

DISTRIBUTION OF HEAVY METALS IN THE AGRICULTURAL SOIL OF THE FERRARA ALLUVIAL PLAIN

DARIO DI GIUSEPPE

Dipartimento di Scienze della Terra, Università di Ferrara, Via Saragat 1, 44100 Ferrara

INTRODUCTION

The knowledge on the chemical composition of terrains and its regional variability is essential to understand the origin (natural vs. anthropogenic) of potentially harmful elements; moreover, it is very important to assess the human impact and to fix guide values and quality standards.

In particular, in alluvial areas the geochemistry of sediments records complex tectonic, climatic and hydrological processes occurring within a river basin. The varying contributions of confluents which drain geologically different sub-basins lead to various geochemical signatures on the sedimentary deposits, reflecting the geochemistry of the mother rocks and the weathering mechanisms. Moreover, in urbanized areas, anthropogenic contributions can overprint the pristine (geogenic) geochemical signatures of the alluvial sediments.

This study investigates the easternmost part of the Po River Plain in northern Italy, *i.e.* a sedimentary basin bordered by the Alps and Apennines that hosts about 30-40% of the Italian population and most of Italy's total productive activities.

The outcropping sedimentary facies reflect climatic changes and human impacts that deeply modified the configuration of the local drainage system, represented by the evolving Po River (containing significant part of the Alpine belt in his catchment) and minor rivers, such the Reno River, flowing down from the Apennines (Amorosi *et al.*, 2002; Bianchini *et al.*, 2002; Stefani & Vincenzi, 2005; Simeoni & Corbau, 2009).

In the easternmost and terminal part of the basin, in historical times, high lateral mobility of the active channel belts also permitted the development of fens and swamps (probably developed in few decades) characterized by peat deposition. When the high-energy alluvial deposition outranged the organic deposition, the peat level was buried and incorporated into the stratigraphic record (Miola *et al.*, 2006).

In this paper we focus the attention on the geochemistry of sediments collected in the surrounding of the city of Ferrara, around the towns of Argenta and Vigarano, where alluvial sediments, consisting of sands, silts and clays related to both the Po River and the Reno River, have been recognised. A fourth sampling zone has been focused close to the Town of Ostellato (Mezzano Zone) where the organic-rich fine sediments prevail.

The data, presented as GIS-based geochemical maps, intend to define the geochemistry of the main facies of the area, highlighting the local backgrounds of potentially harmful elements, such as the heavy metals, and nutrients (such as nitrogen), which are progressively affecting the interacting waters causing eutrophication problems (Mastrocicco *et al.*, 2009). The results should be taken in consideration by the local authorities to provide guidelines for the agricultural activities.

SAMPLING STRATEGIES AND ANALYTICAL METHODS

The sampling sites were selected taking into consideration the geological-geomorphological map of the area (geologic map of Ferrara, 1:50000, 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, in order to investigate all the different terrains outcropping in the area. Each sampling point was georeferenced by using a portable global positioning system (GPS), for locating the points and for setting up future field surveys.

In each selected site, according to the procedure delineated by Ungaro *et al.* (2008), samples were taken at depths of 30-40 cm and at 90-120 cm, in order to evaluate the magnitude of possible Top Enrichment Factor

(TEF) induced by anthropogenic contributions. Samples were divided into distinct aliquots, to carry out grain-size and chemical/mineralogical investigations.

The amount of organic material was evaluated on thermo-gravimetric basis; a known weight of sample, placed in a ceramic crucible, was heated between 350 and 440°C overnight. Samples were cooled in a desiccator and then weighted. Organic matter content is calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%.

Mineralogical characterization was carried out by X-ray diffraction (XRD) using a Philips PW1860/00 diffractometer, using graphite-filtered $\text{CuK}\alpha$ radiation (1.54 Å) to recognise the constituent mineralogical phases. Diffraction patterns were collected in the 2θ angular range 3-30°, with a 6 s/step (0.02 2 θ). Further mineralogical characterization was obtained by electron microprobe using a Cameca SX 50 electron microprobe at the IGG-CNR Institute of Padova.

