

## Review Article

# Metal Availability and Transfer along Food Chains in Siena, a Small Medieval Town in Italy

Emilia Rota , Nicola Bianchi, and Roberto Bargagli

Department of Physics, Earth and Environmental Sciences, University of Siena, Siena, Italy

Correspondence should be addressed to Emilia Rota; [rota@unisi.it](mailto:rota@unisi.it)

Received 28 March 2018; Revised 13 July 2018; Accepted 16 September 2018; Published 9 October 2018

Academic Editor: Samuel B. Dampare

Copyright © 2018 Emilia Rota et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Heavy metals originating from vehicular emissions and other anthropogenic sources pose one of the main environmental health risks in urban areas. The assessment of metal bioaccumulation in selected species of synanthropic organisms allows evaluating their bioavailability and the transfer along food chains in urban ecosystems. An overall view of the results achieved in Siena on urban ecosystems shows that the mean Cd, Cu, Pb, and Zn concentrations in biological crusts covering urban walls ( $0.66$ ,  $34$ ,  $65$ , and  $184 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) are higher than the respective concentrations in tree leaf litter ( $0.19$ ,  $9.5$ ,  $9.2$ , and  $38 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) and topsoil ( $0.40$ ,  $44$ ,  $34.2$ , and  $102 \mu\text{g}\cdot\text{g}^{-1}$  d.w.). Furthermore, the epilithic moss *Tortula muralis* accumulated much higher levels of Cd, Cu, Pb, and Zn ( $0.34$ ,  $65$ ,  $17.6$ , and  $106 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) than epiphytic lichens ( $0.22$ ,  $11.6$ ,  $2.1$ , and  $47.3 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) or the holm oak live foliage ( $0.15$ ,  $14$ ,  $1.51$ , and  $26.5 \mu\text{g}\cdot\text{g}^{-1}$  d.w.), respectively. However, analyses of the soft tissues of *Papillifera papillaris*, a snail dwelling on stone walls, show that metals deposited on urban walls are scarcely bioavailable. *Papillifera* accumulates (and transfers to the next trophic level) amounts of Cd, Cu, Pb, and Zn ( $1.7$ ,  $171$ ,  $1.1$ , and  $71 \mu\text{g}\cdot\text{g}^{-1}$  d.w., respectively) that are comparable or inferior to those found in a ground-dwelling snail ( $3.3$ ,  $88$ ,  $2.0$ , and  $880 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) and two earthworm species ( $2.0$ – $4.4$ ,  $18$ – $23$ ,  $1.4$ – $2.2$ , and  $356$ – $594 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) from the same urban green area.

## 1. Introduction

Between now and 2050, the world's urban population is expected to increase by 2.5 billion people, with about 66% of the global population residing in urban areas [1]. This continued growth poses significant challenges for policy-makers, practitioners, and scientists to ensure environmental quality and human welfare. Among the possible measures to address these challenges, a prominent role is played by the multiple ecological services provided by urban ecosystems that contribute to the well-being of residents through the reduction of local air pollution, noise, heat waves, and flooding [2, 3]. Lead, Cd, Zn, Cu, and other heavy metals released from vehicular traffic, domestic heating, and other anthropogenic sources are among the most common pollutants in urban environments [4]. The ecological and health risks posed by these are often assessed through the exposure of sentinel species in the laboratory (e.g., [5]) or in urban areas (e.g., [6]). However, these approaches oversimplify the complexity of the processes

involved in the metal uptake in urban ecosystems and the results can be significantly different from those achieved by field investigations [7].

Biotic communities in urban ecosystems are chronically exposed to a complex mixture of atmospheric pollutants, which have a variable composition in space and time and can cause additive or synergistic biological effects [8]. In addition, the time exposure in laboratory experiments and microcosms (usually a few weeks) may be too short to evaluate the actual bioaccumulation and the potential transfer of metals to higher trophic levels [9]. Because of the changing physico-chemical properties of metals in different substrata (in wet and dry atmospheric deposition, in soils, etc.) and the mutable physiological conditions of exposed organisms (diet, age, metabolic rate, and reproductive state), the bioavailability, uptake, and bioaccumulation of metals are dynamic processes [10]. Recent studies analyzing the possible correlations between metal bioavailability estimated chemically in urban soil and the amount actually accumulated in soil fauna

(e.g., [11, 12]) have found that the metal content in different soil fractions does not allow to predict its bioaccumulation. As discussed by Pauget et al. [11], the chemical analysis of soil only informs about the easiness of metal leaching by weak extractions (i.e., the environmental availability) and not about the actual bioavailability and/or bioaccumulation, which also depend on the physiological traits and conditions of the target organisms [13]. Thus, although the basic ecophysiological data and life-history traits of many species of organisms in urban ecosystems are not well-known, and soil pollutants and biotic communities most often have a patchy distribution [14], the analytical determination of internal concentrations of metals in representative samples of appropriate plant and animal species is the most suitable approach to assess the bioavailability of persistent pollutants and their potential transfer along food chains. This information is very useful for assessing ecological and health risks deriving from metals and for formulating goals for the protection of the urban environment in terms of ecosystem services [15]. Several species of lichens, mosses, higher plants, soil invertebrates (mainly earthworms and snails), birds, or small mammals are quite common in urban environments. These organisms have a suitable biomass for the analysis of pollutants, they are rather easy to sample, accumulate persistent atmospheric pollutants, and have been widely used as biomonitors in many cities (e.g., [16–23]).

