

Fate of Trace Elements in Urban Surface Drainage Deposits of the Athens Basin, Greece

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Introduction

Urban deposits (road dust and gully sediment) are reflective of a wide range of anthropogenic activities, and are a useful medium for evaluating the level and distribution of trace element contaminants in the surface environment. The drainage system of cities plays an important role in terms of capturing and/or releasing trace element contaminants to the receiving aquatic bodies (Duzgoren-Aydin *et al.*, 2014). Monitoring of the urban environment of Greece's capital, Athens, provided important information about how trace element concentrations behave between seasons and how they contribute to the urban pollution. Chemical partitioning of contaminants in both road dust and gully sediment can, therefore, be useful to evaluate the long-term fate of contaminants in the urban system. Urban sediment samples have been collected and analysed from different altitudes within the Athens basin, based on the hydrographic network of the area.

Sampling and analysis

A total of 26 urban sediment samples were collected and analysed for 33 elements following hot *aqua regia* dissolution and measured by Inductively Coupled Plasma Emission Spectroscopy. Soil organic carbon content, soil pH and grainsize distribution and magnetic susceptibility measurements have been determined, and mineralogical analysis by powder X-ray diffraction was also performed in order to identify possible factors explaining the variability of elemental concentrations. The BCR sequential extraction protocol (Ure, 1992; Ure *et al.*, 1993) was subsequently applied to a set of ten selected samples with the highest concentrations of trace elements (Cd, Co, Cr, Cu, Ni, Pb, Zn). Seasonal sampling at selected sampling sites over one year was also performed, followed by determination of the reactive content of trace elements after extraction with dilute (0.43 M) HNO₃ at room temperature (Rodrigues *et al.*, 2010) and measurement by Flame Atomic Absorption Spectroscopy.

Results and discussion

Basic statistical parameters of *aqua regia* concentrations of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sediment samples are tabulated in Table 1. With the exception of Co and As, both maximum and median values were found to be much higher in this work than those presented for Athens topsoil in a previous study (Kelepertzis and Argyraki, 2015).

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Element	This study (n = 26)		Kelepertzis and Argyraki (2015) (n = 45)	
	Range	Median	Range	Median
As (mg/kg)	8-18	12.5	4.4 - 227	27.1
Cd (mg/kg)	0.5 - 2	0.93	0.09 - 2.35	0.37
Co (mg/kg)	6-14	8	8.7 - 52.8	14.5
Cr (mg/kg)	54 - 193	215	21.1 - 558	82.4
Cu (mg/kg)	43 - 640	98.2	15.1 - 316	59.2
Fe (%)	1.03 - 2.56	1.72	0.99 - 4.06	2.35
Mn (mg/kg)	269 - 648	390	246 - 2810	564
Ni (mg/kg)	43 - 112	69.7	25.4 - 762	94.5
Pb (mg/kg)	44 - 3092	267	9.6 - 823	106
Zn (mg/kg)	147 - 1469	598	37.2 - 783	146

Table 1. Statistical summary of aqua regia extractable concentrations of major and trace elements for the
investigated sediment samples from Athens basin (n = 26), and comparison with topsoil values reported by
Kelepertzis and Argyraki (2015: Table 1, p.66).

Cluster analysis performed on the results identified two major groups of elements based on a >43.6% criterion of similarity. The first cluster contains elements of geogenic origin including Co, Fe, Mn and Ni. The parameters of soil organic carbon, magnetic susceptibility, Cu and Cr are grouped together in a second cluster showing similarity level >65%, while a third cluster groups together Pb, Zn and Cd and is interpreted as anthropogenic. Sequential extraction results support this grouping as the anthropogenic elements tend to be released in the first two extraction steps. Cadmium and Zn are the only trace elements showing significant association with the exchangeable fraction, reaching 40%, suggesting that they are the most susceptible elements to mobilisation during runoff. Moreover, Cu and Pb are largely associated with the oxidisable fraction. Trace element fractions identified as showing larger associations with the reducible and oxidisable fractions will continue to be vulnerable to mobilisation as a result of changes in ambient pH

and/or redox conditions (Robertson *et al.*, 2002). No significant seasonal variation has been observed for all the studied elements, except Cd which displayed significantly lower concentrations during the December sampling period.

Soil and dust in cities and towns that are contaminated by trace elements, of anthropogenic origin, represent a potential risk for the residents through several pathways (Kelepertzis *et al.*, 2013). Urban surface drainage deposits are the main sinks where dust, urban soil and anthropogenic sediments can be trapped. Briefly, it was documented that the type and extent of contamination in the surface environment of the Athens basin reflects the characteristics of prevalent anthropogenic activities, and that traffic-related activities are the primary sources of contaminants in the city.



Figure 1. Dendrogram showing grouping of measured parameters in surface drainage deposits of the Athens Basin.

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