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Title: Geochemical proxies of sediment provenance in alluvial plains with interfering fluvial systems: a study case from NE Italy

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Keywords: Padanian plain; Po and Adige rivers; geochemical proxies; palaeohydrographic reconstruction

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Abstract: This paper demonstrates that geochemistry is useful for the identification of sediment origin and provenance in alluvial plains characterised by a complex hydrographic evolution. The study is focused on the northeastern Padanian plain (Italy), an area primarily characterised by sedimentary contributions from the two largest Italian river systems (Po and Adige), which intimately interacted during the last millennia. X-ray fluorescence analyses of 120 soils and alluvial sediments define three diverse geochemical affinities that have distinctive siderophile/chalcophile elemental ratios. The sample group characterised by high Ni/Zn and Cr/Pb values conforms to modern Po River sediments, whereas a second group showing low Ni/Zn and Cr/Pb values conforms to the geochemical signature of modern Adige River sediments. A third sample group defines a "transitional" affinity that represents a geochemical mixture of Po (70%) and Adige (30%) sedimentary end-members. Based on these geochemical features, it is possible to distinguish alluvial sediments of the Po River basin (Ni/Zn > 1.0 and Cr/Pb > 4.2) from those of the Adige River basin (Ni/Zn < 0.6 and Cr/Pb < 1.9) and to provide evidence of the migration of these rivers during the evolution of the Padanian plain. The interpretation of transitional samples is less constrained and could imply an ancient connection between the two fluvial systems, possibly due to the development of wetlands where both the Po and Adige rivers variably delivered their sedimentary contributions. This study approach, therefore, provides important implications for palaeohydrographic and palaeoenvironmental reconstructions in a complex area that is characterised by significant geomorphological modifications during the last millennia.

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Geochemical proxies of sediment provenance in alluvial plains with interfering fluvial systems: ~~a~~ A study case from NE Italy

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Abstract

This ~~contribution~~ paper demonstrates that geochemistry is useful for the identification of sediment origin and provenance in alluvial plains characterised by a complex hydrographic evolution. The study is focused on the northeastern Padanian plain (Italy), an area primarily~~mainly~~ characterised by sedimentary contributions from the two largest Italian river systems (Po and Adige), which ~~that~~ intimately interacted during~~in~~ the last millennia. X-ray fluorescence analyses of 120 soils and alluvial sediments define three diverse geochemical affinities ~~having~~ that have distinctive siderophile/chalcophile elemental ratios. The sample group characterised by high Ni/Zn and Cr/Pb values conforms to ~~the~~ modern Po ~~river~~ River sediments, whereas a second group showing low Ni/Zn and Cr/Pb values conforms to the geochemical signature of ~~the~~ modern Adige ~~river~~ River sediments. A third sample group defines a "transitional" affinity ~~representing~~ that represents a geochemical mixture of Po (70%) and Adige (30%) sedimentary end-members. Based on these geochemical features, it is possible to distinguish alluvial sediments of the Po ~~river~~ River basin (Ni/Zn > 1.0 and Cr/Pb > 4.2) from those of the Adige ~~river~~ River basin (Ni/Zn < 0.6 and Cr/Pb < 1.9) and to provide evidence of~~clues on~~ the migration of these rivers during the evolution of the Padanian plain. The interpretation of transitional samples is less constrained and could imply an ancient connection between the two fluvial systems, possibly due to~~plausibly by~~ the development of wetlands where both the Po and Adige rivers variably delivered their sedimentary contributions. Th~~is~~ise study approach, therefore, provides important implications for palaeohydrographic and palaeoenvironmental reconstructions in a complex area that ~~was~~ is characterised by significant geomorphological modifications during~~in~~ the last millennia.

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Introduction

The sedimentary infill of continental basins is related to climatic and tectonic processes that influence rock weathering, erosion, transport of clastic particles and deposition. The interplay of varying subsidence rates and sediment supplies results in the development of different sedimentary environments, ranging from fluvial to a variety of lacustrine settings. The resulting floodplains are complex landscape assemblages~~ of landscapes~~ composed of active landforms (e.g., channels) and stabilis~~z~~ed units of various ages and origins (e.g., abandoned channels and banks), which are often formed~~derived~~ by the overlap~~ping in space and time~~ of multiple riverine systems in space and time.

The development of human settlements~~settlings~~ and their interactions with the hydrographic networks causes~~provides~~ additional complexities in~~to~~ the natural evolution of these environments. Floodplains are, therefore, paleoclimatic and ~~hystorical~~historical archives~~,~~ that record~~ing~~ human activities and the hydroclimatic evolution,~~ and human activities that~~ which are typically~~usually~~ revealed by the~~deciphered~~ coupling of geomorphological, sedimentological and archaeological studies (Gautier et al., 2009, Hoffmann et al., 2010; D'Haen et al., 2012). In this framework, the ~~understanding of~~ sedimentary dynamics in alluvial plains can be determined~~implemented by the~~ using~~e of~~ geochemical tracers that are~~represent~~ powerful tools for the identification of~~ the~~ sediment source areas (e.g., Macklin et al., 2006; Singh, 2010; Campodonico et al., 2016). This~~e~~ approach has been widely used in the Emilia-Romagna region~~ in order~~ to distinguish the alluvial sediments in~~of~~ the Po ~~river~~River, which drains~~ing~~ the Western Alps, from those of other riverine systems that drain~~ing~~ the Northern Apennines (Amorosi, 2012; Bianchini et al., 2012; 2013). Conversely, the potential of this~~e~~ method has been scarcely~~ been~~ tested northward, where the Po ~~river~~ River system interfered with other fluvial depositional systems during the ~~development of the~~ Padanian plain development. In~~ particular, in~~ this work we particularly investigated a sector of the plain, located between the towns of Ferrara and Rovigo, that is bordered to the north~~ward~~ and south~~ward~~ by the Adige and Po rivers, respectively (Fig. 1). The purpose was to identify geochemical proxies for~~of~~ distinct sedimentary end-members and to analyse their spatial distribution, ultimately providing evidence~~clues~~ for the palaeohydrographic evolution of the area. To achieve this~~In this view~~, 120 major and trace element geochemical analyses of soils and alluvial sediments have been statistically studied~~elaborated in order~~ to identify the geochemical trends related to weathering of different mother rocks that outcrop~~ping~~ in separate hydrological basins. Moreover, 18 samples of bed and suspended sediments from the Po and Adige rivers have been ~~also~~ sampled and analysed~~, in order~~ to verify their geochemical affinity and to compare the current and past daily~~y~~ trends~~ with those occurred in the past~~. The results represent a powerful complementary tool to the geomorphological approach for~~in~~ the reconstruction of the palaeohydrographic patterns of the northeastern Padanian plain, which~~that~~ are currently~~so far~~ hypothetical and primarily~~mainly~~ based on the interpretation of landforms and~~ findings of~~ archaeological remains (Piovan et al., 2010; Corrò and Mozzi, 2016).

Geological and geomorphological outlines

The study area is located in the easternmost part of the Padanian plain in northern Italy, a sedimentary basin between the Alps and the Apennines that was progressively filled by Neogene marine sediments and finally capped by fluvial sediments since the Pleistocene. During the~~In~~ Late Holocene, the sedimentary discharge was supplied by two primary~~main~~ fluvial systems (Po and Adige), and the configuration of the local drainage system was predominantly~~mainly~~ controlled by the interaction between~~among~~ tectonic, climatic, eustatic, and sedimentary processes (Garzanti et al., 2011). The geological features of the~~ir~~ basins are briefly described below.

The Po ~~river~~ River drains the western Alps (Marchina et al., 2015), which~~that~~ are characterised by a prevalent crystalline basement~~,~~ consisting of felsic plutonic rocks (granitoids) and metamorphic rocks (Boriani et al., 2003). Jurassic ophiolites consisting of serpentinis~~z~~ed peridotites, gabbros and basalts are also observed in the western Alps, together with sedimentary rocks such as Mesozoic (Triassic and Jurassic) limestones that become significant only in the central Alps (in Lombardy;

Bosellini, 2004) and subordinate Tertiary silico-clastic rocks (Maino et al., 2013). Ore deposits recorded in the Po basin primarily~~mainly~~ consist of Fe-Ni and PGE (platinoids) elements, typically~~usually~~ associated with~~to~~ ultramafic rocks (Garuti and Rinaldi, 1986; Rossetti and Zucchetti, 1988; Carbonin et al., 2015).

The Adige ~~river~~ River drains metamorphic rocks of the Austroalpine domain in the upper part of the basin, rhyolitic rocks of the Atesian volcanic complex between Bolzano and Trento, and ~~then~~ the carbonate units of the Southalpine domain (Natali et al., 2016). Zn-Pb-Cu-Fe sulphide-bearing ore deposits are renowned in the Adige basin (Nimis et al., 2012), which are occasionally~~sometimes~~ associated with barite and fluorite (Bakos et al., 1972).

The study area ranges in elevation between 5 and 3.5 m a.s.l. and is characterised by a complex network of alluvial ridges formed by the aggradation of sandy and silty channel deposits, natural levees, and minor~~,~~ proximal crevasse splays. The depressions contain finer distal levee deposits, such as silty clays, that are ~~sometimes~~occasionally associated with abundant organic matter~~,~~ suggesting the local development of swamps (Piovan et al., 2008; 2010).

The soils developed on these alluvial deposits are generally characterised by a limited profile development, in which the lack of soil maturity is related to the young depositional age (Late Holocene), fluvial reworking and extensive agricultural activities (ploughing). These young soils, therefore, preserve the geochemical signature of the alluvial sediments from which they are derived, which in turn are related to ~~the nature of~~ the parent rocks that outcrop~~ping~~ in the various hydrological basins that delivered sediments to the alluvial plain.

Materials and methods

Alluvial soils and sediments were collected from 60 sampling sites distributed in 5 distinct agricultural areas of the Rovigo province (Boara Pisani, Concadirame, Lusia, Fratta Polesine-Bosaro, Stienta), located between the Po and Adige rivers (Fig. 1). According to the 1:250,000 soil map of the Veneto region (Osservatorio Regionale Suolo dell'ARPAV, 2015), the investigated soils are primarily~~mainly~~ Cambisols, subordinately Fluvisols and rarely Calcisols. Following the sampling strategy adopted by Bianchini et al. (2012) and (2013), two samples were collected by an Eijkelkamp hand auger at each ~~selected~~ site: one representative sample of the soils just beneath the root~~s~~ zone (at a depth of 20-30 cm) and another ~~one~~ representative sample of the underlying alluvial sediments (at a depth of 90-110 cm). ~~Taking into c~~Consider~~ation~~ing that the tillage depth ~~of tillage~~ for the~~involving~~ soil digging, stirring, and overturning is typically~~usually~~ ca 50 cm, the shallower samples are considered representative of the soil portion affected~~interested~~ by agricultural activity, while the deepest samples are interpreted as representative of horizons unaffected by anthropogenic activities. Samples were air-dried and divided into distinct aliquots for grain-size and geochemical investigations. The grain size determination was obtained on a sample subset, following the notional classification of Wentworth, by sieving the sand~~y~~ from the fine (<63 µm) fraction, and then using wet gravitational separation in deionised water to separate~~divide~~ the clay and~~from the~~ silt fractions using~~by~~ a "Micrometrics Sedigraph 5100".

