

The Po river water from the Alps to the Adriatic Sea (Italy): new insights from geochemical and isotopic ($\delta^{18}\text{O}$ - δD) data

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Abstract

Although the Po river is the most important fluvial system of Northern Italy, the systematic geochemical and isotopic investigations of its water are rare and were never reported for the whole basin. The present contribution aims to fill this knowledge gap, reporting a comprehensive data-set including oxygen and hydrogen stable isotopes, as well as major and trace element concentration of dissolved species for 54 Po river water samples, mainly collected in different hydrological conditions (peak discharge in April, drought in August) at increasing distance from the source, i.e. from the upper part of the catchment to the terminal (deltaic) part of the river at the confluence with the Adriatic Sea.

The isotopic compositions demonstrate that the predominant part of the runoff derives from the Alpine sector of the catchment through important tributaries such as Dora Baltea, Ticino, Adda and Tanaro rivers, whereas the contribution from the Apennines tributaries is less important. The geochemical and isotopic compositions show that the Po river water attains a homogeneous composition at ca. 100 km from the source. The average composition is characterized by $\delta^{18}\text{O}$ -9.8‰, δD - 66.2‰, TDS (Total Dissolved Solids) 268 mg/L, chloride 17 mg/L and by a general Ca-HCO₃ hydrochemical facies, which is maintained for most of the river stream, only varying in the terminal part where the river is diverted in a complex deltaic system affected by more significant evaporation and mixing with saline water evidenced by higher TDS and chloride content (up to 8,198 mg/L and 4,197 mg/L, respectively). Geochemical and isotopic maps have been drawn to visualize spatial gradients, which reflect the evolution of the river water composition at progressive distance from the source; more detailed maps were focused on the deltaic part in order to visualize the processes occurring in the transitional zone toward the Adriatic Sea. The data also highlight anthropogenic contributions, mainly represented by significant concentrations of nitrate (average 8 mg/L) and possibly arsenic (average 12 µg/L). These data allow the calculation of geochemical fluxes transferred from the river to the sea, and generally they contribute to the definition of a “hydro-archive” which is useful to highlight ongoing variations in the related ecosystems.

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 km² (about a quarter of the national territory), including about 3,200 municipalities of 6 distinct regions (Piemonte, Valle D'Aosta, Lombardia, Veneto, Liguria, Emilia-Romagna). It is the longest Italian river (length of 652 km), having an average discharge rate of 1,500 m³/s and maximum peak flows of 10,300 m³/s at Pontelagoscuro, which is located close to city of Ferrara, before the delta initiation (Vörösmarty et al. 1998; Kettner and 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 that covers an area of more than 380 km². 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 contribution we present 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.

The data are discussed in order to constrain the river dynamics, characterizing the areas of recharge, the processes that contribute to the water chemistry and the related water quality in terms of inorganic pollutants such as nitrates, arsenic, chromium and nickel.

Considering that the river water is a dynamic multi-component system, in which chemical concentration varies as a function of time and distance from the source, our contribution intends to provide geochemical backgrounds along the river course from the Alps to the Adriatic Sea, also evaluating variations that occur in distinct hydrological periods (e.g.: peak discharge, drought).

The data, considered for the first time at the whole basin scale, are useful to discriminate - for the various geochemical components - between natural (geogenic) and anthropogenic sources.

In particular, the oxygen/hydrogen isotope ratios are temperature dependent, and therefore give a snapshot of the current climatic conditions that can be compared with literature data and updated by future measurements in order to provide a hydro-archive that can be used as a tool to evaluate on-going climatic changes (Zuppi and Sacchi 2004). In this light, to retrieve more information the data have to be elaborated and decoded defining geochemical and isotopic gradients, which are potentially sensitive to environmental changes.

The resulting insights are important considering that the Po river water is: 1) distributed within a widespread network of artificial channels largely used to irrigate the agricultural fields (Petrini et al., 2014); 2) often connected with the aquifer reservoirs, some of which are exploited for drinking purposes (Rapti Caputo and Martinelli 2009).

Background information on the investigated area

The Po plain (Fig. 1a) is a sedimentary basin bound to the N by the Alpine mountains, to the SW by the Apennine hills and to the E by the Adriatic Sea. From the geological point of view the basin was characterized by a marine sedimentation in the Pliocene to Early Pleistocene, followed by fluvial sedimentation that was enhanced during the glaciation periods (Garzanti et al. 2011). Within the plain, the most important fluvial system is represented by the Po river, which is progressively fed by many tributaries (and groundwater flows) from both the Alps and the Apennines. The Alpine streams are mainly fed by snow melting and show a seasonal peak flow during the spring-early summer period, while the Apennines streams have a rainy, and therefore intermittent, influence showing a minimum seasonal flow (drought) during the summer. These tributaries account for the annual regime of the Po river, which is characterized by two low-level hydrometric periods (winter and summer) and two flood periods (late fall and spring; Fig. 1b and c). The

first flood period reflects the intense late fall rains, while the second is due to snow melt from the higher sectors of the catchment (Zanchettin et al. 2008; Coppola et al., 2014; Fatichi et al., 2014).

