OPHIOLITE INHERITANCE IN THE PO PLAIN SEDIMENTS: INSIGHTS ON HEAVY METALS DISTRIBUTION AND RISK ASSESSMENT

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ABSTRACT

High heavy metals backgrounds, in particular chromium and nickel, are renowned in soils and sediments of the Po Plain. New XRF data, synthetized in geo-referenced geochemical maps, emphasize that the anomalously high Cr-Ni backgrounds are related to the fine alluvial sediments of the Po River. A comparison with the regolith composition of ophiolite rocks cropping out within the Po River basin suggests that the observed geochemical features reflect sedimentary components deriving from the weathering of femic and ultrafemic rocks. The elevated Cr-Ni backgrounds are therefore a geogenic character of the Po River alluvial sediments, unrelated to anthropogenic contamination. Electron microprobe investigation focused on femic minerals highlights that nickel is mainly sequestrated in serpentine (up to 0.4 wt%) whereas chromium is mainly hosted in chlorite (up to 2.5 wt%). Extraction tests, in which leachates have been analysed by ICP-MS, reveal that the mobility of chromium is limited; coherently the natural water of the area usually display concentration lower than the national drinking standards. Unfortunately, this element is considered toxic and dangerous even at extremely low concentration if oxidized in the hexavalent form that is prevalent in supergene conditions, thus posing serious environmental concerns. Nickel, on the other hand, displays a higher mobility, possibly due to the metastable behaviour of serpentine. Coherently the Cr/Ni is always higher than one in the investigated sediments and soils, whereas is always lower than one in both the natural waters and agricultural products of the area. Therefore, the high nickel concentration represents further geochemical risk and the relative content has to be monitored in the local agricultural crops. For the same reasons, aquaculture activities such as mussels and clam farms developed in the lagoons widespread around the delta of Po River are also potentially exposed to nickel bio-accumulation and the related products have to be carefully monitored.

INTRODUCTION

The weathering of femic and ultrafemic lithologies included in ophiolite associations usually generate sedimentary deposits and soils anomalously enriched in heavy metals such as nickel (Ni), Cobalt (Co), Chromium (Cr), Vanadium (V). Similar weathering products are significantly represented in the hydrological basin of the Po River, because Tethyan ophiolite complexes crop out on the bordering Alpine and Apennine orogenic chains (Garzanti et al., 1998; Amorosi, 2012). This in turn explains the presence of ophiolite-inherited components within the sediments of the Po River, currently cropping out in the Po Plain.

In this paper, we implement the studies reported by Bianchini et al. (2002; 2012) investigating a new sample population collected close to the town of Ferrara, including a wider variety of sedimentary facies. Samples have been characterized with 112 new XRF (X-ray fluorescence) major and trace element analyses and with 22 aqua regia extraction tests in which the heavy metal contents of leachates have been analysed by ICP-MS. We also report in situ electron microprobe analyses (EMPA) of distinct minerals included in these sediments in order to understand in which mineral phases the heavy metals are concentrated.

The chemical-mineralogical characterization of these alluvial terrains and their regional variability are essential in order to understand the origin (natural vs. anthropogenic) of potentially harmful elements. The purpose is to define and monitor the local heavy metal backgrounds, as well as to understand in which grain-size/mineralogical fraction they are concentrated. The mobility of distinct heavy metals is also discussed to evaluate if the potentially toxic elements are mobile, and thus bio-accessible and transferable in the food chain causing harmful health problems.

GEOMORPHOLOGY AND LITHOLOGICAL OUTLINES

The soils of the Po Plain consist of alluvial deposits, characterized by a limited profile development, in which the lack of soil maturity is related to young depositional age (Holocene), fluvial reworking and extensive agricultural activities (ploughing).

The geochemistry of sediments in alluvial areas records the complex tectonic, climatic and hydrological processes which occur within a river basin (Pennisi et al., 2009). The varying contributions of confluents which drain geologically different sub-basins, lead to sedimentary deposits with different geochemical signatures, reflecting the geochemistry of the parent rocks and the weathering mechanisms. Moreover, in urbanized areas, anthropogenic contributions can overprint the pristine (geogenic) geochemical signatures of the alluvial sediments. In particular, this study investigates the easternmost part of the Po River plain in Northern Italy, i.e., a sedimentary basin bordered by the Alps and the Apennines, which hosts about 30-40% of the Italian population and most of the Nation's industrial and agricultural activities (Fig. 1).

In the studied area, the cropping out sedimentary facies

(and the related soils) reflect climatic changes and human impacts that deeply modified the configuration of the local drainage system, which is represented by the migrating branches of the Po River (Amorosi et al., 2002; Bianchini et al., 2002; 2012; Stefani and Vincenzi, 2005; Simeoni and Corbau, 2009; Garzanti et al., 2011; Amorosi, 2012). In the terminal part of the basin the delta environment is characterized by high lateral mobility of the active channel belts, with recurrent avulsion and channel bifurcation, which redistribute the water and sediment fluxes throughout the system. This dynamic scenario permitted, in historical times, the development of fens and swamps (probably developed over the period of a few decades) sometimes characterized by peat deposition.

In the same sector of the plain sediments of Apennine provenance transported in historical times by Reno River are also represented, giving further complexity to the geomorphological evolution of the plain, in turn reflected in the sediment stratigraphy.

MATERIAL AND METHODS

This study implements the paper recently published by Bianchini et al. (2012), which focused on agricultural terrains collected in the vicinity of the villages "Vigarano Mainarda" and "Vigarano Pieve", sampling a neighbouring sector of the Po River plain closer to the town of Ferrara (Fig. 1). The identification of sampling sites was based on the geological-geomorphological map of the area (Geological Map of the Emilia-Romagna Plain, 1:250,000 scale, 1999) in which the different alluvial facies of the Po and Reno Rivers were identified. The rationale behind the site selection was to consider all the different lithological-geomorphological units cropping out in the area, sampling a wider variety of sedimentary facies, also including deltaic deposits.

The sampling was carried out with an Edelman auger (Eijkelkamp) geo-referencing the site by a portable global positioning system (GPS), to locate the points and to set up future field surveys. 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. The samples were air-dried and divided into distinct aliquots for grain-size and chemical/mineralogical investigations. The grain size investigation was obtained, following the notional classification of Wentworth as described by Salemi et al. (2010), by sieving the sandy fraction from the fine (< 63 μm) one, and then using wet gravitational separation in deionized water to divide the clay from the silt fraction. Stokes' law was applied to calculate the settling time for the silt fraction in order to siphon out the resulting supernatant containing the clay particles.

Major (expressed as wt%) and trace elements (Ni, Co, Cr, V, Sc, Pb, Zn, and Cu, expressed as ppm) were analysed 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 are based on systematic re-analyses of standards; for major elements they are 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%. On a subset of samples XRF analyses were duplicated on separated grain-size fractions, i.e., the coarse fraction > 63 μm and the fine fraction < 63 μm to find out the relationships between heavy metals content and grain-size. A further investigation was carried out using tests of metal extraction. According to the official Italian methods for soil analysis heavy metal extractions were obtained by using suprapure grade reagents, following the procedure proposed by Barbafieri et al. (1996). According to this protocol: a) 1 g of powdered sample is wet with a few millilitres (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 hours; e) the obtained solutions are centrifuged, filtered and transferred to other flasks that are taken to the final volume of 100 ml. Subsequently, the ICP-MS analyses were carried out using an X Series Thermo-Scientific spectrometer at the Department of 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 the 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 (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.

Mineral investigation was focused on femic fractions that plausibly host the heavy metals. These fractions were isolated using a Frantz magnetic separator, and then mounted on thin sections and properly polished. Subsequently, mineral compositions were obtained at the CNR–IGG Institute of Padova using a Cameca SX 50 electron microprobe, fitted with three wavelength-dispersive spectrometers, using natural silicates and oxides as standards.

COMPOSITION OF SEDIMENTS IN THE FERRARA SURROUNDINGS

Previous studies reporting petrographic observations and XRD analyses indicate that the alluvial sediments of both Po (Ps) and Reno (Rs) Rivers include quartz, feldspars, calcite, and micas, which are prevalent in the coarse sand, as well as phyllosilicates such as illite, kaolinite, chlorite, serpentine and smectite, which tend to prevail in the finer fraction (Chiorboli and Lenzi, 1992; Bianchini et al., 2002). In this contribution, emphasis has been devoted to the distinction of different sediment types (i.e., grain-size characteristics), and Ps and Rs sediments have been further subdivided in the following subgroups:

• Ps1, i.e., coarse sediments (sands) attributable to the Po River;

• Ps2, i.e., loamy sediments attributable to the Po River;

• Ps3, fine sediments attributable to the Po River;

