

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment, Archaeometry and Cultural Heritage*

Soil-water interaction in soils of the Po River Plain (Ferrara, Northern Italy): insights on heavy-metal mobility and phytoavailability

Gianluca Bianchini^{1,2,*}, Dario Di Giuseppe¹ and Livia Vittori Antisari³

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

²Istituto di Geoscienze e Georisorse, C.N.R., Via Moruzzi 1, 56124 Pisa, Italia

³Dipartimento di Scienze Agrarie, Alma Mater Studiorum, Università di Bologna, Via G. Fanin 40,
40127 Bologna, Italia

*Corresponding author: bncglc@unife.it

Abstract

The soils of the Po River Plain, developed on the alluvial sediments, are often characterized by high concentrations of heavy metals, in particular chromium and nickel. These geochemical anomalies are geogenic, i.e. related to the nature of the rocks outcropping in the basin that typically include mafic and ultramafic lithologies. The elevated heavy metal backgrounds of soils potentially represent an effective geochemical risk considering the toxicity of these elements. In order to delineate soil quality thresholds and to provide guidelines for human activities (e.g. agriculture) the current legislation takes into consideration the “pseudototal” metal concentration obtained with aqua regia extraction tests. However, only a fraction of this chemical budget is available for plant and human uptake. Soil leaching tests with deionized water plausibly provide a better analogue to simulate soil-water interactions, in order to predict the behavior of metals in the environment. In particular, in this paper we investigate with water leaching tests agricultural soils sampled in the surrounding of Ferrara (eastern part of the Po River Plain) that were previously characterized by XRF bulk analyses and aqua regia extractions. The approach gives insights on the specific transport parameters of distinct elements, giving clues for a) the possible contamination of natural waters and b) the soil-to-plant uptake processes and phytoavailability. The results, expressed as solid-water partition coefficients, highlight that nickel and arsenic are mobile and bioavailable and should be monitored in the local agricultural products to avoid its possible transfer and bioaccumulation in the food chain.

Key words: soils; Po River Plain; heavy metals; element-specific transport parameters; soil-to-plant uptake; water contamination.

Introduction

The soils are very complex multiphase dynamic systems and their understanding necessary requires the integration of several scientific disciplines, including geochemistry. The results of these multidisciplinary studies give insights on the soil development processes, the interaction processes at the water-soil interface, as well as the possible occurrence of pollution processes. Coherently, the characterization of potential pollutants in topsoil and their fate along the soil profile is important to evaluate the hazard of groundwater contamination and the availability for plants. The understanding of these processes is therefore an important goal for the scientific community (Carlon et al., 2004; Peralta-Videa et al., 2009; Watson et al., 2012; Wennrich et al., 2012). In this framework, the geochemical study of soils can also provide background information for the sustainability of agricultural practices.

In particular, this contribution investigates agricultural soils outcropping in the Padanian Plain (Northern Italy) close to the city of Ferrara, where anomalously high contents of metals (in particular chromium and nickel) were highlighted by previous studies (Amorosi et al., 2002; Bianchini et al., 2002; 2012; Sammartino, 2004). These studies mainly focused on bulk chemical analyses and chemical extractions by aqua regia or EDTA, while the aim of this study is to assess the mobility and availability of metals using water leaching tests of soil rhizosphere (samples collected at depth between 30 and 40 cm) that give more reliable indications of the element-specific transport parameters in natural conditions. In fact, the chemistry of water leachates represents the soil porewater integrated with soluble elements. The liable components result from reactions between the interacting fluid and the surface of minerals and organic matter. This approach gives indications for understanding both environmental pollution and

phytoavailability of heavy metals (Kabata-Pendias, 2004; Cappuyns and Swennen, 2008; Rennert and Rinklebe, 2010).

Geological and geochemical outlines

The study area is included in the eastern part of the Po River Plain (Northern Italy), i.e. a sedimentary basin bordered by the western-central Alps and the northern Apennines (Figure 1). The samples were collected in the vicinity of the village of Vigarano Mainarda (near Ferrara) where soils have formed and developed from alluvial deposits. A simplified pedological description, taken from the soil map available in the Emilia Romagna Region web site (www.suolo.it), is reported in supplementary Table 1*. These soils are characterised by a young depositional age (Holocene), fluvial reworking and extensive agricultural activities (ploughing). The pristine alluvial sediments, consisting of sand, silt and clay are referred to both the Po and Reno rivers (Figure 1). Coherently, samples are hereafter subdivided in two distinct affinity groups 1) soils developed from Po alluvial sediments (Ps hereinafter) and 2) soils developed from Reno alluvial sediments (Rs hereinafter). Previous studies (Amorosi et al., 2002; Bianchini et al., 2002; 2012; Amorosi, 2012) highlighted the differences in bulk chemical composition of Rs and Ps, emphasizing that Ps are significantly enriched in heavy metals (in particular Cr and Ni) with respect to Rs (supplementary Table 2*). The high Cr-Ni contents of Ps are related to the presence of Cr- and Ni-rich phyllosilicates such as chlorite and serpentine, deriving from the weathering process of femic and ultrafemic rocks that significantly crop out in the Po River basin (Bonifacio et al., 2010; Amorosi, 2012). On the contrary, femic and ultrafemic rocks do not crop out in the basin of the Reno River that drains the Bolognese sector of the Apennines, thus explaining the paucity of heavy metals in the related alluvial sediments.

