



Strontium isotopic composition of the Po river dissolved load: Insights into rock weathering in Northern Italy

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ABSTRACT

Strontium isotopic composition ($^{87}\text{Sr}/^{86}\text{Sr}$) of river water provides insight on the nature of rocks involved in the weathering processes and important constraints for reconstructing silicate versus carbonate weathering in large scale basins. New data, presented in the context of a geochemical map of the Po river basin, highlight that the Po river water evolves from the upper part of the catchment, where $^{87}\text{Sr}/^{86}\text{Sr}$ approaching 0.7097 relates to the weathering of igneous and metamorphic silicate rocks, to the middle part, where less radiogenic compositions ($^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7089$) are driven by the confluence of the tributaries draining Mesozoic carbonate rocks of the South Alpine domain and from inflow of Apennine streams characterized by less radiogenic Sr signatures due to weathering of marly sediments and mafic magmatic rocks. Down flow, the Sr isotopic compositions of Po river water rises at 0.7091 either by the confluence of the last Apennine tributary (Panaro, $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7095$) and/or by the possible contribution from hyporheic exchanges. Po river isotopic signatures reveal slightly more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ in comparison to other important Alpine river systems (e.g. Danube, Rhine and Rhône), likely suggesting that silicate rocks are comparatively contributing more weathering byproducts in the Po basin.

1. Introduction

Strontium (Sr) is an element normally present in trace levels in rocks (Faure et al., 1978; Faure, 1986), where it substitutes for calcium (Ca) in mineral structures having similar charge and size. Coherently, carbonates and Ca-bearing silicates (plagioclase, clinopyroxene, amphibole etc.) invariably have relatively high Sr concentrations (Faure et al., 1978; Goldstein and Jacobsen, 1987; Palmer and Edmond, 1992). The natural variation in $^{87}\text{Sr}/^{86}\text{Sr}$ is also linked with the radioactive ingrowth of ^{87}Sr from the decay of ^{87}Rb . In magmatic and metamorphic rocks, the $^{87}\text{Sr}/^{86}\text{Sr}$ is a function of both the geological age and composition; in terrigenous (i.e. siliciclastic) sedimentary rocks $^{87}\text{Sr}/^{86}\text{Sr}$ is strictly related to the nature of the parent rocks, whereas in marine carbonate rocks it reflects the isotopic composition of seawater from which they precipitated. In river waters, Sr mainly derives from weathering, providing both congruent and incongruent dissolution products of calcium-bearing minerals present in variable abundance in igneous, metamorphic and sedimentary rocks. During weathering the $^{87}\text{Sr}/^{86}\text{Sr}$ in the solution approaches that of the destabilized minerals of the parent rock in the presence of carbonate lithologies, or it is slightly

more radiogenic (on the order of 0.0001) in the case of weathering of silicate rocks (Blum et al., 1993; Bullen et al., 1996). The shift in isotopic ratio recorded between the solution and silicate rocks is linked with the higher weathering susceptibility of some minerals such as biotite, which are characterized by higher $^{87}\text{Sr}/^{86}\text{Sr}$ (Blum and Erel, 1996). Consequently, Sr concentration and its isotopic ratio in river water are mainly governed by both the lithological features of the catchment area and the weathering rate of the different rock-forming minerals (Palmer and Edmond, 1992; Négrel et al., 1997; Gaillardet et al., 1999; Grosbois et al., 2000; Gillis et al., 2005). Collectively, a number of studies highlighted that Sr isotopes represent a powerful tool to constrain weathering reactions, weathering rates, flow pathways and mixing scenarios (Singh et al., 1998; Galy et al., 1999; Gaillardet et al., 1999; Dalai et al., 2003; Pennisi et al., 2006; Shand et al., 2007; Tripathy et al., 2010, 2012; Bakari et al., 2013; Wu et al., 2013; Kim et al., 2013; Gislason et al., 2009; Rao et al., 2015; Zieliński et al., 2017; Negrél et al., 2017; Sharma et al., 2017). However, for a comprehensive interpretation, extended data-sets (elaborated with geostatistical methods) reporting $^{87}\text{Sr}/^{86}\text{Sr}$ variation at the catchment scale, are necessary to understand fluvial dynamics (Bowen et al., 2009). Here we

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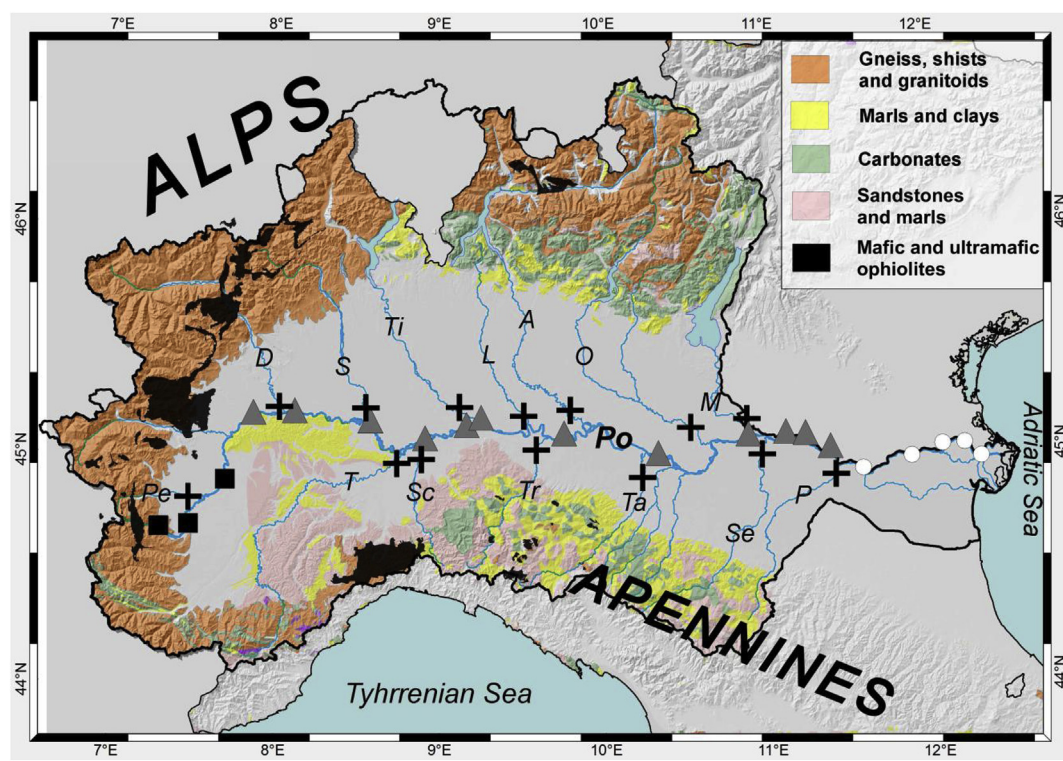


