Carbon, nitrogen, and sulphur isotope analysis of the Padanian Plain sediments: backgrounds and provenance indication of the alluvial components

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Abstract

This work reports an *ab initio* study on the carbon (C), nitrogen (N), and sulphur (S) elemental and isotope compositions of the Padanian Plain sediments collected in the province of Ferrara (Northern Italy). The investigated sediments were already characterized by previous research that highlighted a bimodal provenance, as some sediments are from the Alpine chain and were conveyed to the plain by Po River, whereas others are from the Apennine chain and were conveyed to the plain by the Reno River. This information was obtained considering the concentration of heavy metals retrieved from hundreds of X-ray fluorescence analyses available in the literature, whereas CNS elemental and isotope compositions are unknown. These tracers are generally considered scarcely useful to identify the sediment source areas, as influenced by multiple environmental factors. However, this work challenges these assertions observing that $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$ are significantly different in Po and Reno River sediments. Our hypothesis is that the CNS geochemical signal is 1) mainly regulated by the organic fraction included in the alluvial sediments, and 2) these organic fraction has in turn a specific composition in the distinct source catchments. More in general, the presented data increase knowledge on the local elemental and isotopic backgrounds. This is important because many pollutants contain significant CNS concentration and specific isotope composition. Therefore, they

serve as baseline and will provide new tools to recognize possible anthropogenic anomalies in the studied area.

Keywords: CNS isotopes, alluvial sediments, Padanian Plain, Po River, Reno River, isotopic fractionation, biogeochemical processes

1. Introduction

The geochemical signatures of sediments in alluvial plains record the geochemistry of the parent rocks and the weathering mechanisms occurred in the source areas. However, geochemical signatures are often complex to be interpreted because distinct rivers (and tributaries) drain geologically different sub-basins, sometimes conveying different sediments in the same alluvial plain. In general, major and trace elements are used to trace the sediments' provenance as they reflect the source rock composition (Bianchini et al., 2012; Balabanova et al., 2016; Nyobe et al., 2018; Salomão et al., 2020; Vicente et al., 2021). However, secondary pedological processes, related to the local climatic conditions could affect the primary signature (Costantini et al., 2002; Caporale and Violante, 2016). In addition, the natural (geogenic) geochemical fingerprint of the alluvial sediments can be overprinted by anthropogenic contributions in agricultural, industrial, and urban areas (Galán et al., 2014; Barbieri et al., 2018). Therefore, in order to better constrain the sources of alluvial sediments, new geochemical proxies have to be tested to delineate the provenance of sediments and features of the relative depositional environments. Among the various case-studies, alluvial sediments in the province of Ferrara, located in the easternmost sector of the Padanian Plain (Northern Italy), have been widely studied from the geochemical point of view (Amorosi et al., 2002; Amorosi, 2012; Bianchini et al., 2012; 2013, 2019; Di Giuseppe et al., 2014a; 2014b; 2014c). The soils of this specific sector of the plain are composed by young (Holocene in age) alluvial deposits transported by Po and Reno fluvial systems. Previous investigations on these sediments were mainly focused on major elements having lithophile affinity (Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K, P) and heavy metals (Ni, Co, Cr, V, Sc, Cu, Pb, Zn) to constrain the distribution of potentially toxic elements (Di Giuseppe et al., 2014a; 2014b; 2014c, Bianchini et al., 2012; 2013; 2019). They were important to define the local geochemical backgrounds, as well as the sediments provenance, *i.e.*, which fluvial system conveyed its alluvial load in the plain (Bianchini et al., 2012). In particular, specific trace element such as nickel (Ni) and chromium (Cr) were effective in discriminating between alluvial sediments from Po and Reno Rivers, the two fluvial systems that are interacting in the area (Bianchini et al., 2012; 2013; 2019). In fact, the Po River sediments are richer in Ni and Cr than Reno River sediments, because the parent rocks outcropping in the Po River catchment include mafic and ultramafic lithologies rich in heavy metals (Amorosi, 2012). In the above-mentioned studies essential elements such as carbon (C), nitrogen (N), and sulphur (S) have been scarcely investigated, and information on their isotopic ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$) is missing. The stable isotope compositions of C, N, and S of soils and sediments vary significantly, reflecting the nature of the parent rock material, the current and past climates and vegetation, and the effects of other organisms (Anderson, 1988). Therefore, they could be used as additional proxies to trace the source areas of the weathered material, which was mobilized by erosion, transported by rivers in the catchments and finally deposited in alluvial plains.

In order to test the effectiveness of CNS elemental and isotopic data in the provenance analysis, sediment samples were selected from the collections of previous geochemical studies that emphasized the origin of Padanian alluvial sediments on the basis of Ni and Cr content (Bianchini et al., 2012; 2013; Di Giuseppe et al., 2014a; 2014b; 2014c). This new investigation deals with the analysis of the elemental and isotopic composition of C, N, and S of selected sample sediments having "Po affinity" (*i.e.*, high Ni-Cr contents) and "Reno affinity" (*i.e.*, low Ni-Cr contents). The goal is to define CNS elemental and isotopic backgrounds and to verify if these tracers can be used as additional proxies to define the sediment provenance.

2. Study area

The Padanian Plain is the widest alluvial plain (~ 48,000 km^2) of the Italian peninsula (Campo et al., 2020). It is the morphological expression of the homonymous basin, which is bounded by the Alpine and Apennine chains, at north and south respectively (Fig. 1a). The plain was characterized by marine sedimentation in Pliocene to Early Pleistocene before progradation of fluvial sediments that was enhanced during glaciation periods (Amorosi et al., 2019; 2021; Campo et al., 2020). The easternmost part of the plain, where the Ferrara province is located, received sedimentary contributes from i) the Po River, which is the principal Italian fluvial system crossing from west to east the Padanian Plain with numerous tributaries from distinct parts of the Alps and the north-western Apennines (Marchina et al., 2015; 2016; 2018), and ii) several torrents flowing from the north-eastern Apennines (Fig. 1; Bianchini et al., 2002; 2012; 2014).