With regard to the water budget, the main Alpine tributaries (left bank) often display discharge higher than 100 m³/s (Dora Baltea, 110 m³/s, Ticino 290 m³/s, Adda up to 160 m³/s), whereas the Apennine tributaries (right bank) usually show discharge lower than 50 m³/s. The Tanaro river draining the Maritime Alps (Liguria) is the only right bank tributary with high average discharge (up to 130 m³/s). These tributaries transfer their water budget to the Po river, which progressively increases its average discharge from the upper to the lower part of the basin: 1.1 m³/s after 5 km from the source, 50 m³/s after ca. 90 km from the source, 958 m³/s at Piacenza (300 km from the source), 1115 m³/s at Cremona (350 km from the source), 1,500 m³/s at Pontelagoscuro (Montanari 2012; Tarpanelli et al. 2013; integrated with data provided by the Basin Authority of the Pedimont Region).

Downstream of Pontelagoscuro, the Po river approaches a delta consisting of six major distributaries; from the main course the first diversion (southward) is represented by Po di Goro, which drains ca. 15 % of the original flow. A second diversion (northward) is represented by Po di Levante, which is artificially regulated and separated from the main course, which is known as Po di Venezia. The latter progressively distributes water to Po di Gnocca (southward; 13% of the flow) and Po di Maistra (northward; 2% of the flow) finally subdividing in Po di Tolle (15% of the flow) and Po di Pila (55% of the flow).

The current hydrographic network has been variably constrained by anthropogenic activities that: a) embanked the river to avoid the recurrent avulsions and diversions (Castellarin et al. 2011); b) constructed dams to store water reservoirs (Zampieri et al., 2014); c) organized a widespread network of artificial canals that are used to regulate the hydrological flow as well as to irrigate agricultural fields (Bozzola and Swanson 2014).

According to the hydrological balance provided by Montanari (2012) the annual river recharge consists of ~ 78 km³ of water, 25 of which are lost by evapotranspiration while 6.5 are consumed by civil, agricultural and industrial uses, leading to a discharge of ~ 47 km³ of river water within the Adriatic Sea, roughly in agreement with the previous estimation of Artina et al. (1990) which proposed an annual flow of 42.6 km³ of river water toward the sea.

The chemical composition of the studied waters is directly related to the nature of the lithologies included in the basin and to the related weathering processes. It is important to note that from the geological point of view, the western Alps are mainly made of crystalline (metamorphic and granitoid) basement rocks that pertain to the Alpine and Hercynian orogenic cycles and by Jurassic ophiolites (serpentinized peridotites, gabbros and basalts), with only subordinate limestones of Triassic and Jurassic age. The northern Apennines are mainly made of Tertiary flysh (alternation of sandstone and pelite rocks) and by Jurassic ophiolites (Garzanti et al. 2011; 2012). The Padanian plain is obviously made of alluvial sediments representing the weathering products of the rocks mentioned above (Amorosi 2012; Bianchini et al. 2012; 2013; 2014).

Sampling and analytical methods

In this study 54 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, mainly in April and August 2012 (Table 1 and Fig.1). The rationale behind the selection of sampling locations was to monitor the water geochemistry along the river profile, before/after the confluence of important tributaries, settlements and/or zones of important productive activities, but logistical criteria (i.e. easy site accessibility) were also taken into consideration. Each sampling location was geo-referenced by a portable global positioning system (GPS), to locate the points and to set up future field surveys. Surface water was collected at 40-50 cm depth using a bucket, possibly far from the shore (using boats, piers, or sampling above bridges). Electrical conductivity (EC), pH and temperature were directly measured in the field (Table 1), then water samples were filtered by 0.45 µm filters (Minisart® NML syringe cellulose acetate filters) and stored in two distinct 100 ml bottles, one for the analysis of anions and oxygen/hydrogen isotopes and a second (acidified with 0.5 mL of concentrated Suprapur HNO₃) for the determination of cations and trace elements.

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 analyzer and reported in Table 2. The isotopic ratios of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ are expressed as δ notation [$\delta = (R_{\text{sample}}/R_{\text{standard}} - 1) \cdot 1000$] 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 $\delta^{18}\text{O}$ 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 M Ω 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 (www.scpscience.com). 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 mentioned analyses are reported in Table 3. The coherence of chemical data has been verified checking the ionic balance, as the sum cations (expressed in meq/L) approaches that of anions with relative error, $[(\sum_{\text{cations}} - \sum_{\text{anions}}) / (\sum_{\text{cations}} + \sum_{\text{anions}})] \cdot 100$, which is generally minor than 5%.

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 \log_{10} 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 (Bowen and Wilkinson 2002) that would introduce high amplitude variability in the interpolated surface over short length scales.