Fig. 1. Simplified geological map of the Po river basin showing the sampling locations. Distinct symbols have been used for the three different part of the Po river as indicated in Marchina et al. (2015) (Upper Part, UP, black squares; Middle Part, MP, grey triangles; Terminal Part, TP, white circles). Crosses indicate sampling locations of tributaries (Pe = Pellice, D = Dora Baltea, S = Sesia, Ti = Ticino, L = Lambro, A = Adda, O = Oglio, M = Mincio, T = Tanaro, Sc = Scrivia, Tr = Trebbia, Ta = Taro, Se = Secchia, P = Panaro).

apply this approach to the Po river catchment, which crosses W-E the whole Northern Italian peninsula conveying to the Adriatic Sea the weathering products of lithologies outcropping in the surrounding Alpine and Apennine mountain belts (Fig. 1). The presented data, together with those from earlier studies discussing elemental and oxygen, hydrogen, carbon, sulphur isotopic compositions of the Po river waters at the catchment scale (Marchina et al., 2015, 2016a) constitute a hydro-archive useful to understand on-going environmental processes. The Sr isotopic signature usefully identifies lithologies involved in exogenous processes in distinct sub-basins. Results observed in the Po river basin are compared with those observed in other important Alpine river systems to emphasize regional analogies and differences.

2. Geological background

The Po river flows within the main alluvial plain of Northern Italy, which is a sedimentary basin bounded to the N by the Alpine mountains, to the SW by the Apennine hills and to the E by the Adriatic Sea (Fig. 1). The western Alps (Piemonte) are characterized by the widespread outcropping of the crystalline basement, which mainly consists of plutonic (granitoids s.l.) and metamorphic rocks. The latter includes gneisses, schists and phyllites, but also lithologies containing a significant amount of carbonate such as calc-schists and minor marbles. Jurassic ophiolites consisting of serpentinized peridotites, gabbros and basalts are also observed in the western Alps; sedimentary rocks such as Mesozoic (Triassic and Jurassic) limestones become significant only in the central Alps (in Lombardy). The Northern Apennines are mainly made of Tertiary flysch (alternation of sandstone, marls and pelite rocks) and by Jurassic ophiolites (Amorosi, 2012). The plain has been infilled by alluvial sediments representing the weathering products of the rocks mentioned above (Garzanti et al., 2012; Bianchini et al., 2012, 2013).

3. Hydrological background

The Po river basin constitutes the most important fluvial system of the Padana plain, which is fed by many tributaries (and groundwater flows) from both the Alpine and the Apennine chains. The Alpine streams are mainly fed by snow melt and accordingly show a seasonal peak flow during the spring to early-summer period, whereas the temporary Apennine streams show a minimum seasonal flow (drought) during the summer, being generally fed by rains. These tributaries account for the annual regime of the Po river (Marchina et al., 2017 and references therein), which is characterized by two low-level hydro-metric periods (winter and summer) and two flood periods (late fall and spring). In terms of water budget, the main Alpine tributaries (left bank) often display discharge higher than $100 \text{ m}^3/\text{s}$ (Dora Baltea, $110 \text{ m}^3/\text{s}$, Ticino $290 \text{ m}^3/\text{s}$, Adda up to $160 \text{ m}^3/\text{s}$), whereas the Apennine tributaries (right bank) usually show discharge lower than $50 \text{ m}^3/\text{s}$. The Tanaro river, draining the Maritime Alps (Liguria), is the only right bank tributary with high average discharge (up to $130 \text{ m}^3/\text{s}$). These tributaries transfer their water budget into the Po river, progressively increasing its average discharge from the upper to the lower part of the basin: $1 \text{ m}^3/\text{s}$ after 5 km from the source, $50 \text{ m}^3/\text{s}$ after ca. 90 km from the source, $960 \text{ m}^3/\text{s}$ at Piacenza (300 km from the source), $1115 \text{ m}^3/\text{s}$ at Cremona (350 km from the source), $1500 \text{ m}^3/\text{s}$ at Pontelagoscuro, (560 km from the source; Montanari, 2012; Tarpanelli et al., 2013). The current hydrographic network has been variably modified by anthropogenic activities including river embankment for flood management, dam construction for water storage and hydroelectric power, organization of a network of artificial canals to regulate the hydrological flow and to irrigate agricultural fields.

4. Methods

Water samples were collected along the entire course of the Po river

Table 1

Strontium elemental and isotopic composition of Po River water. Elemental concentration was analysed by ICP-MS at the University of Ferrara, and isotopic composition was measured both by TIMS at the IGG-CNR (waters collected in August 2010 and August 2012) and by MC-ICP-MS at New Hampshire University (waters collected in May 2014). See [Supplementary Table 1](#) for more complete chemical analyses.

