

Influence of sediment provenance on background values of potentially toxic metals from near-surface sediments of Po coastal plain (Italy)

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Abstract Systematic variability in metal concentrations is recorded in near-surface (1 m deep) Late Quaternary sediments of Po coastal plain, across the boundary between alluvial deposits of Apenninic provenance and a formerly active, now abandoned, delta lobe of the Po River. In the latter area, high Cr and Ni concentrations, exceeding the national standard limits, are attributed to sediment provenance from ultramafic source rocks of Po catchment basin, and not to anthropogenic impact. Spatial distribution of carbonate-related elements, such as Ca and Sr, displays consistent differences between the two areas, confirming a primary control of provenance domains on sediment composition. Accurate facies characterization of near-surface sediments, coupled with detailed information on sediment dispersal patterns, enable a reliable interpretation of the spatial variability of major elements and trace metals in the study area. Particularly, detailed reconstructions of source area composition and changes in flow directions through historical times allow precise correlation of apparently anomalous geochemical patterns with distinctive depositional events, such as shifts in channel course, crevasse splay formation and beach-ridge evolution. The findings of unusually high, natural (provenance-controlled) heavy metal concentrations in pre-industrial near-surface levels highlight the contribution of a sedimentological approach to a reliable interpretation

of geochemical data. This should be taken into account when determining background values versus anthropogenic impact.

Keywords Sediment provenance · Background values · Heavy metals · Quaternary · Po Plain

Introduction

It is widely held that total element concentrations in the natural surficial environment may vary by several orders of magnitude (Tarvainen and Kallio 2002), depending primarily on the different geological properties of sediments and related source rocks. When dealing with unconsolidated Quaternary deposits, the type of sedimentary facies and composition, which reflect distinctive sediment provenance and grain size, play a fundamental role in controlling the spatial distribution of heavy metals. In spite of this, integration of accurate sedimentological studies with geochemical analyses is relatively uncommon, and very few studies have examined in detail the relationships between facies associations and chemical composition of sediments (Miller 1997; Box and Wallis 2002).

The Po Plain is the surface expression of a thick sedimentary basin, bounded by the Alps to the north and the Apennines to the south that records a complex depositional history and tectonic evolution. Surface geology, depicted by the Geological Maps produced by the Emilia-Romagna Geological Survey, used detailed geomorphologic investigations that have been carried out in the last decades (Ciabatti 1967; Nelson 1970; Veggiani 1974; Castiglioni et al. 1990;

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Bondesan et al. 1995). A considerable knowledge exists on subsurface geology beneath the present coastal plain, where sedimentological data from tens of continuously cored boreholes (Amorosi et al. 1999, 2003) and hundreds of piezocone penetration tests (Amorosi and Marchi 1999) have recently led to the three-dimensional reconstruction of the stratigraphic architecture within the uppermost 30–40 m. Given the large amount of geologic information available for this area, the Po Plain provides an excellent site to test the influence of drainage basin lithology and depositional dynamics on heavy metal distribution.

The drainage pattern of the Po Plain, with a catchment area of about 70,000 km², includes a major trunk river, the Po, that flows into the Adriatic Sea. It receives sediment from numerous tributaries emerging from the surrounding Alpine and Apenninic chains. The modern Po delta is very recent in origin: in ancient times (before twelfth Century A.D.) the Po River flowed in a more southerly position, between Ferrara and Ravenna. Several coalescing delta lobes were then fed by four major distributary channels, such as Po di Ariano, Po di Volano, Po di Spina, and Po di Primaro (Fig. 1). After the Ficarolo avulsion event (Ciabatti 1967), in 1152, about 10 km NW of Bondeno (Fig. 1), the Po River shifted to the north, toward its present position. Its four distributary channels became progressively inactive, and the ancient Po delta lobe was

abandoned. As a consequence, the lower reaches of its southern branch (Po di Primaro) were incorporated into the Apenninic network, receiving sediments from Sillaro, Santerno and Senio rivers. At present, the Po di Primaro coincides with the Reno River, which flows from the Apennines in the Bologna area (Fig. 1).

