Preliminary evaluation of heavy metal pollution in fluvial sediments within peri-urban areas – a Portuguese case study

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Abstract. Heavy metal pollution is a serious problem because living organisms may incorporate heavy metals into their tissues and transfer the heavy metals into the food chain, leading to their bioaccumulation. There are several sources of heavy metals, such as mining, industries, waste disposal, fuel combustion and phytosanitary treatments in agricultural fields. Although the EU’s strategy has led to good progress in reducing heavy metal emissions within member states, it is a worthwhile subject to evaluate the already diffused heavy metals and their concentrations in the pedosphere.

Peri-urban areas have been subject to greater land-use changes and urbanisation pressure. This study evaluates the potential heavy metal pollution over a stream network located in a peri-urban catchment (~6 km²) near the city of Coimbra in Portugal. High contents of heavy metals were recorded in fluvial sediments, reaching, for example, 188.0 mg/kg Cu, 658.9 mg/kg Zn and 154.5 mg/kg Pb. However, high heavy metal concentrations were not equally dispersed over the stream network. Hence, it is considered that runoff, sediment sources and their mobilisation are important parameters for assessing the unequal dispersion of heavy metals in peri-urban areas.

Keywords: EU strategy, food chain, heavy metal, peri-urban, sediment.

1. Introduction

At present, there is much concern regarding the effects of perturbations on the environment such as climate change, acid rain and water pollution [e.g. Barrett & Rosenberg, 1981]. Industrialisation and urbanisation have intensified environmental risks and pollution, and an estimated 12.6 million people died from environmental health risks in 2012 [World Bank Group, 2016].

It is considered that heavy metal pollution in soil is one of the most severe problems because living organisms may face a risk due to the transfer of heavy metals into the food chain and their bioaccumulation [cf. Barrett & Rosenberg, 1981; Szefer et al., 1997]. Measurement of heavy metal concentrations in the environment is important to assess potential contamination levels and harmful effects to humans and other organisms. It is therefore the purpose of this manuscript to evaluate pedospheric heavy metals and their concentrations in the fluvial sediments which were sampled in a Portuguese peri-urban area.

2. Background information

The necessary fundamentals and the terms used are briefly reviewed first, followed by a main description.

2.1. Heavy metals

The term "heavy metals" has been used extensively in the past to describe metals which are environmental pollutants. For a metal to be considered "heavy", it must have a density relative to water greater than five [Barrett & Rosenberg, 1981]; however, this term has been replaced in recent years by a classification scheme that considers their chemistry rather than density [review in Appenroth, 2010]. Metals are non-biodegradable – unlike some organic pesticides, metal cannot be broken down to less harmful components [Barrett & Rosenberg, 1981]. Several metal ions are essential for the metabolism of cells. They are necessary at low concentrations but toxic at high concentrations, resulting in bell-shaped dose-response relationships [cf. Marschner, 1995]. The pollution effects are aggregated by improper disposal systems that result in the bioaccumulation of metals in the food chain, and the non-biodegradability of metal ions results in their accumulation in living organisms, with the effect manifested in various forms of disease [review in Matoka et al., 2015].

The sources of heavy metal pollutants are metal mining, metal smelting, metallurgical and other metal-using industries, waste disposal, corrosions of metals in use, phytosanitary treatments (i.e. control of plant diseases) in agriculture, fossil fuel combustion and so on [Oliver, 1997]. Hot spots of heavy metal pollution are located close to industrial sites, around large cities and in the vicinity of mining and smelting plants [Oliver, 1997].
Agriculture in the areas near heavy metal sources faces major problems due to heavy metal transfer into crops and subsequently into the food chain [Puschenreiter et al., 2005]. On sites with low or medium contamination levels, metal concentration in crops is mostly not high enough to cause acute toxicity, but in the long term it may provoke chronic damage to health [Adriano, 2001]. Due to the heavy metal burden in human nutrition, there is a need for measures to reduce the metal transfer into agricultural plants.