Name		Date	Distance from the source (Km)	Sr (µg/L)	Rb (µg/L)	⁸⁷ Sr/ ⁸⁶ Sr	2σ
Po river							
Pian del Re	UP	05/2014	0	24	0.42	0.709745	0.000006
Sanfront	UP	05/2014	15	112	0.66	0.709601	0.000007
Carignano	UP	05/2014	68	309	2.15	0.709702	0.000009
Crescentino	MP	05/2014	123	360	1.11	0.709187	0.000009
Frassineto Po	MP	05/2014	158	345	0.88	0.709269	0.000009
Balossa Bigli	MP	05/2014	196	259	0.97	0.709453	0.000010
Rea	MP	08/2012	217	287	0.76	0.709273	0.000010
Rea	MP	05/2014	217	310	0.91	0.709108	0.000010
Senna Lodigiana	MP	08/2012	258	290	0.67	0.709110	0.000009
Piacenza	MP	08/2012	268	225	0.71	0.709122	0.000027
Cremona	MP	08/2012	292.6	200	0.71	0.709224	0.000006
Cremona	MP	05/2014	292.6	238	1.12	0.709154	0.000011
Coltaro	MP	08/2012	327.6	218	0.79	0.709079	0.000008
Coltaro	MP	05/2014	327.6	275	1.34	0.709148	0.000010
Revere	MP	08/2010	444	271	1.37	0.709220	0.000022
Revere	MP	08/2012	401.6	235	0.72	0.708980	0.000007
Revere	MP	05/2014	401.6	289	1.05	0.708957	0.000010
Occhiobello	TP	08/2012	443.6	239	0.68	0.708944	0.000014
Occhiobello	TP	05/2014	443.6	286	0.99	0.708956	0.000006
Crespino	TP	08/2010	468	275	1.43	0.709157	0.000018
Crespino	TP	08/2012	467.6	237	1.01	0.708923	0.000009
Crespino	TP	05/2014	467.6	252	1.53	0.709185	0.000008
Bottrighe	TP	08/2010	486	307	1.30	0.709079	0.000012
Bottrighe	TP	08/2012	486	234	0.89	0.708931	0.000068
Taglio di Po	TP	08/2010	495	288	1.45	0.709224	0.000034
Taglio di Po	TP	08/2012	494.6	237	0.79	0.708959	0.000018
Taglio di Po	TP	05/2014	494.6	257	1.33	0.709172	0.000007
Po di Levante	TP	05/2014	518.6	663	8.48	0.709267	0.000007
Tributaries							
Pellice	UP	05/2014		54	0.91	0.712335	0.000008
Dora Baltea	UP	05/2014		215	1.45	0.708627	0.000009
Sesia	UP	05/2014		121	0.84	0.709998	0.000008
Tanaro	UP	05/2014		310	0.77	0.709258	0.000010
Scrivia	MP	05/2014		675	0.64	0.709501	0.000009
Ticino	MP	08/2012		150	0.90	0.708850	0.000017
Ticino	MP	05/2014		180	1.62	0.709055	0.000008
Lambro	MP	05/2014		272	3	0.708981	0.000009
Trebbia	MP	05/2014		448	0.79	0.708843	0.000007
Adda	MP	08/2012		181	0.55	0.709683	0.000021
Adda	MP	05/2014		230	1.83	0.709738	0.000006
Oglio	MP	05/2014		461	1.06	0.708765	0.000008
Mincio	MP	08/2012		288	1.14	0.708649	0.000027
Mincio	MP	05/2014		134	1.49	0.708801	0.000007
Taro	MP	05/2014		543	1.35	0.708558	0.000008
Secchia	MP	05/2014		1117	1.43	0.708524	0.000010
Panaro	MP	05/2014		481	1.45	0.709514	0.000007

(Fig. 1) in distinct periods over the years 2010, 2012 and 2014. Electrical conductivity (EC), pH, and temperature were directly measured in the field ([Supplementary Table 1](#)), and then water samples were filtered at 0.45 µm pore size (Minisart® NML syringe cellulose acetate filters). The results of the following analyses are notionally attributed to the dissolved load fraction, even if we are aware of the possible contribution of colloidal components.

Chemical analyses were carried out at the Department of Physics and Earth Sciences of the University of Ferrara by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument calibrated with a Merck CertiPUR-ICP multi-element standard solution. Samples were diluted 1:10 by deionized Milli-Q water (resistivity of ca. 18.2 MΩ × cm) and spiked with known amount of Re and Rh as an internal standard. In each analytical session, the accuracy was evaluated by the analysis of the reference solutions ES-L1 (a natural groundwater) and EU-L-1 (a waste water) provided by SCP-Science (<http://www.scpscience.com>) and the obtained results were always within the certified confidence interval. Results are reported in [Supplementary Table 1](#).

The Sr isotopic compositions of Po river water were determined in two laboratories. Samples collected in August 2010 and 2012 were analysed by Thermal Ionization Mass Spectrometry (TIMS) at IGG-CNR of Pisa. Strontium was concentrated using standard cation exchange chromatographic columns and eluted with 2.5 N HCl, in order to leach undesired elements that can create interference during the analyses and to isolate the investigated element. Resulting Sr-rich salts were dried down, then re-dissolved with 2 µL of HNO₃ and deposited on previously outgassed tungsten filaments that were subsequently loaded in a Finnigan MAT 262 V multi-collector mass-spectrometer. Measured ⁸⁷Sr/⁸⁶Sr values were normalized to ⁸⁶Sr/⁸⁸Sr = 0.1194. During the collection of isotopic data, replicate analyses of the NIST SRM 987 (SrCO₃) isotopic standard gave an average ⁸⁷Sr/⁸⁶Sr value of 0.710247 ± 20 (2σ, n = 9). Samples collected in May 2014 were analysed at the Department of Earth Sciences at the University of New Hampshire. River waters were acidified to 3 M HNO₃ and were loaded onto a 0.5 mL column filled with Eichrom Sr-Spec resin. Repeated washing with 3 M HNO₃ removed major elemental interferences, with the resulting elution of the Sr fraction in 0.05 N HCl. Samples were

analysed by Multi-Collector Inductively Coupled Plasma-Mass Spectrometry (MC-ICP-MS) on a Nu Plasma II ES instrument. Data were normalized to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and corrected for Rb and Kr interferences as described in Kontar and Storm (2014). During the collection of isotopic data, replicate analyses of the NIST SRM 987 isotopic standard gave an average $^{86}\text{Sr}/^{88}\text{Sr}$ value of 0.710248 ± 18 (2σ , $n = 87$).

Geostatistical modelling has been carried out to assess 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 focus on large - scale features ($> 10 \text{ km}^2$) 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.

5. Results

Po river (and tributary) water samples were first characterized for main dissolved cations, selected trace elements, and oxygen-hydrogen stable isotopes (see background data in the Supplementary Table 1). As described in Marchina et al. (2015; 2016a), the recorded variations in concentration of major dissolved ions and those of isotopic gradients are significant only in the first part of the river, close to the Pian del Re sources (Western Alps), followed downflow by the attainment of a compositional homogeneity that is maintained for most of the riverine profile.

Sr isotopic compositions of Po river waters reported in Table 1 and in Figs. 2–4, describe variations along the riverine course. As indicated in Fig. 1, Po river course has been subdivided in Upper Part (UP), Middle Part (MP) and Terminal Part (TP), as previously proposed by Marchina et al. (2015; 2016a).

