



New insights on mobility and bioavailability of heavy metals in soils of the Padanian alluvial plain (Ferrara Province, northern Italy)



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ABSTRACT

Heavy metals having both natural and anthropogenic origin are common contaminants in soils and sediments, and can be transferred and bioaccumulated at all levels of the food chain, posing serious environmental concern to the local population. In this paper, agricultural soils from the Province of Ferrara (easternmost part of the Padanian Plain, northern Italy) were investigated to assess the levels of potentially toxic metals in relation to their phytoavailability. Agricultural soils have been sampled in order to identify the origin, mobility and bioavailability of heavy metals, collecting superficial and deeper (depths of 20–30 and 100–120 cm, respectively) horizons. The “total” XRF analyses properly elaborated with a statistical approach reveal that soils evolved from two distinct types of alluvial sediments, in turn related to the Po and Reno rivers; the former type is distinctively enriched in heavy metals (particularly Cr and Ni), reflecting the presence of femic and ultrafemic rocks in the hydrological basin of River Po. The absence of Top Enrichment Factors for Ni, Co, Cr, V, and Pb suggests that the content of these elements is natural and unaffected by contamination, whereas superficial enrichments of Cu (and Zn) is ascribed to anthropogenic inputs related to agricultural activities. Multiple extraction tests using variously aggressive reactants (aqua regia, DTPA, EDTA, NH₄NO₃, and H₂O) analyzed by ICP gave insights on the specific mobility of the distinct elements, which decreases in the following order: Pb > Cu > Cd > Co > Ni > Cr. Taking into consideration the elements that are inducing the main concerns, Cr appears scarcely mobile, whereas Ni could be more phytoavailable and has to be monitored in the local agricultural products. Cd although scarcely abundant has to be monitored for its mobility and toxicity, whereas Cu although abundant and extremely mobile doesn't induce concerns as it is not hazardous for the living receptors.

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1. Introduction

Heavy metal distribution in soil systems can derive by the weathering of rocks or by anthropogenic pollutants. Obviously, the anthropogenic sources related to agriculture, industry, and urban emission overprint the natural “geogenic” heavy metals backgrounds and consequently increase the risk of contamination for the food chain (Peralta-Videa et al., 2009).

This paper investigates the heavy metal distribution in soils from the easternmost part of the Padanian Plain (northern Italy), implementing previous studies that emphasized the presence of natural anomalies consisting of high contents of nickel and chromium (Amorosi et al., 2002; Amorosi, 2007; Bianchini et al., 2002, 2012, 2013).

The new data (124 XRF and 224 ICP analyses) integrate those existing in the literature (Bianchini et al., 2012, 2013), thus forming an extended data set useful to understand the heavy metals distribution and their behaviour. Moreover, this paper re-evaluate the potential geochemical risks, highlighting that the studies available in the literature were mainly based on total (or pseudo-total) analyses of heavy metals, whereas environmental monitoring and assessment have to take into consideration the specific elemental mobility and phytoavailability (Kabata-Pendias, 2004). In fact, the active fraction of metal, available for organisms and plants, is related to the metal speciation, in turn depending to the mineralogical, chemical and biochemical characteristics of soils. These concepts have been introduced to predict plant uptake and potential bioaccumulation processes, and therefore many soil extracting procedures are used to define the specific elemental phytoavailability (Gupta and Sinha, 2007). The main question is: do high metal concentrations of the Padanian soils imply a geochemical risk? In our view, a priori expectation is unknown. The answer necessarily

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requires the investigation of the elemental mobility that could be evaluated with specific extraction tests, including aggressive reagents such as aqua regia, or weak chelating agents such as EDTA and DTPA that are widely used to simulate chelating solution in the soils (Kabata-Pendias, 2004). Accordingly, we leached the studied soils both with EDTA and DTPA and we also tested the rhizosphere-based extraction method that uses low-molecular-weight organic acids (Feng et al., 2005) to simulate the exudates released by plant roots as well as the products of fungi and bacteria activity (Fox and Comerford, 1990). Finally, we tested extractions with NH_4NO_3 that induces cation-exchange, as well as extractions with simple water. This approach therefore provides for the first time series of combined extraction tests to define potential bioaccumulation in the agricultural soils of the Padanian plain, in order to predict the extent to which living receptors are exposed to heavy metal contaminants.

2. Physiographic outlines and sampling strategies

The Padanian plain is located in the homonymous basin between the Alps and the Apennines and receives sedimentary contributes from numerous tributaries having a distinct provenance. In particular this basin can be considered the retroforeland of the Alps and the foredeep of the Apennines, and was characterized by marine sedimentation in Pliocene to Early Pleistocene, before progradation of fluvial sediments that was enhanced during glaciation periods. Fluvial sediments were conveyed in the Plain by rivers coming from both the Alps and the Apennines (Garzanti et al., 2011). The sedimentary deposits of Alpine rivers (e.g., Po River) formed extensive tabular bodies, whereas the sedimentary deposits of Apennine rivers (e.g., Reno River) are constituted by relatively small fans (Garzanti et al., 2011). As reported in the recent CARG geological maps of the Emilia-Romagna region and synthesized by Amorosi and Pavesi (2010) these Quaternary continental sediments are mapped as UBSU (unconformity-bounded stratigraphic units) and notionally grouped within the Emilia-Romagna super-synthem, in which the upper part is called Upper Emilia-Romagna synthem.

