Università degli Studi di Ferrara

DOTTORATO DI RICERCA IN
SCIENZE DELLA TERRA

CICLO XXVII

COORDINATORE Prof. Massimo Coltorti

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

Settore Scientifico Disciplinare GEO/09

Dottorando	**Tutore**
Dott. Marchina Chiara	Prof. Bianchini Gianluca
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Anni 2012/2014

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Abstract

The Po river cross east-west the whole Northern Italy and flows within a densely populated area characterized by intense agriculture and industrial activities. In spite of its importance, systematic geochemical and isotopic investigations of its water are rare and never reported for the whole basin scale. The aim of this study was to fill this knowledge gap investigating the Po river water through a chemical and multi-isotopic approach that includes oxygen, hydrogen, carbon, nitrogen sulphur and strontium isotope data.

The Po river flows within the Padanian plain, which 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 and cover an area of more than 71,000 km^2 (a quarter of the national territory). 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 enhanced during the glaciation periods. 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). The first flood period reflects the intense late fall rains, while the second is due to snow melt from the higher sectors of the. The average discharge rate is 1,500 m^3/s and maximum peak flows of 10,300 m^3/s at section of Occhiobello, which is located in the lower reach of the river (close to the city of Ferrara), right upstream of the deltaic system.

The isotopic compositions (δ^{18}O - δD) 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 of the Apennines tributaries is less important. Geochemical and isotopic data show that the Po river water attains a homogeneous composition at ca. 100 km from the spring. The average composition measured at Occhiobello is characterized by δ^{18}O 9.6‰, δD 64.0‰, TDS (Total Dissolved Solids) 260 mg/L, chloride 15 mg/L and by a general Ca–HCO_3 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 8,000 mg/L and 4,000 mg/L, respectively). The comparison of the data presented in this thesis with historical chemical analyses of Po river (available for the past fifty years) indicates that the major components (i.e. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO3, Cl, SO4) of the runoff water remained constant over the last decades suggesting that they reflect natural compositions unaffected by anthropogenic activities; in contrast, nitrate drastically increases from less than 1 mg/L to an average value of 9 mg/L as result of diffuse contamination. Coherently, $\delta^{13}C$ (between -11.4‰ and -4.4‰) and $\delta^{34}S$ (between 4.2‰ and 8.0‰) and also the $^{87}Sr/^{86}Sr$ (between 0.70896 and 0.70974) are compatible with the weathering and dissolution processes that involve the lithologies outcropping in the basin, while extremely variable $\delta^{15}N$ (between -4.1‰ and 18.0‰) indicates contribution from pollutants of urban origin as well as components released by the agricultural and zootechnical activities. These observations confirm that although the origin of the main constituents of the Po river water is geogenic, anthropogenic contributions are also effective. The data also highlight an evolution of the dissolved nitrogen species that appear extremely reactive, especially in the deltaic part of the river, which is characterized by denitrification processes.

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. It has to be noted that the presented data represent a snapshot of the nowadays river condition, and that future monitoring will be useful to highlight a) progressive involvement of further anthropogenic components and b) on-going environmental (climatic) changes. For these reasons this research contribute to integrate the GLObal River Chemistry (GLORICH) database (Hartmann et al. 2014, Proc Earth Plan Sci) which is a useful tool to monitor earth surface processes at extensive scales and high resolution, and also to implement existing isotopic hydro-archives that provide additional information that cannot routinely be recovered from elementary chemistry alone (Bowen et al. 2009, Earth Plan Sc).

1 PREFACE

The current PhD project is the follow up of my undergraduated thesis that was focused on the geochemical study of Po River waters in the surrounding of Ferrara (Marchina, 2011). Developing this thesis I familiarized with the analytical facilities (ion chromatography, ICP-MS) available at the University of Ferrara (Department of Physics and Earth Sciences) in order to obtain information on major and trace elements of the riverine waters. In this framework, I also spent a period at the IGG-CNR of Pisa under the supervision of Dr. Luigi Dallai to analyze stable isotopes ($\delta^{18}O$ – δD) in water samples by IRMS (isotope ratio mass spectrometry). In the PhD project I decided to extend the geochemical study to the whole river that was sampled in different seasons during the three year of the project (April 2012, August 2012, March 2013, May 2013, May 2014) in several sites located between the Monviso sources to the delta, where the river flows toward the Adriatic Sea. Note that PhD project was greatly favoured by the acquisition (just in the initial period of my PhD project) of a new instrument (CRDS Los Gatos LWIA 24-d isotopic analyser) for the analyses of the water stable isotopes that became essential for the development of the current research. My geochemical background was subsequently enriched by another stage at the CNR of Pisa (June 2012, November-December 2013) devoted to the analyses of the strontium isotopes of Po River water in collaboration with Dr. Maddalena Pennisi, and by a 4 months research period in the framework of a “Erasmus Placement program” (from March 2013 to July 2013) at the Helmholtz-Zentrum für Umweltforschung (UFZ) of Leipzig/Halle (Germany), where I developed a fruitful collaboration with Prof. Kay Knöller in order to investigate the carbon-nitrogen-sulphur isotopes of the dissolved components of Po river water. In the third year I implemented the geochemical and isotopic analyses of the dissolved components investigating the suspended matter in the Po river waters using an additional new IRMS instrument acquired by the Department of Physics and Earth Sciences of the University of Ferrara. Finally, thanks to an additional scholarship (specifically dedicated to youth researchers), provided by the University of Ferrara, I spent a three months visiting period in the USA at the New Hampshire University, where the Po River water were investigated by MC-ICP-MS, under the supervision of Professor Julie Bryce and her collaborators. This period was of fundamental importance to discuss the existing hypothesis and to initiate the writing of this thesis (and of related papers) in the english language. In the following sections I report the outcome of these distinct research periods, in order to provide new insights on the processes and dynamics occurring in this important river.

2 OVERVIEW ON THE PO RIVER AND ITS BASIN

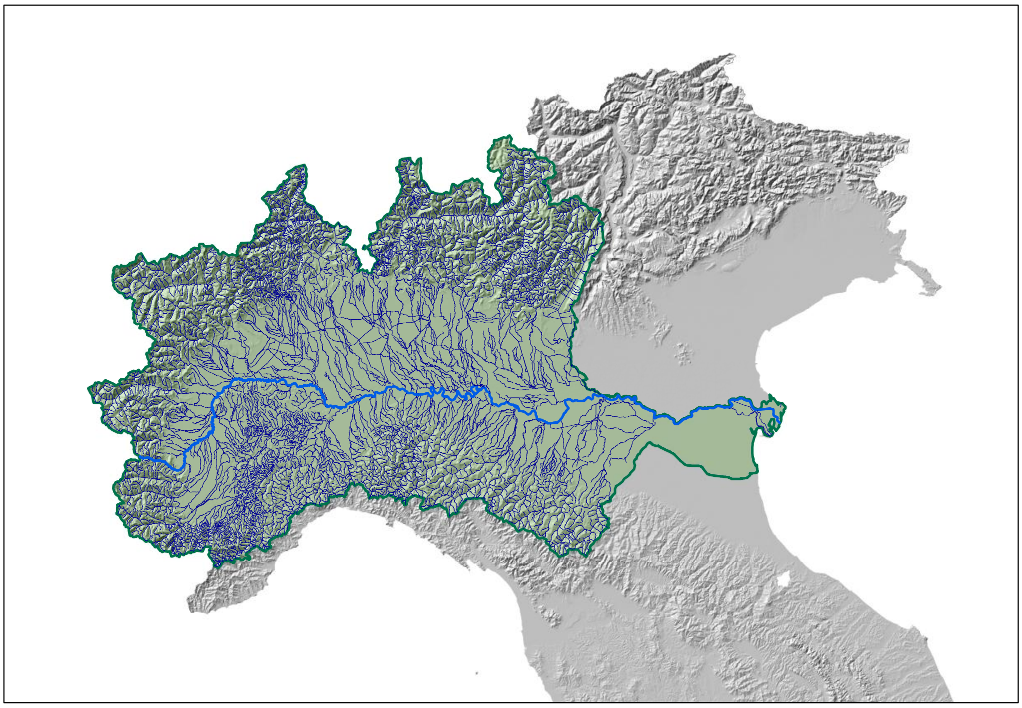

Figure 1: Po River catchment area (Northern Italy). The Po river course is represented in light blue.

The Po plain (Figs 1 and 2 Ch. 2) 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 becomes more important with the addition of 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). 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).

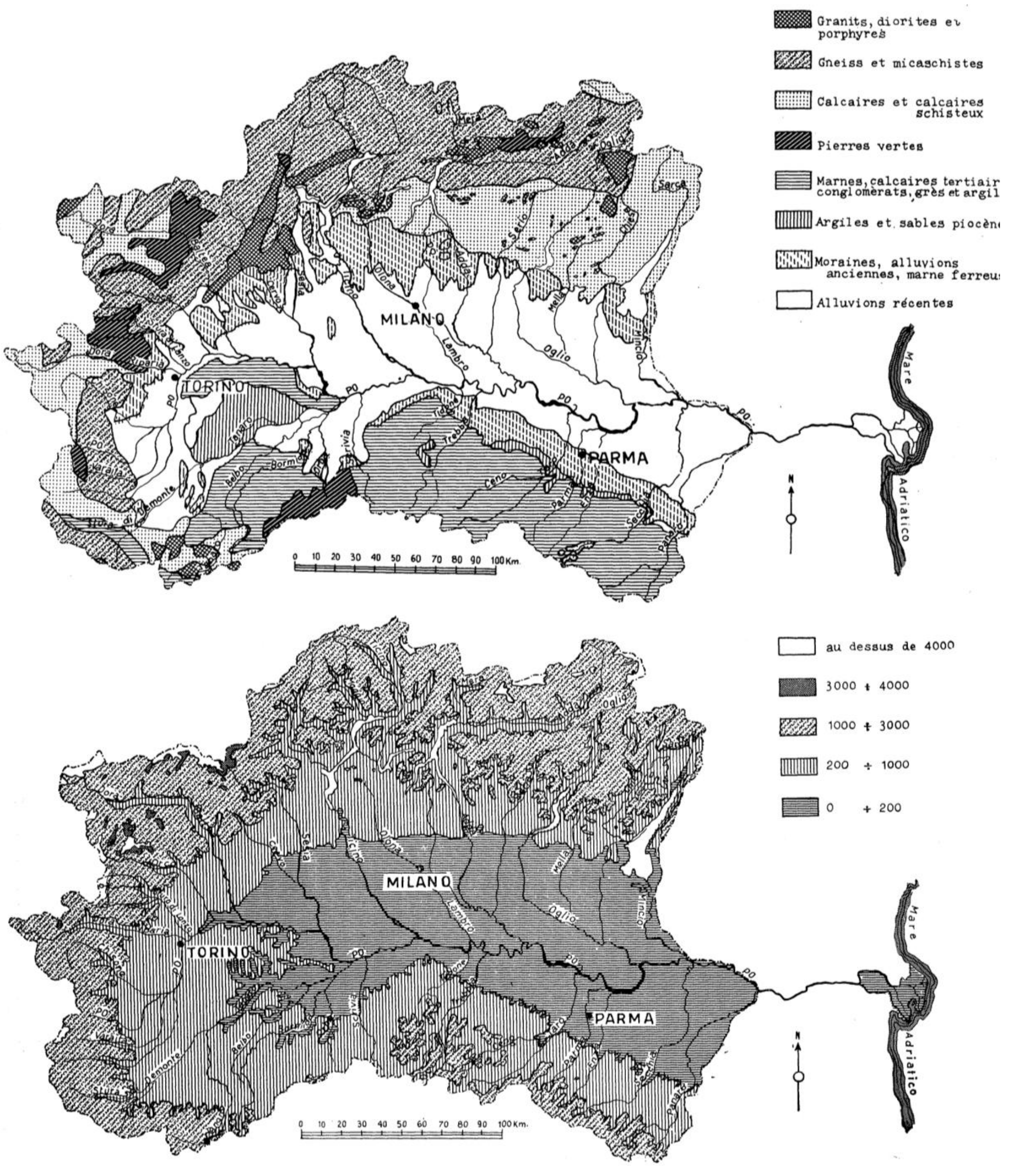

Fig. 3

Figure 2: Schematic lithological map of the Po River drainage basin and relative elevation map from Canali and Allodi (1962)

With regard to the water budget, the main Alpine tributaries (left bank) often display discharge higher than 100 m^3/s (Dora Baltea, 110 m^3/s, Ticino 290 m^3/s, Adda up to 160 m^3/s), whereas the Apennine tributaries (right bank) usually show discharge lower than 50 m^3/s. The Tanaro river draining the Maritime Alps (Liguria) is the only right bank tributary with high average discharge (up to 130 m^3/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 m^3/s after 5 km from the spring, 50 m^3/s after ca. 90 km from the source, 958 m^3/s at Piacenza (300 km from the spring), 1115 m^3/s at Cremona (350 km from the spring), 1,500 m^3/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 comprised 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 limestone compositions of Triassic and Jurassic age. The northern Apennines is mainly made of Tertiary flysh (alternation of sandstone and pelite rocks) and 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).

3 PRELIMINARY GEOCHEMICAL INVESTIGATION ON THE PO RIVER IN THE SURROUNDINGS OF FERRARA (years 2010 - 2011)

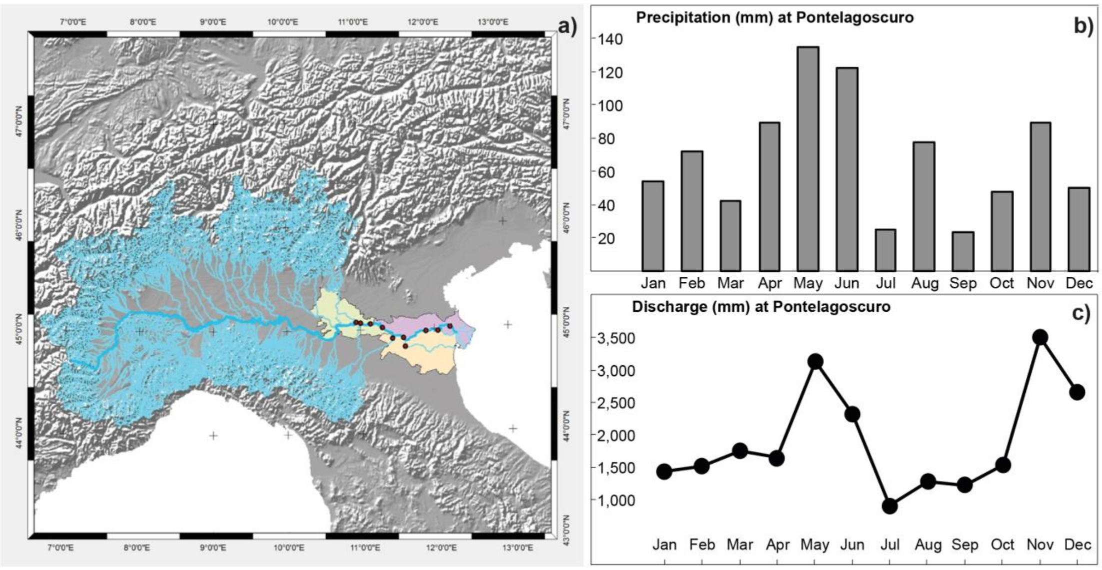

Figure 1: a) Location of the Po River watershed (investigated area) in Northern Italy and relatively sampling station (red dots) of the sampling campaigns in the years 2010 – 2011; b) Average monthly precipitation at Pontelagoscuro station (Ferrara) during the year 2010; c) Discharge of the Po river in the section of Pontelagoscuro (Ferrara) during the year 2010.

This chapter briefly reports the data carried out in the period August 2010, November 2010 and February 2011, available for the restricted zone in the surrounding of Ferrara (Fig. 1a, Ch. 3). This represents the incipit of the current PhD project on the geochemistry of Po river water. This sampling and the relative data were carried out under the supervision of Dr. Claudio Natali in a phase in which I wasn't independent yet. Therefore a more detailed description of the analytical methods will be reported in the next chapters for the subsequent sampling campaigns in which my operative role has been predominant.

Table 1, Ch. 3 reports some parameters measured in the field (temperature, pH and water conductivity) as well as major and trace elements (reported in mg/L and µg/L respectively). The investigated waters display a Ca-HCO_3 hydrochemical facies, with limited seasonal variation. As concerns dissolved heavy metals V, Cr, Mn, Fe, Ni never exceed the drinking water tolerance threshold. Anomalous concentration of iron (1,200 µg/L), aluminium (650 µg/L) and manganese (89 mg/L) is recorded only in Crespino site during the flood of November 2010 (Q= 6050 m^3/s), whereas arsenic is generally high (15-21 µg/L) throughout the whole sample population. Note that in Fig. 2 a) and b), Ch. 3 a significant Fe-Al correlation is observed among the samples collected in the summer season, and the sample collected at Crespino during the flood of November 2010 has the highest value registered.

a)

n.	Name	Date	T (°C)	pH	EC (µS/cm)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/L)	SO_4^{2-} (mg/L)	Cl^-(mg/L)	Br^- (mg/L)	NO_3^- (mg/L)	TDS (mg/L)
1	*Ficarolo*	08/2010	25	7.6	499	50.0	11.2	8.92	2.07	213	30.2	11.7	nd	5.23	332
2	*Castelmassa*	08/2010	25	7.9	507	50.5	11.0	8.81	2.05	214	30.5	12.2	nd	5.25	334
3	*Sustinente*	08/2010	26	7.9	494	49.7	11.4	8.76	1.96	183	27.9	11.7	nd	4.46	299
4	*S,Benedetto Po*	08/2010	25	7.8	510	54.3	11.7	9.40	2.13	183	32.2	12.8	nd	5.48	311
5	*Revere*	08/2010	25	7.9	505	52.7	11.9	9.44	2.07	214	31.1	12.5	nd	3.91	337
6	*Occhiobello*	08/2010	26	4.1	506	52.3	11.6	9.14	2.09	195	30.7	12.1	0.02	4.69	318
7	*Crespino*	08/2010	18	8.2	420	51.1	11.6	10.3	2.33	183	31.0	12.5	nd	8.22	310
8	*Papozze*	08/2010	19	8.3	420	48.5	11.0	9.80	2.20	183	30.6	12.5	0.05	8.44	306
9	*Loreo*	08/2010	20	8.0	550	61.3	18.3	12.7	3.36	256	32.2	17.0	nd	11.0	412
10	*Taglio di Po*	08/2010	19	8.4	450	54.6	12.7	11.9	2.29	183	32.8	14.1	0.03	8.25	320
11	*Crespino*	11/2010	12	8.3	310	44.1	9.16	6.01	2.18	na	43.7	19.6	0.06	11.2	nd
12	*Revere*	11/2010	7	8.4	520	na	na	na	na	na	44.6	19.9	0.05	11.4	nd
13	*Castelmassa*	02/2011	7	8.3	510	na	na	na	na	na	44.0	19.2	0.07	11.0	nd
14	*Bottrighe*	02/2011	7	8.4	520	na	na	na	na	na	45.2	19.7	0.10	11.2	nd
15	*Loreo*	02/2011	6	8.5	1150	na	na	na	na	na	75.7	124	0.35	22.9	nd
16	*Ca Morosini (Lendinara)*	11/2010	10	8.2	380	48.2	12.0	5.9	1.8	120	41.0	15.0		7.10	104

b)

n.	Name	Date	Li	Rb	Sr	Fe	Al	V	Cr	Mn	Ni	As
1	*Ficarolo*	08/2010	6.69	1.31	271	6.42	28.6	1.11	0.62	5.96	3.09	16.5
2	*Castelmassa*	08/2010	1.59	1.10	265	11.8	23.2	1.09	11.9	2.43	2.06	17.2
3	*Sustinente*	08/2010	1.63	1.11	245	2.68	12.6	1.05	0.35	1.54	2.03	16.4
4	*S,Benedetto Po*	08/2010	1.48	1.14	288	9.94	54.6	1.08	0.48	2.20	2.56	18.3
5	*Revere*	08/2010	1.55	1.37	275	117	96.8	1.44	0.71	3.35	1.84	17.7
6	*Occhiobello*	08/2010	1.48	1.31	278	na	0.31	1.21	0.33	6.46	1.80	17.8
7	*Crespino*	08/2010	9.01	1.43	278	na	na	1.01	0.50	na	2.11	17.3
8	*Papozze*	08/2010	1.75	1.30	266	2.84	na	0.94	0.70	na	2.05	15.7
9	*Loreo*	08/2010	3.63	1.43	222	na	30.0	1.91	0.07	na	1.48	20.6
10	*Taglio di Po*	08/2010	2.23	1.45	307	153	92.5	1.14	1.50	10.1	2.90	17.4
11	*Crespino*	11/2010	3.06	2.23	252	1224	652	2.37	4.06	89.0	9.33	14.5
12	*Revere*	11/2010	na	na	na	na	na	na	na	na	na	na
13	*Castelmassa*	02/2011	na	na	na	na	na	na	na	na	na	na
14	*Bottrighe*	02/2011	na	na	na	na	na	na	na	na	na	na
15	*Loreo*	02/2011	na	na	na	na	na	na	na	na	na	na
16	*Ca Morosini (Lendinara)*	11/2010	2.7	1.88	185	280	200	1.02	1.09	13.2	2.19	14.7

Table 1 : a) Physico-chemical parameters of surface waters of the Po river measured in the field in the different locality and chemical composition. Major elements are represent in mg/L b) trace elements (in µg/L). *"na"* for samples not analyzed, *"nd"* for the elements not detected.

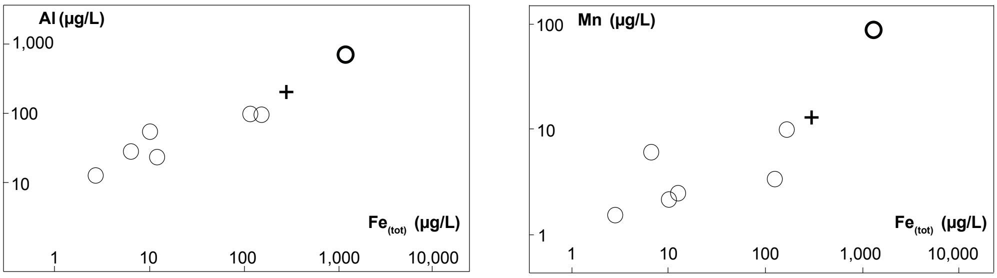

Figure 2: Po river waters in the terminal part of the river a) binary diagram Fe vs Al; b) binary diagram Fe vs Mn.

These waters have been also analysed by IRMS at the IGG-CNR of Pisa, under the supervision of Dr. Luigi Dallai to measure the isotopic composition oxygen and hydrogen. The data have been also useful to calibrate a new instrument that was acquired in that period at the Department of Physics and Earth Sciences of the University of Ferrara. This instrument is a Los Gatos, CRDS LWIA *24-d* (Fig 3 a and b. Ch. 3).

Figure 3: a) The Los Gatos CRDS LWIA *24-d* liquid-water stable isotope instrument; b) vacuum pump, drierite column are shown in the background.

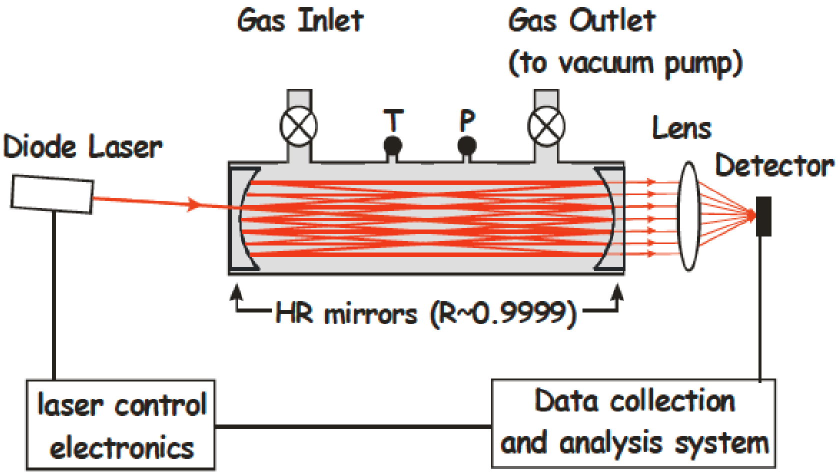

Fig. 4: Technical Overview Off-Axis Integrated Cavity Output Spectroscopy

I actively contributed to the set up of this instrument that allows an innovative quick and cost effective method to analyse isotopic composition of waters alternative to the more established IRMS technique.

The Off-axis integrated cavity output spectroscopy (OA-ICOS) exploits Beer-Lambert's law (Ricci et al., 1994) to relate the absorption of a laser light passing through a vaporized water sample to the isotopic composition of the sample (Fig. 4, Ch.3). Another important feature of this instrument is the simultaneous analysis of ^{2}H and ^{18}O for each injection of water, reducing time and operational expenses per measured sample. In addition, simultaneous measurements exclude the potential relative error of two separate measurements of hydrogen and oxygen isotopes at different times.

A certificate attesting my experience and competence on this analytical technique is reported in the appendix A.

It has to be noted that the cross-check between the oxygen and hydrogen isotopic composition obtained by IRMS and those obtained by CRDS Los Gatos LWIA-24d revealed a good precision and accuracy inn the order of 0,1‰ and 0,4 ‰ for δ^{18}O and δD, respectively. The data, reported in Table 2 and Fig. 3, represent the preliminary results of an hydro-archive on the Po river waters, that has been greatly improved in the subsequent years of the PhD project.