Significant provenance changes in the Late Quaternary evolution of the Po Plain, south of the present Po River, have recently been documented by sand petrography (Marchesini et al. 2000) and geochemical characterization of fine-grained (silt and clay) deposits (Amorosi et al. 2002). Results have enabled detailed reconstruction of the paleogeographic evolution during the last 30 ky. Geochemical and mineralogical variations along 16 core profiles have revealed that Late Quaternary deposits of the Po Plain preserve signatures of the related catchment basins. Particularly, Cr and Ni among the metals and serpentine minerals detected in the clay fraction by XRD analysis have been proved to be unequivocal provenance indicators in the Po River drainage basin, reflecting a significant contribution from ophiolites, serpentinites and ultramafic source rocks to the Po delta and the adjacent coastal plain, via longshore drift (Amorosi et al. 2002). On the other hand, Cr and serpentine concentrations are invariably lower in fine-grained fluvial sediments from the Romagna Apennines. Average absolute Cr values for these core sediment samples of Apenninic provenance are 125 ± 16 ppm (E. Dinelli, personal communication, 2003). By contrast, Cr in cores from Po River deposits averages 216 ± 34 ppm. The latter values obviously represent natural Cr concentrations and are devoid of anthropogenic disturbance. They lie above the maximum contaminant level (150 ppm) for Cr in soils, as designated by the Italian environmental legislation (Decr. Min. 471/99) for residential and recreational land use. Previous work by Amorosi et al. (2002) has been confirmed by Vignati et al. (2003), showing that Cr levels in the Po river sediments are higher than most of the published sediment quality guidelines.

The surficial geology of the Po coastal plain, north of Ravenna, offers a great diversity of facies associations. It comprises a northern sector that, in part, coincides with the abandoned Po delta lobe. Its southern part reflects sediment contribution from Apenninic sources (Fig. 1). This peculiar setting, thus, provides an excellent case to investigate how changes in the geochemical background can be closely related to variations in sediment provenance.

The geochemical background is commonly defined as the natural abundance of an element in a given material (soil, sediment or rock), with reference to a

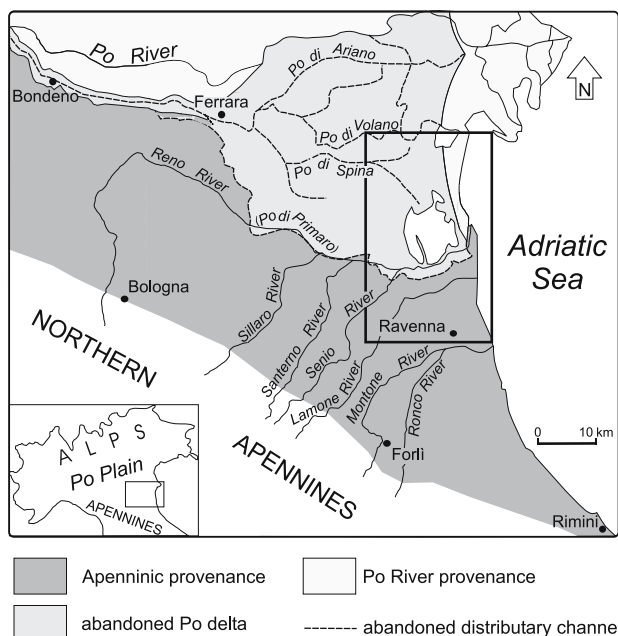


Fig. 1 Location of the study area showing drainage patterns and the southern Po Plain. The study area corresponds to Sheet 205 (Comacchio) + Sheet 223 (Ravenna) of the Geological Map to 1:50,000 scale

particular area or data set (see discussion in Salminen and Gregorauskienė 2000). Geochemical baseline values (Darnley 1997) have regional and local variations that may have a wide range, according to changes in basic geology (Salminen and Tarvainen 1997), grain size and depositional environment (Ruiz 2001).

The purpose of this paper, which expands upon previous subsurface studies from the Po coastal plain, is to provide a case study for the assessment of background values for potentially toxic metals in near-surface sediments that bear strong geochemical signatures of source rock composition. Specific aim is to document how interpretation of geochemical data based upon a detailed sedimentological framework can represent an innovative, powerful tool for a reliable mapping of hazardous levels of heavy metal concentration.