Results and discussion

pH, temperature and conductivity of Po river waters

Physico-chemical parameters measured in-situ such as pH, temperature and conductivity of Po river water have been reported in Table 1. In order to appreciate physico-chemical changes along the flow path the sample population has been geographically subdivided in three subsets corresponding to increasing distance from the river source, defined as UP (upper part), MP (middle part), TP (terminal part), and the related variability has been also evaluated in order to delineate spatial-temporal changes.

pH was rather homogeneous, i.e. 7.8-8.9 in UP, 7.7-8.7 in MP, 7.5-8.5 in TP, without systematic trends in the distinct sampling periods. On the other hand, the water temperature shows significant spatial-temporal variation; in UP it varied between 6 °C (locality Pian del Re, April 2012) to 21 °C (locality Carignano, August 2012); in MP it varied between 16 °C (April 2012) to 28 °C (August 2012); in TP it varied between 16 °C (in April 2012) to 31°C (in August 2012).

Water conductivity was also variable, increasing from UP (average 200 $\mu\text{S}/\text{cm}$) through MP (average 370 $\mu\text{S}/\text{cm}$), up to TP where samples were more heterogeneous (average 410 $\mu\text{S}/\text{cm}$). Higher conductivity (up to 8,500 $\mu\text{S}/\text{cm}$) has been sporadically observed in some samples from the deltaic part of the river. This indicates progressively higher amounts of dissolved components moving from the UP, to the MP, and to the TP catchment areas.

Isotopic composition of Po river waters

The $\delta D\text{‰}$ and $\delta^{18}O\text{‰}$ isotopic ratios have been measured for Po river water sampled in distinct hydrological periods of the year 2012. $\delta D\text{‰}$ ranges from -92.0‰ to -48.0‰ in winter-spring and from -94.7‰ to -55.1‰ in summer, whereas $\delta^{18}O\text{‰}$ ranges from -13.1‰ to -7.0‰ in winter-spring and from -13.4‰ to -6.9‰ in summer. These data are plotted in Fig. 2a together with the global (GMWL; Craig 1961) and local meteoric water lines (northern Italy; Longinelli and Selmo 2003; Longinelli et al. 2006); the presented data were also compared with the compositions of meteoric precipitation of prevalent Atlantic provenance (e.g. rain in Germany; Stumpp et al., 2014) and meteoric precipitation of prevalent eastern Mediterranean provenance (e.g. rain in Greece; Dotsika et al., 2010) which can provide the isotopic fingerprint of vapor mass end-members potentially influencing the study-area.

The recorded isotopic compositions of hydrogen and oxygen in the Po river water mainly reflects the isotopic composition of the meteoric precipitations (rain, snow, glacier ice melting) in the drainage area which is in turn related to altitude and continental effects. Noteworthy, most Po river isotopic compositions conform to those of precipitations occurring at high altitudes in the north/northwestern-most part of the basin (UP), i.e. from high Alpine zones (Fig. 2b, modified after Longinelli and Selmo 2003). Coherently, Montanari (2012) showed that the prevalent meteoric contribution (up to 1,600 mm/yr of precipitation) in the Po river basin is confined within the mountainous Alpine sectors, which collect most of the catchment precipitations. In particular:

1) 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), display $\delta^{18}O$ varying from -13.4‰ to -11.1‰ and δD varying from -94.7‰ to -75.3‰ . The average $\delta^{18}O$ recorded in April (-12.5‰) is slightly more negative than the average value observed in August (-12.2‰) whereas the average δD value are nearly constant in the two seasons.

2) Samples from the middle part of the river (MP), located between the localities of Frassineto Po and Revere, display $\delta^{18}O$ varying from -12.5‰ to -8.4‰ and δD varying from -84.7‰ to -60.1‰ . The average $\delta^{18}O$ recorded in April (-9.8‰) is analogous to the average value observed in August (-9.8‰), and also the average δD values are nearly constant in the two seasons.

3) Samples from the terminal part of the river (TP), also including the deltaic area, display $\delta^{18}O$ 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 (-9.1‰) is slightly more negative than the average value observed in summer (-8.1‰) whereas the average δD values are nearly constant in the two seasons.

The isotopic variability observed along the river profile is presented in Fig. 3, which reports the $\delta^{18}O$ value as a function of the distance from the river source, also emphasizing relationships with the discharge of the main course and the principal tributaries. 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 $d - \delta\text{‰}$ 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 is 0.2‰ $\delta^{18}O$ and 1.7‰ δD per 10 km. The trends recorded in Figs. 2 and 3 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 is negatively correlated with $\delta^{18}O$ by a logarithmic relationship ($r^2 = 0.98$), while in the MP a linear regression better describes the relations between these parameters ($r^2 = 0.90$). The mean altitude gradient recorded along the UP and MP is -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 and Bortolami (1982). The $\delta^{18}O$ /100 m gradient defined in this study is also higher than the global gradient defined by Bowen and Wilkinson (2002), but it is comparable with that defined by precipitations occurring in Germany (Stumpp et al., 2014), possibly suggesting an origin from similar vapor masses of prevalent Atlantic provenance. These notable correlations describing the morphoclimatic effects in the UP and MP parts of the river do not characterize the TP part, which is 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 ($\delta^{18}O \sim -9.5\text{‰}$) 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 disappear after few kilometers being homogenized within the riverine water mass, whereas isotopic variations due to the confluence of Apennine tributaries (having $\delta^{18}\text{O} \sim -8.0$ and -8.9‰ ; Iacumin et al. 2009) are 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 (April and August 2012) allow us to evaluate relationships between the $\delta\text{‰}$ values and the temperature. From the data presented in Fig. 1 (air temperature), Table 1 (water temperature), and Table 2 (isotopic values) 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 $\Delta\delta^{18}\text{O}/\text{temperature}$ gradient of $\sim 0.1\text{‰}$, which is scarcely significant. The lack of significant variation for water samples collected in distinct hydrological phases (peak discharge in April, drought in August) 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 are slowly released in the summer period b) by sub-surface inflow which variously delay the meteoric contributions; c) by man-made dams which create reservoirs where meteoric contribution of different seasons mix together.

