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Soil Contamination by Trace Metals: Geochemical Behaviour as an Element of Risk Assessment

Monika Zovko and Marija Romić
*University of Zagreb, Faculty of Agriculture
Croatia*

1. Introduction

Trace metals occur naturally in rocks and soils, but increasingly higher quantities of metals are being released into the environment by anthropogenic activities. Metals are chemically very reactive in the environment, which results in their mobility and bioavailability to living organisms. People can be exposed to high levels of toxic metals by breathing air, drinking water, or eating food that contains them. As a consequence, metals get into the human body by different routes - by inhaling, through skin, and via ingestion of contaminated food.

Every decision on the application of any measures in the environment related to soil quality and management, whether statutory regulations or practical actions, must be based on reliable and comparative data on the status of this part of environment in the given area. Various aspects have to be considered by the society to provide a sustainable environment, including a soil clean of heavy metal pollution. The first step is to identify environments (or areas) in which anthropogenic loading of heavy metals puts ecosystems and their inhabitants at a health risk.

Long-term and extensive use of land for agriculture with frequent application of agrochemicals is one of the major causes of trace metal, such as copper, nickel, zinc and cadmium, accumulation in soil. Accumulation of Cu in agricultural soil is a consequence of the century - old practice of using copper-sulphate (Bordeaux mixture) and other copper containing fungicides to control vine downy mildew. It is estimated that every time vines are sprayed with copper-containing solutions, some 2 to 5 kg ha⁻¹ of copper enter the soil (Romić & Romić, 2003).

Widespread distribution of Cd and its high mobility makes it a potential contaminant in a wide range of natural environments. Generally, soil Cd concentrations exceeding 0.5 mg kg⁻¹ are considered evidence of soil pollution (McBride, 1994). Phosphatic fertilizers are one of the most ubiquitous sources of Cd contamination in agricultural soils throughout the world. Total Cd inputs to soils through fertilizers in the countries of the European Union have been estimated to be around 334 t yr⁻¹ (Alloway & Steinnes, 1999). Long-term investigations worldwide have shown that application of phosphate fertilizers has resulted in soil enrichment with Cd (0.3-4.4 g ha⁻¹ year⁻¹), depending on the rates and kinds of fertilizers applied (Singh, 1994). Andrews et al. (1996) and Gray et al. (1999) also determined a highly significant correlation between total concentrations of Cd and phosphorus in agricultural

soils of New Zealand, which they attributed to long-term application of phosphate fertilizers. Chen et al. (2008) observed significant correlations between Cd and Pb and soil phosphorus in California vegetable croplands, indicating the application of P-fertilizers contributes significantly to the accumulation of Cd and Pb in soils. Zinc belongs to a group of trace metals that are potentially most dangerous for the biosphere. The main sources of the pollution are industry and use of liquid manure, composted materials and agrochemicals such as fertilizers and pesticides in agriculture.

Beside anthropogenic sources, trace metals can be also found in the parent material from which the soils developed. Whether the said inputs will become toxic and to what degree mobile depends on a number of factors: specific chemical and physical trace metal characteristics, soil type, land use, geomorphological characteristics within the soil type and exposure to emission sources. Processes that control the mobility, transformation and toxicity of metals in soil are of special importance in the soil root developing zone – the rhizosphere. For this reason, there is a considerable interest in understanding trace metals behaviour in soil, with special emphasis on the way they build-up in soil and on processes of by which plants take up metals.

2. Factors controlling trace metals behaviour in soil

2.1 Trace metal characteristics

Two thirds of all elements found in nature are metals. According to their chemical definition, metals are elements and as such cannot be synthesized or degraded by biological or chemical processes, though these processes can change chemical forms of metals. Metals are contained in the Earth's crust and in parent rocks, by whose weathering soils are formed, so their presence differs in different geographic regions. Terms like heavy metals, metalloids and microelements are the most commonly encountered in ecological studies. Among the 96 known metals, 17 are semimetals or metalloids (e.g., B, Si, Ge, As, Sn, Te, Po ...). The term heavy metal refers to a group of 53 metals with density higher than 5 g/cm³. From the geochemical point of view, trace elements are metals whose percentage in rock composition does not exceed 0.1% (e.g., Cu, Cr, F, Fe, Mo, Ni, Se, Zn, As, Cd, Hg, Pb). In very small amounts, some of these elements are essential for normal growth and development of living organisms and they are, from the physiological point of view, called micronutrients or microelements (e.g., Fe, Mn, Zn, Cu, Mo, Ni, Se), while others are toxic even in small concentrations. The issue of toxicity is usually merely a matter of quantity, with the range varying for each element.

Regardless of whether soil metals originate from a natural source or are a consequence of anthropogenic activity, metals appear in groups; one element by itself is rarely the source of contamination. Hence, synergistic and antagonistic interactions of metals should not be disregarded in assessing bioavailability. For example, Zn and Cd are usually present together in ores and have similar physical and chemical properties.

Distribution, mobility, bioavailability and toxicity of metals depend not only on metal concentration but also on the form in which metal exist. Full understanding and prediction of chemical behaviour of an element in the environment is possible only by identification of all forms in which that element can be found under different environmental conditions. Metal speciation is one of the most important properties that determine the behaviour and toxicity of metals in the environment. Chemical speciation of an element refers to its specific form characterized by a different isotopic composition, molecular structure, and electronic

or oxidation state (Manouchehri et al., 2006). Speciation is the process of identification and determination of different chemical and physical forms of elements present in a sample (Wang et al., 2006). Metals that occur in cationic forms have a higher ability of binding to negatively charged soil colloids, and are thus less bioavailable, but more easily accumulate in soil, unlike the anionic forms that are mainly present in soil solution and are more bioavailable, but are more readily leached from the soil.

2.2 Soil properties

Because of their very low abundance, trace elements are particularly sensitive to surrounding environmental conditions, which influence their physico-chemical speciation and their behaviour in the ecosystems (N'guessan et al., 2009). In agricultural environment soil is the main sink and source of trace metals. Not all soil properties have equal influence on the mobility and availability of a particular metal. For each metal it is therefore important to know the dominant soil property that will control the behaviour of that metal in that particular soil. With regard to bioavailability, the following metal fractions have an important role in soil: metals in soil solution; precipitated metals; metals bound to clay minerals, oxides and hydroxides, organic matter, and metals in the soil mineral matrix. All fractions of metals are in dynamic equilibrium, and only metals in aqueous soil solution are directly available to plants. Soil solution is in direct contact with the soil solid phase and transformations going on in it are a consequence of mineral equilibrium, exchange processes and sorption processes in the soil mineral phase and organic matter, as well as complexation with organic matter in the solid phase and in solution (figure 1). Major soil properties that affect changes in metal speciation, and thereby also their fractionation, are soil reaction, redox-potential, and existence of different organic and inorganic reactants – ligands.