• Rs1, i.e., coarse sediments (sands) attributable to the Reno River;
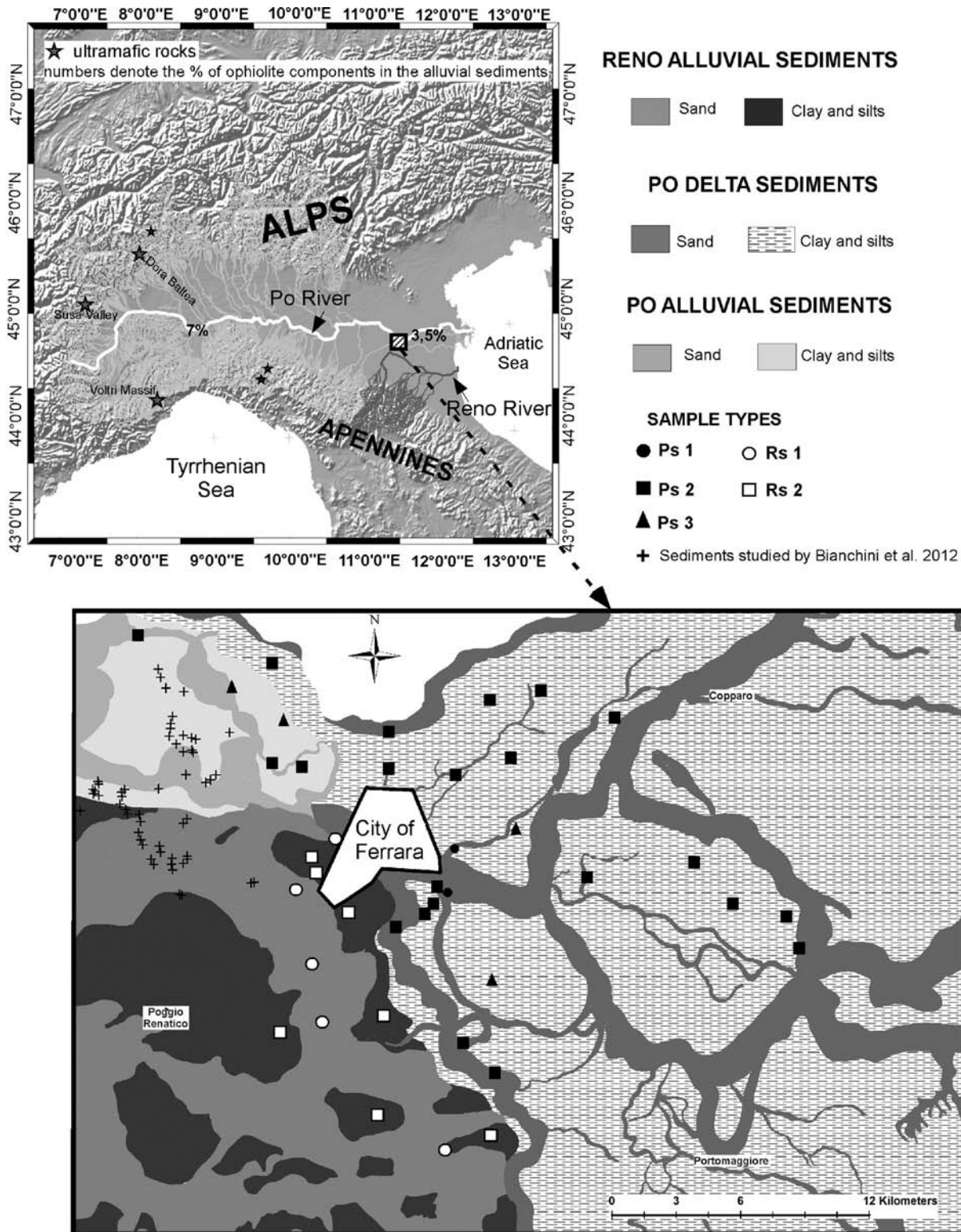
Fig. 1 - Localization of the studied area close to the city of Ferrara (44°50'00''N; 11°35'47''E) reporting a geographic overview of the whole Po River basin showing the main outcrops of ultramafic lithologies (Amorosi, 2012), as well as the percentage of ophiolite components in the Po alluvial sediments (Garzanti et al., 2012). A lithological sketch map showing the main sedimentary facies and the sampling sites is also reported.

• Rs2, i.e., fine sediments (sands) attributable to the Reno River;

Ps1 and Rs1 mainly consist of sandy sediments deposited in high-energy fluvial environments, and plausibly represent paleochannels of Po and Reno Rivers, respectively. Ps2 consists of sediments composed of sand, silt, and clay in rela-tively even concentration, representing interfluvial deposi-tional sequences of Po River. Ps3 and Rs2 consist of clay sediments typical of low-energy sedimentation, possibly in wetlands formed between active river branches of Po and Reno Rivers, respectively.

The relative chemical compositions (Table 1 refers to

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Table 1 - Bulk XRF major (wt%) and trace (ppm) element composition of sediments collected in the surroundings of Ferrara at a depth of 100-120 cm.

| Sample	F9	FE11	FE12	FE13	FE16	FE19	FE22	FE24	FE2	FE3	F7	F8P	FE9	FE10	F13	FE14	FE15	FE17	FE18	FE20
Affinity	Ps1	Ps1	Ps1	Ps1	Ps1	Ps1	Ps1	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2
SiO$_2$ (wt%)	63.65	60.13	60.29	60.43	62.00	57.19	63.45	47.06	51.47	48.95	46.69	49.22	52.01	52.30	46.66	45.23	52.04	52.11	47.57	49.57
TiO$_2$	0.31	0.48	0.47	0.54	0.51	0.54	0.46	0.72	0.70	0.73	0.71	0.64	0.60	0.71	0.68	0.72	0.73	0.67	0.75	0.71
Al$_2$O$_3$	9.39	11.11	10.45	10.94	11.43	10.71	10.44	14.37	13.94	13.82	14.90	13.21	12.36	13.79	14.01	13.80	14.38	12.39	14.25	13.11
Fe$_2$O$_{3\,tot}$	2.71	4.01	3.78	4.31	4.31	4.28	3.76	7.28	6.12	6.52	6.09	5.35	5.05	5.73	5.84	7.17	6.40	5.31	7.17	5.73
MnO	0.09	0.10	0.10	0.11	0.10	0.13	0.10	0.19	0.13	0.13	0.15	0.13	0.15	0.11	0.13	0.17	0.14	0.11	0.23	0.15
MgO	2.67	4.21	3.68	3.95	3.54	4.14	3.89	3.44	3.87	3.93	2.73	4.12	2.55	4.37	3.96	3.96	3.70	4.27	3.63	4.04
CaO	4.64	10.08	10.19	10.03	7.08	11.67	8.51	10.00	9.80	10.60	10.10	12.65	12.35	9.68	11.77	11.55	8.19	11.51	9.92	11.20
Na$_2$O	1.12	1.48	1.40	1.49	1.33	1.29	1.58	0.34	0.63	0.48	0.32	0.71	0.62	0.76	0.51	0.44	0.54	0.80	0.40	0.56
K$_2$O	1.73	2.49	2.15	2.40	2.35	2.14	2.35	2.61	2.49	2.58	2.54	2.23	2.40	2.50	2.24	2.53	2.73	2.22	2.61	2.32
P$_2$O$_5$	0.08	0.10	0.11	0.11	0.28	0.13	0.13	0.15	0.16	0.12	0.13	0.16	0.12	0.15	0.13	0.12	0.33	0.16	0.13	0.13
LOI	13.63	5.82	7.39	5.68	7.08	7.79	5.34	13.83	10.69	12.14	15.63	11.57	11.79	9.90	14.08	14.31	10.82	10.45	13.33	12.48
Co ppm	7	6	8	8	9	7	10	14	14	16	18	16	10	15	18	15	14	13	15	14
Cr	115	150	164	172	165	155	147	212	205	223	139	193	104	208	199	206	211	191	208	188
Ni	48	70	76	75	73	79	66	129	118	164	95	133	60	116	143	136	117	109	124	122
Pb	13	15	15	16	27	14	17	13	15	20	17	18	13	16	18	16	19	15	15	14
V	42	66	65	66	72	72	63	121	108	115	111	98	88	104	106	117	106	93	123	105
Zn	32	34	38	37	70	37	35	74	67	73	76	62	55	61	65	66	82	55	75	63
Cu	11	15	16	14	34	18	15	53	43	49	56	40	40	41	45	53	57	35	53	46
Sc	8	10	12	12	13	12	12	16	17	16	14	15	12	15	14	14	16	14	16	14

Sample	FE21	FE23	FE25	FE26	FE28	FE6	F12	FE29	F4	F5	FE4	F11	FE31	FE1	FE5	F6	FE7	FE8	F10	FE30
Affinity	Ps2	Ps2	Ps2	Ps2	Ps2	Ps3	Ps3	Ps3	Rs1	Rs1	Rs1	Rs1	Rs1	Rs2	Rs2	Rs2	Rs2	Rs2	Rs2	Rs2
SiO$_2$ (wt%)	46.90	50.25	47.37	52.68	53.21	51.61	47.95	49.88	53.25	49.86	53.00	49.24	53.13	46.77	49.81	45.26	48.54	48.28	49.06	49.18
TiO$_2$	0.71	0.65	0.70	0.69	0.71	0.88	0.74	0.79	0.47	0.59	0.66	0.60	0.66	0.78	0.78	0.78	0.78	0.83	0.76	0.76
Al$_2$O$_3$	13.83	12.70	13.61	13.16	14.09	20.45	16.23	16.12	12.22	13.80	12.84	13.58	12.93	18.55	14.84	17.73	15.10	16.29	15.93	15.10
Fe$_2$O$_{3\,tot}$	7.24	5.82	6.61	5.87	6.23	8.24	6.65	7.82	4.19	5.19	5.29	5.04	5.33	9.00	6.91	6.88	6.86	7.21	6.51	6.73
MnO	0.18	0.12	0.15	0.12	0.11	0.05	0.14	0.12	0.14	0.14	0.13	0.14	0.14	0.13	0.16	0.13	0.15	0.15	0.15	0.14
MgO	3.28	4.30	3.90	4.77	4.21	3.11	3.68	4.15	1.97	2.34	2.42	2.48	2.59	2.59	2.58	2.39	2.61	2.72	2.53	2.44
CaO	10.76	11.56	11.36	9.41	8.03	1.90	6.21	6.97	10.78	9.27	10.97	10.54	10.78	6.33	9.19	7.64	9.67	8.50	9.22	9.56
Na$_2$O	0.34	0.65	0.53	0.78	0.70	0.41	0.36	0.45	0.69	0.46	0.64	0.47	0.66	0.23	0.41	0.23	0.35	0.31	0.37	0.38
K$_2$O	2.48	2.24	2.53	2.46	2.57	4.15	2.68	3.14	2.27	2.38	2.61	2.30	2.50	4.06	2.97	3.23	3.05	3.42	2.92	3.00
P$_2$O$_5$	0.13	0.15	0.13	0.14	0.16	0.10	0.14	0.14	0.12	0.26	0.13	0.12	0.14	0.13	0.12	0.14	0.12	0.12	0.13	0.12
LOI	14.15	11.56	13.10	9.92	9.97	9.11	15.21	10.43	13.92	15.70	11.31	15.48	11.15	11.41	12.22	15.59	12.79	12.16	12.42	12.59
Co ppm	17	15	12	15	12	17	18	21	11	12	9	12	8	16	14	15	14	13	17	12
Cr	189	204	193	215	206	219	223	265	77	107	102	94	106	156	127	135	127	139	124	121
Ni	128	140	128	127	109	110	145	178	55	67	60	65	59	79	71	77	75	66	77	66
Pb	13	18	16	16	15	25	21	16	16	20	18	15	16	17	17	17	16	13	19	13
V	122	98	111	102	106	163	117	134	71	84	92	86	90	146	121	130	127	134	121	122
Zn	71	59	65	59	64	109	83	89	53	90	61	61	57	92	82	85	81	70	88	74
Cu	62	39	47	35	44	79	52	65	39	74	44	45	45	59	53	60	56	55	56	54
Sc	14	14	13	15	17	19	15	19	11	13	14	12	13	16	17	15	16	16	17	16

