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Review

Bioavailability and bioaccessibility in soil: a short review and a case study

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Abstract: In industrialized countries, there is a growing concern about the possible negative effects on human health induced by high levels of heavy metals in soil. It is recognized that high levels of heavy metals are not necessarily indicative of the adverse effects. These effects are related to bioavailable fractions, which are involved in plant uptake and transfer to the food chain. Bioavailability is a complex issue that is essential to evaluate to determine if heavy metals present in soil may pose hazards to humans and the environment. In the case of direct ingestion of soil, it is essential to consider also bioaccessibility. Bioavailability and bioaccessibility are related to several soil processes and may be largely determined by soil characteristics. This review deals with the influence of soil properties on metal bioavailability and bioaccessibility. A case study on bioavailability and bioaccessibility of heavy metals is reported, considering a large uncontaminated area influenced by deposition from a cement plant.

Keywords: soil characteristics; soil bioavailability; soil bioaccessibility; heavy metals; soil use

1. Introduction

In industrialized countries the relationship between the soil and health is a central issue which requires appropriate tools in order to transfer the scientific knowledge into intervention strategies [1,2]. Evaluating whether, and to what extent, soil contamination causes significant risks to human health is key in formulating strategies for reducing the negative health impact of soil contamination. The appropriate strategy depends on the specific characteristics of the pollutants and the soils.

The exposure scenarios that link the quality of the soil to health vary in complexity. A relatively simple scenario is that of sites polluted by contaminants whose environmental presence and specific health effects have been ascertained. In these cases, a risk assessment procedure leads to implementation of environmental remediation interventions, while an epidemiological and health surveillance quantifies the effectiveness of the adopted reclamation procedures. More complex scenarios are typically found in areas characterized by agricultural, urban and natural soils, in presence of productive activities where, even if the soil is uncontaminated, heavy metals may be present. Heavy metals may derive from different sources, such as traffic, fertilizers, urban and industrial wastes, etc, and may also involve the food chain due to the transfer from soil to plant.

Soil is a very complex three-phase system characterized by a significant number of processes and reactions (distribution between phases, desorption-adsorption, degradation, etc.), which give it a high spatial and temporal variability. The three phases of the soil: solid, liquid and gaseous, are accompanied by a fourth very important phase, the living phase. In fact, one gram of soil contains on average of 10 billion organisms, which drastically influence many of the processes that take place in the soil environment. This complex system is the primary source of the elements and substances that humans absorbs through their diet. In fact, most of the food is produced in the soil: plants uptake the substances from the soil and transfer them to the food chain. The elements absorbed by plants are ingested directly in the consumption of plants, or indirectly through meat, milk, etc.

Human health is largely determined by the quality of nutrition and therefore by the absorption of substances whose primary source is the soil. Soil quality is thus key for human health and the study of soil processes that determine the fate of contaminants in soil enables their potential adverse effects on human health to be estimated [3,4].

Understanding the mechanisms that link soil quality and human health involves identifying the bioavailability processes that regulate the transfer of substances from the soil to humans through the food chain and other exposure pathways.

2. Bioavailability processes in soil

In the soil, bioavailability is the result of a series of complex mass transfer and sorption processes which are determined by the properties of the substances, the soil characteristics, and the biology of the organisms involved [5,6]. To account for this complexity, a set of interactions need to be considered, which are characterized by different aspects and different temporal phases, and which determine the exposure of an organism to a chemical substance present in the soil (Figure 1).

The first of these processes (Step A) is the passage of an element from the solid phase in which it is essentially unavailable for any environmental process, to the liquid phase, in which every element is potentially available for most of the organisms that live in or on the soil. When a contaminant reaches the soil, the bond with the solid phase can occur through adsorption processes both in the mineral matrix (clays, oxides, hydroxides) and the organic matrix (humic substances). Depending on the contaminant properties and the specific soil conditions, the contaminants are retained by the surfaces of the soil with bonds of a different nature and strength [7].