The amount of ~~S~~soil ~~O~~organic ~~M~~matter (SOM) was estimated through thermogravimetry performed at 500°C and expressed as percent weight (wt%) loss with respect to the starting weight of the material (Nelson and Sommers, 1996; Abella and Zimmer, 2007).

For~~As concerns~~ the modern river sediments, sampling was performed~~carried out~~ following the method~~approach~~ described by Corazzari et al. (2016). The solid suspended load of the Adige and Po rivers was obtained by collecting 10 litres of river water in plastic containers; after the particles settled~~ing~~, the supernatant liquid was removed using~~by~~ a siphon, and the residue was dried in an oven at 60°C. Bed sediments (ca. 1 kg) were collected from the river bank and dried in an oven at 60°C.

For the geochemical analysis, the samples were powdered in an agate mill and approximately~~about~~ 4 g of powder was hydraulically pressed with~~ addition of~~ boric acid~~ by hydraulic press~~ to obtain powder pellets. Simultaneously, a sample aliquot of 0.5–0.6 g was heated for approximately~~about~~ 12 h in a furnace at~~ temperature of~~ 1000 °C~~ in order~~ to determine the ~~L~~loss ~~O~~on ~~I~~ignition (LOI). This parameter measures the total concentration of volatile species contained in the sample. The Wavelength Dispersive X-Ray Spectrometry (WDXRF) analysis of the powder pellets was performed~~carried out~~ using an ARL Advant'X spectrometer Thermo Scientific (Waltham, MA, USA). Calibrations were obtained analysing certified reference materials, and a matrix correction was performed according to the method proposed by Trail and Lachance (1966). Precision and accuracy calculated by repeated analyses of international standards (with matrices comparable to~~with~~ the studied samples, Di Giuseppe et al., 2014) were generally better than 3% for Si, Ti, Fe, Ca and K, and 7% for Mg, Al, Mn and Na. For the trace elements (above 10 ppm), the errors were generally better than 10%.

Comment [QCE1]: Please be consistent with the inclusion of a space between the number and degree symbol.

Geostatistical modelling was performed~~carried out in order~~ to show the spatial variation of geochemical data. Interpolated maps along the geographical extension were produced in ArcGIS 9.3 (Geostatistical Analyst extension) at a resolution of 100 m using a~~by~~ generalised linear regression technique (ordinary kriging)~~, using~~ and a spherical semivariogram model with the nugget on log_{10}-transformed data.

Results

The bulk rock geochemical composition of 120 soil and sediment samples from the alluvial sector located between the Adige and Po rivers are presented in Supplementary Table 1-5~~,~~ and summarised in Table 1. For most samples, the textural composition~~,~~ is reported based on the classification scheme of Wentworth~~, is also reported~~.

The WDXRF and textural analyses reveal that the collected samples span~~ over~~ a wide range of chemical and grain size compositions. ~~In particular f~~For the major elements, SiO_2 varies from 35.70 ~~up~~ to 72.79 wt%, Al_2O_3 from 8.40~~ up~~ to 17.24 wt%, CaO from 1.09~~ up~~ to 11.56 wt% and Fe_2O_3 from 2.95~~ up~~ to 10.56 wt%. The grain size distribution also shows significant~~a great~~ variability for~~with~~ the sand and clay contents varying in the ranges of 0.1 - 92.4 % and 3.0 – 65.4 %, respectively, whereas the SOM varies between 0.7 and 24.8. The sand content (%) is positively

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correlated with SiO_2 (wt%), whereas the clay and SOM contents (%) are positively correlated with Fe_2O_3, K_2O and Al_2O_3 (wt%).

For each sampling site, athe comparison between the metal concentration at 20-30 and 90-110 cm in depth was performed toallowed the evaluateeion theof possible Ttop Eenrichment Ffactors (TEF) induced by anthropogenic activities. In this view, tThe trace element budget of the studied soils/sediments preserves a "geogenic" signature as demonstrated by the general lack of TEFs (Trevisan et al., 2016). The heavy metal distribution highlights different backgrounds in the distinct sampling areas: Stienta and to ain lesser extent Bosaro-Fratta Polesine show comparativeare relatively enrichedment of in siderophile elements (Cr, Ni, Co, V) and depletedion in chalcophile elements (Zn, Cu, Pb), whereas the opposite is observed at Boara Pisani, Concadirame and Lusia. These observations, shownhighlighted by box-plots (Trevisan et al., 2016), are emphasised in the geochemical maps (Fig. 2), which show a northward increase of Zn and Pb (chalcophile elements) and a southward enrichment in Ni and Cr (siderophile elements) in the alluvial sediments of this sector of the Padanian plain, suggesting that different geochemical affinities characterise the Po and Adige river basins. Discrimination diagrams, useful to identify the provenance of the investigated samples, are reported in Fig. 3. The Ni *vs* Zn diagram (Fig. 3a) allows identifiesying two data series that possiblyplausibly indicatereferred to the sedimentary contributions from the Po and Adige rivers, respectively, whereas a third sample group delineates a "transitional" series with an intermediate character. In particular, sSediments from the Po river River basin (45 samples, r^2 = 0.67) are characterised by the highest Ni/Zn values (average 1.78, SD = 0.28), whereas sediments from the Adige river River basin (49 samples, r^2 = 0.56) haveby the lowest Ni/Zn values (average 0.38, SD = 0.09); the transitional series also displays a very good correlation between Ni and Zn (28 samples, r^2 = 0.79) and intermediate Ni/Zn values (average 0.74, SD = 0.13). Coherently, the Ni/Zn values of the sediments attributed to the Po river closely correspond to those characteristic of the Po sediments (average 1.81, SD = 0.37) that outcropping southward in the Province of Ferrara (Bianchini et al., 2013). The discriminated series are also characterised by other distinctive siderophile/chalcophile values such as Cr/Pb (Fig. 3b), which is highest in the Po (average 7.95, SD = 2.1), lowest in the Adige (average 1.41, SD = 0.35) and intermediate in the transitional (average 2.39, SD = 0.75) sediments. The existence of tThree sample groups areis also shownhighlighted inby the Ba *vs* Al_2O_3 diagram (Fig. 3c), that indicates a general enrichment of Ba in the fine fraction, and comparatively higher values in the Adige alluvial sediments with respect to those from the Po sediments. The different concentrations of siderophile/chalcophile elements in the recognised sample groups is generalised in the Cr+Ni+Co+V *vs* Zn+Pb+Cu+Ba diagram (Fig. 4a) and schematiszed in the Ni/Zn *vs* Cr/Pb diagram (Fig. 4b) that provideallow a geochemical classification scheme for the sediment provenance of sediments in the investigated area. Discrimination is also provided by tThe relationships between alkaline and alkaline-earth elements are also used to distinguish the sediments: Po sediments are relativelycomparatively enriched in Sr (ppm), whereas the Adige sediments are relativelycomparatively enriched in K_2O (wt%) and Ba (ppm). Further geochemical differences are showngiven by P_2O_5 and MnO (wt%), which that are generally higher in the Adige and Po samples, respectively.

The bulk rock geochemical composition of 18 bed and suspended sediments from the Po and Adige rivers are presented in Supplementary Table 6, and summarised in Table 2. The major element composition of the bed sediments is, in general, relativelycomparatively enriched in SiO_2 compared to thewith respect to suspended sediments, whichthat are in turn enriched in Al_2O_3 and K_2O (wt%). This observation reflects the prevalencecet presence of quartz in the coarser bed sediments and of clay minerals and carbonates in the finer suspended particles. The Bbed sediments are in generally depleted in Ni, V, Zn, Pb, and Cu comparedwith respect to the suspended sediments, which indicatesing that most heavy metals are preferentially partitioned in clay minerals and/or in the associated amorphous matter. AThe comparison between sediments from the Po and Adige rivers showsreveals that the former isare relativelycomparatively enriched in CaO comparedwith respect to MgO (wt%). For theAs concerns heavy metals, the Po river River sediments are characterised by higher concentrations of siderophile elements whereas the Adige river River sediments are comparatively enriched in chalcophile elements, showing with geochemical trends overlapping those of their alluvial counterparts (Figs. 3 and 4). Coherently, the Po river River sediments haveshow higher Ni/Zn (average 1.46, SD = 0.28) and Cr/Pb (average 5.36, SD = 1.10) ratios comparedwith respect to the Adige river River sediments (average Ni/Zn = 0.32, SD = 0.04; average Cr/Pb = 1.21, SD = 0.38). The Po sediments haveshow a relatively high Sr content of Sr (ppm), whereas the Adige sediments are characterisszed by a comparative Ba enrichment of Ba (ppm).

Discussion

The reported geochemical data foron alluvial sediments from the northeastern Padanian plain provide constraints for the Holocene palaeohydrographic evolution of the area, whichthat is primarilymainly determinedknown by geomorphological studies (often based on remote sensing data), archaeological discoveriesfindings and historical chronicles (e.g., Castiglioni, 1999).

The major element composition primarily reflects the mineralogical features of distinct depositional facies. The positive correlation between sand content (%) and SiO_2 (wt%) suggests that the coarse fraction (channel deposits) is generally dominated by quartz and feldspars, whereas the increase of clay and SOM contents in parallel with Fe_2O_3, K_2O and Al_2O_3 (wt%) suggests that the fine fraction (distal levee deposits) includes iron-rich clay minerals, such as chlorite and smectite, and that it is intimately associated with the organic matter. However, major elements are scarcely discriminant for the sediment provenance in the study area, where the Po and Adige river systems variablyously migrated and interfingered during the last millennia. In fact, aAmong the major elements, only CaO and MgO (wt%) give an approximate rough indication forabout the sediment provenance, as the CaO/MgO ratio is generally higher in the Po river River deposits.

In contrast,On the contrary, in the for the current case study, we have demonstrated that the trace element signature is a precise tool for the identification of the Po and Adige end-members, which refinesing the discrimination criteria previously proposed by Amorosi et al. (2008) and Picone et al. (2008). According to our inferences, alluvial sediments with Ni/Zn > 1.0 and Cr/Pb > 4.2 are clearly attributable to the Po river River basin. This geochemical fingerprint, characterised by a relative enrichment in siderophile elements, is related to the presence of mafic and ultramafic rocks (primarilymainly included in ophiolite sequences) that outcropping within the Po river River hydrological basin (Amorosi, 2012; Bianchini et al., 2012; 2013). Conversely,On the other hand, alluvial sediments with Ni/Zn < 0.6 and Cr/Pb < 1.9 are clearly attributable to the Adige river River basin, where the relative enrichment of chalcophile elements is related to the presence of Zn-Pb-Cu sulphide ore deposits, which are occasionally~~sometimes~~ associated with barite in the mountainous part of the catchment. These discrimination criteria have been validated by~~with~~ the Po and Adige river sediment~~s of Po and Adige~~ data retrieved from the available literature (Boldrin et al., 1989; Dinelli and Lucchini, 1999). The Po soils and sediments are relatively~~comparatively~~ enriched in Sr (ppm) resulting from the weathering of plagioclase-bearing mafic rocks~~,~~ in addition to the geochemical budget related to carbonates. Conversely,~~ the~~ Ba (ppm) enrichment of the Adige sediments is possibly related to the weathering of alkaline feldspar-bearing felsic rocks and/or to barite deposits. Moreover, the Adige sediments are generally enriched in P_2O_5 (wt%) whereas the Po sediments are enriched in MnO (wt%).~~, whereas~~ However, the distribution of other elements, such as Zr and REEs, do~~esn't~~ not differentiate the sediments of the two riverine systems.