Fig. 2 - Hierarchical cluster analysis of samples collected at depths of 100-120 cm. Note that samples related to the distinct typologies Ps1, Ps2, Ps3, Rs1, Rs2 are generally grouped in specific clusters, with only few exceptions that appear misclassified.
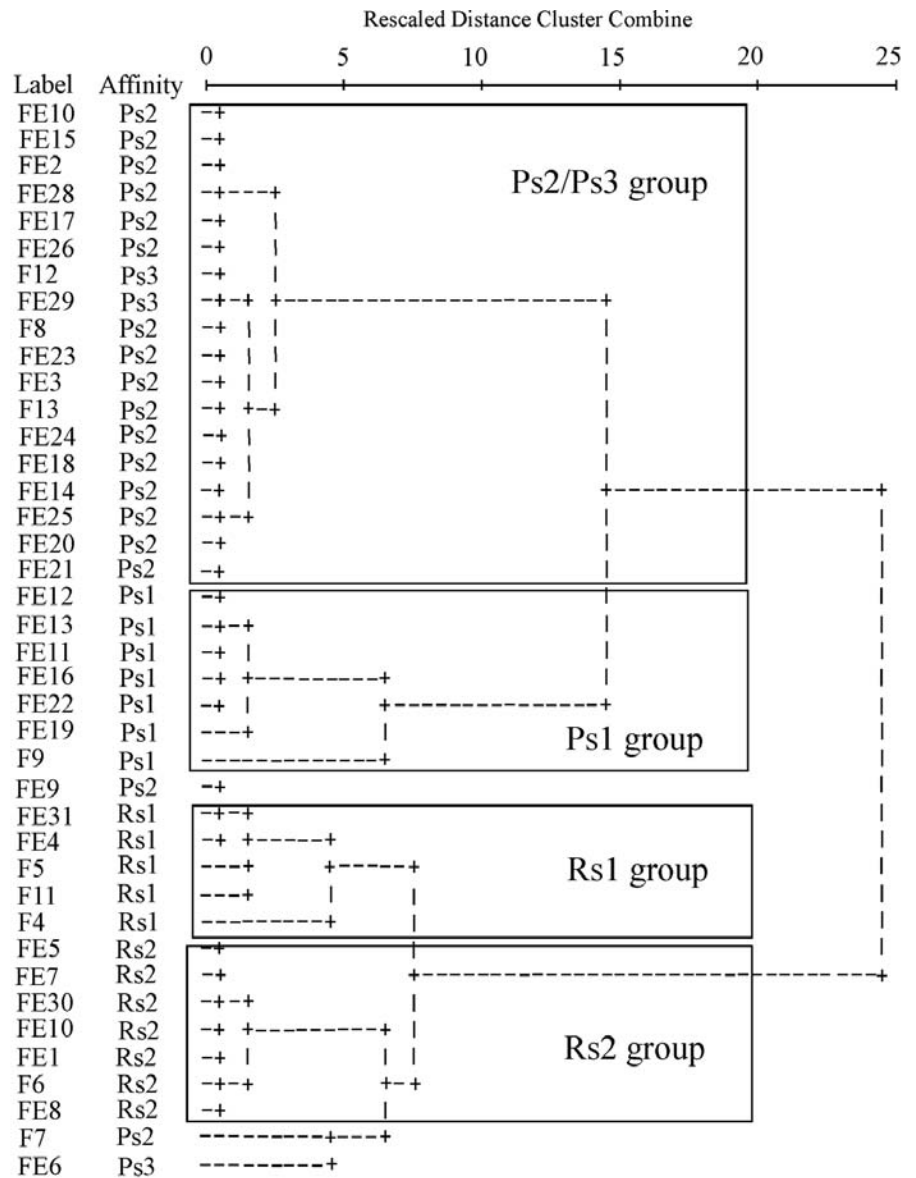
sediments sampled at a depth of 100-120 cm; Table 2 refers to sediments sampled at a depth of 20-30 cm) are obviously related to the presence and relative abundance of the above mentioned minerals.

The preliminary elaboration of the data has been obtained using the statistical processing system SPSS. The results, reported in the dendrogram of Fig. 2, reveal that the sample types defined in the field by grain-size observations can be discriminated by a cluster analysis. Samples pertaining to the distinct typologies Ps1, Ps2, Ps3, Rs1, Rs2 are, with few exceptions, coherently grouped in distinct clusters, thus demonstrating that the composition of alluvial sediments reflects both the provenance of the clastic components and the dynamic of the depositional environment.

In both Ps and Rs sample populations Al_2O_3 is positively correlated with K_2O and negatively correlated with SiO_2, suggesting that the investigated samples represent a mixture of various proportions of quartz and clay minerals (Fig. 3). Fe_2O_3, TiO_2 but also several transition elements such as Cr, Ni (Co, V) show correlation with Al_2O_3 indicating their partitioning in the fine fraction that is enriched in clay minerals (Fig. 4). These diagrams also highlight significant differences between the Ps and Rs sample populations that are significantly discriminated by transition elements such as chromium and nickel. In fact, although the Cr-Ni content is correlated to the amount of clay, significant difference exists between Rs and Ps. This is also confirmed by the analysis of separated grain-size fractions (Table 3) that are reported in Fig. 5. This diagram emphasizes that within each sample Cr-Ni budget is concentrated in the fine (clay-rich) particles.

To emphasize these differences between Ps and Rs, other Authors (Amorosi and Sammartino, 2007; Amorosi, 2012) proposed the use of elemental ratios such as Cr/Al_2O_3, Ni/Al_2O_3 that plausibly rules out artefacts related to difference in the grain-size. Confirming these indications, we report some geo-referenced geochemical maps (Fig. 6) highlighting the Cr/Al_2O_3, Ni/Al_2O_3 spatial distribution that show the clear difference between Ps and Rs lithologies. In particular, Ps lithologies generally show Cr/Al_2O_3 and Ni/Al_2O_3 ratios higher than 11.5 and 6.0, respectively.

Within this sampling collection, terrains of different provenance, i.e., Ps and Rs, are perfectly discriminated in term of MgO (wt%), Cr and Ni (ppm) and the following differences can be observed: i) Rs are characterized by a MgO content lower than 3 wt%, with an average composition of

Table 2 - Bulk XRF major (wt%) and trace (ppm) element composition of sediments collected in the surroundings of Ferrara at a depth of 20-30 cm.

Sample	F9	FE11	FE12	FE13	FE16	FE19	FE22	FE24	FE2	FE3	F7	F8	FE9	FE10	F13	FE14	FE15	FE17	FE18	FE20
Affinity	Ps1	Ps2	Ps2	Ps2	Ps1	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps3	Ps2	Ps2	Ps2	Ps2
SiO_2 (wt%)	60.03	51.12	54.96	53.62	70.26	55.60	52.36	50.69	54.41	55.29	49.68	54.11	51.46	52.31	48.31	50.08	52.52	51.84	51.57	51.39
TiO_2	0.45	0.66	0.67	0.66	0.32	0.62	0.67	0.69	0.68	0.68	0.64	0.63	0.62	0.73	0.70	0.77	0.73	0.69	0.69	0.69
Al_2O_3	11.16	15.26	13.52	13.59	9.74	12.06	13.78	14.44	13.96	14.03	14.05	13.74	13.34	14.69	14.96	15.94	14.47	13.60	15.15	13.78
$Fe_2O_{3\,tot}$	3.73	6.00	5.43	5.48	2.75	4.77	5.80	6.90	5.83	5.70	5.47	5.24	5.41	6.29	6.38	7.26	6.43	5.70	6.41	5.83
MnO	0.09	0.11	0.13	0.13	0.09	0.11	0.12	0.14	0.13	0.13	0.14	0.12	0.15	0.10	0.14	0.14	0.14	0.12	0.12	0.12
MgO	3.20	4.06	4.18	4.01	3.48	4.16	4.09	3.53	4.32	4.05	2.81	3.86	2.67	4.28	3.83	3.80	3.73	4.03	3.84	3.97
CaO	5.70	8.93	8.46	9.53	5.53	10.38	8.81	8.61	8.02	8.24	9.97	6.87	10.74	8.44	6.97	6.51	7.64	9.78	8.02	9.92
Na_2O	1.03	0.52	0.77	0.69	1.80	1.01	0.67	0.50	0.75	0.77	0.44	0.73	0.52	0.70	0.39	0.42	0.53	0.61	0.50	0.58
K_2O	2.00	2.79	2.58	2.48	2.36	2.22	2.70	2.70	2.60	2.75	2.49	2.38	2.59	2.61	2.48	2.87	2.72	2.49	2.87	2.39
P_2O_5	0.20	0.16	0.28	0.23	0.07	0.22	0.36	0.34	0.23	0.22	0.18	0.30	0.23	0.16	0.22	0.20	0.30	0.23	0.18	0.18
LOI	12.41	10.39	9.02	9.57	3.61	8.84	10.64	11.46	9.06	8.15	14.12	12.01	12.26	9.68	15.63	12.01	10.80	10.90	10.65	11.14
Co ppm	11	10	9	10	2	6	9	11	9	9	15	14	6	11	20	15	10	10	10	9
Cr	144	198	201	195	126	183	199	192	250	220	140	187	110	212	212	224	204	194	214	195
Ni	67	118	102	107	47	90	107	108	112	105	83	97	65	117	141	141	112	111	120	114
Pb	16	5	4	7	2	2	15	4	9	10	20	24	6	4	22	9	4	3	4	4
V	62	104	88	90	42	81	91	101	95	98	95	84	88	106	104	126	105	97	110	101
Zn	46	56	61	54	22	42	70	63	69	62	82	70	62	64	78	83	75	56	70	58
Cu	24	46	52	39	12	27	55	53	51	48	64	53	51	54	54	65	53	44	51	44
Sc	11	11	10	11	6	9	12	11	10	12	14	13	10	12	14	12	11	9	11	12