It should be noted that Rapti-Caputo and Martinelli (2009) on the basis of $\delta^{18}\text{O}$ - δD data highlighted, in the MP of the plain, communication and water exchanges between the River Po and the first confined aquifer (depth of 20 to 50 m, in the Ferrara surroundings). In this scenario, the un-expected $\delta^{18}\text{O}$ shift toward more negative values (-1‰) observed in Fig. 3 at ~ 480 km from the source, just before the diversion of the deltaic branches (localities of 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, with $\delta^{18}\text{O}$ up to -9.0‰ and δD up to -6.9‰ , in relation to a more effective evaporation due to the reduction of the water flow velocity, and mixing with saline water.

In Table 2 we also report the values of the deuterium excess calculated as: $d\text{-exc} = \delta\text{D} - 8 \cdot \delta^{18}\text{O}$ on the basis of the world meteorological water line as defined by Dansgaard (1964). This variable provides additional information on the prevailing moisture conditions at the source region but is also related to the temperature recorded at the precipitation site and to the evaporation effects, thus providing a further criterion in the distinction of waters having different origins. The UP samples are characterized by averages $d\text{-exc}$ of 16.8‰ and 14.3‰ for April and August, respectively. This parameter is very constant in the MP samples with averages of 12.6‰ and 12.8‰ , respectively. These $d\text{-exc}$ values recorded in the UP and MP river sectors are intermediate between those recorded in north-European precipitations (e.g. in Germany $6\text{-}12\text{‰}$; Stumpp et al., 2014) and those of south-Mediterranean precipitations (e.g. in Greece $12.9\text{-}20\text{‰}$; Dotsika et al., 2010). The $d\text{-exc}$ is significantly lower in TP samples that are characterized by extremely heterogeneous values (down to negative values in the August period). This observation confirms the occurrence of a high evaporation rate only in the terminal part of the river.

Summarizing, the compositions of the water from the first two groups (UP and MP) are roughly aligned along the above mentioned meteoric water lines, whereas water belonging to the third group (TP) shows a $\delta^{18}\text{O}$ shift toward less negative compositions (Fig. 2a). The observed isotopic differences along the trunk of the Po river are emphasized in the Fig. 3 where isotopic values are plotted along the riverine profile at increasing distance (km) from the source. Noteworthy, the more pronounced isotopic gradients are observed in the upper part (UP) and in the terminal part (TP) of the river, whereas the middle part is characterized by slight, but systematic, variation. The isotopic fingerprint of the central part of the river, compared with the dataset of the meteoric compositions in northern Italy (Longinelli and Selmo 2003; Longinelli et al. 2006) indicates that most of the river recharge occurs in the north-western part of the basin, i.e. conveyed mainly from the Alpine highlands. It has to be noted that the isotopic composition of the river water remained constant in the last years, as the $\delta^{18}\text{O}$ value reported by Iacumin et al. (2009) for Po river close to Cremona is nearly identical to the values recorded by our survey in the same site.

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 (Gibbs 1970; Meybeck 1987; Gaillardet et al. 1999; Gaillardet 2014; Viers

et al. 2014), specific regional researches performed on the Po river catchment are rare. The amount of the dissolved species are related to the nature of lithologies outcropping in the catchment and the weathering processes typically occurring in the region (Voss et al. 2014 and references therein). Moreover, the anthropogenic contribution related to human activities cannot be neglected.