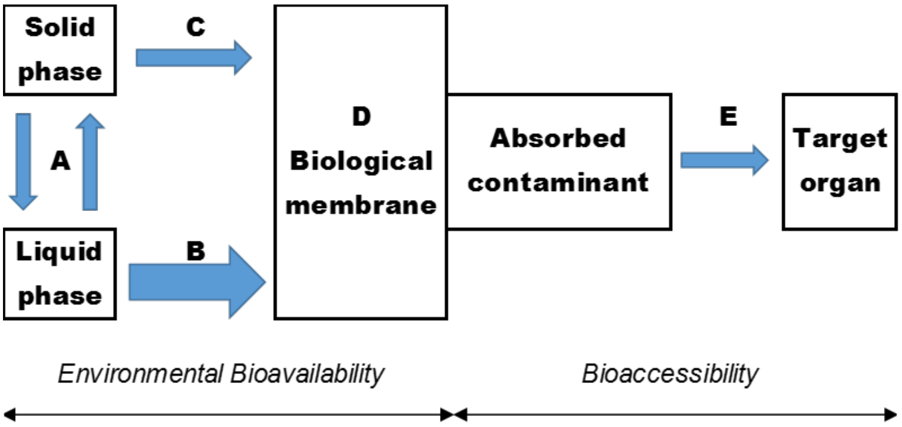

Figure 1. Bioavailability processes as indicated by NRC 2002 [5].

Contaminant are released from the soil surfaces in the liquid phase in response to changes in the chemical environment of the soil solution. Once released into the liquid phase, a contaminant can move freely to a living organism as a result of transport processes (diffusion, dispersion, etc.), which bring it into contact with the organism membrane (Step B). The same mechanisms can also transport substances that are bound to solid particles of very small dimensions, such as those of a colloidal nature (Step C). During the transport phase, the contaminants may be subjected to further reactions (oxidation-reduction, hydrolysis, photolysis, degradation, etc.) which can modify both their toxicity and bioavailability.

After a contaminant enters a living system (Step D), the influence of the soil on the bioavailability processes continues to be important only in the case of direct ingestion of soil. For this last pathway (Step E), it is essential to consider a further parameter: bioaccessibility. Bioaccessibility measures the fraction of the total contaminant present that is solubilized in the stomach and becomes available to be absorbed in the intestine [8]. Bioaccessibility takes into account additional contamination pathways to those deriving from the soil-plant-food chain. These contamination routes are the direct ingestion of soil (e.g., hand-to-mouth in children), skin contact, and the inhalation of soil particles.

When evaluating human health risks associated with contaminated soils, it is necessary to consider the exposure pathway soil ingestion especially by children. When soil contamination levels are high, the direct ingestion of soil is often the route of exposure that creates the greatest health risks [9]. After the contaminated soil has been ingested, the digestive processes may release the contaminants from the soil itself. This process starts in the oral cavity and continues into the stomach where the pH is low (1–4). In the intestine, the pH returns to neutrality when the absorption of contaminants is greatest, given the high surface area of microvilli (approximately 200 m^2 for adults) [10].

Ingestion via hand-to-mouth has been estimated as a mean of 50–200 mg soil/day [11,12], thus the bioaccessibility of contaminants in soil is a very important factor to consider. Because bioaccessibility is determined by the release of contaminants from the solid phase of ingested soil, an evaluation of the influence of soil properties on the bioaccessibility is essential in order to accurately evaluate the health risk posed by contaminants. Bioavailability and bioaccessibility are related to the characteristics of soil and contaminants, but identify different routes of exposure.

The size and nature of the effects of a contaminant are determined not only by the concentration but also by the chemical species, which interacts with an organism [7]. To understand how the specific characteristics of each soil influence the potential transfer of contaminants to humans by the bioavailability and bioaccessibility processes, let us take the example of heavy metals, considering the parameters that determine the release from the solid phase and their chemistry in the soil solution. Heavy metals are the most persistent elements in the soil, and their negative effects on human health are well known [13–16]. Metals that are bioaccumulated in plants or animals become available to the higher organisms that feed on them. Depending on the degree of bioaccumulation in each organism, the final receptors may be exposed to higher concentrations than those found in the soils from which the contaminant originates (biomagnification) [17]. If the plant is the fundamental step in the passage of a contaminant from the soil to a human, any substance, to be absorbed by the root system, must be dissolved in the liquid phase. In bioavailability processes, this fundamental step, from the solid phase to the soil solution, is governed by the specific characteristics of the soil.

3. The influence of soil characteristics on contaminant bioavailability/bioaccessibility

The fate and transport of pollutants in soil, is determined by complex processes due to the fact that soil is a dynamic system characterized by a very high heterogeneity. Heavy metals in soils are present in different pools [3]:

- In soil solution as simple or complex soluble ions;
- Adsorbed on mineral particles in exchangeable forms;
- Adsorbed or complexed by organic matter;
- Occluded or precipitated with oxides, carbonates and phosphates, or other secondary minerals;
- Included in the crystal lattice of hydroxides, clay minerals.

The first three pools are considered as the most important to release available forms of heavy metals for plants, while the remaining pools are characterized by metals with decreasing availability.