In Siena, a small medieval city in central Italy, where the main source of metal pollution is vehicular traffic, several studies have been conducted on the metal accumulation in soils, lichens, tree leaves, earthworms, and land snails from urban parks and avenues (e.g., [16, 24–29]). Vegetated walls are rather common in Siena as in many other urban environments, and these vertical structures are colonized by primary producers (cyanobacteria, algae, cryptogams, and higher plants), a variety of primary consumers (molluscs, isopods, millipedes, and ants), and their predators, such as firefly larvae, spiders, scorpions, lizards, birds, and small mammals. Marbles, limestones, and bricks in these artificial ecosystems have a more homogenous composition than minerals in soils, and our preliminary results indicate that biological crusts, epilithic mosses, and molluscs from these ecosystems are very sensitive indicators of metal deposition in the urban environment [21, 29]. Through an overall evaluation of the results of previous environmental investigations carried out in Siena and those deriving from ongoing research, this review aims to evaluate and compare the metal bioavailability in urban soil and vegetated walls, their accumulation in primary consumers, and the possible transfer along the food chains.

## 2. Materials and Methods

**2.1. Study Area and Methodology.** The urban area of Siena (Tuscany, 55,000 inhabitants) is located in a hilly area (elevation between 300 and 350 m); the old town centre has narrow, winding streets, and vehicular traffic is concentrated mainly in ring-roads around the medieval walls. The climate is sub-Mediterranean with an average annual temperature of 13.9°C and an average annual rainfall of about 750 mm·yr<sup>-1</sup>.

The prevailing winds are from S and NNW, and the climate and topographic characteristics favor the dispersal of atmospheric pollutants, which are mainly released from vehicular traffic and domestic heating. Except for tropospheric O<sub>3</sub>, that sometimes in summer reaches above 120 µg·m<sup>-3</sup>, concentrations of pollutants are low to moderate: in 2016 the annual average was 38, 21, and 13 µg·m<sup>-3</sup> for NO<sub>2</sub>, PM<sub>10</sub>, and PM<sub>2.5</sub>, respectively [30].

This review focuses on the elemental composition of several environmental matrices from Siena urban area and control stations (soil, litter, epiphytic lichens, holm oak live foliage, earthworms, and land snails from green areas and roadside; biological crusts, epilithic mosses, and shells, soft tissues, and excreta of stone-dwelling snails from vegetated walls). Details on the collection, preparation, and analysis of biotic and abiotic samples are reported in previous works [25–29]. In short, representative samples of soil, biological crusts, unwashed lichen thalli, moss shoots, and tree leaves (of comparable size and age) were air-dried, homogenized, and sieved to <250 µm. Earthworms and snails were rinsed with water and placed in plastic Petri dishes containing filter paper to remove gut contents; samples of snail excreta and shells were also collected. Analytical determinations of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn concentrations were performed after digestion of samples with HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> (in Teflon bombs using a Milestone Ethos 900 microwave lab station) with graphite furnace atomic absorption spectrometry (GF-AAS), inductively coupled plasma emission spectrometry, or ICP-mass spectrometry. As a rule, the precision of the analytical determinations estimated through repeated analysis of the same samples was <7.5% for all elements. The accuracy was checked by concurrent chemical digestion and analysis of standard reference materials and recoveries ranging from 82% to 116%, depending on the element and nature of sample. All metal concentrations are expressed in µg·g<sup>-1</sup> dry weight.

**2.2. Calculation and Statistical Analyses.** The normal distribution of analytical results was ascertained by using the Shapiro-Wilks *W* test; for normally distributed data, the statistical significance (at 5% level) of differences between datasets was determined by the parametric Student's *t*-test; and for nonnormally distributed data by the nonparametric Mann-Whitney *U* test. The correlations between metal concentrations in earthworm and snail tissues and those in soils, biological crusts, and epilithic mosses were determined by Spearman's correlation test (*p* < 0.05). Regression analyses were used to investigate the relationships between the two different food chains.

## 3. Results and Discussions

**3.1. Metal Bioavailability and Bioaccumulation in Urban Green Areas.** Soils in Siena have a sandy-loam texture, pH values >7.4, and high CaCO<sub>3</sub> concentrations (up to 32.5%) [27]. Soil samples collected at a distance of 2–4 m from roads usually have higher mean content of Ba, Cd, Cu, Pb, Sb, and Zn than those from control areas and differences are

statistically highly significant ( $p < 0.01$ ), especially for Pb and Sb [16, 27]. The highest metal concentrations are usually recorded in areas with slow traffic (especially near traffic lights, crossroads, and roundabouts), indicating that fuel combustion, brake, clutch, and tire-wear are the main sources of metal pollution in urban soils. In the last decades, atmospheric deposition of metals in the urban environment has been investigated by using thalli of the epiphytic lichen *Flavoparmelia caperata* as quantitative biomonitors [16, 24, 25]. Due to the resuspension of soil and road dust particles by vehicular traffic, the concentrations of lithophilic elements such as Al, Cr, Fe, Mn, as well as those of metals released by anthropogenic sources (e.g., Cd, Cu, Pb, and Zn) were generally higher in urban lichens than in control samples (Table 1). However, the differences for the latter elements were not always statistically significant ( $p < 0.05$ ). Unpublished data from student practicals indicate that, in the last 30 years, only Pb among all metals analysed showed markedly and significantly lower concentrations (from 50 to about  $2 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) in the lichens of Siena.