Sampling strategy and methods

Samples were collected at 120 different locations by hand drilling. Sampling depth was 90–110 cm, corresponding to the B-horizon of soils. Sediment description includes colour, grain size (assessed by visual inspection of cores), accessory materials (roots, organic matter, shell fragments), and facies associations. Sampling was carried out on an area of 820 km², according to 2.5 × 2.5 km² cells. Sites for sampling, however, did not follow regular grids, but were selected accurately on the basis of surficial geology (see Geological Map of the Emilia-Romagna Plain 1999), in order to encompass the wide spectrum of deposits cropping out in the study area.

Six facies associations were identified. Four of them (beach-ridge sands, 36 samples; channel-levee and crevasse splay silty sands, 16 samples; floodplain clays, 27 samples; distributary channel silts and sands, 13 samples) coincide with depositional units defined by the Geological Map. The remaining two facies associations (interdistributary bay fossil-rich clays, 19 samples; interdistributary area organic-rich clays and peats, 9 samples) were identified during the hand-drilling campaign, and represent a subdivision of the former interdistributary area deposits.

Samples for XRF-analysis were not sieved, and analysed as bulk. They were air dried at 40°C and powdered in an agate swing mill. The ground samples, pressed into tablets, were analysed for major and trace elements in a Philips PW1480 spectrometry with a Rh tube, using matrix correction methods of Franzini et al. (1972, 1975), Leoni and Saitta (1976) and Leoni et al.

(1986). The accuracy of determinations for trace elements is 5%, except for elements with concentration of 10 ppm or lower, where the accuracy is 10–15%.

Provenance indicators in near-surface sediments of Po coastal plain

Use of near-surface sediments to estimate background values of potentially toxic metals

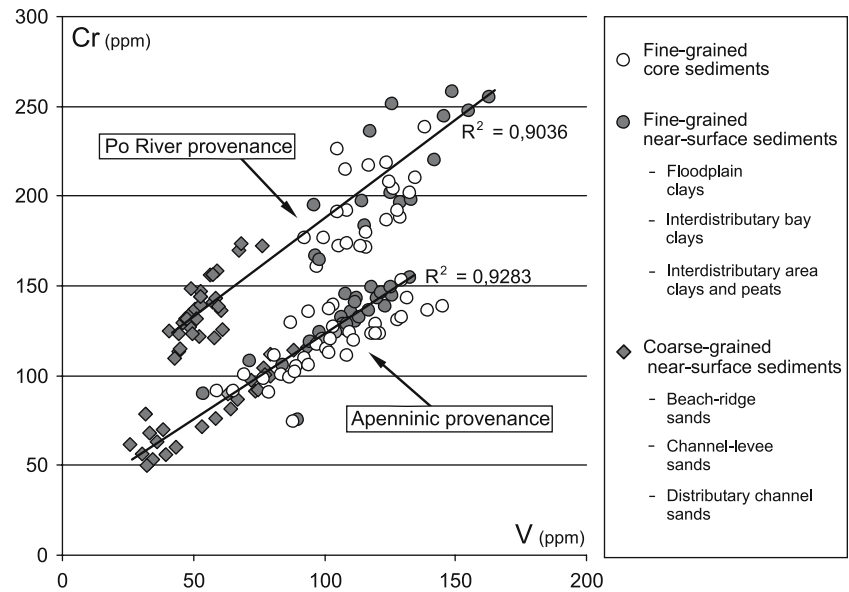
Unlike surface sediments, which strongly reflect the recent human contribution, samples collected from cores below any anthropogenic influence may enable a reasonable estimation of the background levels (Liaghati et al. 2003). It is assumed that near-surface samples, collected at 1 m depth, accumulated under pre-industrial conditions and have been shown to be suitable to determine natural background values for potentially toxic metals, even in highly industrialized areas (Huisman et al. 1997). However, to test the reliability of near-surface sediments as indicators of background levels in the Po coastal plain, a comparison was made with fine-grained (silt and clay) samples collected in the same area from 5–40 m deep cores (Amorosi et al. 2002), i.e. far below the possible effects of the pre-industrial concentration of metals or other pollution caused by agricultural activity.