			IRMS			***LWIA 24-d***		
	Name	**Date**	**δ^{18}O (‰)**	**δD (‰)**	**d-exc (‰)**	**δ^{18}O (‰)**	**δD (‰)**	**d-exc (‰)**
1	*Ficarolo*	08/2010	-9.5	-66.9	10.1			
2	*Castelmassa*	08/2010	-9.7	-68.8	9.8			
3	*Sustinente*	08/2010	-9.2	-64.8	9.7			
4	*S,Benedetto Po*	08/2010	-10.1	-69.4	12.4			
5	*Revere*	08/2010	-9.6	-66.2	11.6			
6	*Occhiobello*	08/2010	-9.4	-64.5	11.6			
7	*Crespino*	08/2010	-9.6	-65.5	12.3			
8	*Papozze*	08/2010	-9.6	-67.0	10.8			
9	*Loreo*	08/2010	-9.2	-64.1	10.4			
10	*Taglio di Po*	08/2010	-9.5	-63.5	13.5			
11	*Crespino*	11/2010	-9.9	-65.4	14.8	-9.8	-65.1	14.7
12	*Revere*	11/2010				-9.4	-65.1	11.3
13	*Castelmassa*	02/2011	-10.8	-66.4	21.0			
14	*Bottrighe*	02/2011	-10.7	-66.7	19.8			
15	*Loreo*	02/2011	-8.6	-62.5	7.1			
16	*Ca Morosini (Lendinara)*	11/2010	-10.2	-70.0	12.6	-10.8	-75.3	11.9

Tabella 2: Hydrogen and oxygen isotope ratios in the Po river waters in the terminal part of the river. Data are expressed in ‰ respect to the SMOW standard.

The recorded δ ^{18}O values ranging between -10.8‰ and -8.6‰, and δ D values ranging between -69.4‰ and -62.5‰ are compared with the local groundwaters (Rapti Caputo and Martinelli, 2008), the Northern Italy Meteoric Water Line (Longinelli and Selmo, 2003) and the Global Meteoric Water Line (GMWL) from Craig (1961) in Fig. 5 Ch. 5. In spite of the sampling area is located in lower part of the river course (close to the Adriatic sea), the surface waters mainly reflect isotopic composition of precipitation in the Upper Part of the basin located in Piedmont region and reported in Longinelli and Selmo (2003; 2006).

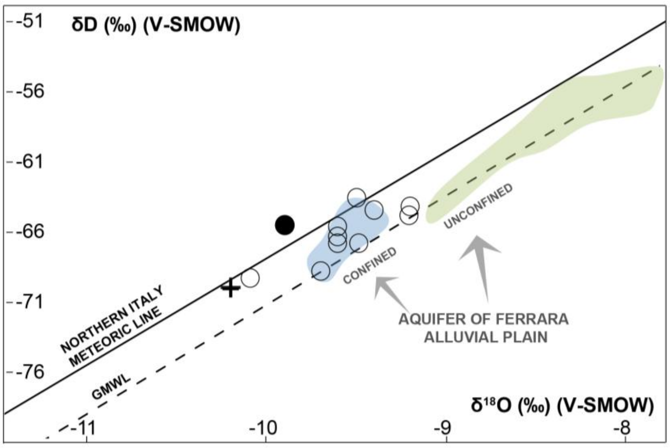

Figure 5: $\delta^{18}O$ - δD isotopic composition of Po river water for the sampling campaign of August 2010. Po river waters are represent with white circles, Meteoric water lines are also reported for comparison: the dotted line represents the global meteoric water line (GMWL; Craig 1961); the dashed line represents the local meteoric water line (LMWL), defined for Northern Italy (Longinelli and Selmo 2003). The black cross represents sample collected in the Adige river in November 2011.

4 ACTIVITY OF THE FIRST YEAR, BASED ON THE SAMPLING CAMPAIGNS 2012

In this period I carried out the first systematic sampling of the whole river that was thoroughly investigated using the analytical facilities available at the University of Ferrara. The outcome of the activity of this year has been synthetized in a paper titled “The Po river water from the Alps to the Adriatic Sea (Italy): new insights from geochemical and isotopic ($\delta^{18}O$-δD) data” that is currently in press on “Environmental Sciences an Pollution Research” (Marchina et al., in press).

4.1 Sampling strategies and analytical methods

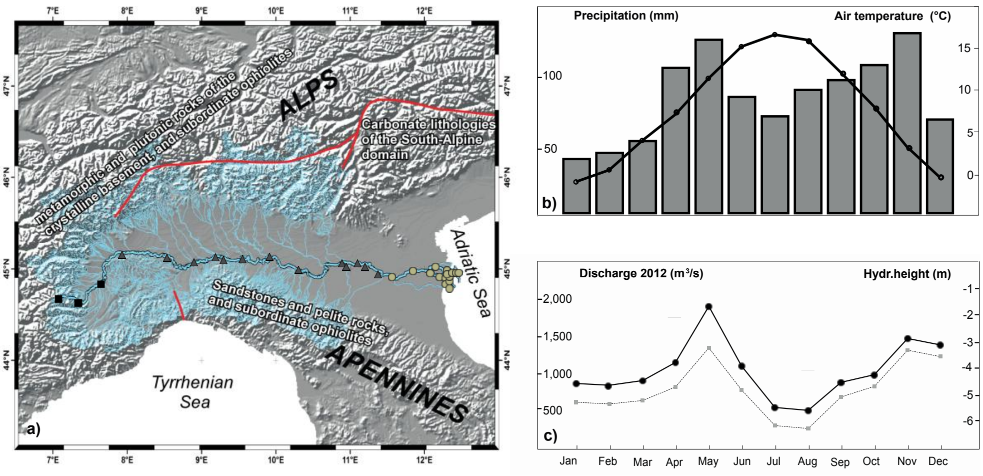

Figure 1: a) Hillshade map of the Po river catchment (based on NASA SRTM data) reporting the sampling locations where Po river water samples have been collected. Distinct symbols have been used for water sampled at increasing distance from the source in the upper part (UP, black squares), middle part (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

In the first year two sampling campaigns were plan in order to investigate the runoff water of the Po river at basin scale. For this purpose 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 (Tab. 1, Ch. 4 and Fig.1 Ch. 4). 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 (Tab. 1, Ch. 4), 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 HNO_3) 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 Tab. 2, Ch. 4. The isotopic ratios of $^2H/^1H$ and $^{18}O/^{16}O$ are expressed as δ notation [$\delta = (R_{sample}/R_{standard} - 1)*1000$] 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 $\delta^{18}O$ 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 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 (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 Tab. 3, Ch. 4. 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, [(Σcations−Σanions)/(Σcations+Σanions)]*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 log10 transformed data. Considering that I was interested in the reflection of large-scale features (>10 km) of the river water composition, I 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.

4.2 Results and discussion

pH, temperature and conductivity of Po river waters

Parameters measured in-situ such as pH, temperature and conductivity of Po river water have been reported in Tab. 1, Ch. 4. 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 µS/cm) through MP (average 370 µS/cm), up to TP where samples were more heterogeneous (average 410 µS/cm). Higher conductivity (up to 8,500 µS/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.

n.	Name	Data	Latitude	Longitude	pH	T (°C)	EC (µS/cm)
	Upper Part (UP)						
1	*Pian del Re*	04/2012	44°42' 04.00"	07° 05' 42.00"	8.9	6	80
2		08/2012			8.8	6	110
3	*Sanfront*	04/2012	44° 39' 03.89"	07° 19' 58.90"	8.2	9	120
4		08/2012			8.8	16	190
5	*Carignano*	04/2012	44° 54' 31.37"	07° 41' 29.93"	8.0	16	470
6		08/2012			7.8	21	510
	Middle Part (MP)						
7	*Settimo Torinese*	08/2012	45° 07' 29.63"	07° 46' 15.37"	8.6	24	540
8	*Crescentino*	04/2012	45° 10' 32.96"	08° 05' 55.61"	8.2	17	470
9		08/2012			8.2	23	566
10	*Frassineto Po*	04/2012	45° 08' 39.77"	08° 32' 27.29"	8.6	19	490
11		08/2012			8.5	28	450
12	*Balossa Bigli*	04/2012	45° 03' 58.00"	08° 54' 48.80"	8.0	18	380
13		08/2012			7.7	25	310
14	*Rea*	08/2012	45° 07' 27.90"	09° 09' 31.96"	8.0	26	200
15	*Ticino river (Vaccarizza)*	04/2012	45° 08' 40.88"	09° 13' 48.62"	8.2	16	230
16		08/2012			8.4	26	450
17	*Senna Lodigiana*	04/2012	45° 07' 46.41"	09° 38' 07.16"	8.0	18	370
18		08/2012			8.6	26	440
19	*Adda river (Crotta d'Adda)*	08/2012	45° 09' 18.97"	09° 51' 13.62"	8.0	25	500
20	*Piacenza*	08/2012	45° 03' 41.76"	09° 41' 53.51"	8.7	25	430
21	*Cremona*	04/2012	45° 07' 43.34"	09° 59' 45.93"	8.0	18	350
22		08/2012			8.7	26	430
23	*Coltaro*	04/2012	44° 59' 03.67"	10° 18' 27.70"	8.2	17	360
24		08/2012			7.8	27	420
25	*Mincio river (Governolo)*	08/2012	45° 05' 11.58"	10° 57' 43.99"	8.6	24	310
26	*Revere*	04/2012	45° 03' 27.46"	11° 07' 52.80"	8.0	16	370
27		08/2012			7.8	27	420
	Terminal Part (TP)						
28	*Occhiobello*	04/2012	44° 55' 04.78"	11° 34' 46.10"	8.5	16	360
29		08/2012			8.0	27	480
30	*Crespino*	04/2012	44° 58' 37.64"	11° 52' 53.06"	8.2	17	400
31		08/2012			8.0	28	480
32	*Bottrighe*	04/2012	45° 01' 15.17"	12° 04' 44.24"	8.4	17	400
33		08/2012			7.6	29	460
34	*Taglio di Po*	04/2012	45° 00' 36.12"	12° 13' 09.12"	8.2	17	410
35		08/2012			7.5	30	450
36	*Po di Levante (Porto Levante)*	04/2012	45° 02' 43.00"	12° 19' 27.52"	8.0	19	1,010
37		08/2012			7.5	31	450
38	*Po di Goro (mouth)*	08/2012	44° 47' 36.80"	12° 23' 44.80"	7.9	28	8,500
39	*Po di Goro (Gorino Veneto)*	08/2012	44° 50' 15.54"	12° 20' 42.18"	7.8	29	5,700
40	*Po di Gnocca (Santa Giulia)*	08/2012	44° 50' 18.30"	12° 22' 30.08"	7.8	29	3,600
41	*Po di Gnocca (Polesinino)*	08/2012	44° 52' 28.70"	12° 20' 27.60"	7.7	29	1,780
42	*Po di Gnocca (Donzella)*	08/2012	44° 55' 54.10"	12° 19' 31.40"	7.7	30	450
43	*Po di Venezia (Villa Regia)*	08/2012	44° 57' 14.30"	12° 17' 56.00"	7.7	31	430
44	*Po della Pila (Cà Zuliani)*	08/2012	44° 57' 25.90"	12° 25' 14.30"	7.8	30	810
45	*Po della Pila (near Pila)*	08/2012	44° 57' 25.00"	12° 27' 05.00"	7.7	30	1,127
46	*Busa Dritta (mouth)*	08/2012	44° 58' 00.00"	12° 31' 47.00"	7.8	30	5,500
47	*Po di Goro (Serravalle)*	12/2011	44° 58' 09.85"	12° 03' 27.05"	7.9	6	470
48		08/2012			7.7	28	440
49	*Po di Goro (Ariano)*	12/2011	44° 56' 35.07"	12° 07' 23.17"	8.1	6	480
50		08/2012			7.7	28	440
51	*Po di Goro (Mesola)*	12/2011	44° 55' 27.29"	12° 13' 17.96"	8.4	6	460
52		08/2012			7.6	28	440
53	*Po di Goro (S. Giustina)*	12/2011	44° 53' 36.51"	12° 17' 03.35"	8.2	6	470
54		08/2012			7.6	28	1,160

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.

Isotopic composition of Po river waters

The δD‰ and δ^{18}O‰ isotopic ratios have been measured for Po river water sampled in distinct hydrological periods of the year 2012. δD‰ ranges from -92.0‰ to -48.0‰ in winter-spring and from -94.7‰ to -55.1‰ in summer, whereas δ^{18}O‰ 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, Ch.4 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 Mediterranean provenance (e.g. rain in Greece; Dotsika et al., 2010) which can provide the isotopic fingerprint of vapour mass end-members potentially interesting in this 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. 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, Ch. 4 modified after Longinelli and Selmo 2003). Coherently, Montanari (2012) shows 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 δ^{18}O varying from -13.4‰ to -11.1‰ and δD varying from -94.7‰ to -75.3‰. The average δ^{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 δ^{18}O varying from -12.5‰ to -8.4‰ and δD varying from -84.7‰ to -60.1‰. The average δ^{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 δ^{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

n.	Name	Data	$\delta^{18}O$ (‰)	δD (‰)	d-exc (‰)
	Upper Part (UP)				
1	*Pian del Re*	04/2012	-13.1	-92.0	14.4
2		08/2012	-13.4	-94.7	13.7
3	*Sanfront*	04/2012	-12.7	-82.9	19.8
4		08/2012	-12.1	-84.2	13.9
5	*Carignano*	04/2012	-11.6	-78.9	15.0
6		08/2012	-11.1	-75.3	14.6
	Middle Part (MP)				
7	*Settimo Torinese*	08/2012	-10.7	-74.9	11.9
8	*Crescentino*	04/2012	-11.0	-71.6	17.8
9		08/2012	-10.6	-74.0	11.9
10	*Frassineto Po*	04/2012	-11.0	-75.4	14.0
11		08/2012	-10.4	-72.2	11.6
12	*Balossa Bigli*	04/2012	-9.7	-67.4	11.1
13		08/2012	-9.8	-69.4	10.3
14	*Rea*	08/2012	-9.8	-69.4	10.3
15	*Ticino river (Vaccarizza)*	04/2012	-9.1	-64.5	9.0
16		08/2012	-8.9	-62.8	9.6
17	*Senna Lodigiana*	04/2012	-9.5	-62.7	14.4
18		08/2012	-9.6	-60.4	17.6
19	*Adda river (Crotta d'Adda)*	08/2012	-9.2	-62.3	12.6
20	*Piacenza*	08/2012	-9.2	-62.8	11.9
21	*Cremona*	04/2012	-9.4	-63.8	12.4
22		08/2012	-9.2	-62.4	12.4
23	*Coltaro*	04/2012	-9.3	-61.1	14.0
24		08/2012	-9.3	-62.0	13.5
25	*Mincio river (Governolo)*	08/2012	-9.1	-62.3	11.3
26	*Revere*	04/2012	-8.9	-63.5	8.2
27		08/2012	-9.2	-60.6	14.3
	Terminal Part (TP)				
28	*Occhiobello*	04/2012	-8.8	-58.0	12.9
29		08/2012	-8.7	-60.1	13.2
30	*Crespino*	04/2012	-9.6	-61.2	16.2
31		08/2012	-8.9	-60.9	12.8
32	*Bottrighe*	04/2012	-9.9	-59.4	21.0
33		08/2012	-9.1	-58.8	14.7
34	*Taglio di Po*	04/2012	-9.8	-59.6	19.8
35		08/2012	-9.0	-58.8	14.1
36	*Po di Levante (Porto Levante)*	04/2012	-7.0	-48.0	8.7
37		08/2012	-6.9	-55.1	0.6
38	*Po di Goro (mouth)*	08/2012	-7.8	-57.2	5.7
39	*Po di Goro (Gorino Veneto)*	08/2012	na	na	-
40	*Po di Gnocca (Santa Giulia)*	08/2012	na	na	-
41	*Po di Gnocca (Polesinino)*	08/2012	-7.3	-59.4	0.0
42	*Po di Gnocca (Donzella)*	08/2012	-7.4	-60.4	-0.4
43	*Po di Venezia (Villa Regia)*	08/2012	-7.5	-60.8	0.0
44	*Po della Pila (Cà Zuliani)*	08/2012	-7.3	-60.2	-1.0
45	*Po della Pila (near Pila)*	08/2012	na	na	-
46	*Busa Dritta (mouth)*	08/2012	-8.1	-58.6	6.9
47	*Po di Goro (Serravalle)*	12/2012	-9.3	-64.0	11.6
48		08/2012	-8.6	-61.7	7.9
49	*Po di Goro (Ariano)*	12/2012	-9.6	-62.1	15.7
50		08/2012	-8.7	-61.2	9.4
51	*Po di Goro (Mesola)*	12/2012	-9.3	-63.1	12.1
52		08/2012	-8.8	-61.2	9.8
53	*Po di Goro (S. Giustina)*	12/2012	-9.6	-61.6	16.3
54		08/2012	-8.5	-60.3	8.4

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 δ‰ respect to the SMOW standard. na = not analyzed.

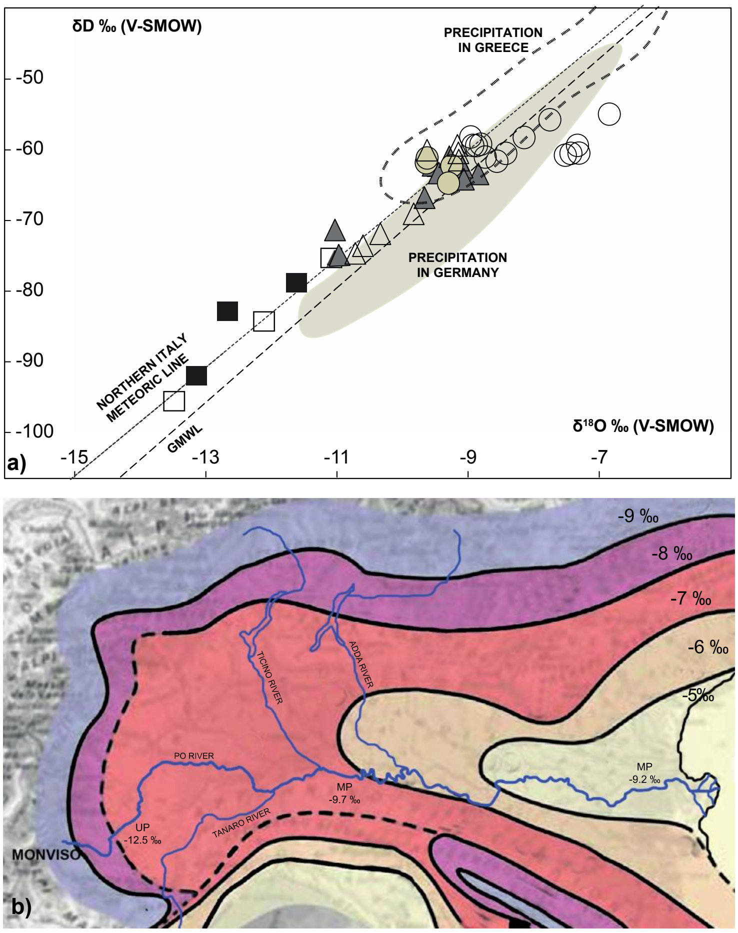

Figure 2: a) δ^{18}O-δD isotopic composition of Po river water. Meteoric water lines are also reported for comparison: the dotted line represents the Global Meteoric Water Line (GMWL; Craig 1961); the dashed line represents the Local Meteoric Water Line, defined for Northern Italy (LMWL; Longinelli and Selmo 2003), together with compositional fields relative to meteoric precipitation of prevalent Atlantic provenance (e.g. rain in Germany; Stumpp et al., 2014) and meteoric precipitation of prevalent 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.

The isotopic variability observed along the river profile is presented in Fig. 3, Ch. 4 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 (r2 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 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 (r2 = 0.98), while in the MP a linear regression better describes the relations between these parameters (r2 = 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 ($\delta^{18}O$ ~ -9.5 ‰) suggests that the associated riverine system integrate multiple contributions, which are mixed and homogenized. This indicates that significant water volumes, which buffer further variations, already characterize the MP sector of the river. Changes observed at the most important tributary confluence (Ticino river), progressively disappear after few kilometres being homogenized within the riverine water mass, whereas isotopic variations due to the confluence of Apennine tributaries (having $\delta^{18}O$ ~ -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.

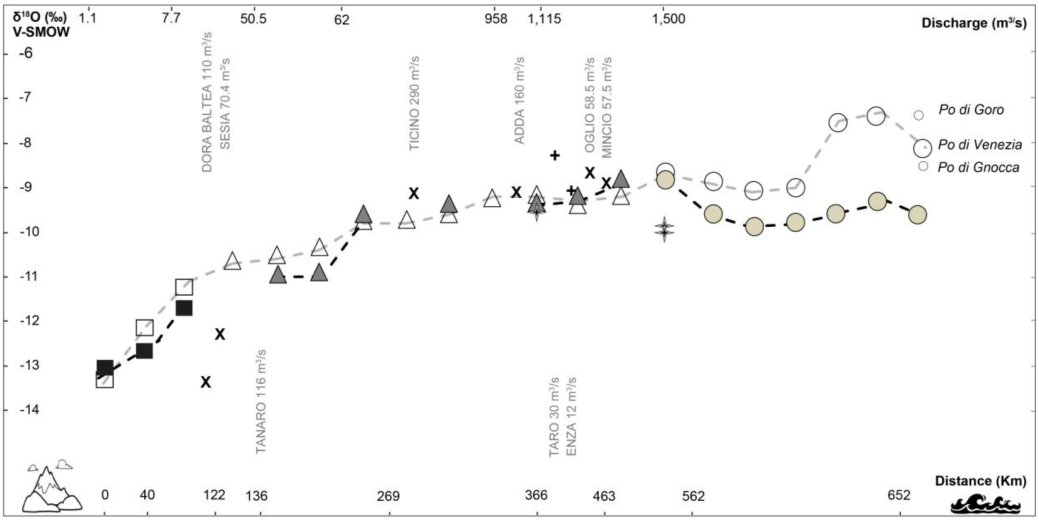

Figure 3: Variation of the $\delta^{18}O$ signature in function of the distance from the source of the Po river. The relation with the discharge of the main course and the principal tributaries is also reported. Filled symbols (black square for UP, grey triangle for MP, light grey circle for TP) for 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 divided in two different size: 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).

The presented data, including isotopic composition of river water sampled in distinct periods (April and August 2012) allow us to evaluate relationships between the δ‰ values and the temperature. From the data presented in Fig. 1b Ch. 4 (air temperature), Tab. 1, Ch. 4 (water temperature), and Tab. 2, Ch. 4 (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 $\Delta\delta^{18}O/T°C$ gradient of ~ 0.1‰, 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 in which meteoric contribution of different seasons mix together.

Noteworthy, the UP-MP Po river water displays remarkable $\delta^{18}O$-δD similarity to the groundwater from the first confined aquifer (depth of 20 to 50 m, in the Ferrara surroundings) of the alluvial plain, suggesting a common Alpine origin and/or repeated river-aquifers exchanges; on the contrary water of the shallow phreatic aquifers displays less depleted isotopic compositions more influenced by local precipitations, and is scarcely influenced by interaction with the Po river (Rapti-Caputo and Martinelli, 2009). Particular emphasis has to be 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 $\delta^{18}O$ 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 Tab. 2, Ch. 4 it is also report the values of the deuterium excess calculated as: d-exc = $\delta D - 8 * \delta^{18}O$ 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-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-exc values recorded in the UP and MP river sectors are intermediate between those recorded in north-European precipitations (e.g. in Germany, 6-12 ‰; Stumpp et al., 2014) and those of south-Mediterranean precipitations (e.g. in Greece12.9-20‰; Dotsika et al., 2010). The d-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 $\delta^{18}O$ shift toward less negative compositions (Fig. 2a, Ch. 4). The observed isotopic differences along the trunk of the Po river are emphasized in the Fig. 3, Ch. 4 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 remained constant in the last years, as the $\delta^{18}O$ value reported by Iacumin et al. (2009) for Po river close to Cremona is nearly identical to the values recorded by my 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 (Tab. 3, Ch. 4).

