GEOCHEMICAL AND ISOTOPIC INVESTIGATION ON THE PO RIVER WATERS FROM MONVISO SOURCES TO ITS DELTA: NATURAL AND ANTHROPOGENIC COMPONENTS

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INTRODUCTION

The Po River is located in the Padanian Plain, which is the largest hydrological basin of Italy covering an area of more than 71,000 km^2 (about a quarter of the national territory). It is the longest Italian river (652 km), having an average discharge rate of 1,500 m^3/s and a maximum peak flows of 10,300 m^3/s at Pontelagoscuro, which is located close to city of Ferrara, before the delta initiation (Kettner & Syvitsky, 2008; Montanari, 2012). The river originates from the Monviso Mountain in the Pian del Re locality (Piemonte), and it is fed by 141 tributaries before flowing into the Adriatic Sea through its delta, which covers an area of more than 380 km^2. Its basin is characterized by widespread human activities, having a population of about 16 million inhabitants, and economically represents the most important area of the country where 40% of Italy's Gross Domestic Product (GDP) is produced. In fact, the area concentrates industrial, zootechnical, and agricultural activities that can potentially affect the water quality.

Unfortunately, investigations on the chemical and isotopic composition of the river water are scarce and were never reported for the whole river course. In this PhD project I have analyzed major and trace element concentrations of dissolved species, as well as oxygen and hydrogen isotope composition of the Po River water sampled all along its main course, with particular attention to the deltaic part. In addition, the thesis presents, for the first time, systematic analysis of carbon, sulphur and nitrogen isotopes (δ^{13}C, δ^{34}S, δ^{15}N), that provide additional information to understand sources and origin of the dissolved components, thus constraining the river geochemical cycles and dynamics. The data are also useful to discriminate natural compositions and superimposed anthropogenic geochemical components, considering that the riverine geochemistry gives first-order constraints on the processes affecting the continental surface (weathering of rocks, erosion and dissolution as well as human pollution) in turn resulting on the amount and nature of geochemical fluxes transferred to the sea. Finally, the thesis also presents new strontium isotope analyses of the Po River water, which varies along the riverine course in function of the specific lithotypes outcropping in the basin.

SAMPLING AND ANALYTICAL METHODS

Water samples were collected along the whole stream of the Po River, from its source (Pian del Re spring) to the deltaic area, in distinct seasonal periods of the years 2010, 2012, 2013 and 2014.

Laboratory analyses were carried out at the Department of Physics and Earth Sciences of the University of Ferrara. Hydrogen and oxygen isotope ratios were determined using the CRDS Los Gatos LWIA 24-d isotopic analyser. The isotopic ratios of ^{2}H/^{1}H and ^{18}O/^{16}O were expressed as δ notation [$\delta = (Rsample/Rstandard - 1)*1000$] with respect to the V-SMOW (Vienna Standard Mean Ocean Water) international standard. Four bracketing standards that cover the whole range of isotopic values of the Po River water were run throughout the analytical sessions. These standards, obtained from the Los Gatos Research Company, were calibrated with international standard such as V-SMOW and SLAP (Standard Light Antarctic Precipitation). Analytical precision and accuracy were better than 0.3‰ and 1.0‰ for δ^{18}O and δD respectively.

Major cations and trace elements were detected by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument on samples previously diluted 1:10 (or 1: 100 for samples having high EC) by deionized Milli-Q water (resistivity of ca. 18.2 MΩ x cm), also introducing known amount of Re and Rh as internal standard; in each analytical session the analysis of samples was verified with that of the reference materials EU-L-1 and ES-L1 provided by SCP-Science. The major anions were determined by ion chromatography using a Dionex ICS-1000 calibrated using solutions obtained by different dilutions of the Dionex "7-ion standard". Accuracy and precision, based on the repeated analyses of samples and standards, were better than 10% for all the considered parameters. The coherence of chemical data was verified checking the ionic balance, as the sum cations (expressed in meq/L) approaches that of anions with relative error, $[(\Sigma\text{cations}-\Sigma\text{anions})/(\Sigma\text{cations}+\Sigma\text{anions})]*100$, which generally resulted < 5%.