Major and trace elements (Ni, Co, Cr, V, Rb, Ba, Sr, Nb, Zr, Pb, Zn, and Cu) were analyzed by X-ray fluorescence (XRF) on powder pellets, using a wavelength-dispersive automated ARL Advant'X spectrometer at the Department of Earth Sciences of the University of Ferrara. Accuracy and precision for major elements are estimated as better than 3% for Si, Ti, Fe, Ca, and K, and 7% for Mg, Al, Mn, and Na; for trace elements (above 10 ppm) they are better than 10%.

Further investigations of these samples were performed with leaching tests. These tests of heavy metals extraction were done with HNO_3 and HCl 1:3 (according to the Italian official methods of soil analysis) and analysed by ICP-MS. The analyses were done using a VG Plasma Quad2 plus at the Department of Earth Sciences of the University of Ferrara. Accuracy and precision, based on replicated analyses of samples and standards, were estimated as 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 as cross-check. The analyzed solutions were also added of known amount of Rh, In, and Re used as internal standard to correct instrumental drifts. These data indicated the mobility of metals under the different chemical-physical conditions and, therefore, they were useful to determine a potential geochemical risk to cultivations and natural waters.

As concerns the analysis of soluble salts, including nitrate that represents a key parameter to envisage anthropogenic contributions, the Italian Legislation (Italian Ministerial Decree 13/09/1999 "Official methods for the analysis of soils") prescribes the following analytical protocol: 30 g of the sediments is taken in contact with 150 ml of deionized Milli-Q water stirring for 2 hours, leaving to settle overnight, and then filtering with a Whatman Grade No. 42 Filter Paper. The resulting solutions were subsequently analyzed by ion chromatography using an ICS-1000 Dionex instrument.

COMPOSITION OF THE SEDIMENTS

Petrographic observations, XRD analyses, and microprobe data indicated that the alluvial sediments of both Po River (Ps) and Reno River (Rs) included quartz, feldspars, calcite, and micas that were prevalent in the coarse sands, as well as phyllosilicates such as illite, kaolinite, chlorite, serpentine and smectite that tended to prevail in the finer fractions.

The relative chemical compositions were obviously related to the presence and relative abundance of the above mentioned minerals. In both the sample populations (Ps and Rs) K_2O and Rb were positively correlated with Al_2O_3 , thus suggesting that they were associated with Al-bearing mineral phases (such as the clay minerals), whereas CaO was inversely correlated with Al_2O_3 and SiO_2 suggesting that most of the CaO budget was related to the presence of a carbonatic mineral fraction.

The chemical analyses of samples that were investigated by grain size characterization revealed that heavy metals were mainly partitioned in the fine fraction, plausibly in association with the clay minerals.

However, within our sampling collection, sediments of different provenance, *i.e.* Ps and Rs were perfectly discriminated in the diagrams reporting Cr and Ni (ppm) *versus* MgO and Al_2O_3 (wt.%).

For example, in the zone around Vigarano we observed the following differences between Ps and Rs sediments:

i) Rs showed MgO content lower than 3 wt.%, with an average composition of 2.30 wt.%, and a median composition of 2.33 wt.%; Ni content was lower than 100 ppm, with an average composition of 59 ppm and a median composition of 60 ppm; Cr content is lower than 142 ppm, with an average composition of 103 ppm and a median composition of 102 ppm;

ii) Ps showed MgO content higher than 3 wt.%, with an average composition of 3.51 wt.% and a median composition of 3.54 wt.%; Ni content was higher than 90 ppm, with an average composition of 116 ppm and a median composition of 114 ppm; Cr content is higher than 135 ppm, with an average composition of 190 ppm and a median composition of 185 ppm.

The same elements appeared also correlated with other metals such as V and Co, and within each population a positive correlation is observed also with the Al₂O₃ content.