Samples having transitional characteristics between the Po and Adige geochemical affinities represent a mixture of the above described end-members. They could result from the juxtaposition of several alluvial events for~~of~~ the two fluvial vectors occurring~~ed~~ in historical times when both the Po and Adige rivers were scarcely channelled, thus more frequently subjected to overflow and avulsion (Stefani and Vincenzi, 2005). However, remarkable inter-element correlations (Figs. 3 and 4) suggest that the transitional series represents a~~ quite~~ precise mixture of the Po and Adige sediments in the proportions of 70% and 30%, respectively. This homogeneity implies the existence of an ancient fluvial system collecting water and sediments from both river basins~~,~~ and flowing between the current stream paths of the Po and Adige rivers, which is possibly~~plausibly~~ represented by a series of palaeochannels known as "Po di Fratta", "Cona-Saline" (Bronze age) and "Po di Adria" (Iron age-Roman times; Piovan et al., 2010; 2012; Ravazzi et al., 2013). The existence of these ancient branches of the Po ~~river~~ River has been confirmed by petrographic studies on coarse-grained sediments from alluvial ridges near Rovigo~~,~~ that highlighted the presence of key minerals (glaucophane and serpentine) attributable to the weathering of rocks (blueschists and serpentinites) that outcrop~~ping~~ exclusively in the Po ~~river~~ River basin. Unfortunately, the approach adopted by previous studies is appropriate only for palaeochannel deposits, whereas it cannot be applied to finer sediments, such as those of distal levee facies, which~~ that~~ can only be interpreted using~~only by~~ bulk sample geochemistry. Our new data suggests that this ancient Po ~~river~~ River stream path possibly captured a branch of the Adige fluvial system (also including minor distributaries oriented southward, Castiglioni, 1999), thus acquiring part of its sedimentary load that effectively mixed and generated the transitional sediments widespread in the study area. However, this hypothesis is scarcely constrained by the available geomorphological evidence (Piovan et al., 2012; Fontana et al., 2014) and historical chronicles (Calzolari, 2008)~~,~~ and, therefore, it is more plausible that the interaction between the Po and Adige fluvial systems (that variably~~ously~~ interfingered~~interfered~~ in space and time during~~in~~ the last millennia) occurred through the development of wetlands fed by both the Po and Adige rivers, especially in Pre-Roman times (Stefani and Vincenzi, 2005). This interpretation is supported by the prevalent fine texture of samples belonging to the transitional series, as well as by historical chronicles that~~which~~ describe the widespread presence of flooded zones in the studied area (Whitehouse, 2001).

Conclusions

The geochemical fingerprint of the ~~sediments from the~~ Province of Rovigo sediments clearly characterises~~reflects the affinity of~~ the solid load transported by the two primary~~main~~ riverine systems that envelope the area, i.e., the Po ~~river~~ River containing~~having~~ sediments characteris~~z~~ed by notable concentrations of Ni and Cr, and the Adige ~~river~~ River containing~~having~~ sediments relatively~~comparatively~~ enriched in chalcophile elements such as Pb and Zn. Therefore, ~~G~~geochemistry~~ therefore~~ represents a fundamental tool to correlate~~relate~~ the investigated alluvial soils and sediments to a specific basin characterised by distinct parent rocks. ~~In this view, g~~Geochemical maps showing~~reporting~~ the spatial distribution of key elements are useful to define geochemical gradients and local anomalies, but the precise identification of the sediment provenance can only be~~ only~~ assessed~~ by the~~ using~~e of~~ key elemental ratios. The current study shows~~highlights~~ the potential of the geochemical approach in the reconstruction of palaeohydrographic patterns. We demonstrated that the ~~sedimentary influence of~~ Po ~~river~~ River sedimentary influence extends northward compared to~~respect to~~ its current stream path (as also proposed by authors that studied sediments in the Adriatic Sea; Amorosi et al., 2008; Picone et al. 2008)~~, and that~~ and that the Po ~~river~~ River sediments are locally present very close to the modern Adige stream path. Moreover, the presented geochemical data suggest that in historical times a branch of the Po ~~river~~ River crosscutting the studied area was characterised by a sedimentary load with~~having~~ a hybrid signature intermediate between those currently recognised in the Po and Adige rivers~~, nowadays~~. ~~The existence of t~~These transitional sediments may suggest that at that time the two fluvial systems were connected, i.e., that a branch of the Adige was a tributary of the Po ~~river~~ River upstream with respect to the study area or, more probably, that the interference of the two fluvial systems developed through marsh/swamp environments that are recorded in historical chronicles and in geomorphological reconstructions (Vincenzi and Stefani, 2005). These sedimentary facies could, therefore, represent the expression of depositional domains in which both the Po and Adige rivers delivered sedimentary inputs~~, and were~~ that probably originated within wetlands developed among major fluvial ridges.

Acknowledgments

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Table captions:

Table 1 – Geochemical composition of soils and sediments from the investigated sector of the Padanian plain (Province of Rovigo, NE Italy).

Table 2 – Average geochemical composition of modern bed and suspended sediments from the Po and Adige rivers.

Geochemical proxies of sediment provenance in alluvial plains with interfering fluvial systems: A study case from NE Italy

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Abstract

This paper demonstrates that geochemistry is useful for the identification of sediment origin and provenance in alluvial plains characterised by a complex hydrographic evolution. The study is focused on the northeastern Padanian plain (Italy), an area primarily characterised by sedimentary contributions from the two largest Italian river systems (Po and Adige), which intimately interacted during the last millennia. X-ray fluorescence analyses of 120 soils and alluvial sediments define three diverse geochemical affinities that have distinctive siderophile/chalcophile elemental ratios. The sample group characterised by high Ni/Zn and Cr/Pb values conforms to modern Po River sediments, whereas a second group showing low Ni/Zn and Cr/Pb values conforms to the geochemical signature of modern Adige River sediments. A third sample group defines a "transitional" affinity that represents a geochemical mixture of Po (70%) and Adige (30%) sedimentary end-members. Based on these geochemical features, it is possible to distinguish alluvial sediments of the Po River basin (Ni/Zn > 1.0 and Cr/Pb > 4.2) from those of the Adige River basin (Ni/Zn < 0.6 and Cr/Pb < 1.9) and to provide evidence of the migration of these rivers during the evolution of the Padanian plain. The interpretation of transitional samples is less constrained and could imply an ancient connection between the two fluvial systems, possibly due to the development of wetlands where both the Po and Adige rivers variably delivered their sedimentary contributions. This study approach, therefore, provides important implications for palaeohydrographic and palaeoenvironmental reconstructions in a complex area that is characterised by significant geomorphological modifications during the last millennia.

Keywords: Padanian plain; Po and Adige rivers; geochemical proxies; palaeohydrographic reconstruction

Introduction

The sedimentary infill of continental basins is related to climatic and tectonic processes that influence rock weathering, erosion, transport of clastic particles and deposition. The interplay of varying subsidence rates and sediment supplies results in the development of different sedimentary environments, ranging from fluvial to a variety of lacustrine settings. The resulting floodplains are complex landscape assemblages composed of active landforms (e.g., channels) and stabilised units of various ages and origins (e.g., abandoned channels and banks), which are often formed by the overlap of multiple riverine systems in space and time. The development of human settlements and their interactions with the hydrographic networks causes additional complexities in the natural evolution of these environments. Floodplains are, therefore, paleoclimatic and historical archives that record human activities and the hydroclimatic evolution, which are typically revealed by the coupling of geomorphological, sedimentological and archaeological studies (Gautier et al., 2009, Hoffmann et al., 2010; D'Haen et al., 2012). In this framework, the sedimentary dynamics in alluvial plains can be determined using geochemical tracers that are powerful tools for the identification of sediment source areas (e.g., Macklin et al., 2006; Singh, 2010; Campodonico et al., 2016). This approach has been widely used in the Emilia-Romagna region to distinguish the alluvial sediments in the Po River, which drains the Western Alps, from those of other riverine systems that drain the Northern Apennines (Amorosi, 2012; Bianchini et al., 2012; 2013). Conversely, the potential of this method has been scarcely tested northward, where the Po River system interfered with other fluvial depositional systems during the Padanian plain development. In this work we particularly investigated a sector of the plain, located between the towns of Ferrara and Rovigo, that is bordered to the north and south by the Adige and Po rivers, respectively (Fig. 1). The purpose was to identify geochemical proxies for distinct sedimentary end-members and to analyse their spatial distribution, ultimately providing evidence for the palaeohydrographic evolution of the area. To achieve this, 120 major and trace element geochemical analyses of soils and alluvial sediments have been statistically studied to identify the geochemical trends related to weathering of different mother rocks that outcrop in separate hydrological basins. Moreover, 18 samples of bed and suspended sediments from the Po and Adige rivers have been sampled and analysed to verify their geochemical affinity and to compare the current and past daily trends. The results represent a powerful complementary tool to the geomorphological approach for the reconstruction of the palaeohydrographic patterns of the northeastern Padanian plain, which are currently hypothetical and primarily based on the interpretation of landforms and archaeological remains (Piovan et al., 2010; Corrò and Mozzi, 2016).

Geological and geomorphological outlines

The study area is located in the easternmost part of the Padanian plain in northern Italy, a sedimentary basin between the Alps and the Apennines that was progressively filled by Neogene marine sediments and finally capped by fluvial sediments since the Pleistocene. During the Late Holocene, the sedimentary discharge was supplied by two primary fluvial systems (Po and Adige), and the configuration of the local drainage system was predominantly controlled by the interaction between tectonic, climatic, eustatic, and sedimentary processes (Garzanti et al., 2011). The geological features of the basins are briefly described below.

The Po River drains the western Alps (Marchina et al., 2015), which are characterised by a prevalent crystalline basement consisting of felsic plutonic rocks (granitoids) and metamorphic rocks (Boriani et al., 2003). Jurassic ophiolites consisting of serpentinised peridotites, gabbros and basalts are also observed in the western Alps, together with sedimentary rocks such as Mesozoic (Triassic and Jurassic) limestones that become significant only in the central Alps (in Lombardy; Bosellini, 2004) and subordinate Tertiary silico-clastic rocks (Maino et al., 2013). Ore deposits recorded in the Po basin primarily consist of Fe-Ni and PGE (platinoids) elements, typically associated with ultramafic rocks (Garuti and Rinaldi, 1986; Rossetti and Zucchetti, 1988; Carbonin et al., 2015).

The Adige River drains metamorphic rocks of the Austroalpine domain in the upper part of the basin, rhyolitic rocks of the Atesian volcanic complex between Bolzano and Trento, and the carbonate units of the Southalpine domain (Natali et al., 2016). Zn-Pb-Cu-Fe sulphide-bearing ore deposits are renowned in the Adige basin (Nimis et al., 2012), which are occasionally associated with barite and fluorite (Bakos et al., 1972).