The isotopic analyses of carbon, sulphur and nitrogen were carried out in the Po River water sampled in March and May 2013, as well as on some samples collected in the year 2012, previously studied by Marchina *et al.* (2015). These isotopic analyses were preformed in the laboratories of the Helmholtz-Zentrum für Umweltforschung (UFZ) of Leipzig/Halle (Germany). Isotopic analyses of carbon and associated oxygen have been carried out on Dissolved Inorganic Component (DIC) using the method described in Atekwana & Krishnamurthy (1998). The technique uses evacuated glass septum tubes, pre-loaded with phosphoric acid, and a magnetic stir bar. Water samples were injected into the septum tubes and transferred to the vacuum line during the DIC extraction. Isotopic measurements were performed using a Delta V plus mass spectrometer (Electron with a Gasbench II, Thermo Electron GmbH). The $^{13}C/^{12}C$ isotope ratios were reported as δ notation with respect to the PDB (Pee Dee Belemnite) international standard. Repeated analyses of standards (NBS-19) and samples revealed $\delta^{13}C_{DIC}$ precision and accuracy of 0.1‰. The associated $(^{18}O/^{16}O)_{DIC}$ ratios were reported as δ notation with respect to the SMOW international standard.

Isotopic analyses of sulphur and associated oxygen were carried out on sulphate recovered using the method described in Knöller *et al.* (2005), where $BaSO_4$ precipitation was induced at 70 °C, after the pH of the solution was adjusted to 2.5. Subsequently, isotopic measurements were performed after conversion of $BaSO_4$ to SO_2 using the continuous flow combustion technique coupled with a delta S, Finnigan MAT mass spectrometer. The $^{34}S/^{32}S$ and associated $(^{18}O/^{16}O)_{SO4}$ were reported as δ notation with respect to the VCDT (Vienna Canion Diablo Troilite) and SMOW, respectively. Analyses of $\delta^{34}S_{SO4}$ were corrected using international sulphur isotopic standards NBS 127 ($BaSO_4$) and IAEA-S1 (Ag_2S). Analytical accuracy and precision were generally 0.3‰ and 0.5‰ for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ respectively.

Isotopic analyses of nitrogen and associated oxygen were carried out on Dissolved Inorganic Nitrogen (DIN) using the bacteria denitrification method described by Sigman *et al.* (2001) and Casciotti *et al.* (2002). This method involves the use of bacteria to transform $(NO_3)^-$ in N_2O. Isotopic measurements were performed using a Delta V plus mass spectrometer (Electron with a Gasbench II, Thermo Electron GmbH). The $^{15}N/^{14}N$ and associated $(^{18}O/^{16}O)_{NO3}$ were reported as δ notation with respect to the AIR and SMOW International Standards, respectively. The measured $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ were corrected using international (IAEA) nitrogen isotopic standards USGS-32, USGS-34, USGS-35, NO_2-1, NO_2-2. Analytical accuracy and precision were generally 0.2‰ for $\delta^{15}N_{NO3}$ and 0.7‰ for $\delta^{18}O$.

For the strontium isotopic investigation, that represents the topic of this paper, the analyses were carried out in two distinct laboratories. The samples collected in August 2010 and 2012 were analysed in the laboratories at IGG-CNR in Pisa by TIMS. Strontium was concentrated using chromatographic columns eluted by HCL 2.5N, allowing to leach undesired elements that could create interference during the analyses and to isolate the investigated element. Subsequently, samples were dried down and this fraction was re-taken with 2 μL of HNO_3^- and deposited on (handmade) tungsten filaments that are loaded to the TIMS (Thermal Ionization Mass Spectrometry) instrument. In particular, measurements were obtained by a Finnigan MAT 262 V multi-collector mass-spectrometer. Measured $^{87}Sr/^{86}Sr$ ratios were normalized to $^{86}Sr/^{88}Sr = 0.1194$. During the collection of isotopic data, replicate analyses of the Sr SRM-NIST 987 ($SrCO_3$) isotopic standard gave an average $^{86}Sr/^{88}Sr$ value of 0.710253 ± 13 (2σ, N = 30) The samples collected in May 2014 were prepared as discussed above and then analysed by Multi-Collectors Inductively Coupled Plasma-Mass-Spectrometry (MC-