The sediments of Po River mainly derive from the western and central Alps and north-western Apennines, where limestones, sandstones, as well as mafic and ultramafic rocks (*i.e.*, ophiolites) crop out (Amorosi et al., 2002). On the other hand, sediments from north-eastern Apenninic rivers derive from Cretaceous to Pliocene sedimentary rocks, such as sandstones, marls, and evaporites (Amorosi et al., 2002; Manzi et al., 2007).

In particular, this study focused on the geochemistry of agricultural soils collected close to i) the town of Ferrara (labels FE, F), and ii) the nearby village of Vigarano Mainarda (labels VM, VP). These soils developed from alluvial sediments (sand, silt and clay carried by the Po and Reno Rivers) that have been geochemically characterized by Bianchini et al. (2012; 2013). In these studies, the Po or Reno related provenance of each sediment sample was identified based on their Ni and Cr contents.

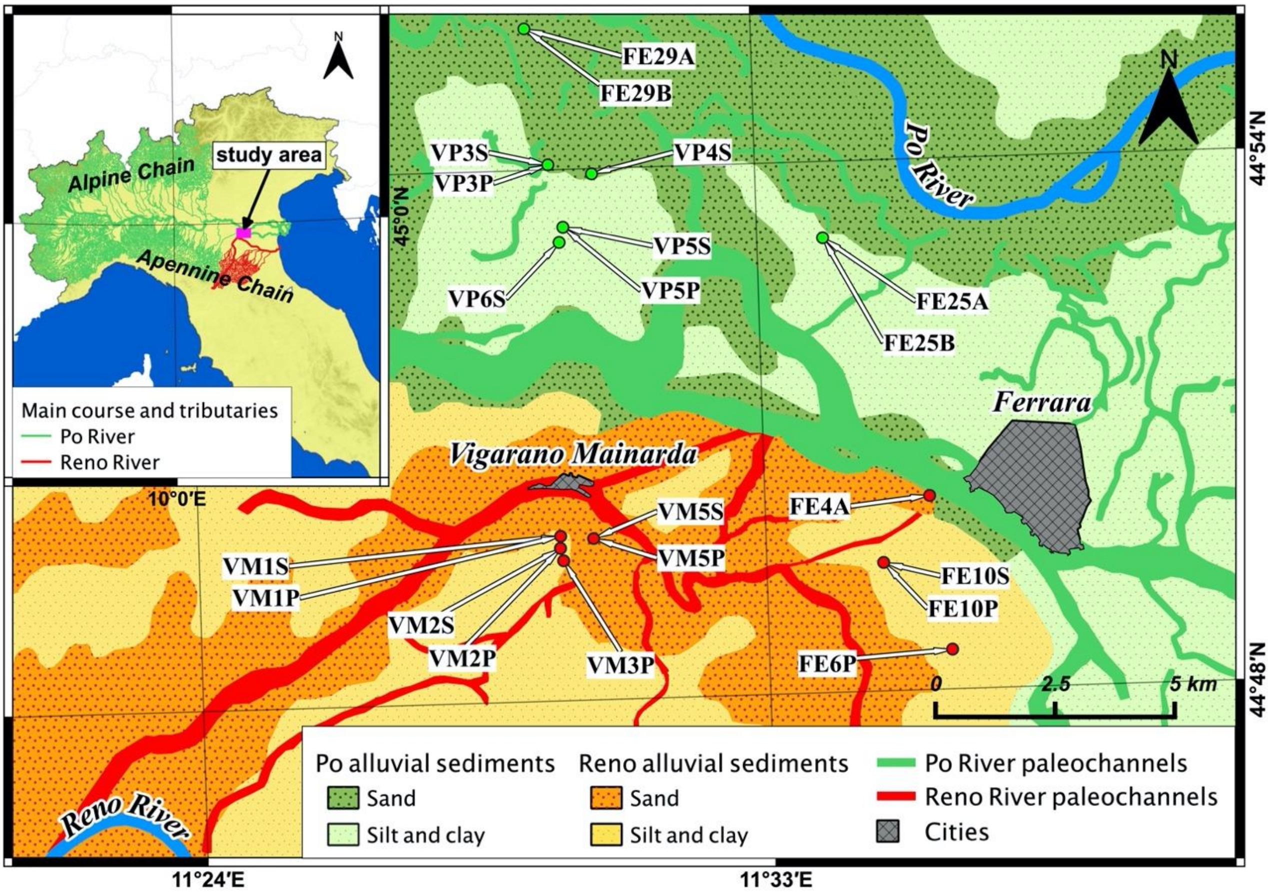

Figure 1. Sedimentological map (modified from Bertolini et al., 2009) of the study area reporting the paleochannels and the location of the sediment samples. Samples collected near Ferrara are labelled FE, F; samples collected near Vigarano Mainarda are labelled VM, VP. The inset reports the location of the study area in Northern Italy and the main courses and tributaries of the Po and Reno fluvial systems.

3. Materials and methods

3.1. Sample selection

Ten sediment samples with "Po affinity" and eleven sediment samples with "Reno affinity" were selected. The samples were collected at two distinct depths: one representative of the plough horizon (just beneath the roots zone, at a depth of 30–40 cm) and the other representative of the underlying undisturbed layer (at a depth of 100–120 cm). The samples were powdered and homogenized within an agate mill before to proceed with further analyses.

3.2 C, N, S elemental and isotopic composition

The analyses of C, N, S contents (expressed in wt%) and the relative isotope ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$) were carried out at the Department of Physics and Earth Science of University of Ferrara

(Italy) using an elemental analyser (EA) Vario PYRO Cube (Elementar) operating in combustion mode and coupled with the isotope ratio mass spectrometer (IRMS) precisION (Elementar). Homogenous powdered samples (around 40 mg) were weighed in tin capsules, wrapped, and finally loaded in the EA autosampler to be analyzed.