Soil characteristics (pH, organic matter, texture etc.), as well as the intrinsic properties of each element, determine the distribution in the different pools, which in itself is related to the sorption and release process in soil. The fate and behaviour of heavy metals in soil are determined by these retention/release processes, which regulate the concentration of heavy metals in the soil solution and thus their bioavailability. The sorption/desorption reactions strictly depend on the specific characteristics of the soil. Therefore, knowledge of soil characteristics is crucial to assess the mobility and the concentration of metals in soil solution, and thus their bioavailability for plants and humans.

3.1. pH

The nature of the mineralogical substrate from which the soil originated determines the soil pH, and this is the most important parameter that governs the concentration of inorganic elements in the soil solution [18,19]. The solubility of most metals tends to decrease as the pH increases, however, there are some important contaminants such as arsenic and chromium, which behave inversely. The pH also regulates the specific adsorption and complexation processes. The adsorption of the metals is often proportional to the pH due to competition of the H+ ions for the same adsorption sites on the surfaces of the soil [6].

3.2. Clays

Clays, which are primary constituents of the soil, retain the metals through ion exchange reactions or specific adsorption by interacting with metals by hydroxyl ions to which the metals are bonded, or by the formation of bonds directly with metals and the displacement of a proton [20]. Depending on the type of clays, there are considerable differences in adsorptive capacities. Adsorption and retention processes are higher in expandable clays in which adsorption takes place in the interlayer spaces. The importance of the soil texture on the distribution of contaminants between the phases has a direct impact on the bioavailability, which is always higher in soils of sandy nature [6].

3.3. Organic matter

Complex chemical forms characterize the organic matter in the soil; which is of great importance for bioavailability, due to the tendency of humic substances to form complexes with metals and to act as adsorbent matter [21]. The complexes formed with the substances with the lower molecular weight (fulvic acids) are soluble, and tend to increase the metal content in the soil solution. Conversely, higher molecular weight humic acids form very stable complexes with metals, removing them from all environmental processes and reducing their bioavailability. Carboxylic and amine phenolic functional groups are essential in the retention of metals by humic substances, and the increase of these functional groups during humification increases the stability of the complexes over time, thus reducing the bioavailability of metals [22].

3.4. Cation exchange capacity

The cation exchange capacity expresses the charge density on the surfaces of the soil colloids. It is determined by the organic substances and by the quantity and type of clays. The negative charges on the surfaces of the solid phase of the soil can be permanent or may depend on the pH. Thus, ions with a positive charge in the soil solution can be bound to the surfaces by weak electrostatic bonds, which thus decreases their bioavailability [6].

3.5. Redox potential

Many oxidation-reduction reactions occur in the soil, which are controlled by the activity of free electrons in solution expressed as the redox potential (Eh) that is a measure of the electron availability in the soil environment. High levels of Eh are characteristic of dry and well-ventilated soils, while soils that are submerged or particularly rich in organic substances tend to have low Eh values [23]. Soils that are rich in organic substances tend to promote the solubilization of iron oxi-hydroxides, and a consequent greater bioavailability of some contaminants such as arsenic anions, which are released from the surfaces of the hydroxides. This effect can however be counterbalanced by the formation of heavy metal sulfites, which are characteristic of soils in anaerobic conditions [24].

3.6. Oxides and hydroxides

The hydrated oxides of iron aluminium and manganese can reduce the metal concentrations in the soil solution both by specific adsorption and precipitation reactions. Metal ions can also enter the oxides, within the structure of the mineral lattice or in micro pores, after being superficially adsorbed. The specific adsorption of metals by oxides drastically reduces their bioavailability [25].

3.7. Time

Time governs the interactions between the solid phase of the soil and the contaminants. Over time, a contaminant is subject to transformations that lead it to be more strongly retained by the solid phase and thus less available for environmental processes [26]. This aspect is particularly important for organic compounds, but also involves inorganic compounds, which decrease in the soil over time, in bioavailable forms.

3.8. Measuring bioavailability/ bioaccessibility

The concept of bioavailability has long been used in soil science, for example to define the quantity of an element (N, P, K, etc.) that is available for plant nutrition, which often represents the basis for deciding the amount of fertilizer to be used.

This concept is not immediately utilizable in environmental studies where it is necessary to understand the pollution mechanisms in order to define both the risks that derive from pollution and the possible measures to eliminate it. Bioavailability is determined by a complex series of different processes, involving chemistry, biology and ecotoxicology [27].