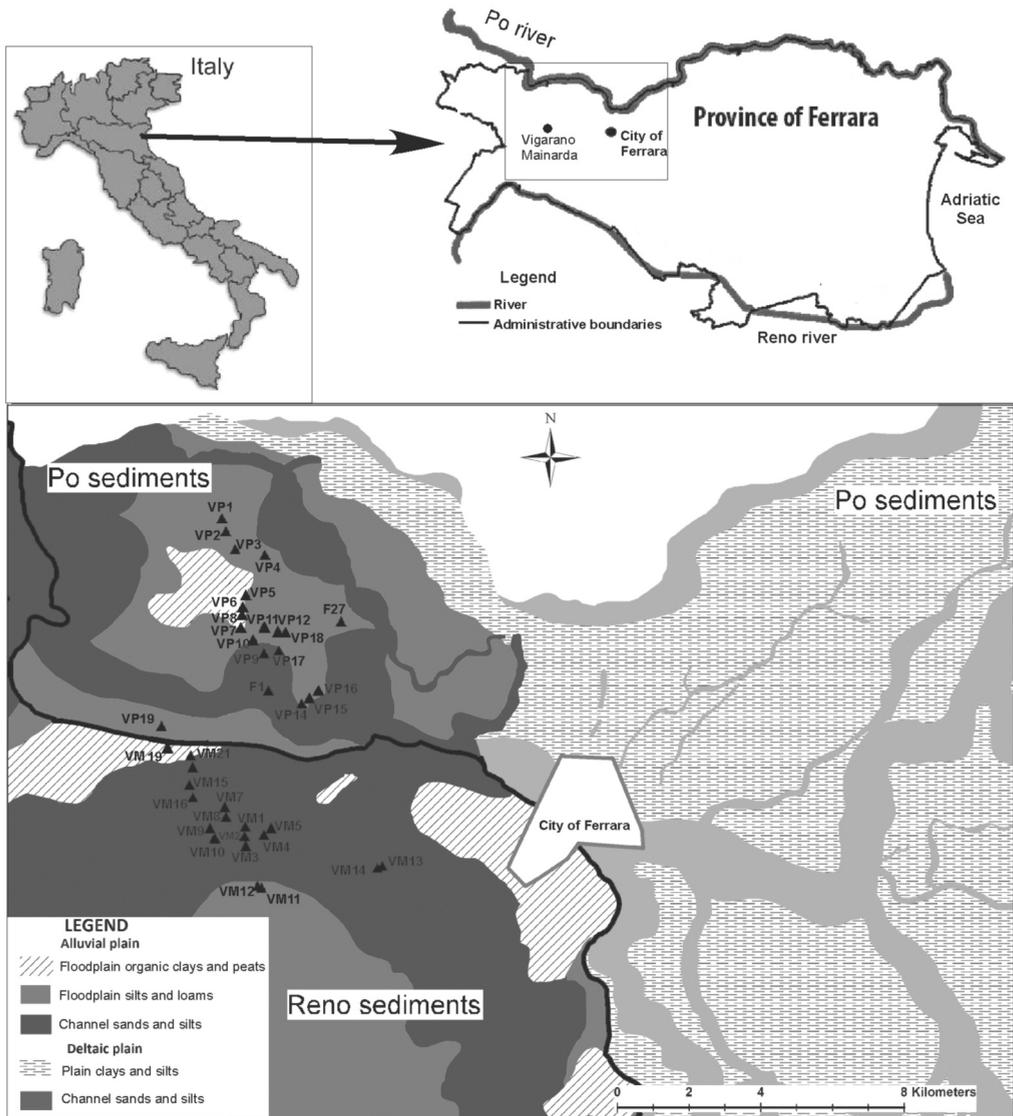


Figure 1. Geographic and geological outlines of the studied area, reporting the sites of sample collection (modified after Bianchini et al., 2012). In the geological sketch, the boundary between the alluvial sediments of the Po River (Ps) and those of the Reno River (Rs) is represented by a tick black line.

Materials and methods

Geo-referenced sites were carefully selected to include the different soil types of the area, and

samples were preliminarily characterized by Bianchini et al. (2012); the studied soils are Inceptisols and Vertisols and the samples were collected from the rhizosphere zone (30 - 40 cm

depth) using an Edelman auger (Eijkelkamp). The soil sampling was carried out when the crops (wheat and corn) were still cultivated, and a few of these plants were also harvested for grain analysis (supplementary Table 3*). The soil samples have been characterized by a) grain-size investigation; b) XRF bulk analysis; c) ICP-MS bulk analysis after total acid (HF + HNO₃) digestion; d) aqua regia extraction (HCl + HNO₃) and ICP-MS analysis of the solutions (Bianchini et al., 2012). In this contribution we implement the available data presenting and discussing a series of extraction tests in which the studied soils were leached with ultra-pure deionized water obtained from a Milli-Q purifier system (Millipore Corp., Bedford, MA, USA). In particular, experiments were carried using a soil/water weight ratio of 1/5 (5 mg of soil powder in 25 ml of water); the soils and water were mixed and sealed in beakers, then shaken for 1 h, and centrifuged for 1 h at 25 °C to separate the sediment and the solution, then analyzed using ICP-MS. 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 analyzed solutions as an internal standard, in order to correct for instrument drift. Accuracy and precision, based on replicated analyses of samples and standards are better than 10% for all elements, well above the detection limit. As reference standards, the E.P.A. Reference Standard SS-1 (B type naturally contaminated soil) and the E.P.A. Reference Standard SS-2 (C type naturally contaminated soil) were also analyzed to cross-check and validate results.