The study area ranges in elevation between 5 and 3.5 m a.s.l. and is characterised by a complex network of alluvial ridges formed by the aggradation of sandy and silty channel deposits, natural levees, and minor proximal crevasse splays. The depressions contain finer distal levee deposits, such as silty clays, that are occasionally associated with abundant organic matter suggesting the local development of swamps (Piovan et al., 2008; 2010).

The soils developed on these alluvial deposits are generally characterised by a limited profile development, in which the lack of soil maturity is related to the young depositional age (Late Holocene), fluvial reworking and extensive agricultural activities (ploughing). These young soils, therefore, preserve the geochemical signature of the alluvial sediments from which they are derived, which in turn are related to the parent rocks that outcrop in the various hydrological basins that delivered sediments to the alluvial plain.

Materials and methods

Alluvial soils and sediments were collected from 60 sampling sites distributed in 5 distinct agricultural areas of the Rovigo province (Boara Pisani, Concadirame, Lusia, Fratta Polesine-Bosaro, Stienta), located between the Po and Adige rivers (Fig. 1). According to the 1:250,000 soil map of the Veneto region (Osservatorio Regionale Suolo dell'ARPAV, 2015), the investigated soils are primarily Cambisols, subordinately Fluvisols and rarely Calcisols. Following the sampling strategy adopted by Bianchini et al. (2012) and (2013), two samples were collected by an Eijkelkamp hand auger at each site: one representative sample of the soils just beneath the root zone (at a depth of 20-30 cm) and another representative sample of the underlying alluvial sediments (at a depth of 90-110 cm). Considering that the tillage depth for the soil digging, stirring, and overturning is typically ca 50 cm, the shallower samples are considered representative of the soil portion affected by agricultural activity, while the deepest samples are interpreted as representative of horizons unaffected by anthropogenic activities. Samples were air-dried and divided into distinct aliquots for grain-size and geochemical investigations. The grain size determination was obtained on a sample subset, following the notional classification of Wentworth, by sieving the sand from the fine (<63 μm) fraction, and then using wet gravitational separation in deionised water to separate the clay and silt fractions using a "Micrometrics Sedigraph 5100".

The amount of soil organic matter (SOM) was estimated through thermogravimetry performed at 500°C and expressed as percent weight (wt%) loss with respect to the starting weight of the material (Nelson and Sommers, 1996; Abella and Zimmer, 2007).

For the modern river sediments, sampling was performed following the method described by Corazzari et al. (2016). The solid suspended load of the Adige and Po rivers was obtained by collecting 10 litres of river water in plastic containers; after the particles settled, the supernatant liquid was removed using a siphon, and the residue was dried in an oven at 60°C. Bed sediments (ca. 1 kg) were collected from the river bank and dried in an oven at 60°C.

For the geochemical analysis, the samples were powdered in an agate mill and approximately 4 g of powder was hydraulically pressed with boric acid to obtain powder pellets. Simultaneously, a sample aliquot of 0.5–0.6 g was heated for approximately 12 h in a furnace at 1000 °C to determine the loss on ignition (LOI). This parameter measures the total concentration of volatile species contained in the sample. The Wavelength Dispersive X-Ray Spectrometry (WDXRF) analysis of the powder pellets was performed using an ARL Advant'X spectrometer Thermo Scientific (Waltham, MA, USA). Calibrations were obtained analysing certified reference materials, and a matrix correction was performed according to the method proposed by Trail and Lachance (1966). Precision and accuracy calculated by repeated analyses of international standards (with matrices comparable to the studied samples, Di Giuseppe et al., 2014) were generally better than 3% for Si, Ti, Fe, Ca and K, and 7% for Mg, Al, Mn and Na. For the trace elements (above 10 ppm), the errors were generally better than 10%.

Geostatistical modelling was performed to show the spatial variation of geochemical data. Interpolated maps along the geographical extension were produced in ArcGIS 9.3 (Geostatistical Analyst extension) at a resolution of 100 m using a generalised linear regression technique (ordinary kriging) and a spherical semivariogram model with the nugget on $\log_{10}$-transformed data.

Results

The bulk rock geochemical composition of 120 soil and sediment samples from the alluvial sector located between the Adige and Po rivers are presented in Supplementary Table 1-5 and summarised in Table 1. For most samples, the textural composition is reported based on the classification scheme of Wentworth.

The WDXRF and textural analyses reveal that the collected samples span a wide range of chemical and grain size compositions. For the major elements, SiO_2 varies from 35.70 to 72.79 wt%, Al_2O_3 from 8.40 to 17.24 wt%, CaO from 1.09 to 11.56 wt% and Fe_2O_3 from 2.95 to 10.56 wt%. The grain size distribution also shows significant variability for the sand and clay contents varying in the ranges of 0.1 - 92.4 % and 3.0 – 65.4 %, respectively, whereas the SOM varies between 0.7 and 24.8. The sand content (%) is positively correlated with SiO_2 (wt%), whereas the clay and SOM contents (%) are positively correlated with Fe_2O_3, K_2O and Al_2O_3 (wt%).
For each sampling site, a comparison between the metal concentration at 20-30 and 90-110 cm in depth was performed to evaluate the possible top enrichment factors (TEF) induced by anthropogenic activities. The trace element budget of the studied soils/sediments preserves a "geogenic" signature as demonstrated by the general lack of TEFs (Trevisan et al., 2016). The heavy metal distribution highlights different backgrounds in the distinct sampling areas: Stienta and to a lesser extent Bosaro-Fratta Polesine are relatively enriched in siderophile elements (Cr, Ni, Co, V) and depleted in chalcophile elements (Zn, Cu, Pb), whereas the opposite is observed at Boara Pisani, Concadirame and Lusia. These observations, shown by box-plots (Trevisan et al., 2016), are emphasised in the geochemical maps (Fig. 2), which show a northward increase of Zn and Pb (chalcophile elements) and a southward enrichment in Ni and Cr (siderophile elements) in the

alluvial sediments of this sector of the Padanian plain, suggesting that different geochemical affinities characterise the Po and Adige river basins. Discrimination diagrams, useful to identify the provenance of the investigated samples, are reported in Fig. 3. The Ni *vs* Zn diagram (Fig. 3a) identifies two data series that possibly indicate the sedimentary contributions from the Po and Adige rivers, respectively, whereas a third sample group delineates a "transitional" series with an intermediate character. Sediments from the Po River basin (45 samples, $r^2 = 0.67$) are characterised by the highest Ni/Zn values (average 1.78, SD = 0.28), whereas sediments from the Adige River basin (49 samples, $r^2 = 0.56$) have the lowest Ni/Zn values (average 0.38, SD = 0.09); the transitional series also displays a very good correlation between Ni and Zn (28 samples, $r^2 = 0.79$) and intermediate Ni/Zn values (average 0.74, SD = 0.13). Coherently, the Ni/Zn values of the sediments attributed to the Po river closely correspond to those characteristic of the Po sediments (average 1.81, SD = 0.37) that outcrop southward in the Province of Ferrara (Bianchini et al., 2013). The discriminated series are also characterised by other distinctive siderophile/chalcophile values such as Cr/Pb (Fig. 3b), which is highest in the Po (average 7.95, SD = 2.1), lowest in the Adige (average 1.41, SD = 0.35) and intermediate in the transitional (average 2.39, SD = 0.75) sediments. Three sample groups are also shown in the Ba *vs* Al_2O_3 diagram (Fig. 3c) that indicates a general enrichment of Ba in the fine fraction, and comparatively higher values in the Adige alluvial sediments with respect to those from the Po sediments. The different concentrations of siderophile/chalcophile elements in the recognised sample groups is generalised in the Cr+Ni+Co+V *vs* Zn+Pb+Cu+Ba diagram (Fig. 4a) and schematised in the Ni/Zn *vs* Cr/Pb diagram (Fig. 4b) that provide a geochemical classification scheme for the sediment provenance in the investigated area. The relationships between alkaline and alkaline-earth elements are also used to distinguish the sediments: Po sediments are relatively enriched in Sr (ppm), whereas the Adige sediments are relatively enriched in K_2O (wt%) and Ba (ppm). Further geochemical differences are shown by P_2O_5 and MnO (wt%), which are generally higher in the Adige and Po samples, respectively.

The bulk rock geochemical composition of 18 bed and suspended sediments from the Po and Adige rivers are presented in Supplementary Table 6 and summarised in Table 2. The major element composition of the bed sediments is, in general, relatively enriched in SiO_2 compared to the suspended sediments, which are enriched in Al_2O_3 and K_2O (wt%). This observation reflects the prevalence of quartz in the coarser bed sediments and of clay minerals and carbonates in the finer suspended particles. The bed sediments are generally depleted in Ni, V, Zn, Pb, and Cu compared to the suspended sediments, which indicates that most heavy metals are preferentially partitioned in clay minerals and/or in the associated amorphous matter. A comparison between sediments from the Po and Adige rivers shows that the former is relatively enriched in CaO compared to MgO (wt%). For the heavy metals, the Po River sediments are characterised by higher concentrations of siderophile elements whereas the Adige River sediments are comparatively enriched in chalcophile elements with geochemical trends overlapping those of their alluvial counterparts (Figs. 3 and 4). Coherently, the Po River sediments have higher Ni/Zn (average 1.46, SD = 0.28) and Cr/Pb (average 5.36, SD = 1.10) ratios compared to the Adige River sediments (average Ni/Zn = 0.32, SD = 0.04; average Cr/Pb = 1.21, SD = 0.38). The Po sediments have a relatively high Sr content (ppm), whereas the Adige sediments are characterised by a comparative Ba enrichment (ppm).

Discussion

The reported geochemical data for alluvial sediments from the northeastern Padanian plain provide constraints for the Holocene palaeohydrographic evolution of the area, which is primarily determined by geomorphological studies (often based on remote sensing data), archaeological discoveries and historical chronicles (e.g., Castiglioni, 1999).

The major element composition primarily reflects the mineralogical features of distinct depositional facies. The positive correlation between sand content (%) and SiO_2 (wt%) suggests that the coarse fraction (channel deposits) is generally dominated by quartz and feldspars, whereas the increase of clay and SOM contents in parallel with Fe_2O_3, K_2O and Al_2O_3 (wt%) suggests that the fine fraction (distal levee deposits) includes iron-rich clay minerals, such as chlorite and smectite, and that it is intimately associated with the organic matter. However, major elements are scarcely discriminant for the sediment provenance in the study area, where the Po and Adige river systems variably migrated and interfingered during the last millennia. Among the major elements, only CaO and MgO (wt%) give an approximate indication for the sediment provenance, as the CaO/MgO ratio is generally higher in the Po River deposits.