To evaluate bioavailability from a chemical point of view, it is essential to determine the quantity of metals present in the soil solution and/or the most easily releasable from the solid phase. This is done by either the direct analysis of the soil solution or using tests with mild extractants (water or solutions of alkaline salts) which provide a good indication of the potential bioavailable metals present in a soluble form in the liquid phase of the soil [28,29].

When focusing on the relationship between soil and human health in addition to the bioavailable fraction, it is also essential to consider bioaccessibility. Ignoring any semantic issues [30], the bioaccessible fraction can be considered as the maximum amount of contaminants available for human absorption. The effective health risks from contaminants in ingested soil are strongly determined by the amount soluble in the gastrointestinal tract and thus available for absorption [31,32]. To determine the bioaccessibility, several methods are commonly used in soil chemistry that take into account the problems previously described for the determination of bioavailability. Some methods involve sequential extractions in order to assess the processes that occur in the gastrointestinal tract [33–35], while other tests are based on the reproduction of acid pH conditions to simulate the gastric environment [36].

The use of several chemical, biological, and toxicological methods must be combined with an in-depth knowledge of the specific characteristics of the soil, which enables the most important contaminants-involving processes to be identified.

Both bioavailability and bioaccessibility are highly dependent on the specific soil and the specific receptor, thus the results obtained by different methods are affected by a significant component of natural variability deriving from soil heterogeneity.

4. A case study

In this case study, the bioaccessibility and bioavailability of chromium (Cr), copper (Cu), lead (Pb), zinc (Zn), and nickel (Ni) were investigated in a large area affected by deposition from a cement plant. This area is located in northern Italy (Figure 2).

Figure 2. Map of the sampling sites in the investigated area. In yellow the sampling points and in red the cement plant.

4.1. Materials and methods

4.1.1. Soil sampling

The cement plant in this area is considered the possible source of heavy metals. The best soil sampling strategy in cases of a possible point source contamination is to consider theoretical circles at increasing distances from the cement plant [37–39]. The soil samples were taken approximatively in five circles at a distance of 1, 2, 3, 5 and 7 km from the cement factory (1C, 2C, 3C, 5C and 7C) also taking into account the main wind directions. A total of 27 georeferenced soil samples (Figure 2) were taken. The samples were collected at a depth of 0–3 cm. This depth has been selected to evaluate any atmospheric emission from the cement plant [37–39]. Background values of studied metals were considered by collecting soil in the same places at a depth of 1 m, where it was assumed that there was no influence of anthropogenic activities. According to the land use, soils have been subdivided in agricultural (A), where agricultural activity was underway, natural (N) in the presence of non-cultivated wild grassland or wooded areas, and urban (U) within the urban residential areas.

4.1.2. Soil analysis

Soils samples were air-dried and then ground to pass through a 2 mm sieve. Standard methods of soil analysis [40] were followed to determine texture, pH, cation exchange capacity (CEC) and organic matter. To quantify the total concentrations of chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn), the EPA method 3051a was used. Each sample of mineralized soil was collected quantitatively in 25 mL bottles and filtered before the analysis using atomic absorption spectroscopy (Varian AA240FS). To determine the bioaccessibility, a simulated gastric fluid [36] was prepared by adding 30 mL of concentrated HCl to 1 L of 0.4 M of glycine solution, and adjusting the final pH of the solution to 1.5. The solution (100 mL) was added to 1 g of soil and then stirred at 37 °C for 1 hour, centrifuged at 15,000 rpm and filtered to 0.45 mm before analysis [31]. The potential bioavailability of heavy metals was determined by mean of extraction with a 0.1 M solution of $CaCl_2$ with a soil / extract ratio of 1:10 and a stirring period of three hours [6,41].

4.1.3. Quality assurance and quality control

Quality assurance and control were performed by testing a standard solution every 10 samples. Certified reference materials BCR 141, BCR 142, BCR 143 were used to control the quality of the analytical system. The values obtained from the certified references were always in good agreement with the certified values. The recovery of spiked samples (5%) ranged from 95% to 101%, with an RDS of 1.90% of the mean.

4.1.4. Statistical analysis

Statistical analysis was performed using STATISTICA version 6.0 (Statsoft, Inc., Tulsa, OK, USA). The concentrations of heavy metals in soils at increasing distance from the cement plant were analyzed using one-way analysis of variance (ANOVA). Differences among means were compared and a post-hoc analysis of variance was performed using the Tukey Honestly Significant Difference test ($P < 0.05$). The effects of soil properties on metal bioavailability and bioaccessibility was evaluated by multiple linear regressions. Regression models were performed by stepwise selection with a significance level of $P < 0.05$ for variables to remain in the predictive equations.