ICP-MS) at the Department of Earth Sciences of the New Hampshire University. In particular, measurements were obtained by a "Nu Plasma" MC-ICP-MS instrument (Nu Instruments). Even in this case data were normalized to $^{86}Sr/^{88}Sr = 0.1194$. During the collection of isotopic data, replicate analyses of the Sr SRM-NIST 987 isotopic standard gave an average $^{86}Sr/^{88}Sr$ value of 0.710248 ± 17. The good agreement between the values obtained in the two distinct laboratories on the same standard implies that the values obtained on the samples can be properly compared.

Geostatistical modelling has been carried out in order to visualize the spatial variation of the obtained geochemical data. Interpolated maps along the Po River geographical extension were produced in ArcGIS 9.3 (Geostatistical Analyst extension) at a resolution of 170 m by generalized linear regression technique (ordinary kriging), using a spherical semivariogram model with nugget on log10 transformed data. Considering that we were interested in the reflection of large-scale features (> 10 km) of the river water composition, we chose to conduct the interpolation without the use of ancillary variables such as elevation that would introduce high amplitude variability in the interpolated surface over short length scales.

In the next discussion the Po River water are divided in three distinct part, that typically display significant compositional changes, at increasing distance starting the source: *i*) an *upper part* (**UP)** from Pian del Re to Carignano; *ii*) a *middle part* (**MP)** from Crescentino to Revere; *iii*) a *terminal part* (**TP**) from Occhiobello, close to the city of Ferrara right upstream the Delta del Po, to Port Levante.

RESULTS AND DISCUSSION

Dissolved components

A detailed understanding of the processes controlling the water chemistry of a river is crucial to define geochemical cycles within a given catchment. Although natural studies of riverine chemistry at the global scale have been widely discussed (Gaillardet *et al*., 2014; Viers *et al.,* 2014), specific regional researches performed on the Po River catchment are rare. The amount of the dissolved species is related to the nature of lithotypes outcropping in the catchment basin and to the weathering processes typically occurring in the region. Moreover, the anthropogenic contribution related to human activities cannot be neglected.

The investigation was refined taking into consideration the chemical analyses of the major cations and anions. The Total Dissolved Solids (TDS), calculated as a sum of the major chemical species, coherently increased from the upper part of the catchment, where the UP samples had TDS < 130 mg/L, to the central part, where the MP samples had a TDS between 170 and 330 mg/L. Higher TDS values were generally observed in the deltaic samples (up to 1,000 mg/L), with localized high saline samples (TDS up to 5,864 mg/L at the Po di Goro mouth) which possibly resulted from effective mixing with sea water during momentary high tide influence.

It is extremely interesting to note the chemical variations along the river course, starting from the source of Pian del Re, that were synthetized in the notional Gibbs diagram where TDS values (y-axis) were plotted against the $[Na^+/(Na^++Ca^{2+})]$ ratio (x-axis). It can be observed that the UP water, and in particular that from Pian del Re, already displayed a significant degree of water-rock interaction. According to the Langelier Saturation Index the initial Po River water (close to the Pian del Re source) was calcite undersaturated, but it quickly reached calcite saturation, being buffered from further interaction with the scarce carbonate lithologies outcropping in the basin. Conversely, reactions with silicate-rocks and their constituent minerals continued all along the river course, explaining the comparatively higher TDS and $[Na^+/(Na^++Ca^{2+})]$ ratios observed in the MP samples. More extreme $[Na^+/(Na^++Ca^{2+})]$ ratios characterized the TP samples from the deltaic area, confirming the mixing with saline sea (and lagoon) water, as also evidenced by the isotopic signature of these samples. A more comprehensive examination was given by the Piper classification diagram, where it could be observed that Po River water mainly exhibits a bicarbonate-alkaline earth hydrochemical facies, with slight but significant differences between the delineated UP, MP, TP groups of samples. Very few TP samples showed a chloride-alkaline hydrochemical facies that indicate effective mixing with saline water. The calculation of a correlation matrix highlighted coherent elemental relationships along the whole sample suite; in particular, Cl^- positively correlated with Br^- and $(SO_4)^{2-}$ but also with alkaline elements such as Na^+, K^+, and trace element such as Li and Rb, whereas Ca^{2+} mainly correlated with Sr.