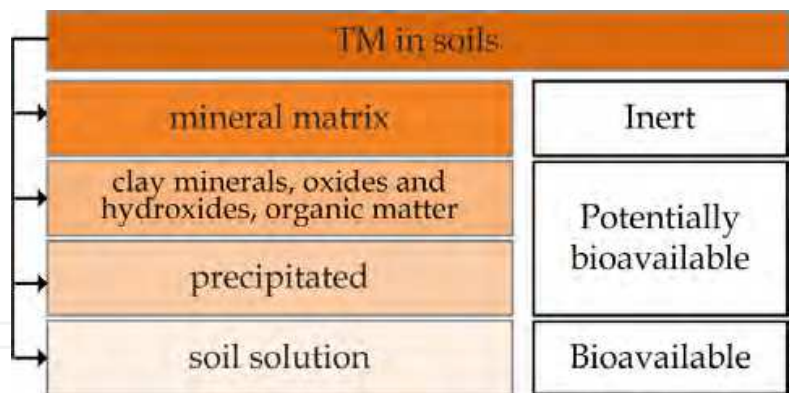


Fig. 1. Simplified schematic presentation of different trace metal (TM) fractions in soil

Whether soil metals will form complexes with organic matter, mineral colloids, inorganic complexes or exist as free ions depends on the soil solution reaction. Constant changes in soil pH are a consequence of cation/anion balance, leaching of organic acids, root respiration and oxidation-reduction reactions. Each change in pH alters the adsorption capacity of minerals and organic colloids. Positive charge prevails at low pH conditions under which anion exchange capacity is dominant, while at high pH negative charge prevails and cation exchange capacity predominates. Solubility of Mn and Zn is strongly dependent on soil reaction. The lower the pH, the stronger the Mn and Zn competition with H^+ and Al^{3+} ions for places in the soil cation exchange complex, and higher the Mn and Zn solubility and proportion of readily available free ions in soil solution. Soil reaction will

affect Cu speciation, its solubility and adsorption; however, a weak correlation was determined between soil reaction and Cu concentration in soil solution (Wang et al., 2002) since dissolved Cu has high affinity for organic matter, that is, for phenolic groups and groups of weak acids of humic compounds (Cornu et al., 2007). Gummuluru et al. (2002) showed that Cu complexes with dissolved organic matter are the most dominant species, averaging 97.1, in the neutral and mildly acidic soils.

The presence of carbonate, high contents of organic matter and percentages of clay may suggest that trace metals could be retained in these soils, as these properties increase the adsorption capacity of metals by soil (Peris et al., 2008). Organic substances and oxyhydroxides have the highest surface charge density and are thus the most important and strongest sorbents of trace metals. Carboxylic groups ($-\text{COO}^-$) of organic compounds can form stable complexes with metal ions, which leads to changes in the metal fraction available to biota. Surface charge of organic matter and oxyhydroxides is strongly dependent on soil pH, contrary to surface charge of clay (except kaolinite), which does not depend on pH (Reichman, 2002). Organic matter affects the soil redox potential. Fe and Mn hydroxides are especially susceptible to changes in soil redox potential. Electrons are released through organic matter decomposition, which results in a decrease in redox potential and reduction of Fe(III) into the easily soluble Fe(II) form. Manganese ions display similar behaviour. Organic matter can also influence temporary immobilization of Zn. Available Fe and Mn ions inhibit Zn uptake, which can affect precipitation of dissolved Zn into the mineral franklinite (ZnFe_2O_4).

Selective sequential extraction was applied to investigate the potential of mobilizing trace elements in agricultural soils of northwestern Croatia (Romić & Romić, 2003). In alluvial soils developed on Quaternary (Upper Pliocene to Holocene) deposits, extraction with 1M $\text{Mg}(\text{NO}_3)_2$ (pH 7) (Shuman, 1985) indicated possible remobilization of elements from the solid phase into soil solution, particularly in the case of copper. There are several possible mechanisms that increase solubility of metals in the surface layer: 1) the soil mineral component is more susceptible to weathering in shallower than in deeper soil layers owing to faster infiltration of precipitation, higher biological activity and greater changes in temperature; 2) shallower soil horizons are richer in organic matter, which can stimulate metal desorption by formation of soluble organic complexes; and 3) exchangeable complex of shallower soil layers contains more basic cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), which can also reduce sorption of metals by increasing the competition for exchange sites. All these processes are even more pronounced in the anthropogenic horizon of arable soils.

For trace metals to be translocated by water through the soil profile, they have either to be in the soluble phase or bound to mobile particles. Metals can form complexes with particles of organic matter in topsoil and as such can be translocated vertically along the profile depth. It is generally taken that the water-soluble and exchangeable fractions, and sometimes also the organic fraction, are bioavailable forms. Investigations dealing with the leaching of metals from soil revealed a marked vertical distribution of organometallic compounds that can be leached up to 3 times deeper compared to metals not complexed with organic matter. This phenomenon is particularly pronounced in application of organic soil amendments. The observed enhanced mobility of metals in soils improved by different organic conditioners (Al-Wabel et al., 2002) is a consequence of metal binding to dissolved organic carbon (DOC) formed through decomposition of such conditioners. An increase in DOC concentration increases metal complexation with organic matter, that is, the proportion of metals in the soil liquid phase, and thereby also their mobility. In their investigations, Al-Wabel et al.

(2002) assessed that more than 99% of Cu and Zn in soil solution and about 90% of Pb were complexed with dissolved organic carbon or mineral colloids without being in the form of free ions or inorganic complexes. In contrast to Cu and Zn, speciation of Cd in soil solution was not strongly influenced by organic matter, but Cd existed in solution as a free divalent cation (Cd^{2+}) or with inorganic complexes Cl^- , SO_4^{2-} or HCO_3^- . It has been well documented in the literature that complex formation between metals and inorganic ligands Cl^- and SO_4^{2-} inhibits the adsorption of Cd on soil and soil constituents due to the formation of cadmium complexes that were not strongly adsorbed by soil (McLean & Bledsoe, 1992). In many arid and semiarid regions, including European Mediterranean region, saline irrigation water containing high level of chloride might aggravate trace metals pollution problem, as a result of metals mobilisation due to the formation of metals-chloride complexes (Ghallab & Usman, 2007). Soil salinity strongly increased the concentration of dissolved chloride (Cl^-) ligands, and significantly influenced Cd solubility and thereby its bioavailability and phytoaccumulation. Exposure to increasing NaCl salinity in the rhizosphere environment increased accumulation of Cd in muskmelon and radish leaves (Ondrašek et al., 2009).