The Gibbs diagram indicates that the water composition at the Po river close to the source is already influenced by the chemical interaction with the main outcropping lithologies (Marchina et al., 2015). Notably, the less mineralized river water collected at Pian del Re is characterized by a Total Dissolved Solids (TDS) of 75 mg/L largely exceeding that of wet deposition over the Alps (typically lower than 5 mg/L; Rogora et al., 2006). Weathering contributions to the river water continue throughout the riverine course explaining the comparatively higher TDS and $[\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})]$ ratios observed downflow. More extreme $[\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})]$ ratios characterize the samples from the deltaic area, and coherently the relative $^{87}\text{Sr}/^{86}\text{Sr}$ provides evidence for interaction with saline-rich components. Pian del Re water contains 24 $\mu\text{g/l}$ of Sr and is characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70975, a value that is higher than those generally recorded in precipitation over the Alps (0.7088–0.7089; Schmitt and Stille, 2005; Negrel et al., 2007). Plausibly, the pristine meteoric components rapidly leach strontium from the outcropping rocks reaching the observed elemental and isotopic compositions.

Surface water rapidly evolves and in the UP water with $\text{TDS} < 300 \text{ mg/L}$ has $^{87}\text{Sr}/^{86}\text{Sr}$ ranging between 0.70960 and 0.70974; in the MP, more mature water (TDS generally around 300 mg/L) has $^{87}\text{Sr}/^{86}\text{Sr}$ ranging between 0.70896 and 0.70945, and in the TP, where water has the higher TDS (up to 400 mg/L), $^{87}\text{Sr}/^{86}\text{Sr}$ ranges between 0.70892 and 0.70927 (Table 1, Fig. 2).

A more detailed Sr elemental and isotopic variation along the Po

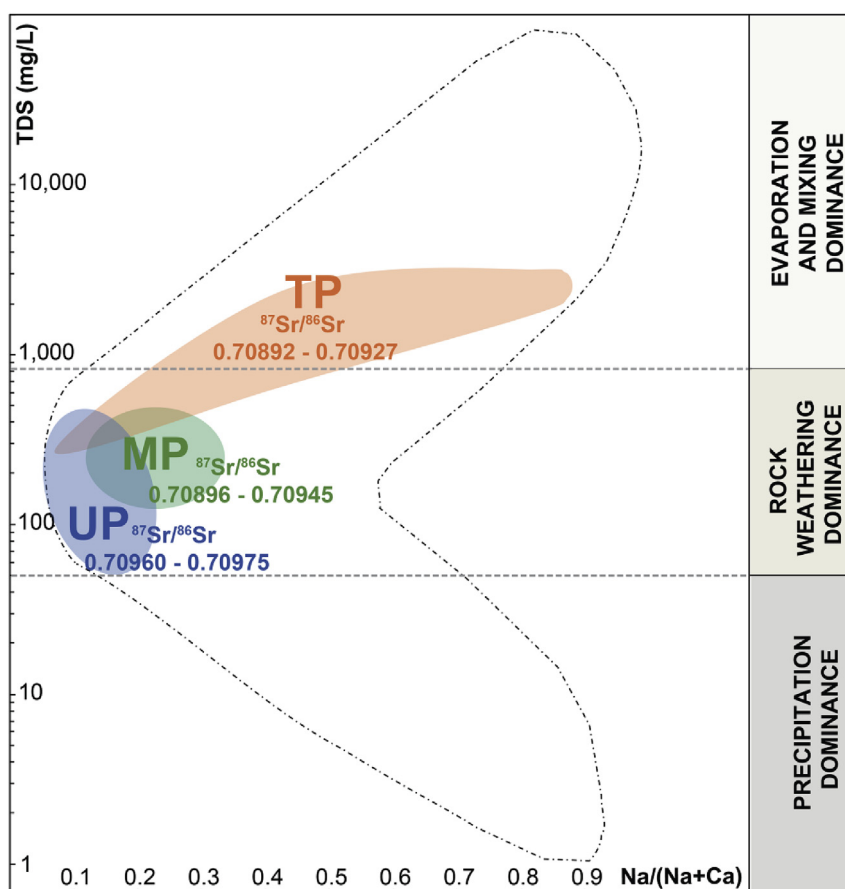


Fig. 2. Gibbs diagram reporting the main dissolved components and the relative range of $^{87}\text{Sr}/^{86}\text{Sr}$ for the Po river water in the UP, MP and TP. The diagram suggests the main processes responsible for hydrochemistry of rivers.