Results and discussion

The concentrations of metals in water leachates of the different soils are reported in Table 1. The hazard of groundwater pollution was measured comparing results with legislative

limits that define groundwater quality standards (column A in Table 2). The comparison highlights that the studied soils release harmful amounts of Ni, Co, Cr (total), As, Al, Fe, Mn and Pb. Additional insights are provided by the comparison with the maximum threshold admissible in leaching test of waste material (column B in Table 2), confirming that the samples release worrying amounts of Ni, Cr, As, Pb and V, thus indicating a potential geochemical risk for the interacting surface and groundwaters. Conversely, concentrations of Cu and Zn do not exceed the reported legislative thresholds defined for drinking water and do not induce environmental concerns.

It is interesting to note that the average contents of the different metals (Figure 2) subdivide the samples of rhizospheric soil in two distinct populations as a function of their developing on the Ps or Rs, respectively. This is also observed in the relative XRF bulk analyses (supplementary Table 2). The difference between the two populations is emphasized in Figures 2 and 3, showing that the water leachates of the Ps soils are significantly enriched in Ni and Cr. Results of a more general elaboration that include all the analyzed elements in the water leachates are reported as correlation matrix (CM) in Table 3 in which the different Pearson coefficients measure the link between two quantitative variables, highlighting inter-element relationships that can provide interesting information on element sources and pathways. The CM of Table 3 confirms that the Rs and Ps soils are well discriminated from each other and Ni and Cr are extremely correlated with Mg (Figure 3) and Fe. In the Ps leachates Ni, Co, Cr and V are extremely correlated also with Al, Li and subordinately K, indicating release from Mg-bearing clay minerals such as serpentine and chlorite. Arsenic, although less abundant than the above mentioned metals, is recorded in the Ps leachates with values up to 0.28 ppm; in these samples the correlation between As and Fe is

significant, suggesting that As is released from iron oxides/hydroxides.

Origin of heavy metals and insights on their mobility

The elevated background concentrations of heavy metals are renowned in the Po River Plain and are interpreted as a natural feature of the local environment, unrelated to anthropogenic activities (Amorosi et al., 2002; Bianchini et al., 2002; 2012). This conclusion is supported by

1) absence of top enrichment factor along the considered soil profiles (Bianchini et al., 2012);

2) analogous compositions recorded in sediments from deep (up to 40 m) cores of the Plain (Amorosi et al., 2002);

3) similar heavy metal concentrations in suspended particles of the River Po water (Vignati et al., 2003);

4) similar composition of ancient bricks and mortars from historical buildings of Ferrara made with local sediments and manufactured in times preceding any significant form of anthropogenic pollution (Bianchini et al., 2004; 2006).

The concentrations of heavy metals measured in studied Ps soils are thus a geogenic characteristic to be related to the peculiar features of the pristine alluvial sediments, in turn including components released by the weathering of femic and ultrafemic rocks widespread in the basin of Po River (Amorosi, 2012).

Do these soil features imply a geochemical risk? This question has to be addressed evaluating specific transport parameters of distinct heavy metals, i.e. evaluating their real mobility. In this light, the presented leaching tests obtained with deionized water give some clues, as they simulate water-soil interaction that commonly occur in the environment. Partition coefficients ($K_d = C_{\text{Soil}}/C_{\text{Leachate}}$) are obtained for the distinct elements of each sample comparing the leachate compositions of Table 1 to the bulk compositions of supplementary Table 2*. As

proposed by similar studies (Allen et al., 1995; Carlon et al., 2004; Luo et al., 2006; Wennrich et al., 2012), the $\log K_d$ of the elements have been plotted in Figure 4 to give an idea of their relative mobility. It can be observed that in the studied soils, the elevated background of chromium (and vanadium) is not associated to a high elemental mobility in water. Elements such as nickel, zinc and lead are decidedly more mobile. A more accurate estimation of the mobilized percentage of an element *i* needs to consider the amounts of powder and water actually used in the leaching experiments, i.e. the milligrams of *i* in 5 grams of soil and those in 25 ml of extracting solution, as expressed in Table 4 for Ni, Cr and As as an example. The results of this approach, reported in Figure 5, indicate that the leaching experiments are effective in mobilizing up to 5% Ni and 3% Cr with respect to the original budget. According to these results, natural waters of the area invariably display higher nickel than chromium (Bianchini et al., 2013); however, the absolute concentrations of the natural surface- and ground-water are always lower than a) the WHO (World Health Organization) limits for drinking water and b) the concentrations of the leachates, also indicating that more reliable experiments would require different solid/water ratios and times of interaction. As concerns arsenic, being the XRF bulk composition not available, its remarkable mobility (Table 4) has been estimated considering the concentrations of the aqua regia extracts as a pseudo-total (Ruiz-Cortés et al., 2005). The mobility of this element poses concerns on quality of the local natural waters that often display concentration exceeding the 10 ppb thresholds defined by WHO for drinking purposes (unpublished Authors data).