Unlike lichens, which have no roots and are dependent on atmospheric depositions for water and nutrients, trees absorb most elements essential for their metabolism from soil; however, their leaves intercept airborne gaseous and particulate pollutants. Due to the widespread occurrence of holm oaks in many Italian urban environments, *Quercus ilex* leaves have been extensively used as quantitative biomonitors of metal deposition (e.g., [26, 31–33]). Leaf samples from Siena green areas and avenues show generally higher average concentrations of several metals than in extraurban maquis (Table 1); however, such differences are statistically significant ( $p < 0.05$ ) only for Al, Fe, and Pb. During the last two decades, the average content of metals did not change significantly in urban *Q. ilex* leaves, except for a continuous decrease of mean Pb concentrations (from  $13 \mu\text{g}\cdot\text{g}^{-1}$  d.w. over the 1990s to nearly  $1 \mu\text{g}\cdot\text{g}^{-1}$  d.w. in 2011); the average Cu and Zn concentrations decreased by about 50% up until 2001, then remained fairly constant. In the urban area of Siena, variations in spatio-temporal metal deposition patterns in leaves of *Q. ilex* have roughly mirrored those in epiphytic lichens. They both showed essentially greater bioaccumulation of metals in areas with rather intense and slow traffic and a net temporal decrease in Pb concentrations, probably due to the introduction of unleaded fuel in Italy. Because the historic centre of Siena has been a restricted traffic area since 1965, and most vehicles are concentrated in roads around the old city walls, average metal concentrations in urban soils, lichens, or holm oak leaves are generally lower than in other Italian urban environments (Figure 1) (e.g., [34–36]). Despite the low levels of metal contamination, by estimating the biomass of *Q. ilex* leaves [26], the Al, Cd, Cr, Cu, Fe, Pb, and Zn burden was found to be from 1.8 to 2.6 times higher in an urban park than in an extraurban stand. Thus, urban trees play an important ecological service in Siena through the interception of airborne metals. Furthermore, by analyzing the litter and topsoil in urban and extraurban holm oak stands, it was found that Cd, Cu, Pb, and Zn concentrations were 16–55% higher in urban samples than in extraurban ones

(Table 1) [26]. The sclerophyllous litter produced by *Q. ilex* has a very slow decomposition rate, resulting in a thick, complex, and structured humus [37], and in the urban environment, a large proportion of metals deposited by dry deposition, leaf fall, stem flow, and throughfall waters become stored in the organic horizon of soil. As emphasized by Setälä et al. [38], the sinking of C and other essential and nonessential elements in soils beneath trees is a very important and often disregarded ecological service of urban green areas.

To evaluate the bioavailability of metals in Siena urban soil under holm oak, we recently determined metal concentrations and bioaccumulation factors (BAF; the ratio of the element concentration in the organism and in the litter or topsoil) in the epigeal earthworm *Dendrobaena cognettii*. Earthworms are a major component of the soil biota and for their stationary mode of life, adequate biomass for analytical determinations and ability to accumulate metals, they are considered among the most reliable biomonitors of metals in soils (e.g., [39]). Moreover they represent an important route for the transfer of potentially toxic metals to higher trophic levels, because they are food sources for carabid beetles, birds, and small mammals. Among the metals analysed in *D. cognettii* tissues (Al, Cd, Cr, Cu, Fe, Mo, Mn, Ni, Pb, Sb, Sr, and Zn), we found BAF > 1 only for Cd and Zn, whereas for other potentially toxic metals values were much lower (Figure 2; Table 1).

*Dendrobaena cognettii* is a litter-dwelling and non-burrowing species, but other earthworm species inhabit the topsoil or the subsoil, or build deep vertical burrows. Soil is a very complex polyphasic matrix and earthworms belonging to different ecological categories can help evaluate the metal bioavailability in different soil horizons. Nannoni et al. [27] compared metal concentrations in soils and tissues of *Nicodrilus caliginosus* (an earthworm dwelling in horizontal burrows in the upper 20–25 cm of soil) sampled in urban, peri-urban, green urban, and nonurban areas of Siena municipality, and they found that the metal body burden in worms increased with increasing soil metal contamination [27]. Cadmium, Cu, Pb, Sb, and Zn concentrations were usually higher in earthworms from urban and peri-urban sites than in samples from nonurban areas; BAF median values were in the same range as those calculated for *D. cognettii* (Cd = 11.2, Zn = 5.9, Cu = 0.49, and Pb = 0.03). Although comparisons between the two species are made difficult by their different ecophysiological characteristics, the higher Cd and Pb concentrations in the litter-dwelling *D. cognettii* than in the subsurface soil-dwelling *N. caliginosus* in the same urban green areas suggest a different bioavailability of metals in different soil horizons. Data on the chemical availability of metals in soil, determined by sequential extraction procedures, did not always agree with metal accumulation in *N. caliginosus* tissues, especially for essential elements such as Cu and Zn, and for Cd [12]. Regardless of the bioavailable amount of Cu and Zn in soils, earthworms efficiently regulate internal concentrations by actively modulating their elimination and uptake rates [10, 40]. Possible toxic effects of the nonessential Cd are minimized (within certain exposure intervals) by binding

TABLE 1: Mean Cd, Cu, Pb, and Zn concentrations ( $\mu\text{g}\cdot\text{g}^{-1} \pm \text{SD}$ ) in biotic and abiotic matrices from Siena urban green areas (U) and extraurban control sites (C).