Therefore, the relative metal enrichment of Ps indicated that the minerals included in their fine fractions are peculiarly enriched in MgO, Ni, Cr, V, and Co. This evidence was already recorded by Chiorboli & Lenzi (1992) who recognized the significant presence of serpentine in Ps, and by Bianchini *et al.* (2002) who indicated that within Ps samples chlorite was peculiarly abundant and enriched in MgO. This implies that the mother rocks included in the Po River catchment are more enriched in metals, because they include femic and ultrafemic rocks that are unknown in the catchment of Reno River.

Therefore, this high concentration of metals in some of the local sediments has to be considered a natural (geogenic) geochemical anomaly.

This conclusion was further verified by taking into account the composition of ancient bricks from the historical buildings of Ferrara (Bianchini *et al.*, 2006). These bricks, made with local clay-rich sediments, analogous to those considered in this study, in ages preceding any significant form of anthropogenic pollution, showed composition strictly comparable with those presented in this study.

This statement was also confirmed by the lack of enrichment in the uppermost part of the soil profile, *i.e.* by the lack of TEF (Ungaro *et al.*, 2008), calculated as the ratio between topsoil and subsoil estimated concentrations.

The only surprising evidence, provided by the more superficial samples, was the existence of samples with intermediate features between Ps and Rs; these hybrid samples were collected in a sector where the Ps and Rs were juxtaposed in the outcrop and plausibly interlayered along a depth profile. The intermediate compositions thus represent the result of homogenization induced by agricultural (ploughing) activities.

Samples from the surroundings of Ferrara and Argenta displayed an analogous bimodal distribution with both Ps and Rs compositions. On the other hand, samples from the Mezzano were extremely enriched in organic material (up to 10%) thus representing a sedimentary facies resulting from a marshy environment; similar environments are quite widespread in the easternmost part of the Po River along its terminal delta. The geochemical composition of these samples was characterized by very high Cr, Ni, and V contents, thus suggesting a remarkable role of the organic matter in the metal complexation. This hypothesis is supported by various experimental studies (*e.g.* Twardowska & Kyziol, 2003, and references therein) and it is typically verified in natural peats (Bonnett & Cousins, 1987).

The obtained analyses were geo-referenced on a GIS basis providing various geochemical maps in which symbols with different colours express a different magnitude of metal enrichment, overlying geological/geomorphological information on the sedimentary facies, such as the grain-size of the sediment provenance (Po River *vs.* Reno River).

INSIGHTS ON THE ENVIRONMENTAL MANAGEMENT OF THE AREA

The high content of metallic elements recorded in the investigated samples causes environmental concerns. The concentrations of transition elements recorded in the sediments sampled in the Ferrara

surroundings were compared with the maximum concentrations admissible in terrains used for residential purposes and public “green areas” (Italian Legislative Decree n. 152, 03/04/2006). Within the Ps group of samples, the concentration of Ni and Cr tended to be higher than the maximum admissible concentration (120 ppm for Ni; 150 ppm for Cr). The reported analyses also involved guidelines for agricultural activities. For example, following the Italian Legislative Decree n. 99 (27/01/1992), some terrains included in the Ps group and containing more than 75 ppm of Ni could not to be treated and fertilized with sewage sludge (Minnini & Sartori, 1987).

However, it has to be noted that these tolerance limits expressed by the Italian legislation are not referred to the “bulk” concentration of the solid matrix, but to the amount of metal “extractable” by a leaching solution as described above. Therefore, metals were analysed by ICP-MS on the solutions obtained according with the legislative guidelines. Results showed that the metal concentration of the “extracted” solutions were usually lower than the bulk concentration. Comparing average XRF analyses on the bulk sample and ICP-MS analyses on the “extracted” solution we can state that about 45% of the total Cr budget is mobile, and that about 75% of the total Ni budget is mobile.

The Cr concentration appeared to be below the tolerance limits in all the investigated samples, whereas Ni concentration of some Ps sediment exceeded the legislative limit.