Conclusions

The data presented above have important implications for the agricultural activities of the

Table 1. ... Continued

Po affinity (Ps)

Sample	VP9	VP10	VP11	VP12	VP13	VP14	VP15	VP16	VP17	VP18	VP19
Element (ppm)											
Li	0.21	0.42	0.32	0.28	0.22	0.25	0.23	0.28	0.15	0.22	0.31
Na	1.07	1.94	1.10	1.51	1.96	1.36	1.55	1.48	2.01	1.81	1.50
Mg	96.9	146	117	107	96.1	114	93.0	99.7	81.9	105	115
Al	135	270	206	185	142	157	157	176	89.5	130	183
K	20.9	33.2	31.6	33.2	26.5	24.9	23.6	21.1	18.1	19.1	23.9
Ca	390	469	295	386	332	423	216	473	360	509	286
V	0.24	0.49	0.44	0.35	0.30	0.29	0.31	0.36	0.18	0.26	0.36
Cr	0.85	1.43	1.13	1.19	0.92	1.01	0.95	1.05	1.12	0.85	1.07
Mn	6.25	6.78	5.88	6.26	6.22	6.50	6.19	10.9	6.01	6.73	9.54
Fe	130	226	191	161	136	149	153	193	103	137	190
Co	0.12	0.19	0.15	0.13	0.11	0.13	0.12	0.16	0.09	0.12	0.16
Ni	0.76	1.31	1.03	0.88	0.80	0.91	0.88	1.04	0.62	0.81	1.12
Cu	0.47	0.39	0.34	0.28	0.43	0.42	0.32	0.77	0.20	0.28	0.32
Zn	0.66	0.92	0.70	0.67	0.73	0.61	0.59	0.79	0.53	0.56	0.72
As	0.14	0.20	0.16	0.16	0.13	0.16	0.14	0.32	0.12	0.17	0.16
Sr	1.28	1.60	1.07	1.43	1.17	1.29	0.69	1.43	1.18	1.65	1.16
Cd	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01
Pb	0.13	0.18	0.15	0.13	0.12	0.13	0.16	0.17	0.10	0.10	0.15
U	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01

Reno affinity (Rs)

Sample	VM12	VM13	VM14	VM15	VM16	VM19	VM20	VM21
Element (ppm)								
Li	0.30	0.17	0.24	0.23	0.22	0.33	0.27	0.25
Na	1.94	1.13	2.01	1.82	2.14	1.33	0.97	1.39
Mg	75.7	58.4	75.4	64.3	65.5	58.9	61.3	58.5
Al	182	104	138	151	158	221	159	159
K	35.2	23.7	29.0	28.0	30.1	31.9	29.8	27.7
Ca	522	373	580	375	462	385	403	375
V	0.49	0.31	0.41	0.40	0.41	0.33	0.25	0.29
Cr	0.49	0.41	0.44	0.41	0.42	0.48	0.44	0.38
Mn	7.49	4.87	7.69	6.01	7.22	5.94	5.94	6.19
Fe	204	150	187	173	170	194	158	175
Co	0.09	0.04	0.08	0.07	0.07	0.09	0.11	0.07
Ni	0.53	0.37	0.51	0.42	0.43	0.46	0.43	0.40
Cu	0.39	0.41	0.74	0.29	0.26	0.34	0.37	0.37
Zn	0.46	0.29	0.45	0.31	0.31	0.53	0.67	0.47
As	nd	nd	nd	nd	nd	nd	0.15	nd
Sr	1.97	1.34	2.32	1.37	1.73	1.39	1.53	1.34
Cd	nd	nd	nd	nd	nd	nd	0.01	nd
Pb	0.11	0.10	0.26	0.09	0.09	0.09	0.12	0.10
U	nd	nd	nd	nd	nd	nd	0.01	nd

Table 2. Minimum, average and maximum concentrations in the leachates of the Vigarano Mainarda soils, compared with legislative compositional thresholds.

Element	Min (ppb)	Average(ppb)	Max (ppb)	A	B
				Italian legislative Decree 152/2006 thresholds for groundwater quality (ppb)	Italian Ministerial Decree dated 5/2/1998 waste material leachates maximum thresholds (ppb)
Al	87760	161137	269500	200	-
V	133	337	550	-	250
Cr	369	781	1432	50	50
Mn	4873	6475	10880	50	-
Fe	103400	172957	242500	200	-
Co	41	119	191	50	250
Ni	372	739	1311	20	10
Cu	199	344	773	1000	50
Zn	183	625	952	3000	3000
As	0	64	317	10	50
Pb	73	129	256	10	50

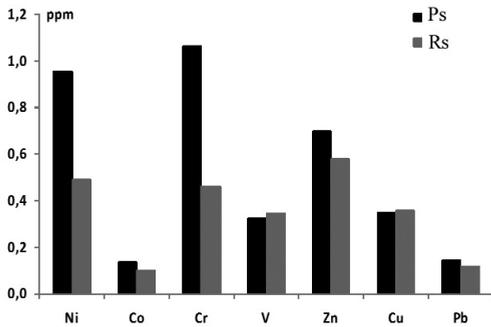


Figure 2. Average heavy metal concentrations recorded in the leachates of the Vigarano Mainarda soils. Ps and Rs indicate the alluvial sediments of the Po River and Reno River, respectively.