Table 1. Threshold values (mg/kg) for metals in soils (adapted from MEF, 2007)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Symbol</th>
<th>Threshold value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>2</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>5</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>0.5</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>1</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>20</td>
</tr>
<tr>
<td>Chrome</td>
<td>Cr</td>
<td>100</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>100</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>60</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>50</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>200</td>
</tr>
</tbody>
</table>

It can be considered that the standards set in Finnish legislation for contaminated soils [MEF, 2007] are representative because the Finnish standard values (Table 1) are a good approximation of the mean values of different national systems in Europe [Carlon et al., 2007], and these Finnish values (Table 1) have been applied in an international context for agricultural soils [Voet et al., 2013].

2.2. EU strategy against heavy metal pollution

Coupled with improved control and abatement techniques for heavy metal emissions, targeted international and EU legislation has led to good progress in most EEA-33 countries (i.e. EU-28 countries and EFTA-4 countries) in reducing heavy metal emissions. Such legislation includes various prescriptions [European Environment Agency, 2010]:

- the 1998 Aarhus Protocol on Heavy Metals targets three particularly harmful substances: Cd, Hg and Pb.
- the EU Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants (LCP Directive) aims to limit heavy metal emissions via dust control and absorption of heavy metals.
- the EU Directive 2010/75/EU on industrial emissions (integrated pollution prevention and control) aims to prevent or minimize pollution of water, air and soil. The directive targets certain industrial, agricultural, and waste treatment installations.

- emissions from a number of heavy metal sources linked with certain industrial facilities are also estimated and reported under the requirements of the European Pollutant Release and Transfer Register Regulation (166/2006/EC).
- the EU Directive on Ambient Air Quality and Cleaner Air for Europe (2008/50/EC) and Directive 2004/107/EC relating to heavy metals and polycyclic aromatic hydrocarbons in ambient air contain provisions, and target and limit values for the further control of air pollutants.

As stated above, the EU strategy has led to good progress in reducing heavy metal emissions within member states. It is necessary to provide an overview of heavy metals and actually evaluate heavy metal contents in European soils in order to prove the successful abatement of heavy metals based on the legislative measures. However, the quality of available databases is questionable, due to, for example, doubts regarding standardisation of data (sampling method and digestion method), mapping of soil parent material, qualified comparison of data by country and so on.

2.3. Fluvial sediment

When loose sand, clay, silt and other particles are transported by water, they become sediments that settle at the bottom of a body of water [cf. MARC, 2006]. Fluvial deposits are the principal source of information regarding terrestrial processes [review in Nedyba et al., 2010] – modern fluvial sediments, particularly in industrial areas, provide numerous data about the impact of human activities on natural systems, and the content of hazardous components represents strategic information about the quality of the environment and for sediment management.

While natural erosion produces nearly 30% of the total sediment, accelerated erosion from human use of land accounts for the remaining 70% in the United States [cf. MARC, 2006]. Sediment entering storm water degrades the quality of water for drinking, wildlife and the land surrounding streams. Sediment pollution annually causes US$16 billion of environmental damage in the United States [cf. MARC, 2006].

2.4. Peri-urban areas

Peri-urban areas are defined by the structure resulting from the process of pre-urbanisation [e.g. Le Jeannic, 1996], and this process can be described as the landscape interface between urban and rural areas.

A peri-urban area attracts new types of housing, transport infrastructure and multifunctional agriculture, with a diverse range of recreation sites and ecosystem services. Urban development, by far the most rapidly expanding land use type in Europe (see Figure 1), 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 [Pirro et al., 2011]. European-wide projections of built development in peri-urban areas are for 1.4-2.5% per annum, and the total built development in peri-urban areas will double between 2040-2060 [Pirro et al., 2011].
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 Figure 2) is 6.2 km² in area, is aligned north-south and ranges in altitude 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 [INMG, 1941-2000].

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%.

3.1. Soil type

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

3.2. Vegetation type

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 robur L., Q. faginea brotero and Q. suber L. trees (1%). Generally, eucalypt plantations occur on sandstone.