The ratio between two relatively immobile elements, such as Cr and V, traditionally regarded as a good provenance indicator (McLennan et al. 1990; Wronkiewicz and Condie 1990; Cullers 1994; Bauluz et al. 2000), was used to compare two different sets of samples. Figure 2 shows a good correspondence between the fine-grained samples from cores and the fine-grained near-surface sediments, proving that the latter may serve efficiently as reliable indicators of background values for these metals. The Cr/V diagram of near-surface samples (Fig. 2) reveals two distinct linear trends, which represent a clear indication of two different source rocks types: (a) the Cr-poor lithologies of the northern (Romagna) Apennines and (b) the relatively Cr-rich rocks of the Po River drainage basin (see “Geochemical indicators of sediment provenance”).

Geochemical indicators of sediment provenance

Natural background concentrations show remarkable variations, reflecting differences in sediment provenance and grain size (Salminen and Tarvainen 1997). The important influence of grain size on heavy metal distribution in the near-surface sediments of the study

Fig. 2 Scatterplots of Cr versus V content from fine-grained (clay and silt) core samples (data from Amorosi et al. 2002) and near-surface (1 m) samples (this work). The two lines reflect separation between Apenninic (low Cr) and Po River (high Cr) provenance. Note the good overlap between the two sets of fine-grained deposits, suggesting that samples at 1 m depth can be used confidently as indicators of background values. Coordinates representing concentrations within coarse-grained (sand) deposits plot further down the tie lines



area is documented by substantial covariation between Cr and V (Fig. 2), with increasing values from coarse-grained deposits (beach-ridge, channel-levee and distributary-channel sands in Fig. 2) to fine-grained sediments (floodplain, interdistributary bay and interdistributary area silts and clays in Fig. 2). This implies that, for a given source area (Apenninic or Po River provenance), silt and clay material appears to contain invariably more trace metals than sandy sediments, irrespective of the type (marine, brackish or continental) of depositional environment. This consistent difference between clays and sands is interpreted to reflect the different hydrodynamic behaviour of suspended sediment relative to bed load, and emphasizes the role of transport mechanisms and hydraulic sorting in the physical dispersal of heavy metals (see also Singh and Rajamani 2001; Whitmore et al. 2004).

Owing to this high facies variability and the consequent geochemical heterogeneity as a function of grain size, provenance interpretations based on absolute element concentrations alone could be misleading. Therefore, to highlight the influence of sediment provenance and to avoid grain-size effects on element concentration, we applied a common normalization procedure, by plotting onto the geological map (Fig. 3) a key element, such as Cr, against Al_2O_3 (Daskalakis and O'Connor 1995; Huisman et al. 2000; Ruiz 2001; Liaghati et al. 2003).

Excluding seven samples, six of which are aligned along a N–S elongated beach ridge, north of Ravenna, a clear separation in terms of $\text{Cr}/\text{Al}_2\text{O}_3$ distribution is recorded across Reno River, which was active as the southern branch (Po di Primaro) of the Po delta

(Fig. 3). Almost all samples from the northern area, corresponding to the abandoned Po delta lobe, show increased $\text{Cr}/\text{Al}_2\text{O}_3$ values. Conversely, $\text{Cr}/\text{Al}_2\text{O}_3$ ratios decline sharply south of Reno River, suggesting sediment provenance from the adjacent Apenninic chain.

Unlike sand deposits from the northern distributary channels (Po di Spina and Po di Volano), which invariably display high $\text{Cr}/\text{Al}_2\text{O}_3$ values, crevasse splays from Po di Primaro show alternatively high and low $\text{Cr}/\text{Al}_2\text{O}_3$ values (black and white dots in Fig. 3), in roughly equal proportion. In this instance, crevasse splays with high $\text{Cr}/\text{Al}_2\text{O}_3$ values are interpreted to have formed before the Ficarolo avulsion (Ciabatti 1967), when Po di Primaro acted as a distributary channel of the Po delta. After 1152 AD, when Po di Primaro was incorporated into the Apenninic network, a new sediment source, of Apenninic origin, was supplied into an area previously dominated by Po River sediments, forming the Cr-poor crevasse splays. It is, thus, apparent how detailed sedimentological information may enable a refined interpretation of geochemical data, forming the basis to detect historical changes in drainage patterns and reconstruct source area composition.