In general, the more extreme variations were observed in the terminal part of the river, where evident mixing trends can be observed on the more conservative elements (Cl^- *vs.* Br^-, $(SO_4)^{2-}$, Na^+, Li, B), with theoretical mixing lines with seawater indicating that up to 20% of marine influence could affect the river waters. Other less conservative elements, if plotted and compared with the theoretical seawater mixing lines, showed that the mixing process was largely not ideal and not conservative, possibly as result of ion-exchange processes with suspended solid particles (Bianchini *et al.*, 2005).

Nitrate concentration was extremely variable throughout the main course of the river; it was less than 1 mg/L at the spring (Pian del Re) but suddenly increased in Carignano (last sample of the UP) reaching the extreme value of 18 mg/L in March 2013. Downstream, the MP samples were characterized by an average composition of 9 mg/L, with significant seasonal fluctuations. Therefore, nitrate concentrations along the river course were heterogeneous and plausibly related to anthropogenic inputs that were spatially and temporally variable. The data described above were also compared with past compositions recorded in Po River water since *ca.* 50 years ago, when human impacts were less pronounced. Useful literature data were provided by Gherardelli & Canali (1960) and Fossato (1971) that reported temperature, pH, $(HCO_3)^-$, Ca^{2+}, Mg_2^+ and $(NO_3)^-$ values for Po River water collected at the boundary of MP and TP during the years 1959, 1968, and 1969. It is important to note that the values of conductivity, $(HCO_3)^-$, Ca^{2+}, Mg^{2+}, and Mg/Ca ratio are comparable with those recorded nowadays, whereas NO_3^-concentration measured in the past had an average value of 2 mg/L in the fifties and 4 mg/L in the sixties, reaching concentrations higher than those recorded in the eighties (up to 10 mg/L, according to a data-set provided by Arpa-Veneto) and then declining to the current values.

Isotopic composition of Po River waters

The recorded isotopic compositions of hydrogen and oxygen in the Po River water mainly reflected the isotopic composition of the meteoric precipitations (rain, snow, glacier ice melting) in the drainage area which was in turn related to altitude and continental effects. Noteworthy, most Po River isotopic compositions conformed to those of precipitations occurring at high altitudes in the north/northwestern-most part of the basin (UP), *i.e.*, from high Alpine zones (Longinelli & Selmo 2003). Coherently, Montanari (2012) showed that the prevalent meteoric contribution (up to 1,600 mm/yr of precipitation) in the Po River basin was confined within the mountainous Alpine sectors, which collected most of the catchment precipitations.

In particular: *i*) samples from the upper part of the river (UP), located from the spring of Pian del Re downward to the locality of Carignano (before the town of Torino), displayed $\delta^{18}O$ varying from -13.4‰ to -11.1‰ and δD varying from -94.7‰ to -75.3‰. The average $\delta^{18}O$ recorded in spring was slightly more negative than the average value observed in summer, whereas the average δD values were nearly constant in the different seasons. *ii*) Samples from the middle part of the river (MP), located between the localities of Frassineto Po and Revere, displayed $\delta^{18}O$ varying from -12.5‰ to -8.4‰ and δD varying from -84.7‰ to -60.1‰. The average $\delta^{18}O$ recorded in spring was analogous to the average value observed in summer, and also the average δD values were nearly constant in the two seasons. *iii*) Samples from the terminal part of the river (TP), also including the deltaic area, displayed $\delta^{18}O$ varying from -9.9‰ to -6.90‰ and δD varying from -65.1‰ to -48.0‰. The average $\delta^{18}O$ recorded in winter-spring was slightly more negative than the average value observed in summer (-8.1‰) whereas the average δD values were nearly constant in the two seasons.