4. Methodology

Fluvial sediments were sampled in 22 sites within the stream network (Figure 2), on three distinct occasions.

4.1. Sampling

Sediment samples were taken with a stainless steel trowel from the upper 3 cm of the stream bank, a few centimetres below the water level. Each sample represents a composite sample of several sub-samples collected in a 1 m length section. The samples were transferred to plastic bags and transported to a laboratory.

4.2. Pre-treatment and analysis

All the samples were oven-dried at 38°C for at least 48 h. The dry samples were disaggregated using a mortar and pestle. The disaggregated samples were sieved to recover the fraction below 63μm (i.e. equivalent to suspended sediment). After this sieving operation, the samples were analysed by X-ray fluorescence (Niton X-ray fluorescence elemental analyzer) in order to quantify metal elements.

For data quality control, the multi-element standard (reference RCRA) was used before and after every 10 samples, for quantification of elemental concentrations.

5. Results

As seen in Figure 3, site No. 20 shows great concentrations of Pb (154.5 mg/kg), Zn (658.9 mg/kg) and Cu (136.6 mg/kg).
mg/kg). This site receives runoff from major road construction (cf. Figure 2). Site Nos. 3, 4 and 6 also show high concentrations of Zn, Cu and Cr. These sites also receive road runoff contributions (cf. Figure 2). Site No. 9 encompasses the outlet of an urban storm drainage system, and this site recorded the greatest level of Cu (188 mg/kg). On the other hand, fluvial sediments sampled in site No. 1 (catchment outlet, Figure 2) exhibit relatively low concentrations of heavy metals compared with those from the other sampling sites.

6.1. Sampling density and overview of contamination level

There has been no sufficient data to provide a reliable view on the real extent of the heavy metal problem in Europe and worldwide [Toth et al., 2016]. FOREGS data produced by the EuroGeoSurvey and the derived continuous map sheet [Lado et al., 2008] have been the most comprehensive source of information to date. However, the low sampling density (1 site per 5000 km²) of the FOREGS study allows only limited interpretation apart from the provision of a continental-scale overview without the possibility of comparing the concentrations by land use type.

The sample density was 1 site per 0.28 km² on average in the performed field study. In such high-density conditions, the metal contents varied considerably; e.g. the Zn content varied from values below the limit of detection to 658.0 mg/kg. It may be possible to separately interpret the metal levels at each sampling site, but it is quite difficult to obtain a reliable overview of metal levels from a macroscopic standpoint. This implies that the problem of heavy metal assessment lies in not only the sample density but also the choice of site characteristic and time of sampling.

6.2. Metal type and bioaccumulation

Bioavailability is the proportion of total metals that are available for incorporation into biota (bioaccumulation). Geologic and (or) environmental conditions that enhance dissolved metal abundances (for example, lower pH) result in greater metal bioavailability [McKinney and Rogers, 1992].

Therefore, in a discussion of the bioaccumulation of heavy metals, it is necessary to classify metals into two types – bioavailable and non-bioavailable one. The total metal concentrations of metals were measured by an X-ray analyzer; however, the total metal concentrations do not necessarily correspond with metal bioavailability [cf. Kikuchi and Gorbacheva, 2006]. Some high concentrations were determined in the study catchment, but it cannot be concluded that the peri-urban areas are at environmental risk. It may be correct to say that they are potentially at risk.

7. Conclusion

It is reported that the rapid change of land use puts peri-urban areas under environmental pressure. The obtained preliminary results support the notion of such environmental pressure, driven by the number of sites with high heavy metal concentrations. As the next step, long-term monitoring will help to enhance understanding of the land use impact and the potential heavy metal sources in the peri-urban area.

Although metal bioavailability is related to the bioaccumulation risk, it remains for a future research to provide an overview of bioavailable metals in the study area. This subject will contribute to a proper assessment of the EU strategy against heavy metal pollution.

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References

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