The historical evolution of the Po di Primaro-Reno River system also provides the basis to interpret Cr distribution along the N–S trending beach ridge north of Ravenna, with remarkably higher $\text{Cr}/\text{Al}_2\text{O}_3$ values compared to the adjacent units. This beach ridge represents an ancient delta front-strandplain system, which received sediment directly from the Po River prior to the Ficarolo avulsion, with subsequent

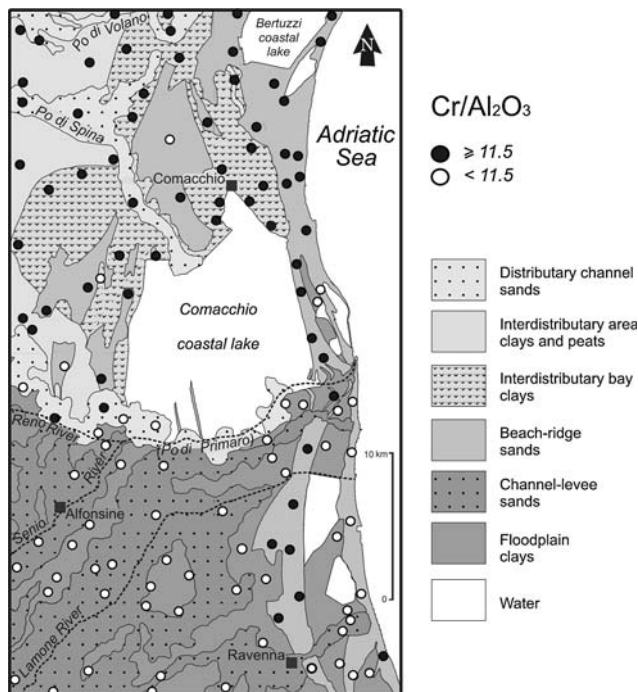


Fig. 3 Spatial distribution of $\text{Cr}/\text{Al}_2\text{O}_3$ in near-surface sediments of Po coastal plain, based on 120 sampling sites. Surficial geology modified from the Geological Map of the Emilia-Romagna Plain (1999)

alongshore dispersion of Cr-rich sediments by wave-induced currents. By contrast, the beach sediments forming the present Adriatic coast, east of Ravenna, are evidently depleted in Cr, reflecting sediment delivery from the Apennines by the Reno River during the last few centuries. Of note also is the spatial variability of $\text{Cr}/\text{Al}_2\text{O}_3$ along the beach ridge, with low concentrations typical for an Apenninic origin recorded at the southern margin of the study area (white dot south of Ravenna, in Fig. 3). This is likely to reflect a progressive contribution of sediment of Apenninic provenance, with increasing distance from the Po di Primaro fluvial mouth.

$\text{Ni}/\text{Al}_2\text{O}_3$ values do not display a discernible change compared to $\text{Cr}/\text{Al}_2\text{O}_3$, and for this reason their spatial distribution is not shown here. Despite a general trend

toward higher concentrations in the finer-grained (floodplain and interdistributary area) facies associations, deltaic sediments fed by the Po River have invariably higher $\text{Ni}/\text{Al}_2\text{O}_3$ values than alluvial plain sediments deriving from the Romagna Apennines, with no overlap (Table 1), allowing an obvious separation of the two provenance domains.

CaO distribution from near-surface sediments of the study area mirrors the geochemical behaviour of Cr and Ni, pointing to a similar distinction between sediments of Apenninic versus Po River origin (Fig. 4). The majority of samples from the northern area show uniformly low Ca concentrations. By contrast, a great uniformity of chemical composition characterizes the study area south of Reno River, with significantly higher Ca values (Table 1). Similarly to what observed for $\text{Cr}/\text{Al}_2\text{O}_3$ distribution (cf. Fig. 3), CaO displays remarkable variations along the Primaro/Reno distributary channel, and a Po river affinity is recognized for the beach ridge cropping out north of Ravenna (Fig. 4). Similarly to Ca, strontium appears as another provenance indicator, showing a clear distinction between samples of Apenninic and Po River provenance, regardless of grain size variations (Table 1).