		Major dissolved ions (mg/L)											Trace elements (μg/L)							
Number	Name	Data	Na^+	Mg^{2+}	K^+	Ca^{2+}	$Fe_{(tot)}$	Cl^-	Br^-	NO_3^-	SO_42^-	HCO_3^-	TDS	Li	B	Rb	Sr	As	Cr	Ni
Upper part (UP)																				
1	*Pian del Re*	04/2012	0.38	2.14	0.11	14.3	nd	0.86	0.06	1.44	5.01	45	69	nd	nd	nd	20.0	nd	nd	nd
2		08/2012	0.57	0.89	0.32	19.0	nd	0.18	0.21	1.51	5.42	45	73	0.13	nd	0.21	26.5	3.00	nd	0.88
3	*Sanfront*	04/2012	1.00	3.53	0.56	17.8	nd	2.55	0.05	2.64	12.4	66	107	nd	nd	nd	100	nd	nd	nd
4		08/2012	1.93	5.06	0.55	25.1	nd	2.76	nd	2.29	17.6	90	145	0.13	nd	0.13	129	4.59	nd	0.36
5	*Carignano*	04/2012	6.11	13.2	1.82	68.0	0.02	10.1	0.06	2.64	48.4	470	620	1.40	nd	1.01	412	12.9	0.31	2.19
6		08/2012	4.00	10.1	1.30	61.4	nd	12.7	nd	3.12	50.4	510	653	0.51	nd	0.06	259	13.7	nd	nd
Middle part (MP)																				
7	*Settimo Torinese*	08/2012	7.52	11.4	1.44	46.4	nd	20.5	0.02	18.4	86.4	186	378	1.78	nd	0.39	455	12.1	nd	nd
8	*Crescentino*	04/2012	9.70	14.0	1.39	63.6	nd	16.1	nd	7.59	59.0	225	396	nd	nd	nd	380	10.0	nd	nd
9		08/2012	10.2	13.6	1.80	82.7	nd	18.6	0.04	9.05	41.6	210	388	2.00	nd	0.31	405	15.1	nd	0.21
10	*Frassineto Po*	04/2012	13.8	16.3	2.84	71.2	nd	15.0	nd	5.98	na	171	296	nd	nd	nd	470	10.0	nd	nd
11		08/2012	8.05	10.9	1.58	63.1	0.03	17.0	0.02	11.7	55.0	nd	167	1.87	nd	1.18	354	9.64	nd	1.00
12	*Balossa Bigli*	04/2012	8.43	8.68	1.86	45.8	0.01	16.4	0.05	0.06	58.7	120	260	nd	nd	nd	280	10.0	nd	nd
13	*Rea*	08/2012	11.5	12.8	2.99	68.9	nd	25.8	0.05	7.23	46.4	nd	176	1.61	nd	0.76	287	15.4	nd	3.22
14	*Ticino river* (*Vaccarizza*)	04/2012	4.72	4.30	1.19	32.2	nd	7.47	0.05	4.81	30.6	99	184	nd	nd	nd	150	6.00	nd	nd
15		08/2012	5.60	5.74	1.31	44.1	nd	9.07	nd	9.41	32.2	90	197	0.44	nd	0.9	150	8.44	nd	nd
16	*Senna Lodigiana*	04/2012	13.8	10.7	2.93	54.9	nd	15.5	0.06	0.18	38.2	126	262	nd	nd	nd	290	10.0	nd	nd
17		08/2012	9.84	8.57	1.68	60.4	nd	23.1	0.08	11.7	40.1	156	311	1.08	nd	0.67	227	11.7	nd	nd
18	*Adda river* (*Crotta d'Adda*)	08/2012	6.41	10.2	1.57	42.3	nd	13.1	nd	5.81	42.3	151	273	0.94	nd	0.55	181	16.8	nd	nd
19	*Piacenza*	08/2012	9.64	8.84	1.92	63.2	nd	12.0	0.09	8.18	30.1	145	279	1.08	nd	0.71	225	11.6	nd	nd
20	*Cremona*	04/2012	8.88	9.00	2.59	48.8	nd	15.1	0.05	6.47	38.1	150	279	nd	nd	nd	260	10.0	nd	nd
21		08/2012	7.97	8.63	2.08	57.3	nd	22.0	0.04	7.46	78.2	165	349	1.09	nd	0.71	200	10.8	nd	0.74
22	*Coltaro*	04/2012	9.44	9.07	1.66	57.3	0.01	12.1	0.04	4.70	32.9	84	211	nd	nd	nd	300	10.0	nd	nd
23		08/2012	8.15	8.26	1.71	51.9	nd	19.7	0.06	10.1	38.7	165	304	1.24	nd	0.79	218	9.34	nd	nd
26	*Mincio river* (*Governolo*)	08/2012	9.40	11.7	2.13	54.3	nd	12.8	nd	5.48	32.2	183	311	1.48	14.9	1.14	288	18.3	0.48	2.56
27	*Revere*	04/2012	13.7	11.5	2.59	63.3	nd	23.3	0.05	4.64	43.2	150	312	nd	nd	nd	330	10.0	nd	nd
28		08/2012	8.97	8.71	1.58	56.8	0.01	23.3	0.07	4.64	43.2	150	297	1.43	nd	0.72	235	10.6	nd	0.45
Terminal part (TP)																				
29	*Occhiobello*	04/2012	10.7	9.85	2.14	54.0	3.55	12.7	0.04	6.40	31.8	165	293	nd	nd	nd	310	10.0	nd	nd
30		08/2012	11.4	10.6	1.61	63.9	nd	24.8	nd	4.49	42.8	180	340	1.59	nd	0.68	239	9.68	nd	nd
31	*Crespino*	04/2012	13.0	11.2	1.82	62.6	0.06	15.1	0.07	7.12	37.6	150	299	nd	nd	nd	340	10.0	nd	nd
32		08/2012	11.7	10.7	2.14	58.6	nd	25.3	0.04	3.95	42.0	135	289	1.79	20.0	1.01	237	11,2	nd	1.21

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.. nd = not detected.

Table 3 (continued)

		Major dissolved ions (mg/L)											Trace elements (μg/L)							
Number	Name	Data	Na^+	Mg^{2+}	K^+	Ca^{2+}	$Fe_{(tot)}$	Cl^-	Br^-	NO_3^-	SO_42^-	HCO_3^-	TDS	Li	B	Rb	Sr	As	Cr	Ni
33	*Bottrighe*	04/2012	14.1	11.8	2.70	57.8	0.05	15.4	0.05	7.06	37.8	120	267	nd	nd	nd	340	10.0	nd	nd
34		08/2012	14.3	13.4	1.91	63.3	nd	24.7	0.05	4.32	45.5	135	302	1.69	20.0	0.89	234	10,7	3.00	0.75
35	*Taglio di Po*	04/2012	13.4	11.8	1.82	61.5	nd	14.7	0.07	3.50	37.0	156	300	nd	nd	nd	330	10.0	nd	nd
36		08/2012	11.4	10.8	1.76	61.2	nd	24.6	0.09	0.25	16.2	150	276	1.65	20.0	0.79	237	11.6	nd	0.57
37	*Po di Levante (Porto Levante)*	04/2012	1919	262	92.5	115	nd	4827	11.2	7.44	730	234	8198	40.0	830	30.0	1790	20.0	nd	10.0
38		08/2012	1096	151	43.8	73.8	nd	4197	nd	7.73	603	135	6307	20.5	1000	11.8	953	15.5	nd	1.12
39	*Po di Goro (mouth)*	08/2012	1099	153	45.4	90.8	nd	3886	9.51	7.39	573	na	5864	18.0	479	11.0	966	17.0	nd	5.00
40	*Po di Goro (Gorino Veneto)*	08/2012	681	96.8	27.4	71.9	nd	2468	6.10	2.56	332	na	3685	11.9	324	7.47	692	13.8	nd	2.50
41	*Po di Gnocca (Santa Giulia)*	08/2012	374	59.1	16.8	69.4	0.08	1421	nd	nd	226	na	nd	7.00	179	4.05	485	13.0	nd	4.79
42	*Po di Gnocca (Polesinino)*	08/2012	172	32.7	8.17	62.7	nd	596	1.48	2.65	114	na	990	4.00	91.0	2.68	347	11.2	nd	2.28
43	*Po di Gnocca (Donzella)*	08/2012	12.3	9.95	2.36	49.6	nd	30.4	0.06	3.11	40.4	na	148	16.1	24.0	1.12	236	11.5	nd	2.24
44	*Po di Venezia (Villa Regia)*	08/2012	13.2	12.2	2.47	62.2	nd	25.4	0.09	4.55	46.4	na	167	16.4	25.0	0.99	254	12.2	nd	2.01
45	*Po della Pila (Cà Zuliani)*	08/2012	15.0	12.8	2.48	64.1	nd	169	0.44	0.68	19.6	na	285	16.4	25.0	0.98	241	12.7	nd	1.17
46	*Po della Pila (near Pila)*	08/2012	56.2	17.9	3.22	64.7	nd	170	0.79	0.68	19.6	na	333	2.29	42.0	0.99	272	10.3	nd	1.67
47	*Busa Dritta (mouth)*	08/2012	580	83.4	25.3	70.2	nd	2334	5.65	3.60	361	na	3463	11.2	292	6.97	679	13.3	nd	1.68
48	*Po di Goro (Serravalle)*	12/2012	19.1	13.6	2.68	60.0	0.08	22.4	0.09	10.6	46.6	150	325	2.36	59.2	1.52	379	14.9	nd	3.50
49		08/2012	15.6	15.2	2.59	51.9	nd	23.2	0.09	6.01	44.8	171	330	1.93	38.3	1.58	341	13.4	nd	nd
50	*Po di Goro (Ariano)*	12/2012	17.2	13.0	2.25	63.4	0	22.0	0.06	11.1	46.7	156	332	2.42	38.2	1.59	390	14.5	nd	2.34
51		08/2012	16.0	16.0	2.07	52.3	nd	22.5	0.07	5.49	44.0	141	299	1.95	35.8	1.72	338	10.9	nd	nd
52	*Po di Goro (Mesola)*	12/2012	17.3	13.0	1.58	60.5	0	21.7	0.07	11.0	46.2	144	315	2.55	36.0	1.46	370	10.2	nd	0.40
53		08/2012	16.2	16.5	2.42	56.4	nd	22.8	nd	6.55	45.6	135	301	2.05	36.5	1.90	363	13.1	nd	nd
54	*Po di Goro (S. Giustina)*	12/2012	16.8	12.8	2.05	65.1	0.06	21.3	0.08	10.4	46.4	150	325	2.51	33.8	1.50	389	14.7	nd	1.71
55		08/2012	149	32.6	5.47	62.2	nd	320	0.85	5.52	81.7	144	801	4.05	92.8	3.70	465	11.8	nd	nd

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 that the chemical variations along the river course, starting from the sources of Pian del Re, synthetized in the notional Gibbs diagram where TDS values (y-axis) are plotted against the $[Na^{+/}(Na^{+}+Ca^{2+})]$ ratio (x-axis, Fig. 4, Ch. 4).

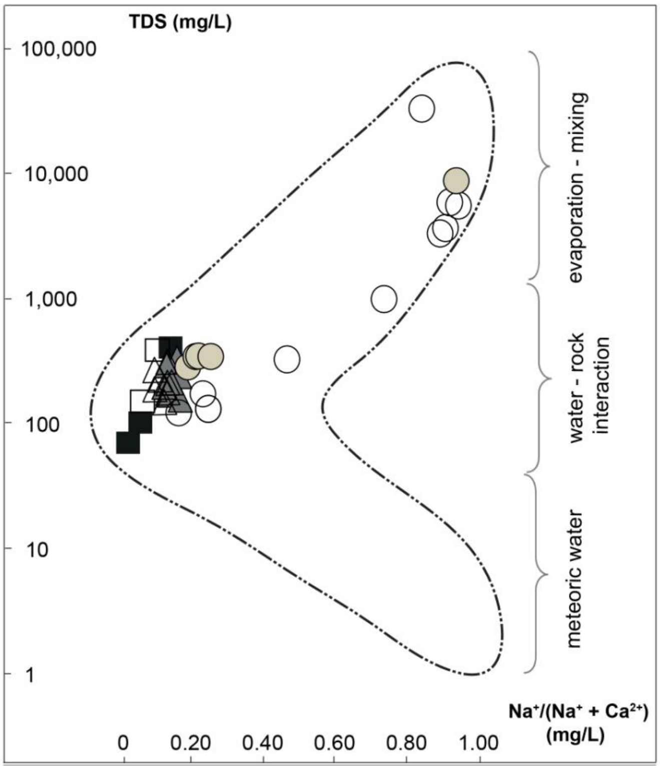

Figure 4: Gibbs diagram: TDS vs [Na/(Na+Ca)] reported in mg/L for the Po river water. Filled symbols (black square for UP, grey triangle for MP, light grey circle for TP) for samples collected in winter-spring; open symbols (square for UP, triangle for MP, circle for TP) for the samples collected in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

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 $[Na^{+/}(Na^{+}+Ca^{2+})]$ ratios observed in the MP samples. More extreme $[Na^{+/}(Na^{+}+Ca^{2+})]$ 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, Ch. 4 where it can be observed that Po river water mainly exhibits a bicarbonate-alkaline earth hydrochemical

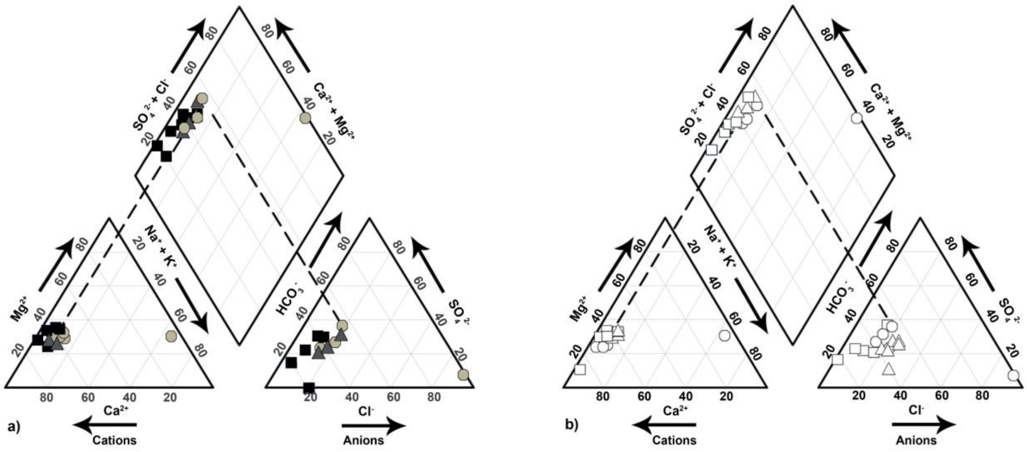

Figure 5: Piper classification diagram reporting composition of River Po water a) samples collected in winter-spring, b) samples collected in summer.

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: Ca^{2+}/Na^+ (molar) is 21.6-6.4 and 3.8-2.3 for UP and MP, respectively; Mg^{2+}/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 analysed 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, Ch. 4 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).

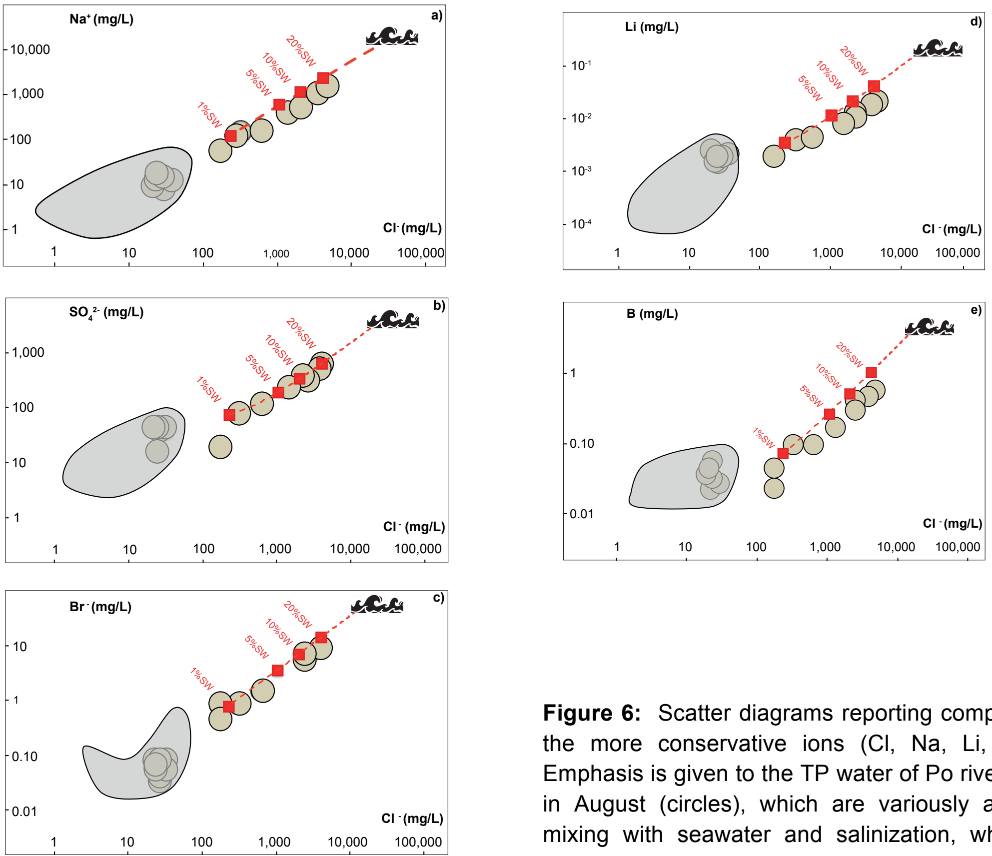

Figure 6: Scatter diagrams reporting compositions of the more conservative ions (Cl, Na, Li, Br, SO_4). Emphasis is given to the TP water of Po river collected in August (circles), which are variously affected by mixing with seawater and salinization, whereas the remaining UP and MP samples are grouped 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 ≈ 20% of mixing with seawater.

Anthropogenic contributions are superimposed on the geochemical fingerprint, as indicated by the concentration of nitrate (Fig. 7a, Ch. 4) that reaches the highest values in the MP samples (12 mg/L). It is interesting to note that in the MP of the river the dissolved NO_3^- is systematically higher in winter-spring than in summer, whereas in the TP of the river 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 higher nitrate concentration has been detected close to the city of Parma and Piacenza where agricultural 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.

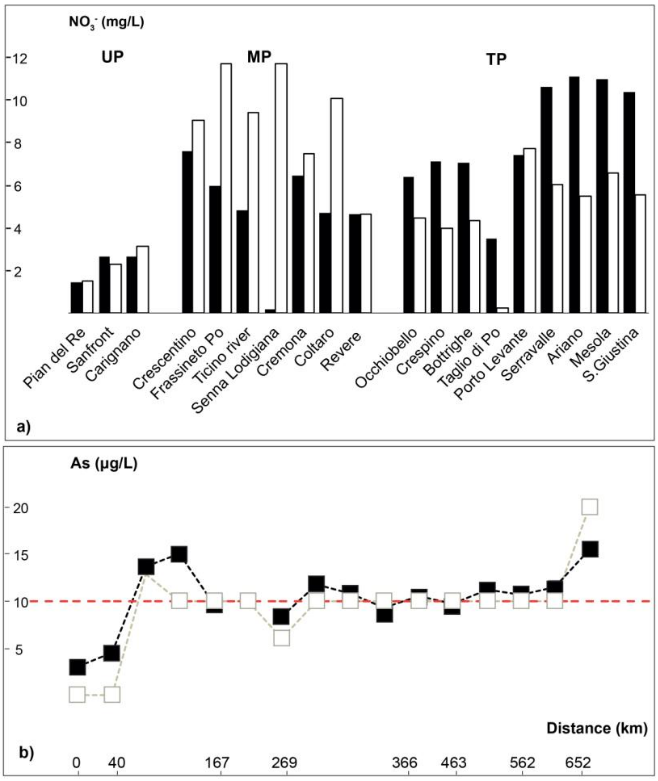

Figure 7: a) Histograms representing the NO_3^- dissolved in different Po river sites in distinct hydrological periods (expressed in mg/L; white color, winter-spring; black color, summer). b) arsenic concentration (expressed in µg/L) along the Po river profile (white squares, winter-spring; black squares, summer).

Emphasis is also given to elements that are potentially toxic and hazardous in water for drinking purposes (e.g.: As, Ni, Cr; Tab. 3, Ch. 4). For example, arsenic (Fig. 7b, Ch. 4) 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 µg/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). The analyses (Tab. 3, Ch. 4) 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 µg/l in the natural water of the area, i.e. significantly lower than the European drinking standards (20 and 50 µg/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 one in the Po river sediments, whereas it is always lower than one 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 Nikel 2005).

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 neighbours, 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).

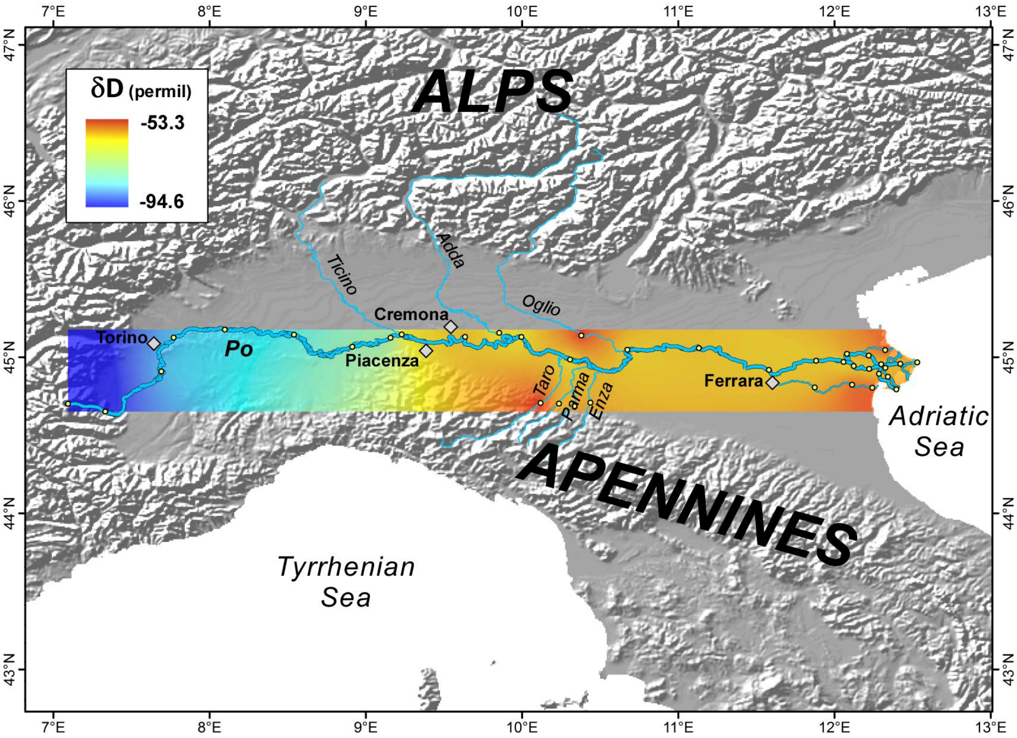

Figure 8: Geochemical map showing the δD (‰) spatial variation along the geographical extent of Po river. For interpretation refer to the colored web version of the paper.

In this study, spatial interpolation techniques have been used to define the geochemical variability of Po river waters along its main channel, also considering the potential contribution of some alpine and apennine tributaries (additional data from Iacumin et al. 2009; Delconte et al. 2014). The 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.

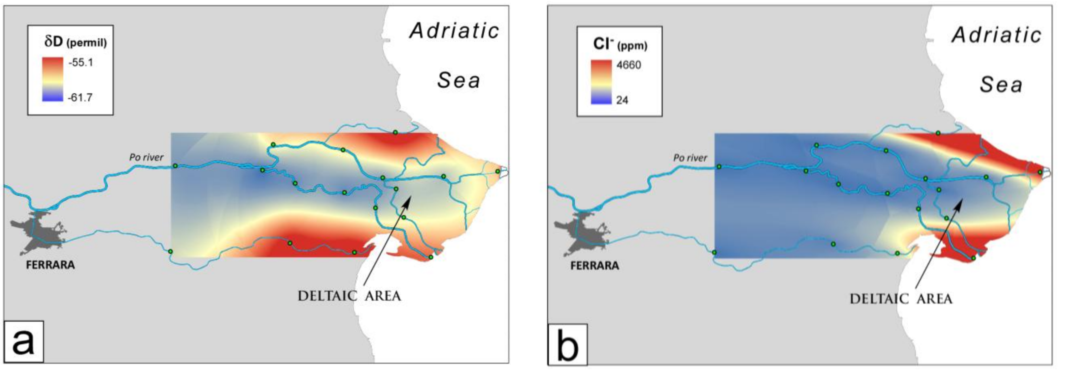

Figure 9: Geochemical maps focused on the deltaic part of the Po river showing a) the δD (‰) and b) the chloride (mg/l) spatial variation, respectively. For interpretation refer to the colored web version of the paper.

Interpolation models reveal that the Po riverine distribution of both $\delta^{18}O$ 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, Ch. 4 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, Ch. 4 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, Ch. 4 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, which 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 vapour 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.

5 ACTIVITY OF THE SECOND YEAR, BASED ON THE SAMPLING CAMPAIGNS 2013

The activity of the second year started with other two sampling campaigns (March 2013, May 2013) in which samples have been collected in the same sites delineate in the previous chapter. The related samples have been investigated to carry out major ions as well as oxygen and hydrogen isotopes. In addition, this chapter presents the analyses of other isotopic tracers such as carbon, sulphur and nitrogen ($\delta^{13}C$, $\delta^{34}S$, $\delta^{15}N$) that provide further information to understand the river geochemical cycles and its dynamics. Furthermore, the current chapter reports the analyses of suspended matter collected during the same year in the Po river water. The presented data implement the discussion of the previous chapters in order to discriminate natural compositions and superimposed anthropogenic components. In fact, as widely described in the literature (Mook, 2005; Garrels et al, 1973; Schulte et al. 2011) 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 components transferred to the sea. A manuscript containing the outcome of this chapter has been already submitted to the Journal “Environmental Monitoring and assessment”.