4.2. Results and discussion

4.2.1. Soils characteristics

Soils were mainly sandy with a mean value of 83.6% in a range from 72.3 to 91.9%. Clay content ranged from 1.62 to 14.6% with a mean value of 5.25%. Silt content ranged from 4.35 to 21.4% with a mean value of 11.1%. Soils were characterized by a pH mean value of 6.2, an average organic matter content 7.8% and a mean CEC value of 27.1 cmol(+) kg^{-1}.

The heavy metals values were within the limits of non-contaminated Italian soils [42] and also the contamination factor calculated by the equation CF = $[M_{tot}]/[M_{background}]$ was negligible [43]. The bioaccessibility and bioavailability metal values were examined in relation to both the distance from the cement plant and the use of the soil. Three different soil uses were considered (natural, agricultural, urban). The bioavailability and bioaccessibility were reported for only Pb, Cu, Zn and Ni, since the concentration values of Cr in both the bioavailable and bioaccessible fractions were below the detection limit of all soil samples. Heavy metals concentrations in plants of the investigated area were negligible often below the detection limit (data not reported), thus it was impossible to correlate them with bioavailable concentrations of metals determined by chemical extraction.

4.2.2. Distance from the cement plant

Total heavy metal content of soil samples collected at increasing distance from the cement plant is reported in Table 1.

Table 1. Total concentration of heavy metals (mg kg^{-1}) in soil samples grouped by distance from cement plant. Data are expressed as mean values of concentration ± standard deviation of all sampling points on each circle

Distance from cement plant	Cu	Zn	Ni	Pb
1C	26.5 ± 3.9	81.5 ± 9.5	15.1 ± 2.0	35.4 ± 4.8
2C	22.6 ± 3.8	70.4 ± 7.2	18.2 ± 2.6	36.2 ± 3.4
3C	26.2 ± 3.3	79.8 ± 7.7	14.7 ± 3.4	41.9 ± 3.7
5C	26.3 ± 4.5	71.0 ± 6.2	19.9 ± 4.4	40.4 ± 5.2
7C	28.9 ± 4.7	80.8 ± 7.6	18.1 ± 2.6	37.7 ± 3.7

These results show that for these metals, there were no statistically significant differences between the concentration values in the circles at increasing distance from the cement plant considering the cement plant as the main point source of metal emission, The metal concentrations are within the range of Italian uncontaminated soils, largely below the levels that define soil pollution according to Italian legislation [42].

The trend of bioavailable (Bav) and bioaccessibile (Bac) fractions at different distances from the cement plant are reported in Figure 3.

For all the metals, the bioavailable fraction showed a trend with no significant differences among the five circles, which thus suggests that the distance from the cement plant did not affect the bioavailability of the metals. The bioavailable quantities of Cu ranged from about 1 mg kg^{-1} to about 1.8 mg kg^{-1}, which was on average around 15% of the total content. Bioavailable Pb varied from about 2.5 mg kg^{-1} to 4.3 mg kg^{-1} and around 12% of the total. Bioavailable Ni accounted for 20% of the total content, ranging from about 2.5 mg kg^{-1} to 3.9 mg kg^{-1}. The amount of bioavailable Zn varied from about 7.6 mg kg^{-1} to 12.5 mg kg^{-1} and about 21% of total soil content.