If we take into account the seasonal sampling of August in the UP and MP parts, a remarkable correlation can be observed between the distance (d) from the source (expressed in km) and both $\delta^{18}O$ and δD (R^2 better than 0.9). Distinctive d – δ‰ linear relationships characterize the UP and MP water, the former giving higher regression slopes (*e.g.*, 3.5 and 0.5 respectively for $\delta^{18}O$). The mean UP-MP gradient observed from the source was 0.2‰ $\delta^{18}O$ and 1.7‰ δD per 10 km. The trends can be referred to altitude variation of the meteoric recharge along the river course, as the water budget along the profile progressively integrate meteoric contributions related to lower altitudes. In particular, in the UP part the elevation of the sampling sites was negatively correlated with $\delta^{18}O$ by a logarithmic relationship ($R^2 = 0.98$), whereas in the MP a linear regression better described the relations between these parameters ($R^2 = 0.90$). The mean altitude gradient recorded along the UP and MP was -0.5‰ $\delta^{18}O$ per 100 m rise, slightly higher than that defined for meteoric water of the area (-0.3‰ $\delta^{18}O$) by Zuppi & Bortolami (1982). The $\delta^{18}O$ /100 m gradient defined in this study was also higher than the global gradient, but it was comparable with that defined by precipitations occurring in Germany, possibly suggesting an origin from similar vapour masses of prevalent Atlantic provenance. These notable correlations describing the morphoclimatic effects in the UP and MP parts of the river did not characterize the TP part, which was plausibly influenced by local effects that disturb the original isotopic fingerprint of the meteoric water that feed the river. The relative isotopic consistency of Po River MP water samples irrespective to seasonal variability ($\delta^{18}O \sim -9.5$‰) suggests that the associated riverine system integrate multiple contributions, which are mixed and homogenized. This indicates significant water volumes, which buffer further variations, already characterized the MP sector of the river. Changes observed at the most important tributary confluence (Ticino River), progressively disappeared after few kilometres being homogenized within the riverine water mass, whereas isotopic variations due to the confluence of Apennine tributaries (having $\delta^{18}O \sim -8.0$ and -8.9‰) were not recorded in the main stream, due to their negligible contribution to the Po River water budget.

The presented data, including isotopic composition of river water, sampled in distinct periods, allowed to evaluate relationships between the δ‰ values and the temperature. From the data it can be noted that limited isotopic variation is coupled with significant temperature changes of both water and air (in the order of 10 °C). This is reflected in a $\Delta\delta^{18}O$/temperature gradient of ~0.1‰, which is scarcely significant. The lack of significant variation for water samples collected in distinct hydrological phases along the whole stream path is possibly due to: a) delayed effect of winter meteoric contributions caused by snow melt (and alpine glacier melting) that were slowly released in the summer period; b) sub-surface inflow, which variously delayed the meteoric contributions; c) man-made dams, which create reservoirs where meteoric contribution of different seasons mixed together.

It should be noted that Rapti-Caputo & Martinelli (2009) on the basis of $\delta^{18}O$ -δD data highlighted, in the MP of the plain, communication and water exchanges between the River Po and the first confined aquifer (depth from 20 to 50 m, in the Ferrara surroundings). In this scenario, the unexpected $\delta^{18}O$ shift toward more negative values (- 1‰) observed at ~ 480 km from the source, just before the diversion of the deltaic branches (Crespino, Bottrighe, and Taglio di Po), could be ascribed to a significant groundwater flow toward the river. More in general, emphasis is given to the isotopic composition of the TP, where the river develops a complex deltaic system. In this sector, the isotopic composition evolve toward less negative values, in relation to a more effective evaporation due to the reduction of the water flow velocity and mixing with saline water.