5.1 Sampling strategies and analytical methods

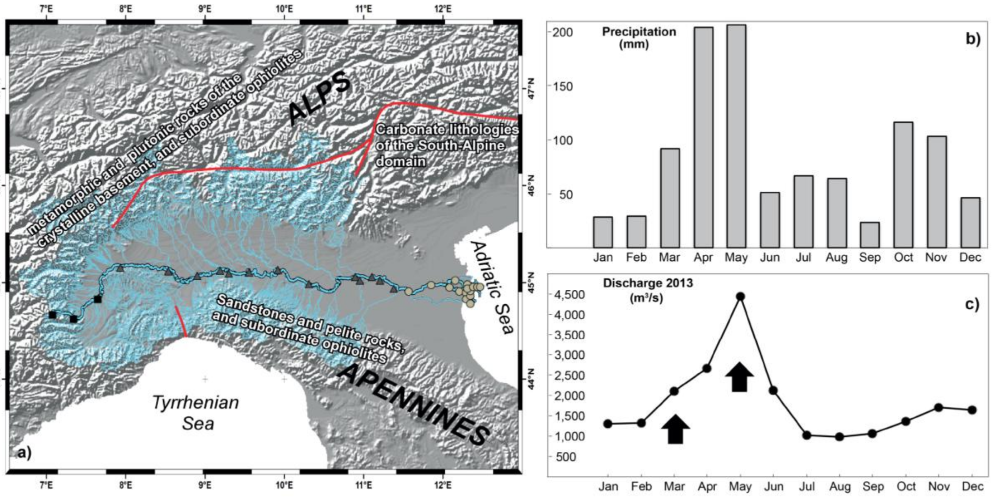

Figure 1: a) Po river catchment area (based on NASA SRTM data) and relative sampling stations Distinct symbols have been used for water sampled at increasing distance from the source in the upper part (UP, black squares), middle part (MP, grey triangles), and terminal part (TP, light grey circles); b) Monthly precipitation (2013) in the Upper Part of the Po river catchment (data provided by ARPA PIEMONTE); c) Po river discharge (Q, m3/s) 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 2013 (data provided by ARPA EMILIA ROMAGNA).

In this year 36 water samples were collected along the whole stream of the Po river (Fig. 1, Ch. 5) from its source (Pian del Re spring) to the deltaic area in March and May 2013. As described before, 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 from bridges). Electrical conductivity

(EC), pH and temperature were directly measured in the field, then water samples were filtered by 0.45 µm filters (Minisart® NML syringe cellulose acetate filters) and stored in distinct 100 ml bottles; one for the analysis of anions and oxygen/hydrogen isotopes, one acidified with 0.5 mL of concentrated Suprapur HNO_3 for the determination of cations, and additional two bottles for the measurement of carbon, nitrogen and sulphur isotopes ($\delta^{13}C$-$\delta^{18}O$; $\delta^{15}N$- $\delta^{18}O$; $\delta^{34}S$- $\delta^{18}O$).

Analyses were carried out at the Department of Physics and Earth Sciences of the University of Ferrara (Italy). As described above cations were measured by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series instrument on samples previously diluted 1:10 by deionized Milli-Q water (resistivity of ca. 18.2 MΩ x cm), 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 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.

Hydrogen and oxygen isotope ratios were determined using the *CRDS LOS GATOS LWIA 24-d* isotopic analyzer and reported in Table 2, Ch. 5. The isotopic ratios of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ are expressed as δ notation [$\delta = (R_{sample}/R_{standard} - 1)*1000$] with respect to the V-SMOW (Vienna Standard Mean Ocean Water) international standard. Four bracketing standards covering 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 standards such as V-SMOW and SLAP (Standard Light Antarctic Precipitation). Analytical precision and accuracy were better than 0.3‰ and 1.0‰ for $\delta^{18}O$ and δD respectively. A cross check of the obtained $\delta^{18}O$ - δD values have been done re-analysing a data subset with a PICARRO L2120-i water isotope analyser (Fig. 2, Ch. 5) at Helmholtz Centre for Environmental Research (UFZ) in Halle (Germany).

Figure 2: PICARRO L2120-i water isotope analyser at Helmholtz Centre for Environmental Research (UFZ) in Halle (Germany).

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. (2014). These isotopic analyses were preformed in the laboratories of the Helmholtz-Zentrum für Umweltforschung (UFZ) of Leipzig/Halle (Germany). Most of the lab-activities have been carried out by myself during the “Erasmus Placement program” (as attested by the relative certificate; Appendix B).

Carbon (and associated oxygen) isotopic analyses have been carried out on Dissolved Inorganic Component (DIC) using the method described in Atekwana et al., 1998. The technique uses evacuated glass septum tubes pre-loaded with phosphoric acid and a magnetic stir bar. Water samples are injected into these septum tubes and transferred to the vacuum line during the DIC extraction. $^{13}C/^{12}C$ isotope ratios are reported as δ notation with respect to the PDB (Pee Dee Belemnite) international standard. The associated $^{18}O/^{16}O$ ratios are reported as δ notation with respect to the SMOW international standard. Repeated analyses of standards (NBS-19) and samples reveal $\delta^{13}C$ precision and accuracy of 0.1‰.

Sulphur (and associated oxygen) isotopic analyses have been carried out on sulphate recovered using the method described in Knöller et al (2005), where $BaSO_4$ precipitation is induced at 70°C after the pH of the solution was adjusted to

2.5 (Fig. 3, Ch. 5). Subsequentely, isotopic measurements were performed after conversion of $BaSO_4$ to SO_2 using the continuous flow combustion technique coupled with an isotope-ratio mass spectrometry (delta S, Finnigan MAT). $^{34}S/^{32}S$ and and associated $^{18}O/^{16}O$ isotope ratios are 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 (Ag2S). Analytical accuracy and precision was generally 0.3‰ and 0.5‰ for $\delta^{34}S$ and $\delta^{18}O$ respectively.

Figure 3: $BaSO_4$ precipitation for the analyses of the dissolved sulphate

Nitrogen (and associated oxygen) isotopic analyses have been carried out on Dissolved Inorganic Nitrogen (DIN) using the *bacteria denitrification method* (Fig. 4, Ch. 5) described by Sigman et al. (2001) and Casciotti et al. (2002). This is a method that involves the use of bacteria to transform NO_3^- in N_2O. $^{15}N/^{14}N$ and associated $^{18}O/^{16}O$ isotope ratios are reported as δ notation with respect to the AIR and SMOW international standards, respectively. Analyses of $\delta^{15}N_{NO3}$ were corrected using international nitrogen isotopic standards IAEA: USGS-32, USGS-34 (KNO_3 $\delta^{15}N$ = -1.8‰), USGS-35 ($NaNO_3$), NO_2-1 (KNO_2), NO_2-2 $NaNO_2$. Analyses of $\delta^{18}O_{NO3}$ were corrected respect to international nitrate isotopic standards USGS-34 ($\delta^{18}O$ = -27.9‰) and USGS-35 ($\delta^{18}O$ = +57.5‰) (Bölke et al. 2003). Analytical accuracy and precision was generally 0.2‰ for $\delta^{15}N$ and 0.7‰ for $\delta^{18}O$.

Denitrified Method

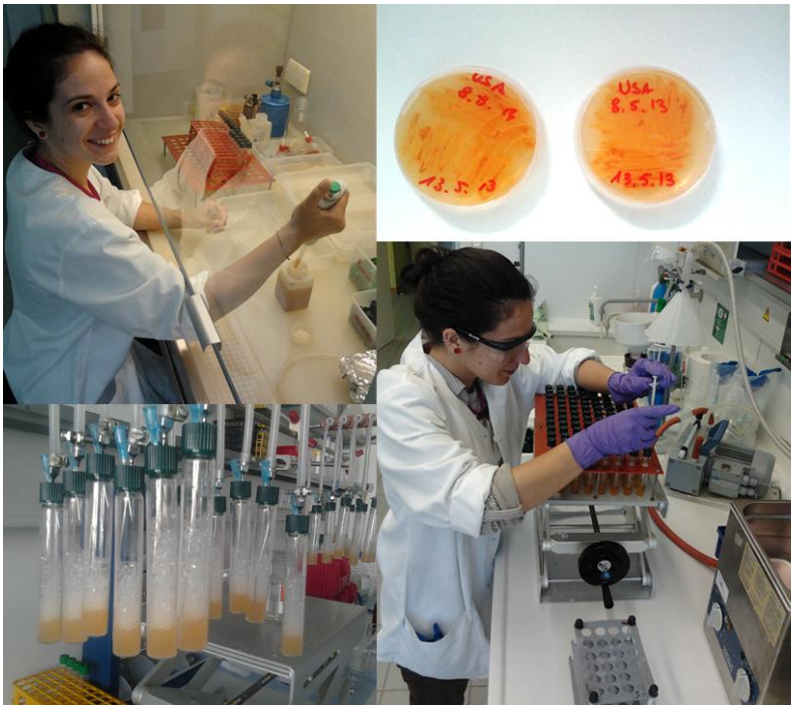

Figure 4: Sample preparation for the analyses of nitrogen isotopes using the bacteria *Pseudomonas chlororaphis* (ATCC #13985) (Helmholtz-Zentrum für Umweltforschung (UFZ) of Leipzig/Halle, Germany

The denitrifier method is based on the isotope ratio analysis of nitrous oxide generated from sample nitrate by denitrifying bacteria. In particular it provides additional issues associated with $^{18}O/^{16}O$ analysis of nitrate. It is interesting to note that is the first method tested for $^{18}O/^{16}O$ analysis of nitrate in seawater.

Respect to other methods, this approach has higher sensitivity, lack of interference by other solutes, and ease of sample preparation.

The denitrifier method for $^{15}N/^{14}N$ analysis of nitrate, described also by Sigman et al., is based on bacterial conversion of nitrate to N_2O and, therefore, can also offer oxygen isotope information. The degree of exchange varies greatly among bacterial strains and may be related to the biochemistry of nitrite reduction. Bacteria possessing the heme-type nitrite reductase (as Pseudomonas chlororaphis does) were shown to catalyze a relatively large amount of exchange (39-76%), while Pseudomonas aureofaciens, known to possess the copper-type nitrite reductase, was shown to cause relatively little incorporation of oxygen atoms from water into N_2O (6%).

5.2 Hydrochemistry

Physico-chemical parameters measured in-situ such as pH, temperature and conductivity of Po river water are reported in Table 1, Ch. 5. Note that the sample population has been geographically subdivided in three subsets according to Marchina et al. (2015): Upper Part (UP), Middle Part (MP), Terminal Part (TP) of the river. Few anomalous samples (or values) have been evidenced in italic font. These outliers are referred to samples collected in March 2013 in the UP at *Carignano* (intensive vineyard production), in the MP at *Torino* (important urban settlement), *Crescentino* (rice paddies activites) and *Balossa Bigli* (multiple agro-zoothecnical activities). An additional outlier is represented by the sample of *Porto Levante*, last site in the TP, possibly interested by mixing with seawater.

The value of pH varies in the three distinct parts of the river between 8.1 and 9.0, with the lowest value in *Porto Levante* and the higher value in *Pian del Re* (Spring). This variation doesn't show a systematic trend and is in the same range of that recorded from Marchina et al. (2015). Water temperature shows significant spatial-temporal variation; in UP it varied between 5 °C (locality *Pian del Re*, March 2013) to 13 °C (locality *Carignano*, May 2013); in MP it varied between 9 °C (March 2013) to 16 °C (May 2013); in TP it varied between 10 °C (in March 2013) to 17°C (in May 2013).

Water conductivity was also variable, increasing from UP (average 137±45 µS/cm) through MP (average 335±62 µS/cm), up to TP where samples were more heterogeneous (average 430±9 µS/cm). The highest value was recorded seaward at *Porto Levante* (1,280 µS/cm). These values were compared with water conductivity of the previous sampling campaigns (of the year 2012; Marchina et al., 2015) and evidence nearly constant values in particular for UP and MP samples (170±45 µS/cm and 350±25 µS/cm respectively). Chemical analyses of the major cations and anions are also reported in Table 1, Ch. 5. These data, especially the concentration of Ca^{2+}, HCO_3^-, SO_4^{2-} and NO_3^-, will help in constraining carbon, nitrogen and sulphur isotope data presented in the next sections.

Name	Date	Latitude	Longitude	pH	T (°C)	EC (µS/cm)	Na^+	Mg^{2+}	K^+	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	HCO_3^-	TDS
Upper Part (UP)															
Pian del Re	03/2013	44° 42' 04.00"	07° 05' 42.00"	9	5	110	0.79	3.95	0.07	8.81	0.63	0.85	6.25	45	66
	05 2013			8.2	6	90								44	
Crissolo	05 2013	44° 41' 52.38"	07° 09' 33.9"	8.4	9	150								58	
Sanfront	03/2013	44° 39' 03.89"	07° 19' 58.90"	8.7	9	160	3.23	5.45	0.70	9.74	3.35	4.38	11.9	60	99
	05 2013			8.7	9	100								45	
Carignano	03/2013	44° 54' 31.37"	07° 41' 29.93"	8.4	10	*560*	*10.2*	*21.0*	*1.73*	*64.3*	*13.0*	*18.0*	*46.4*	*135*	*310*
	05 2013			7.3	13	210	1.97	4.95	1.62	22.1	3.28	5.20	12.6	75	127
Middle Part (MP)															
Torino	03/2013	45° 04' 12.20"	07° 43' 12.15"	8.5	10	*550*	11.8	18.7	2.55	42.2	*19.2*	4.03	*47.8*	*165*	*311*
	05 2013			7.5	13	210	0.85	1.72	0.44	9.03	4.63	6.75	13.4	60	97
Casale Monferrato	05 2013	45° 08' 30.79"	08° 26' 51.07"	8.2	14	180	2.08	4.01	0.60	13.5	3.86	4.52	12.3	90	131
Crescentino	03/2013	45° 10' 32.96"	08° 05' 55.61"	8.5	9	*510*	13.5	17.0	2.00	27.2	*20.4*	*13.7*	*51.2*	135	*280*
Balossa Bigli	03/2013	45° 03' 58.00"	08° 54' 48.80"	8.5	9	400	18.1	15.7	2.31	30.1	20.6	*31.4*	35.4	135	289
Rea	05 2013	45° 07' 27.90"	09° 09' 31.96"	8.00	15	200	2.65	4.01	1.32	17.6	4.79	4.49	13.5	90	138
Ticino River	03/2013	45° 08' 40.88"	09° 13' 48.62"	8.7	10	310	12.5	8.20	1.65	19.3	11.9	8.27	26.1	165	235
	05 2013			8.00	14	170					7.03	3.88	26.1	45	
Senna Lodigiana	05 2013	45° 07' 46.41"	09° 38' 07.16"	8.00	14	230					11.3	4.98	35.7	90	
Adda river	05 2013	45° 09' 18.97"	09° 51' 13.62"	8.3	13	260					10.7	5.80	35.0	105	
Piacenza	03/2013	45° 03' 41.76"	09° 41' 53.51"	9.00	9	390	11.1	10.8	1.26	30.0	15.0	6.95	28.1	nd	
	05 2013			8.5	10	390					12.9	4.56	26.1	120	
Cremona	03/2013	45° 07' 43.34"	09° 59' 45.93"	8.5	9	440	15.9	15.5	1.99	32.0	17.5	8.88	31.1	165	288
	05 2013			8.2	15	260					13.2	5.79	30.4	60	
Coltaro	03/2013	44° 59' 03.67"	10° 18' 27.70"	8.8	8	420	13.6	17.6	2.14	54.4	13.6	8.31	25.0	195	330
	05 2013			8.3	14	260					12.4	6.01	26.5	75	
Boretto	03/2013	44° 54' 24.67"	10° 33' 25.50"	9.00	9	440	15.2	17,1	2.10	59.0	16.1	10.4	28.5	165	314
	05 2013			8.3	14	250					12.6	5.97	31.9	105	
Revere	03/2013	45° 03' 27.46"	11° 07' 52.80"	8.5	10	520	16.8	16.6	2.10	64.0	20.7	12.0	39.9	144	316
	05 2013			8.2	15	310					13.0	7.32	38.2	120	
Terminal Part (TP)															
Occhiobello	03/2013	44° 55' 04.78"	11° 34' 46.10"	8.5	10	520	16.8	16.5	2.41	63.7	19.2	11.4	38.2	135	303
	05 2013			8.2	16	350	12.7	13.3	2.93	33.5	14.3	7.01	40.0	120	244
Crespino	03/2013	44° 58' 37.64"	11° 52' 53.06"	8.7	10	490	18.4	20.8	3.79	82.5	18.0	8.86	33.9	165	351
	05 2013			8.3	17	360	15.4	15.6	2.81	52.4	13.8	6.74	35.3	120	261
Bottrighe	03/2013	45° 01' 15.17"	12° 04' 44.24"	8.3	10	500					12.7	6.15	40.1	150	
	05 2013			8.2	17	360	25.4	24.5	5.99	66.8	12.1	6.27	39.2	150	330
Taglio di Po	03/2013	45° 00' 36.12"	12° 13' 09.12"	8.4	10	500					18.7	10.6	42.7	180	
	05 2013			8.2	17	360					15.2	7.91	45.6	150	
Po di Levante (Porto Levante)	03/2013	45° 02' 43.00"	12° 19' 27.52"	8.1	12	1,280	89.6	44.1	7.24	97.8	164	29.9	108	270	811
Historical samples by Fossato (1971); Gherardelli and Canali (1960)															
Polesella	03/1969			7.4	9			14.3		33.0		4.65		192	
	03/1969			7.5	9			14.8		30.4		4.6		187	
	04/1969			7.3	13			16.8		28.0		4.30		177	
	04/1969				17			13.9		33.0		4.32		193	
	05/1969				19			9.20		24.0		3.30		137	
	02/1959			7.3		409	17.0	12.9	2.20	60.6	19.8	absent	53.1	187	
	05/1959			7.7		225	7.00	8.40	1.80	33.6	9.00	only traces	29.1	108	

Table 1: Physico-chemical parameters measured in the field and 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.

Total Dissolved Solids (TDS) coherently increases from the upper part of the catchment, where the UP samples have TDS average of 97 (±30) mg/L, to the central part where the MP samples have a TDS average of 250 (±85) mg/L. In particular, Ca^{2+} varies between 9 mg/L (*Pian del Re*, UP) and 98 mg/L (*Porto Levante*, TP), with average values of 14 (±7) mg/L, 34 (±18) mg/L, 60 (±18) mg/L in UP, MP and TP respectively. HCO_3^- varies between 45 mg/L to 135 in the UP samples, becomes more homogeneous in the MP and TP waters (average 143±25 mg/L) and increases seaward in the locality of *Porto Levante* (270 mg/L).

It is interesting to note that the chemical variations along the river course observed for the year 2013, (synthetized in the notional Gibbs diagram; Fig. 5 Ch. 5), are quite similar to those recorded in the year 2012 (Marchina et al. 2015); the UP water rapidly evolves and then reaches a notable constancy which is maintained in most of the river course up to the terminal part. The Piper classification diagram (not shown) indicates that the ubiquitous hydrochemical facies of these waters is bicarbonate-alkaline earth.

Sulphate concentration increases in the UP water from 6 mg/L to 12 mg/L) and then became more stable in MP and TP with an average value of 30 (±7) mg/L, except for the last sample, influenced by mixing process with seawater). It is interesting to note that sulphate evidences a positive spike at *Carignano* (UP, March 2013), with a notable value of 46 mg/L, probably due to agricultural practices specifically used for vineyards. High SO_4 values are also recorded in March 2013 at *Torino* and *Crescentino* site.

Nitrate concentration is extremely variable throughout the main course of the river; it is less than 1 mg/L at the spring (*Pian del Re*) but suddenly increase in *Carignano* (last sample of the UP) reaching the extreme value of 18 mg/L in March 2013. Down-stream, the MP samples are characterized by an average composition of 9 mg/L, with two anomalous samples collected in March 2013 at *Torino* and *Balossa Bigli*, having 14 mg/L and 31 mg/L respectively. NO_3 values recorded in March 2013 are in general higher respect to the values recorded in May 2013 and also respect to those recorded in April 2012 (Marchina et al. 2015). Therefore nitrate concentrations along the river course are heterogeneous and plausibly related to anthropogenic inputs that are spatially and temporally variable. The data above described are also compared with past compositions recorded in Po river water since ca. 50 years ago, when human impacts were less pronounced. Useful literature data, provided by Gherardelli and Canali (1960) and Fossato (1971), report 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 and 1968 – 1969. I noted that the values of conductivity, HCO_3^-, Ca^{2+} and Mg^{2+} (and Mg/Ca ratio) are comparable with those recorded nowadays, whereas NO_3^- concentration has an average value of 2 mg/L in the fifties and 4 mg/L in the sixties, reaching in the eighties concentrations up to 10 mg/L, and then finally declining to the current values (data ARPA VENETO). The same temporal trend has been envisaged by the data compilation reported by Viaroli et al. 2013.

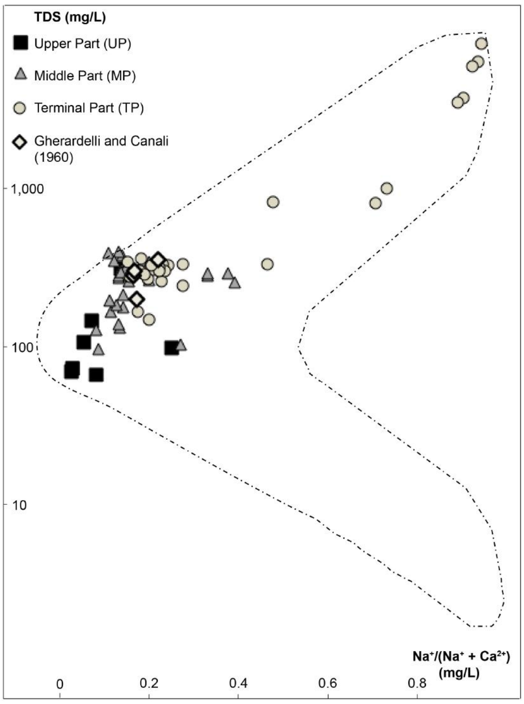

Figure 5: Gibbs diagram. TDS vs [Na+/(Na++Ca2+)] reported in milligrams/liter for the Po river water. Filled symbols (black square for UP, grey triangle for MP, light grey circle for TP) for samples collected in the years 2012 and 2013. White diamonds report chemical composition of the Po river waters in the year 1959 (Gherardelli et al., 1959).

5.3 Oxygen and Hydrogen isotopes in Po river waters

The δD‰ and δ^{18}O‰ isotopic ratios have been measured on Po river water in March and May 2013. Results are presented in Table 2, Ch. 5 and reported in Fig. 6, Ch. 5. δD‰ ranges from -86.8‰ to -59.0‰ in March and from -88.8‰ to -65.7‰ in May, whereas δ^{18}O‰ ranges from -12.5‰ to -8.6‰ in March and from -12.9‰ to -9.7‰ in May. The isotopic values recorded in May are slightly more negative, possibly in relation to the contribution of snow-melt that becomes preponderant in the late spring. In Fig. 6a, Ch. 5 the new δ^{18}O values presented in this paper are compared with those recorded in Po river during the year 2012 (Marchina et al. 2015). The isotopic differences recorded in each site, during distinct periods are quite limited. In particular, in the UP waters the temporal δ^{18}O differences are in the order of 0.6‰, whereas in the MP waters temporal δ^{18}O differences are slightly higher in the order of 1‰. Therefore, it appears that isotopic differences along the river profile are more significant than those recorded locally (i.e. in the same site) in distinct seasons (±0.5‰ at *Pontelagoscuro* in the period 2005-2007; Martinelli et al. 2014); for this reason in the δ^{18}O – δD diagram (Fig. 6b, Ch. 5) the data are simply presented with distinct symbols for the three river sectors, highlighting a progressive shift towards less negative composition from the UP to the TP.

Name	**Date**	**δD‰**	**δ^{18}O‰**
Upper Part (UP)			
Pian del Re	03/2013	-86.8	-12.5
	05/2013	-88.8	-12.9
Crissolo	05/2013	-86.9	-12.6
Sanfront	03/2013	-82.0	-11.9
	05/2013	-84.2	-12.2
Carignano	03/2013	-81.2	-11.7
	05/2013	-76.8	-11.2
Middle Part (MP)			
Torino	03/2013	-81.9	-11.6
	05/2013	-71.8	-10.5
Casale Monferrato	05/2013	-69.5	-10.3
Crescentino	03/2013	-77.5	-11.2
	05/2013	-69.9	-10.2
Balossa Bigli	03/2013	-74.5	-10.8
Rea	05/2013	-67.4	-10.1
Ticino River	03/2013	-66.1	-9.7
	05/2013	-63.5	-9.4
Adda river	05/2013	-66.2	-9.8
Piacenza	03/2013	-71.2	-10.4
	05/2013	-66.6	-9.8
Cremona	03/2013	-70.2	-10.1
	05/2013	-66.6	-9.9
Coltaro	03/2013	-72.0	-10.5
	05/2013	-66.6	-9.9
Boretto	03/2013	-71.2	-10.4
	05/2013	-66.6	-10.0
Revere	03/2013	-68.1	-9.9
	05/2013	-67.8	-10.3
Terminal Part (TP)			
Occhiobello	03/2013	-67.6	-9.9
	05/2013	-66.3	-9.9
Crespino	03/2013	-71.0	-10.4
	05/2013	-66.9	-10.1
Bottrighe	03/2013	-70.8	-10.2
	05/2013	-65.7	-9.8
Taglio di Po	03/2013	-70.5	-10.4
	05/2013	-65.9	-9.7
Po di Levante (Porto Levante)	03/2013	-59.0	-8.6

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 δ‰ respect to the SMOW standard.