The Vario PYRO Cube consists of a combustion oven operating at 1150°C. After the sample has been burnt, the released C, N, and S gaseous species are transferred in a reduction column operating at 850°C that contains chips of native copper to reduce the nitrogen oxides (NO_x) to N_2. The analyte gases pass into the original purge and trap module before to enter in the IRMS. Only N_2 is not trapped and is introduced directly in the IRMS to be analyzed for isotopic composition determination. CO_2 and SO_2 are trapped respectively in two distinct traps. When the N isotopic analysis terminated, the CO_2 trap is heated at 110°C to release CO_2 which flows in the IRMS to start the isotopic C analyses. After that, the SO_2 trap is heated at 220°C to release the gas.

In the mass spectrometer the molecules of the sample gas are ionized by the source (*i.e.*, a thorium oxide filament), and the ions pass through a magnet, which deflects and sorts them into beams with distinctive mass/charge ratios (m/z). Then ion beams arrive at the collector where three Faraday cups detect the ions of each of the three different masses of analyzed gas simultaneously (*i.e.*, for N_2 the masses 28, 29, and 30, for CO_2 the masses are 44, 45, and 46 and for SO_2 the masses 64 and 66).

The detection of the distinct isotopic masses of the sample is bracketed between those of reference gases (N_2, CO_2, SO_2, 5 grade purity), which have been calibrated using reference materials. In the cups, the impact of the ions is translated into a recordable electrical signal, forming peaks, which area is proportional to the number of incident ions. The isotope ratios are calculated through peak definition and integration through the ionOS software.

The signal intensity is amplified by an integrated Amplifier and is expressed in nano-ampere (nA). The signal intensity is referred as “peak height”, and the minimum acceptable signal is 1 nA (optimum between 2 and 10 nA) in amplitude and at least 5 seconds in duration.

Additional data on the distinct carbon fractions (organic carbon, OC; inorganic carbon IC) were carried out with the EA Vario MICRO cube coupled with the IRMS Isoprime100 (Elementar), following the thermal speciation analytical approach defined by Natali et al. (2018).

Calibration of the instruments were performed using several standards: the limestone JLs-1 (Kusaka and Nakano, 2014), the Carrara Marble (Natali and Bianchini, 2015), the Jacupiranga carbonatite (Beccaluva et al., 2017), the peach leaves NIST SRM1547 (Dutta et al., 2006), the caffeine IAEA-600, the Tibetan human hair powder USGS42 (Coplen and Qi, 2011), the Barium Sulfate IAEA-SO-5 (Halas and Szaran, 2001).

The $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$ isotopic ratios (R) were expressed with the δ notation (in ‰ units):

$$\delta = (R_{sam}/R_{std} - 1) \times 1000$$

where R_{sam} is the isotopic ratio of the sample and R_{std} is the isotopic ratio of the international isotope standards Pee Dee Belemnite (PDB), air N_2, and Canyon Diablo troilite (CDT) for C, N, and S respectively.

Analytical uncertainties (1 sigma) for the isotope analyses were in the order of ± 0.1‰ for $\delta^{13}C_{TC}$ and ± 0.3‰ for $\delta^{15}N$ and $\delta^{34}S$, as indicated by repeated analyses of samples and standards.

3.3 Statistical analysis

The data interpretation was supported by a statistical analysis that was carried out by R (R Core Team, 2017). The analysis of variance (ANOVA test) was applied to test if element composition and/or isotopic ratios were affected by the provenance of the sediments. The PCA was applied to examine differences in elemental and isotopic parameters between sediments having Po and Reno affinity (package “FactoMineR” [Le et al., 2008]; package “factoextra” [Kassambara, 2017]).

The spatial variation of the various parameters was also investigated. Among the various proxies, the $\delta^{13}C_{TC}$ (‰) isotopic signatures appears influenced by the depositional facies, hence a geochemical map was prepared with Q-GIS 3.14.

4. Results

The contents of C, N, and S as well as the respective isotopic ratios of alluvial sediments with Po or Reno River affinity are reported in Table 1.

Table 1. C, N, and S elemental and isotopic composition of alluvial sediments in the surroundings of Ferrara. Sediments are ascribed to Po and Reno River contributions according to previous studies (Bianchini et al., 2012; 2013).

	Depth (cm)	TC (wt%)	$\delta^{13}C_{TC}$ (‰)	N (wt%)	$\delta^{15}N$ (‰)	S (wt%)	$\delta^{34}S$ (‰)
Po River affinity							
VP3S	30-40	2.81	-10.9	0.13	9.7	0.05	1.9
VP3P	100-120	3.10	-7.5	0.06	9.8	0.04	2.8
VP4S	30-40	2.55	-10.5	0.10	8.9	0.03	3.0
VP5S	30-40	2.76	-14.4	0.14	8.7	0.03	2.6
VP5P	100-120	1.23	-21.4	0.08	7.3	0.03	0.2
VP6S	30-40	2.63	-13.0	0.12	8.1	0.03	2.9
FE25A	30-40	2.04	-12.0	0.12	8.2	< 0.01	0.5
FE25B	100-120	2.55	-8.2	0.08	10.7	< 0.01	0.8
FE29A	30-40	2.48	-9.8	0.12	12.5	< 0.01	1.8
FE29B	100-120	2.04	-9.4	0.12	10.3	< 0.01	0.7
Average		**2.42**	**-11.7**	**0.11**	**9.4**	**0.04**	**1.7**
Reno River affinity							
VM1S	30-40	2.62	-11.0	0.10	6.4	0.04	-2.0
VM1P	100-120	2.58	-7.3	0.05	7.0	0.03	-1.9
VM2S	30-40	2.45	-8.7	0.06	6.3	0.04	-2.6
VM2P	100-120	2.64	-8.0	0.05	6.7	0.05	-4.0
VM3P	100-120	2.71	-9.9	0.07	5.7	0.03	-3.1
VM5S	30-40	2.47	-7.6	0.06	7.6	0.03	-4.1
VM5P	100-120	2.50	-5.9	0.03	9.0	0.03	-1.6
F6P	100-120	2.43	-9.9	0.13	8.0	< 0.01	-0.9
F10S	30-40	2.74	-11.0	0.15	7.3	< 0.01	-0.1
F10P	100-120	2.41	-7.6	0.10	7.8	0.11	-4.5
FE4A	30-40	2.74	-9.2	0.15	9.0	< 0.01	-0.4
Average		**2.57**	**-8.7**	**0.09**	**7.3**	**0.04**	**-2.3**

The Total Carbon (TC) concentration of the whole sample population varies between 1.2 and 3.1 wt% and $\delta^{13}C_{TC}$ ranges from -7.3 to -21.4‰. Significant differences can be observed between sediments with Po and Reno affinity (Fig. 2a, b).