	Cd	Cu	Pb	Zn
<i>Quercus ilex</i> live foliage (U) <sup>a</sup>	0.15 ± 0.07	14.0 ± 0.15	1.51 ± 0.16	26.5 ± 2.2
<i>Quercus ilex</i> live foliage (C) <sup>a</sup>	0.06 ± 0.03	7.80 ± 2.33	0.59 ± 0.07	13.5 ± 0.9
<i>Flavoparmelia</i> lichen (U) <sup>b</sup>	0.22 ± 0.04	11.6 ± 5.0	2.10 ± 0.81	47.3 ± 10.2
<i>Flavoparmelia</i> lichen (C) <sup>b</sup>	0.09 ± 0.02	7.21 ± 2.35	1.12 ± 0.45	32.4 ± 6.7
<i>Quercus ilex</i> litter (U) <sup>a</sup>	0.19 ± 0.07	9.5 ± 0.9	9.2 ± 2.7	38 ± 21.3
<i>Quercus ilex</i> litter (C) <sup>a</sup>	0.16 ± 0.12	4.3 ± 0.3	7.0 ± 0.6	27 ± 10.1
Topsoil (0–3 cm) (U) <sup>a</sup>	0.40 ± 0.36	44.1 ± 18.2	34.2 ± 19.8	102 ± 45
Topsoil (0–3 cm) (C) <sup>a</sup>	0.25 ± 0.11	15.0 ± 13.3	24.8 ± 18.8	54.3 ± 18.5
Soil (0–20 cm) (U) <sup>c</sup>	0.16 ± 0.08	39.0 ± 11.3	54.2 ± 17.5	90.7 ± 31.6
Soil (0–20 cm) (C) <sup>c</sup>	0.15 ± 0.03	23.2 ± 1.1	23.0 ± 7.8	77.6 ± 9.0
<i>Dendrobaena cognettii</i> earthworm (U) <sup>d</sup>	4.42 ± 0.50	12.7 ± 2.2	3.21 ± 0.8	356 ± 77
<i>Dendrobaena cognettii</i> earthworm (C) <sup>d</sup>	2.22 ± 0.86	14.0 ± 5.6	1.15 ± 0.48	324 ± 87
<i>Nicodrillus caliginosus</i> earthworm (U) <sup>c</sup>	2.01 ± 1.03	22.8 ± 6.7	1.40 ± 0.38	594 ± 188
<i>Nicodrillus caliginosus</i> earthworm (C) <sup>c</sup>	1.90 ± 0.71	13.8 ± 3.9	1.20 ± 0.43	479 ± 170
<i>Pomatias elegans</i> snail (U) <sup>d</sup>	3.32 ± 0.92	88.1 ± 24.7	1.98 ± 0.64	880 ± 23
<i>Pomatias elegans</i> snail (C) <sup>d</sup>	1.67 ± 0.34	58.1 ± 19.3	1.05 ± 0.42	714 ± 186

Data sources: <sup>a</sup>[26]; <sup>b</sup>unpublished; <sup>c</sup>[27]; <sup>d</sup>[49].

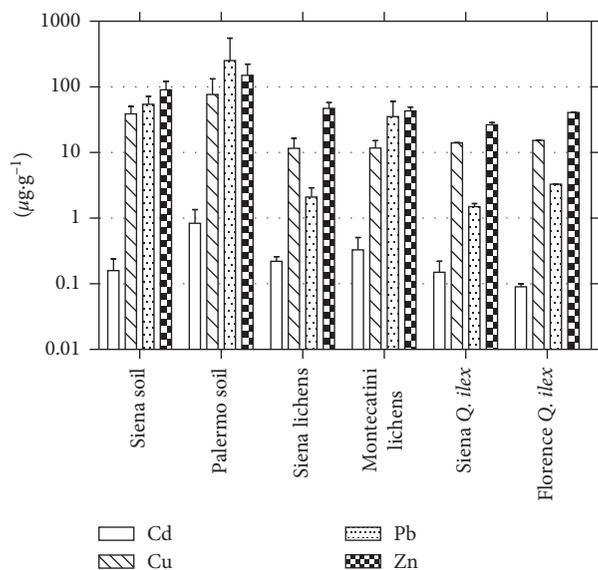


FIGURE 1: Average metal concentrations  $\pm \text{SD}$  ( $\mu\text{g}\cdot\text{g}^{-1}$  d.w.) in soil, epiphytic lichens, and holm oak live foliage from Siena and other urban areas in Italy (data sources: Palermo [34]; Montecatini [35], Florence [36]).

the metal to the isoform 2 of metallothionein (MT-2) [40] or by storing Cd in phosphate-rich structures in the chlorogenous tissue [41]. Both detoxification processes contribute to a low elimination rate of Cd and its consequent bioaccumulation [40]. Earthworms can detoxify Pb by storing it in waste amorphous granules, which are kept in the inert form within coelomic cells or are excreted through the segmental nephridia [42].

Like earthworms, land snails and slugs are large, move only short distances, can take metals via the gastrointestinal tract and the integuments, and represent an important route for the transfer of potentially toxic elements to higher trophic levels, because they are preyed upon by many urban animals.

Under chronic exposure to metals, such as that occurring in urban green areas, detoxification processes of snails involve a storage strategy for Cd [43] and the bioaccumulation of Cd, Cu, Pb, and Zn (e.g., [44]). However, unlike earthworms, land mollusks feed on plant material and their chemical composition mainly reflects the metal uptake from food, by skin contact and also through respiratory organs [45]. A preliminary survey on the elemental composition of soft tissues of the litter-dwelling snail *Pomatias elegans* from an urban park in Siena showed higher mean Cd, Cu, Pb, and Zn concentrations than in individuals of the same species and size range from extraurban sites (Table 1). These snails accumulated higher Cu and Zn concentrations and slightly lower Cd and Pb concentrations than the litter-dwelling earthworm *D. cognettii* from the same park (Figure 2; Table 1).