The mobilization potential of trace metals, like Cd, Cu, Pb and Zn, may get increased in dredged (oxidised) sediments compared to submerged (reduced) sediments (Tack et al. 1998; Vandecasteele et al., 2007). Indeed, an important factor in the metal mobilization is changing redox conditions. In that sense, the Mn behavior is particularly varying. In oxic environment Mn precipitates as oxides with large mineral surfaces entering into the reactions with both trace metals and soil organic matter (Kaiser & Guggenberger, 2003).

3. Assessment of soil contamination by trace metals – geochemical methods

Various chemical methods, geochemical models and biotests are used for assessment of the bioavailable metal fraction in soil. However, these methods are not universally applicable for all elements and different soil characteristics. Chemical methods for assessment of metal bioavailability are commonly grouped within methods for assessment of total metal content in soil, methods for assessment of currently available and potentially available fractions, methods for assessment of metal speciation in soil solution.

Determination of the total content of metals in soils is an important step in estimating the hazards to the vital roles of soil in the ecosystem, and also in comparison with the quality standards in terms of the effects of pollution and sustainability of the system. Methods for assessment of total metal content are based on soil digestion with strong acids such as HNO_3 , HF, HClO_4 and aqua regia. Although the total metal content in soil does not show a good correlation with the bioavailable fraction, it is still used in most countries as a statutory regulation for assessment of soil contamination.

From the ecotoxicological aspect, however, it is equally important to determine the bioavailability of trace metals accumulated in agricultural soils. Single and sequential extraction methods are applied for assessment of currently available and potentially available metal fractions in soil. There are several kinds of extraction solutions, the most commonly used being 0.001 to 1 M salt solutions (CaCl_2 , $\text{Ca}(\text{NO}_3)_2$, NaNO_3), weak acids (acetic acid, citric acid) and strong complexes (EDTA, DTPA). Extraction methods are based on complexometric reactions between extractants and metals. In complexometric titrations use is made of suitable indicators, commonly compounds that can produce a less stable coloured product with a free (hydratized) cation. Extraction methods are extensively applied in bioavailability investigations, but are not acceptable for all kinds of metals; for

example, EDTA is not suitable for metal bioavailability assessment in contaminated soils, particularly for Cu assessment (Brun et al., 2008). Available Cu in topsoils of the wine-growing regions in north-western Croatia was evaluated with DTPA extraction and calcium chloride extraction methods. Highly significant positive correlation was determined between total copper content and DTPA-extractable copper contents. Such strong correlation indicates that the DTPA extraction method is not suitable for assessing copper availability to plants (Romić et al., 2003).

There are two approaches to determining metal speciation in solution: analytical determination and chemical balance models. Direct measurements of metal ion speciation in soil solution are rare. Measurements are mostly conducted in solutions extracted with dilute salts (0.005 M HNO₃) of soil metals. Precise measurement of different forms of metals present in aqueous solution is the most demanding procedure, since it requires analytical methods of high selectivity and sensitivity; hence, different computer models (GEOCHEM, SOILCHEM) are mostly used for metal speciation determinations. These models are based on geochemical thermodynamic principles (Peijnenburg et al., 2003). Despite their high efficiency, computer models still have shortcomings that must not be disregarded in interpretation of the results obtained. The problem in the application of geochemical models for calculation of element speciation is the modelling of organic matter-metal complexation, since there are no reliable values for stability constants of dissolved organic matter, the properties of which can vary considerably in dependence on environmental conditions.

The main flaw of all chemical methods for bioavailability assessment is that they invalidate all complexity of the mechanism of metal uptake by plants and neglect the very important role of root metabolism and of the microorganisms that surround it. For this reason, these tests are not adequate for assessment of plant available metals in soil (Chaignon et al., 2003). An ideal method for metal phytoavailability assessment should simulate soil-plant interactions as closely as possible (Fang et al., 2007). Further, such a method should extract the amount of metal that corresponds to metal concentration taken up by the plant. Along these lines, the RHIZO - method (rhizosphere based method) was developed. It is based on the application of extraction of 0.01 M solution of organic acids of low molecular mass in wet rhizosphere soil. In laboratory investigations, Feng (2005) demonstrated the efficiency of the RHIZO method application in acid, neutral and alkaline soils, which makes this method more suitable than other bioavailability assessment methods. However, the results were satisfactory only for Cr, Cu, Zn, and Cd, while the method was not a good indicator of Pb and Ni phytoavailability.

Application of bioassays with plants offers a different approach to assessment of metal bioavailability in contaminated soils. Biotests can be done in nutrient solutions or in soil, depending on the research goal. Nutrient solutions can be considered as models of the soil system, more precisely, soil solution. Whether a nutrient solution will be a good soil solution model depends on the experimental design, but it should still be pointed out that this is a simplified soil system and that metal-plant interactions are different in solution and in soil. Thus, the interaction between Zn and Cu is of synergistic character in soil, and of antagonistic character in solution. It is also important to know metal rhizotoxicity because some metals, e.g., Cu, accumulate much more in roots than in stalks (Chaignon et al., 2003). Therefore it is essential for bioavailability assessment to develop biotests that will enable an unobstructed approach to root and rhizosphere studies.

4. Assessment of soil contamination by trace metals: A case of NW Croatia

4.1 Environmental soil functions

Soil plays many important roles in the environment. As being situated at the interface between the atmosphere and the lithosphere it acts as a filter and a buffer: it may weaken and degrade environmentally harmful compounds protecting the air quality. It also has an interface with hydrosphere and therewith it affects surface and groundwater quality. Furthermore, soil, as a part of biosphere, provides nutrient-bearing environment that sustains the growth of plant and animals. As a habitat and protecting media of flora and fauna it contributes to the maintaining of the global nutrient cycling as well as biomass production, whether by natural vegetation growing or plant cultivation. Beside these ecological functions, soil is ground to build and live on, raw material and reserve of cultural heritage.

Because soil quality and its utilization are directly linked, each of above mentioned functions or use mode requires a certain soil quality level. Otherwise, any change of soil quality may affect its utilization potential. Soil is a natural resource essential for the food production and global economy. The way and rate of soil degradation on the global scale point out the importance of the sustainable land use. Harris et al. (1996) define the soil quality as a capacity of the certain soil volume in given conditions (land use, relief, and climate) to protect water and air quality, to sustain plant and animal growth, promoting thus the human health. Out of total degraded land on the global scale that are estimated to 1,965 mha, about 55% was water eroded, about 28% wind eroded, and about 12% is polluted by chemicals (Adriano et al., 1995). Land degradation caused by physical, biological and chemical processes runs up the changes of the key soil properties that have a pivotal role in geochemical cycling.