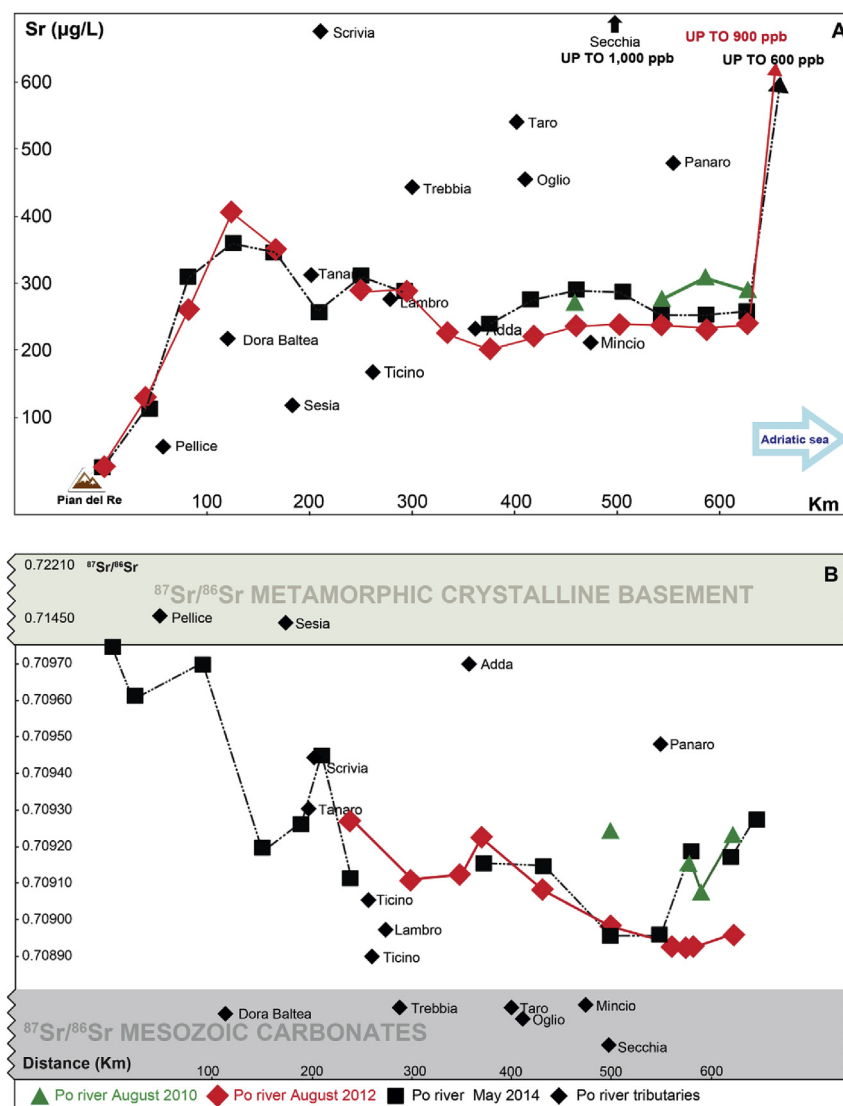


Fig. 3. a) Sr variation along the Po river in different periods, from the Pian del Re source to the Adriatic Sea; b) $^{87}\text{Sr}/^{86}\text{Sr}$ variation along the Po river in different periods of the years 2010–2014 from the Pian del Re source to the Adriatic sea. Isotopic ratios of waters are compared with the isotopic fingerprint of the Mesozoic carbonates and crystalline basement of the region (Faure et al., 1978; Voshage et al., 1987). Isotopic signatures of the main tributaries are also reported to highlight the contribution of distinct sub-basin having specific lithology.

river course and its tributaries, in different periods of the years 2010–2014 is reported in Fig. 3. The geochemical influence of tributaries is related to their water geochemistry, but also to the discharge relative to the Po river.

The amount of dissolved Sr increases from 24 $\mu\text{g/L}$ up to 300 $\mu\text{g/L}$ in the mountainous part of the basin, and then remains nearly stable for most of the riverine course, significantly changing only in the TP due to interaction with saline-rich components in the deltaic system (Fig. 3a). This means that along the UP river water progressively records incremental contributions from the weathered lithologies that sharply increase the dissolved Sr concentration. From the MP the Po river water initially shows a decrease in Sr concentration that becomes progressively more attenuated due to the increasing river discharge and “water maturity” approaching CaCO_3 saturation. Although it is clear that in some riverine systems part of the Sr dissolved load could be related to anthropogenic contributions (Roy et al., 1999), the homogeneous Sr elemental concentration throughout most of the Po river waters (before and after important urban settlements, industrial and agricultural sites) indicates that anthropogenic activities scarcely modify the budget of this element. This interpretation is supported by similarities between

modern Po river Sr contents and those assessed in “historical” (1950s) analyses of Po river water (300 $\mu\text{g/L}$; Gherardelli and Canali, 1960). Interestingly, $^{87}\text{Sr}/^{86}\text{Sr}$ variation along the river course appears less buffered than the elemental concentration. In particular, the river water in the mountainous part of the basin is characterized by very radiogenic isotopic values (up to 0.70974 at Pian del Re), compatible with the isotopic fingerprint of the lithologies outcropping in the Alpine sector of the catchment, which mainly consist of crystalline magmatic and metamorphic rocks of the basement (Fig. 3b). Among the tributaries of the UP part, the Pellice river shows the most extreme $^{87}\text{Sr}/^{86}\text{Sr}$ value (0.71233), coherent with the lithologies outcropping in its sub-basin that includes the Dora-Maira Massif constituted by Paleozoic metamorphic rocks (gneisses and mica-schists; see the Geological Map of Italy, sheet n. 154 entitled “Susa”) having $^{87}\text{Sr}/^{86}\text{Sr}$ values up to 0.79510 (Tilton et al., 1989).

In the MP, close to the city of Torino, the Po river water shows less radiogenic isotopic composition (0.70919), and especially after the confluence of the Dora Baltea tributary, the water displays a totally distinct composition (0.70863) probably related to the presence of Jurassic ophiolites in its sub-basin (Geological Map of Italy, sheet n. 90