The $\delta^{13}C_{DIC}$ isotopic compositions of Po River water collected in March 2013 along the river course evidenced a sharp variation trend in the UP samples where we recorded a $\delta^{13}C_{DIC}$ value of -4.4‰ in the river source of Pian del Re, of -6.7‰ in Sanfront (14 km from the source), and of -9.8‰ at Carignano (85 km from the source). Downflow in most samples of MP we noted a remarkable isotopic homogeneity in the range $\delta^{13}C_{DIC}$ (-10.5‰ ±0.4). The $\delta^{13}C_{DIC}$ isotopic trend along the Po River course was congruent with that observed in other riverine systems such as the Rhone River, where starting from the source area progressively more negative isotopic values were observed downstream, until more evolved waters attained an isotopic homogeneity. The $\delta^{13}C_{DIC}$ evolution was at first dominated by isotopic exchange with atmospheric CO_2, and then, progressively, by the increasing water-rock interaction and biochemical activities (*i.e.*, photosynthesis). It is interesting to note that the average $\delta^{13}C_{DIC}$ value was very similar to that recorded in the particles suspended in the Po River waters, where $\delta^{13}C$ ranged from -11.4‰ to -9.9‰. This compositional analogy suggests that the carbon associated to the suspended solid particles has the same origin and is affected by the same processes that influence the dissolved inorganic carbon. Relatively homogeneous isotopic values were maintained in the MP sector of the river and significantly changed only in the TP, where mixing with seawater induced a trend toward less negative $\delta^{13}C_{DIC}$

isotopic values. It is interesting to note that the $\delta^{13}C_{DIC}$ signature coupled with the HCO_3^- dissolved in the river Po appears equilibrated with CO_2 of air (especially in the UP waters) and subsequently reflects nonequilibrium dissolution of carbonates, whereas HCO_3^- deriving from weathering of silicate lithologies and dissolution of soil organic components (usually characterized by extremely negative $\delta^{13}C_{DIC}$) seems subordinate. Although carbonate bearing lithotypes are subordinate in the upper part of the catchment, calcite was observed in sporadic marble outcrops (having δ $\delta^{13}C_{DIC}$ 0-2‰) that are included in the crystalline basement. Further carbon can be released in the river waters by interaction with carbonate sedimentary rocks (Permian-Triassic ages), which are characterized by $\delta^{13}C_{DIC}$ varying between -3.7 and 4.1. The outcrops of these sedimentary rocks become more significant at the border between the UP and MP sectors of the river, in particular in the Ticino and Adda sub-basins.

Moreover it has to be noted that a very good relation was observed between the isotopic composition of the oxygen associated to carbon ($\delta^{18}O_{DIC}$) and that recorded in the water molecules ($\delta^{18}O_{H2O}$) as resulted from the following equation:

$$\delta^{18}O_{DIC} = 1.52 \cdot \delta^{18}O_{H2O} + 5.56 \ (R^2 = 0.9).$$

This suggests an attainment of an isotopic equilibrium between the dissolved inorganic carbon and the water solvent. This relationship could be interesting because isotope fractionation between carbonate and water is temperature-dependent and may, in principle, be used as a further climatic proxy.