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 (Longinelli and Selmo 2003) and the gradual increase along the river course is due to the progressive contribution of meteoric components from lower altitudes.

The hydrogen and oxygen isotopic ratios are dependent on the temperature of water condensation, (Dansgaard 1964), and give therefore a snapshot of the current climatic conditions that concur to create a hydro-archive useful to evaluate climatic changes (Rozansky 1985; Zuppi and Sacchi 2004; Henderson and Shuman 2010). For this reason it is extremely interesting to compare current meteoric components that dominate surface water bodies with groundwater of the same region, because aquifers have longer residing times and contain paleo-meteoric waters that were influenced by climatic condition at the time of recharge (Fontes et al. 1993).

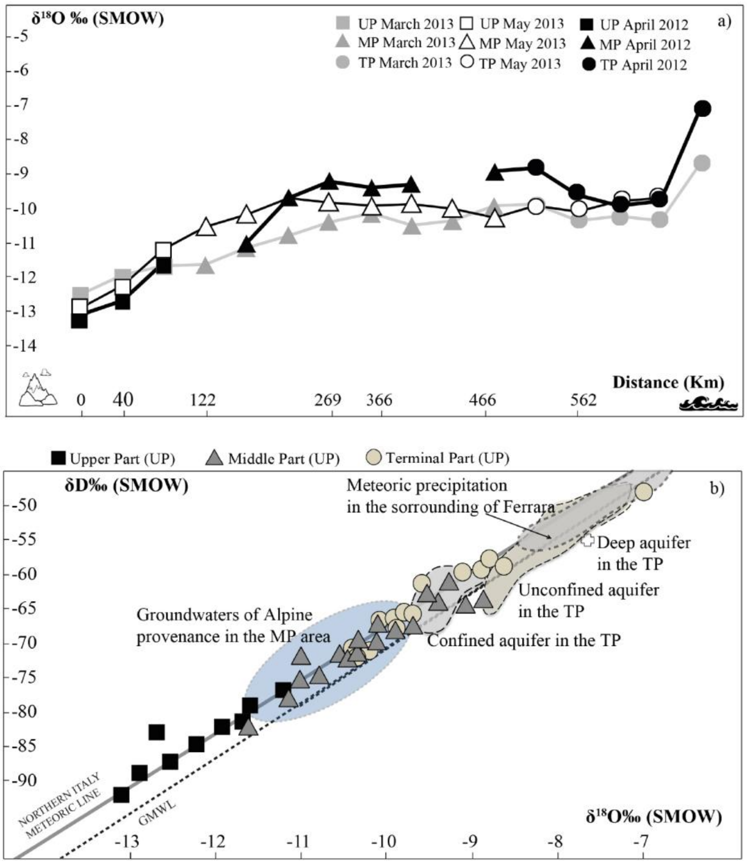

Figure 6: a) Variation of the $\delta^{18}O$ signature in function of the distance from the source of the Po river fro three different sampling campaign (April 2012 from Marchina et al., 2014; March and May 2013); b) $\delta^{18}O$-δD isotopic composition of Po river water. Meteoric water lines are also reported for comparison: the black line represents the global meteoric water line (GMWL; Craig 1961); the red line represents the local meteoric water line (LMWL), defined for Northern Italy (Longinelli and Selmo 2003), together with compositional fields relative to confined and unconfined aquifer in lower Padanian Plain (Rapti Caputo et al., 2009) and meteoric precipitation in the area of Ferrara.

Confined aquifers of the Padanian plain represent suitable hydro-archives being characterized by steady-state flow regime and hydraulic continuity (Zuppi and Sacchi 2004). In this view, Fig. 6b, Ch. 5 shows the isotopic fingerprint of aquifers in the MP and TP sectors (Rapti Caputo and Martinelli 2009; Martinelli et al. 2014), and deep aquifer (100 m depth; authors' unpublished data) located close to Ferrara, compared to the Po river water.

Based on radiocarbon data, Martinelli et al. (2014) recently proposed ages from 594 to the 35,000 yr for the Padanian plain groundwater of Alpine provenance hosted at depths ranging from 60 to 237 meters. The groundwater investigated in this study has and average ^{14}C age of 23,750 yr that is associated with an $\delta^{18}O$ average value of -10.2‰ (±0.5; n=21) that is very similar to that reported for Holocene groundwater by Zuppi and Sacchi (2004). These values are very close to the $\delta^{18}O$ isotopic fingerprint of Po river water at Pontelagoscuro (which is located in the lower reach of the river, right upstream of the deltaic system) that was -10.0‰ in the seventies (Zuppi and Bortolami 1982), -9.8‰ in the years 2005-2007, -9.9‰ in the year 2013. This slight difference between river and groundwater disappears if we consider as representative of the Po river the MP sector which has an average $\delta^{18}O$ value of -10.2‰. Groundwater $\delta^{18}O$ values down to -11.5‰, proxies of colder climatic condition, have been mentioned by Zuppi and Sacchi (2004) but have not been confirmed by more recent investigation. Analogous consideration could be obtained if we take into consideration the associated δD parameters, and in any case we don't observed the δD shift of +12‰ that should reflect an important warming trend occurred during the Holocene, as suggested by Rozansky (1985).

Coherently, calculation of d-excess (from data reported in Table 2, Ch. 5, using the equation: d-exc= $\delta D - 8*\delta^{18}O$) indicates values ranging between 11.8‰ and 13.6‰, in the MP Po river water. These values overlap with those recorded in groundwater (ranging between 11‰ and 14‰; Martinelli et al. 2014), suggesting a quite constant relative humidity conditions over the source areas in the last millennia.

Based on the above considerations, additional information concerning groundwater isotopic composition and dating are needed to constrain the debate on climatic changes, avoiding speculation. At this preliminary stage, it can be suggested that the present day Po river waters (MP sector) show a remarkable analogy with the composition of groundwater of the Padanian plain confined aquifers defined as paleoarchives; this analogy, in my view, precludes that significant climatic warming occurred at least during the last thousands years.

5.4 Carbon, Sulphur and Nitrogen isotopic composition of dissolved components

In Table 3, Ch. 5 are reported the C-N-S isotopic composition of the Po river waters in distinct periods of the year 2013 (and subordinately of the year 2012). These parameters, as far as I know, were never analysed systematically in Po River water.

$\delta^{13}C_{DIC}$ isotopic compositions of Po river water collected in March 2013 are reported in Fig. 7a, Ch. 5 in order to highlight compositional variation along the river course. It can be noted that a sharp variation trend can be observed in the UP samples where we recorded a $\delta^{13}C_{DIC}$ value of -4.4‰ in the river source of *Pian del Re,* a value of -6.7‰ in *Sanfront* (14 km from the source) and a value 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 is congruent with that observed in other riverine systems such as the Rhone river, where starting from the source area progressively more negative isotopic values are observed downstream, until more evolved waters attain an isotopic homogeneity (Telmer and Veizer 1999; Mook 2005). The $\delta^{13}C_{DIC}$ evolution is at first dominated by isotopic exchange with atmospheric CO_2, and then progressively increasing water-rock interaction and biochemical activities (i.e. photosynthesis).

The observed $\delta^{13}C_{DIC}$ range of the Po river water is partially overlapped with that typical of groundwater of the Padanian plain that displays $\delta^{13}C_{DIC}$ between -12.7‰ and -9.4‰ (Pilla and Sacchi 2006). The shift toward more negative $\delta^{13}C_{DIC}$ composition observed in groundwater may reflect a more effective interaction with sediment/soils and their organic components.

Furthermore, it is interesting to note that the average $\delta^{13}C_{DIC}$ value is very similar to that recorded in the particles suspended in the Po river waters, where $\delta^{13}C$ range from -11.4‰ to -9.9‰ (authors' unpublished data). 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 are maintained in the MP sector of the river and significantly change only in the TP, where mixing with seawater induces a trend toward less negative $\delta^{13}C_{DIC}$ isotopic values. Fig. 4b emphasizes that the carbon isotopic evolution is coupled with significant variation of HCO_3^-, as also observed in other important rivers originating from the Alps (i.e. Rhone river; Mook 2005). Fig. 4 also resumes the $\delta^{13}C_{DIC}$ signature expected for distinct processes occurring in river systems (Barth et al. 2003); on this basis, 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 $\delta^{13}C$) seems subordinate.

Although carbonate bearing lithologies are subordinate in the upper part of the catchment, calcite is observed in sporadic marble outcrops (having $\delta^{13}C$ 0-2‰, Baker 1988) that are included in the crystalline basement. Further carbon can be released in the river waters by interaction with carbonate sedimentary rocks, having Permian – Triassic ages, which are characterized by $\delta^{13}C_{DIC}$ varying between -3.7 and 4.1 (Newton at al. 2004). 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 is observed between the isotopic composition of the oxygen that is associated to carbon ($\delta^{18}O_{DIC}$) and that recorded in the water molecules ($\delta^{18}O_{H2O}$):

$$\delta^{18}O_{DIC} = 1{,}52 \cdot \delta^{18}O_{H2O} + 5{,}56 \ (R^2 = 0.9)$$

thus suggesting 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 and dependent and may, in principle, be used as a further climatic proxy (Beck et al. 2005; Affek et al. 2013).

The sulphur isotopic compositions ($\delta^{34}S_{SO4}$) of Po river water, available only for MP and TP samples collected in May 2013, are reported in Table 3 and Fig. 5a in order to observe compositional variation along the river course. It can be noted that a sharp variation trend can be observed in the first part of MP where it is recorded a value of 4.2‰ in the *Rea* locality, before the *Ticino* river confluence (11.0‰), whereas 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 age that includes sulphate-bearing horizons (Cortecci et al. 1981; Newton et al. 2004). Downstream both MP and TP waters maintain a remarkable isotopic homogeneity in the $\delta^{34}S_{SO4}$ range of 7.3‰ ±0.7 that persists along the entire river course. Additional charts are used to delineate the origin of sulphate in riverine waters: in Fig. 5b sulphur isotopic composition plotted vs SO_4^{2-} concentration, shows a rough correlation and an evolution trend. In particular, MP waters are divided in two different groups: *1)* waters collected before the Ticino river confluence are 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 have higher SO_4^{2-} concentration (average 34 mg/L) and $\delta^{34}S_{SO4}$ (average 7.3‰).

Further information can be extrapolated from Fig. 5c, where sulphur isotopic composition is compared with the associated oxygen isotopic composition ($\delta^{18}O_{SO4}$, varying from 5.3‰ to 8.4‰.). In this diagram the compositions of the Po river water are compared with those that characterize sulphur bearing lithologies existing within the Po river basin, such as a) the metamorphic and igneous rocks of the basement that contains accessory sulphides (having $\delta^{34}S$ 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 anthropogenic contributions to the sulphur budget, e.g. equilibration with atmospheric gases and/or deposition of atmospheric particles (Mayer 2005; Panettiere et al. 2000) cannot be excluded a priori, but are not highlighted by the observed geochemical trends. In other words, although we cannot exclude a minor contribution from antropogenic sources which are pronounced in the urbanized/industrialized sector of the plain (Panettiere et al. 2000), I emphasize that the isotopic compositions observed in the Po river waters recall those of the mentioned lithologies and don't 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 we recorded anomalous SO_4^{2-} concentrations. Note 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 lithologies.

$\delta^{15}N_{NO3}$ isotopic compositions of Po river water are reported in Fig. 6a in order to bring out compositional variation along the river course. In this case, I observed a systematic isotopic variation in the two investigated periods of the year 2013 (March and May). These temporal differences in the nitrogen isotopic composition are 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, from the site of *Carignano* that is characterized by a remarkable isotopic spike toward heavy $\delta^{15}N_{NO3}$. In March the initial UP waters have $\delta^{15}N_{NO3}$ varying from -2.2‰ at *Pian del Re* to 1.8‰ at *Sanfront* and then it remains relatively homogeneous for the rest of the river course with an average composition of 7.7‰. In May the initial UP waters have $\delta^{15}N$ varying from -1.7‰ at *Pian del Re* to -0.1‰ at *Sanfront*, and then it shows a progressive - systematic - downflow increase up to 8.2‰ in the locality of Occhiobello 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 $\delta^{15}N$ 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 $\delta^{15}N$ distribution observed in March is quite fluctuating around an average value of ($\delta^{15}N$ 7.7‰) with significant oscillation of ± 2.9‰, whereas the distribution observed in May is more regular and characterized by a lower average value (3.9‰) and a systematic smooth increase. This systematic $\delta^{15}N$ differences observed in May could be related to the combined effect of dilution and concomitant fertilization practices that employ chemical compounds having $\delta^{15}N$ approaching 0‰, that usually occur at the begin of the spring season.

Nitrogen isotopic compositions of the Po river waters are plotted vs NO_3^- in Fig. 7a and compared with the groundwater collected in the MP area (Lombardy plain) from Sacchi et al. (2013) and Delconte et al. (2014). In spite of lower concentration of nitrate, the $\delta^{15}N_{NO3}$ signature of the Po river is comparable with that of the aquifers, suggesting a common origin. More detailed information on the nitrogen sources are given in Fig. 7b ($\delta^{15}N_{NO3}$ vs $\delta^{18}O$) 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 (Clark and Fritz 1997) in order to provided specific information about natural/anthropogenic sources of dissolved nitrate.

It can be observed that the observed isotopic signature of Po river water conforms to those of soil organic matter and manure, also suggesting an incipient denitrification trend that seems to be more effective in the TP waters. Although denitrification is scarcely documented in riverine systems, it has to be noted that analogous trends were also observed in the Oglio river by Bartoli et al. (2012). Accordingly, during denitrification the $\delta^{15}N_{NO3}$ and $\delta^{18}O_{(NO3)}$ values of the remaining nitrate increase; coherently, in the TP samples collected in March 2013 a rough positive correlation ($R^2 = 0.6$) is observed between $\delta^{18}O_{(NO3)}$ and $\delta^{18}O_{(H2O)}$ as expected during denitrification processes (Lee et al. 2008). This relation suggests that the $\delta^{18}O_{(NO3)}$ values are significantly controlled by the $\delta^{18}O_{(H2O)}$ values in the river during microbial activity (Kroopnick and Craig, 1972; Kumar et al., 1983; Hollocher, 1984).

Table 3: Stable isotopes ($\delta^{13}C$, $\delta^{15}N$, $\delta^{14}S$ and the relative oxygen) for the Po river waters. Data are expressed in ‰ respect to the PDB standard for $\delta^{13}C$, AIR standard for $\delta^{15}N$ and VCDT for $\delta^{14}S$. The $\delta^{18}O$ is expressed in ‰ respect to the SMOW for carbon, nitrogen and sulphur isotopes.

Name	Date	$\delta^{13}C_{DIC}$‰	$\delta^{18}O_{DIC}$‰	$\delta^{15}N_{NO3}$‰	$\delta^{18}O_{NO3}$‰	$\delta^{34}S_{SO4}$‰	$\delta^{18}O_{SO4}$‰
Upper Part (UP)							
Pian del Re	04/2012	-8.5	-13.8	-2.0	4.4		
	08/2012	-5.9	-15.6	-4.1	-7.0		
	03/2013	-4.4	-13.6	-2.2	6.4		
	05/2013			-1.7	4.5		
Crissolo	05/2013			-1.6	-36.0		
Sanfront	04/2012	-8.7	-13.4	4.6	10.1		
	08/2012	-9.2	-14.5	18.6	-2.4		
	03/2013	-6.7	-12.7	1.8	0.1		
	05/2013			-0.1	3.5		
Carignano	04/2012	-9.7	-11.1				
	08/2012	-11.0	-12.2				
	03/2013	-9.8	-11.5	9.5	14.8		
	05/2013			5	6.6		
Middle Part (MP)							
Settimo Torinese	08/2012	-10.6	-12.8				
Torino	03/2013	-10.2	-11.6	7.4	-0.2		
	05/2013			1.9	7		
Casale	05 2013			3.4	6.4	5.2	nd
Crescentino	04/2012	-10.9	-11.3				
	08/2012	-11.2	-11.9				
	03/2013	-10.4	-10.8	8.7	11.4		
	05/2013						
Balossa Bigli	04/2012	-11.4	-10.6				
	08/2012						
	03 2013	-10.8	-10.6	7.1	8.8		
Rea	08/2012			5.4	8.8		
	05 2013			3.3	5.6	4.2	nd
Ticino River	04/2012	-9.7	-10.3	6.5	7.5		
	08/2012	-10.6	-10.8				
	03/2013	-11.5	-9.8	7.1	5.9		
	05/2013			3.2	3.1	11	9.5
Senna Lodigiana	04/2012			10	1.4		
	08/2012			3.5	-8.5		
	05/2013			4.1	4.6	8.0	8.4
Adda river	05/2013			5	4.2	9.0	7
Piacenza	08/2012	-10.9	-10.3	8.2	2.2		
	03/2013	-10.4	-10.5	5.5	4.9		
	05/2013			4.6	4.3	7.2	6.1
Cremona	04/2012	-10.5	-10.9				
	08/2012	-11.3	-10.9	8.4	7.6		
	03/2013	-10.3	-10.4	8.4	9.2		
	05/2013			5	3.9	8.0	7.3
Coltaro	04/2012	-11.0	-10	8	-10.1		
	08/2012	-11.0	-11.4				
	03/2013	-10.7	-10.7	6.2	6.2		
	05/2013			5.3	2.2	6.7	nd
Boretto	03/2013	-10.9	-10.6	9.5	14.9		
	05/2013			6	4.6		
Revere	04/2012	-9.8	-9.7	9.5	2.6		
	08/2012						
	03/2013	-9.7	-9.8	8.8	3.3		
	05/2013			6.8	4.3	6.29	5.3
Terminal Part (TP)							
Occhiobello	04/2012	-10.3	-9.9				
	08/2012						
	03/2013	-9.8	-9.6	11.5	14.6		
	05/2013			8.2	5.2	7.3	6.3
Crespino	04/2012	-10.3	-10	8.7	1.7		
	08/2012						
	03/2013	-10.8	-10.2	8.3	11.1		
	05/2013					7.3	7.7
Bottrighe	04/2012	-10.5	-10.6	12.1	12.3		
	08/2012						
	03/2013	-10.6	-9.6	7.3	10.2		
	05/2013			8.3	5.3	7.5	6.9
Taglio di Po	04/2012	-8.0	-9.1				
	08/2012						
	03/2013	-10.3	-10.1	8.9	11.1		
	05/2013			8.2	4.4	7.5	6.3
Po di Levante (Porto Levante)	04/2012	-7.5	-6.7				
	08/2012						
	03/2013	-8.7	-6.3	11.6	14.6		

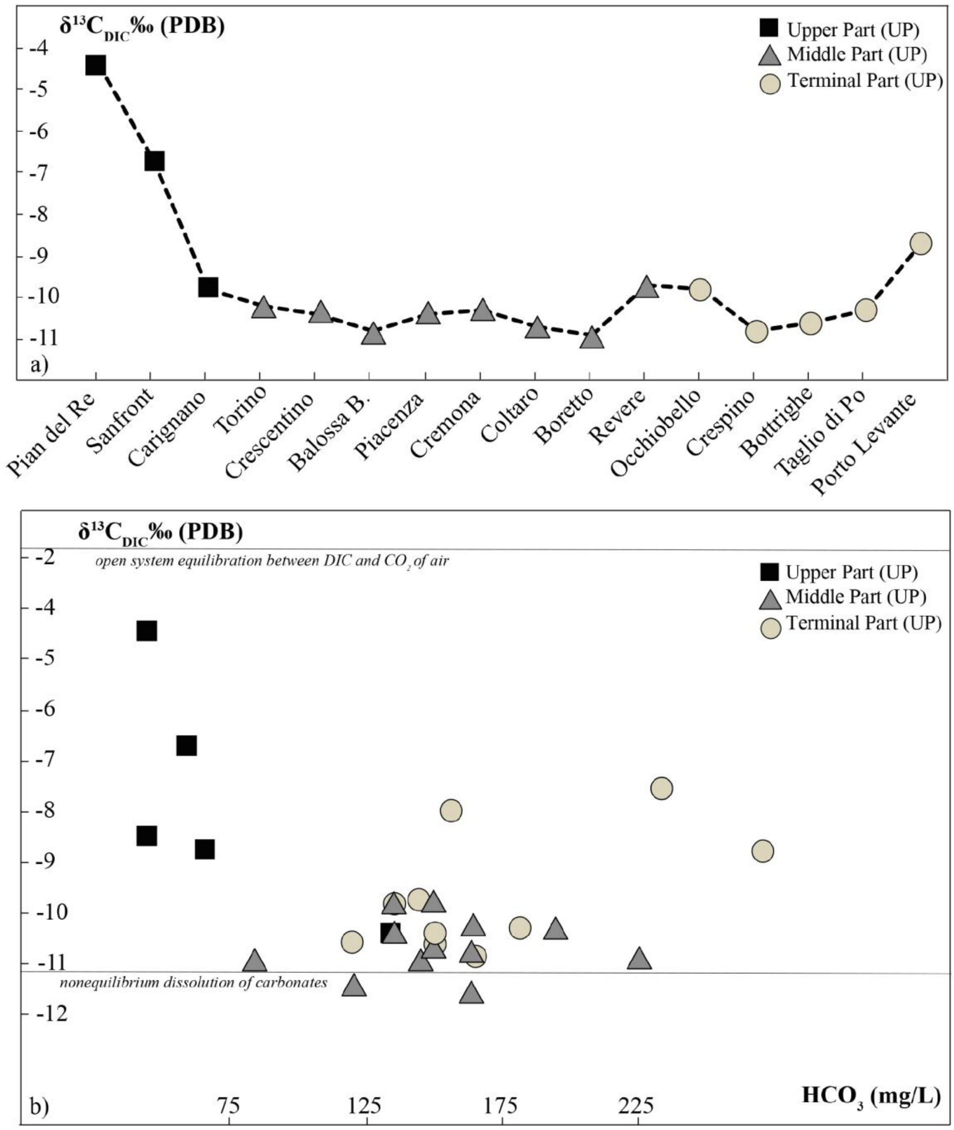

Figure 7: a) Variation of the δ^{13}C$_{DIC}$ signature in function of the distance from the source for Po river waters collected in March 2013; b) HCO$_3^-$ vs δ^{13}C$_{DIC}$, also reporting the δ^{13}C values expected for dissolved carbon having distinct origin (Barth et al. 2003). The δ^{13}C$_{DIC}$ typically recorded in Po river water is intermediate between that expected for an open system equilibrium between DIC and CO$_2$ of air and that expected for nonequilibrium dissolution of carbonates; Note that nonequilibrium dissolution of silicates would give extremely negative δ^{13}C (down to - 22‰) that are not recorded in the studied water.

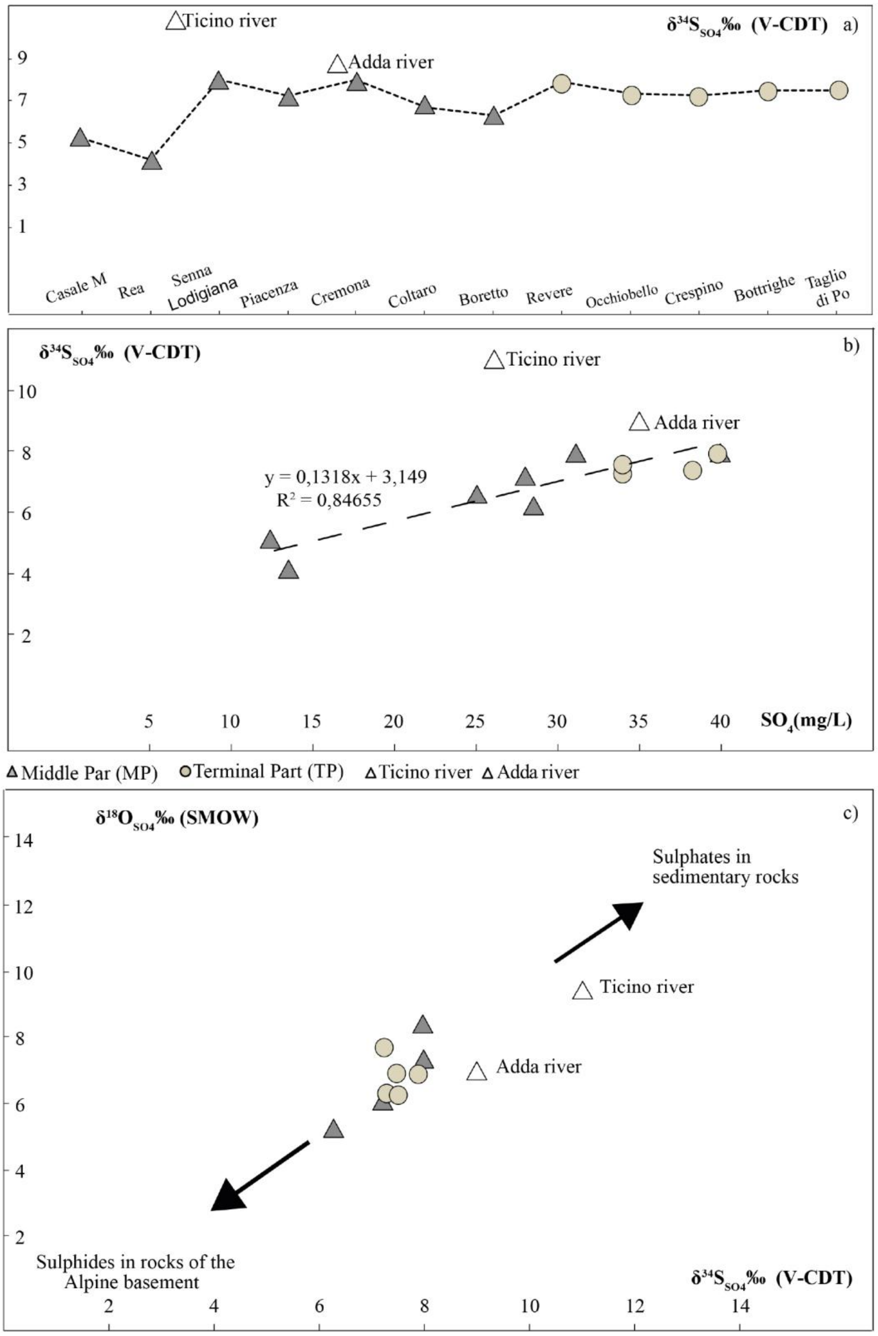

Figure 8: a) Variation of the $\delta^{34}S_{SO4}$ signature in function of the distance from the source of the Po river. Two main tributaries of the Po river (*Ticino* and *Adda*) are also represented; b) SO_4^{2-} vs $\delta^{34}S_{SO4}$; c) $\delta^{34}S_{SO4}$ vs $\delta^{18}O_{(SO4)}$ isotopic composition of the Po river and its two main tributaries (*Ticino* and *Adda*). Arrows delineating possible geogenic sources are taken from Nordstrom et al. (2007). Note that within the Po river basin sulphide-bearing lithologies are observed in the metamorphic and igneous rocks of the basement (Garuti et al. 1986; Fantone et al. 2014;

Giacometti et al. 2014), whereas sulphates are observed in Permian-Triassic sedimentary sequences (Cortecci et al. 1981; Newton et al. 2004).

