



# Distribution of toxic elements between biotic and abiotic components of terrestrial ecosystem along an urbanization gradient: Soil, leaf litter and ground beetles



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## ABSTRACT

Urbanization and anthropogenic activities are the major source of environmental pollution which may cause damage in terrestrial ecosystems and their organisms. Toxic elements can accumulate in soil and leaf tissue; thus, through the food chain they can accumulate in predatory organisms. The aim of our study was to investigate the effects of urbanization on toxic element concentration in soil, leaf litter and *Carabus violaceus* and *Pterostichus oblongopunctatus* specimens along an urbanization gradient. The studied predator species were common and their distribution is widespread along the urbanization gradient. Soil, leaf litter and ground beetles were collected from three forested area: urban park, suburban forest and rural forest. The following toxic element concentrations were analyzed in all samples: Al, Ba, Cd, Cu, Fe, Mn, Ni, Pb, Sr and Zn. In the soil there was no significant difference in toxic element concentration between areas, except in seasons. Significantly higher toxic element concentration was found in autumn than in spring in the soil. In the case of leaf litter we found significant differences between areas in the following toxic elements: Ba, Cu, Mn, Sr and Zn. The concentrations of all elements were significantly higher in autumn than in spring. Significantly higher concentration was found in *P. oblongopunctatus* specimens than in *C. violaceus* for all studied elements, except Sr. We found significant differences in elemental concentrations between sexes in both species. Significantly higher Cu and Pb concentration was found in male beetles than in female ones. Just the opposite was true for the Sr concentration. We found positive correlation between toxic element concentration of *C. violaceus* and leaf litter for Mn and Zn. Negative correlations were found between toxic elements of ground beetles and soil for Al, Ba, Fe, Sr and Zn. Our study confirms that different breeding strategies and sexes cause differences in the accumulation of toxic elements. In summary, we demonstrated that ground beetles, leaf litter and soil were suitable bioindicators for monitoring the effects of urbanization and anthropogenic activities on terrestrial ecosystem.

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## 1. Introduction

Several studies demonstrated the effects of anthropogenic activities and urbanization on invertebrates' population (Heikens et al., 2001; Van Straalen et al., 2001; Magura et al., 2006, 2010).

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Invertebrates are especially useful to assess the effects of anthropogenic activities on the terrestrial ecosystem, because they are in close contact with toxic elements in the soil and in the leaf litter (Heikens et al., 2001).

Among terrestrial invertebrates carabid beetles are frequently used to study the effects of environmental changes (Avgin and Luff, 2000; Bednarska et al., 2013; Lagisz and Laskowski, 2008) because of they are one of the most resistant insect group to metals and inhabit highly contaminated areas (Sklaski et al., 2011). Carabid beetles can accumulate metals from soil through dermal absorption

during larval period, feeding on contaminated food during larval and adult period (Brunsting and Heessen, 1984). They are usually predators and/or scavengers representing the second trophic level; they can also accumulate toxic elements through biomagnifications (Kramarz and Laskowski, 1997). Thus, ground beetles are potentially exposed to increased level of toxic elements (Lagisz et al., 2005; Purchart et al., 2010). Heikens et al. (2001) studied the Pb, Cd and Cu concentration in many taxonomic groups. Their study demonstrates that the Cd and Pb accumulation depends on the total soil concentration, i.e. the internal Pb concentration increased strongly with increasing concentration in the soil (Heikens et al., 2001). Jelaska et al. (2007) showed that the internal Cu and Zn concentration also correlated with the elemental concentration of soil. Studied about metal kinetics of ground beetles indicated that metals probably due to the efficient detoxification by excretion (Bednarska et al., 2013; Janssen et al., 1991; Kramarz, 1999; Mozdzer et al., 2003; Talarico et al., 2014). At the same time, ground beetles as holometabolous insects are present in the soil during their development phases, so they are poor metal accumulator (Cortet et al., 1999).

Variation of toxic element accumulation depends on feeding preferences, breeding, sex, development stage, season and physiological conditions (Butovsky, 2011; Jelaska et al., 2007). Feeding preferences and breeding were studied by Purchart and Kula (2007). Sex specific accumulation of elements were studied by Lindqvist and Block (1997, 1998, 2001), and Purchart and Kula (2007). Similar to earlier findings, Butovsky (2011) also found large variation in the accumulation of metals caused by sex-specific metabolism.