The investigation has been refined taking into consideration the chemical analyses of the major cations and anions (Table 3). The Total Dissolved Solids (TDS), calculated as a sum of the major chemical species, coherently increases from the upper part of the catchment where the UP samples have TDS < 100 mg/L, to the central part where the MP samples have a TDS between 250 and 300 mg/L. Higher TDS values are generally observed in the deltaic samples (> 500 mg/L), with localized high saline samples (TDS up to 5,864 mg/L) which possibly result 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 are synthetized in the notional Gibbs diagram where TDS values (y-axis) are plotted against the $[\text{Na}^+(\text{Na}^+\text{+Ca}^{2+})]$ ratio (x-axis, Fig. 4). It can be observed that the UP water, and in particular that from Pian del Re, already displays 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) is calcite under-saturated, 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 continue all along the river course explaining the comparatively higher TDS and $[\text{Na}^+(\text{Na}^+\text{+Ca}^{2+})]$ ratios observed in the MP samples. More extreme $[\text{Na}^+(\text{Na}^+\text{+Ca}^{2+})]$ ratios characterize 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 is given by the Piper classification diagram of Fig. 5, where it can 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 show a chloride-alkaline hydrochemical facies that indicate effective mixing with saline water. The calculation of a correlation matrix highlights coherent elemental relationships along the whole sample suite; in particular, Cl^- positively correlates with Br^- and SO_4^{2-} but also with alkaline elements such as Na^+ , K^+ , and trace element such as Li and Rb (r^2 is better than 0.9 for all the mentioned elements), whereas Ca^{2+} mainly correlates with Sr ($r^2=0.72$). Elemental ratios have been also taken into account because they can highlight the different lithologies that have been weathered releasing chemical component in the interacting water (Viers et al. 2014; Voss et al. 2014). In the Po river water: $\text{Ca}^{2+}/\text{Na}^+$ (molar) is 21.6-6.4 and 3.8-2.3 for UP and MP, respectively; $\text{Mg}^{2+}/\text{Na}^+$ (molar) is 5.3-2 and 1.4-0.7 for UP and MP, respectively. These values have been compared with those provided by Meybeck (2003) for water of mono-lithological basins which interacted with distinct carbonate and plutonic/metamorphic silicate rocks; the comparison reveals that the UP water preferentially dissolves carbonate components, whereas the MP water is progressively influenced by silicate rocks (igneous and metamorphic) components, which are particularly abundant in the catchment. The trace element ratio could provide further useful information; according to the findings provided by Natale et al (2013), who analyzed little mono-lithological alpine catchments, the rubidium/strontium ratio can highlight if the weathered rocks are mainly composed by carbonates (low Rb/Sr) or silicates (high Rb/Sr). It has to be noted that the Po river water is usually characterized by Rb/Sr between 0.004 and 0.009, values suggesting prevalent interaction with silicate rocks that predominate in the highlands of the catchment, and only a subordinate interaction with carbonate lithologies.

In general, the more extreme variations are observed in the terminal part of the river, where evident mixing trends can be observed in the bi-variate diagrams of Fig. 6, which are based on the more conservative elements (Cl^- vs Br^- , SO_4^{2-} , Na^+ , Li , B). In these diagrams, the real TP compositions compared with theoretical mixing lines with seawater indicate that up to 20 % of marine influence could affect the river waters. Other less conservative elements, if plotted and compared with the theoretical sea water mixing lines, show that the mixing process is largely not ideal and not conservative, possibly as result of ion-exchange processes with suspended solid particles (Bianchini et al. 2005).

Anthropogenic contributions are superimposed on the geogenic geochemical fingerprint, as indicated by the concentration of nitrate (Fig. 7a) that reaches the highest values in MP samples (12 mg/L). It is interesting to note that in MP waters the dissolved NO_3^- is systematically higher in winter-spring than in summer, whereas in TP waters NO_3^- becomes preponderant in the summer period, possibly suggesting a diverse origin in the

two zones. The precise origin of NO_3^- in water from the Po plain was recently investigated by Sacchi et al. (2013) that evidenced: a) diffuse contamination related to the agricultural activities that use abundant nitrogen-bearing fertilizers, b) punctual (direct) pollution from zootechnical activities that produce nitrogen rich manure, c) sewers from densely inhabited lower Po plain settlements. In particular, the highest NO_3^- concentration has been detected close to the city of Parma and Piacenza where pigs breeding practices are widely developed. The obtained results also complement the studies of the Po river solid load (Cozzi and Giani 2011), suggesting the first order role of Po river in regulating the nitrogen budget of the Adriatic Sea. Emphasis is also given to elements that are potentially toxic and hazardous in water for drinking purposes (e.g.: As, Ni, Cr; Table 3). For example, arsenic (Fig. 7b) is generally high throughout the whole sample population and often exceeds the tolerance limits for drinkable water defined by the European Council Directive 98/83/EC (on the quality of water for human consumption) and by the World Health Organization (10 $\mu\text{g/L}$). Attention also has to be paid to nickel and chromium that are known to be enriched in the alluvial sediments of the area due to widespread outcrop of ophiolite ultramafic rocks in the Po river catchment (Bianchini et al. 2012; 2013; 2014). Our analyses (Table 3) reveal that the mobility of chromium is limited (probably due to the Eh and pH conditions of the studied waters), as indicated by concentration $<10 \mu\text{g/l}$ in the natural water of the area, i.e. significantly lower than the European drinking standards (20 and 50 $\mu\text{g/l}$ for Ni and Cr, respectively). Nickel displays a higher mobility, possibly because it is associated with serpentine that is a metastable mineral phase (Kierczak et al. 2007). Coherently the Cr/Ni is always higher than 1 in the Po river sediments, whereas it is always lower than 1 in the studied waters; therefore, the high bio-accessibility of nickel represents a potential geochemical risk for the area and has to be carefully monitored (Cempel and Nickel 2005). In UP and MP waters boron is generally not detectable, and always below 15 $\mu\text{g/L}$, thus significantly lower than the EU drinking standards (1 mg/L).

