40°13'N), located 3 km north-west of Coimbra, the largest city in central Portugal.

The catchment (see Fig.1 left) is 6.2 km^2, aligned north-south, with altimetry ranging from 34 to 205 m a.s.l. The area has a Mediterranean climate, with a mean annual temperature of 15°C and an average annual rainfall of 892 mm [16]. Between 1958 and 2007, the urban area expanded from 6% to 32% and woodland expanded from 44% to 64%, at the expense of agricultural land, which showed a marked decrease from 48% to 4%.

The catchment is underlain by sandstone (57%) and limestone (43%). Soils developed on sandstone are classified as Fluvisols and Podsols, whereas in limestone they are Leptic Cambisols.

The woodland area consists mainly of *Eucalyptus globulus Labill.* plantations (55%), but with some mixed stands of eucalypt and pine (29%), scrubland (15%) and relict oak woodland composed of *Quercus roburL., Q. faginea broteroi* and *Q. suber L.* trees (1%). Generally, eucalypt plantations occur on sandstone. The agriculture areas are mainly comprised of backyards, used for family consumption as a complementary income, and by relatively small pasture fields and few remaining olive groves.

4. Methods

Twenty four soil surface samples (0-2cm) were collected in distinct farmland areas within Ribeira dos Covões on 16/08/2017. The collected samples were dried at room temperature. The dry samples were disaggregated using a mortar and pestle and put through a sieve with a 2 mm grid. After this sieving operation, metal elements were extracted from the pre-treated samples using two different methods — (i) a 1.7 g sample was mixed with 50 ml of 1M ammonium acetate and shaken for 2 hours [17]. Then, the extracted metals from the sample were filtrated, and they are denoted as bioavailable

fractions in this paper; and (ii) a 1.7g sample was mixed with 10 ml concentrated HNO_3 and heated. Furthermore, 20 ml $HCLO_4$ was added to this mixture and again heated [18]. After cooling, 20 ml HCl was used as the final reflux acid for chemical analysis. Then, the extracted metals were filtered, and they are denoted as the total metal portion in this paper. The following elements were simultaneously determined by inductively coupled plasma spectrometry (Perkin Elmer, Optima 5300 DV) – Cu, Pb, Cr and Zn.

5. Results and Discussion

The bioavailable fraction of metals represents a relatively low portion of the total heavy metals. For example, less than 0.01% of the total content of nitrogen generally exists in plant-available form [19]. As stated above, analytical attention was given to quantifying the element content that would be available for plant uptake. The amounts of elements extracted with ammonium acetate can be mainly considered plant-available [20]. Given the large number of sampling sites and the limited space, this paper presents data from only two representative sites (Fig. 2): site 10, a typical horticulture garden, and site 18, representative of local backyards. As expected, the obtained results prove that the total element content is much different from the plant-available content.
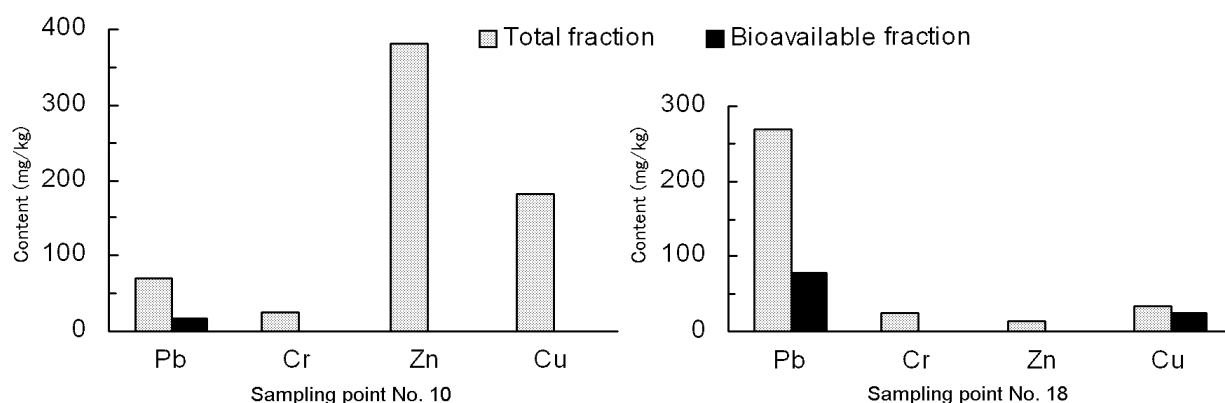

Fig. 2: Metal contents at sampling point Nos. 10 and 18 in Ribeira dos Covões study site.

6. Conclusion

Environmental science and legislation over recent years have supported the view that total content of metals in soil by itself is not a good measure for assessing their bioavailability and not a very useful tool for determining potential risks from soil contamination (review in [21]). Environmental strategies are currently moving towards implementation of risk-based legislative frameworks, and it is possible that the use of a single extraction may not provide a proper assessment of heavy metal forms. It is therefore advisable to combine different extraction methods in order to correctly perform risk-based evaluation.

Acknowledgements

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