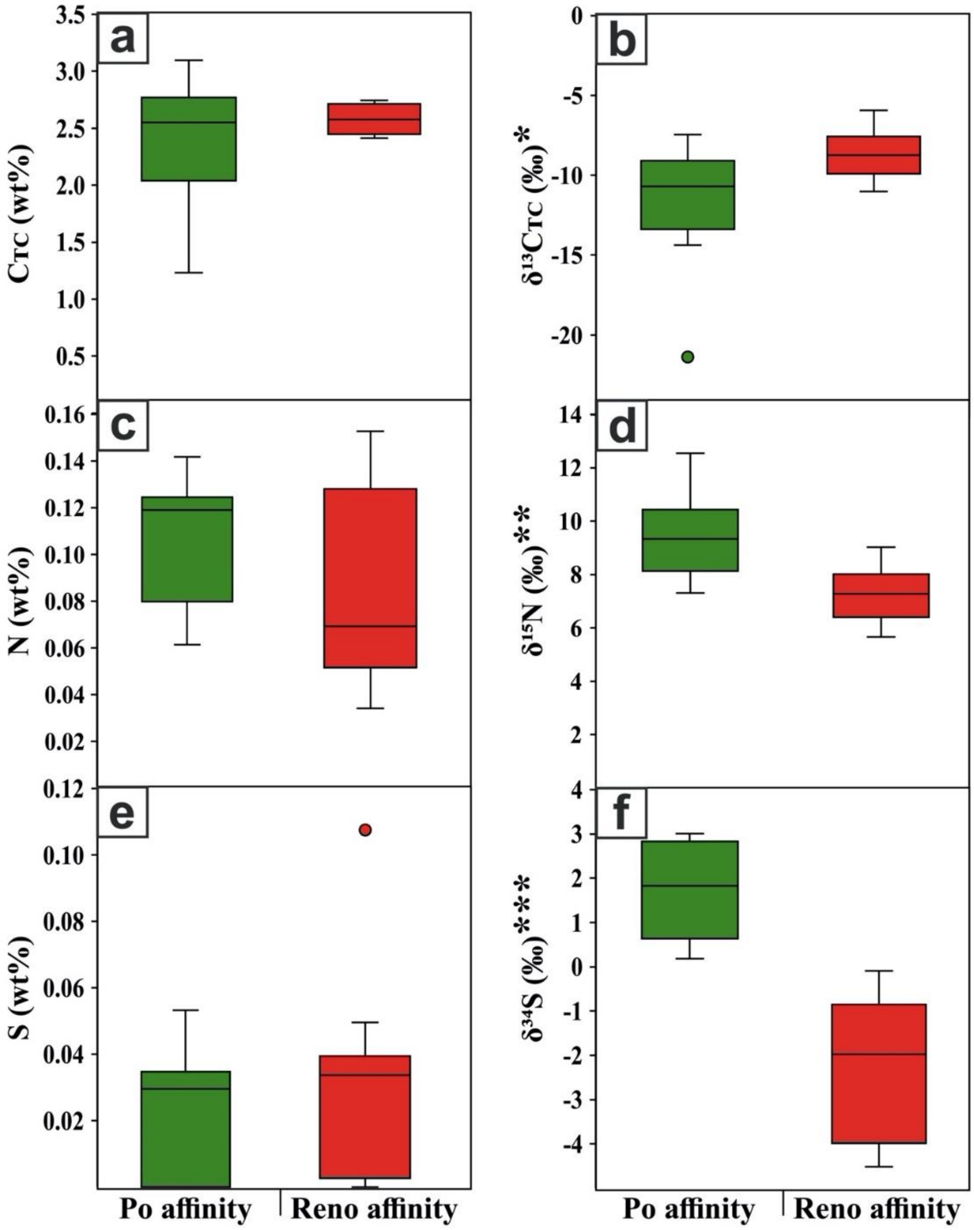

Figure 2. Box plots of the C, N, and S elemental and isotopic composition of alluvial sediments in the surroundings of Ferrara. Sediments are ascribed to Po and Reno River contributions according to previous studies (Bianchini et al., 2012; 2013). For the isotopic parameters, the one-way ANOVA results are also reported (* $p < 0.01$; ** $p < 0.001$; *** $p < 0.0001$), while for the elemental contents, the one-way ANOVA results are not significant.

Po River sediments are characterized by TC between 1.2 and 3.1 wt% and $\delta^{13}C_{TC}$ between -7.5 and -21.4‰ with average value of 2.4 wt% and -11.7‰, respectively. Reno River sediments are characterized by more restricted elemental and isotopic ranges than those of Po River, having TC between 2.4 and 2.7 wt% and $\delta^{13}C_{TC}$ between -7.3 and -11.0‰, with average values of 2.6 wt% and -8.7‰, respectively. This difference is primarily related to the inorganic and organic carbon (IC and OC, respectively) ratios, as IC typically has $\delta^{13}C_{IC}$ approaching 0‰ and OC typically has very negative $\delta^{13}C_{OC}$ down to -25‰ (Natali and Bianchini, 2015). However, our analyses of the distinct carbon fractions (Table 2) revealed that also OC and IC have distinct isotopic values in Po and Reno River sediments.

Table 2. Elemental and isotopic composition of distinct carbon fractions (Organic Carbon, OC; Inorganic Carbon, IC) of alluvial sediments in the surroundings of Ferrara. Sediments are ascribed to Po and Reno River contributions according to previous studies (Bianchini et al., 2012; 2013).