In contrast, for the current case study, we have demonstrated that the trace element signature is a precise tool for the identification of the Po and Adige end-members, which refines the discrimination criteria previously proposed by Amorosi et al. (2008) and Picone et al. (2008). According to our inferences, alluvial sediments with Ni/Zn > 1.0 and Cr/Pb > 4.2 are clearly attributable to the Po River basin. This geochemical fingerprint, characterised by a relative enrichment in siderophile elements, is related to the presence of mafic and ultramafic rocks (primarily included in ophiolite sequences) that outcrop within the Po River hydrological basin (Amorosi, 2012; Bianchini et al., 2012; 2013). Conversely, alluvial sediments with Ni/Zn < 0.6 and Cr/Pb < 1.9 are clearly attributable to the Adige River basin, where the relative enrichment of chalcophile elements is related to the presence of Zn-Pb-Cu sulphide ore deposits, which are occasionally associated with barite in the mountainous part of the catchment. These discrimination criteria have been validated by the Po and Adige river sediment data retrieved from the available literature (Boldrin et al., 1989; Dinelli and Lucchini, 1999). The Po soils and sediments are relatively enriched in Sr (ppm) resulting from the weathering of plagioclase-bearing mafic rocks in addition to the geochemical budget related to carbonates. Conversely, Ba (ppm) enrichment of the Adige sediments is possibly related to the weathering of alkaline feldspar-bearing felsic rocks and/or to barite deposits. Moreover, the Adige sediments are generally enriched in P_2O_5 (wt%) whereas the Po sediments are enriched in MnO (wt%). However, the distribution of other elements, such as Zr and REEs, do not differentiate the sediments of the two riverine systems.

Samples having transitional characteristics between the Po and Adige geochemical affinities represent a mixture of the above described end-members. They could result from the juxtaposition of several alluvial events for the two fluvial vectors occurring in historical times when both the Po and Adige rivers were scarcely channelled, thus more frequently subjected to overflow and avulsion (Stefani and Vincenzi, 2005). However, remarkable inter-element correlations (Figs. 3 and 4) suggest that the transitional series represents a precise mixture of the Po and Adige sediments in the proportions of 70% and 30%, respectively. This homogeneity implies the existence of an ancient fluvial system collecting water and sediments from both river basins and flowing between the current stream paths of the Po and Adige rivers, which is possibly represented by a series of palaeochannels known as “Po di Fratta”, “Cona-Saline” (Bronze age) and “Po di Adria” (Iron age-Roman times; Piovan et al., 2010; 2012; Ravazzi et al., 2013). The existence of these ancient branches of the Po River has been confirmed by petrographic studies on coarse-grained sediments from alluvial ridges near Rovigo that highlighted the presence of key minerals (glaucophane and serpentine) attributable to the weathering of rocks (blueschists and serpentinites) that outcrop exclusively in the Po River basin. Unfortunately, the approach adopted by previous studies is appropriate only for palaeochannel deposits, whereas it cannot be applied to finer sediments, such as those of distal levee facies, which can only be interpreted using bulk sample geochemistry. Our new data suggests that this ancient Po River stream path possibly captured a branch of the Adige fluvial system (also including minor distributaries oriented southward, Castiglioni, 1999), thus acquiring part of its sedimentary load that effectively mixed and generated the transitional sediments widespread in the study area. However, this hypothesis is scarcely constrained by the available geomorphological evidence (Piovan et al., 2012; Fontana et al., 2014) and historical chronicles (Calzolari, 2008) and, therefore, it is more plausible that the interaction between the Po and Adige fluvial systems (that variably interfingered in space and time during the last millennia) occurred through the development of wetlands fed by both the Po and Adige rivers, especially in Pre-Roman times (Stefani and Vincenzi, 2005). This interpretation is supported by the prevalent fine texture of samples belonging to the transitional series, as well as by historical chronicles that describe the widespread presence of flooded zones in the studied area (Whitehouse, 2001).

Conclusions

The geochemical fingerprint of the Province of Rovigo sediments clearly characterises the solid load transported by the two primary riverine systems that envelope the area, i.e., the Po River containing sediments characterised by notable concentrations of Ni and Cr, and the Adige River containing sediments relatively enriched in chalcophile elements such as Pb and Zn. Therefore, geochemistry represents a fundamental tool to correlate the investigated alluvial soils and sediments to a specific basin characterised by distinct parent rocks. Geochemical maps showing the spatial distribution of key elements are useful to define geochemical gradients and local anomalies, but the precise identification of the sediment provenance can only be assessed using key elemental ratios. The current study shows the potential of the geochemical approach in the reconstruction of palaeohydrographic patterns. We demonstrated that the Po River sedimentary influence extends northward compared to its current stream path (as also proposed by authors that studied sediments in the Adriatic Sea; Amorosi et al., 2008; Picone et al. 2008) and that the Po River sediments are locally present very close to the modern Adige stream path. Moreover, the presented geochemical data suggest that in historical times a branch of the Po River crosscutting the studied area was characterised by a sedimentary load with a hybrid signature intermediate between those currently recognised in the Po and Adige rivers. These transitional sediments may suggest that at that time the two fluvial systems were connected, i.e., that a branch of the Adige was a tributary of the Po River upstream with respect to the study area or, more probably, that the interference of the two fluvial systems developed through marsh/swamp environments that are recorded in historical chronicles and in geomorphological reconstructions (Vincenzi and Stefani, 2005). These sedimentary facies could, therefore, represent the expression of depositional domains in which both the Po and Adige rivers delivered sedimentary inputs that probably originated within wetlands developed among major fluvial ridges.

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References

Abella, S.R., Zimmer, B.W., 2007. Estimating Organic Carbon from Loss-On-Ignition in Northern Arizona Forest Soils. Soil Sci. Soc. Am. J. 71, 545-550.

Amorosi, A., 2012. Chromium and nickel as indicators of source-to-sink sediment transfer in a Holocene alluvial and coastal system (Po Plain, Italy). Sediment. Geol. 280, 260-269.

Amorosi, A., Pavesi, M., Ricci Lucchi, M., Sarti, G., Piccin, A., 2008. Climatic signature of cyclic fluvial architecture from the Quaternary of the central Po plain, Italy. Sed. Geol. 209, 58-68.

Bakos, F., Brondi, A., Perna, G., 1972. The Age of Mineral Deposits in the Permian Volcanites of Trentino-Alto Adige (Northern Italy). Geologija 15, 181-194.

Bianchini, G., Natali, C., Di Giuseppe, D., Beccaluva, L., 2012. Heavy metals in soils and sedimentary deposits of the Padanian Plain (Ferrara, Northern Italy): Characterisation and biomonitoring. J. Soil. Sediment. 12, 1145-1153.

Bianchini, G., Di Giuseppe, D., Natali, C., Beccaluva, L., 2013. Ophiolite inheritance in the Po plain sediments: insights on heavy metals distribution and risk assessment. Ofioliti 38, 1-14.

Boldrin, A., Juracic, M., Menegazzo-Vitturi, L., Rabitti, S., Rampazzo, G., 1989. Geochemical considerations on trace elements distributions in suspended matter and sediments at the river-sea interface, Adige river mouth, Northern Adriatic Sea. Appl. Geochem. 4, 409-421.

Boriani, A., Burlini, L., Caironi, V., Colombo, A., Giobbi Mancini, E., Tunesi, A., Zappone, A. (2003). The abundance of 54 elements and petrovolumetric models of the crust in Val d'Ossola – Lago Maggiore and Valtellina (site2). Acc. Naz. Sci. 32, 97-162.

Bosellini, A., 2004. The western passive margin of Adria and its carbonate platforms. Spec. Vol. It. Geol. Soc. for IGC 32, Florence.

Calzolari, M., 2008. 'Athesis Veronensium in Padum decurrit'. Una nota sul corso dell'Adige in età romana , in P. Basso , A. Buonopane , A. Cavarzere & S. Pesavento Mattioli (eds.), 'Est enim ille flos Italiae'. Vita economica e sociale nella Cisalpina romana. Atti delle giornate di studi in onore di Ezio Buchi (Verona , 30 novembre - 1 dicembre 2006), Verona, pp. 397-402.

Campodonico, V.A., Garcia, M.B., Pasquini, A.I., 2016. The geochemical signature of suspended sediments in the Parana River basin: Implications for provenance, weathering and sedimentary recycling. Catena 143, 201-214.

Carbonin, S., Martin, S., Tumiati, S., Rossetti, P., 2015. Magnetite from the Cogne serpentinites (Piemonte ophiolite nappe, Italy). Insights into seafloor fluid–rock interaction. Eur. J. Mineral. 27, 31-50.

Castiglioni, G.B., 1999. Geomorphology of the Po Plain. Supplement of Geografia Fisica e Dinamica Quaternaria 3-3, 7-20.

Corazzari, L., Bianchini, G., Billi, P., Marchina, C., Natali, C., 2016. A preliminary note on carbon and nitrogen elemental and isotopic composition of Po River suspended load. Rend. Lincei 27, 89-93.

Corrò, E., Miozzi, P., 2016. Water matters. Geoarchaeology of the city of Adria and palaeohydrographic variations (Po Delta, Northern Italy). J. Archaeol. Sci., http://dx.doi.org/10.1016/j.jasrep.2016.08.001.

D'Haen, K., Verstraeten, G., Degryse, P., 2012. Fingerprint historical fluvial sediment fluxes. Prog. Phys. Geogr. 36, 154–186.

Di Giuseppe, D., Bianchini, G., Faccini, B., Coltorti, M., 2014a. Combination of WDXRF analysis and multivariate statistic for alluvial soils classification: a case study from the Padanian Plain (Northern Italy). X-ray Spectrom. 43, 165-174.

Dinelli, E., Lucchini, F., 1999. Sediment supply to the Adriatic Sea basin from the Italian rivers: geochemical features and environmental constraints. Giornale di Geologia 61, 121-132.

Garuti, G., Rinaldi, R., 1986. Platinum group and related minerals from the Ivrea-Verbano sulphide deposits. Rendiconti Società Italiana di Mineralogia e Petrologia 41, 229-244.

Garzanti, E., Andó, S., France-Lanord, C., Censi, P., Vignola, P., Galy, V., Lupker M., 2011. Mineralogical and chemical variability of fluvial sediments 2. Suspended-load silt (Ganga–Brahmaputra, Bangladesh). Earth Planet. Sci. Lett. 302, 107–120.

Gautier, E., Corbonnois, J., Petit, F., Arnaud-Fassetta, G., Brunstein, D., Grivel, S., Houbrechts, G., Beck, T., 2009. Multi-disciplinary approach for sediment dynamics study of active floodplains. Géomorphologie 15, 65-78.

Fontana, A., Mozzi, P., Marchetti, M., 2014. Alluvial fans and megafans along the southern side of the Alps. Sediment. Geol. 301, 150-171.

Hoffmann, T., Thorndycraft, V.R., Brown, A.G., Coulthard, T.J., Damnati, B., Kale, V.S., Middelkoop, H., Notebaert, B., Walling, D.E., 2010. Human impact on fluvial regimes and sediment flux during the Holocene: Review and future research agenda. Global Planet. Change 72, 87-98.

Macklin, M.G., Benito, G., Gregory, K.J., Johnstone, E., Lewin, J., Michczyńska, D.J., Soja, R., Starkel, L., Thorndycraft, V.R., 2006. Past hydrological events reflected in the Holocene fluvial record of Europe. Catena 66, 145–154.

Maino, M., Decarlis, A., Felletti, F., Seno, S., 2013. Tectono-sedimentary evolution of the Tertiary Piedmont Basin (NW Italy) within the Oligo–Miocene central Mediterranean geodynamics. Tectonics 32, 593–619.