**3.2. Metal Deposition and Bioavailability in Urban Vegetated Walls.** Vegetated walls are common structures in many urban environments and these artificial ecosystems can host a variety of primary producers and consumers. Like epiphytic lichens on tree trunks, organisms living in these vertical spaces are exposed to air pollutants from mobile and stationary sources. We began environmental studies on urban and control green walls in Siena [21] assuming that these ecosystems are more suitable than horizontal green areas for the assessment of metal deposition and bioavailability in urban environments. Marble, limestones, or bricks have a much more homogenous composition than soil and previous environmental surveys showed that the chemical composition of black crusts from historical buildings and monuments reflects temporal changes in atmospheric pollutant patterns and can help shed light on their sources (e.g., [46]). Samples of biogenic crusts, the moss *Tortula muralis*, and a small land snail (*Papillifera papillaris*) specialized in dwelling on stone surfaces, fractures, and interstices were collected from the same wall stones and bricks in the city and control sites. In general,

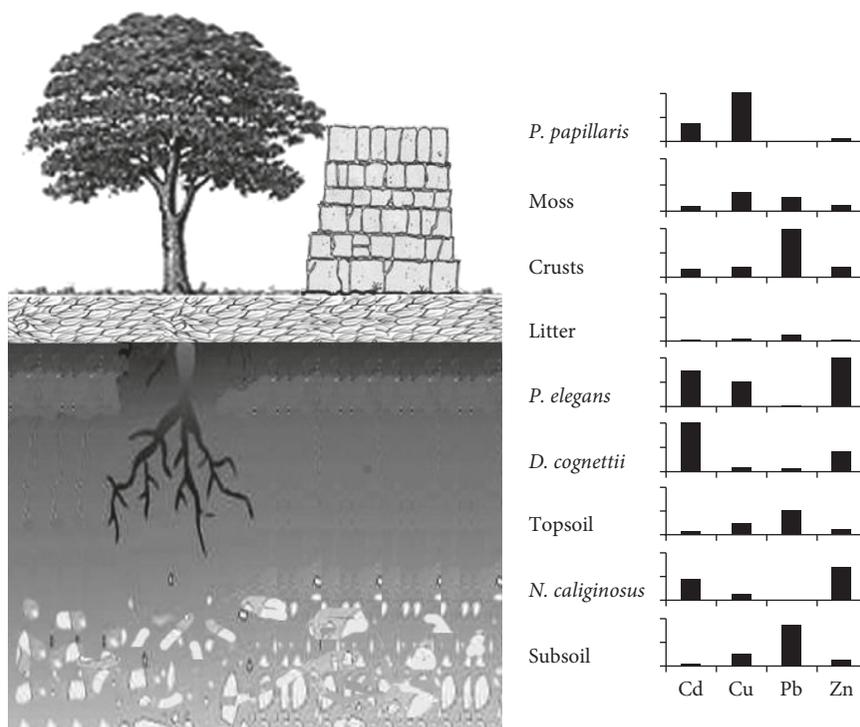


FIGURE 2: Comparisons between average Cd, Cu, Pb, and Zn concentrations in the different environmental matrices from the urban park and vegetated walls in Siena. Values are reported as % of the highest metal concentration in all matrices (all data sources as for Tables 1 and 2).

samples more exposed to the metal emission from vehicular traffic had significantly higher average Cd, Pb, Zn, and Cu concentrations than those from control walls (Table 2). Comparisons between the mean elemental composition of abiotic and biotic matrices from urban green areas (Table 1) and vegetated walls (Table 2) (Figure 2) showed higher mean Cd, Pb, and Zn concentrations in biological crusts than in the litter or topsoil under holm oak canopy; the epilithic moss *T. muralis* accumulated much higher levels of Cd, Cu, Pb, and Zn than epiphytic lichens or holm oak leaves. However, despite the metal accumulation in mosses, soft tissues of the stonewall-dwelling *P. papillaris*, purged of the gut content, had slightly higher Cu concentrations and lower Cd and Zn concentrations than the litter-dwelling *Pomatias elegans* from urban parks (Figure 2; Tables 1 and 2). Mosses accumulate a large amount of barely bioavailable metals through the entrapment of soil and rock dust particles [47], and their shoots are seldom consumed by vertebrate or invertebrate herbivores [48]. Probably, the small snail *P. papillaris* mainly eats algae, microfungi, or higher plants. The chemical composition of excreta (feces) indicates that through mechanical scraping of stones and fractures, this snail ingests large amounts of lithophile elements such as Al, Cr, or Fe, which are scarcely absorbed in the gastrointestinal tract. The snail feces contain relevant Pb concentrations (mean =  $30.4 \pm 12.8 \mu\text{g}\cdot\text{g}^{-1}$  d.w.) indicating that the bioavailability of this metal is negligible and/or Pb is easily excreted by snails.

#### 4. Conclusions

Exposure to heavy metals originating from emissions of vehicles, domestic heating, and other anthropogenic sources is a major environmental/health hazard in urban areas.

Green areas such as parks, gardens, and avenues contribute to the well-being of residents through multiple ecological services such as the reduction in local air pollution, noise, heat waves, and flooding and are very useful to assess spatio-temporal variations of metal deposition, bio-availability, and transfer along food chains. The results of past and ongoing research in biotic and abiotic matrices from Siena urban ecosystems show that Cd, Cu, Pb, and Zn are among the most widespread metal pollutants and they are mainly released by vehicular traffic. Although levels of environmental contamination are lower than those usually reported for other cities, the outcomes of metal bio-availability in Siena soils and vegetated walls and their accumulation in earthworm and snail tissues may have application in other urban contexts. While confirming that epiphytic lichens and *Q. ilex* leaves are reliable biomonitors of spatio-temporal variations in deposition patterns, our surveys showed that litter and topsoil under holm oak trees are important metal sinks. The analysis of earthworms is probably one of the most reliable approaches to evaluate metal bioavailability in polluted soils and potential environmental health risks. Our research in Siena shows that earthworm tissues accumulate Cd and Zn above all, and the differing elemental compositions found in litter-dwelling (*D. cognettii*) and soil-dwelling species (*N. caliginosus*) seem to indicate that these organisms can be used to evaluate the metal bioavailability in different soil horizons. Unlike earthworms, land snails feed on live or dead plant material, and individuals of *P. elegans* sampled in urban green areas showed higher concentrations of Cd, Cu, Pb, and Zn in their tissues than snails of the same species and size collected in extraurban sites. Zinc, Cu, and Cd seem to

TABLE 2: Mean Cd, Cu, Pb, and Zn concentrations ( $\mu\text{g}\cdot\text{g}^{-1} \pm \text{SD}$ ) in biotic and abiotic matrices from Siena vegetated walls (U) and extraurban control walls (C).