Spatial variability of water isotopes and chloride

Geochemical maps are a useful tool to describe the state of environmental resources of a territory. In this light, interpolation of point measurements using geostatistical techniques can be used to estimate values in the neighbors, i.e. to extend predictions to non-sampled locations. The geostatistic approach is based on the spatial autocorrelation concept defining that nearby objects are more related than distant objects. It has been traditionally applied to emphasize geochemical backgrounds and anomalies of soils (Goovaerts 1998) but is also useful, and progressively more used, for hydrological applications (Dutton et al. 2005; Bowen 2010; Timsic and Patterson 2014).

In this study, spatial interpolation techniques have been used to define the geochemical variability of Po river waters along its main path, also considering the potential contribution of some alpine and apennine tributaries (additional data from Iacumin et al. 2009; Delconte et al. 2014). Our goal is to visualize geochemical changes within the riverine system, providing a spatial snapshot of the summer conditions, which may represent a tool to understand ongoing processes. The most appropriate method of spatial interpolation to map the isotopic and geochemical variability of the Po river is the “kriging” algorithm in which the weights assigned to nearby data during the interpolation process are determined by a model of the covariance structure of the observational data (Isaaks and Srivastava 1990). A spherical semivariogram model has been fitted by automatic calculation of its parameter by the Geostatistical Analysis tool (ArcGis 9.3) in which anisotropy has been also considered evaluating its significant directional differences.

Interpolation models reveal that the Po riverine distribution of both $\delta^{18}\text{O}$ and δD delineates a rough but systematic isotopic gradient, with values that become less negative as the water reaches the lowlands along the river course. This “weighting” trend is particularly evident for hydrogen isotopes and is depicted by the thematic map of Fig. 8, which allows the definition of a precise δD gradient obtained by an interpolation algorithm relating the geographical distance with the considered parameter. This is particularly evident in the UP and MP parts, reflecting the mean elevation of the relative sub basins and the isotopic composition of the associated meteoric waters (Dutton et al. 2005; Kendall and Coplen 2001). The δD spatial distribution indicates that the Po river isotopic fingerprint acquired in the MP is buffered and maintained irrespective to the confluence of the tributaries having distinct compositions, only varying with the distance from the source. In particular, the geostatistical approach is extremely useful in the deltaic sector where the river is subdivided in several branches. Accordingly, emphasis is given to the TP of the river in order to highlight geochemical

variation related to mixing processes with marine water; in Fig. 9a it can be observed that the main deltaic branch (Po di Venezia) nearly preserves the unaltered original composition, whereas waters of the second order (outer) branches such as Po di Levante, Po di Maistra, Po di Gnocca, Po di Tolle, Po di Goro) display a more marked δD "positivization"; this observation is plausibly due to their lower discharge and flow velocity which make them more sensitive to seawater intrusion. This hypothesis is supported by the geochemical map of Fig. 9b which reports the chloride spatial variation in the same TP sector. Further constraints would require the preparation of analogous geochemical maps taking also into consideration the tidal characteristics that could influence the mixing between river and marine water.

The spatial correlation of the d-excess, which amplifies small differences between the observed δD and $\delta^{18}O$ parameters, has been also taken into consideration in order to identify the ultimate origin of the vapor air masses circulating within and around the Po river basin. The ordinary kriging interpolation of this parameter along with the Po river highlights an initial d-exc composition around +14‰ which conforms with the fingerprint of precipitations of Atlantic provenance; d-exc gradually decreases to ca. +10‰ down flow to the confluence of Ticino River and is followed by a re-increase up to +17,6‰ in the, MP, which plausibly reflects meteoric contribution from both Atlantic and Mediterranean (d-exc up to +27‰; Cruz-San Julian et al. 1992; Lambs et al. 2013) provenance. The prediction map finally exhibits a sharp d-exc decrease (down to negative values) in the deltaic portion of TP, where evaporation and mixing processes have been described above.

Summary and conclusions

This contribution presents geochemical data of Po river waters including major and trace elements as well as oxygen-hydrogen stable isotopes. In most sampling sites which are uniformly distributed along the river course, from the Alps to the Adriatic Sea, the isotopic variation observed in distinct hydrological periods (peak discharge in April, drought in August) is limited, plausibly due to homogenization of distinct contributes related to surface run off (rain and snow melt) and groundwater recharge. In general, the isotopic fingerprint of local precipitations is predominant in the upper part of a river course, whereas in the lower part of the basin the contribution of local precipitations to the river water budget is minor, except during floods, and in general the isotopic composition is more complex to be interpreted.