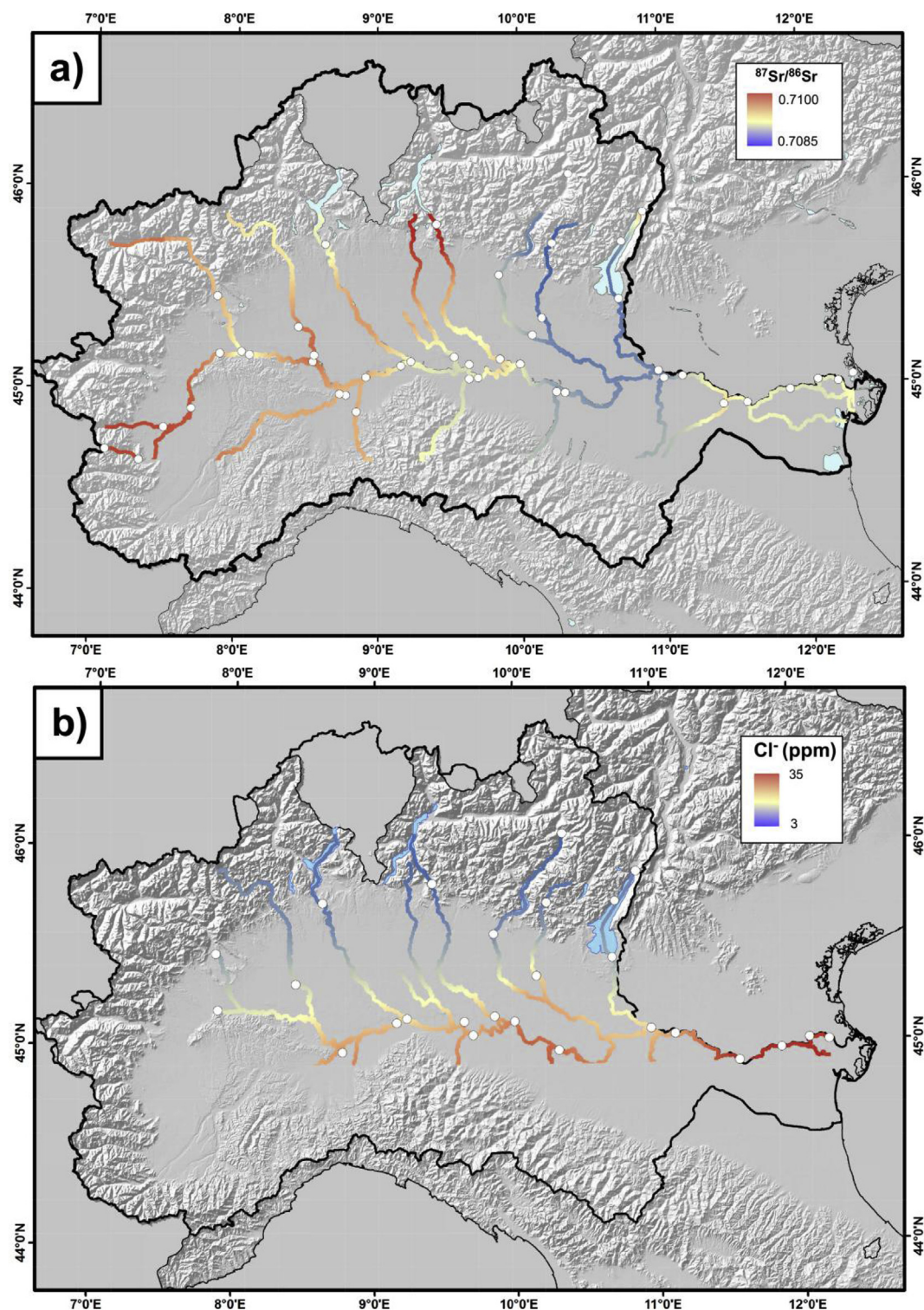


Fig. 4. Geochemical maps showing the spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ (a) and Cl^- (b) in river water within the Po basin, obtained merging original data presented in this paper with those by [Donnini et al. \(2016\)](#).

entitled “Aosta”). Down flow, the confluences of Tanaro, Scrivia (right bank), Sesia and Adda (left bank) rivers modify the Po river water, shifting its isotopic composition toward radiogenic values. In fact, Sesia and Adda are characterized by high $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.71000 and 0.70974, respectively) due to the outcrop of Paleozoic metamorphic rocks (Geological Map of Italy, sheet n. 56 entitled “Sondrio”) having very high $^{87}\text{Sr}/^{86}\text{Sr}$ in their catchments (up to 0.71470, [Pinarelli et al., 2008](#)) and Tanaro river shows $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70926, a value that is

coherent with the geology of its basin that includes silico-clastic rocks of Mesozoic to Tertiary age ([Maino et al., 2013](#)). Other confluences such as Ticino, Lambro, Oglio, Mincio (left bank) and Trebbia, Taro, Secchia (right bank) modify the Po river water, shifting its isotopic composition toward less radiogenic values. Ticino, Lambro, Oglio and Mincio are characterized by low isotopic values (down to 0.70877) due to widespread sedimentary Mesozoic carbonate outcrops in their sub-basins. Trebbia, Taro and Secchia have low $^{87}\text{Sr}/^{86}\text{Sr}$ values (average 0.70864)

in relation to the lithologies outcropping in their basins that include a sequence of Mesozoic to Tertiary sediments (with carbonates marls and flysches) and ophiolites (Geological Map of Italy, sheets n. 199 entitled “Parma sud” and n. 200 entitled “Reggio Emilia”). The last Apennine tributary is the Panaro river that drains Pliocene clays, and displays relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.70951). The TP of the river progressively shows more radiogenic values, plausibly reflecting an interaction with saline-rich components that could be represented by seawater, but also by saline-rich groundwater and/or sediments.

Seasonal variabilities of Po river water are not notable in the MP, which is characterized by relatively homogeneous $^{87}\text{Sr}/^{86}\text{Sr}$ (average 0.70910). By contrast, significant variations are observable in the TP where the hydrological conditions have a greater influence on the water geochemistry (Marchina et al., 2016b, 2017).

6. Discussion

6.1. Tracking weathering processes within the Po river catchment

Previous studies on the Po river water revealed that the oxygen and hydrogen isotopic composition is rather homogeneous along most of the riverine profile and in distinct hydrological periods, constantly preserving a Ca-HCO_3 hydrochemical facies (Marchina et al., 2015, 2016a). Preliminary considerations on the Rb/Sr ratio highlighted that the Po river water is usually characterized by values between 0.004 and 0.009, suggesting prevalent interaction with silicate rocks that predominate in the highlands of the catchment (Marchina et al., 2015), whereas interaction with carbonate lithologies (characterized by significantly lower Rb/Sr) seems to be subordinated. This is also supported by Supplementary Fig. 1, reporting Ca/K vs Sr/Rb in the Po river water, tributaries and water end-members circulating in crystalline and carbonate rocks, respectively. $^{87}\text{Sr}/^{86}\text{Sr}$ provides further constraints on the nature of rocks involved in the weathering processes that are variable in the different part of the hydrographic network. The presented data, coupled with those reported by Donnini et al. (2016) represent an extensive georeferenced Sr-isotopic hydroarchive of the Po river basin that allows geostatistical elaboration, properly finalized in the isotopic map of Fig. 4a. The map highlights that $^{87}\text{Sr}/^{86}\text{Sr}$ in Po basin evolves from the UP, where the highest $^{87}\text{Sr}/^{86}\text{Sr}$ values are recorded in relation to the weathering of igneous and metamorphic silicate rocks, to the MP where less radiogenic composition (down to 0.70890) are mainly driven by the confluence of the Oglio and Mincio tributaries which drain carbonate rocks of the South alpine domain. The lowering of $^{87}\text{Sr}/^{86}\text{Sr}$ value in this particular sector of the river is also induced by the inflow of Apennine rivers such as Trebbia, Taro and Secchia characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ value down to 0.70850. Down flow of these confluences, the Sr isotopic composition of Po river water rises to 0.70910 in relation to the confluence of the last Apennine tributary (Panaro, $^{87}\text{Sr}/^{86}\text{Sr}$ ca. 0.70951) and/or by hyporheic exchanges that were already identified by oxygen and hydrogen isotopes in the TP sector of the Po river (Marchina et al., 2015), as also indicated by the chlorine distribution shown in Fig. 4b.