	Cd	Cu	Pb	Zn
Biological crusts (U)	$0.66 \pm 0.90$	$33.7 \pm 19.8$	$64.8 \pm 55.9$	$184 \pm 123$
Biological crusts (C)	$0.25 \pm 0.13$	$60.9 \pm 48.0$	$22.4 \pm 13.4$	$82 \pm 38$
<i>Tortula muralis</i> moss (U)	$0.34 \pm 0.13$	$64.6 \pm 24.7$	$17.6 \pm 6.1$	$106 \pm 28$
<i>Tortula muralis</i> moss (C)	$0.21 \pm 0.02$	$40.8 \pm 24.5$	$9.2 \pm 6.6$	$53.8 \pm 6.74$
<i>Papillifera papillaris</i> snail (tissues) (U)	$1.70 \pm 1.55$	$171 \pm 53$	$1.09 \pm 0.42$	$71.1 \pm 51.2$
<i>Papillifera papillaris</i> snail (tissues) (C)	$0.69 \pm 0.44$	$132 \pm 72$	$0.50 \pm 0.43$	$28.7 \pm 5.2$
<i>Papillifera papillaris</i> snail (feces) (U)	$0.34 \pm 0.14$	$157 \pm 68$	$30.4 \pm 12.8$	$62.3 \pm 46$
<i>Papillifera papillaris</i> snail (feces) (C)	$0.45 \pm 0.20$	$240 \pm 117$	$31.1 \pm 23.4$	$37.7 \pm 23.2$
<i>Papillifera papillaris</i> snail (shell) (U)	$0.24 \pm 0.09$	$46.6 \pm 15.2$	$1.82 \pm 0.46$	$261 \pm 78$
<i>Papillifera papillaris</i> snail (shell) (C)	$0.14 \pm 0.04$	$38.3 \pm 9.8$	$1.70 \pm 0.91$	$346 \pm 111$

Data source: [29].

be the most abundant metals transferred from snails to secondary consumers.

The elemental composition of biological crusts, mosses, and snails from vegetated walls showed that these environmental matrices are reliable and sensitive biomonitors of metal deposition in urban environments. Although biological crusts and epilithic mosses accumulate very high concentrations of metals, the metal accumulation in soft tissues of a stone-wall dwelling snail (*P. papillaris*) was not significantly higher than in other snail species living in the soil of urban parks and gardens. The analysis of *P. papillaris* feces showed an efficient excretion of Pb, Al, Fe, Cr, and Ni. Thus, Cd and Cu are the metals of greatest concern for *P. papillaris* predators. For a better understanding of soil metal transfer along urban food chains, future research should involve other invertebrates such as isopods, which are very common in urban environments and graze on fungal hyphae (very efficient accumulators of soil metals), and the non-destructive sampling and analysis of tissues from lizards, birds, and small mammals living in our cities.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## References

- [1] United Nations, Department of Economic and Social Affairs, Population Division, *World Urbanization Prospects: The 2014 Revision, Highlights (ST/ESA/SER.A/352)*, United Nations, New York, NY, USA, 2014.
- [2] D. Haase, N. Larondelle, E. Andersson et al., "A quantitative review of urban ecosystem service assessments: concepts, models, and implementations," *AMBIO*, vol. 43, no. 4, pp. 413–433, 2014.
- [3] F. Baró and E. Gómez-Baggethun, "Assessing the potential of regulating ecosystem services as nature-based solutions in urban areas," in *Nature-Based Solutions to Climate Change Adaptation in Urban Areas, Theory and Practice of Urban Sustainability Transitions*, N. Kabisch, H. Korn, J. Stadler, and A. Bonn, Eds., pp. 139–158, Springer Open, Cham, Switzerland, 2017.
- [4] B. J. Alloway, *Heavy Metals in Soils. Trace Metals and Metalloids in Soils and their Bioavailability*, Springer, Dordrecht, Netherlands, 2013.
- [5] M. Boshoff, K. Jordaens, S. Baguet, and L. Bervoets, "Trace metal transfer in a soil-plant-snail microcosm field experiment and biomarkers responses in snails," *Ecological Indicators*, vol. 48, pp. 636–648, 2015.
- [6] F. Regoli, S. Gorbi, D. Fattorini et al., "Use of the land snail *Helix aspersa* as sentinel organism for monitoring ecotoxicological effects of urban pollution: an integrated approach," *Environmental Health Perspectives*, vol. 114, no. 1, pp. 63–69, 2006.
- [7] D. J. Spurgeon and S. P. Hopkin, "Comparisons of metal accumulation and excretion kinetics in earthworms (*Eisenia fetida*) exposed to contaminated field and laboratory soils," *Applied Soil Ecology*, vol. 11, no. 2-3, pp. 227–243, 1999.
- [8] R. Bargagli, *Trace Elements in Terrestrial Plants: An Ecophysiological Approach to Biomonitoring and Biorecovery*, Springer-Verlag, Berlin, Germany, 1998.
- [9] C. Fritsch, M. Coeurdassier, F. Gimbert, N. Crini, R. Scheifler, and A. de Vaufléury, "Investigations of responses to metal pollution in land snail populations (*Cantareus aspersus* and *Cepaea nemoralis*) from a smelter impacted area," *Ecotoxicology*, vol. 20, no. 4, pp. 739–759, 2011.
- [10] M. M. Ardestani, N. M. van Straalen, and C. A. M. van Gestel, "Uptake and elimination kinetics of metals in soil invertebrates: a review," *Environmental Pollution*, vol. 193, pp. 277–295, 2014.
- [11] B. Pauget, O. Faure, C. Conord, N. Crini, and A. de Vaufléury, "In situ assessment of phyto and zooavailability of trace elements: a complementary approach to chemical extraction procedures," *Science of the Total Environment*, vol. 521-522, pp. 400–410, 2015.
- [12] F. Nannoni and G. Protano, "Chemical and biological methods to evaluate the availability of heavy metals in soils of the Siena urban area (Italy)," *Science of the Total Environment*, vol. 568, pp. 1–10, 2016.
- [13] B. Pauget, F. Gimbert, M. Coeurdassier, C. Druart, N. Crini, and A. de Vaufléury, "How contamination sources and soil properties can influence the Cd and Pb bioavailability to snails," *Environmental Science and Pollution Research*, vol. 23, no. 4, pp. 2987–2996, 2016.
- [14] E. Rota, T. Caruso, F. Monaci et al., "Effects of soil pollutants, biogeochemistry and microbiology on the distribution of enchytraeid communities in urban and suburban holm oak stands," *Environmental Pollution*, vol. 179, pp. 268–276, 2013.
- [15] V. E. Forbes and P. Calow, "Developing predictive systems models to address complexity and relevance for ecological risk assessment," *Integrated Environmental Assessment and Management*, vol. 9, no. 3, pp. e75–e80, 2013.