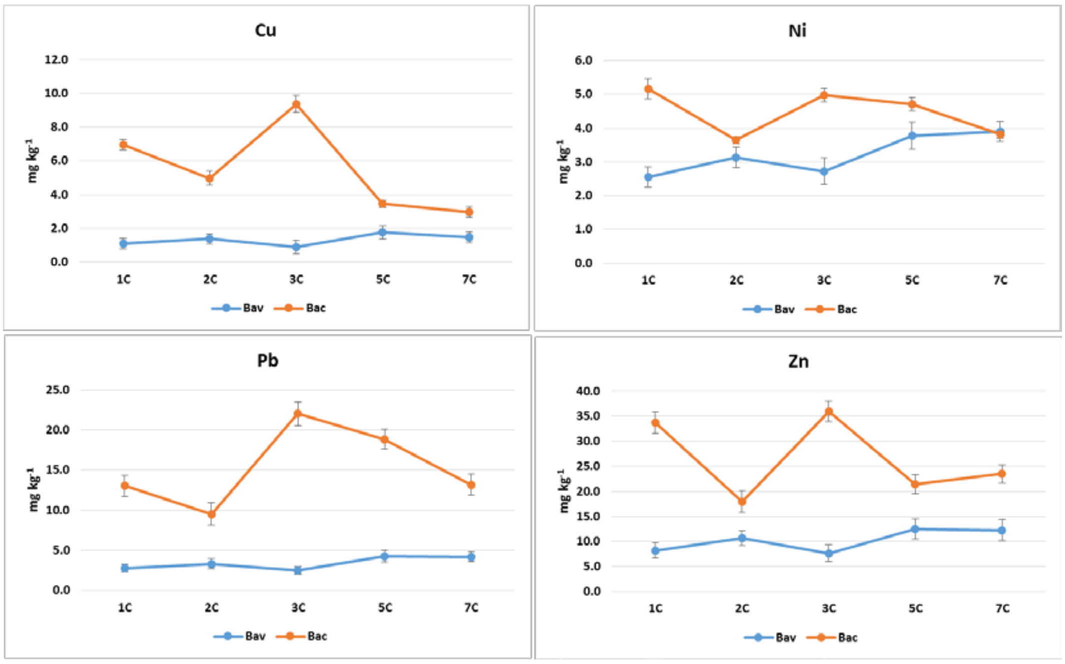

Figure 3. Metal bioavailable (Bav) and bioaccessible (Bac) at increasing distance from the cement plant.

Concerning the metals in the bioaccessible form; the Zn concentrations were significantly higher in circles 1 C and 3 C (around 35 mg kg^{-1}) compared to other circles and also the Pb concentration was highest in circle 3C, with values of about 20 mg kg^{-1}. The Ni and Cu bioaccessible concentrations were similar, around 5 mg kg^{-1} with a slight, but not significant increase in circles 1 C and 3 C.

Although it is difficult to attribute this trend to the influence of the cement plant with certainty, the different pattern in heavy metals bioavailability and bioaccessibility in the soils of the study area needs highlighting. In general, no correlation was detected between the concentration of metals extracted with glycine (bioaccessible) and the concentrations derived from the extraction with $CaCl_2$ (bioavailable). A similar lack of correlation has also been reported by Luo et al. 2012 [9]. One explanation may lie in the different actions of the two extractants: extraction with $CaCl_2$ induces an ion exchange reaction, while glycine decreases soil pH, which in turn promotes the solubilization of the metals.

4.2.3. Land use

Bioavailability and bioaccessibility were also examined in relation to the different land uses: agricultural (A), urban (U) and natural (N) (Figure 4).

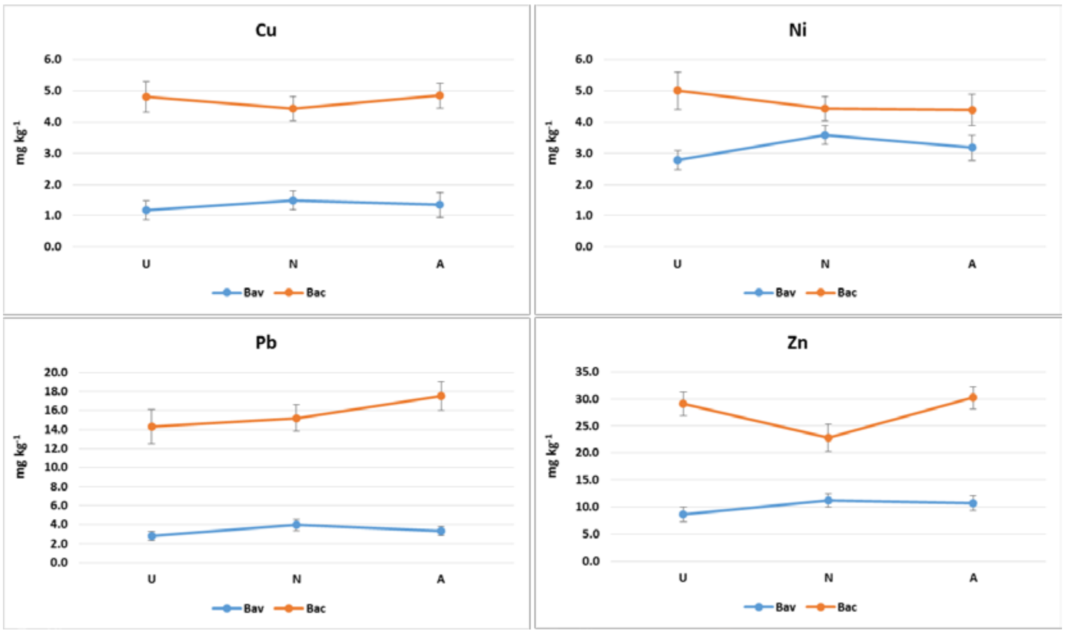

Figure 4. Bioavailability and bioaccessibility value in relation to the different land uses.