Stable isotopes of the Po river water display $\delta^{18}O$ between -13.1‰ and -7.0‰ and δD between -92.0‰ and -48.0‰ suggesting that most of the recharge is confined in the north and northwestern part of the basin, conveying water to the river mainly from the Alpine highlands. This statement, mainly based on the observation of the isotopic compositions, conforms with the available data on the tributaries discharge, which indicate that the various streams conveying in the Po river from the Apennine hills are of second order importance respect to those flowing down from the Alpine mountains. The river waters in the middle part of the course (MP) maintain a nearly constant isotopic signature that becomes variable only in the terminal part, in response to more effective evaporation and mixing with saline waters that induce an isotopic shift of $\delta^{18}O$ and δD toward less negative values. Since these isotopic tracers are affected by fractionations, which are temperature dependent, their monitoring has to consider that long term isotopic variations in river systems can be induced by climatic changes such as variation in the environmental temperature, change of precipitation distribution in the drainage area, but also by anthropogenic influences on the hydrological regime. We emphasize that the effectiveness of such monitoring is greatly enhanced if the available isotopic data are decoded in terms of linear and altimetric gradients along the river profile, acquired in distinct hydrological periods (comparing isotopic values during peak discharge and drought), and properly georeferenced and presented with spatially resolved geochemical maps. In this light, we present a series of geochemical maps (by ArcGIS software), highlighting geochemical variations occurring in the catchment area. For example, Fig. 8 shows the existence of a significant δD gradient along the whole river catchment. Although less marked, also $\delta^{18}O$ displays similar evolution along the catchment, showing a regular increase of $\delta^{18}O$ from the Po source up to the Ticino intersection (269 Km), a relative consistency from the Ticino confluence up to the Taglio di Po site with $\delta^{18}O$ variation slightly fluctuating ($\pm 0.5\%$) around the value of -9.5‰, and then a $\delta^{18}O$ progressive positivization in the deltaic branches. This hydro-archive could be useful as background information for future "hydrograph separation" studies in order to distinguish between pre-event and event water in the stream (Klaus and McDonnel, 2013).

The processes occurring at the transition with the sea are emphasized in the geochemical maps of Fig. 9a, that is a zoom in the terminal part of the river, based only on the summer δD data (August 2012), i.e. a period preferentially affected by evaporation and mixing processes. These maps focused on the delta show that secondary branches (smaller and located in the delta periphery) are affected by more relevant interaction with seawater and salinization respect to the principal deltaic branch (Po di Venezia). This phenomenon is plausibly due to a remarkable inertia of the main branch which has comparatively higher discharge and flow velocity that prevent significant seawater intrusion.

The dissolved solutes result by the weathering of the rocks outcropping in the basin, i.e. processes that are particularly effective in the surrounding Alpine and Apennine reliefs; therefore the presented geochemical analyses of the Po river water gives insights on the erosion and denudation processes of these orogenic belts. The TDS progressively increases from the initial value of 70 mg/L at the river source to values of 250-300 mg/L (the average and median of 39 measurements are 268 and 292 mg/L, respectively for MP samples) that characterize most of the stream length, and increase significantly only in the terminal sector of the delta. In this area the river freshwater is affected by mixing with saline water of the Adriatic sea (and that of the connected lagoons). The magnitude of the salinization processes and their geographical distribution should be monitored periodically and systematically (also considering the tidal effects) taking into consideration that climatic changes influence both the sea-water level and the river discharge.

In general the presented data can contribute to calculate geochemical fluxes conveyed by the Po into the Adriatic Sea. Considering that the annual Po water volume is of 47 km³, the observed TDS implies a solute flux in the order of 13,600,000 t/yr transferred from the Po river toward the Adriatic Sea. Assuming that the solutes represent a fraction (accounting for ca. 20%; Hinderer et al 2013) of the weathering products, we estimated a denudation (chemical weathering plus physical erosion) and mass transport of 68,000,000 t/yr within the Po river drainage basin. The weathering processes are also intrinsically related to the annual temperature, meteoric precipitation and CO₂ activity (Viers et al. 2014). The presented data represent therefore a snapshot of the current conditions and contribute to the definition of a hydro-archive useful to interpret potential climatic and river dynamic changes.

The study also identifies potential anthropogenic contaminations that deserve further monitoring and assessment. The presence of NO₃⁻ (average 8 mg/L), for example, delineates a notable flux toward the sea (370,000 t/yr) that can contribute to eutrophication processes. This evaluation of reactive nitrogen flux is obviously underestimated because significant amount of this element is associated with suspended particulate (Tesi et al 2013). Further concern is represented by the presence of arsenic, that in many samples exceeds the 10 µg/l threshold defined for drinking water. In this case, the origin and geochemical behavior of this element is not straightforward (Molinari et al 2012) and additional research will be necessary to understand if the presence of this hazardous element is a "natural" ("geogenic") anomaly or the result of direct anthropogenic contamination.

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Captions:

Table 1 Physico-chemical parameters measured in the field. According to the geographical distribution, the investigated samples have been subdivided in three distinct groups, representative of the UP (upper part), MP (middle part) and TP (terminal part) of the Po river course. This subdivision is reflected in distinct parameters, as emphasized by electrical conductivity progressively increasing from UP, to MP and TP water. Some important tributaries (Ticino, Adda, Mincio), sampled close to the confluence with Po river have been also taken into account.