- [16] F. Monaci and R. Bargagli, "Barium and other trace metals as indicators of vehicle emissions," *Water, Air, and Soil Pollution*, vol. 100, no. 1-2, pp. 89–98, 1997.
- [17] G. J. Komarnicki, "Tissue, sex and age specific accumulation of heavy metals (Zn, Cu, Pb, Cd) by the populations of the mole (*Talpa europaea* L.) in a central urban area," *Chemosphere*, vol. 41, no. 10, pp. 1593–1602, 2000.
- [18] J. Nahmani, M. E. Hodson, and S. Black, "A review of studies performed to assess metal uptake by earthworms," *Environmental Pollution*, vol. 145, no. 2, pp. 402–424, 2007.
- [19] M. Marcheselli, L. Sala, and M. Mauri, "Bioaccumulation of PGEs and other traffic-related metals in populations of the small mammal *Apodemus sylvaticus*," *Chemosphere*, vol. 80, no. 11, pp. 1247–1254, 2010.
- [20] J. Kekkonen, I. Hanski, R. A. Väisänen, and J. E. Brommer, "Level of heavy metals in House Sparrows (*Passer domesticus*) from urban and rural habitats in southern Finland," *Ornis Fennica*, vol. 29, pp. 91–98, 2012.
- [21] E. Rota, D. Barbato, S. Ancora, N. Bianchi, and R. Bargagli, "Papillifera papillaris (O.F. Müller), a small snail living on stones and monuments, as indicator of metal deposition and bioavailability in urban environments," *Ecological Indicators*, vol. 69, pp. 360–367, 2016.
- [22] A. Enuneku, E. Biore, and L. Ezemonye, "Levels, distribution, characterization and ecological risk assessment of heavy metals in road side soils and earthworms from urban high traffic areas in Benin metropolis, Southern Nigeria," *Journal of Environmental Chemical Engineering*, vol. 5, no. 3, pp. 2773–2781, 2017.
- [23] P. Bauerová, J. Vinklerová, J. Hraníček et al., "Associations of urban environmental pollution with health-related physiological traits in a free-living bird species," *Science of the Total Environment*, vol. 601–602, pp. 1556–1565, 2017.
- [24] R. Bargagli, P. L. Nimis, and F. Monaci, "Lichen bio-monitoring of trace element deposition in urban, industrial and reference areas of Italy," *Journal of Trace Elements in Medicine and Biology*, vol. 11, no. 3, pp. 173–175, 1997.
- [25] F. Monaci, R. Bargagli, and D. Gasparo, "Air pollution monitoring by lichens in a small medieval town of central Italy," *Acta Botanica Neerlandica*, vol. 46, no. 4, pp. 403–412, 1997.
- [26] F. Fantozzi, F. Monaci, T. Blanusa, and R. Bargagli, "Holm oak (*Quercus ilex* L.) canopy as interceptor of airborne trace elements and their accumulation in the litter and topsoil," *Environmental Pollution*, vol. 83, pp. 89–95, 2013.
- [27] F. Nannoni, S. Rossi, and G. Protano, "Soil properties and metal accumulation by earthworms in the Siena urban area (Italy)," *Applied Soil Ecology*, vol. 77, pp. 9–17, 2014.
- [28] F. De Nicola, D. Baldantoni, L. Sessa, F. Monaci, and R. Bargagli, "Distribution of heavy metals and polycyclic aromatic hydrocarbons in holm oak plant-soil system evaluated along urbanization gradients," *Chemosphere*, vol. 134, pp. 91–97, 2015.
- [29] E. Rota, B. Braccino, R. Dei, S. Ancora, and R. Bargagli, "Organisms in wall ecosystems as biomonitors of metal deposition and bioavailability in urban environments," *Environmental Science and Pollution Research*, vol. 25, no. 11, pp. 10946–10955, 2018.
- [30] ARPAT, "Annuario 2017 dei dati ambientali della Provincia di Siena," in *Agenzia Regionale per la Protezione Ambientale della Toscana*, ARPAT, Firenze, Italy, 2017, <http://www.arpat.toscana.it/annuario>.
- [31] A. Alfani, F. De Nicola, G. Maisto, and M. V. Prati, "Long-term PAH accumulation after bud break in *Quercus ilex* L. leaves in a polluted environment," *Atmospheric Environment*, vol. 39, no. 2, pp. 307–314, 2005.
- [32] A. Alfani, D. Baldantoni, G. Maisto, G. Bartoli, and A. Virzo De Santo, "Temporal and spatial variation in C, N, S and trace element contents in the leaves of *Quercus ilex* within the urban area of Naples," *Environmental Pollution*, vol. 109, no. 1, pp. 119–129, 2000.