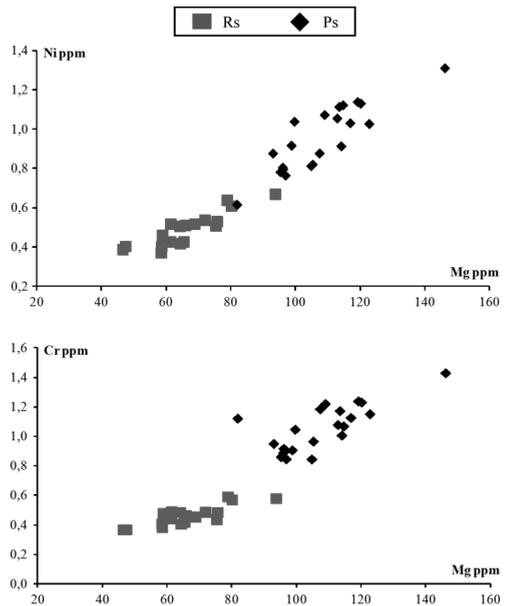


Figure 3. Mg vs. Cr and Ni concentrations, respectively, in the leachates of the Vigarano Mainarda soils; note the significant difference between the results obtained on Ps and Rs soils. Ps and Rs as in Figure 2.

Table 3. Correlation matrix that highlights relationships (in terms of Pearson coefficients) between the different elements in the leachates of the Vigarano Mainarda soils; a) refers to soils evolved from Po River alluvial sediments (Ps); b) refers to soils evolved from Reno River alluvial sediments (Rs).

	Ps	Li	Na	Mg	Al	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Pb
Li	1.00																	
Na	0.08	1.00																
Mg	0.90	0.17	1.00															
Al	0.98	0.10	0.87	1.00														
K	0.73	0.16	0.73	0.73	1.00													
Ca	0.30	0.19	0.35	0.24	0.24	1.00												
V	0.95	0.07	0.79	0.97	0.66	0.14	1.00											
Cr	0.81	0.31	0.73	0.83	0.83	0.25	0.79	1.00										
Mn	0.40	-0.18	0.24	0.38	0.00	0.12	0.41	0.30	1.00									
Fe	0.94	0.19	0.79	0.91	0.65	0.28	0.91	0.76	0.48	1.00								
Co	0.96	0.05	0.83	0.92	0.58	0.30	0.90	0.76	0.58	0.95	1.00							
Ni	0.96	0.13	0.87	0.91	0.64	0.25	0.89	0.75	0.51	0.96	0.34	1.00						
Cu	0.23	-0.31	0.09	0.26	-0.02	0.30	0.28	0.04	0.56	0.28	0.34	0.26	1.00					
Zn	0.81	0.29	0.75	0.82	0.70	0.37	0.78	0.73	0.40	0.81	0.80	0.42	0.80	1.00				
As	0.57	0.18	0.36	0.54	0.25	0.54	0.54	0.45	0.58	0.75	0.67	0.64	0.57	0.57	1.00			
Sr	0.50	0.50	0.47	0.46	0.42	0.70	0.42	0.49	0.12	0.61	0.48	0.48	0.13	0.59	0.67	1.00		
Pb	0.78	0.28	0.64	0.80	0.56	0.18	0.78	0.67	0.35	0.83	0.78	0.80	0.34	0.79	0.61	0.44	1.00	

	Rs	Li	Na	Mg	Al	K	Ca	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Pb
Li	1.00																	
Na	0.23	1.00																
Mg	0.75	0.51	1.00															
Al	0.78	0.25	0.57	1.00														
K	0.65	0.41	0.56	0.80	1.00													
Ca	0.25	0.37	0.37	-0.24	0.04	1.00												
V	0.57	0.69	0.78	0.62	0.55	0.05	1.00											
Cr	0.90	0.28	0.83	0.58	0.51	0.41	0.55	1.00										
Mn	0.51	0.66	0.77	0.48	0.53	0.50	0.69	0.51	1.00									
Fe	0.85	0.45	0.92	0.81	0.66	0.17	0.80	0.80	0.75	1.00								
Co	0.75	0.19	0.52	0.23	0.26	0.63	0.26	0.75	0.38	0.44	1.00							
Ni	0.85	0.41	0.88	0.47	0.46	0.61	0.56	0.94	0.67	0.81	0.80	1.00						
Cu	0.16	0.23	0.48	0.25	0.17	0.04	0.48	0.44	0.22	0.47	-0.05	0.29	1.00					
Zn	0.63	0.07	0.33	0.16	0.07	0.45	0.26	0.61	0.23	0.30	0.91	0.62	0.04	1.00				
As	0.12	-0.16	-0.17	-0.43	-0.31	0.55	-0.33	0.18	-0.21	-0.31	0.70	0.22	-0.42	0.73	1.00			
Sr	0.30	0.47	0.50	-0.04	0.12	0.85	0.35	0.39	0.74	0.36	0.57	0.60	0.32	0.47	0.34	1.00		
Pb	0.21	0.36	0.50	0.09	0.10	0.38	0.39	0.28	0.53	0.37	0.25	0.42	0.87	0.27	-0.05	0.60	1.00	