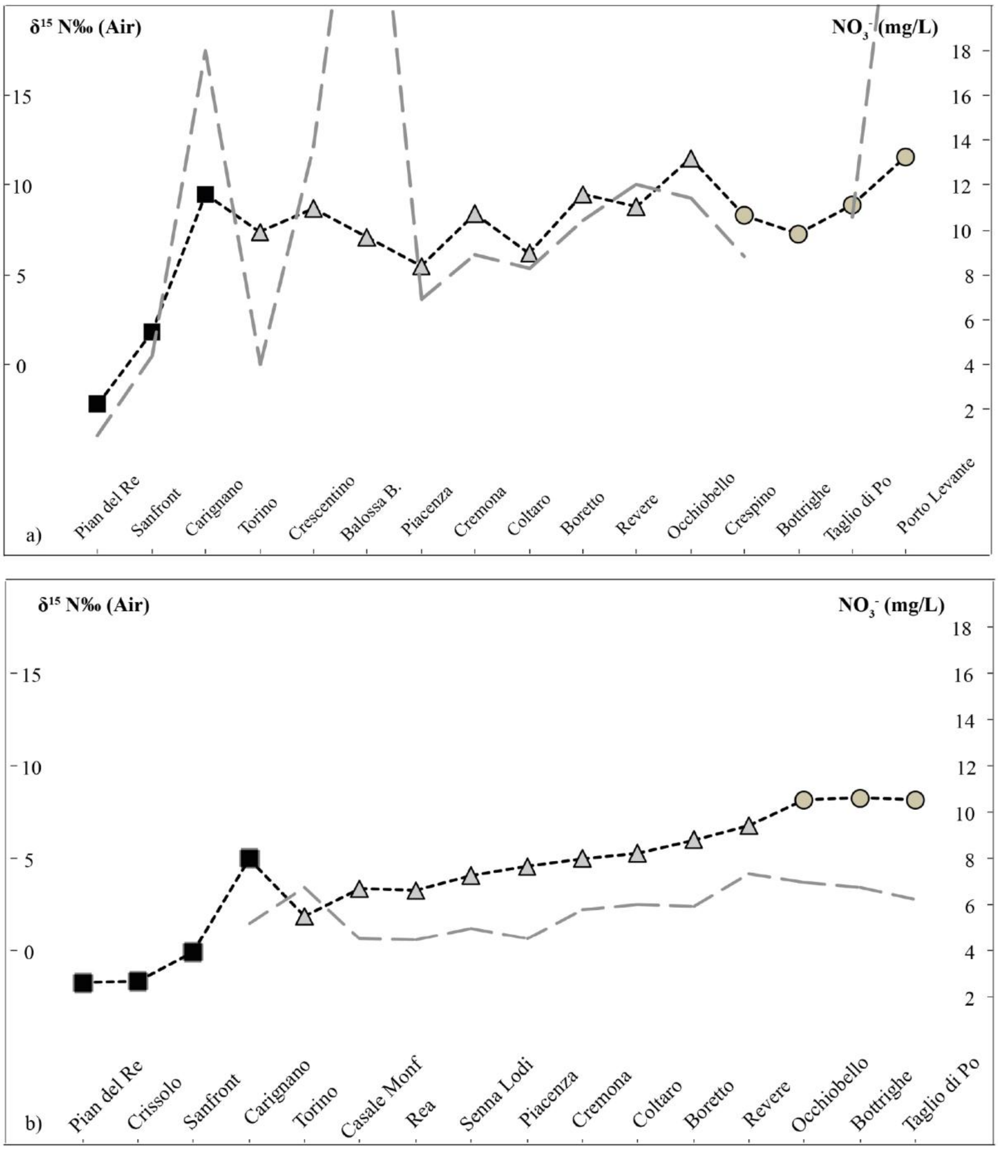

Figure 9 Variation of the δ^{15}N signature in function of the distance from the source of the Po river in a) March 2013 and b) May 2013. Grey dotted line represents NO_3^- variation along the river course.

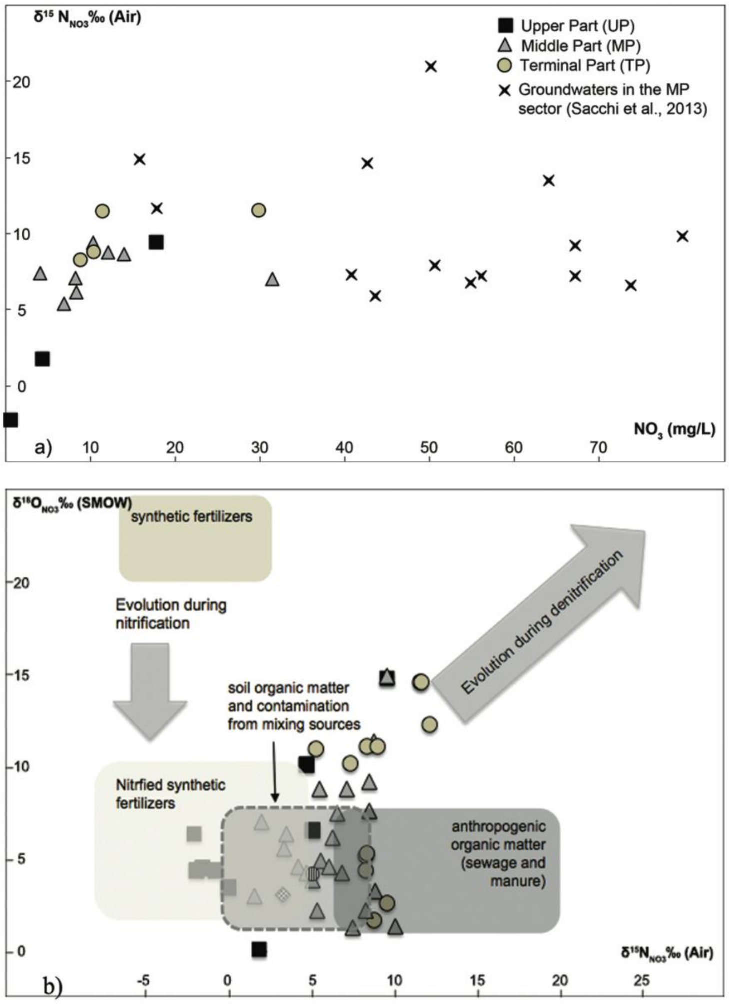

Figure 10: a) NO_3^- vs $\delta^{15}N_{NO3}$ in the three distinct sectors of the river compared to the isotopic range typical of groundwater in the Lombardia plain; b) $\delta^{15}N_{NO3}$ - $\delta\ ^{18}O_{(NO3)}$ of the Po river waters compared to the isotopic composition of groundwater (Sacchi et al. 2013) and the potential sources of nitrate (after Clark and Friz 1997): synthetic fertilizers; anthropogenic organic matter (sewage and manure); soil organic matter and contamination from mixed sources. Evolution trends during nitrification and denitrification are also reported.

5.5 Carbon and nitrogen isotopic composition of suspended matter

In the Po river site of Occhiobello, which is the located before the beginning of the deltaic sector of the river, the suspended matter was also sampled in three distinct periods (October 2013, January and February 2014). For this purpose, solid particles were recovered settling 10 litres of water in suitable buckets, extracting the water and then drying the precipitated particles.

The particles suspended in the Po river water were investigated using a new instrument that is operative at the Department of Physics and Earth Sciences since June 2013. Note that I actively contributed to the set up of the system during the installation and the training phases with the technicians of the producing company (See the certificate reported as Appendix C). The analytical system consist of an Elemental Vario Micro Cube elemental analyser in line with an ISOPRIME 100 Isotopic Ratio Mass Spectrometer operating in continuous-flow mode. (Fig. 10, Ch. 5).

Figure 11: Elemental vario MICRO cube analyser and the IRMS Isoprime100 for the measurement of the elemental composition of carbon and nitrogen and relative isotopes ($\delta^{13}C$ and $\delta^{15}N$)

Powdered samples are introduced in tin capsules that are wrapped and weighed; these capsules, that allow to load up to 40 mg of sample, are subsequently introduced in the Vario Micro Cube autosampler to be analyzed. Flash combustion at 950 °C takes place in a sealed quartz tube filled with copper oxide grains (padded with corundum balls and quartz wool) which acts as catalyst, in excess of high purity (6 grade purity) O2 gas. Freed gaseous species are transferred through a reduction quartz tube (at 550°C) filled with metallic copper wires that reduce the nitrogen oxides (NOx) to N2. The formed analyte gases (N_2, H_2O and CO_2), carried by dry He (5 grade purity) gas, pass through a water-trap filled with sicapent ensuring complete removal of moisture, are sequentially separated by a temperature programmable desorption column (TPD) and quantitatively determined on a thermo-conductivity detector (TCD). Sample N_2 goes directly to the interfaced IRMS for isotopic composition determination, while CO_2 is held by the TPD column, kept at room temperatures 20–25°C. When N_2 isotopic analysis is over, CO2 is desorbed from the TPD column raising the temperature to 210°C, and finally reaches the IRMS compartment for the determination of carbon isotopic ratios. The detection of the distinct isotopic masses of the sample are sandwiched between those of reference N_2 and CO_2 (5 grade purity) gases, which have been calibrated using a series of reference materials, in turn calibrated against IAEA international standards, such as the limestone JLs-1, the peach leaves NIST SRM1547, the Carrara Marble (calibrated at the Institute of Geoscience and Georesources of the National Council of Researches of Pisa), and the synthetic sulfanilamide provided by Isoprime Ltd. Mass peaks were recalculated as isotopic ratios by the Ion Vantage software package. Reference and carrier gases of certified purity were provided by SIAD Ltd. The elemental precision estimated by repeated standard analyses, and accuracy estimated by the comparison between reference and measured values, were in the order of 5% of the absolute measured value. Uncertainties, increase for contents approaching the detection limit (0.001 wt %). Carbon and nitrogen sotope ratios are expressed in the standard (δ) notation in per mil (‰) relative to the notional standards that are the Vienna Pee Dee Belemnite (V-PDB) and Air, respectively. $\delta^{13}C$ and $\delta^{15}C$ values were characterized by an average standard deviation of ±0.1‰ and ±0.2‰, defined by repeated analyses of the above mentioned standards.

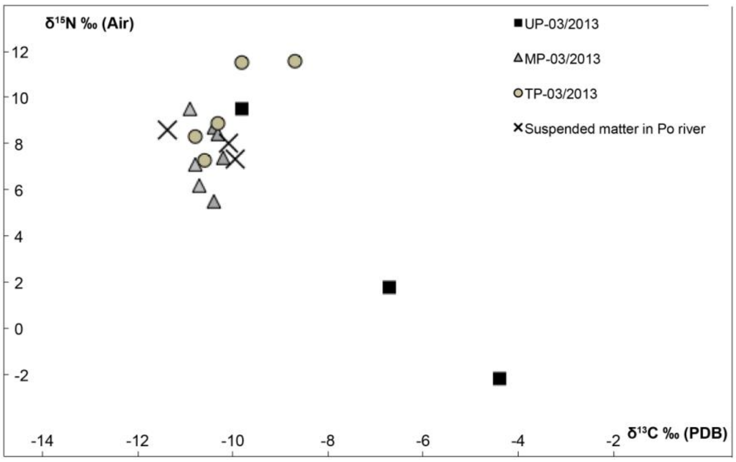

Figure 12: $\delta^{13}C$ - $\delta^{15}N$ isotopic composition of the dissolved components in the Po river waters and in the suspended matter collected in three different sampling campaign in the Occhiobello site (the first sample of the TP). Isotopic composition of the suspended matter is similar to the dissolved components in the same site, suggesting an equilibrium system between the different solutions.

The data, reported in Table 4, Ch. 5, are referred to three distinct periods in which waters have been collected from the same site of Occhiobello. These sampling periods were characterized by distinct discharge that is reflected in different solid load contents, varying from 70 mg/L in October 2013, 80 mg/L in January 2014 and 280 mg/L in February 2014.

These solid particles contain a carbon concentration varying from 4.9% to 5.1%, and a $\delta^{13}C$ ranging from -11.4‰ to -9.9‰. The same particles have nitrogen concentration varying from 0.3% to 0.6%, and $\delta^{15}N$ ranging from 7.3‰ to 8.6‰. The $\delta^{13}C$ and $\delta^{15}N$ isotopic data, plotted in Fig. 11, Ch. 5, shows a remarkable similarity with the isotopic fingerprint recorded in the dissolved components described above. This compositional analogy suggest that the carbon – nitrogen associated to the suspended solid particles has the same origin and is affected by the same processes that were described in the previous chapter.

Considering that the activity of dissolved carbon species are strictly influenced by complex equilibria, in turn related to the temperature and the atmospheric CO_2 content, the presented data represent a snapshot of the current environmental condition and could be taken into account by future investigations to evaluate possible on-going changes. Total suspended material (TSM) data of the three distinct periods were also presented in Table 4, Ch. 5 together with the daily discharge. The Po River discharge (~ 1500 m^3/s) alone accounts for about 60% of the total freshwater inflow into the study area, and it is also the major source of nutrients (Degobbis & Gilmartin, 1990, Justić et al. 1995). It is evident that the value of the TSM recorded in this study overlap the value reported in Tesi et al. (2013) in a period characterized by an average discharge less than 1500 m^3/s. The weight (%) of carbon and nitrogen are also comparable and reported in Table 4, Ch. 5. Total carbon (TC) of each sample range from 3036 µg/L to 13244 µg/L whereas the total nitrogen (TN) ranges from 256 µg/L to 896 µg/L.

Elemental composition of carbon and nitrogen in the suspended matter could be useful to refine the estimate of the geochemical fluxes toward the Adriatic Sea. Considering an average discharge of 1500 m^3/s and a consequent volume of 47,3 km^3, it is possible to calculate the volume of total carbon and nitrogen transferred from the Po river to the Sea (318,000 t/yr and 24,000 t/yr for C and N respectively).

Nitrogen amount in the suspended matter was finally compared with that of the dissolved components, calculated considering that a NO_3^- concentration in riverine waters is around 98% respect to NO_2 and NH_3 (Tesi et al., 2013). The data, reported in Table 4, Ch. 5, suggest that dissolved nitrogen in the Po river waters is nearly 4 times grater that that transported by suspended matter.

5.6 Synthesis and considerations on geochemical and isotopic data

The chemical and isotopic analyses of the Po river water presented in this chapter properly compared with data referred to previous periods, allow the following conclusion:

- River geochemistry remained remarkably homogeneous from the end of the fifties respect to the main water components; on the contrary nitrate drastically increases from less than 1 mg/L in the sixties to more than 10 mg/L in the eighties, and then stabilized around 9 mg/L in the last years. This observation suggests that, although the main hydrochemical facies is geogenic (derived by natural processes), anthropogenic contributions are also influencing the river water. The slight decrease of NO_3^- in Po river water recorded after the eighties, possibly reflects the effects of environmental policy and governance which imposed the treatment of waste water (*s.l.*) and a more sustainable (i.e. limited) use of fertilizers (Bouraoui and Grizzetti 2011).

- Carbon, sulphur and nitrogen isotopic signatures, systematically investigated for the first time are compatible with the weathering and non-equilibrium dissolution of lithologies outcropping in the basin (4.4‰ <$\delta^{13}C_{DIC<}$ -11.0‰; 4.2‰ <$\delta^{34}S_{SO4}$ <8.0‰), whereas $\delta^{15}N_{NO3}$ (between -4.1‰ and 18.0‰) confirms urban (sewage waste waters), agricultural and zoo-technical contributions (fertilizers, animal manure) (Sacchi et al. 2013). The data also highlight reactivity of the dissolved nitrogen species that, in the deltaic part of the river, are affected by denitrification processes.

It is interesting to note that the aquifers of the Padanian plain have the same nitrogen isotopic signature of the Po river, but are characterized by significantly higher concentration (Sacchi et al. 2013). This is probably due to a higher interaction of groundwater with soils that are interested by agricultural practices. This suggests that the severe pollution of the aquifers is not ascribed to inflow of current river water. Noteworthy, the attenuation of the nitrogen load recorded in the river is not observed in groundwater, where NO_3^- continued to increase in the first years of the new millennium reaching a peak in the years 2007-2008 (Sacchi et al. 2013), due to lower resilience, i.e. longer residing times of groundwater and associated longer periods to recover from contamination.

Considering that the outflow of the Po river provides over 50% of the freshwater budget into the Adriatic sea (Pettine et al. 1998), the presented data can contribute to calculate nutrient fluxes by the river to northern Adriatic basin. Calculation should consider updated river discharge (that in the last years is higher than the historical average value of 1,500 m^3/s), chemical composition recalculated considering that NO_3^- concentration in riverine waters is around 98% of the total nitrogen budget (Tesi et al. 2013), and speciation between dissolved and suspended components.

The data presented in this chapter allow to calculate fluxes in two distinct hydrological periods of the year 2013: in March 2013 we recorded higher average NO_3^- concentration respect to May 2013 (10.6 mg/L and 6 mg/L, respectively), but the monthly discharge was decidedly lower in March respect to May 2013 (2,110 m^3/s and 4,450 m^3/s respectively). As result the nitrogen flux from the river to the sea was 426 t/day and 521 t/day in March and May respectively. These balances calculated on annual basis show that the sight NO_3^- decrease respect to the eighties is counterbalanced by an anomalous high average discharge (1,830 m^3/s) that characterized the year 2013. The calculation indicates that the total amount of dissolved nitrogen conveyed by the Po river to the Adriatic sea in the year 2013 was $10.7*10^4$ t/yr. According to the preliminary investigation on the suspended particles this estimation should be increased by ca 25% if we take into consideration also the suspended load. The new flux calculation is slightly lower than previous estimates of the total dissolved nitrogen flux that are in the order of $13 – 16 *10^4$ (Pettine et al. 1998). These estimations contribute to define more detailed models that investigate the nutrient loads in the Adriatic costal ecosystem that is affected by frequent eutrophication processes (Artioli et al. 2005; Palmeri et al. 2005; Viaroli et al. 2013).

Concerning the oxygen-hydrogen stable isotopes (proxies of climatic conditions influencing the hydrological cycle), it is extremely interesting the comparison between the Po river that can be considered a megascale pluviometer recording the current meteoric contribution and the Padanian plain aquifers that are a hydro-archive that store paleo-waters recharged in the last millennia. In this view, the striking $\delta^{18}O$-δD analogies between the riverine water in the middle part of its course ($\delta^{18}O$ between -11.6‰ and -9.9‰; δD between -81.9‰ and -68.1‰) and groundwater of Alpine provenance in confined aquifers of the Padanian plain ($\delta^{18}O$ between -11.4‰ and -9.6‰; δD between -78.8‰ and -63.7‰), seems to preclude that significant climatic warming occurred, in the studied region, during in the last thousands of years.

I emphasize that the current data represent a snapshot of the nowadays river condition, and that future monitoring are useful to highlight a) progressive involvement of further anthropogenic components and b) on-going environmental (climatic) changes.

More in general, the presented data also contribute to integrate the GLObal River Chemistry (GLORICH) database (Hartmann et al. 2014) which is a useful tool to monitor earth surface processes at extensive scales and high resolution, and also to implement existing isotopic hydro-archives that provide additional information that cannot routinely be recovered from elementary chemistry alone (Bowen et al. 2009).

6 ACTIVITY OF THE THIRD YEAR, BASED ON THE SAMPLING CAMPAIGNS 2013-2014

Analysis of Sr isotopes by TIMS at IGG-CNR (Pisa) and by MC – ICP – MS at the University of New Hampshire

The begin of the third year has been devoted to the analyses of the strontium isotopic composition of the Po river waters performed at the IGG-CNR of Pisa under the supervision of Dr. Maddalena Pennisi.

Isotopic analyses of $^{87}Sr/^{86}Sr$ have been carried out on samples collected in August 2010 and 2012 in the MP and TP section respectively. The relative major and trace elements related to this study are reported in the Chapter 4.

Strontium isotopic composition is an important geochemical tracer. It is used in a wide range of applications, including rock dating (Rb–Sr geochronological system), understanding of petrological processes (Faure 1978; Faure, 1986; Hoefs, 2009), understanding of sedimentary processes (Jenkins et al.1995).

The natural variation in the $^{87}Sr/^{86}Sr$ ratio is derived from the radioactive decay of ^{87}Rb to ^{87}Sr. In magmatic and metamorphic rocks, the ratio is a function of the geological age and composition; in terrigenous (i.e. silico-clastic) sedimentary rocks Sr isotopes are strictly related to the composition of the mother rocks from which the particles derived, whereas in marine carbonate rocks $^{87}Sr/^{86}Sr$ reflects the isotopic composition of seawater from which they were precipitated. Over geological history the isotopic composition of seawater has varied considerably and, thus, the isotopic composition of Sr in carbonates is a useful tool in the reconstruction of the geological history. Morover, strontium isotopic composition is an important tool also in hydrology and hydrogeology, enabling tracing of groundwater flow and water mixing. However, in order to use this isotopic tracer, high precision isotopic measurement (better than 0.005%) is required.

In natural waters, the geochemistry of dissolved Sr is very similar to that of Ca. The Sr isotope fractionations in geochemical processes are considered negligible, and the $^{87}Sr/^{86}Sr$ variations in natural systems are mainly controlled by geological age and Rb/Sr ratio (Pennisi.et al. 2006). It is important to remember that the isotopic composition of Sr is constant in present-day seawater, with $^{87}Sr/^{86}Sr$ = 0.7091 (Goldstein and Jacobsen, 1987), whereas published studies of the isotopic composition of Sr in some major rivers (Brass, 1976) support a global average value of $^{87}Sr/^{86}Sr$ for rivers of ~ 0.711. Coherently, in recent years, riverine Sr isotopic compositions have been widely used as a tracer to reveal chemical weathering in the drainage basin, fluxes variation of dissolved load into the oceans and their contributions to seawater $^{87}Sr/^{86}Sr$ ratio change (Wu et al, 2009; Yongbin et al, 2011). Furthermore, in fluvial environment strontium isotopic composition is a useful geo-indicator to investigate: (i) groundwater inflow; (ii) origin of salinity and (iii) mixing processes (Faure, 1978; Brass, 1975; Faure, 1986; Negrel and Roy, 1998; Aubert et al., 2002; Drouet et al., 2005; Rose and Fullagar, 2005).

For running waters draining multi-lithological systems, solute chemistry and isotopic composition ratios in any water parcel can be regarded as a chemical mixture from several sources, and the discrimination of the contribution from each geological formation is a difficult task (Galy et al., 1999). In rivers, strontium derives from dissolution of Ca-bearing minerals, that are widely present in igneous, metamorphic and sedimentary rocks. During weathering reactions the $^{87}Sr/^{86}Sr$ isotopic ratio in solution is the same of the source mineral since no isotopic fractionation occurs. Similarly, strontium isotopic fractionation is negligible when this element is removed from water by either mineral precipitation or cation exchange process (e.g. Bullen et al., 1996). As a consequence, Sr content and Sr isotope composition in river waters are mainly governed by both the lithological features of the catchment area and the weathering rate of the different rock-forming minerals (Négrel, 1997; Négrel et al., 2000).