The mean values of the bioavailable forms were very low with respect to total heavy metals content and differences related to the use of soil were not statistically significant.

Cu extractability was around a value of 1.30 mg kg^{-1}. Ni concentrations were around 3.20 mg kg^{-1} in all the three kind of soils considered (agricultural, natural and urban). The same trend occurred for Pb, with a mean value of 3.40 mg kg^{-1} from agricultural, natural and urban soils. Also for Zn, the maximum bioavailability value (around 11.0 mg kg^{-1}) was found in agricultural and natural soils, and the minimum value (8.66 mg kg^{-1}) in an urban soil.

The use of the soil did not significantly influence metal bioaccessibility. In fact, mean Cu and Ni concentrations in the glycine extracts were around 4.5 mg kg^{-1}. Pb varied from about 14 mg kg^{-1} to 18 mg kg^{-1} and Zn from 22 to 30 mg kg^{-1}.

Although the differences were not statistically significant, generally the highest bioavailability of metals was found in natural soils, while the bioaccessibility values were higher in urban and agricultural soils.

Interactions of the contaminants with the soil constituents can greatly affect the metal availability in environmental processes. The metal distribution among the solid and liquid phases determines the quantities, which can have immediate adverse effects [44,45]. The amount of metals in mobile form in the soil solution is related to the physical and chemical characteristics of the soil [7,46]. We therefore assessed the bioavailability and bioaccessibility data in relation to the main properties of the soil, i.e. pH, organic matter, sand and clay content, C.E.C, and total metal content. Data obtained by multiple regression linear analysis are reported in Table 2.

Table 2. Effect of soil characteristics on bioavailability of metals (M-Bav) and bioaccessibility of metals (M-Bac). OM indicates organic matter.

Equation	R^2
Cu-Bav = 8.18 − 1.09 pH − 0.0016 Clay − 0.0074 OM%	0.9205
Ni-Bav = 14.3 − 1.75 pH + 0.0040 Clay − 0.025 OM%	0.8651
Pb-Bav = 16.9 − 2.13 pH − 0.010 Clay − 0.020 OM%	0.8769
Zn-Bav = 55.6 − 7.12 pH + 0.041 Clay − 0.17 OM%	0.9606
Cu-Bac = − 8.53 + 2.40 pH + 0.050 Clay − 0.23 OM%	0.3032
Ni-Bac = − 3.20 + 0.74 pH + 0.030 Clay + 0.38 OM%	0.1207
Pb-Bac = − 7.91 + 3.63 pH + 0.014 Clay + 0.16 OM%	0.1055
Zn-Bac = − 43.4 + 13.8 pH − 1.01 Clay − 1.29 OM%	0.4289

Positive terms in the equation indicate a direct proportionality between the soil property and bioavailability or bioaccessibility while negative terms indicate inverse proportionality. Validation of the correlation model was obtained by the value of R^2 [47,48]. Results show that the obtained equations accurately described the effect of soil properties on metal bioavailability, with values of R^2 ranging from 0.8651 to 0.9606. While there is no correlation among soil properties and metals bioaccessibility as depicted by the lower values of R^2 from 0.1055 to 0.4289.