	Depth (cm)	**OC (wt%)**	**$\delta^{13}C_{OC}$ (‰)**	**IC (wt%)**	**$\delta^{13}C_{IC}$ (‰)**
Po River affinity					
VP3S	30-40	0.85	-21.8	1.73	-1.2
VP3P	100-120	0.39	-20.5	2.32	-1.5
VP4S	30-40	0.77	-21.1	1.64	-1.4
VP5S	30-40	1.13	-22.0	1.36	-2.2
VP5P	100-120	0.60	-28.1	0.43	-4.1
VP6S	30-40	0.93	-22.4	1.48	-2.7
FE25A	30-40	0.70	-24.5	2.75	-3.3
FE25B	100-120	0.31	-23.6	0.77	-0.4
FE29A	30-40	0.84	-22.8	1.32	0.2
FE29B	100-120	0.56	-22.8	1.32	-0.5
Average		**0.71**	**-23.0**	**1.51**	**-1.7**
Reno River affinity					
VM1S	30-40	0.75	-22.5	1.59	-0.5
VM1P	100-120	0.43	-21.3	1.98	-0.5
VM2S	30-40	0.48	-22.1	1.72	-1.0
VM2P	100-120	0.49	-22.1	1.88	-1.1
VM3P	100-120	0.34	-20.0	1.86	-0.8
VM5S	30-40	0.54	-20.7	1.88	-0.2
VM5P	100-120	0.63	-21.7	1.92	-0.1
F6P	100-120	0.76	-23.1	1.27	-0.9
F10S	30-40	0.90	-22.7	1.32	-1.5
F10P	100-120	0.50	-22.5	1.53	-1.3
FE4A	30-40	0.80	-22.3	1.80	0.2
Average		**0.60**	**-21.9**	**1.70**	**-0.7**

Samples with Po affinity have on average 0.7 wt% of OC characterized by $\delta^{13}C_{OC}$ of -23.0‰ and 1.5 wt% of IC with $\delta^{13}C_{IC}$ of -1.7 ‰, whereas those with Reno affinity have on average 0.6 wt% of OC characterized by $\delta^{13}C_{OC}$ of -21.9 ‰ and 1.7 wt% of IC characterized by $\delta^{13}C_{IC}$ of -0.7 ‰.

The N concentration of the whole sample population varies between 0.03 and 0.15 wt% and $\delta^{15}N$ varies between 5.7 and 12.5 ‰. From the elemental point of view Po and Reno River sediments are indistinct (0.0-0.1 wt%), but they differ in the isotopic composition (Fig. 2 c, d). Po River sediments are characterized by $\delta^{15}N$ between 7.3 and 12.5‰ with average of 9.4‰, whereas Reno River sediments are characterized by $\delta^{15}N$ between 5.7 and 9.0‰ with average of 7.3‰. The S concentration of the whole sample population varies from < 0.01 wt% up to 0.11 wt%, whereas $\delta^{34}S$ varies between -4.5 and 3.0‰. Po River sediments are characterized by positive $\delta^{34}S$ values (between 0.2 and 3.0‰, average of 1.7‰), whereas Reno River sediments are characterized by negative $\delta^{34}S$ values (between -4.5 and -0.1‰, average of -2.3 ‰; Fig. 2 e, f).

The one-way ANOVA test was used to verify if the composition and/or isotopic ratios were affected by the provenance of the sediments (Po or Reno River catchment). The test showed that TC, N, S, OC, IC, and $\delta^{13}C_{OC}$ of alluvial sediments were not significantly influenced (*p*-values > 1) by fluvial system which transported and deposited the sediments on the Padanian Plain. On the other hand, the $\delta^{13}C_{TC}$, $\delta^{13}C_{IC}$, are moderatly affected (*p*-values < 0.01) by the fluvial system, and $\delta^{15}N$, $\delta^{34}S$ are significantly (*p*-value < 0.001) and extremely (*p*-value < 0.0001) influenced by the origin of the alluvial sediments, respectively.

5. Discussion

The difference between Reno and Po River sediments was already pointed out on the basis of selected trace elements such as Ni and Cr as their high concentration is related to the presence of the ophiolite rock sequences in the Po River hydrological basin and are largely subordinate in the Reno River catchment (Bianchini et al., 2012; 2013, 2019). However, following the ANOVA results and the box plots, the isotopic ratios of C, N, and S are further good parameters to discriminate the sediments for their provenance. Such discrimination is also emphasized by the multivariate statistical analysis (PCA, Fig. 3), where the isotopic ratios of C, N, and S were used as principal components. The PCA plot explains more than 80% of the total variance and well clusters the samples according to the Po and Reno River affinity. In the PCA plot the arrays show a similar length indicating that the isotopic parameters contribute equally to discriminate the two sample populations.