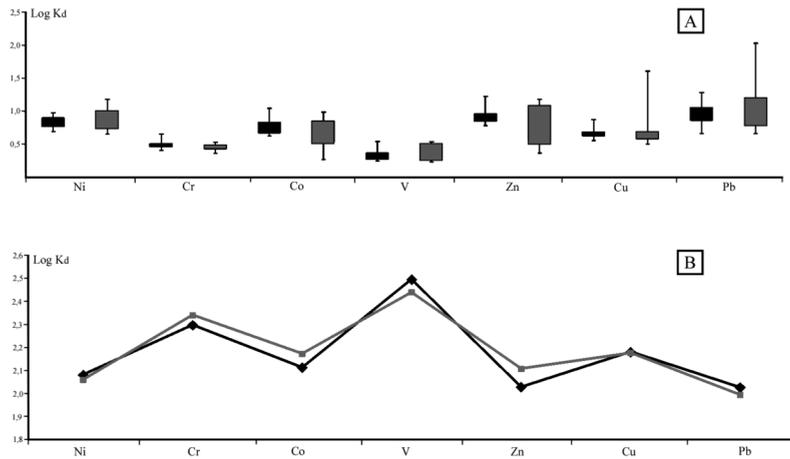


Figure 4. Soil/water partition coefficients obtained by leaching experiments on the Vigarano Mainarda soils. Results are expressed as log Kd ($K_d = C_{\text{Soil}}/C_{\text{Leach}}$), and plotted as box plots (A) and averages (B). Grey and black colours denote Rs and Ps samples, respectively.

Table 4. Specific chromium, nickel and arsenic percent extracted by leaching experiments on soil samples collected in the surroundings of Vigarano Mainarda (close to Ferrara, Po River Plain, Northern Italy).

Sample	Nickel			Chromium			Arsenic		
	ppm		%	ppm		%	ppm		%
	XRF bulk composition	ICP-MS leached		XRF bulk composition	ICP-MS leached		ICP-MS aqua-regia composition	ICP-MS leached	
F1	110	0.78	3.55	182	0.86	2.38	17.8	0.18	5.05
FE27	153	1.07	3.51	229	1.22	2.67	22.2	0.22	5.05
VP1	101	0.81	4.00	189	0.89	2.36	15.7	0.16	5.02
VP2	113	0.92	4.07	203	0.91	2.23	16.8	0.17	5.16
VP3	127	1.06	4.14	212	1.08	2.55	18.6	0.20	5.39
VP4	103	0.82	3.98	190	0.97	2.54	15.1	0.16	5.38
VP5	122	1.14	4.67	215	1.24	2.88	24.3	0.28	5.69
VP6	144	1.12	3.86	232	1.18	2.53	24.9	0.25	5.12
VP7	106	1.03	4.83	190	1.15	3.03	13.7	0.18	6.41
VP8	144	1.13	3.92	240	1.23	2.56	23.2	0.23	5.04
VP9	92	0.76	4.14	205	0.85	2.07	14.0	0.14	5.10
VP10	133	1.31	4.93	217	1.43	3.31	15.6	0.20	6.37
VP11	125	1.03	4.14	226	1.13	2.49	16.3	0.16	5.06
VP12	114	0.88	3.85	224	1.19	2.65	16.2	0.16	5.02
VP13	83	0.80	4.82	181	0.92	2.54	12.1	0.13	5.53
VP14	121	0.91	3.79	197	1.01	2.56	16.2	0.16	5.07
VP15	98	0.88	4.47	210	0.95	2.27	13.5	0.14	5.06
VP16	137	1.04	3.80	224	1.05	2.34	30.2	0.32	5.24
VP17	68	0.62	4.53	219	1.12	2.56	12.2	0.12	5.12
VP18	105	0.81	3.87	181	0.85	2.34	16.7	0.17	5.06
VP19	124	1.12	4.51	235	1.07	2.28	14.1	0.16	5.70

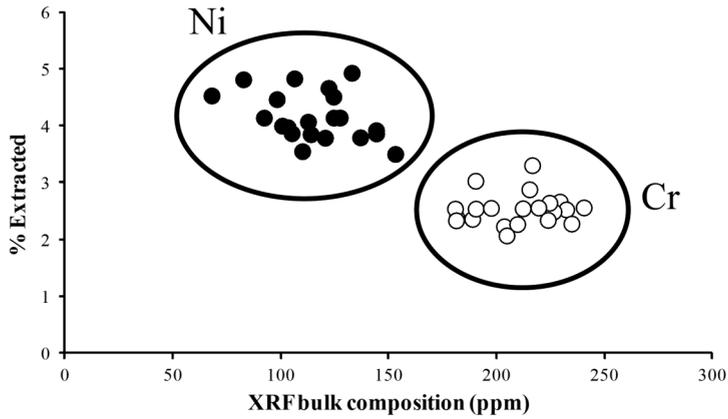


Figure 5. Percent nickel and chromium extracted by the leaching tests on the Vigarano Mainarda soils.