From the standpoint of soil degradation, the presence of some trace elements in a toxic concentration may be due to both natural and anthropogenic factors. Therefore, it may become quite difficult to discriminate among the different causes. The parent material largely influences trace metals content in many soil types, with concentration sometimes exceeding the critical values (Palumbo et al., 2000; Romić & Romić, 2003; Salonen & Korkka-Niemi, 2007). Some metals, such as Ni, Cr and Mn, are contained as trace elements in some rock types of volcanic and metamorphic origin (Alloway, 1995). During weathering processes the primary crystalline structures of some rock minerals are completely broken, relevant chemical elements may be thus either adsorbed in the topsoil or transported towards surface water or ground water targets. The transformation of metals and metalloids is influenced significantly by adsorption-desorption reaction in soil environments; these reactions are affected by physicochemical and biological interfacial interactions, which should be especially important in rhizosphere (Huang, 2008). Soil buffer capacity may be defined as its ability to postpone the negative effects of more or less continuous input of toxic substances by inactivation of contaminants (Moolenaar & Lexmond, 1999). This inactivation can generally be reached by effective binding of contaminant and soil particles, or by forming of insoluble complexes. When the contaminant input exceeds the level of so-called «critical content», their buffer capacity is getting overcome as well and then the soil is characterized as polluted (de Haan, 1996). So that, buffer capacity of the diverse soil types defers considerably regarding the soil characteristics reflecting thus its vulnerability or resistance.

Generally, two main types of pollution may be distinguished: diffuse pollution or non-point source, and point source (O'Shea, 2002). The example of the non-point source is atmospheric deposition as a result of urban, transport and construction activities, as well as mineral

fertilizer or sewage sludge application in agriculture. Diffuse sources of pollution are not easy to control, and the best methods for soil pollution control often depend on the legal regulations and management strategies. It becomes easier to control point sources of pollution, because it usually refers to the single source that is easy to identify (local pollution caused by chance, accidentally or undertaking prohibited activities). Sources of agricultural land contamination, especially if places near urban or industrial area, certainly have a diffuse nature.

Geochemical maps are good visual demonstration of contaminant changes in the space, and enable the identification of the areas that are likely to contain harmful substances (Goodchild et al., 1993). The knowledge on spatial variability becomes equally important both for the assessment of the study site and for the prediction of the possible risks. The procedure of the geochemical surveys, including exhausting field work, long-lasting and expensive chemical analysis, require the sampling scheme optimization for the efficient interpolation and mapping.

4.2 Soil pollution assessment

A soil pollution assessment becomes very difficult to carry out when different sources of contamination are present and their products are variably distributed. In these cases the spatial variability of the trace metal concentrations in soils is basic information for identifying the possible sources of contamination and to delineate the strategies of site remediation. An approach was described that interpolate sampled trace metal concentrations using numerous environmental predictors and then represent the overall pollution by using the continuous limitation scores, as proposed by Romić et al. (2007). Such visualizations can supplement maps of separate trace metals so that the areas of high overall pollution can be more easily delineate presenting the basis for further studies on risk assessment or decision making.

In Europe, decision makers and spatial planners more and more require information on soil quality for different purposes: to locate areas suitable for organic (ecologically clean) farming and agro-tourism; to select sites suitable for conversion of agricultural to non-agricultural land, particularly for urbanization; setting up protection zones for groundwater pumped for drinking water; to estimate costs of remediation of contaminated areas and similar. Every decision on the application of any measures in the environment relating to soil quality and management, whether statutory regulations or practical actions, must be based on reliable and comparable data on the status of this part of environment in the given area. Various aspects must be considered by the society to provide a sustainable environment, including a soil clean of heavy metal pollution. The first among them is to identify environments (or areas) in which anthropogenic loading of heavy metals puts ecosystems and their inhabitants at health risk. Maps indicating areas with pollution risks can provide decision-makers or local authorities with critical information for delineating areas suitable for the planned land use or soil clean up (Van der Gaast et al., 1998; Broos et al., 1999). Maximum permissible concentrations of trace metals in soil are now regulated by law in many countries.

In urban and industrial environments there are numerous potential sources of contamination with harmful substances, including trace metals, mainly combustion processes in industry and transportation. Lead and cadmium are the main trace elements arising from combustion and are often associated with zinc owing to tyre wear on the roads. Waste water from industrial processes may contain an important load of zinc, copper,

chromium and nickel. Moreover, mining activities for extraction and manufacturing of metal products may result in a large amount of pollutants to be released into the atmosphere and, secondly, in the adjoining soils and waters.

Long-term and extensive use of agricultural land with frequent application of growing practices and use of pesticides (Nicholson et al., 2003) may cause heavy metals such as copper, nickel, zinc and cadmium to be strongly accumulated in the topsoil.

The estimation of the total trace metals content and spatial variability of these elements in soil is the main indicator of the degree of contamination, but is not sufficient for establishing the relevant guidelines or decision making. GIS-based mapping techniques in conjunction with statistical and geostatistical analysis of the data are widely used to highlight the influence of human activities on the trace metals content of topsoils in urban and sub-urban areas (Kelly et al., 1996) and to assess the transport pathways, sinks, and impact of particulate associated trace metals in the various spheres making up the urban environment (Charlesworth et al., 2011). Intensive urbanisation of the Croatian capital of Zagreb has led to a situation where very good agricultural soils, particularly for vegetable production, are entrapped within urban and suburban areas. On the example of the Zagreb region (Northwest Croatia), different approaches to the assessment of the soil trace metals spatial variability and level of contamination will be demonstrated.

4.2.1 Data acquisition

The research on pollution in agricultural soils of the Zagreb region and establishment of the monitoring on a regional scale has started in 1997. At the beginning, the survey was carried out on approximately 860 km² of urban and suburban areas of the city of Zagreb. Later on, the research was extended for about 3000 km², covering agricultural soils of the City of Zagreb and the surrounding Zagreb County.

A total of 916 topsoil (0-20 cm) samples were collected using a systematic sampling on a 2-km grid, with sampling density increasing to 1 km within the industrial and residential area and wine-growing areas (Fig. 2). The observation sites were spatially referenced using GPS and data were stored in different GIS layers. Site survey, carried out during sampling process, provided site-specific information related to land use and other human activities near the sampling points.

For the determination of soil properties, the surface soil samples (average weight of 2 kg) were air-dried and mixed well. A subsample of about 1 kg soil was sieved through a 0.5-mm mesh. Digestion in aqua regia (HRN ISO11466, 2004) was done by the microwave technique on a PerkinElmer Multiwave 6MF 100 (1000W) apparatus in closed TFM vessels and with automatic pressure and temperature regulation. Heavy metal concentrations in soil digests were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a VistaMPX AX (Varian).