Discussion

Data shown in the previous sections clearly document that the strong chemical contrast in near-surface sediments from the Po coastal plain was caused predominantly by the changes in sediment source composition through space and time. Although Cr (and Ni) invariably show maximum concentrations within finer-grained deposits (see Fig. 2), spatial distribution of $\text{Cr}/\text{Al}_2\text{O}_3$ and $\text{Ni}/\text{Al}_2\text{O}_3$ does not appear to be controlled by grain size (Figs. 3, 4). In this respect, Cr and Ni may serve efficiently as provenance indicators (Feng and Kerrich 1990; Bauluz et al. 2000) and can be used successfully to differentiate Alpine-derived Po River deposits from sediments from an Apenninic source. These metals are commonly contained in minerals of

Table 1 Average concentration of selected provenance indicators from near-surface sediments of Po coastal plain, with subdivision of sediments with Po River versus Apenninic provenance into facies associations

Provenance	Facies association	$\text{Cr}/\text{Al}_2\text{O}_3$	$\text{Ni}/\text{Al}_2\text{O}_3$	CaO (%)	Sr (ppm)
Po River	Beach ridge	13.7 ± 2.2	7.9 ± 1.6	8.6 ± 2.2	248 ± 33
	Distributary channel-levee	14.2 ± 1.4	9.1 ± 1.0	9.6 ± 2.6	265 ± 38
	Interdistributary bay	13.4 ± 1.1	8.1 ± 1.6	6.4 ± 4.2	227 ± 74
	Interdistributary area	15.1 ± 1.4	9.4 ± 2.1	3.4 ± 3.8	161 ± 95
Apennines	Beach ridge	8.6 ± 2.1	4.8 ± 0.6	17.9 ± 5.3	375 ± 85
	Fluvial channel-levee	8.4 ± 1.1	5.3 ± 0.6	15.8 ± 1.9	337 ± 50
	Floodplain	10.4 ± 1.0	6.4 ± 0.6	14.7 ± 2.0	379 ± 37

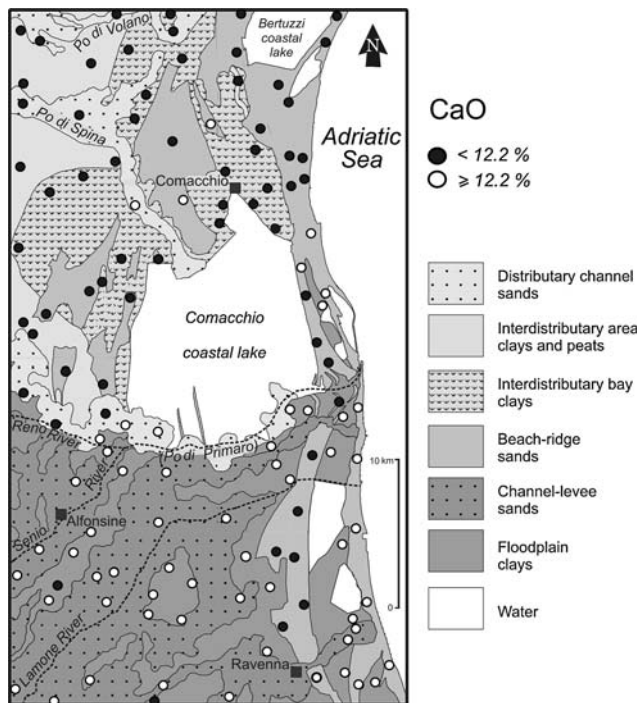


Fig. 4 Spatial distribution of CaO in near-surface sediments of Po coastal plain, based on 120 sampling sites. Surficial geology modified from the Geological Map of the Emilia-Romagna Plain (1999)

ultrabasic igneous rocks, such as forsterite-olivine, chrome diopside and chromite (van de Kamp and Leake 1995).