Table 2 Hydrogen and oxygen isotope ratios in the Po river waters. Some important tributaries (Ticino, Adda, Mincio), sampled close to the confluence with Po river have been also taken into account. Data are expressed in $\delta\%$ respect to the SMOW standard. na = not analyzed.

Table 3 Chemical composition of Po river waters. Some important tributaries (Ticino, Adda, Mincio), sampled close to the confluence with Po river have been also taken into account. A more complete set of trace elements analyses including Al, Fe, Mn, Cu, Zn, Se, Cd, Sb, U can be provided upon request to the corresponding author. nd = not detected; na = not analysed.

Fig. 1 a) Hillshade map of the Po river catchment (based on NASA SRTM data) reporting the sampling locations where Po river water samples have been collected. Distinct symbols have been used for water sampled at increasing distance from the source in the upper part (UP, black squares), middle part (MP, grey triangles), terminal part (TP, light grey circles) that typically display significant compositional changes. b) Average (2002-2010) monthly precipitation (grey histograms) and air temperature (black line) of the UP sector of the Po river basin (Fatichi et al., 2014); c) discharge (Q, m³/sec; black line) and water level height (grey line) of Po River in the section of Pontelagoscuro which is located at the boundary between the MP and UP sector delineated in this study; the values are specifically referred to the year 2012, and black arrows denote the sampling periods.

Fig. 2 a) $\delta^{18}\text{O}$ - δD isotopic composition of Po river water. Meteoric water lines are also reported for comparison: the dotted line represents the Global Meteoric Water Line (GMWL; Craig 1961); the dashed line represents the Local Meteoric Water Line, defined for Northern Italy (LMWL; Longinelli and Selmo 2003), together with compositional fields relative to meteoric precipitation of prevalent Atlantic provenance (e.g. rain in Germany; Stump et al., 2014) and meteoric precipitation of prevalent eastern Mediterranean provenance (e.g. rain in Greece; Dotsika et al., 2010). Filled symbols (black square for UP, grey triangle for MP, light grey circle for TP) represent samples collected in winter-spring; open symbols (square for UP, triangle for MP, circle for TP) represent samples collected in summer. b) Contour lines reporting the geographical distribution of the oxygen isotopic composition of precipitation in Italy and the Po river course together with the more significant fluvial elements (modified after Longinelli and Selmo 2003; for interpretation refer to the colored web version of the paper). In this map the average isotopic composition of UP, MP, TP Po river water is also reported. See text for further explanation.

Fig. 3 Variation of the $\delta^{18}\text{O}$ signature in function of the distance from the source of the Po river. The relation with the discharge of the main course and the principal tributaries is also reported. Filled symbols (black square for UP, grey triangle for MP, light grey circle for TP) for samples collected in April 2012; open symbols (square for UP, triangle for MP, circle for TP) for the samples collected in August 2012; ✦ represents additional analyses of Po river water available in the literature, whereas + and x represent the right bank and left bank tributaries, respectively; (Zuppi and Bortolami 1982; Delconte et al. 2014; Iacumin et al. 2009; Rapti Caputo and Martinelli 2009). As concerns the TP deltaic sector, open circles are further subdivided in different sizes: big circles represent samples taken in Po di Venezia (the main distributary) whereas the small circles represent Po di Goro and Po di Gocca (minor/secondary branches).

Fig. 4 Gibbs diagram: TDS vs [Na/(Na+Ca)] reported in mg/L for the Po river water. Filled symbols (black square for UP, grey triangle for MP, light grey circle for TP) for samples collected in winter-spring; open symbols (square for UP, triangle for MP, circle for TP) for the samples collected in summer.

Fig. 5 Piper classification diagram reporting composition of River Po water a) samples collected in winter-spring, b) samples collected in summer.

Fig. 6 Scatter diagrams reporting compositions of the more conservative major ions (Cl⁻, Na⁺, SO₄²⁻, Br⁻) and trace elements (Li, B). Emphasis is given to the TP water of Po river collected in August (circles), which

are variously affected by mixing with seawater and salinization, whereas the remaining UP and MP samples are grouped within a compositional field. Note that real TP compositions are compared with theoretical seawater mixing trends, showing that the more saline TP samples correspond to $\approx 20\%$ of mixing with seawater.

Fig. 7 a) Histograms representing the NO_3^- dissolved in different Po river sites in distinct hydrological periods (expressed in mg/L; white color, winter-spring; black color, summer). b) arsenic concentration (expressed in $\mu\text{g/L}$) along the Po river profile (white squares, winter-spring; black squares, summer).

Fig. 8 Geochemical map showing the δD (‰) spatial variation along the geographical extent of Po river. For interpretation refer to the colored web version of the paper.

Fig.9 Geochemical maps focused on the deltaic part of the Po river showing a) the δD (‰) and b) the chloride (mg/L) spatial variation, respectively. For interpretation refer to the colored web version of the paper.