Therefore, $^{87}\text{Sr}/^{86}\text{Sr}$ values are coherent with information provided by key elemental ratios useful to discriminate contributions by silicate rocks from the basement, that are prevalent in the upper Alpine part of the catchment (Piemonte), and carbonate rocks, that become widespread in the central part of the catchment where Po river receives contributions from the South-Alpine geological domain (Lombardia) and the Northern Apennines (Emilia-Romagna), where mafic ophiolite rocks are also present. Additional information can be retrieved by the $1/\text{Sr}$ (mg/L) vs $^{87}\text{Sr}/^{86}\text{Sr}$ diagram reported in Fig. 5, which highlights that the Po river water in UP has relatively low Sr elemental abundances coupled with highly radiogenic isotopic values, typical of weathering product of rocks included in the crystalline basement (Hosein et al., 2004; Pinarelli et al., 2014). Conversely, down flow in MP the Sr elemental concentration increases and the isotopic

composition become less radiogenic, thus revealing more significant contributions from weathering of carbonate rocks. In this diagram, we also reported the composition of water end-members draining carbonate and silicate rocks, respectively. A suitable water end-member draining carbonates has been identified in a neighbouring Alpine sector and is represented by Tagliamento river that is characterized by a mono-lithological basin dominated by Paleozoic – Mesozoic carbonate rocks (Donnini et al., 2016). The choice of a water end-member draining silicate rocks is more challenging due to the high variability of lithotypes that include a wide spectrum of metamorphic and magmatic rocks. Within the Po river basin, reasonable candidates could be represented by the Pellice river and rivers from the Chiavenna valley (Pinarelli et al., 2014). The carbonate end-member is characterized by very high Sr concentration (1250 $\mu\text{g/L}$) coupled with low $^{87}\text{Sr}/^{86}\text{Sr}$ (down to 0.70773). Silicate end-members are characterized by very low Sr concentration (down to 50 $\mu\text{g/L}$) coupled with high (0.71234, Pellice river) to very high (0.71800, Chiavenna Valley rivers) $^{87}\text{Sr}/^{86}\text{Sr}$ (Fig. 5). Calculations using Sr elemental and isotopic data and mixing equations (Faure, 1986) indicate that the silicate water end-members prevail especially in samples from the UP ($\approx 90\%$), and that the contribution of the carbonate water end-member, although increasing in the MP, remains subordinate (less than 40%). This confirms the insights provided by oxygen and hydrogen stable isotope compositions indicating that the predominant part of the runoff derives from the Alpine sector of the catchment, where silicate rocks are predominant (Marchina et al., 2015). Further constrain could be attained by future studies taking into considerations the geochemical fingerprint of the suspended load that is complementary to the dissolved load for the understanding of the physical weathering (cfr., Gaillardet et al., 1997; Roy et al., 1999). Significant variations are finally observed only in the river delta where trends toward more radiogenic Sr isotopic signatures (and higher TDS, and less negative $\delta^{18}\text{O}$ - δD ; Marchina et al., 2015) are related to interaction with saline-rich components. Sr elemental and isotopic mixing calculations indicate that the maximum seawater contribution recorded in TP do not exceed 5%.

A better understanding of the Po river system would also require the geochemical investigation of the groundwaters of connected aquifer systems that potentially interact with the riverine system, especially during low discharge period.

6.2. Comparison with other Alpine riverine systems

The largest rivers draining the Alps (i.e., the Po, Rhine, Rhône and Danube) are all characterized by calcium-bicarbonate water (Golterman and Meyer, 1985; Gaillardet et al., 1999; Pawellek et al., 2002; Hartmann et al., 2007; Donnini et al., 2016). In spite of this analogy, Po river water typically has a lower dissolved calcium, with respect to that of Rhine, Rhône and Danube, indicating significant differences in mineral equilibria and water-rock interactions in the distinct catchments. The $^{87}\text{Sr}/^{86}\text{Sr}$ values observed in the Po river are also distinctive from those measured in the Danube, Rhine and Rhône waters.

For the Danube river, the available data record $^{87}\text{Sr}/^{86}\text{Sr}$ ranging between 0.7086 and 0.7089 throughout most of the river course (Palmer and Edmond, 1989; Pawellek et al., 2002). For the Rhine river $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7092 was reported by Palmer and Edmond (1989), whereas more recent analyses gave distinctly less radiogenic values around 0.7085 (Tricca et al., 1999; Donnini et al., 2016). All available Rhône river $^{87}\text{Sr}/^{86}\text{Sr}$ data fall in the range 0.7087–0.7089 (Brass, 1976; Palmer and Edmond, 1989; Donnini et al., 2016). On the whole, the data indicate that the $^{87}\text{Sr}/^{86}\text{Sr}$ range between 0.70892 and 0.70975 represents the fingerprint of the weathering of lithologies included in the Alpine (s.l.) chain, including both carbonate and silicate rocks. Among these important catchments slightly more radiogenic compositions are observed in Po river waters, likely indicating that silicate rocks contribute comparatively more to the Po river water.