Before any solution for the problem of soil heavy metal pollution can be suggested, a distinction needs to be made between natural anomalies and those resulting from human activities. Namely, it often happens that also natural concentrations and distribution of potentially toxic metals could present health problems, like in the case of chromium, cobalt, and particularly nickel in ultramafic soils (Proctor & Baker, 1994). Rock type and geological-geochemical processes can change markedly in a relatively small area, resulting in great spatial variability in the soil content of elements. The region exhibits a variety of soils developed on diverse lithologies described in detail by Sollito et al. (2010). The oldest stratigraphic units are represented by the Paleozoic magmatic and metamorphic complex of the deep earth crust (Fig.

3a), mostly comprising diabases, gabbros, greenschist and blueschist facies rocks outcropping at Mt Medvednica (Belak & Tibljaš, 1998). These types of rocks are known to have a chemical composition characterized by high content of heavy metals, such as Ni and Cr, which are accumulated during the weathering processes in the soil (Alloway, 1995). Mesozoic calcareous rocks (mostly dolomite and limestone) outcrop at NW. Paleozoic-Mesozoic massif is rimmed by Miocene sediments due to the presence of tectonic structures. These deposits are composed by a transgressive sequence of calcareous breccias and conglomerates, marls, clays, sands and silts (Vrsaljko et al., 2005). The main geo-lithological features are the Pliocene and Quaternary alluvial sediments of the Sava River basin in the central and southern parts of the studied area. Terraced sediments outcrop mainly in the western and southwestern sectors of the region and consist of gravel and sands, and secondarily of sandy and silty clays. The sediments in the floodplain area and in the recent stream beds consist of coarse grained sandy-clayey silts and silty clays, with thin layers of charcoal that were flooded from the Slovenian coal mines. Moreover, Pleistocene deposits are made of pond sediments and non-carbonate loess mixed with sand and gravel. Quartz is the main component of the light mineral fraction of these sediments.

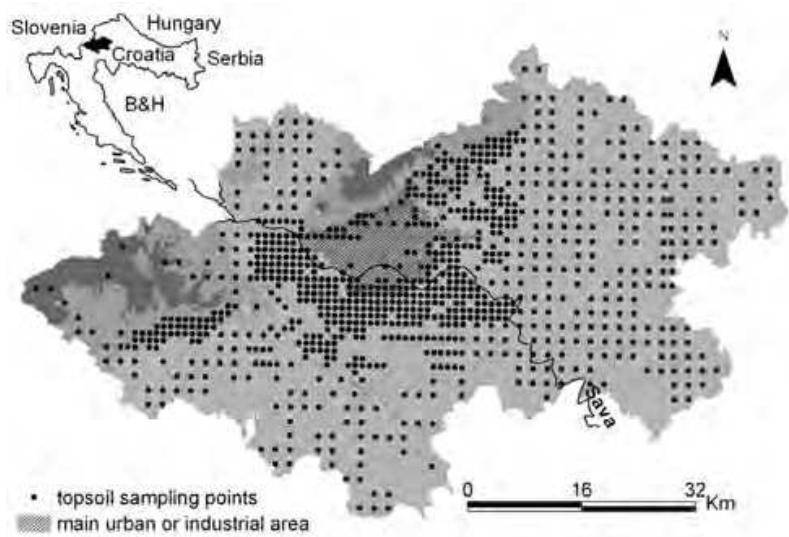


Fig. 2. Study area and sampling locations

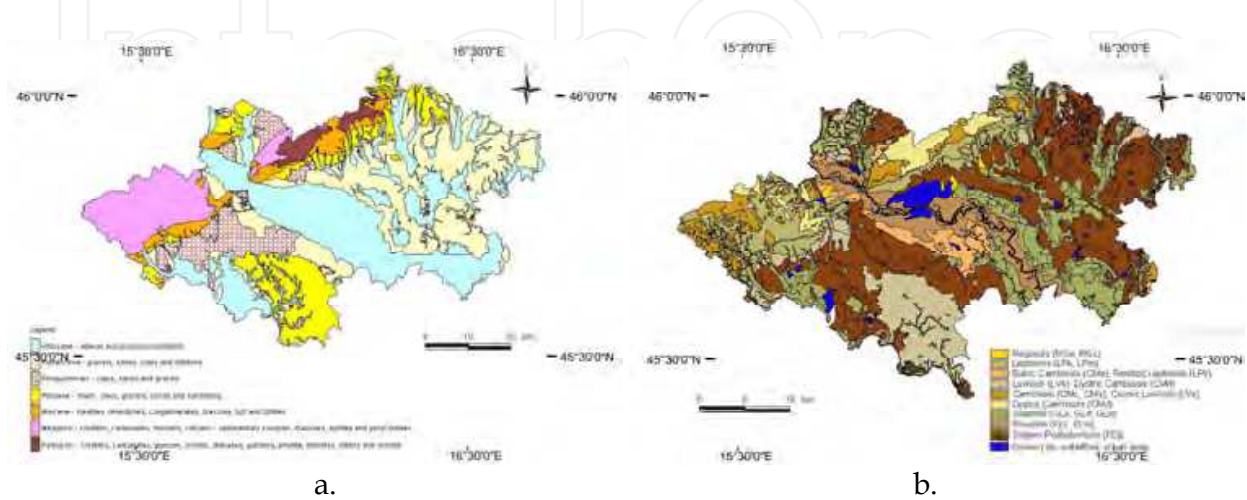


Fig. 3. a) Simplified geologic map of the studied area; b) Simplified soil map of the study area

The large heterogeneity of the parent material, combined with the climate and geomorphology of the Zagreb region, has caused the development of a wide variety of soil types (Fig. 3b). Since the floodplain soils are mixture of the material eroded from the geological units present in the catchment basin, the mineralogical and chemical composition as well as the textural properties of the sedimentary deposits in the alluvial region are largely influenced by the dynamic of the Sava River flow and its solid transportation. Hydromorphic soils prevail in the Sava River valley, where the recent deposits form fluvial terraces. Molic Fluvisols, Calcaric Fluvisols, Eutric Cambisols, Eutric and Calcic Greysols are developed on the Holocene deposits. In the area of Pleistocene terraces, Stagnic Podzoluvisols prevail on the plateau, whereas Stagnic Podzoluvisols and Glayic Podzoluvisols are prevalent on the slopes (FAO, 1998). More than 50% of the land is used for agriculture: soils developed on loamy aeolian materials are mostly used for intensive cultivation of field crops (like cereals), but some of them are under permanent grassland. Anthropogenic vineyard soils, classified as Aric Anthrosols (FAO, 1998), of the Mt Medvednica foothills were formed on Tertiary carbonate deposits of marl and limestone. Moreover, as the Žumberačka Gora piedmont spreads perpendicularly to the mountains, some slopes are firmly interlinked by ridges, forming well protected, amphitheatre-shaped vineyard areas. The presence of intense agricultural activities imposes the risk of soil contamination due to the use of pesticide, which sometimes may constitute a diffuse source over large regions. In addition to agricultural land use other main usage classes are forest, covering the mountain areas and some parts of the terraces, pasture and orchard. Local source of pollution may be related to industrial areas and urban networks, which are scattered distributed over the floodplain, as well as to mining activities which are mainly located in the upstream regions.