Sample	FE21	FE23	FE25	FE26	FE28	FE6	F12	FE29	F4	F5	FE4	F11	FE31	FE1	FE5	F6	FE7	FE8	F10	FE30
Affinity	Ps2	Ps2	Ps3	Ps2	Ps3	Ps3	Ps2	Ps2	Rs1	Rs2	Rs1	Rs1	Rs1	Rs2	Rs2	Rs2	Rs2	Rs2	Rs2	Rs1
SiO_2 (wt%)	50.26	53.62	49.50	50.38	47.94	51.53	51.86	52.69	52.03	48.31	54.00	49.80	52.76	49.02	53.15	48.79	49.33	48.49	49.72	51.98
TiO_2	0.65	0.67	0.77	0.71	0.75	0.84	0.58	0.69	0.52	0.74	0.57	0.57	0.69	0.82	0.71	0.80	0.82	0.79	0.77	0.64
Al_2O_3	13.08	14.55	16.26	14.25	16.13	19.98	13.32	14.20	12.96	15.41	12.80	13.21	14.18	18.12	14.61	17.35	17.87	16.55	15.79	13.99
$Fe_2O_{3\,tot}$	5.82	5.94	7.54	6.39	7.69	8.21	5.04	5.89	4.44	6.48	4.74	4.81	5.81	7.66	5.97	7.21	7.47	7.22	6.64	5.45
MnO	0.15	0.13	0.08	0.14	0.15	0.08	0.11	0.13	0.14	0.15	0.15	0.14	0.15	0.14	0.15	0.15	0.13	0.15	0.15	0.15
MgO	3.79	4.16	3.83	4.15	3.75	3.35	3.61	4.09	2.16	2.26	2.41	2.35	2.56	2.60	2.62	2.46	2.58	2.52	2.47	2.54
CaO	11.02	7.88	6.98	9.12	7.65	1.85	7.19	8.19	8.93	7.15	10.91	9.86	9.15	5.82	8.25	7.50	6.14	7.99	8.44	9.82
Na_2O	0.55	0.67	0.41	0.55	0.39	0.33	0.61	0.63	0.53	0.30	0.67	0.46	0.58	0.28	0.53	0.31	0.29	0.30	0.37	0.55
K_2O	2.30	2.67	3.13	2.60	2.89	3.78	2.17	2.59	2.32	2.63	2.71	2.24	2.74	3.77	2.97	3.43	3.77	3.30	2.95	2.74
P_2O_5	0.18	0.26	0.17	0.21	0.15	0.16	0.20	0.34	0.23	0.23	0.29	0.14	0.18	0.24	0.24	0.24	0.19	0.23	0.18	0.20
LOI	12.21	9.45	11.33	11.51	12.51	9.90	15.31	10.56	15.73	16.35	10.73	16.41	11.19	11.53	10.08	11.76	11.42	12.47	12.52	11.93
Co ppm	10	9	12	12	13	15	15	7	10	15	5	11	7	11	7	18	9	10	16	5
Cr	180	205	221	218	238	260	166	206	85	117	89	88	105	155	115	144	147	138	125	107
Ni	111	111	150	127	155	136	98	112	52	68	54	58	58	71	61	79	73	72	74	56
Pb	6	5	8	2	6	18	19	14	22	18	13	11	11	7	19	20	9	8	17	12
V	96	98	126	106	128	157	80	95	69	108	77	77	93	137	102	129	139	132	119	88
Zn	72	62	84	68	78	111	56	90	67	99	63	56	80	93	80	101	93	84	91	92
Cu	86	42	59	50	60	88	35	123	59	87	74	42	109	65	73	65	63	60	59	61
Sc	10	11	14	12	13	17	13	12	11	14	9	10	10	15	11	18	15	14	17	10

Fig. 3 - SiO$_2$ vs Al$_2$O$_3$ and K$_2$O vs Al$_2$O$_3$ variation diagrams reporting composition of sediments cropping out close to Ferrara. Compositions are referred to sampling depths of 100-120 cm.
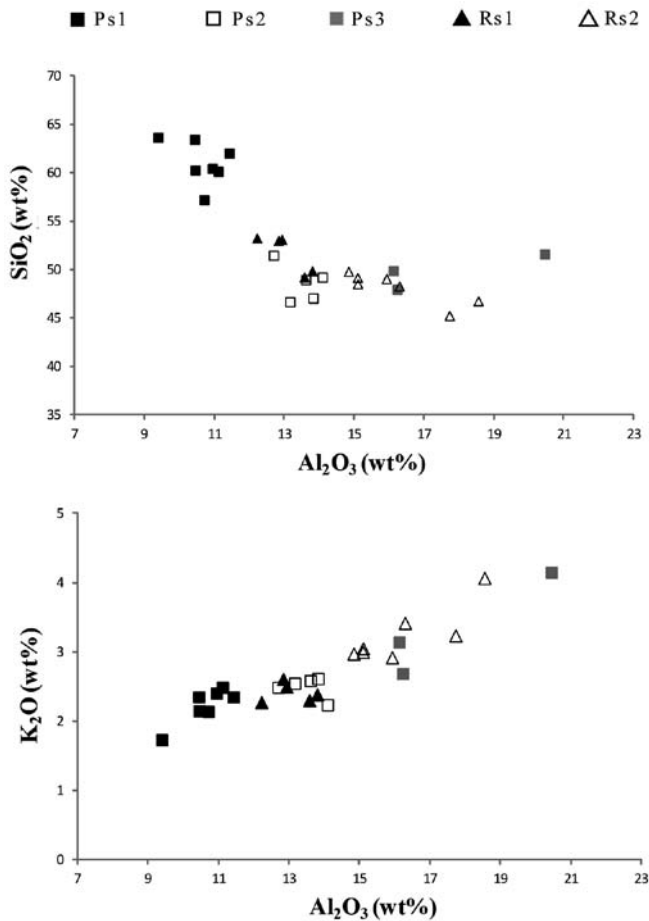

Fig. 4 - Cr vs Al$_2$O$_3$ and Ni vs Al$_2$O$_3$ variation diagrams reporting composition of sediments cropping out close to Ferrara. Compositions are referred to sampling depths of 100-120 cm.

2.47 wt%, and a median composition of 2.51 wt%; the Ni content is lower than 80 ppm, with an average composition of 68 ppm and a median composition of 79 ppm; the Cr content is lower than 160 ppm, with an average composition of 118 ppm and a median composition of 122 ppm; ii) Ps present a MgO content higher than 3 wt%, with an average composition of 3.79 wt% and a median composition of 3.92 wt%; the Ni content is higher than 78 ppm, with an average composition of 111 ppm and a median composition of 117 ppm; the Cr content is higher than 130 ppm, with an average composition of 132 ppm and a median composition of 159 ppm. The mentioned differences are reported as box-plots (i.e., whiskers diagrams) in Fig. 7.

This difference between the Ps and Rs populations is not an artefact related to grain size differences, as demonstrated by the particle size analysis and by the log (Fe$_2$O$_3$/K$_2$O) vs. log (SiO$_2$/Al$_2$O$_3$) diagram, which link chemistry to grain-size distribution (Herron, 1988). Therefore, the relative metal enrichment of Ps indicates that the minerals included in the fine fraction are peculiarly enriched in MgO, Ni, Cr, V, and Co. This evidence was already recorded by Chiorboli and Lenzi (1992) who recognized the significant presence of serpentine in Ps, and by Bianchini et al. (2002) that indicated that within Ps samples chlorite is peculiarly abundant and enriched in MgO.