The outcropping sedimentary facies reflect climatic changes and human impacts that deeply modified the configuration of the local drainage system, which in the studied area is represented by the migrating branches of the Po and Reno rivers (Bondesan et al., 1995; Amorosi et al., 2002; Amorosi, 2012; Bianchini et al., 2002, 2012; Stefani and Vincenzi, 2005). These rivers were characterized by high lateral mobility of the active channel belts, with recurrent flooding and channel bifurcation, which redistributed the water and sediment fluxes throughout the system. The deposition environments were therefore characterized by distinct hydrodynamic energy, and distinct sedimentary facies (Bianchini et al., 2014). The new samples considered in this study were sampled around the town of Argenta ($44^\circ 36' 47''$ N, $11^\circ 50' 11''$ E; Fig. 1). The identification of sampling sites was based on the geological-geomorphological map of the area (geologic map of Ferrara, 1:250,000, Servizio Geologico, Sismico e dei Suoli della Regione Emilia Romagna) in which the different alluvial facies of the Po and Reno rivers' sediments were identified. The rationale behind the site selection was to include all the different geomorphological units (and lithological types) outcropping in the area.

Sampling was carried out as described by Bianchini et al. (2012); taking into consideration that the depth of tillage involving soil digging, stirring, and overturning is usually ca 50 cm, in each selected site, according to the procedure delineated by Facchinelli et al. (2001) and Ungaro et al. (2008), two samples were collected: one representative of the plough horizon (just beneath the roots zone, at a depth of 20–30 cm) and the other representative of the underlying undisturbed layer (at a depth of 100–120 cm). The comparison

allows the evaluation of the magnitude of the possible Top Enrichment Factor (TEF) induced by anthropogenic contributions.

3. Analytical methods

Major and trace elements (Ni, Co, Cr, V, Sc, Pb, Zn, and Cu) were analysed by X-ray fluorescence (XRF) on powder pellets, using a wavelength-dispersive automated ARL Advant'X spectrometer at the Department of Physics and Earth Sciences of the University of Ferrara. Accuracy and precision were based on systematic re-analysis of standards; for major elements they were better than 3% for Si, Ti, Fe, Ca and K, and 7% for Mg, Al, Mn and Na and for trace elements (above 10 mg kg^{-1}) they were better than 10%. Investigation was also carried out with extraction test by aqua regia (AR), as defined by official Italian methods for soil analysis, following the procedure proposed by Barbaferi et al. (1996). According to this protocol: (a) 1 g of powdered sample is wet with a few ml of water and acidified with a few drops of HNO_3 within 250 ml Erlenmeyer flasks (made of high-quality borosilicate glass); (b) 20 ml of hydrogen peroxide (H_2O_2) are added and properly stirred; (c) solutions are evaporated down to 3 ml by heating on a hot plate; (d) further 9 ml of HCl + 3 ml of HNO_3 (i.e. 12 ml of aqua regia) are added and heating continues for 2 h; (e) the obtained solutions are centrifuged, filtered and transferred to other flasks that are taken to the final volume of 100 ml. Subsequently, the analyses were carried out using an X Series Thermo-Scientific spectrometer at the Department of Physics and Earth Sciences of the University of Ferrara. Specific amounts of Rh, In and Re were added to the analysed solutions as an internal standard, in order to correct for instrument drift. Accuracy and precision, based on replicated analyses of samples and standards were better than 10% for all elements, well above the detection limit. As reference standards, the E.P.A. Reference Standard SS-1 (a type B naturally contaminated soil) and the E.P.A. Reference Standard SS-2 (a type C naturally contaminated soil) were also analysed to cross-check and validate the results.

Further extraction tests were performed with less aggressive reactants. Extraction procedures using 0.05 M EDTA, 0.005 M DTPA, 1 M NH_4NO_3 , and a "rhizosphere solution" were carried out according to Feng et al. (2005). Briefly, for the EDTA extraction 2 g soil were dissolved in 20 ml 0.05 M EDTA and adjusted by an ammonia solution to pH 7.0, shaking for 1 h (Wear and Evans, 1968). For the DTPA extraction, 10 g of soil were shaken for 2 h within 20 ml 0.005 M DTPA + 0.01 M TEA + 0.01 M, according to Lindsay and Norvell (1978). The rhizosphere-based extraction protocol was performed on 2 g of soil mixed with 20 ml of acetic, lactic, citric, malic acids in 4:2:1:1 molar concentration, for a total molar concentration of 10 mM; the soil suspension was shaken for 16 h and centrifuged at $300 \times g$ for 10 min and an aliquot of supernatant (10 ml) was removed immediately by a pipette and immediately acidified with suprapure HNO_3 (Feng et al., 2005). All extraction procedures were carried out in triplicate, including the blanks. For the NH_4NO_3 extraction (Gupta and Sinha, 2007), 10 g of soil were added in 50 ml of 1 M NH_4NO_3 and shaken for 2 h at room temperature. Water extraction was performed with deionized water and 10 g soil, which were shaken with 100 ml of deionized water for 16 h, then centrifuged at $300 \times g$ for 15 min and stabilized with suprapure HNO_3 . All solutions were subsequently analysed by ICP-OES (SpectroAmetek) at the Department of Agricultural Science of the University of Bologna.

4. Results

4.1. Soil characterization by XRF analyses

The new XRF analyses reported in supplementary Table [a] represent the "total" composition of soils from the surrounding of the

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