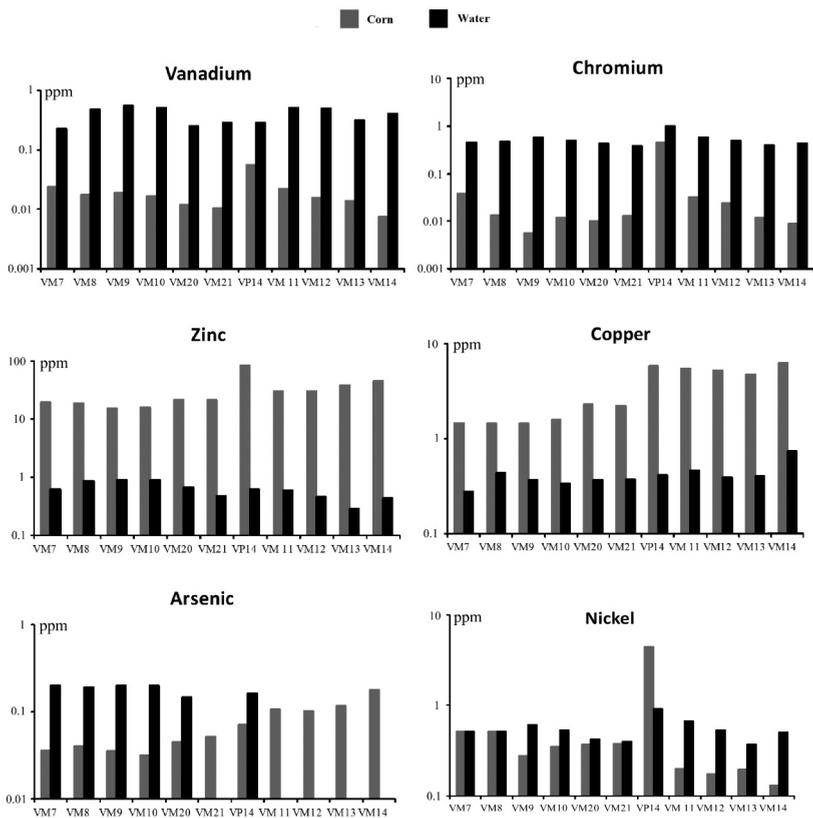


Figure 6. Heavy metal concentrations (ppm) in the leachates of the Vigarano Mainarda soils compared with those analysed in corn grains (Bianchini et al., 2012) cultivated in the same sites.

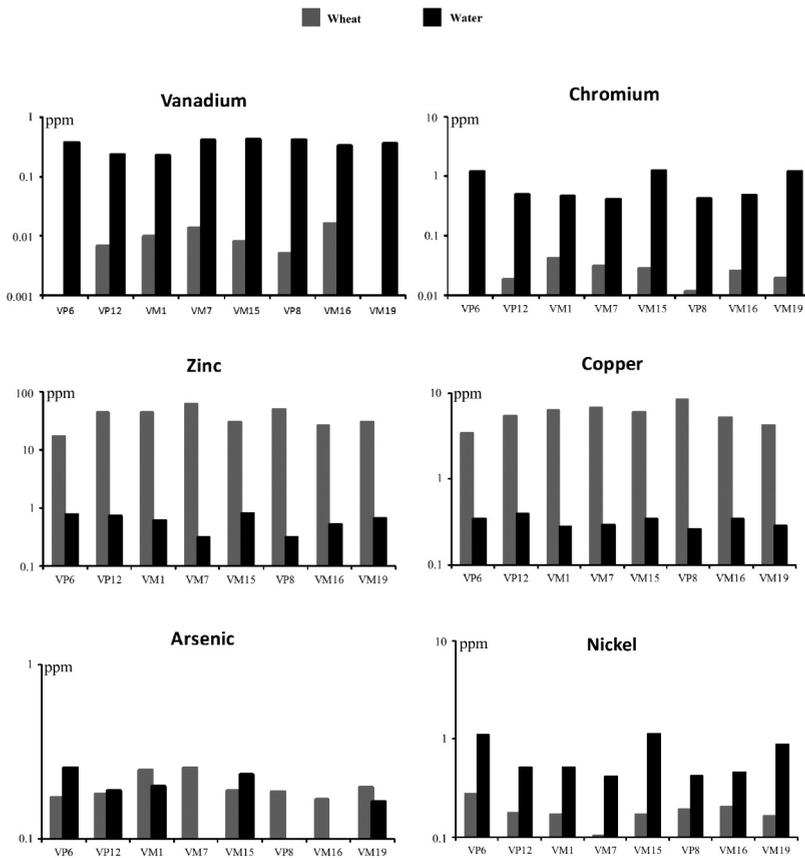


Figure 7. Heavy metals concentrations in the leachates of the Vigarano Mainarda soils compared with those analysed in wheat grains (Bianchini et al., 2012) cultivated in the same sites.

area. The concentrations recorded in the leachates have been compared with the concentrations in the grains of the corn and wheat cultivated in the same sites (Figures 6 and 7). This approach highlights soil-to-plant uptake parameters, i.e. the phytoavailability of the distinct heavy metals, providing clues on the possible occurrence of bioconcentration and bioaccumulation that can potentially transfer toxic components in the human food chain. It can be observed the following order of increasing phytoavailability $Cr, V < As, Ni < Zn, Cu$, and that corn is generally characterized by a higher

tendency to accumulate metals with respect to wheat, with the exception of As that is peculiarly more concentrated in wheat.

The integration of similar studies could indicate the potentially harmful elements to be monitored in the local agricultural products, also suggesting the crop types suitable (or not) for the specific area. Moreover, the use of recycling wastes such as sewage sludge, zootechnical manure, and landfill leachates in the agricultural activities of the area has to be minimized since their heavy-metal contents are often extremely high (Nicholson et al., 2003; Abu-Zeid et al.,

2004) and therefore application rates of these amendments have to be carefully controlled, to obviate the possible accumulation of toxic metals in agricultural soils.

Acknowledgements

The authors thank Dr. R. Tassinari for the analytical support, and Referees and Editors for their constructive comments that helped to improve earlier versions of this manuscript.