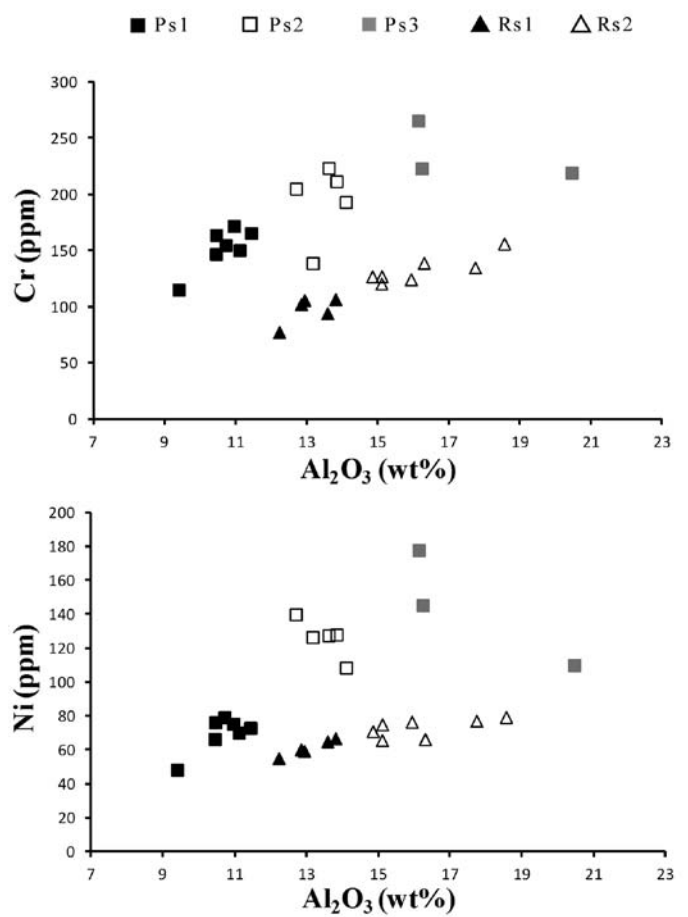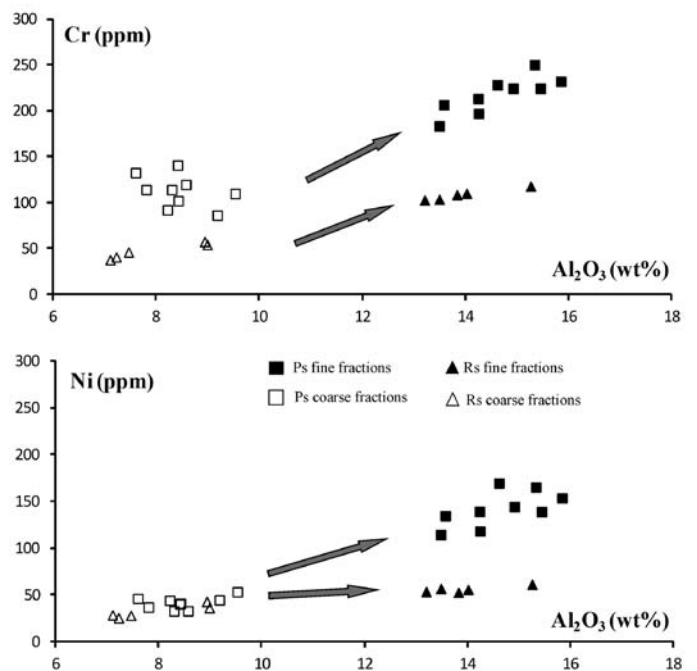Fig. 5 - Cr vs Al$_2$O$_3$ and Ni vs Al$_2$O$_3$ variation diagrams reporting composition of distinct grain-size (coarse, i.e., > 63 µm; fine, i.e., < 63 µm) fractions obtained by sieving. Note that Cr, Ni and Al$_2$O$_3$ decidedly increase in the fine clay-rich fractions.

Table 3 - XRF major (wt%) and trace (ppm) element composition of fine (< 65 mm) and coarse (> 65 mm) fractions of sediments collected in the surroundings of Ferrara preliminarily separated by sieving.

| 20-30 cm | FE16 | | F9 | | FE3 | | FE18 | | FE20 | | FE23 | | FE9 | | FE5 | | FE31 | | F4 | |
| Affinity | Ps1 | | Ps1 | | Ps2 | | Ps2 | | Ps2 | | Ps2 | | Ps2 | | Rs2 | | Rs1 | | Rs1 | |
	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse
SiO_2 (wt%)	49.31	72.87	51.76	74.19	50.64	71.36	48.91	71.30	51.02	66.69	51.32	69.07	49.97	67.62	52.18	67.80	52.93	66.66	54.14	69.44
TiO_2	0.76	0.34	0.72	0.32	0.77	0.43	0.74	0.30	0.70	0.25	0.75	0.28	0.68	0.18	0.73	0.16	0.70	0.18	0.66	0.16
Al_2O_3	15.33	8.29	14.24	8.57	14.92	8.41	15.84	7.59	14.25	8.21	15.45	8.42	14.23	6.36	15.26	7.10	14.01	7.45	13.83	7.22
$Fe_2O_3{}_{tot}$	7.55	2.38	6.41	2.46	6.78	3.04	7.09	2.58	5.90	2.34	6.75	2.34	6.03	1.57	6.18	1.84	5.93	1.81	5.63	1.65
MnO	0.17	0.06	0.16	0.06	0.15	0.08	0.13	0.09	0.12	0.08	0.14	0.06	0.15	0.10	0.15	0.11	0.15	0.10	0.15	0.09
MgO	4.23	2.26	4.23	2.59	3.99	2.63	3.76	2.69	3.92	2.26	4.09	2.54	2.72	1.18	2.62	1.18	2.60	1.19	2.58	1.09
CaO	6.73	5.48	8.00	4.38	8.02	5.79	7.60	6.39	9.50	7.80	7.25	6.92	9.84	10.70	7.80	9.27	8.91	8.99	8.46	8.99
Na_2O	0.49	2.11	0.68	2.08	0.49	1.97	0.37	1.75	0.55	1.63	0.51	1.81	0.43	1.54	0.47	1.64	0.57	1.55	0.59	1.68
K_2O	2.81	1.87	2.64	1.93	2.73	1.88	2.84	1.83	2.38	1.71	2.68	1.78	2.57	1.86	2.96	2.01	2.73	2.07	2.70	2.21
P_2O_5	0.50	0.09	0.36	0.08	0.22	0.09	0.19	0.07	0.18	0.10	0.27	0.12	0.24	0.09	0.22	0.14	0.18	0.18	0.25	0.08
LOI	12.12	4.25	10.80	3.33	11.30	4.32	12.55	5.42	11.47	8.94	10.81	6.67	13.14	8.81	11.44	8.74	11.28	9.81	11.00	7.39
Co ppm	20	nd	12	nd	12	nd	11	nd	8	nd	11	nd	5	nd	6	nd	5	nd	2	nd
Cr	250	114	213	120	224	141	232	132	197	92	224	102	132	42	118	38	110	46	108	41
Ni	165	33	139	33	144	40	154	46	118	44	139	41	72	26	61	29	56	28	53	26
Pb	28	10	15	10	13	8	13	9	11	4	13	4	11	4	17	9	15	7	15	17
V	104	41	96	44	110	51	121	38	105	42	109	43	100	19	106	25	95	24	87	20
Zn	188	29	150	27	96	30	102	30	75	33	89	28	114	24	98	38	90	32	141	28
Cu	88	14	55	12	67	14	61	14	45	19	56	17	63	16	80	26	110	70	79	22
Sc	11	5	12	4	13	6	13	5	11	5	11	6	10	5	10	6	10	5	9	4

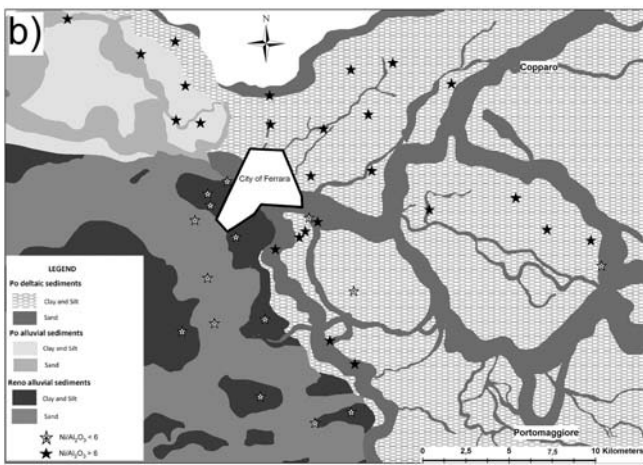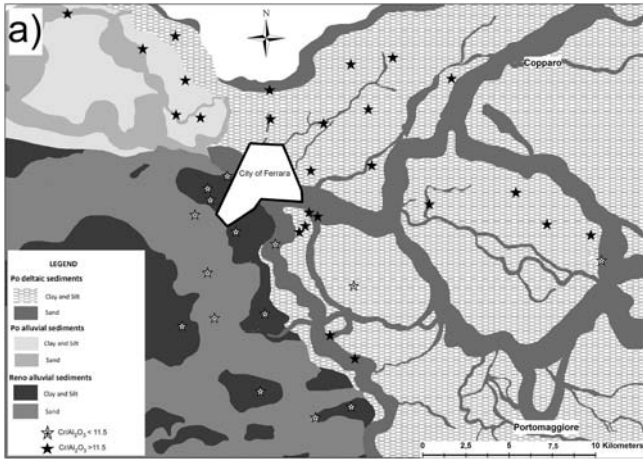| 20-30 cm | FE3 | | FE20 | | FE23 | | FE9 | | FE31 | | F4 | |
| Affinity | Ps2 | | Ps2 | | Ps2 | | Ps1 | | Rs1 | | Rs1 | |
	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse	fine	coarse
SiO_2 (wt%)	46.83	72.55	50.73	66.80	50.31	65.70	50.42	63.97	52.88	61.81	51.25	62.66
TiO_2	0.75	0.32	0.70	0.25	0.68	0.30	0.69	0.20	0.65	0.27	0.65	0.26
Al_2O_3	14.61	7.80	13.48	9.18	13.57	9.53	13.83	7.26	13.20	8.93	13.48	8.98
$Fe_2O_3{}_{tot}$	6.74	2.38	5.47	2.61	5.83	2.82	5.70	2.30	5.28	2.93	5.62	2.77
MnO	0.13	0.06	0.13	0.07	0.12	0.06	0.16	0.12	0.14	0.14	0.16	0.11
MgO	3.91	2.38	4.08	2.42	4.30	2.87	2.63	1.33	2.62	1.64	2.51	1.55
CaO	10.64	5.82	10.71	7.39	10.71	7.64	10.83	11.58	10.44	10.34	11.18	10.62
Na_2O	0.37	1.90	0.63	1.71	0.59	1.60	0.47	1.33	0.61	1.28	0.54	1.25
K_2O	2.59	1.70	2.28	1.98	2.27	2.02	2.42	1.94	2.45	2.25	2.52	2.33
P_2O_5	0.13	0.06	0.14	0.05	0.16	0.07	0.13	0.04	0.13	0.05	0.15	0.06
LOI	13.30	5.04	11.65	7.54	11.47	7.38	12.73	9.92	11.60	10.36	11.94	9.41
Co ppm	11	nd	6	nd	8	nd	7	nd	1	nd	3	nd
Cr	228	114	183	86	206	110	109	47	103	57	103	54
Ni	169	37	114	45	135	53	64	35	53	43	57	36
Pb	8	6	8	4	8	4	8	4	5	2	2	3
V	120	42	100	46	97	51	99	28	88	44	92	39
Zn	82	25	72	36	71	36	80	29	64	37	81	35
Cu	55	14	44	18	43	21	53	19	46	35	52	27
Sc	12	6	10	6	11	6	9	6	10	6	10	6