Rocks that could act as potential sources for Cr and Ni are the ophiolitic complexes cropping out extensively along the Western Alps (Amorosi et al. 2002), although a minor contribution from the northwestern (Emilia) Apennines, which are part of the Po drainage basin, cannot be excluded. An additional possible source for Cr and Ni are the metamorphic equivalents of the above ultrabasic rocks, i.e. the serpentinites, which form under low-grade metamorphism. High values (up to 3% of total rock composition) of serpentinite rock fragments have been reported by Gazzi and Zuffa (1970) from beach sands at the Po River mouth.

The low Cr concentrations recorded south of Reno River are consistent with the lower Cr values found in bed-load sediments from the Romagna Apennines rivers, between Bologna and Forlì (Dinelli et al. 1999), where the mixed carbonate-siliciclastic Miocene “Marnoso-arenacea” turbidites constitute the dominant sedimentary unit of the catchment basin. The significantly higher amount of carbonate rock fragments delivered by the Apenninic rivers to the adjacent coastal plain compared to the Po River (Gazzi and

Zuffa 1970; Dinelli and Lucchini 1999), is interpreted as the major controlling factor of the remarkably high Ca and Sr values recorded south of Reno River.

Results of the present study on fluvial, coastal, and deltaic near-surface sediments of the Po coastal plain are consistent with an earlier work by Amorosi et al. (2002), showing Cr enrichment in core material. Similar enrichments were reported from a small area around the town of Ferrara (Bianchini et al. 2002), and from channel-bed sediments of Po River throughout its catchment (Dinelli and Lucchini 1999; Vignati et al. 2003). The high Cr concentrations in near-surface sediments, related to Po River activity, indicate that such elevated levels are natural and do not reflect land-use practices or artificial contamination. Similarly to the observation by Vignati et al. (2003) for Cr levels in bed-load sediments and suspended sediments of the Po River, natural Cr concentrations found in Po-derived sediments of the Po coastal plain are by far higher than the threshold effect concentration (TEC—concentration above which toxicity may be observed) and the probable effect concentration (PEC—concentration above which toxicity is frequently observed) reported by MacDonald et al. (2000). These values for Cr are 43 ppm (TEC) and 111 ppm (PEC), respectively. Although most Cr does not appear to be bioavailable owing to its natural origin (Sammartino 2004), it is clear how local conditions, instead of “world mean values” are essential for the calculation of background values and for the subsequent evaluation of metals of anthropogenic origin.

In summary, this study documents that background concentrations of potentially toxic metals do not necessarily mean low concentrations (see Matschullat et al. 2000). Natural geological conditions may imply high metal contents, which should be taken into account by environmental legislation locally in the assessment of contaminated soils. A correct determination of background values has important economic implications for soil management, resulting in precise differentiation between contaminated and pollutant-free soils (Salminen and Gregorauskiene 2000). The patterns of metal distribution shown in this study from the Po coastal plain suggest that a large part of the Po Plain, directly fed by the Po River, contains natural concentrations of Cr and Ni that are higher than the Italian standard limits. These values in the Po catchment basin represent the background values against which anthropogenic influence should be assessed. Once background (pre-contamination) values of potentially toxic metals are established on a geological basis, values exceeding the limit between background and anomalous concentrations at specific sites can

be assessed as a clear evidence of contamination (Sammartino 2004).

Conclusions

1. Interpreting heavy metal concentrations on a sedimentological basis may represent an efficient, new methodological approach for mapping metal distribution in areas with contrasting sediment provenance. Facies analysis and accurate reconstruction of historical changes in drainage patterns may greatly assist in understanding apparently anomalous patterns of metal distribution.
2. The unusually high amounts of Cr and Ni recorded in near-surface sediments from the Po coastal plain reflect the geochemical characteristics of the Po River drainage basin, and are considered to represent background levels that do not reflect any anthropogenic influence. Ophiolites and serpentine rock fragments are identified as the major natural sources. The low Ca and Sr values for Po River deposits are also noteworthy, and indicate meaningful differences in source rock composition compared to carbonate-rich deposits fed by Apenninic sources.
3. Because natural background concentrations of metals in soils can be notably different from one area to another, to understand specific pollution problems background values should be defined independently for individual areas that reflect marked differences in sediment provenance. This study demonstrates that in the case of the Po Plain, the limiting values for Cr and Ni concentrations in soils should not follow directives from other countries, but should be modified taking into account the natural distribution of these potentially toxic metals.

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