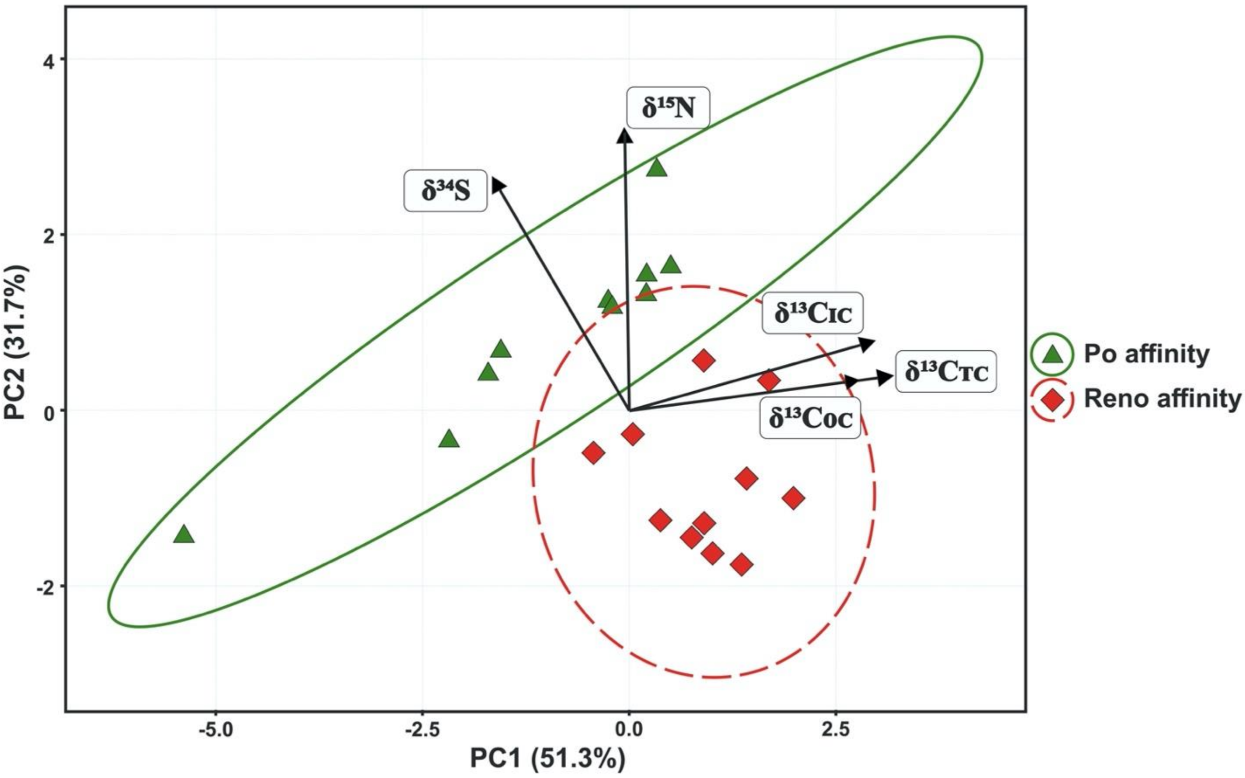

Figure 3. Principal Component Analysis (PCA) for the isotopic ratios of C, N, and S of alluvial sediments in the surroundings of Ferrara having Po and Reno affinity.

To confirm the significant role of these isotopic tracers in the provenance analysis, $\delta^{13}C_{TC}$, $\delta^{15}N$ and $\delta^{34}S$ are plotted vs. the Ni content, *i.e.*, the best marker to discriminate between Po and Reno River sediments according to Bianchini et al. (2012; 2013, 2019; Fig. 4). In the biplot diagrams, each isotopic ratio is effective to discriminate the two sample populations.

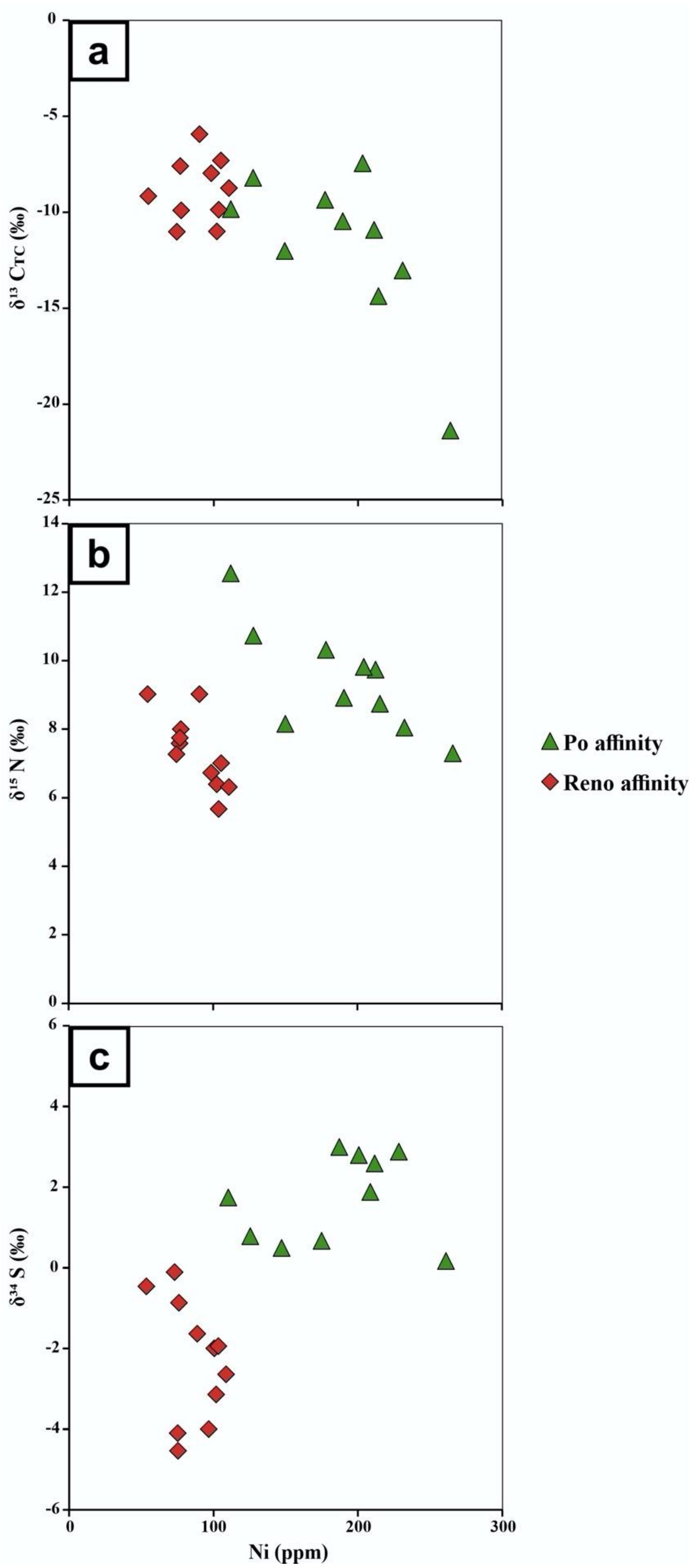

Figure 4. Ni (Bianchini et al. 2012; 2013) vs $\delta^{13}C_{TC}$ (a), $\delta^{15}N$ (b) and $\delta^{34}S$ (c) biplot diagrams discriminate the alluvial affinities in the surroundings of Ferrara from geochemical point of view.

Hypotheses can be done to explain the reasons for the different C, N, and S isotopic fingerprint on the Po and Reno River alluvial sediments.