The As concentration in some of the Ps samples was also exceeding the legislative limit (Italian Legislative Decree n. 152, 03/04/2006) for green areas used for public/private residential purposes that indicates a tolerance threshold of 20 ppm. In this case, the comparison between average XRF analyses on the bulk sample and ICP-MS analyses on the “extracted” solution revealed that this element could be extremely mobile. This geochemical behaviour suggests that it is contained in Fe-Mn oxides/hydroxides and/or in sulphides, *i.e.* in mineral phases that are extremely sensitive to pH and Eh variation and hence that can be easily destabilized (Smedley & Kinniburgh, 2002).

The high level of nitrates seems to represent a further environmental problem, because many of the investigated terrains contained a nitrogen content higher than the tolerance limit stated by the EU’s Nitrates Directive (91/676EC). This evidence implies that the studied zone has to be considered a Nitrate Vulnerable Zone (NVZ) in which nutrient over-enrichment ultimately results in pollution of the coexisting groundwater (Mastrocicco *et al.*, 2009) which, in turn, induce eutrophication and algal blooms in the aquatic ecosystems. In this framework, farmers should minimize the use of nitrogen-rich fertilizers and adopt more sustainable land management practices.

CONCLUSION

The Ferrara province, as most of the Po River plain, is characterized for more than 70% of its territory by agricultural soil. An environmental concern is the elevated concentration of heavy metals in the agricultural soils that can determine a potential toxicity for the plants and for their consumers.

In this framework, the Department of Earth Sciences of the University of Ferrara realized a study on the heavy metals concentration in the agricultural soils, in which the two principal sediment types characterizing the Ferrara alluvial plain (related to the Po River and Reno River respectively) were investigated.

The sampling was done including all the principal geological characteristics representative of the area. Two different samples were collected at each sampling site: a) within depths of 90-120 cm to determine the “background values” of heavy metals in the soil and b) at depths of 30-40 cm to determine the TEF of heavy metals in the soil.

The bulk chemical analysis by X-ray fluorescence (XRF) for the determination of major (wt.%) and trace elements (ppm), discriminated two well-delineated populations of samples, respectively characterized by high values of Cr (> 150 ppm) and Ni (> 100 ppm) in the Po River alluvial sediments and by low values of Cr (< 150 ppm) and Ni (< 100 ppm) in the Reno River alluvial sediments.

The statistic and graphic elaboration of the chemical data showed a positive correlation among the distributions of Cr and Ni ($R_2 > 0.6$). Cr and Ni were also positively correlated with MgO, Al₂O₃, and V, as well with the clay content determined through grain size analysis.

Specific thematic cartography highlighted relationships among the sedimentary facies of the area and the concentration of heavy metals. Cr and Ni showed maximum concentration in the Po floodplain organic clays, whereas lower concentrations were found in the Reno channel-levee sands and silt.

Coherently, the analysis of the fine-grained fraction of the samples (< 63 µm) showed higher (20-60%) concentration of Cr and Ni with respect to the coarse fraction.

The Cr/V and Cr/Al₂O₃ ratios were good geochemical indicators of sediment provenance of the Ferrara alluvial plain: Cr/V > 1.4 and Cr/Al₂O₃ > 10.7 corresponded to the sediments of the Po River; Cr/V < 1.4 and Cr/Al₂O₃ < 10.7 corresponded to the sediments of the Reno River.

The values of the TEF, determined by the ratio between the concentrations of Cr and Ni of the superficial samples and those recorded at the depths of 90-120 cm, are nearly equal to 1 for Cr and smaller than 1 for Ni indicating the absence of heavy metals pollution within the examined agricultural soils.

The agricultural soils that were found in the alluvial sediments of the Po River were characterized by elevated background values of Cr and Ni that represent a natural geochemical anomaly originated by the peculiar mineralogical composition of the fine-grained fraction, probably constituted by Cr-, Ni-rich phyllosilicates such as chlorite and serpentine. This hypothesis was confirmed by *in situ* electron microprobe analyses on these minerals.

Further investigations of these samples were performed with leaching tests. These tests of heavy metals extraction indicate the potential mobility of metals under the different chemical-physical conditions and therefore are useful to determine the potential geochemical risk to cultivations and natural waters. Nevertheless, these tests highlighted, for all the investigated samples, concentration lower than the tolerance limits of the Italian legislation.

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