The $\delta^{15}N_{NO3}$ isotopic values showed a systematic variation along the river course in the two investigated periods of the year 2013 (March and May). These temporal differences in the nitrogen isotopic composition were limited in the initial UP, close to the source of the river (in the order of 2‰), but become greater at ca. 80 km from the source, *i.e.*, from the site of Carignano that was characterized by a remarkable isotopic spike toward heavy $\delta^{15}N_{NO3}$. In March the initial UP waters had $\delta^{15}N_{NO3}$ varying from -2.2‰ at Pian del Re to 1.8‰ at Sanfront and then it remained relatively homogeneous for the rest of the river course with an average composition of 7.7‰. In May the initial UP waters had $\delta^{15}N_{NO3}$ varying from -1.7‰ at Pian del Re to -0.1‰ at Sanfront, and then it showed a progressive and systematic downflow-increase, up to 8.2‰, in the locality of Occhiobello then remaining relatively homogeneous within the TP waters. It is interesting to note that this value is very similar to those recorded in the particles suspended in the Po River waters that are characterized by $\delta^{15}N_{NO3}$ ranging from 7.3‰ to 8.6‰. This compositional analogy suggests that nitrogen associated to the suspended solid particles has the same origin and is affected by the same processes of the dissolved inorganic nitrogen. In the MP samples, the $\delta^{15}N_{NO3}$ distribution observed in March was quite fluctuating around an average value of ($\delta^{15}N_{NO3}$ 7.7‰) with significant oscillation of +/- 2.9‰, whereas the distribution observed in May was more regular and characterized by a lower average value (3.9‰) and a systematic smooth increase. This systematic $\delta^{15}N_{NO3}$ differences observed in May could be related to the combined effect of dilution and concomitant fertilization practices that employ chemical compounds, having $\delta^{15}N_{NO3}$ approaching 0‰, that usually occur at the begin of the spring season.

The nitrogen isotopic compositions of the Po River waters were plotted against NO_3^- and compared with the groundwater collected in the MP area (Lombardy plain) from Sacchi *et al.* (2013). In spite of lower concentration of nitrate, the $\delta^{15}N_{NO3}$ of the Po River are comparable with that of the aquifers, suggesting a common origin. More detailed information on the nitrogen sources are given in $\delta^{15}N_{NO3}$ *vs.* $\delta^{18}O$ plot in which the isotopic composition of the Po waters are further compared with the typical ranges of synthetic fertilizers, animal manure, sewage wastewaters, and soil organic matter in order to provide specific information about natural/anthropogenic sources of dissolved nitrate.

The sulphur isotopic compositions ($\delta^{34}S_{SO4}$) of Po River water were analysed only for MP and TP samples collected in May 2013 in order to observe compositional variation along the river course. It can be noted that a sharp variation trend were observed in the first part of MP where a value of 4.2‰ was recorded in the Rea locality, before the Ticino River confluence (11.0‰); conversely, the highest values for the Po River were measured in Cremona (8.0‰) and after the Adda River junction (9.0‰). This variation marks a progressively more relevant contribution from sedimentary rocks of Permian-Triassic ages that includes sulphate-bearing horizons. Downstream, both MP and TP waters maintained a remarkable isotopic homogeneity in the $\delta^{34}S_{SO4}$ range of 7.3‰ ±0.7 that persisted along the entire river course.

Additional charts were used to delineate the origin of sulphate in riverine waters: the sulphur isotopic composition plotted *vs.* $(SO_4)^{2-}$ concentration, shows a rough correlation and an evolution trend. In particular, MP waters can be divided into two different groups: 1) waters collected before the Ticino River confluence, characterized by low $(SO_4)^{2-}$ concentration (average 13 mg/L) and $\delta^{34}S_{SO4}$ (average 4.7‰); 2) waters collected after the Ticino River confluence, characterized by higher $(SO_4)^{2-}$ concentration (average 34 mg/L) and $\delta^{34}S_{SO4}$ (average 7.3‰).