*C. violaceus* is feeding on snails and earthworms (Turin et al., 2003); *P. oblongopunctatus* is feeding on invertebrate groups and carrions (Turin et al., 2003; Jelaska et al., 2007). Breeding season of the studied species is also different. *P. oblongopunctatus* is a spring breeder with maximum activity in spring or early summer, while *C. violaceus* is an autumn breeder and the maximum adult activity occurs late summer and/or autumn. *C. violaceus* and *P. oblongopunctatus* have widespread distribution both in Europe and Hungary across forested habitats. The aim of our study was to analyze the toxic element concentrations in soil, leaf litter and in *Carabus violaceus* (Linnaeus, 1758) and *Pterostichus oblongopunctatus* (Fabricius, 1787) along an urbanization gradient. We estimated the correlation between toxic element concentrations of ground beetles, leaf litter and soil. Our hypothesis is that feeding preferences and breeding cause differences in the toxic element concentrations in ground beetle species. Earlier studies reported large variation of metal concentration in males and females ground beetles; thus, we tested the effect of sexual dimorphism on the toxic element concentration in *C. violaceus* and *P. oblongopunctatus*. Finally, we assessed the usefulness of ground beetles, leaf litter and soil as indicators for the effect of urbanization and anthropogenic activities on terrestrial ecosystem.

## 2. Material and methods

### 2.1. Study areas and sample collection

Sampling areas were located in and around the city of Debrecen (Hungary). Along an urban–suburban–rural gradient three sampling areas (urban, suburban and rural) were chosen representing different levels of urbanization. The urban sampling area was in a park of the downtown with heavy traffic around. The suburban area was situated between the urban and rural area, with lower traffic and other anthropogenic activities. The rural area was in a protected forest where the traffic and visitors pressure was relatively low lending a more natural and undisturbed character to this area.

In all sampling areas forest stands are dominated by English oak (*Quercus robur*) (Simon et al., 2014). Four sites were selected within each sampling area. The sites were spatial replicates, i.e. they were not differed from each other.

Soil samples were collected at the same time when leaf samples. Soil samples ( $N=24$ ) were collected along an urbanization gradient representing urban, suburban and rural areas. At each sampling site, two repeated bulk samples were collected. All samples were collected at a depth of 0–20 cm. From all samples, 50–100 g soil was dried at room temperature. After drying, stones, plant roots and residues were removed with plastic tweezers. Samples were sieved in 2 mm plastic sieve, homogenized with agate mortar and stored in plastic tubes until pre-treatment (Simon et al., 2013).

Leaf litter samples ( $N=24$ ) were collected from the three studied areas during April and September 2010. In each sampling site two pooled samples were collected in plastic bags. In the laboratory, leaf litter samples were dried for 24 h at 105 °C, homogenized with an electric mixer and stored in plastic tubes until pre-treatment (Simon et al., 2011).

Adult carabids were collected with live trapping during their reproductive period from May to August in 2010. In each site 20 live trap was used. We collected 2 species, *C. violaceus* and *P. oblongopunctatus*. From the studied areas, 74 *C. violaceus* (urban:  $N=24$ , suburban:  $N=12$ , rural:  $N=38$ ) and 42 *P. oblongopunctatus* (urban:  $N=18$ , suburban:  $N=7$ , rural:  $N=17$ ) individuals were collected. Live ground beetles were moved to the laboratory where they were transferred into polyethylene bags. Until sample processing samples were stored in freezing at –18 °C. Before the chemical analysis we assessed the age of the collected the *C. violaceus* specimens. The age of both males and females can be estimated reliably based on mandible wear and physiological characters (Wallin, 1988, 1989). In our study the *C. violaceus* specimens were young adults because of the wear of mandible was just slightly worn.

### 2.2. Toxic element analysis of samples

For toxic element analysis, 0.2 g of soil and leaf litter sample was digested using 4.5 mL 65% (m/m) nitric acid and 0.5 mL 30% (m/m) hydrogen-peroxide in a microwave digestion unit (Milestone 1200 Mega) for 5 min at 300 W and subsequently 5 min at 600 W. Digested samples were diluted to 25 mL with deionised water (Simon et al., 2011). For the elemental analysis 0.2 g of soil samples were digested using 4.5 mL 65% (m/m) nitric acid and 0.5 mL 30% (m/m) hydrogen-peroxide in a microwave digestion unit (Milestone 1200 Mega) for 5 min at 300 W and for 5 min at 600 W, respectively. Digested samples were diluted to 25 mL with deionised water (Simon et al., 2013).

Ground beetles were placed in a plastic sieve and flushed with 250 mL of double deionised water obtained from a Millipore Milli-Q system. Each ground beetle was transferred individually into a 25 mL beaker. Wet body mass of the samples were measured immediately. Samples were dried overnight at 105 °C and reweighed to determine their dry mass. The material was then digested using 2 mL 65% (m/m) nitric acid (Scharlau) in the same container at 80 °C for 4 h. Digested samples were diluted to 20 mL using 1% (m/m) nitric acid (Braun et al., 2009, 2012).

In the case of leaf litter and soil samples Al, Ba, Cu, Fe, Mn, Sr and Zn concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using an IRIS Intrepid II XSP (Thermo Electron Corporation) instrument. The Al, Ba, Cd, Cu, Fe, Mn, Sr, Pb and Zn element analysis in ground beetles was performed by a microwave plasma atomic emission spectrometer (MP-AES 4100, Agilent Technologies). We used six point calibration procedures with multi-element calibration solution (Merck ICP

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