Marchina, C., Bianchini, G., Natali, C., Pennisi, M., Colombani, N., Tassinari, R., Knöller, K., 2015. The Po river water from the Alps to the Adriatic Sea (Italy): new insights from geochemical and isotopic (δ18O-δD) data. Env. Sci. Poll. Res. 22, 5184-5203.

Natali, C., Bianchini, G., Marchina, C., Knöller, K., 2016. Geochemistry of the Adige River water from the Eastern Alps to the Adriatic Sea (Italy): evidences for distinct hydrological components and water-rock interactions. Env. Sci. Poll. Res. 23, 11677-11694.

Nelson DW, Sommers LE (1996) Total carbon, organic carbon, and organic matter. In: Methods of Soil Analysis, Part 2, 2nd ed., A.L. Page et al., Ed. Agronomy. 9: 961–1010. Am. Soc. of Agron., Inc. Madison, WI

Nimis, P., Omenetto, P., Giunti, I., Artioli, G., Angelini, I., 2012. Lead isotope systematics in hydrothermal sulphide deposits from the central-eastern Southalpine (Northern Italy). Eur. J. Mineral. 24, 23-37.

Osservatorio Regionale Suolo dell'ARPAV, 2015. Carta dei suoli della regione Veneto 1:250000.

Picone, S., Alvisi, F., Dinelli, E., Morigi, C., Negri, A., Ravaioli, M., Vaccaro, C., 2008. New insights on late Quaternary palaeogeographic setting in the Northern Adriatic Sea (Italy). J. Quaternary Sci. 23, 489-501.

Piovan, S., Mozzi, P., Stefani, C., 2010. Bronze Age Paleohydrography of the Southern Venetian Plain. Geoarchaeology, 25, 6–35.

Piovan, S., Mozzi, P., Zecchin, M., 2012. The interplay between adjacent Adige and Po alluvial systems and deltas in the late Holocene (Northern Italy). Gèomorphologie 18, 427-440.

Ravazzi, C., Marchetti, M., Zanon, M., Perego, R., Quirino, T., Deaddis, M., De Amicis, M., Margaritora, D., 2013. Lake evolution and landscape history in the lower Mincio River valley, unravelling drainage changes in the central Po Plain (N-Italy) since the Bronze Age. Quat. Int. 288, 195-205.

Rossetti, P., Zucchetti, S., 1988. Early-alpine ore parageneses in the serpentinites from the Balangero asbestos mine and Lanzo massif (Internal Western Alps). Rend. Soc. Ital. Mineral. Petrol. 43, 139-149.

Singh, P., 2010. Geochemistry and provenance of stream sediments of the Gangga river and its major tributaries in the Himalayan region, India. Chem. Geol. 269, 220-236.

Stefani, M., Vincenzi, S., 2005. The interplay of eustasy, climate and human activity in the late Quaternary depositional evolution and sedimentary architecture of the Po Delta system. Mar. Geol. 222/223, 19–48.

Trail, R.J., Lachance, G.R., 1966. Practical solution to the matrix problem in X-ray analysis. Part II. Application to a multicomponent alloy system. Can. J. Anal. Sci. Spectros. 11, 63-71.

Trevisan, F., Bianchini, G., Natali, C., Tassinari, R., Tessari, U., 2016. Heavy Metals Backgrounds In Soils From The Rovigo Province (NE, Italy). EQA-International Journal of Environmental Quality 21, 1-9.

Whitehouse, R., 2001. Investigating surface archaeology on the Po floodplain, northern Italy. Archaeology International. 5, 21–24.

Table captions:

Table 1 – Geochemical composition of soils and sediments from the investigated sector of the Padanian plain (Province of Rovigo, NE Italy).

Table 2 – Average geochemical composition of modern bed and suspended sediments from the Po and Adige rivers.

Research Highlights:

- Padanian Plain landscape results from the interplay of complex fluvial systems
- Po and Adige river systems variously interacted in space and time in the last millennia
- Geochemical analyses allow discrimination between Po and Adige river sediments
- Ni/Zn and Cr/Pb are useful geochemical proxies of sediment provenance
- Geochemical proxies are useful for palaeohydrographic reconstructions

Table 1

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	Boara Polesine				Concadirame				Lusia				Fratta Polesine-Bosaro				Stienta			
	Median	Mean	1st Quart	3rd Quart	Median	Mean	1st Quart	3rd Quart	Median	Mean	1st Quart	3rd Quart	Median	Mean	1st Quart	3rd Quart	Median	Mean	1st Quart	3rd Quart
SiO_2 (wt%)	49.15	49.17	47.12	51.60	51.96	51.97	49.85	54.02	51.22	53.61	48.82	61.34	52.63	52.60	51.94	53.66	51.99	53.65	50.38	55.76
TiO_2	0.69	0.67	0.67	0.71	0.67	0.66	0.63	0.69	0.65	0.62	0.52	0.68	0.63	0.63	0.60	0.65	0.61	0.59	0.58	0.63
Al_2O_3	15.43	14.82	13.46	16.28	13.31	13.28	12.67	14.01	13.32	12.57	10.33	13.90	13.52	13.67	13.30	13.91	12.88	12.68	12.12	13.30
Fe_2O_3	7.36	7.33	5.88	8.65	5.50	5.65	5.16	6.09	5.57	5.15	4.06	5.79	4.92	4.87	4.61	5.16	5.91	5.85	5.40	6.34
MnO	0.09	0.09	0.08	0.10	0.09	0.09	0.09	0.10	0.09	0.08	0.07	0.09	0.09	0.09	0.09	0.10	0.12	0.11	0.10	0.12
MgO	4.47	4.20	3.74	4.76	4.97	4.93	4.58	5.20	5.25	4.87	3.93	5.46	4.73	4.76	4.53	4.90	4.58	4.45	4.34	4.78
CaO	6.35	5.75	3.03	7.65	8.04	7.98	6.97	9.09	7.72	8.17	7.46	8.26	8.82	8.48	8.07	8.97	8.55	8.56	7.92	9.38
Na_2O	0.82	0.89	0.72	1.00	1.12	1.11	1.02	1.20	1.12	1.23	1.05	1.52	1.11	1.14	1.02	1.20	0.87	0.93	0.76	1.04
K_2O	3.21	3.12	3.05	3.33	2.88	2.87	2.77	3.02	2.98	2.94	2.76	3.10	2.40	2.49	2.27	2.64	2.41	2.37	2.20	2.53
P_2O_5	0.19	0.20	0.16	0.22	0.21	0.23	0.17	0.28	0.28	0.28	0.21	0.36	0.23	0.25	0.18	0.28	0.14	0.14	0.11	0.16
LOI	12.46	13.75	11.12	15.43	11.46	11.24	9.66	12.17	11.21	10.47	7.85	12.31	11.01	11.02	10.45	11.57	11.21	10.66	9.66	12.34
Ba (ppm)	512	497	469	554	471	466	448	498	497	460	348	529	400	417	380	440	358	359	337	382
Ce	57	60	51	71	45	46	43	50	49	45	39	51	50	51	47	53	41	42	40	45
Co	24	24	19	29	17	18	15	20	18	17	12	20	19	19	16	22	25	24	22	26
Cr	129	128	83	154	75	93	65	95	73	69	56	80	178	157	108	197	200	192	178	206
Cu	59	64	46	86	38	37	29	45	40	50	34	52	40	44	32	48	46	46	32	51
Ga	24	24	20	28	18	18	16	19	20	18	14	20	17	17	16	18	16	15	14	18
Hf	8	8	7	9	8	8	7	9	8	8	7	8	4	4	4	5	4	4	4	5
La	38	36	27	41	27	27	23	30	25	24	20	27	28	29	24	30	27	26	23	31
Nb	15	15	14	16	15	15	14	16	14	14	12	15	14	15	13	16	10	10	9	13
Nd	32	30	25	37	22	23	20	26	21	21	19	23	27	28	25	30	20	20	18	22
Ni	98	94	64	119	42	57	36	53	39	38	21	48	133	118	76	154	143	144	130	166
Pb	53	57	40	73	49	51	45	57	47	50	33	64	28	36	23	38	24	26	21	29
Rb	143	146	111	184	106	108	102	113	113	109	96	119	106	106	99	114	88	84	73	97
Sc	18	18	16	20	15	15	14	17	15	14	11	16	12	13	12	13	17	17	16	18
Sr	181	181	168	200	189	192	182	198	192	189	168	202	209	213	190	242	250	240	197	296
Th	11	11	9	13	8	8	8	9	8	8	6	9	7	7	6	8	7	7	7	8
V	129	123	96	146	89	89	79	99	96	83	47	102	93	92	84	100	101	99	92	110
Y	24	24	22	27	23	23	20	26	24	22	16	25	26	26	24	28	19	18	15	22
Zn	131	137	108	159	96	105	86	117	97	98	73	115	88	92	78	99	84	90	70	94
Zr	127	132	109	159	169	169	152	182	173	158	127	187	263	268	249	302	130	122	103	147
SOM (wt%)	8.5	9.7	5.9	12.4	11.5	11.2	9.7	12.2	-	-	-	-	3.2	3.0	2.5	3.7	4.6	4.4	3.2	6.0

Footnote: LOI = Loss On Ignition, SOM = Soil Organic Matter, - = not determined.

Table 2
Click here to download Table: Table 2.docx

	Po river		Adige river	
	Bed sediments	*Suspended sediments*	*Bed sediments*	*Suspended sediments*
SiO_2 (wt%)	52.74	47.50	53.46	37.16
TiO_2	0.62	0.62	0.60	0.49
Al_2O_3	12.10	14.00	11.94	13.02
Fe_2O_3	4.54	5.46	3.73	4.93
MnO	0.13	0.12	0.07	0.09
MgO	5.86	4.57	6.31	8.77
CaO	10.53	9.80	9.23	12.27
Na_2O	1.20	0.80	1.45	1.07
K_2O	2.08	2.59	2.54	2.62
P_2O_5	0.21	0.18	0.22	0.17
LOI	10.01	14.37	10.47	19.43
Ba (ppm)	360	424	481	546
Ce	37	52	41	56
Co	27	23	13	16
Cr	241	197	53	70
Cu	33	57	20	57
Ga	14	22	15	21
Hf	5	4	4	2
La	24	33	23	37
Nb	11	15	12	10
Nd	25	21	27	21
Ni	156	187	31	60
Pb	28	36	37	68
Rb	87	129	102	112
Sc	9	14	9	9
Sr	291	321	186	198
Th	6	7	5	3
V	77	117	66	99
Y	25	24	24	23
Zn	97	124	93	202
Zr	227	197	250	180

Footnote: LOI = Loss On Ignition.