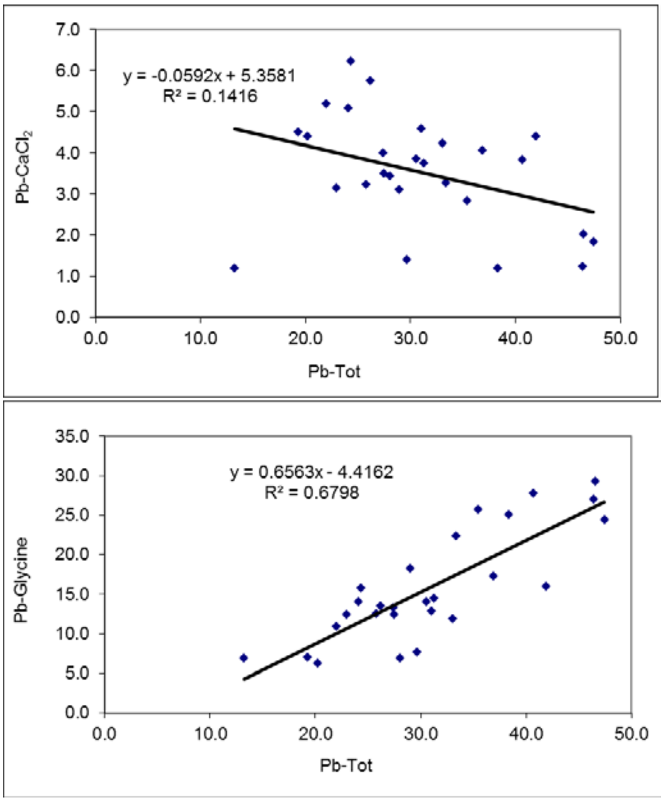

Figure 5. Correlation between Pb total content in soil (Pb-Tot) and $CaCl_2$-extractable Pb (bioavailable) or glycine-extractable Pb (bioaccessible).

This difference between the bioavailable and bioaccessible fractions is also found in relation to the total concentration of heavy metals in the soils. A poor correlation ($R^2 = 0.1$) was found between the $CaCl_2$-extractable heavy metals (bioavailable fraction) and the total metal concentration. On the other hand, the amount of glycine-extractable heavy metals (bioaccessible fraction) was significantly related ($R^2 > 0.6$) to the total metal content in the soil, especially in the case of Pb. As an example, data of Pb with the R^2 values are reported in Figure 5.

The interest in developing ecological surveys on soil contamination has recently increased together with the awareness on the effects of soil properties on metal bioavailability and bioaccessibility in relation to human health. A significant direct risk to human health in fact may also result from the inhalation of soil dust, soil ingestion and dermal contact [49,50]. Oral ingestion is often the critical pathway of exposure for children [51], and the health risks depend on the bioaccessible fraction, which often, but not always, does not depend on the characteristics of the soil. This approach is particularly important in an area characterized by different soil uses, which make it necessary to characterize the health risks considering all the possible pathways: food chain, soil ingestion, inhalation, and dermal contact.

Research on bioaccessibility has focused on contaminated sites [10,52,53], however, unpolluted soils should also be taken into account where aerial deposition can contribute to enriching the metal content of surface soils.

In contrast to agricultural soils where human health is influenced through metals in the food chain, soils in urban and natural areas may be used as recreational parks, thus hand-to-mouth ingestion is a critical pathway of exposure, especially for children [8,9,51] and therefore it is essential to evaluate the risk levels deriving from oral exposure. By assuming a soil ingestion dose of 100 mg day^{-1} for healthy (normal) children, and 10 g day^{-1} for children who deliberately eat soil (soil-pica behaviour) [54], results from this case study showed that in general no risks were found from the bioaccessible fraction of heavy metals in soils. However, the bioaccessible concentration of lead may pose some risks in the case of children with pica behavior. In this case the results from the bioaccessibility test showed a mean value of 158 μg day^{-1} of ingested Pb which is higher than the tolerable daily intake (TDI): 36 μg day^{-1} considered as safe for humans.

Pica behaviour is not common in industrialized countries, however in the developed world, it is the most common eating disorder observed in individuals with developmental disabilities [55,56] and thus should not be underestimated. The results reported in this case study should be considered as a part of a monitoring strategy to evaluate the effects of soil quality on human health, which should also take into account the health risks from multi-elemental exposure.

5. Conclusions

Bioavailability and bioaccessibility are complex issues that need to be assessed to evaluate whether or not there may be adverse effects for human health. Knowledge of these parameters can help in refining risk assessments and offer effective decision-support for managing land where humans are exposed to contaminants.

Although there is still a great variability in the determination of bioavailable and bioaccessible fractions, an assessment of the real risks for humans and the environment must be based on these parameters and not on the total metal concentration. Relationships between contaminant bioaccessibility, bioavailability and soil properties can further clarify the chemical and biological processes of metals also in non-contaminated soils.

The results highlight the need to incorporate physical and chemical parameters in predictive models, which relate heavy metals in soils to human health. The assessment of bioavailability and bioaccessibility in a monitoring strategy should include the variations in these parameters over time due to modifications in some soil parameters or land use. Despite the difficulty of bringing together knowledge from different multidisciplinary skills, which often speak different languages, a more extensive exploration of the relationship between the soil and health is now essential. This is especially the case in today's society, which is characterized by profound imbalances, in which for example, industrialized areas are subjected to pollution caused by excess metals, and areas where a lack of the same elements in the soil leads to irreversible damage to health. Exposure, dose and effects are not independent parameters, but represent successive phases of a continuum, which links the soil to human health through bioavailability processes including bioaccessibility.

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Conflict of interest

The authors declare no conflict of interest.

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