Soils in the vicinity of urban areas and industry are exposed to input of potentially toxic elements, and the situation of agricultural soils gets additionally complicated due to continuous application of agrochemicals.

In practice, soil pollution by heavy metals is commonly assessed by interpolating concentrations of heavy metals sampled at point locations, so that each heavy metal is represented in a separate map (Fig. 4).

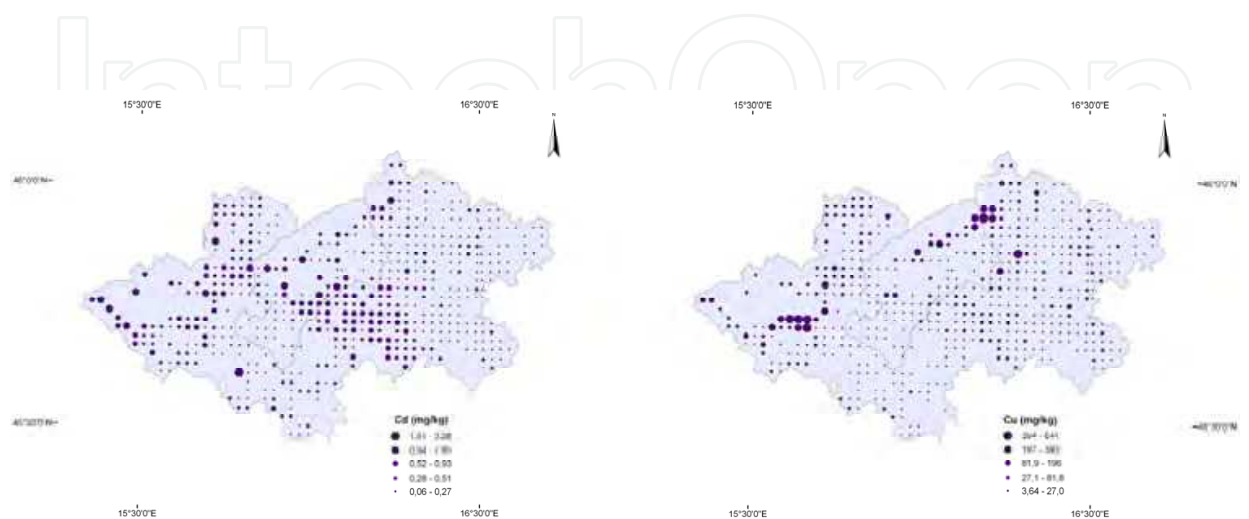


Fig. 4. Cadmium and copper contents at the point locations of the study area

4.2.2 Assessing spatial variability

Spatial variation of soil properties within a field, including trace element contents, is extremely complex, even in a small scale. Therefore it is important to apply methods that may describe this variability. First step in the data processing is the exploratory analysis in spatial data processing. Summary statistics calculation on the dataset (shown in Table 1) provided information about the frequency distribution on the concentrations of chemical elements in the topsoil; the results were compared with some reference values (Table 1).

Variable	Mean	Median	SD	Min	Max	Skewness	Kurtosis	Soils worldwide ^a	Upper continental crust ^b	MPC ^c
Ba (mg kg ⁻¹)	224	220	68.2	12.7	421	0.19	3.09	500	584	-
Ca (g kg ⁻¹)	18.4	5.20	37.3	0.67	214	3.25	13.4	14	29.5	-
Cd (mg kg ⁻¹)	0.40	0.31	0.34	0.02	4.94	5.58	57.7	0.3	0.102	2
Co (mg kg ⁻¹)	10.9	10.8	3.62	2.74	47.2	1.96	16.7	10	24	50
Cr (mg kg ⁻¹)	54.6	51.2	21.1	11.5	400	5.86	91.2	80	126	100
Cu (mg kg ⁻¹)	56.1	23.5	117	3.64	1335	4.56	29.3	25	25	100
Fe (g kg ⁻¹)	29.7	28.9	7.77	5.85	59.1	0.26	2.91	35	30.9	-
Mg (g kg ⁻¹)	8.04	6.51	5.43	0.77	36.6	2.98	12.7	9	13.5	-
Mn (mg kg ⁻¹)	597	556	266	79.2	4537	4.28	56.0	530	527	-
Ni (mg kg ⁻¹)	35.2	29.7	23.8	0.70	488	8.51	148	20	56	60
P (mg kg ⁻¹)	722	675	300	213	3023	2.36	13.6	750	665	-
Pb (mg kg ⁻¹)	23.2	19.6	14.4	1.00	216	5.24	54.2	17	14.8	150
S (mg kg ⁻¹)	407	349	249	47.7	2683	2.52	16.7	800	-	-
Sr (mg kg ⁻¹)	92.9	55.5	136	17.2	1846	6.17	56.5	240	333	-
Zn (mg kg ⁻¹)	77.9	70.7	33.6	27.1	479	4.28	39.6	70	65	300

^a Median, after Reimann and de Caritat (1998)).
^b Mean, after Wedepohl (1995).
^c Maximal permissible concentrations defined by the Croatian government

Table 1. Summary statistics of element concentrations in soils of the study area

The background concentrations of the elements in soils were mostly lower than the average element concentrations in the upper continental crust (Wedepohl, 1995) and were similar to the worldwide median values in soils (Reimann & de Caritat, 1998). Except for the cobalt, the concentrations of all other elements exceeded the maximum permissible concentration (MPC) defined by the Croatian government, with critical conditions recorded for copper, nickel and chromium. For these elements, the maximum concentrations exceed the MPC by up to ten times. Nevertheless, the mean values for all samples were lower than the critical thresholds, meaning that the high values are unevenly distributed in the region. Only a relatively small proportion of samples had concentrations of Ni, Cu and Cr exceeding the MPC (9%, 8% and 1.4% of all samples, respectively). As confirmed by the skewness values (Table 1), the concentrations of elements are characterized by large variability, with positively skewed frequency distributions. This is common for heavy metals, because they usually have low concentrations in the environment, so that the presence of a point source

of contamination may cause a sharp increase of local concentration, so exceeding the thresholds. The concentrations of Ni and Cr higher than the MPC were mainly recorded near the urban area of Zagreb and on the northern edge of the city, whereas the Cu concentration exceeding MPC was found all over the piedmont belt surrounding the northern Paleozoic and Mesozoic relieves. Only the Fe and Ba data distributions are nearly normal, with small differences between the mean and median values and the skewness values close to 0. In contrast, the Mg and Ca concentrations in the topsoil showed a skewed distribution with high values where calcareous rocks outcrop.