For carbon, the TC isotopic fingerprint depends on the OC and IC contents and their relative isotopic ratio. The difference cannot be related to a distinct fertilization history as proposed for other study-cases (Kanstrup et al., 2011) and must be interpreted as a distinctive character of the sediment source area, which is peculiar for every hydrological basin (Li et al., 2020). In general, the $\delta^{13}C_{OC}$ is controlled by the distribution of C_3 and C_4 plants, as according to their photosynthetic pathways the $\delta^{13}C_{TC}$ ranges from -21‰ and -35‰ for C_3 plants and from -9‰ to -20‰ for C_4 plants (O'Leary, 1988; Meier et al., 2014; Brombin et al., 2020). Moreover, in aquatic ecosystems the isotopic composition of the transported organic matter is also influenced by the autochthon growth of biomass constituted by algae and plankton (Finlay and Kendall, 2007).

On the other hand, the $\delta^{13}C_{IC}$ is controlled by the presence of lithogenic (*i.e.*, primary) or pedogenic (*i.e.*, secondary) carbonates, which have $\delta^{13}C_{TC}$ values close to 0‰ or negative, respectively (Gao et al., 2017).

Summarizing, the TC isotopic ratios of Po River sediments are generally more negative than those recorded in Reno River sediments (Table 1; Figs. 2b, 4a). This evidence cannot be related to a different proportion of organic and inorganic compounds, because i) the OC and IC contents of Po and Reno River sediments are similar (Table 2) and ii) both $\delta^{13}C_{OC}$ and $\delta^{13}C_{IC}$ values of Po River sediments are comparatively more negative respect to those of Reno River sediments (Table 2). Indeed, the different distribution of C_3 and C_4 plants could be responsible for the different $\delta^{13}C_{OC}$ of the Po and Reno sediments. The Po River hydrological basin comparatively extends at higher latitude and altitude and is plausibly characterized by a higher C_3/C_4 biomass ratio, with respect to the Reno River ratio. Moreover, it has to be noted that, the embankments of Po River are dominated by *Cyperus* vegetation (Pellizzari, 2020), which are C_3-plants whose $\delta^{13}C$ signature is extremely negative (Puttock et al., 2012; Laceby et al., 2014; Meier et al., 2014). In addition, $\delta^{13}C$ negativization in suspended particles of Po river water can also be induced by comparatively higher development of fresh water plankton (Søballe and Kimmel, 1987; Finlay and Kendall, 2007). The significant presence of such biomass could be responsible for the more negative $\delta^{13}C$ signature recorded in the Po River alluvial sediments. In addition, the samples collected in the interfluvial areas of Po River (VP5S, VP5P, VP6S, FE25A) have comparatively negative $\delta^{13}C_{IC}$ values, which are indicative of the presence of pedogenic carbonates that enhance the difference of the TC isotopic fingerprint of the two sample populations.

Interestingly, the $\delta^{13}C_{TC}$ appears effective, not only to discriminate Po and Reno River sediments, but also to precisely constrain the depositional facies. According to the geochemical map of Fig. 5, irrespectively to the provenance of sediments (Po or Reno Rivers catchment), the paleo-channel deposits, mainly composed of sandy sediments, have less negative $\delta^{13}C_{TC}$ signature respect to the surrounding interfluvial areas which are mainly composed of clayey sediments. In fact, clays usually form aggregates in which the organic matter remains protected from microbial decomposition, and the organic carbon can therefore preserve its original signature (von Lützow et al., 2006; Gunina and Kuzyakov, 2014; De Clercq et al., 2015; Guillaume et al., 2015).