Fig. 6 - Geomorphological sketch map of the alluvial plain close to Ferrara, reporting geo-referenced values of the Cr/Al_2O_3 (a) and Ni/Al_2O_3 ratios (b). As emphasized by Amorosi and Sammartino (2007) and Amorosi (2012) these ratios are useful parameters to discriminate the sediments of the Po River from those of rivers flowing down from the Apennine (e.g., the Reno River).
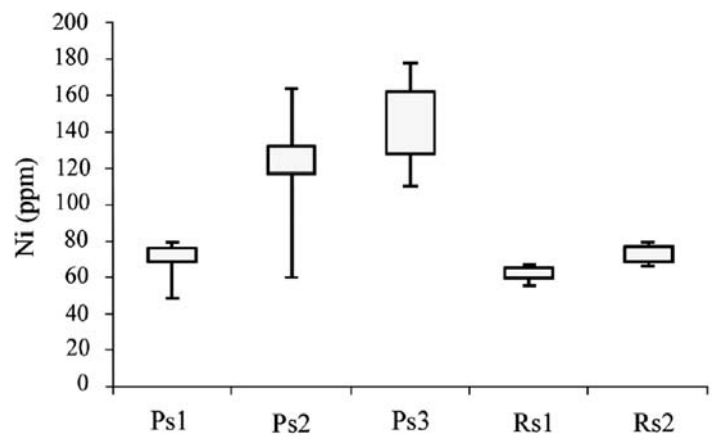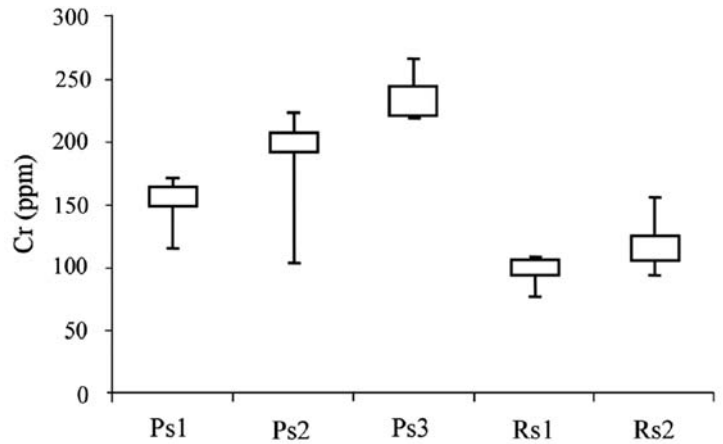
Fig. 7 - Box plots reporting the distribution of Ni and Cr in distinct facies of alluvial sediments related to the Po and Reno Rivers.

GEOCHEMICAL ANOMALIES AND INSIGHTS ON RISK ASSESSMENT

Risk assessment of metal contamination in surface sediments should take into consideration: 1) comparisons of the observed concentrations with those typical of unpolluted sediments generated by similar mother-rocks; 2) investigations on metal distribution and speciation and 3) comparisons with the threshold values of sediment quality guidelines.

As show in Fig. 8, the regolith composition of ophiolite ultramafic rocks cropping out within the basin (Bonifacio et al., 1997; Lombini et al., 1998) suggests that the high Cr-Ni background locally found in sediments of the Po River plain is not related to anthropogenic contamination. Coherently, the current-day solid load of the Po River is also characterized by anomalously high Cr and Ni content due to the significant presence of femic particles suspended in the flowing water (Viganò et al., 2003; Vignati et al., 2003; Farkas et al., 2007). Therefore the geochemical anomaly is plausibly a geogenic feature which indicates that a significant fraction of ophiolite-derived rock fragments and minerals are dispersed and mixed in the studied sediments (Amorosi, 2012). In particular, the percentage of ophiolite components
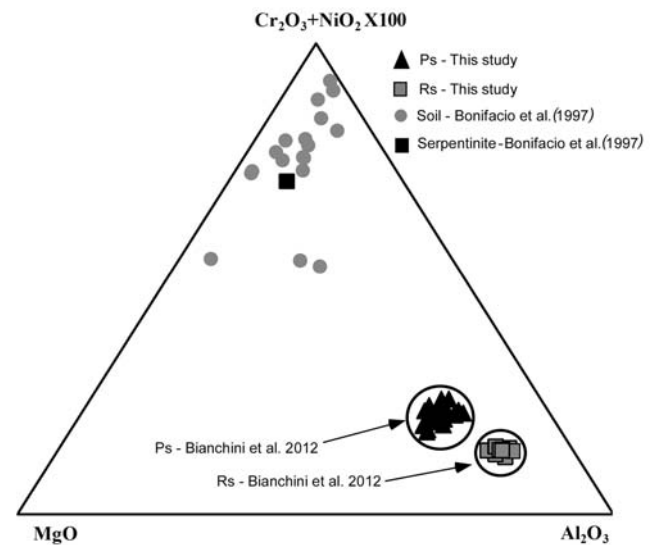

Fig. 8 - MgO - Al_2O_3 - $(Cr_2O_3 + NiO)*1000$ triangular diagram used to discriminate sediments from the Po River from those of the Reno River. Note that compositions of Po sediments trend toward the composition of soils evolved from ophiolite ultramafic rocks.

Table 4 - ICP-MS analyses of aqua regia solutions that extracted trace elements from sediments collected in the surroundings of Ferrara.

Sample	FE1	FE2	FE3	FE4	FE5	FE6	FE7	FE8	FE9	FE10	FE11	FE12	FE13	FE14	FE15	FE16	FE17	FE18	FE19	FE20	FE21	FE22
Affinity	Rs2	Ps2	Ps2	Rs1	Rs2	Ps3	Rs2	Rs2	Ps2	Ps2	Ps2	Ps2	Ps2	Ps3	Ps2	Ps1	Ps2	Ps2	Ps2	Ps2	Ps2	Ps2
$V_{(ppm)}$	51.1	29.6	20.5	28.7	28.8	63.4	42.3	37.6	17.6	26.8	28.7	35.9	32.3	46.9	51.3	5.7	36.8	31.0	20.6	23.9	24.0	26.3
Cr	69.0	133	37.7	93.9	44.6	163	65.7	65.8	52.6	118	107	113	102	135	136	57	114	114	94	105	102	115
Co	16.3	14.0	10.6	13.0	12.1	15.9	13.2	13.5	10.9	13.9	12.4	12.1	11.7	17.0	15.3	7.0	13.3	14.3	9.8	14.8	14.0	14.5
Ni	68.4	95.7	40.7	86.6	49.0	147	68.8	69.7	58.4	117	106	108	101	134	129	56.5	112	111	80.3	109	104	107
Cu	46	36.4	53.2	32.5	49.3	55.5	36.9	37.6	30.1	37.1	26.1	35.7	24.0	42.1	37.9	5.1	29.4	32.8	15.5	32.5	67.4	39.6
Zn	109	71.5	77.2	61.3	80.5	97.6	81.4	83.2	62.9	65.4	54.0	64.1	51.5	86.5	89.2	23.5	66.9	76.1	47.1	69.6	89.0	85.7
As	8.44	10.1	9.6	8.87	10.9	11.7	8.18	8.54	10.0	13.0	11.8	10.7	10.3	13.3	12.2	5.76	11.6	10.8	9.17	11.4	13.3	12.4
Se	0.98	0.91	0.65	0.81	0.65	1.21	0.76	0.75	0.62	0.79	0.78	0.66	0.59	1.07	0.95	nd	0.92	0.92	0.60	0.82	0.74	0.83
Mo	0.70	nd	0.69	nd	0.52	0.60	nd	nd	nd	nd	nd	nd	nd	0.64	nd	nd	nd	0.51	nd	nd	nd	0.55
Cd	0.58	nd	0.53	nd	nd	0.60	nd	0.53	0.52	nd	nd	0.55	0.51	0.68	0.68	nd	0.55	0.58	nd	0.55	0.59	0.69
Sb	nd	nd	nd	nd	nd	0.68	nd	nd	nd	nd	nd	nd	nd	0.61	0.51	nd	nd	nd	nd	nd	nd	0.87
Hg	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Pb	17.4	13.4	18.5	15.0	23.4	19.3	12.6	13.9	13.7	12.1	10.9	11.3	11.5	17.9	16.4	3.79	12.0	15.3	7.40	14.0	16.4	25.8
U	0.69	0.65	0.66	0.55	0.63	0.57	nd	0.70	0.65	0.83	0.83	0.61	0.53	0.71	0.71	nd	0.71	0.67	0.65	0.76	0.59	0.85
ENRICHMENT INDEX	1.3	1.1	0.8	1.0	1.0	1.4	1.1	1.1	0.8	1.1	1.0	1.0	1.0	1.4	1.3	0.5	1.1	1.2	0.8	1.2	1.2	1.2

The enrichment index, EI = Co/20 + Cr/150 + Cu/120 + Ni/120 + Pb/100 +V/90 + Zn/150/7, giving an overall indication of the heavy metal content indicates that some of the investigated samples display comparatively high backgrounds. See text for further details. nd- not detected.

in the Po alluvial sediments surrounding Ferrara appears to be ca. 3.5%, as estimated by Garzanti et al. (2012).