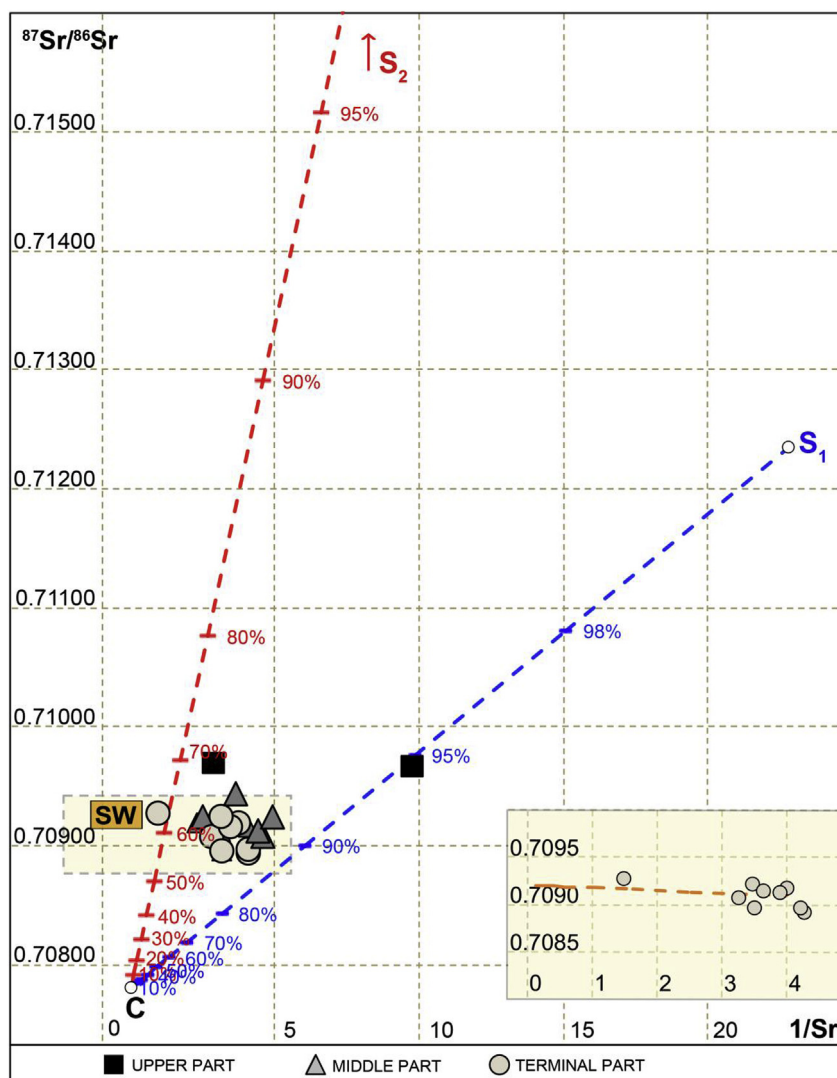


Fig. 5. Binary diagram reporting $1/Sr$ vs $^{87}Sr/^{86}Sr$ of the Po river waters: a) dashed lines represents the mixing between a carbonate water end member (C) and two distinct silicate water end members (S1 Pellice river; and S2 rivers from Chiavenna Valley, Pinarelli et al., 2014); percentages (%) represent the silicate contribution to the water chemistry. b) Inset showing mixing relation with seawater that occurs in the TP. Seawater composition is taken by Capo et al. (1998).

Classical interpretations of enhanced silicate weathering should imply a more relevant outcrop of silicate rocks in the Po river basin respect to the Danube, Rhine, and Rhône catchments, or that weathering in the Po river catchment is preferentially concentrated in sub-basins dominated by silicate rocks (as suggested by Malusà et al., 2017). Alternatively, a different weathering susceptibility of carbonate and silicate rocks in the distinct basins with diverse climatic conditions could be hypothesized may explain our observations. In other words, we consider that this slight isotopic difference between Po and the other Alpine rivers could be related to basin-scale climatic conditions, as the Po river basin is warmer relative to the Danube, Rhine and Rhône basins. The idea is supported by studies that emphasize a temperature dependence on the weathering of silicate rocks (Kump et al., 2000; Oliva et al., 2003; West et al., 2005; Li et al., 2016), and it is corroborated by studies which investigate the different involvements of silicate and carbonate lithologies at varying climatic conditions (Tipper et al., 2006; Tripathy et al., 2010; Rahaman et al., 2011; Hartmann et al., 2014; Donnini et al., 2016; Gaillardet et al., 2018). Noteworthy, the subsequent occurrence/magnitude of calcite precipitation, in turn strictly depending on climatic conditions (and plausibly more efficient in the Po system with respect to other Alpine catchments), could be an additional process which increases $^{87}Sr/^{86}Sr$ of riverine water (cfr. Jacobson et al., 2002;

Liu et al., 2017).

6.3. Geochemical fluxes and inference on the weathering rates of silicate rocks

In terms of geochemical fluxes, we can estimate the budget of the dissolved Sr conveyed by the river to the Adriatic Sea, as an average discharge of $1500 \text{ m}^3/\text{s}$ (at Pontelagoscuro) and a Sr concentration of $300 \mu\text{g}/\text{l}$, implying a total annual flux of ca. 14,050 tons of dissolved Sr transferred by the Po river to the sea. As indicated by isotopic mass balance, at least $\sim 60\%$ of this Sr budget comes from the weathering of silicate rocks, conforming to 12,772 tons/year of Sr. Considering an average concentration of Sr in silicate rocks (ca. $330 \text{ mg}/\text{kg}$; Rudnick and Gao, 2004) we can estimate that the dissolved fraction corresponds to 26 megatons of silicate rocks weathered annually within the Po river basin. This calculation, although not taking into consideration the contribution of the suspended solids (Corazzari et al., 2016), is consistent with previous estimations of the denudation rates of the Alps (Hinderer et al., 2013). Our results imply that the contribution of carbonate lithologies to the Sr budget seems to be subordinate, as also indicated by other authors that studied water geochemistry in Alpine catchments (Donnini et al., 2016).

7. Conclusions

The Sr geochemical and isotopic composition of the Po river represents a tracer of distinct weathering rates of different lithologies outcropping in its basin, whose contributions are progressively integrated from the source to the mouth. The highest $^{87}\text{Sr}/^{86}\text{Sr}$ heterogeneity and the most radiogenic values are recorded in the UP, where the river has a low discharge, low Sr contents and is accordingly particularly susceptible to the confluence of tributaries mainly draining silicate rocks of the crystalline basement. Po river water becomes isotopically less variable and less radiogenic in the MP due to the increase of its water discharge, Sr contents and to the inflow of tributaries draining carbonate lithologies from both South Alpines and Apennine domains. In the final MP and along the TP the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of Po river water approaches 0.7090–0.7091, remaining relatively homogeneous down to the delta, where Sr isotopes and other tracers (Cl^- , TDS, stable isotopes) detect mixing with seawater. The seasonal/annual monitoring of $^{87}\text{Sr}/^{86}\text{Sr}$ in selected sampling sites reveal variations up to 0.0002, and are interpreted as manifestations of the different hydrological contributions observable within the catchment.

Taken as a whole, the slightly more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ composition of the Po river water, with respect to those of other important rivers draining the Alps (Danube, Rhine, Rhône) denotes a comparatively higher weathering of the silicate rocks within its basin. This observation does not necessarily require a higher silicate/carbonate outcrop in the Po river basin, and could be related to a more effective weathering rate of silicate rocks in warmer conditions typical of southern Europe (Fatichi et al., 2014). The existence of relationships between weathering and climatic conditions have been observed in temperate regions by Gaillardet et al. (1999) and Gaillardet et al. (2018) for silicate and carbonate rocks, respectively.

Accordingly, the $^{87}\text{Sr}/^{86}\text{Sr}$ of water from these river systems could usefully serve a proxy of large scale differential weathering rates, which, together with stable isotopes, provides a snapshot of the existing conditions and suggests that future monitoring could be informative of ongoing climatic changes.

Appendix A. Supplementary data

Supplementary data related to this chapter can be found at <https://doi.org/10.1016/j.apgeochem.2018.08.024>.

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