- [33] L. Gratani, M. F. Crescente, and L. Varone, "Long-term monitoring of metal pollution by urban trees," *Atmospheric Environment*, vol. 42, no. 35, pp. 8273–8277, 2008.
- [34] D. Salvagio Manta, M. Angelone, A. Bellanca, R. Neri, and M. Sprovieri, "Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy," *Science of the Total Environment*, vol. 300, no. 1–3, pp. 229–243, 2002.
- [35] S. Loppi, L. Frati, L. Paoli et al., "Biodiversity of epiphytic lichens and metal content of *Flavoparmelia caperata* thalli as indicators of temporal variations of air pollution in the town of Montecatini Terme (central Italy)," *Science of the Total Environment*, vol. 326, no. 1–3, pp. 113–122, 2004.
- [36] F. Ugolini, R. Tognetti, A. Raschi, and L. Bacci, "Quercus ilex L. as bioaccumulator of heavy metals in urban areas: effectiveness of leaf washing with distilled water and considerations on trees distance from traffic," *Urban Forestry & Urban Greening*, vol. 12, no. 4, pp. 576–584, 2013.
- [37] E. Alarcón-Gutiérrez, C. Floch, C. Augur, J. Le Petit, F. Ziarelli, and S. Criquet, "Spatial variations of chemical composition, microbial functional diversity, and enzyme activities in a Mediterranean litter (*Quercus ilex* L.) profile," *Pedobiologia*, vol. 52, no. 6, pp. 387–399, 2009.
- [38] H. Setälä, G. Francini, J. A. Allen, A. Jumpponen, N. Hui, and D. J. Kotze, "Urban parks provide ecosystem services by retaining metals and nutrients in soils," *Environmental Pollution*, vol. 231, pp. 451–461, 2017.
- [39] J. Kumpiene, L. Giagnoni, B. Marschner et al., "Assessment of methods for determining bioavailability of trace elements in soils: a review," *Pedosphere*, vol. 27, no. 3, pp. 3898–4906, 2017.
- [40] K. Veltman, M. A. J. Huijbregts, M. G. Vijver et al., "Metal accumulation in the earthworm *Lumbricus rubellus*. Model predictions compared to field data," *Environmental Pollution*, vol. 146, no. 2, pp. 428–436, 2007.
- [41] A. J. Morgan, S. R. Stürzenbaum, C. Winters, G. W. Grime, N. A. Aziz, and P. Kille, "Differential metallothionein expression in earthworm (*Lumbricus rubellus*) tissues," *Ecotoxicology and Environmental Safety*, vol. 57, no. 1, pp. 11–19, 2004.
- [42] S. P. Hopkin, *Ecophysiology of Metals in Terrestrial Invertebrates*, Elsevier, London, UK, 1989.
- [43] F. Gimbert, A. de Vauflery, F. Douay, R. Scheifler, M. Coeurdassier, and P.-M. Badot, "Modelling chronic exposure to contaminated soil: a toxicokinetic approach with the terrestrial snail *Helix aspersa*," *Environmental International*, vol. 32, no. 7, pp. 866–875, 2006.
- [44] A. Gomot de Vauflery and F. Pihan, "Growing snails used as sentinels to evaluate terrestrial environment contamination by trace elements," *Chemosphere*, vol. 40, no. 3, pp. 275–284, 2000.
- [45] J. Oehlmann and U. Schulte-Oehlmann, "Molluscs as bio-indicators," in *Bioindicators and Biomonitors: Principles, Concepts and Applications*, B. A. Markert, A. M. Breure, and H. G. Zechmeister, Eds., pp. 577–635, Elsevier Science BV, London, UK, 2003.
- [46] S. A. Ruffolo, V. Comite, M. F. La Russa et al., "An analysis of the black crusts from the Seville Cathedral: a challenge to

- deepen the understanding of the relationships among microstructure, microchemical features and pollution sources," *Science of the Total Environment*, vol. 502, pp. 157–166, 2015.
- [47] R. Bargagli, D. H. Brown, and L. Nelli, "Metal biomonitoring with mosses: procedures for correcting for soil contamination," *Environmental Pollution*, vol. 89, no. 2, pp. 169–175, 1995.
- [48] A. Davidson, J. B. Harborne, and R. E. Longton, "The acceptability of mosses as food for generalist herbivores, slugs in the Arionidae," *Botanical Journal of the Linnean Society*, vol. 104, no. 1–3, pp. 99–113, 1990.
- [49] R. Bargagli, S. Ancora, N. Bianchi, and E. Rota, "Biomonitoring and abatement of atmospheric pollutants in urban ecosystems: an overview and suggestions from long-term research in Siena (Central Italy)," *Environmental Monitoring and Assessment*, In press.



**Hindawi**

Submit your manuscripts at  
[www.hindawi.com](http://www.hindawi.com)