The geogenic nature of the observed high Cr and Ni content is corroborated by the lack of Top Enrichment Factor (TEF), determined by the ratio between the concentrations of Cr and Ni of the superficial samples collected at 20-30 cm and those recorded in the same sites at depths of 100-120 cm. This conclusion is further supported by the composition of ancient bricks (and mortars) from historical buildings in Ferrara (Bianchini et al., 2004; 2006). These building materials, made with local sediments analogous to those considered in this study and manufactured in times preceding any significant form of anthropogenic pollution, show compositions strictly comparable with those presented in this study.

The observed concentrations are also compared with legislative thresholds that define contaminated soils. However, it has to be noted that these normative constraints to the soil use usually refer to the metal concentration of the "extracted" solutions, which is usually lower than the bulk concentration. In this light, we re-analysed the investigated sediments according to the normative protocol (see the methods in the previous section) extracting metals with aqua regia (Table 4). Comparing XRF analyses on the bulk samples and ICP-MS analyses on the "extracted" solutions, as reported in Fig. 9, it can be stated that about 50% of the total Cr budget is mobile, and that about 90% of the total Ni budget is mobile.

The Cr concentration appears to be below the tolerance limits in all the investigated samples, whereas Ni concentration of some Ps2-Ps3 soils exceeds the maximum concentration admissible (120 ppm) in terrains that are used for residential purposes and public "green areas" (Italian Legislative Decree 152, 03/04/2006). The reported analyses also provide guidelines for agricultural activities. For example, following the Italian Legislative Decree 99 (27/01/1992), some terrains included in the Ps group (in particular the Ps2 and Ps3) containing more than 75 ppm of Ni could not to be treated and fertilized with sewage sludge (Minnini and Sartori, 1987). The observed Ni content often exceeds the critical thresholds defined for agricultural terrains by Kloke (1993) and Micò et al. (2006 and references therein) in Germany and Spain, respectively. The Enrichment Index is another parameter proposed to evaluate the degree of trace metal contamination (EI; Medici et al., 2011); it averages numerous transition metals preliminary normalized to the tolerance limits of agricultural soils: EI = Co/20 + Cr/150 + Cu/120 + Ni/120 + Pb/100 + V/90 + Zn/150/7. It has to be noted that some Ps2 and Ps3 lithologies display a metal Enrichment Index higher than one, indicating concerns for agricultural activities.

HEAVY METAL SPECIATION

The speciation of chromium and nickel among the different minerals has been investigated by electron microprobe. Attention has been focused on the femic minerals analyzing serpentine, talc, chlorite, amphiboles, pyroxenes, micas, epidotes and oxides. Results indicate that the main carrier of Cr and Ni are represented by chlorite and serpentine, respectively.

Serpentine, and -at least in part- chlorite (Table 5) are inherited from ophiolite lithologies, whereas the provenance of micas and epidotes (Supplementary Table, available in the journal repository) is less constrained. The data-set

Table 5 - Electron microprobe analyses of chlorite, serpentine and talc crystals separated from sediments collected in the surroundings of Ferrara.

Mineral	Chlorite											Talc	
SiO_2	33.83	36.98	33.94	31.40	32.02	29.68	27.08	25.07	25.41	24.95	25.45	59.08	52.24
TiO_2	0.01	0.05	0.01	0.01	0.04	0.03	0.00	0.03	0.02	0.11	0.15	0.01	0.09
Al_2O_3	12.55	12.70	12.46	12.99	16.68	19.42	21.28	21.23	20.00	19.82	20.02	1.05	4.52
Cr_2O_3	1.76	0.71	2.51	0.15	0.38	0.42	0.02	0.00	0.00	0.02	0.00	0.30	1.00
FeOt	3.80	9.53	11.08	15.87	17.67	16.46	24.46	29.77	30.59	30.11	30.68	5.08	3.81
MnO	0.01	0.19	0.04	0.13	0.06	0.00	0.22	0.76	0.69	0.61	0.56	0.00	0.02
NiO	0.18	0.22	0.22	0.11	0.03	0.03	-	-	-	-	-	0.27	0.14
MgO	33.79	25.65	27.25	22.69	20.27	21.52	14.78	10.29	10.85	11.36	10.57	28.47	30.38
CaO	0.05	1.06	0.22	1.24	0.85	0.31	0.04	0.01	0.03	0.05	0.09	0.16	0.10
Na_2O	0.03	0.07	0.01	0.01	0.00	0.06	0.00	0.00	0.00	0.00	0.05	0.00	0.40
K_2O	0.03	0.03	0.06	0.04	0.08	0.00	0.03	0.02	0.00	0.05	0.02	0.05	0.00
V_2O_5	0.02	0.04	0.09	0.02	0.02	0.04	-	-	-	-	-	0.00	0.04
tot	86.61	87.23	87.89	84.66	88.10	87.98	87.91	87.17	87.60	87.07	87.59	94.46	92.74

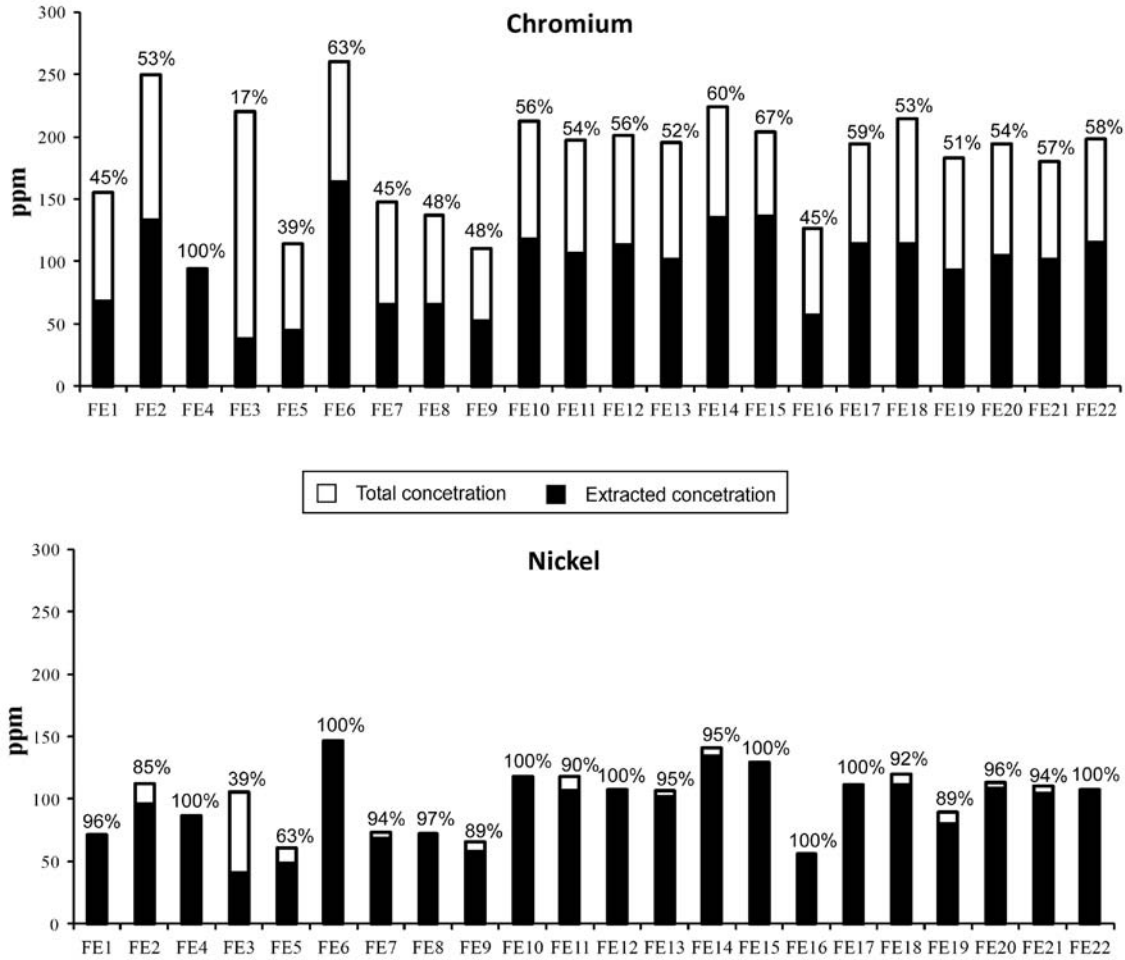| Mineral	Serpentine												Talc							
SiO_2	36.32	36.93	37.92	40.85	39.27	37.53	39.57	39.79	41.18	42.25	44.23	38.59	44.97	42.40	42.07	43.25	44.13	43.92	44.08	43.79
TiO_2	0.00	0.03	0.05	0.01	0.05	0.09	0.03	0.06	0.00	0.01	0.01	0.20	0.02	0.04	0.03	0.02	0.01	0.04	0.04	0.00
Al_2O_3	0.71	3.41	3.18	1.35	3.12	4.98	1.47	3.37	1.62	1.82	0.33	4.17	1.86	3.12	2.70	2.30	1.62	1.97	1.70	2.08
Cr_2O_3	0.02	1.29	0.29	0.28	0.36	1.10	0.03	1.74	0.12	0.19	0.00	0.61	0.05	0.15	0.21	0.18	0.12	0.21	0.40	0.22
FeOt	12.23	8.97	9.98	6.16	10.49	13.14	8.04	4.68	4.31	5.28	4.70	12.28	3.99	7.99	7.35	4.29	2.49	1.68	2.13	1.84
MnO	0.11	0.08	0.10	0.06	0.14	0.12	0.12	0.06	0.09	0.04	0.07	0.13	0.08	0.09	0.13	0.15	0.04	0.06	0.01	0.05
NiO	0.31	0.17	0.33	0.31	0.23	0.35	0.10	0.25	0.12	0.19	0.28	-	-	-	-	-	-	-	-	-
MgO	34.68	33.23	31.15	35.62	30.64	27.59	35.21	35.49	38.74	37.47	37.48	29.81	37.65	34.30	33.78	38.77	40.43	40.32	40.21	40.28
CaO	0.20	0.29	0.53	0.37	0.11	0.69	0.31	0.28	0.10	0.07	0.08	0.31	0.11	0.09	0.07	0.03	0.04	0.02	0.01	0.01
Na_2O	0.03	0.09	0.04	0.02	0.02	0.03	0.05	0.00	0.02	0.04	0.00	0.02	0.06	0.00	0.01	0.03	0.01	0.00	0.00	0.01
K_2O	0.05	0.08	0.03	0.00	0.01	0.03	0.02	0.02	0.01	0.01	0.03	0.07	0.02	0.02	0.03	0.00	0.02	0.03	0.00	0.06
V_2O_5	0.00	0.02	0.03	0.00	0.00	0.00	0.00	0.03	0.01	0.03	0.00	-	-	-	-	-	-	-	-	-
tot	84.65	84.60	83.65	85.03	84.46	85.64	84.96	85.76	86.32	87.40	87.22	86.19	88.81	88.20	86.37	89.01	88.91	88.25	88.59	88.33