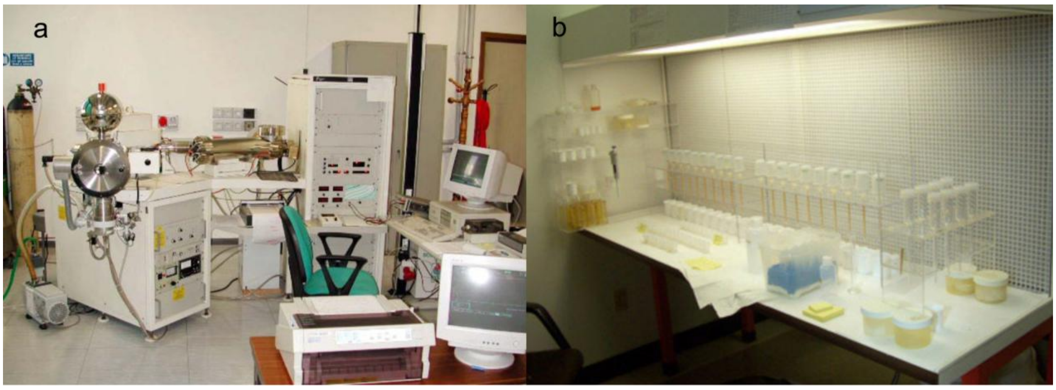

Figure 1: examples of a) theThermal Ionization Mass Spectrometer (TIMS) ; b) the "clean room" similar to those used at IGG-CNR Laboratories of Pisa

From the practical point of view, these analyses require complex (and tedious) preliminary preparation of the samples to separate and concentrate the considered element by a chromatographic technique (Fig. 2a, Ch. 6). This procedure has to be carried out in a "clean room" which is a laboratory with an overpressure and a filtered air inside, where the operator can enter only without shoes and wearing a laboratory coat and gloves that do not generate particles; these particular practices, together with the use of ultrapure reagents, are necessary in order to do not contaminate the samples. For each sample 30 mL were dried and then re-dissolved in 1 mL of HCl 2.5N and then loaded in the chromatographic columns of Fig. 2b, Ch. 6. The columns are subsequently eluted with 6 mL of HCl 2.5N in three steps that leach undesired elements that can create interference during the analyses. Subsequently, strontium is collected with additional 5 mL of HCl 2.5N and dried down. This fraction is re-taken with 2 µL of HNO_3 and deposited on (handmade) tungsten filaments (FiG. 2c, Ch. 6) that are loaded to the TIMS (Thermal Ionization Mass Spectrometry) instrument (Fig. 1 Ch. 6). 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).

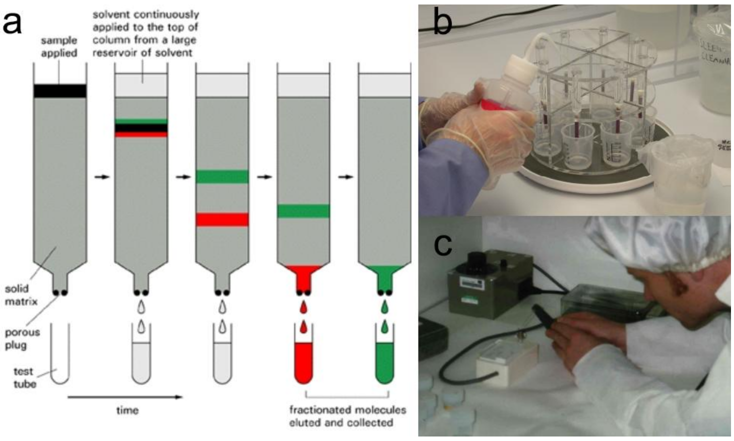

Figure 2: a) Example of chromatographic columns to separate and extract strontium; b) elution of the Sr columns; c) the sample is loaded on the tungsten filament

Results are reported in Table 1 and Fig. 3.

Name	Date	Sr (µg/L)	^{87}Sr/^{86}Sr
Rea	08/2012	287	0.709273
Ticino	08/2012	150	0.708850
Senna Lodigiana	08/2012	290	0.709110
Piacenza	08/2012	225	0.709122
Adda	08/2012	181	0.709683
Cremona	08/2012	200	0.709224
Coltaro	08/2012	218	0.709079
Mincio	08/2012	288	0.708649
Revere	08/2010	271	0.709220
	08/2012	235	0.708980
Occhiobello	08/2012	239	0.708944
Crespino	08/2010	275	0.709157
	08/2012	237	0.708923
Bottrighe	08/2010	307	0.709079
	08/2012	234	0.708931
Taglio di Po	08/2010	288	0.709224
	08/2012	237	0.708959

Table 1: Strontium concentration (by ICP-MS) and the relative isotopic composition measured by TIMS at IGG-CNR on the Po river waters collected in August 2010 and August 2012. Each sample is represented with the relative error.

The $^{87}Sr/^{86}Sr$ value of samples collected in the year 2010 range between 0.709079 and 0.709224, whereas those collected in the year 2012 range between 0.708923 and 0.709273.

If we compare the $^{87}Sr/^{86}Sr$ ratio of samples collected in different years in the same site we observe a very limited variability. More in general, these values are quite similar to the unique value known for the Po river the in literature ($^{87}Sr/^{86}Sr$ 0.70917; Brass et al., 1976). The relative constancy of these isotopic values suggests that this isotopic fingerprint is a geogenic feature. The obtained $^{87}Sr/^{86}Sr$ analyses of the year 2012 are also plotted in Fig. 3, Ch. 6 that emphasizes the isotopic variation along the river course. In this diagram the composition of the Po river water is also compared with that of some important tributaries, such as Ticino and Adda rivers. The Fig. 3, Ch. 6 suggests that Po river in Lombardy display some $^{87}Sr/^{86}Sr$ variations in function of important confluences, whereas downflow in Emilia Romagna the river attains a more homogeneous $^{87}Sr/^{86}Sr$ composition that remains constant with an average value of 0.708948 ± 0.000026.

It can be speculated that although subordinate, carbonatic lithologies are preferentially involved in the weathering processes inducing the typical Ca-HCO_3 hydrochemical facies and a specific strontium isotopic signature ($^{87}Sr/^{86}Sr$ 0.708923 – 0.709273) that is intermediate between that of Mesozoic carbonates (0.7070-0.7088; Faure, 1978) and that felsic igneous and metamorphic rocks (> 0.70145; Voshage, 1987).

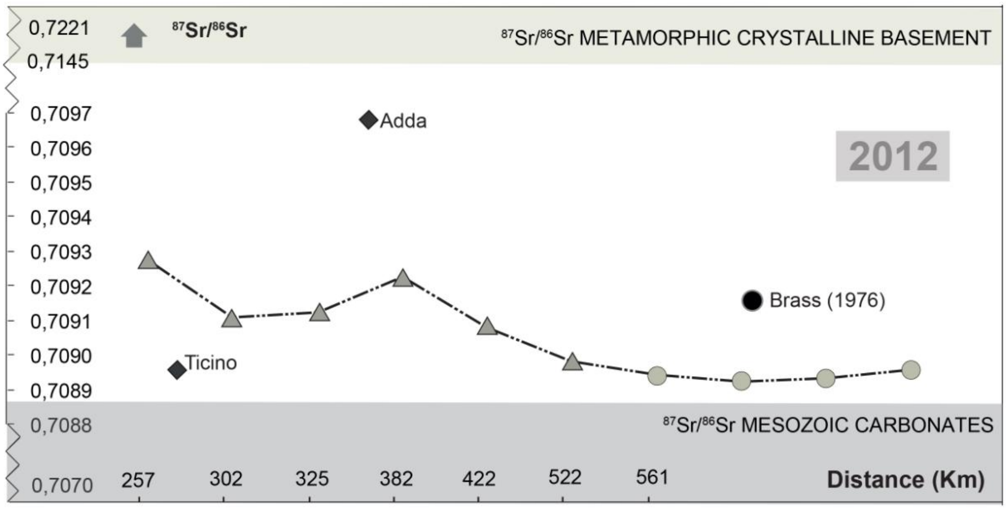

Figure 3: Isotopic variations of the $^{87}Sr/^{86}Sr$ measured by TIMS along the Po River in the MP and TP waters compared with the isotopic ratios of the Mesozoic carbonates (Faure et al. 1978) and metamorphic crystalline basement of the Alpine arc (Voshage et al., 1987). Left bank tributaries (Ticino, Adda and Mincio rivers) isotopic composition is also reported in order to compare and evidence the contribution of the isotopic fingerprint.

The Sr isotope analyses carried out by TIMS at the CNR of Pisa have been implemented thanks to collaboration with Professor Julie Bryce of the New Hampshire University. This collaboration has been possible thanks to an addition scholarship, provided by the University of Ferrara, specifically dedicated for young researchers to spend a study period abroad. In this framework I spent a three months research period (from July to September 2014) at the New Hampshire University (United States).

In this Institution, the additional measurements of $^{87}Sr/^{86}Sr$ have been carried out by a brand new MC-ICP-MS instrument that has been installed in the year 2014 (Fig. 4). Multi Collector ICP – MS that combines a plasma source, a magnetic separator and several Faraday cups. This new generation of instruments represents the new frontier of analytical geochemistry allowing a quicker determination of strontium isotopic ratios (respect to TIMS) that has been performed on a more systematic basis, analysing a higher number of samples.

Note that I have been present during the installation of the mentioned new instrument. This has been very important because I was able to understand the fundamental parts of the technique and I followed the relative training course under the supervision of technicians of the Nu Instrument Company. The set up of the instrument was quite complex, followed by a long period for the calibrations.

Figure 4: The new MC – ICP – MS at the New Hampshire University

It is important to note that a new sampling campaign has been carried out in May 2014 in order to obtain water samples suitable to be investigated by MC-ICP-MS. Po river samples were collected in the same sites of the previous years. Additional samples were taken from some important tributaries from the right bank (Tanaro, Trebbia, Taro, Secchia and Panaro river) and from the left bank (Pellice, Sesia, Dora Baltea, Ticino, Lambro, Adda, Oglio and Mincio river).

As explained in the previous chapters, sampling location was geo-referenced by a portable global positioning system (GPS), to locate the points and to set up future field surveys (Table 2). 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, then water samples were filtered by 0.45 µm filters (Minisart® NML syringe cellulose acetate filters) and stored in two distinct 50 ml bottles, for the analysis of oxygen/hydrogen isotopes. These preliminary analyses analogous to those carried out in the previous years (2010 – 2013) are reported in Tab. 2, Ch. 6.

Name	Date	Latitude	Longitude	pH	T (°C)	EC (µS/cm)	$\delta^{18}O$‰	δD‰	d-exc‰	Na^+	Mg^{2+}	K^+	Ca^{2+}	HCO_3^-
Po river Upper Part (UP)														
Pian della Re	05/2014	44°42' 04.00"	07° 05' 42.00"	8.3	5.5	60	-13.5	-94.8	14.9	0.48	2.63	1.03	9.81	60
Rio Martino (Grotte)	05/2014	44° 42' 5.00"	07° 08' 3.00"				-13.3	-92.6	15.5					
Crissolo		44° 41' 52.38"	07° 09' 33.9"				-13.0	-91.5	13.9					
Sanfront		44° 39' 03.89"	07° 19' 58.90"	8.5	9	110	-12.7	-89.5	13.8	1.13	3.56	1.22	12.77	65
Carignano		44° 54' 31.37"	07° 41' 29.93"	8.2	15	370	-12.2	-85.7	13.9	4.14	9.43	2.62	49.15	135
Po river Middle Part (MP)														
Settimo Torinese		45° 07' 29.63"	07° 46' 15.37"	8.5	17	410	-12.1	-85.0	13.4	7.80	13.42	2.82	47.79	137
Crescentino		45° 10' 32.96"	08° 05' 55.61"	8.4	16	400	-12.2	-86.2	13.1	7.50	12.33	2.78	48.80	140
Frassineto Po		45° 08' 39.77"	08° 32' 27.29"	8.7	16	370	-12.4	-86.6	14.1	6.53	10.21	1.63	45.16	90
Pieve al Cairo		45° 2'10.95"	08° 49' 16.20"	8.6	17	340	-11.8	-82.7	13.5	7.03	9.44	2.96	39.90	120
Balossa Bigli	05/2014	45° 03' 58.00"	08° 54' 48.80"	8.6	16	350	-11.6	-80.3	14.4	8.34	9.75	3.15	38.72	120
Rea		45° 07' 27.90"	09° 09' 31.96"	8.5	17	390	-11.3	-78.9	13.1	9.26	10.19	2.78	43.11	120
Senna Lodigiana		45° 07' 46.41"	09° 38' 07.16"	8.5	18	350	-10.4	-73.2	11.6	10.91	9.56	3.18	43.30	120
Piacenza		45° 03' 41.76"	09° 41' 53.51"	8.6	17	350	-10.5	-72.9	12.2	10.57	9.58	2.25	39.32	147
Cremona		45° 07' 43.34"	09° 59' 45.93"	8.7	18	360	-10.3	-71.3	12.7	8.80	9.67	2.40	37.52	105
Coltaro		44° 59' 03.67"	10° 18' 27.70"	8.5	18	370	-10.1	-70.1	12.3	11.79	12.04	3.34	40.22	126
Revere		45° 03' 27.46"	11° 07' 52.80"	8.7	18	390	-9.9	-68.8	11.8	12.25	11.67	2.50	41.62	102
Po river Termina Part (TP)														
Occhiobello		44° 55' 04.78"	11° 34' 46.10"	8.8	17	380	-10.0	-69.8	11.2	11.98	12.24	3.11	41.16	135
Crespino		44° 58' 37.64"	11° 52' 53.06"	8.6	18	390	-10.2	-70.1	12.7	13.27	11.13	3.52	37.19	130
Bottrighe		45° 01' 15.17"	12° 04' 44.24"	8.5	18	390	-10.0	-71.2	9.8	13.18	11.10	3.69	36.15	130
Taglio di Po		45° 00' 36.12"	12° 13' 09.12"	8.5	19	420	-9.9	-70.8	9.9	12.98	11.32	3.10	36.37	150
Po di Levante (Porto Levante)		45° 02' 43.00"	12° 19' 27.52"	8.7	20	1120	-8.4	-61.7	6.8	868.70	121.20	66.79	69.49	200
Po river Left Bank tributaries														
Pellice	05/2014	44° 48' 43,30"	07° 29' 56,40"	8.2	14	110	-12.9	-90.4	14.6	1.54	2.03	2.86	13.23	60
Dora Baltea		45° 11' 31,80"	08° 02' 28,04"	8.7	14	240	-13.2	-96.1	11.4	4.26	6.84	2.71	27.95	75
Sesia		45° 10' 30,34"	08° 33' 04,02"	8.6	17	190	-11.1	-78.9	11.7	5.85	5.69	3.53	19.72	90
Ticino	05/2014	45° 08' 40,88"	09° 13' 48,62"	8.6	16	230	-9.7	-66.0	12.8	7.42	6.09	2.76	23.99	75
Lambro		45° 09' 56,40"	09° 31' 55,22"	8.3	19	570	-9.2	-60.7	14.0	40.50	14.72	5.12	63.71	132
Adda		45° 09' 18,97"	09° 51' 13,62"	8.6	16	360	-10.6	-66.9	19.2	8.58	11.33	2.37	47.11	93
Oglio		45° 16' 17,01"	10° 05' 0,76"	8.5	18	410	-9.7	-65.1	13.6	5.13	10.17	2.14	57.22	120
Mincio		45° 05' 11,58"	10° 57' 43,99"	8.9	20	330	-7.9	-54.7	9.4	9.83	13.53	2.67	39.39	138
Po river Right Bank tributaries														
Tanaro		44° 59' 4,05"	08° 43' 37,00"	8.6	16.6	420	-11.6	-80.8	13.7	11.84	13.40	2.27	48.86	105
Scrivia	05/2014	44° 53' 41,03"	08° 50' 45,79"	8.7	15	470	-8.5	-55.3	14.1	18.15	9.03	1.70	61.62	144
Trebbia		45° 03' 21,04"	09° 38' 03,22"	9	18	360	-8.6	-56.3	13.3	10.81	10.56	1.13	43.97	75
Taro		44° 59' 20,46"	10° 15' 0,33"	8.8	21	470	-8.5	-56.9	12.4	18.23	17.52	2.56	53.62	138
Secchia		45° 02' 55,80"	11° 00' 0,4"	8.8	16	850	-9.6	-64.9	13.3	78.76	19.70	3.56	92.34	198
Panaro	05/2014	44° 54' 49,80"	11° 24' 45,5"	8.7	16	520	-9.2	-62.4	12.7	24.24	17.13	3.60	61.02	159

Table 2: Physical – chemical parameters measured in field and the isotopic composition ($\delta^{18}O$ – δD and the relative deuterium excess expressed in ‰) of the Po river water and its main tributaries.

Parameters measured in-situ (pH, temperature and conductivity) during the sampling campaign carried out on May 2014 have been reported in Tab. 2, Ch. 6. The Po river water samples have been subdivided in UP, MP and TP as described in the Chapter 4 in order to delineate spatial-temporal changes. The main tributaries of the Po river have been subdivided in *“Left Bank”* – Pellice, Dora Baltea, Sesia, Ticino, Lambro, Adda, Oglio and Mincio – and *“Right Bank”* – Tanaro, Scrivia, Trebbia, Taro, Secchia, Panaro -.

pH was rather homogeneous, i.e. 8.2 – 8.5 in UP, 8.4 - 8.7 in MP, 8.5-8.8 in TP, without a systematic trends along the river course. The main tributaries evidence similar pH values of the Po river nearby the confluence. Water conductivity was also variable, increasing from UP (from 60 μS/cm to 370 μS/cm) through MP (from 340 μS/cm to 410 μS/cm), up to TP where samples reach the highest value of 1,120 μS/cm). This indicates progressively higher amounts of dissolved components moving from the UP, to the MP, and to the TP catchment areas. The Po river water samples analysed in this new sampling campaign display a Ca–HCO_3 hydrological facies that perfectly fit with those of the previous years (2012 and 2013) and described in Chapters 4 and 5.

The Strontium concentration, crucial data to study the relative isotopic composition, is 24 μg/L at *Pian del Re* source and increase gradually throughout the riverine course (average value 292 μg/L ±37 in the MP) and reach in *Porto Levante* the highest value of 663 μg/L. Ca^{2+} varying between 9.81 mg/L and 69.5 mg/L at the *Pian del Re* source to *Porto Levante*, respectively, with and average value of 40 mg/L (±4) for the MP samples.

The tributaries of the Po river evidenced a marked variability in strontium concentration: In the left bank tributaries (of alpine provenance) the Pellice river, located in the UP sector of the basin, records a Sr concentration of 53 μg/L, whereas the Oglio river (MP area) can be considered anomalous, with a Sr concentration of 461 μg/L. The right bank tributaries (of apennine origin) record a higher strontium concentration ranging between 448 μg/L and 1117 μg/L. The Tanaro river, although is a tributary from the right part its source is in the Ligurian alps and has a strontium concentration of 310 μg.

The waters above described have been investigated at the Department of Earth Science of the New Hampshire University to obtain a more complete data set of Sr isotopic analyses. Samples were processed in their “clean room”, through chromatographic techniques similar to those described above, in order to separate strontium from the other elements (Fig. 5).

Name	Date	Sr (µg/L)	^{87}Sr/^{86}Sr	2σ
Po river Upper Part (UP)				
Pian della R	05/2014	23.7	0.709745	0.000006
Rio Martino	05/2014			
Crissolo				
Sanfront		112	0.709601	0.000007
Carignano		309	0.709702	0.000009
Po river Middle Part (MP)				
Settimo Torinese		410		
Crescentino		360	0.709187	0.000009
Frassineto Po		345	0.709269	0.000009
Pieve al Cairo		272		
Balossa Big	05/2014	259	0.709453	0.000010
Rea		310		
Senna Lodigiana		287		
Piacenza		287	0.709614	0.000010
Cremona		238	0.709154	0.000011
Coltaro		275	0.709148	0.000010
Revere		289	0.708957	0.000010
Po river Termina Part (TP)				0.000006
Occhiobello		286	0.708956	0.000008
Crespino		252	0.709185	
Bottrighe		252		
Taglio di Po		257	0.709172	0.000007
Po di Levante (Porto Le		663	0.709267	0.000007
Po river Left Bank tributaries				
Pellice	05/2014	53.7	0.712335	0.000008
Dora Baltea		215	0.708627	0.000009
Sesia		121	0.709998	0.000008
Ticino	05/2014	180	0.709055	0.000008
Lambro		272	0.708981	0.000009
Adda		230	0.709738	0.000006
Oglio		461	0.708765	0.000008
Mincio		134	0.708801	0.000007
Po river Right Bank tributaries				
Tanaro		310	0.709258	0.000010
Scrivia	05/2014	675		
Trebbia		448	0.708843	0.000007
Taro		543	0.708558	0.000008
Secchia		1117	0.708524	0.000010
Panaro	05/2014	481	0.709514	0.000007

Table 3: Strontium concentration and the relative isotopic composition measured by MC – ICP – MS at the University of New Hampshire. Each samples is represented with the relative error.

During the collection of isotopic data, the analysis of the Sr SRM-NIST 987 standard gave a ^{86}Sr$^{/88}$Sr value of 0.710248± 0.000017. This value considered with the associated error is comparable to that obtained on the same standard at the IGG-CNR of Pisa. For this reason the results obtained in the two laboratories can be compare.

Figure 5: Chromatographic columns in the “Clean room” at the Department of Earth Sciences of the University of New Hampshire, USA.

The strontium concentration and the relative isotopic composition of the Po river waters and its main tributaries carried out by MC-ICP-MS on Po river water collected in May 2014 are reported in Table 3 This wider data-set allows to recognise some trends along the riverine course.

The higher value (0.709745) has been recorded at *Pian del Re (*source), and the lower at *Occhiobello* (0.708956). The UP samples have an isotopic signature slightly higher than MP samples, as evident in Fig. 6 and Fig. 7, Ch. 6.

A marked spike toward less radiogenic values are observed in correspondence of *Crescentino* (MP, 0.709187). Then, samples of the MP are generally characterized by an increase of the Sr isotopic ratio along the riverine course up to *Piacenza* (0.709614) and finally decrease along terminal part of the river. The last samples of the terminal part evidence a further increase of the Sr isotopic ratio.

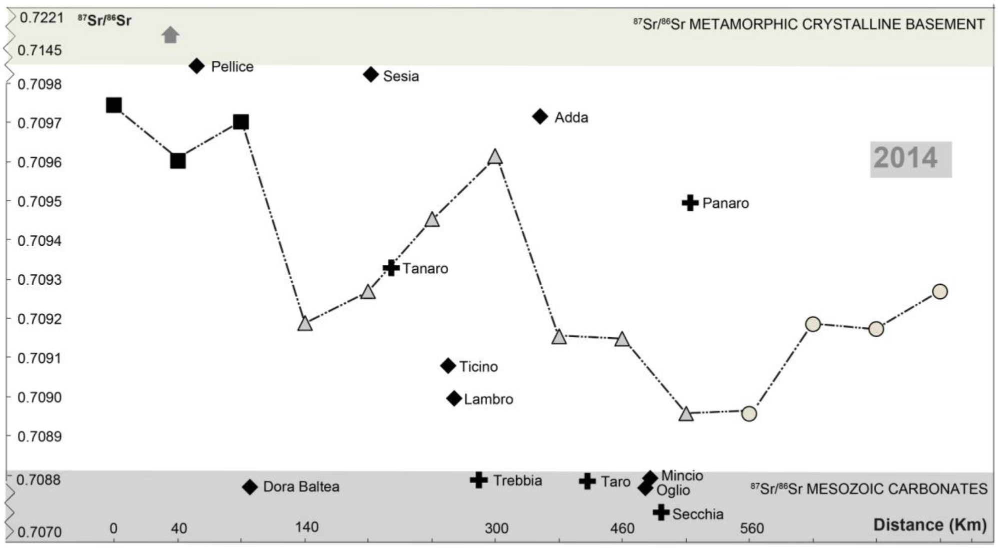

Figure 6: Isotopic variation of $^{87}Sr/^{86}Sr$ measured by MC – ICP - MS along the Po river sampled in May 2014 from the source (Pian del Re) to the Adriatic sea. Istopic ration of the riverine waters are compared with the isotopic ranges of the Mesozoic carbonates (Faure et al. 1978) and metamorphic crystalline basement of the Alpine arc (Voshage et al. 1987). Isotopic signature of the main tribuataries (from the left and right banks) are also represents to evidence the contribution of the isotopic fingerprint.

The tributary distributed in the whole catchment area reports marked variation: Pellice river, located in the Cozie alps in the UP sector reveal the highest value of the tributary of 0.712335. This value is in the range of the isotopic composition of the rocks in the crystalline basement (Fig. 6, Ch. 6). Similar isotopic compositions are evident also in the Sesia river (which flows from Mount Rosa) and Adda river (which flows from the Retic Alps). It is interesting to note that the prevalent lithologies in the catchments of these rivers pertain to the crystalline basement.

The isotopic composition of Ticino and Tanaro river (which are the larger tributaries of the Po river with and average discharge of 290 m^3/s and 116 m^3/s) reveal an isotopic composition similar to most of the samples in the Po river.

Among the left bank tributaries (of Alpine provenance) Dora Baltea is characterized by the lower Sr isotopic value, plausibly in connection with the widespread of ophiolites and calc-shists in its catchment (Garzanti et al., 2012).

Furthermore, Oglio river evidences geochemical differences from the other Alpine river, with an isotopic value of 0.708765, probably due to the carbonate lithologies outcropping in its basin (Mesozoic carbonates).