Figure 1

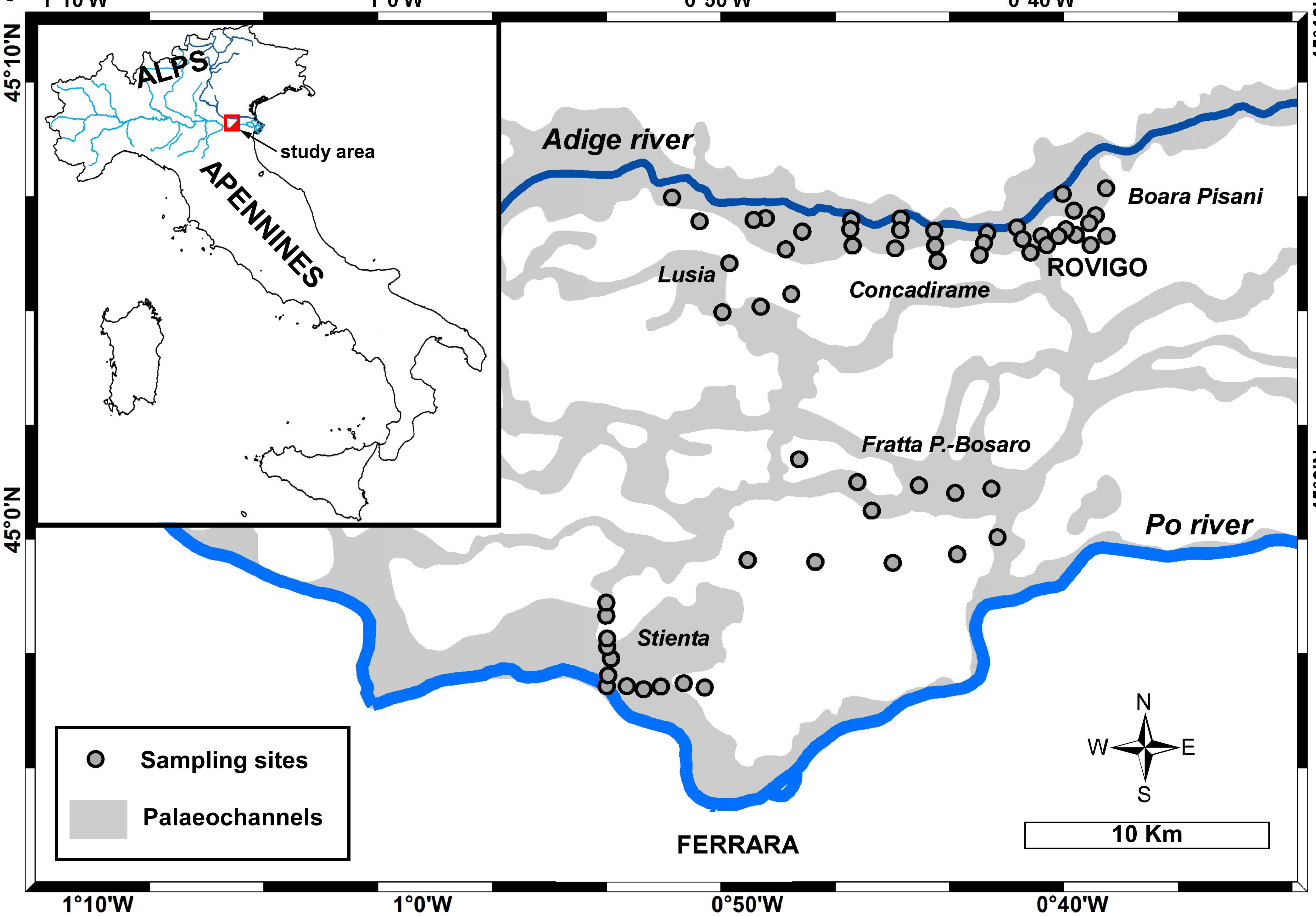
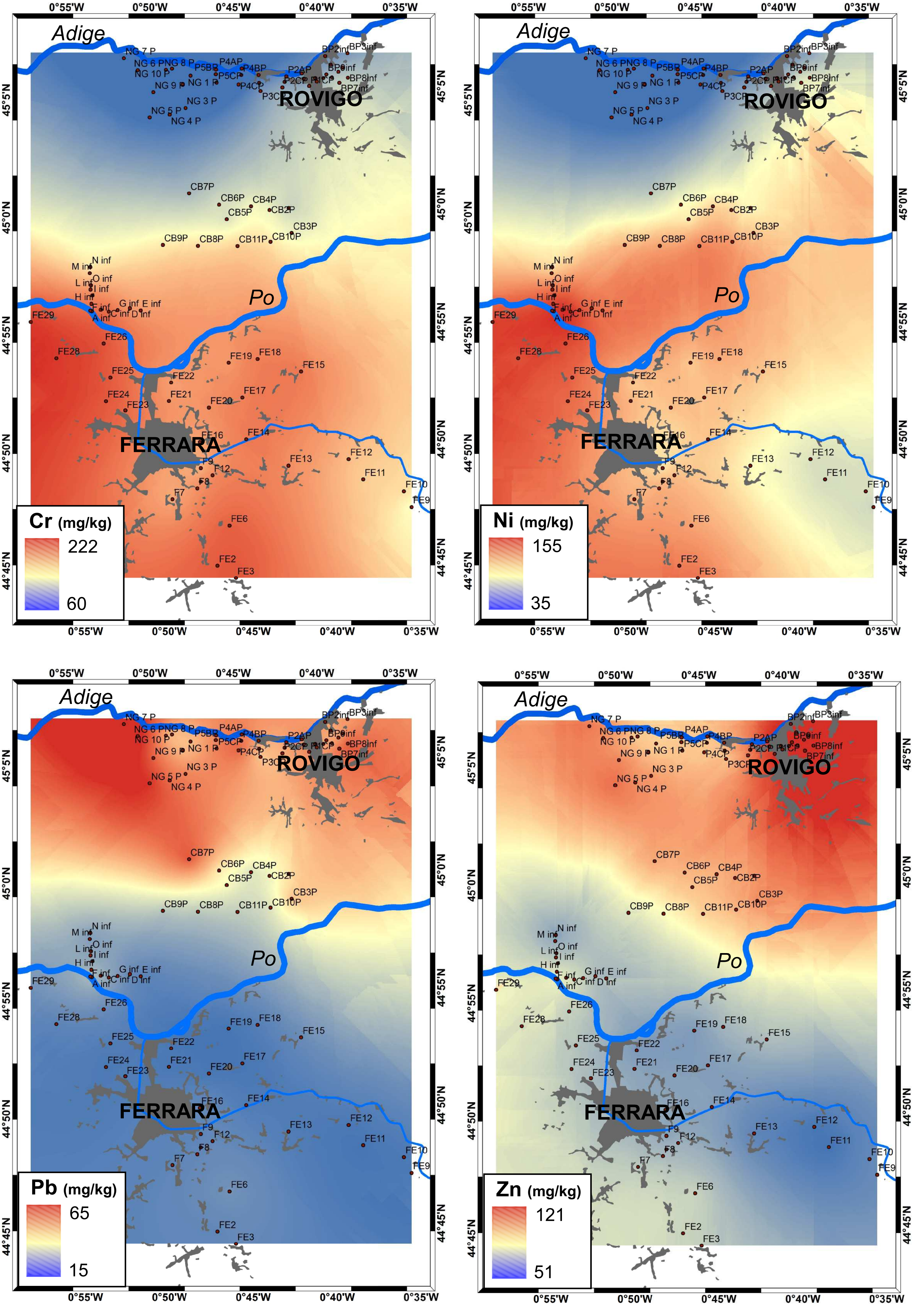
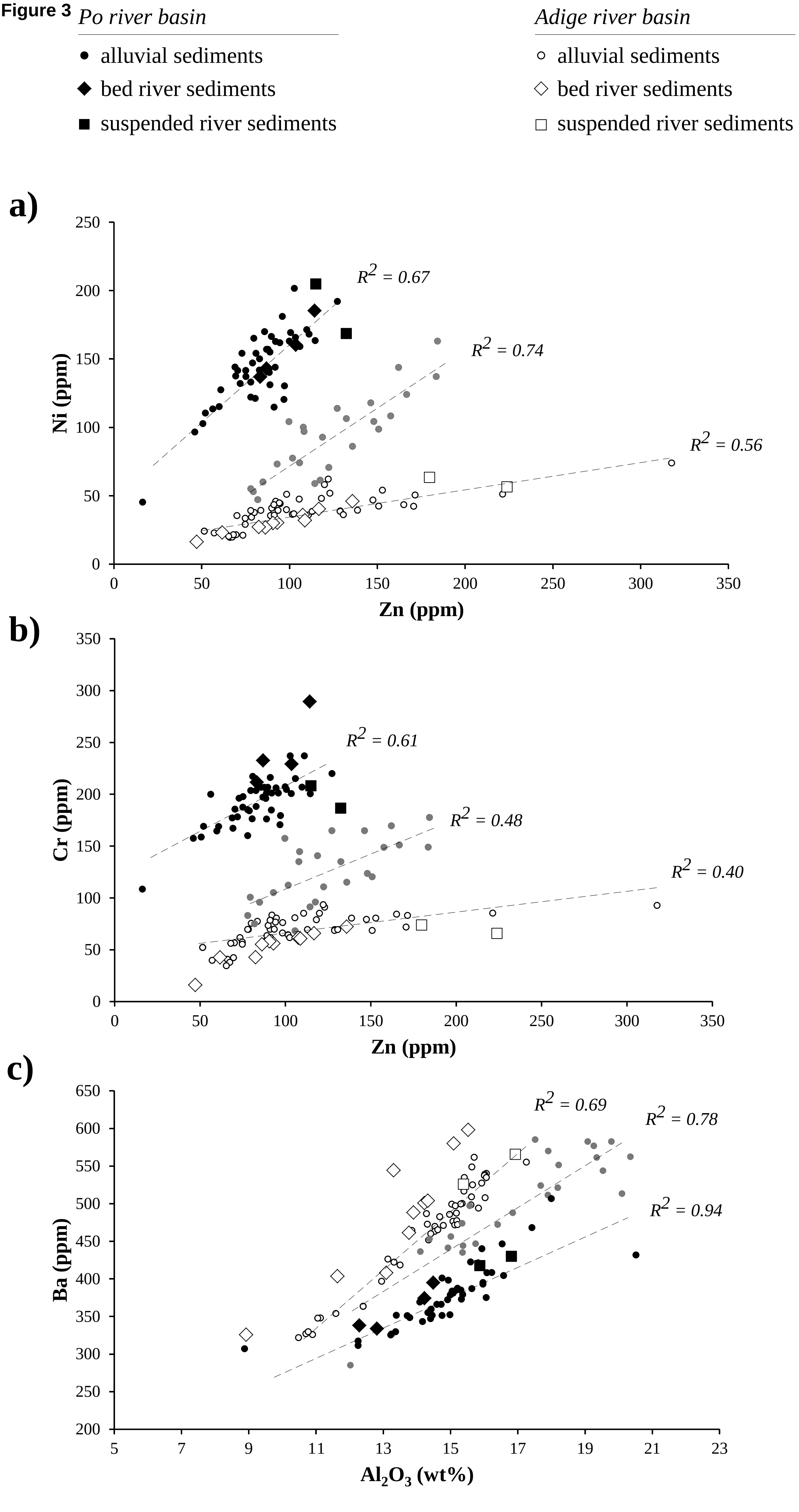

1°10'W
1°0'W
0°50'W
0°40'W
45°10'N
45°0'N
ALPS
APENNINES
study area
Adige river
Boara Pisani
Lusia
Concadirame
ROVIGO
Fratta P.-Bosaro
Po river
Stienta
FERRARA
Sampling sites
Palaeochannels
10 Km
N
W
E
S