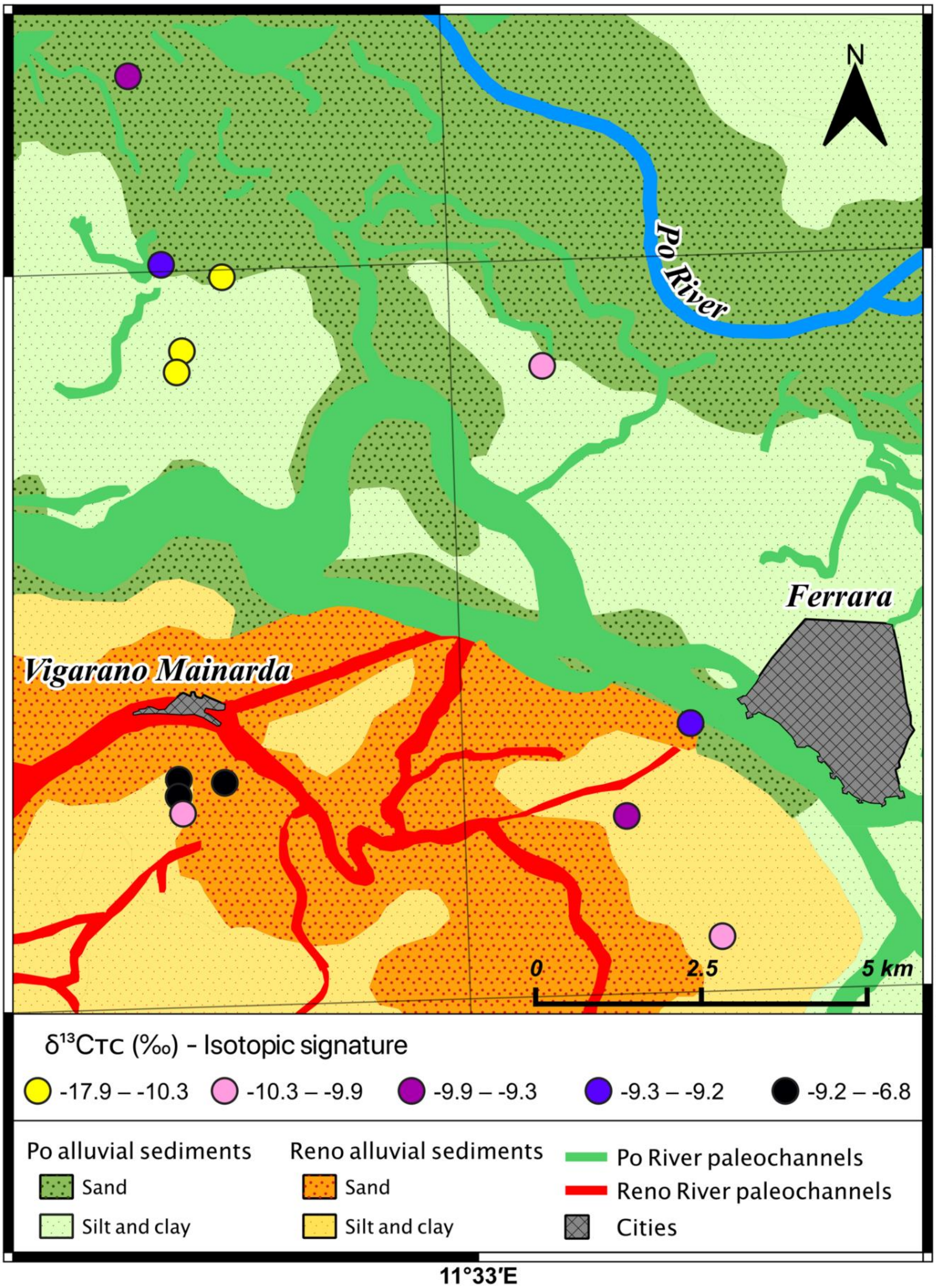

Figure 5. Geochemical map of the $\delta^{13}C_{TC}$ (‰) showing the distribution of the isotopic signatures near Ferrara and Vigarano Mainarda.

The observed differences on the nitrogen isotopic composition of Reno and Po River sediments can be in principle related to that of the organic matter, but soil $\delta^{15}N$ value can be also deeply affected by the agricultural practices and the related fertilization history (Bateman and Kelly, 2007; Xu et al., 2012). Noteworthy, in this case-study the observed difference of the two sample populations indicates that the anthropogenic activities did not obliterate the pristine compositions. In fact, the Po River sediments appear to be systematically enriched in ^{15}N with respect to those from the Reno River, a pristine difference of the associated organic matter that generally tends to develop higher $\delta^{15}N$ as result of the intense biogeochemical transformations (Hobbie and Ouimette, 2009; Craine et al., 2015; Szpak, 2014) occurring in the Po soils which are more mature than those of Reno.

The difference on the sulphur isotopic composition of Reno and Po River sediments is also intriguing. As observed for N, the isotopic differences of S could also be explained in terms of soil maturity, since most of soil sulphur should be hosted in the organic matter (*e.g.*, Edwards et al., 1998). In this case, S isotopic fractionation should be controlled by biogeochemical processes producing fugitive gaseous compounds that are generally $\delta^{34}S$-depleted (Raven et al., 2015) and leave $\delta^{34}S$-enriched residua (Norman et al., 2002). This occurs because during soil biogeochemical processes bacteria preferentially utilize ^{32}S during their metabolism, producing fugitive $\delta^{34}S$-depleted products (Strauss, 1997). Therefore, as the Po River alluvial soils are more mature than those of Reno River, they developed higher $\delta^{34}S$ in response to biochemical isotopic fractionation. Noteworthy, among the biogeochemical processes a particular role is represented by sulphate reduction, where anaerobic bacteria reduce the sulphates into sulphides with more negative $\delta^{34}S$ fingerprint (Guo et al., 2016). This process is associated with the depletion of $\delta^{34}S$ up to 70‰ in the sediments (Habicht and Canfield, 2001), therefore the produced sulphide is depleted in ^{34}S compared to the sulphate from which is formed. This process could explain the different isotopic signature between the alluvial sediments of the surrounding of Ferrara.

On the whole, alluvial soils formed by the deposition of Po River sediments are more mature than those of Reno alluvial soils. This is mainly related to the physiographic difference of the two catchments, as the Po River catchment has a length (652 km) which is four times greater than that of the Reno River catchment (212 km), but also to the timing of sedimentation which appear older for Po River sediments. In fact, locally the interfluvial basins of Po River was definitely reclaimed during the fifteenth century (Bondesan, 1989), whereas the course of Reno River was changed several times until the eighteenth century, when anthropic hydraulic activities defined the actual riverbed (Cremonini, 1989). These different depositional ages are plausibly recorded by the organic matter; Po River soils experienced more complete biogeochemical reactions than that of Reno River sediments. This fact affects the N and S cycles, because as proposed by previous studies organic matter plays a key role in the processes responsible for gaseous loss of nitrogen and sulphur light isotopes (Hobbie and Ouimette, 2009; Norman et al., 2002; Raven et al., 2015).

Conclusions

This paper demonstrates that, although intimately associated and interlayered, alluvial sediments having distinct origin show distinct CNS isotope signature. This is validated for alluvial sediments of the easternmost sector of Padanian Plain, where the distinction between Alpine and Apennine contributions (conveyed Po and Reno Rivers, respectively) was known on the basis of heavy metals concentration.

We found out that the different CNS isotope fingerprint of Po and Reno River sediments is natural and not induced by anthropogenic anomalies, but doesn’t necessarily reflect a lithogenic signature, *i.e.*, it is not solely related to different parent rock types in the Po and Reno River catchments. In fact, we infer that bio-geochemical processes, characterized by distinct ecological conditions in the Po and Reno River catchments, are recorded in the CNS isotopic signatures. Po River sediments are generally few hundreds of years older and pertain to a basin having a path of nearly seven hundred kilometers, much longer that of Reno River. Consequently, soils developed on Po River sediments are comparatively more mature and record more complete biogeochemical processes that were more intense and affected nitrogen/sulphur compounds generating the distinctive isotope signatures.

The important evidence is that the CNS systematics preserve a “memory” of the environment of formation of the conveyed particles, which differs in the distinct basins that feed the alluvial plains. In the considered case-study, this “memory” is not reset by the existing anthropogenic activities.

More in general, the reported data increase knowledge on the local elemental and isotopic backgrounds. This is important because many pollutants contain significant CNS concentration and specific isotope composition. Therefore, the presented data will serve as baseline and provide new tools to recognize possible anthropogenic anomalies in the studied area.

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