The sulphur isotopic composition was also compared with the associated oxygen isotopic composition ($\delta^{18}O_{SO4}$, varying from 5.3‰ to 8.4‰.). The compositions of the Po River water were compared with those that characterize sulphur bearing lithotypes occurring within the Po River basin, such as a) the metamorphic and igneous rocks of the basement that contains accessory sulphides (having $\delta^{34}S_{SO4}$ approaching 0‰) and b) sedimentary rocks of Permian-Triassic ages often containing sulphate-bearing horizons (having $\delta^{34}S_{SO4}$ approaching > 10‰). The latter become more widespread starting from the sub-basins of Ticino and Adda tributaries. The involvement of anthropogenic contributions to the sulphur budget, *e.g.*, equilibration with atmospheric gases and/or deposition of atmospheric particles cannot be excluded *a priori*, but are not highlighted by the observed geochemical trends. In other words, although it cannot be excluded a minor contribution from antropogenic sources, which are pronounced in the urbanized/industrialized sector of the plain, it should be emphasized that the isotopic compositions observed in the Po River waters recall those of the mentioned lithotypes and do not highlight clear pollutions, thus suggesting that the sulphur isotopic signature is mainly geogenic. The definition of the anthropogenic $\delta^{34}S_{SO4}$ fingerprint should be investigated collecting samples during a drought period, possibly in the sites where anomalous $(SO_4)^{2-}$ concentrations were recorded. It should be noted that a relation (although characterized only by $R^2 = 0.5$) can be observed between $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$, thus suggesting significant interaction between the water solvent and the sulphur bearing lithotypes.

Finally, emphasis is given to a more variable proxy, *i.e.*, the strontium element and its isotopes, in order to define the different contribution of the main lithotypes. It can be observed that the amount of dissolved strontium increases from 20 µg/L up to 300 µg/L in the mountainous part of the basin and then remains nearly stable for most of the riverine course, changing only in its terminal part, due to mixing with saline waters occurring in the deltaic system. This means that in the first part the river, water progressively receives contributes from the weathered lithotypes showing sharp variations, whereas, at increasing distance from the mountainous area, the Po River water becomes more mature (possibly reaching $CaCO_3$ saturation) and further variations progressively become more attenuated.

The strontium isotopic variations along the river course appear more variable and less buffered than other proxies. In particular the river water in the mountainous part of the basin is characterized by extremely radiogenic isotopic values, reflecting the isotopic fingerprint of the lithotypes outcropping in the alpine sector of the catchment that mainly consist of crystalline magmatic and metamorphic rocks of the basement. Among the tributaries of this initial part of the catchment the Pellice River showed the most extreme $^{87}Sr/^{86}Sr$ values (0.71234) confirming to the radiogenic composition observed in the Po River main stream. In the initial part of the plain, close to the city of Torino, the Po River water showed less radiogenic isotopic composition (0.70919) as result of the confluence with the Dora Baltea tributary, which displayed a totally distinct composition (0.70863) due to the presence of ophiolites and calcshists in its catchment. Downflow, the most important confluences from the Alps are: Sesia and Adda that are characterized by high $^{87}Sr/^{86}Sr$ values (0.70100 and 0.70974, respectively) and Ticino that is characterized by a lower isotopic value (down to 0.70885) due to widespread sedimentary carbonate outcrops in its catchment. In this sector of the plain, another important tributary is Tanaro River flowing down from the Ligurian Alps which is characterized by $^{87}Sr/^{86}Sr$ of 0.70926.

After these confluences the Po River flows down throughout Lombardy and Emilia Romagna regions receiving contributions from the Apennines tributaries (Trebbia, Taro, Secchia, and Panaro Rivers) that have lower ^{87}Sr/^{86}Sr values (average 0.70887). These rivers, although having different ^{87}Sr/^{86}Sr from the Po River, scarcely influence the isotopic fingerprint of its main course. As a matter of fact, the Po River maintain a quite homogeneous isotopic composition (around 0.70927) up to the Revere station in different hydrological conditions. These prevalent isotopic values approaches the only value reported in the literature for Po River.

Finally, in the Occhiobello site, located in lower reach of the River, right upstream the deltaic system, the Po River registered a slight increase of the ^{87}Sr/^{86}Sr isotopic composition, probably due to the slight decrease of the flow velocity in the main course of the river that become more sensitive to interactions with groundwater. These processes, occurring exactly in this part of the river, were already recognised using oxygen-hydrogen stable isotopes by Marchina *et al.,* 2015. Remarkable ^{87}Sr/^{86}Sr increase (up to 0.70927) was finally observed in the samples collected in the deltaic sector of the river, which may reflect an interaction with sea-water.

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