As confirmed by the skewness values (Table 1), the concentrations of elements are characterized by large variability, with positively skewed frequency distributions. This is common for trace metals, because they usually have low concentrations in the environment, so that the presence of a point source of contamination may cause a sharp increase of local concentration, so exceeding the thresholds. Skewness measures the asymmetry of the observations. Normal distribution is symmetrical and its mean, mode and median coincide at its centre. When the distribution is skewed then the mean does not represent the central data value that causes the unreliability of the statistics. The problem of processing geochemical and environmental data sets is elaborated in details elsewhere (Zang & Selinus, 1998; Reinman & Filmoser, 2000; Webster & Oliver, 2001). Data transformation enables approaching to the normal distribution, reduces the influence of high values, stabilizes variance and thereby enables the next data processing, as shown on Figure 5.

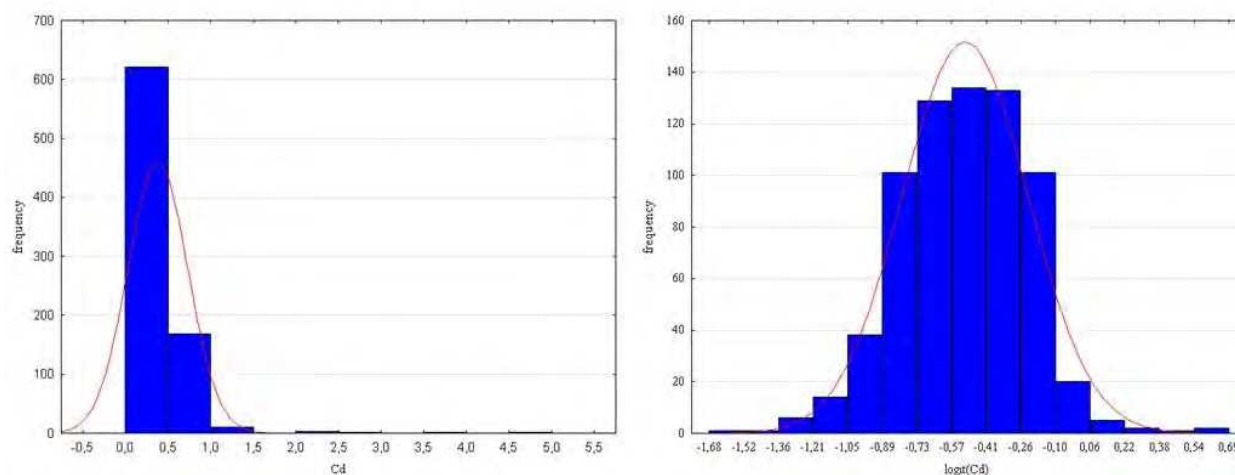


Fig. 5. Histogram of cadmium concentrations before and after logit transformation

Classic geostatistics methods based on univariate analysis can provide distribution maps for each pollutant and delineate the areas where its concentration exceeds the threshold values (Fig. 6). Although the concentration patterns of the elements could suggest probable sources of contamination (Atteia et al., 1995) each chemical element or pollutant might have its own distinctive spatial distribution making difficult to get an overall picture of the contamination.

To solve a problem of presenting overall polluted areas, Romic & Romic (2003) applied factor analysis prior to interpolation and then interpolated factor scores (Fig. 7). As a multivariate method, factor analysis (FA) facilitates the reduction, transformation and organization of the original data by the use of intricate mathematical techniques, which eventually results in a sample form of factor model. Factor analysis creates a new set of

uncorrelated variables, which are the linear combination of the original ones with the same amount of information. Since the FA is conducted if the original variables have significant linear intercorrelations, the first few factors will include the largest part of the total variance. The interpretation of dominant factors was made by taking into account the highest factor loadings on chemical elements. The theoretical details of the FA are given by Johnson (1998).

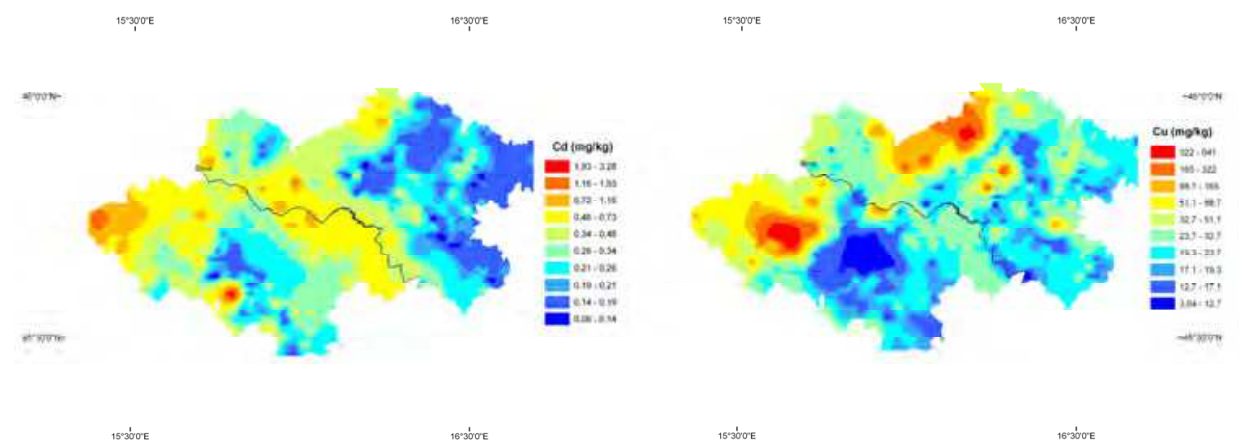


Fig. 6. Interpolated maps of cadmium and copper contents in soils of the study area