Figure 2



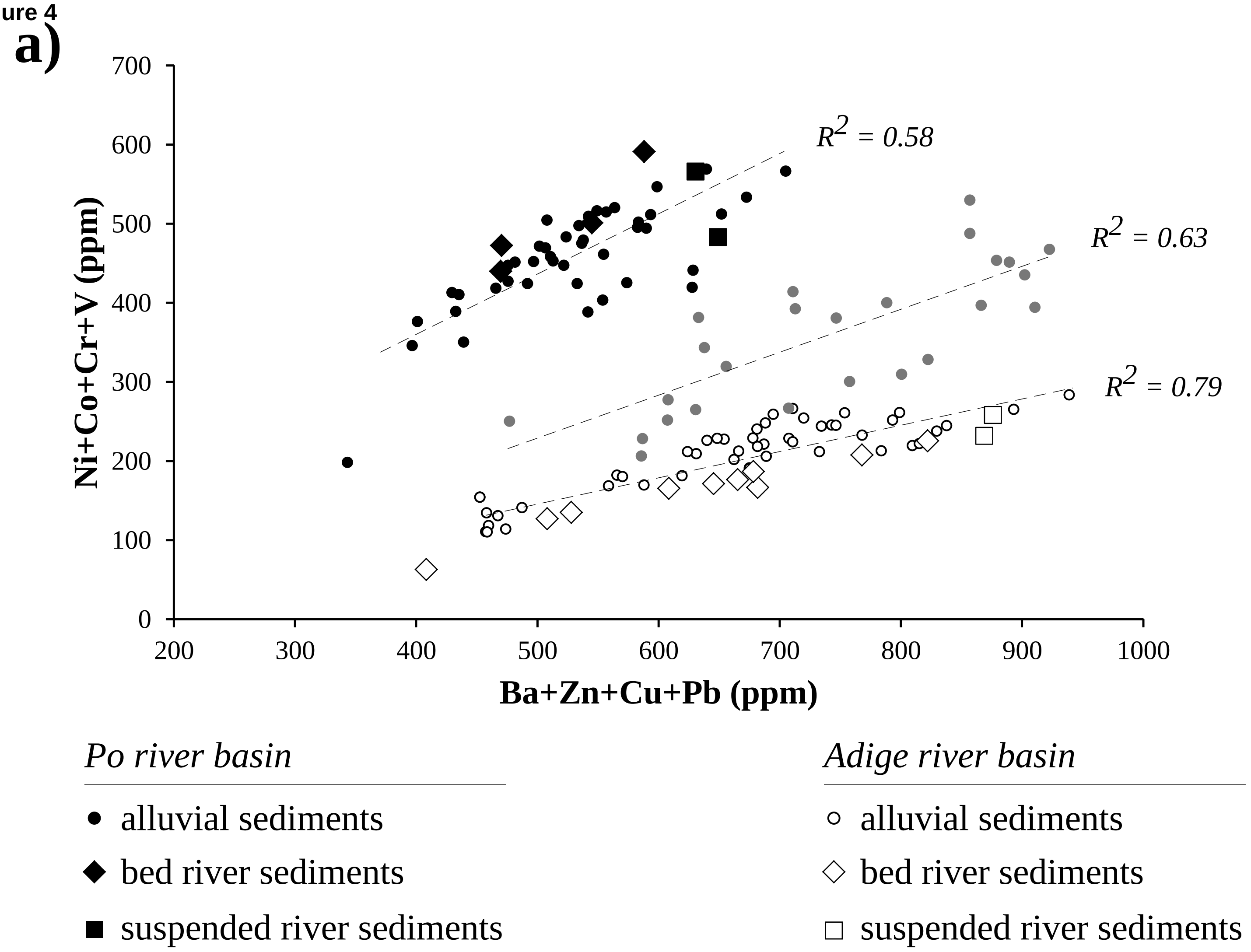
0°55'W
0°50'W
0°45'W
0°40'W
0°35'W
45°5'N
45°0'N
44°55'N
44°50'N
44°45'N
Adige
Po
ROVIGO
FERRARA
NG 7 P
NG 6 P
NG 8 P
NG 10 P
NG 9 P
NG 1 P
NG 3 P
NG 5 P
NG 4 P
P5BP
P4AP
P4BP
P5CP
P4CP
P3CP
P2AP
P2CP
P1CP
BP2inf
BP3inf
BP6inf
BP8inf
BP7inf
CB7P
CB6P
CB4P
CB5P
CB2P
CB3P
CB9P
CB8P
CB11P
CB10P
M inf
N inf
L inf
O inf
I inf
H inf
F inf
G inf
E inf
C inf
D inf
A inf
FE29
FE28
FE26
FE25
FE24
FE23
FE22
FE21
FE20
FE19
FE18
FE17
FE16
FE15
FE14
FE13
FE12
FE11
FE10
FE9
F9
F12
F8
F7
FE6
FE2
FE3
Cr (mg/kg)
222
60
Ni (mg/kg)
155
35
Pb (mg/kg)
65
15
Zn (mg/kg)
121
51

Figure 3



Po river basin
alluvial sediments
bed river sediments
suspended river sediments
Adige river basin
alluvial sediments
bed river sediments
suspended river sediments
a)
Ni (ppm)
Zn (ppm)
R2 = 0.67
R2 = 0.74
R2 = 0.56
b)
Cr (ppm)
Zn (ppm)
R2 = 0.61
R2 = 0.48
R2 = 0.40
c)
Ba (ppm)
Al2O3 (wt%)
R2 = 0.69
R2 = 0.78
R2 = 0.94

Figure 4


a)
700
600
500
400
300
200
100
0
200
300
400
500
600
700
800
900
1000
Ni+Co+Cr+V (ppm)
Ba+Zn+Cu+Pb (ppm)
R2 = 0.58
R2 = 0.63
R2 = 0.79
Po river basin
alluvial sediments
bed river sediments
suspended river sediments
Adige river basin
alluvial sediments
bed river sediments
suspended river sediments

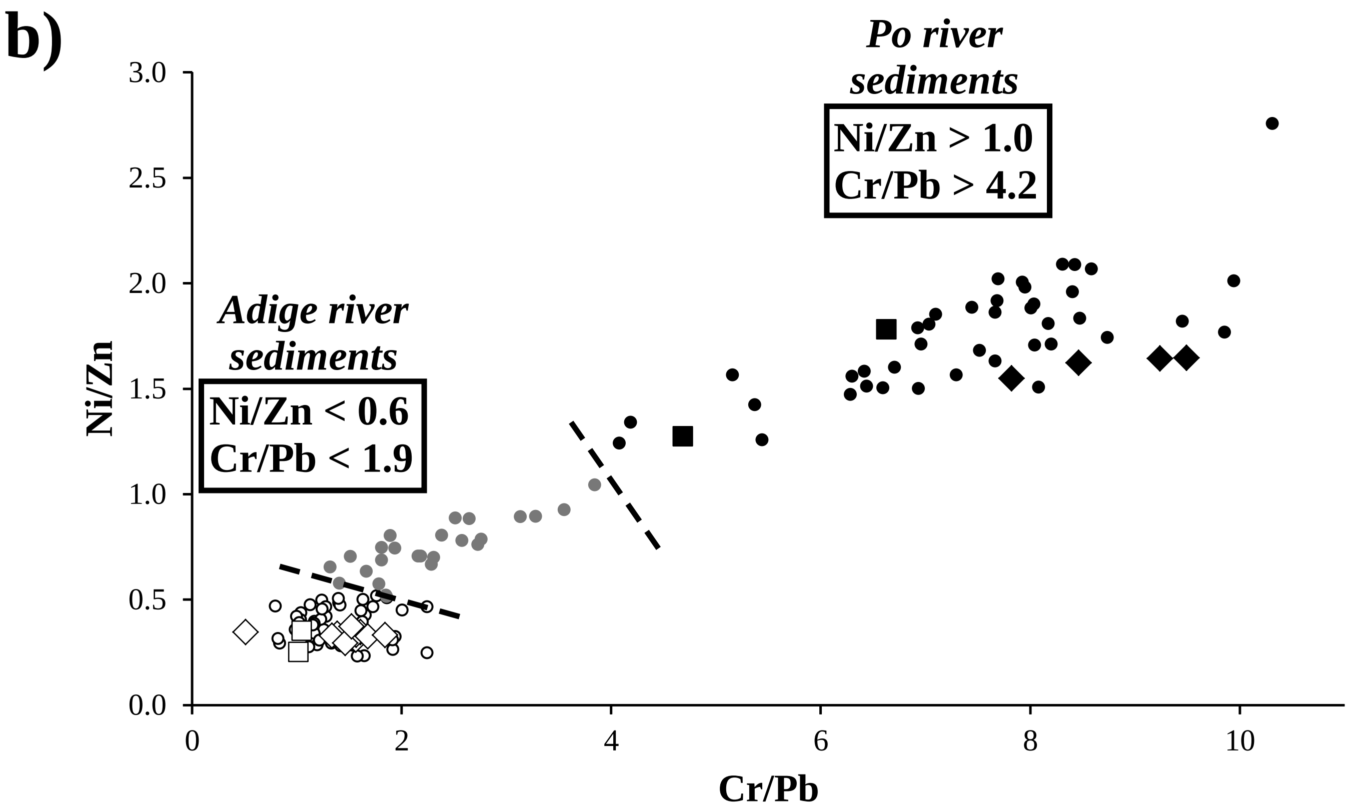

b)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
2
4
6
8
10
Ni/Zn
Cr/Pb
Po river sediments
Ni/Zn > 1.0
Cr/Pb > 4.2
Adige river sediments
Ni/Zn < 0.6
Cr/Pb < 1.9

Figure captions:

Figure 1 – Sketch map of the studied area reporting the Po and Adige river paths, sampling locations of the studied alluvial sediments and palaeochannel distribution retrieved from the Veneto regional soil map 1:250000 (Osservatorio Regionale Suolo dell'ARPAV, 2015). Gauss-Boaga projection (W), datum: Rome 1940.

Figure 2 – Geochemical maps highlighting the spatial distribution of Cr, Ni, Pb and Zn (ppm) in alluvial sediments (collected at 90-110 cm depth) from the studied sector of the Padanian plain. Data from this work and from Bianchini et al. (2013). See text for further details.

Figure 3 – Ni *vs* Zn (a), Cr *vs* Pb (b) and Ba *vs* Al_2O_3 (c) bivariate diagrams highlighting the geochemical features of Po and Adige river sediments. The diagrams report composition of alluvial sediments from the study area (see Supplementary Tables 1-5) and modern bed and suspended sediment from Adige and Po rivers (Supplementary Table 6). Note that the distribution of alluvial sediments identifies three distinct geochemical trends, the most extreme of them conforming to Po and Adige river sediments. The intermediate trend can be interpreted as a mixture of 70% Po and 30% Adige sedimentary end-members.

Figure 4 – Discrimination diagrams based on (a) the sum of siderophile (Cr+Ni+Co+V) *vs* chalcophile (Zn+Cu+Pb+Ba) elements and (b) ratios between siderophile (Ni, Cr) *vs* chalcophile (Zn, Pb) elements.

Supplementary Tables 1-6

Click here to download Supplementary material for on-line publication only: Supplementary Tables 1-6_rev.xlsx