Fig. 9 - Comparison between the bulk sediment (XRF) Cr and Ni concentrations and those recorded on aqua regia extracting solutions (ICP-MS). Numbers represent the amount of metal (% respect to the bulk budget) mobilized by leaching with aqua regia.

shows that serpentine crystals display Mg# [Mg/(Mg + Fe)] usually higher than 0.8, indicating that the genesis is related to the transformation of olivine included in ultrafemic rocks such as the mantle peridotites typically recorded in ophiolite associations. These serpentine crystals host up to 0.4 wt% of nickel, thus suggesting that this element is significantly retained in the lattice during the transformation of pristine olivine-rich peridotite parageneses to serpentine-bearing regoliths. Chlorite is quite heterogeneous ranging from ripidolite, penninite up to diabantitic compositions, being variably enriched in Mg, Cr and Ca, and hosts up to 2.5 wt% of chromium. This heterogeneity plausibly reflects significant differences in the parent rocks, which can be discriminated through the Cr_2O_3 vs MnO diagram of Fig. 10, originally proposed by Zaccarini and Garuti (2008). On this basis, it can be observed that the chromium-rich chlorites are those deriving from the ultrafemic lithologies (i.e., peridotites and serpentinites) of the ophiolite sequences. The analyses of these phases reported on the MgO vs SiO_2 and MgO vs Al_2O_3 diagrams (Fig. 11) reveal that the composition of serpentine and chlorite are quite variable from the ideal stoichiometric formula thus suggesting the complex nature of these phyllosilicates that plausibly consist of mixed serpentine/chlorite, smectite layers (Alietti and Mejsner, 1980). This is confirmed by comparatively high Ca concentration in chlorite crystals of some samples that could be attributed to interlayering with smectite layers (Bettison and Schiff-

man, 1988); according to Miyahara et al. (2005) the presence of smectite in the analysed chlorite grains can be accounted for up to 30%. Therefore, the observed hetero-
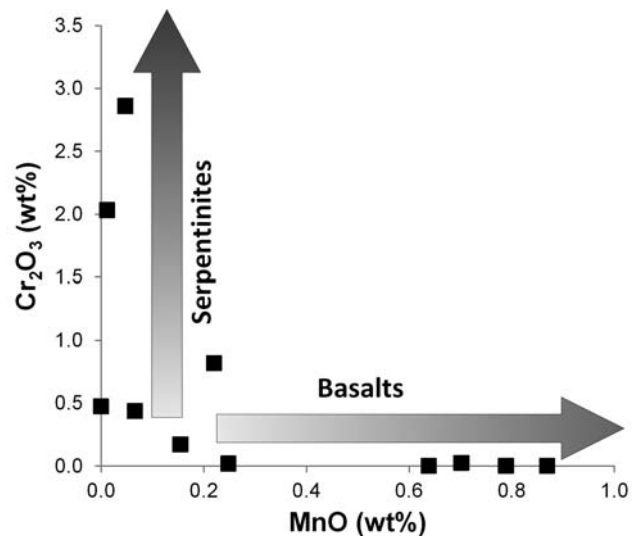
Fig. 10 - Cr_2O_3 vs MnO composition of chlorite crystals included in Po River alluvial sediments that according to Zaccarini and Garuti (2008) is useful to highlight crystals derived from the weathering of ultrafemic parent rocks.
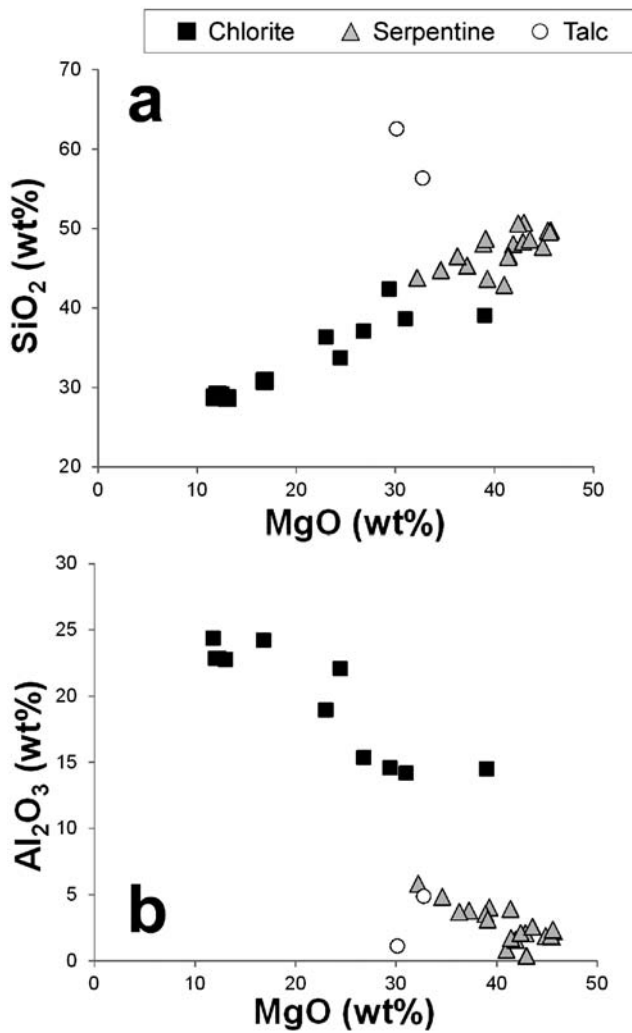
Fig. 11 - SiO$_2$ vs MgO and Al$_2$O$_3$ vs MgO composition of chlorite, serpentine, and talc included in Po River alluvial sediments. Note that the wide compositional spectrum suggests a composite nature of these phyllosicate crystals with alternation of dioctaedral and trioctaedral layers.

geneities of the considered phyllosilicates reflect evolving environments ranging from surface to low-grade metamorphic conditions; this evolution in the supergene environment induces formation of complex phyllosilicates alternating dioctaedral and trioctaedral layers (Šrodoń,1999).

The considered inosilicates (Supplementary Table, available in the journal repository) do not contain Cr and Ni, and merely confirm the presence of ophiolite components in the studied sediments: clinopyroxene and orthopyroxene record the following compositional ranges En$_{53-52}$ Fs$_{21-20}$ Wo$_{27}$ and En$_{75-66}$ Fs$_{23-21}$ Wo$_{4-1}$, respectively, as often observed in femic magmatic rocks; amphibole includes Mg-horneblende as well as pargasite that are compatible with those of ophiolite lithologies.

CONCLUSIONS

High heavy metals backgrounds, in particular chromium and nickel, are renowned in soils and sediments of the Po Plain. This feature, due to ophiolite contributions in the Po River sediments, appears more marked upstream the Ticino confluence (up to 7%) that is relatively close femic/ultra-

femic outcrops, and gradually vanish toward the studied area downstream, where the percentage of ophiolite components is reduced down 3.5% (Garzanti et al., 2012).

The presented geochemical maps emphasize that sediments related to the Reno River (Rs1 and Rs2) display comparatively low Cr-Ni contents, and that the anomalously high Cr-Ni backgrounds are confined on the outcrops of fine alluvial sediments of the Po River (Ps2 and Ps3). This evidence suggests that heavy metals are trapped and sequestrated by specific phyllosilicates (serpentine, chlorite, smectite) that are preferentially deposited in the low-energy anastomosing fluvial system of the Po River delta. Further enrichment of heavy metals is favoured by the presence of organic matter, typically characterizing the deltaic depositional environments of Po River.

Our investigation reveals that the mobility of chromium is limited as this element is effectively sequestrated in chlorite crystals, and the natural water of the area (e.g., the water of Po River) usually display concentration (< 10 mg/l; Authors unpublished data) lower than the national drinking standards (50 mg/l). Unfortunately, this element is considered toxic and dangerous even at extremely low concentration if oxidized in the hexavalent form that is prevalent in supergene conditions and in natural water, thus posing serious environmental concerns. Nickel, on the other hand, displays a higher mobility, possibly because it is associated with serpentine that is a metastable mineral phase (Kierczak et al., 2007). Coherently the Cr/Ni is always higher than one in the investigated sediments and soils, whereas is always lower than one in both the natural waters (e.g., the water of Po River; Authors unpublished data) and agricultural products (Bianchini et al., 2012) of the area. Therefore, the high bio-accessibility of nickel represents further geochemical risk for the area and the relative content has to be carefully monitored in the local crops (Smart and Sherlock, 1987; Cempel and Nikel, 2005).

For these reasons, anthropogenic heavy-metals loads have to be minimized on these terrains limiting the use of sludge fertilization as well as the construction of landfills that could potentially release additional Cr and Ni-rich components (Abu-Zeid et al., 2004) as well as acidic fluids that enhance the contaminant mobility. Moreover, aquaculture activities such as mussels and clam farms developed in the lagoons widespread around the delta of Po River are also potentially exposed to heavy metals bio-accumulation and the related products have to be carefully monitored.

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