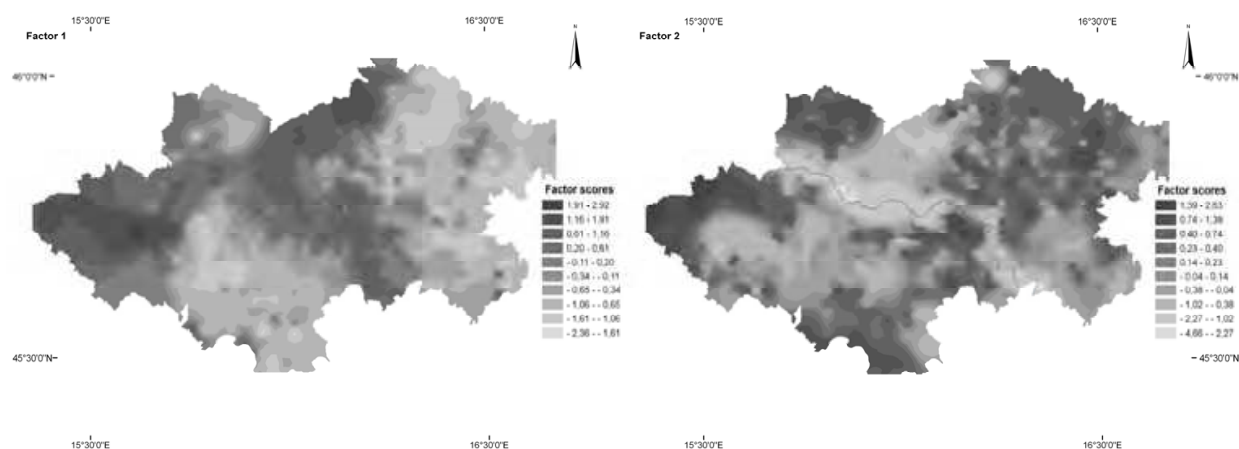


Fig. 7. Contour maps of the distribution of factor scores

Van der Gaast et al. (1998) used maps of background values of soil contaminants focusing on the 90-percentiles. Hanesch et al. (2001) tested fuzzy classification algorithms to distinguish different sources of pollution. Amini et al. (2004) classified HMCs using unsupervised fuzzy k-means to partition the values optimally. The final outputs are maps of memberships to each cluster, which commonly reflect the combination of most correlated heavy metals. In all these examples the procedures are statistically valid, but the meaning of such factors and continuous memberships is hard to interpret. In practice, decision makers usually only wish to see the areas that are polluted without any training in (geo)statistics. Legislative regulations on maximal permitted soil concentrations of potentially toxic elements from practical reasons are setting sharp boundaries. As additional criteria for the soil pollution assessment other soil properties that control metal behaviour in soil are usually set up. Therefore, geochemical data have to be integrated with the detailed soil characterization. Spatial variation of soil properties within a field is extremely complex,

even in a small scale. Main questions interrogating in so doing are how we can measure and model this variability and how this variability affects land use decision-making and environmental quality.

For the study area of NW Croatia, it was assumed that the distribution of trace element contents is systematic, i.e. controlled by natural and anthropogenic factors. The problem appears when the complex interactions between these factors allows for local yield of high natural concentrations of potentially toxic metals in soils, which may exceed the threshold limits designated for contaminated areas (Myers & Thorbjornsen, 2004, Amorosi & Sammartino, 2007). Therefore, statistical and spatial analysis tools were utilised in order to combine the quantitative information obtained from the chemical analysis of the soil samples with the area-specific qualitative information. Romić et al. (2007) applied the regression block kriging for spatial interpolation of heavy metals. A list of potential predictors was used as auxiliary data in the RK model (geological and land cover map, NCVI, water table depth, slope, distance to urban area and roads and wind exposition. After the heavy metal concentrations had been interpolated, they were converted to limitation scores. This study was shown that in the Zagreb region, only 7.2% of the total area is critically polluted by one or more heavy metals.

The applied procedure for geostatistical analysis of heavy metal concentration data successfully identified a number of contamination hotspots in the studied region. The limitation of using the scores is that the high overall pollution can be due to very high values of single element, or due to a cumulative effect of large number of contaminants. But the methodological framework of cumulative limitation scores (CLS) opens several perspectives, i.e. to relate the CLS directly with the remediation costs (Broos et al., 1999), or to observe how heavy metal concentrations change at different scale. In addition, one might consider the methodology of error propagation (Heuvelink, 1998) to derive the composite uncertainty of the final soil pollution map. Geostatistical simulations would help us to get an idea about the propagated uncertainty, but can also be used as an input to a more complex environmental data modelling.

The maps of cumulative limitation scores might be advantageously used to target sampling and/or delineating contaminated zones with lower costs. However, the procedure is suitable in many other decision situations, especially for making decisions about soil remediation, health risk assessment or contaminated land management in general.

5. Conclusion

Risk assessment is the basic element of sustainable management of the agricultural environment because it provides answers to the question about how safe is a studied medium for a population in a given time period and under defined conditions of that medium and population. Risk assessment is the basis for selecting sustainable solutions for allocation of agricultural soils as well as for undertaking efficient measures for remediation of contaminated soils. In the case of trace metals, risk assessment is a demanding and complex task. Metals have a very complex chemical behaviour in the environment and, unlike organic compounds, are not subject to degradation processes. The problem of metals in agricultural environments is enhanced by their potential for mobilization under specific soil physical and chemical conditions. A direct effect of this mobilization is a faster translocation of metals into deeper soil layers, and thereby possible contamination of groundwater. Increased mobility of metals in soil is a frequent effect of fertilization or

application of composts and other organic amendments in a solid form. Therefore, metals risk assessment is an important tool for establishing protective levels in different environmental media. The critical scientific issues that need addressing are the various properties of metals environmental chemistry, bioavailability and bioaccumulation. Bioavailability assessment methods need to be elaborated on as well.

Chemical speciation of metals, their bioavailability, bioaccumulation and toxicity are the key elements in assessing the potential harmful impacts of metals upon the environment and human health. Metal bioavailability is a complex issue that depends on a series of properties related to soil matrix, plant characteristics, and environmental conditions. An interdisciplinary approach is therefore required in risk assessment studies. Bioavailability can be used as an element of risk assessment only if all risk assessors apply the same approach. Such a uniform approach to bioavailability assessment will enable establishment of standard methods for soil analyses and contribute towards developing new legislation on soil protection, particularly those related to persistent immobile substances such as metals and polycyclic aromatic hydrocarbons.

Climate changes are currently the focus of numerous studies because their indirect consequences can affect the geochemical and biological cycling of metals as well. The main aim of these studies is to define the indicators that best describe bioavailability of a metal under given environmental conditions. Reliable information on soil contamination by trace metals is needed, as well as the application of geostatistical methods for determining trace metal variation in soil and identifying possible sources of contamination.

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We are increasingly faced with environmental problems and required to make important decisions. In many cases an understanding of one or more geologic processes is essential to finding the appropriate solution. Earth and Environmental Sciences are by their very nature a dynamic field in which new issues continue to arise and old ones often evolve. The principal aim of this book is to present the reader with a broad overview of Earth and Environmental Sciences. Hopefully, this recent research will provide the reader with a useful foundation for discussing and evaluating specific environmental issues, as well as for developing ideas for problem solving. The book has been divided into nine sections; Geology, Geochemistry, Seismology, Hydrology, Hydrogeology, Mineralogy, Soil, Remote Sensing and Environmental Sciences.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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