References

- Abu-Zeid N., Bianchini G., Santarato G. and Vaccaro C. (2004) - Geochemical characterisation and geophysical mapping of Landfill leachates: The Marozzo canal case study (NE Italy). *Environmental Geology*, 45, 439-447.
- Amorosi A., Centineo M.C., Dinelli E., Lucchini F. and Tateo F. (2002) - Geochemical and mineralogical variations as indicators of provenance changes in Late Quaternary deposits of SE Po Plain. *Sedimentary Geology*, 151, 273-292.
- Amorosi A. (2012) - Chromium and nickel as indicators of source-to-sink sediment transfer in a Holocene alluvial and coastal system (Po Plain, Italy). *Sedimentary Geology* 280, 260-269.
- Allen H.E., Chen Y.-T., Li Y. and Huang C.P. (1995) - Soil partition coefficients for Cd by column desorption and comparison to batch adsorption measurements. *Environmental Science and Technology*, 29, 1887-1891.
- Bianchini G., Laviano R., Lovo S. and Vaccaro C. (2002) - Chemical-mineralogical characterisation of clay sediments around Ferrara (Italy): a tool for an environmental analysis. *Applied Clay Science*, 21, 165-176.
- Bianchini G., Marrocchino E. and Vaccaro C. (2004) - Chemical and mineralogical characterisation of historic mortars in Ferrara (NE Italy). *Cement and Concrete Research*, 34, 1471-1475.
- Bianchini G., Marrocchino M., Moretti A. and Vaccaro C. (2006) - Chemical-mineralogical characterisation of historical bricks from Ferrara: an integrated bulk and micro analytical approach. *London Geological Society, Special Publication*, 257, 127-139.
- Bianchini G., Natali C., Di Giuseppe D. and Beccaluva L. (2012) - Heavy metals in soils and sedimentary deposits of the Padanian Plain (Ferrara, Northern Italy): characterisation and biomonitoring. *Journal of Soils Sediments*, 12, 1145-1153.
- Bianchini G., Di Giuseppe D., Natali C. and Beccaluva L. (2013) - Ophiolite inheritance in the Po plain sediments: insights on heavy metals distribution and risk assessment. *Ofioliti*. doi:10.4454/ofioliti.v38i1.412
- Bonifacio E., Falsone G. and Piazza S. (2010) - Linking Ni and Cr concentrations to soil mineralogy: does it help to assess metal contamination when the natural background is high? *Journal of Soils Sediments*, 10, 1475-1486.
- Carlou C., Dalla Valle M. and Marcomini A. (2004) - Regression models to predict water-soil heavy metals partition coefficients in risk assessment studies. *Environmental Pollution*, 127, 109-115.
- Cappuyns V. and Swennen R. (2008) - The Use of Leaching Tests to Study the Potential Mobilization of Heavy Metals from Soils and Sediments: A Comparison. *Water, Air, & Soil Pollution*, 191, 95-111.
- Kabata-Pendias A. (2004) - Soil-plant transfer of trace elements - an environmental issue. *Geoderma*, 122, 143-149.
- Luo X.-S., Zhou D.-M., Liu X.-H. and Wang Y.-J. (2006) - Solid/solution partitioning and speciation of heavy metals in the contaminated agricultural soils around a copper mine in eastern Nanjing city, China. *Journal of Hazardous Materials*, 131, 19-27.
- Nicholson F.A., Smith S.R., Alloway B.J., Carlton-Smith C. and Chambers B.J. (2003) - An inventory of heavy metals inputs to agricultural soils in England and Wales. *Science of the Total Environment*, 311, 205-219.
- Peralta-Videa J.R., Lopez M.L., Narayan M., Saupe G. and Gardea-Torresdey J. (2009) - The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain. *The International Journal of Biochemistry & Cell Biology*, 41, 1665-1677.
- Rennert T. and Rinklebe J. (2010) - Release of Ni and Zn from contaminated floodplain soils under saturated flow conditions. *Water, Air, & Soil Pollution*, 205, 93-105.
- Ruiz-Cortés E., Reinoso R., Díaz-Barrientos E. and

- Madrid L. (2005) - Concentrations of potentially toxic metals in urban soils of Seville: relationship with different land uses. *Environmental Geochemistry and Health*, 27, 465-74.
- Sammartino I. (2004) - Heavy metals anomalies and bioavailability from soil of southeastern Po plain. *GeoActa*, 3, 35-42.
- Vignati D., Pardos M., Diserens J., Ugazio G., Thomas R. and Dominik J. (2003) - Characterisation of bed sediments and suspension of the river Po (Italy) during normal and high flow conditions. *Water Research*, 37, 2847-2864.
- Watson C.A., Öborn I., Edwards A.C., Dahlin A.S., Eriksson J., Lindström B.E.M., Linse L., Owens K., Topp C.F.E. and Walker R.L. (2012) - Using soil and plant properties and farm management practices to improve the micronutrient composition of food and feed. *Journal of Geochemical Exploration*, 121, 15-24.
- Wennrich R., Daus B., Müller K., Stärk H.-J., Brüggemann L. and Morgenstern P. (2012) - Behaviour of metalloids and metals from highly polluted soil samples when mobilized by water - Evaluation of static versus dynamic leaching. *Environmental Pollution*, 165, 59-66.
- Submitted, November 2012 - Accepted, March 2013*
- * Supplementary tables are available in the contents of the present issue of the Journal (<http://www.periodicodimineralogia.it>).