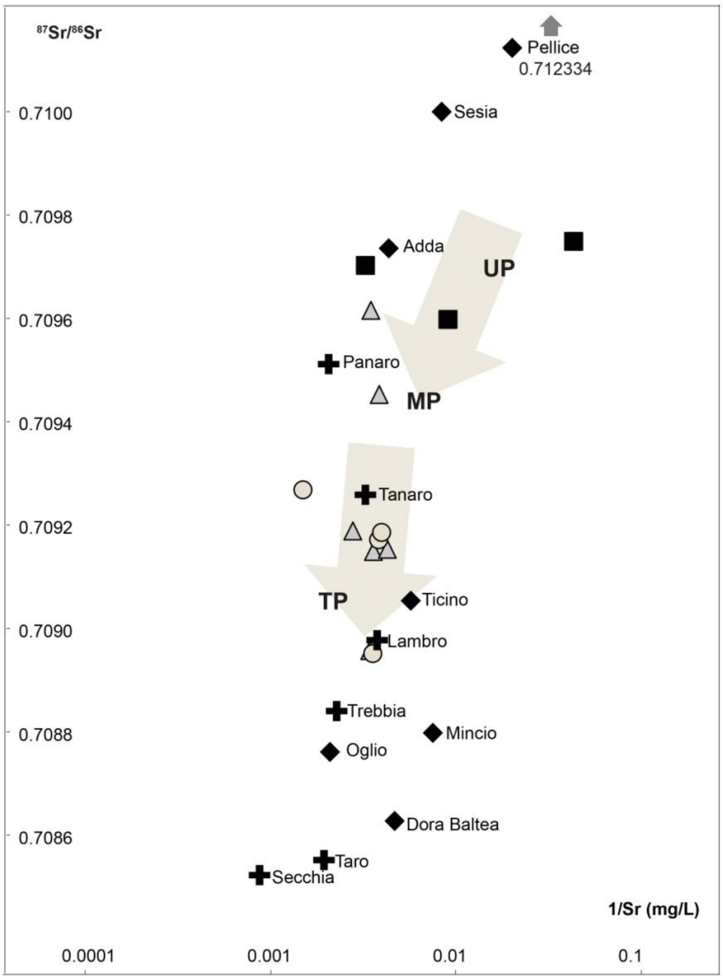

Figure 7: Binary diagram 1/Sr vs $^{87}Sr/^{86}Sr$ of the Po river waters and the main tributaries. Light grey arrows are used to indicate isotopic trend from the UP waters to the MP and TP.

The Appennine tributaries (i.e. Trebbia, Taro and Secchia) evidence a higher strontium concentration coupled with an isotopic range between 0.708843 and 0.708524 that reveal a strong interaction with the carbonate lithologies prevalent in their catchments.

The difference observed between the Sr isotopic data obtained by TIMS at the CNR of Pisa and those obtained by MC-ICP-MS at the University of New

Hamphire, in my view, are not related to analytical flaws. I think that the $^{87}Sr/^{86}Sr$ values of the Po river water are affected by slight variations in distinct hydrological periods. In this framework, I can state that the isotopic variability increases during a high discharge period such as the one in which samples have been collected in the year 2014 (May). I could assume that the average MP isotopic composition carried out at Pisa (0.709131) is representative of the river composition during the low discharge period, whereas the average MP isotopic composition carried out at the New Hampshire University (0.709255) is representative of the river composition during the high discharge period.

Additional isotopic tracers that would be powerful to identify the lithologies that contribute to the Po river water chemistry could be the isotopes of neodymium ($^{143}Nd/^{144}Nd$). This element pertains to the rare earth element group (REE) and has been widely used to investigate petrological processes as well as to date rocks and minerals (Faure, 1986). Potentially the same tracers can be used also in hydrology and hydrogeology: the isotopic composition of waters reflects that of the interacting rocks without significant fractionations. Sr and Nd systematic in riverine water have been taken into consideration by Goldstein and Jacobsen, 1987 and 1988, Palmenr and Edmond, 1992 for American rivers and by Frost 1986 for small catchment in Europe. Unfortunately the practical application for these tracers has been limited - and often related to the suspended loads/ bed sediments - due to the very low concentration usually recorded in natural waters. This limit is going to be bypassed by the new generation of mass spectrometers such as the MC-ICP-MS that was available at the University of the New Hampshire.

Thinking to the isotopic analysis of neodymium, in the sampling performed in May 2014, in each site additional bottles characterized by significant volume (4 L) were taken in order to concentrate the total dissolved salts as well as to separate the suspended matter. After 4 days most part of the suspended particles were deposited on the bottom of the bottles, and was possible to separate the water column from the suspended particles using a syringe. Afterwards the sediment particles were dried down on the hot plate at 110 °C for 8 hours and the recovered water was evaporated on the hot plate at 110°C obtaining the dissolved salts. Both the dissolved salts (DS) and the suspended particles (Total Suspended Matter, TSM) were weighed and expressed as total suspended matter available in the 4L (total amount) and the total suspended matter in 1L (mg/L). The data are presented in Table 4.

PO RIVER - dry samples

n.	Location	TSM mg $_{tot}$	TSM mg/L	DS mg $_{tot}$	DS mg/L
1	*Pian del Re*	na	na	10,0	10,0
2	*Sanfront*	na	na	24,4	24,4
3	*Carignano*	48,2	19,3	97,9	97,9
4	*Settimo Torinese*	19,4	7,76	111	111
5	*Crescentino*	42,7	17,1	443	443
6	*Frassineto Po*	36,8	14,7	259	259
7	*Pieve al Cairo*	75,3	30,1	74,6	74,6
8	*Balossa Bigli*	136	49,5	90,8	90,8
9	*Rea*	120	47,8	114	114
10	*Senna Lodigiana*	92,4	33,6	85,0	85,0
11	*Piacenza*	66,2	26,5	56,7	56,7
12	*Cremona*	78,5	31,4	97,4	97,4
13	*Coltaro*	148	36,9	59,5	59,5
14	*Revere*	223	55,7	61,0	61,0
15	*Occhiobello*	136	33,9	72,6	72,6
16	*Crespino*	108	35,9	92,9	92,9
17	*Bottrighe*	na	na	na	na
18	*Taglio di Po*	21,9	14,6	91,6	91,6
19	*Porto Levante*	278	185	222	222

TRIBUTARIES OF THE PO RIVER

n.	Tributaries	TSM mg $_{tot}$	TSM mg/L	DS mg $_{tot}$	DS mg/L
1	*Pellice*	nd	0	47,3	23,7
2	*Dora Baltea*	20,1	10,1	290	145
3	*Sesia river*	18,0	9,00	84,9	42,5
4	*Ticino*	12,1	6,05	98,9	49,4
5	*Lambro*	158	63,2	502	201
6	*Adda*	49,7	24,9	254	127
7	*Oglio*	267	133	243	121
8	*Mincio*	82,9	27,6	202	67,4
9	*Tanaro*	181	72,4	242	96,8
10	*Scrivia*	17,8	8,90	105	52,4
11	*Trebbia*	174	69,4	364	146
12	*Taro*	204	58,3	384	128
13	*Secchia*	464	133	547	156
14	*Panaro*	175	50,0	627	209

Table 4: Total suspended matter (TSM) and dissolved component (DC) of the Po river waters (total amount and mg/L). TSM (mg$_{tot}$) and DS mg$_{tot}$) is related to the total amount available in 4L.

These powders, representative of the dissolved and suspended matter will be investigated (hopefully) soon at the New Hampshire University, as they represent matrices in which both Sr and Nd isotopic ratios should be detectable.

7 INSIGHTS ON THE MORE SENSITIVE PO RIVER ECOSYSTEM: A FOCUS ON THE GEOCHEMISTRY OF PO DELTA WATERS

Fig. 1: Po di Goro, in the "Delta del Po" area

In this part I present the geochemical and isotopic results of Po river waters in its Delta (Figs. 1 and 2, Ch. 7) .The water of the terminal part of the river was monitored for 4 years, within the framework of several undergraduated theses that I co-supervised, and presented in this section in order to compare geochemical and isotopic data in different periods with different hydrological conditions. In particular the aim of this chapter is to study and compare the water chemistry in the different period of the year. It is also useful compare the data during summers of distinct years, in particular for the years 2012 and 2013 in which water samples were collected in all the branches of the delta using a boat.

The results of this section were fundamentals for evidencing mixing processes with seawater as well as to investigate potential anthropogenic contribution that influence the freshwaters in this complex system. The Delta area, in fact can be considered as a multicomponent sink that involve different biogeochemical processes.

Parameters measured in situ, such as pH, temperature and conductivity of the Po river waters in the Delta del Po have been reported in Table 1. pH is moderately homogeneous and varying from 7,5 to 8,8. The highest value was registered in Occhiobello site during the flood in May 2014.

Electrical conductivity (expressed in µS/cm) is extremely variable as long as the river course approach to the Adriatic sea and in the different branches. The highest value registered is 28000 µS/cm in August 2013 for the sample located at the Po di Tolle mouth, whereas Po di Venezia mouth a value of 6200 µS/cm is registered. TDS, calculated as the sum of the major chemical species, reveal that the highest values registered are 8198 mg/L and 24773 mg/L for August 2012 and August 2013, respectively. The investigated waters although generally maintaining a Ca-HCO_3 hydrochemical facies, show a more marked variation respect to the other parts of the river. This statement is emphasized in the Gibbs diagram (Fig.2, Ch. 7) as well as in the Langelier diagram (Fig. 3, Ch. 7) that evidenced the occurrence of mixing processes with saline waters.

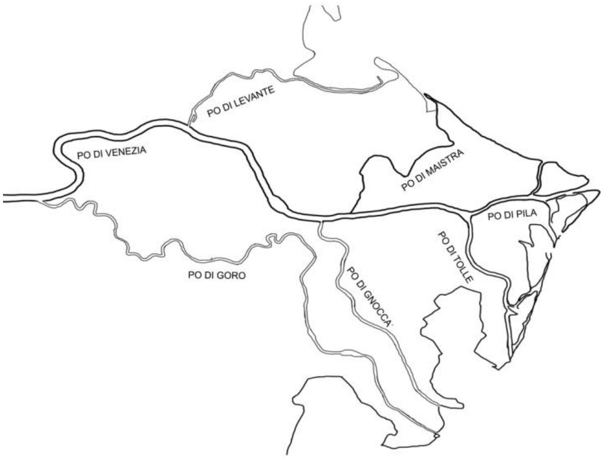

Figure 2: Po river delta consisting of six major distributaries; from the main course the first diversion (southward) is represented by Po di Goro which drains ca. 15 % of the original flow. A second diversion (northward) is represented by Po di Levante, which is artificially regulated and separated 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 isotopic values measured in the different branches of the deltaic part evidenced a remarkable/significant trend toward less negative value and, in particular for the samples collected in August, where evaporation effects are superimposed to the above mentioned mixing processes. These mixing processes are transient because they are strictly related with a) discharge of the riverine system that varies seasonally and b) the tide cycles that in turn influence the river flow into the sea. According to our data I envisaged up to 20% mixing with seawater in the Po di Venezia, that is the main branch of the Delta; whereas a 50% mixing with seawater in the Po di Tolle (one of the peripheral branches). In Fig. 4, Ch. 7 is reported Cl$^-$ vs Na$^+$ in the three different summers (August 2010, 2012 and 2013). The chloride content is extremely variable from the main channel to the peripheral branches where mixing processes are prominent.

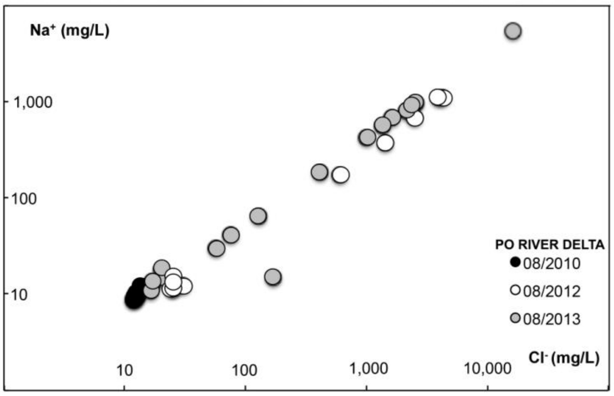

Fig. 4: Binary diagram Cl$^-$ vs Na$^+$ of the terminal part of the Po river waters collected during August (drought period) in three years, 2010 – 2013.

This observation reinforce the hypothesis that salinization become predominant in the outer branches respect to the main course where the discharge (and the flow) are more effective (Fig. 4, Ch. 7).

The isotopic analyses corroborate the delineated hypothesis. The deltaic water became more variable than that of the other parts of the river with δ^{18}O varying between -10,4‰ and 6,9‰ and δD varying from -71‰ to -55,1‰.

Therefore, I emphasize that this part of the river is more sensitive to environmental changes respect of the other sectors of the river and has to be monitored with more attention.

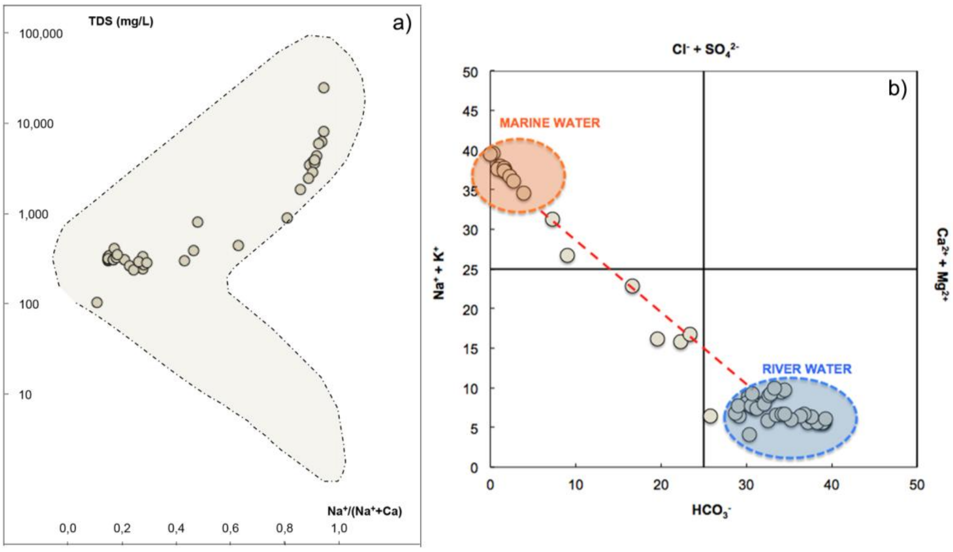

Figure 3: a) Gibbs diagram (TDS vs $[Na^+/(Na^++Ca^{2+})]$) reported in mg/L for the Po river water; b) Ludwig – Langelier diagram where $(Na^++K^+) = (\Sigma r_{Na+K}/\Sigma\ R\ r_{cations})\times 50$ and $(HCO_3)=r_{HCO3}/\Sigma r_{anions})\times 50$, where r is the mEq/L concentration of the constituents.

In Fig. 5, Ch. 7 $\delta^{18}O$ – δD isotopic composition of the Po river water, sampled in different periods, are plotted together with GMWL (Craig, 1961) and the local meteoric water line (LMWL) defined for Northern Italy (Longinelli and Selmo, 2006). Different symbols were used to discriminate samples collected in different seasons.

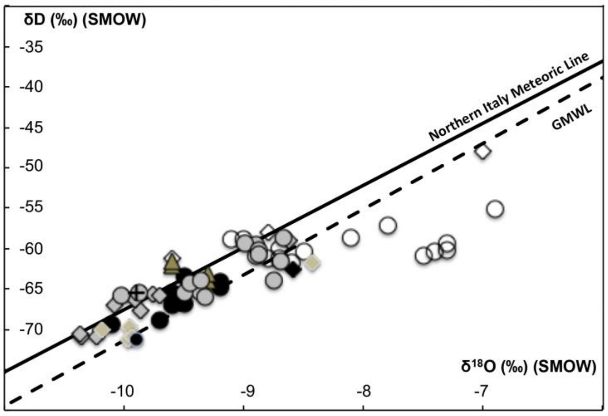

Figure 5: $\delta^{18}O$ – δD isotopic composition of the Po river waters in the Po river Delta in different seasons: black circle □□□ samples collected in August 2010; black cross for sample collected in November 2011, black diamonds □□□ samples collected in February 2011; grey triangle for samples collected in December 2011, □□□□□ diamond for samples collected in April 2012, white circles for samples collected in August 2012, grey diamonds for samples collected in March and May 2013, grey circles for samples collected in August 2013 and light grey diamonds for samples collected in May 2014. The dotted line represents the global meteoric water line (GMWL; Craig, 1961); dashed line represent the local meteoric water line (LMWL) defined for Northern Italy (Longinelli and Selmo, 2003).

Considering that the river water is a dynamic multi-component system, whose bulk chemical composition varies as a function of time and distance from the source, the recorded composition provides a geochemical background that is useful for an environmental monitoring. In this view, the oxygen/hydrogen isotopes provide a snapshot of the current climatic conditions to be compared with the literature data and with the future composition to provide a hydro-archive that should be updated, as a proxy to evaluate on-going climatic changes (Zuppi and Sacchi, 2004). The recorded $\delta^{18}O$ values are compared with the local groundwaters (Rapti Caputo and Martinelli) and with the Northern Italy Meteoric Water Line (Longinelli and Selmo, 2003). These isotopic data, compared with chemical analyses, could be useful to investigate and detect potential industrial, agricultural and urban contaminations, to define mixing processes with the connected alluvial aquifers, and to study the extent of sea-water intrusion and salinization in the terminal (delta) part of the river.

8 COMPARISON BETWEEN ANALYSES CARRIED OUT IN DIFFERENT YEARS AND COMPARISON WITH OTHER RIVERINE SYSTEMS

Within this final chapter the data presented in the previous sections are discussed altogether in a coherent framework valid for the years 2010 – 2014. Isotopic data of the Po river waters at basin scale (from the Monviso to the delta) are registered for the years 2010, 2011, 2012, 2013 and 2014. This discussion is subsequently enriched by comparison with other (coeval) data carried out by myself on the second more important river of Northern Italy, i.e. Adige river. These additional data are included in several theses that I supervised in collaboration with Prof. Gianluca Bianchini, during my official activity of teaching assistance (Appendix D).

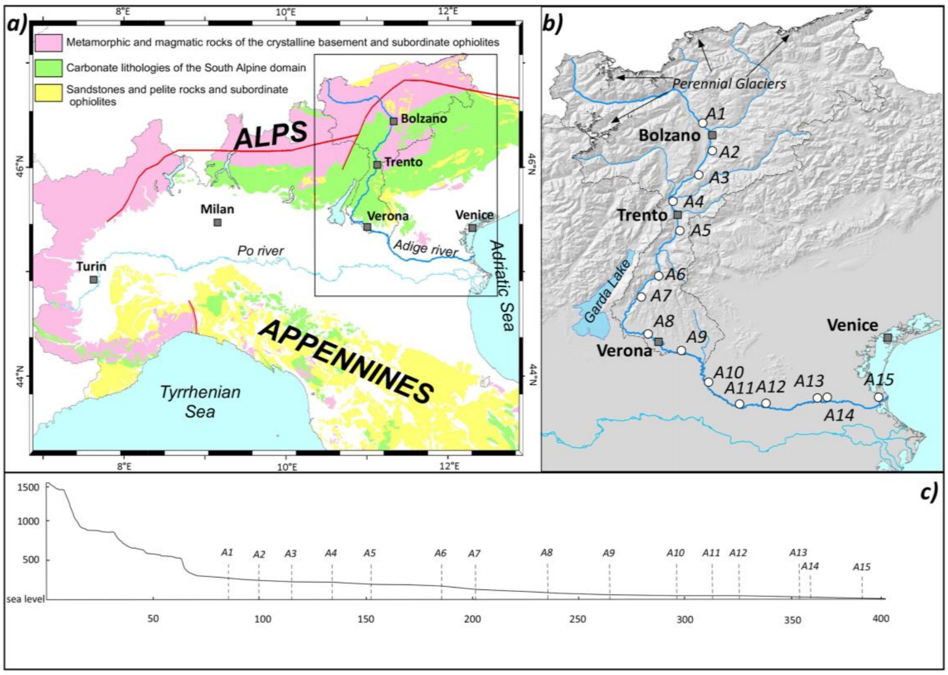

Figure 1: a) Sketch map of the main outcropping lithology of the Northern Italy with Po and Adige river basins; b and c) location of the samples collected in river Adige.

The aim of this chapter is to make comparisons with the analyses of waters collected in several years during particular climatic condition and to evaluate the water chemistry in different fluvial systems.

It is important to note that Po river waters record important evolution trends in the upper and in the terminal parts, whereas are strongly homogeneous in the middle part. In the Upper part the TDS is relatively low and water fingerprint still maintain the meteoric influence. Progressive interactions with the lithologies (Fig. 1 Ch. 8) ultimately lead to the main hydrochemical facies that remains relatively constant and homogeneous starting from the city of Torino to Revere (in the Mantova province). The variations of the terminal part are related to multiple processes, including a flow velocity reduction and a more significant inflow of groundwater to the river, more effective evaporation, and finally mixing with saline water.

This means that the Po river, that already displays a significant degree of water rock interaction in the UP samples (evident in the Gibbs diagram, 2, Ch. 8), maintains a similar geochemical signature throughout the Padanian Plain for ≈ 450 km, with a TDS average of 275 mg/L, 309 mg/L and 254 mg/L for April 2012, August 2012 and March 2013 respectively. The terminal part (TP) widely discussed in the previous chapter reports a TDS variability in distinct branches of the delta, with a TDS that varies from 360 mg/L to 28000 mg/L.

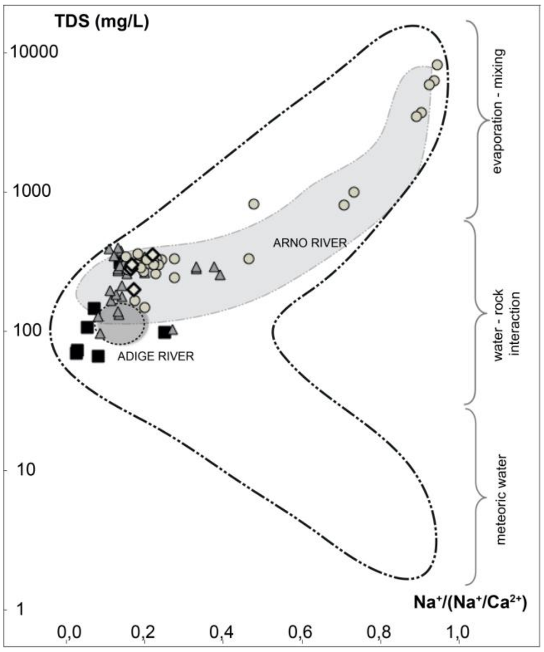

Figure 2: Gibbs diagram: TDS vs $[Na^+/(Na^+ + Ca^{2+})]$ reported in mg/L for the Po river together with compositional fields relative to the Adige river (sampling campaign 2013-2014) and to the Arno river (Nisi, 2008).

It is also important to note that the recorded values are very similar to those available for the Po river since fifty years ago (Gherardelli and Canali, 1960) and that only the nitrate concentration increased in the last decades. Compositional field of Adige and Arno river waters are also reported in Fig. 2, Ch.8 for the comparison. It is evident that the Adige runoff waters maintains a limited variation along the whole path, with HCO_3^- from 54 to 126 mg/L; $Na^+/(Na^++Ca^{2+})$ from 0,1 from to 0,17; Na^+ from 3,9 to 6,4 mg/L, Mg^{2+} from 8,5 to 12,7 mg/L, TDS from 110 to 160 mg/L and generally reflects the interaction with the rocks of upper part of the basin. Arno river (Nisi et al. 2008) reveals a compositional field similar to the Po river, and a water – rock interaction evident since from the headwaters (Capo d'Arno). These estimates have important implications as they can give an idea of the amount of material transported by these rivers to the sea, that in turn reflect the degree of chemical weathering occurring within their hydrological basins. These considerations are very important because the Po river (and in minor amount the Adige river) represent the principal vector of freshwater in the whole Mediterranean basin (Bethoux et al. 1999; Struglia et al. 2004), thus explaining the geochemical features of the northern Adriatic sea that is characterized by relatively low salinity. Therefore the calculation reported in Chapter 5 of this thesis give valuable data to estimate geochemical fluxes toward the sea. The obtained results are on the same order of those calculated by other authors (Pettine et al. 1998) and are essential to understand the eutrophication processes occurring in the costal ecosystems. The same geochemical features, characterized by relatively low salinity and high amount of nutrients (Falcieri et al. 2014; Puddu et al. 1998; Justic et al. 1995, Degobbis et al. 1990) are important to understand the remarkable shellfish production, which characterized the northern Adriatic close to the Po river delta.

Therefore the study of Po river water is essential to understand and monitor the coastal ecosystems. In the investigated years the Po river water shown for most elements a remarkable homogeneity, also attested by Sr isotopic ratios that are discussed in Chapter 6. In fact, the maturity of the Po river water in the MP is attested by $^{87}Sr/^{86}Sr$ that remained constant at cca 0.70913 – 0.70926 in distinct hydrological periods, irrespective to the variable inflow of the various tributaries.

Extremely interesting are also the reported isotopic composition of oxygen and hydrogen (Chapters 3, 4 and 5) that are parameters sensitive to climatic variations. A complete representation of isotopic data is reported in Fig. 3, Ch.8 where $\delta^{18}O$ and δD are plotted together with the global (GMWL; Craig 1961) and local meteoric water lines (northern Italy; Longinelli and Selmo 2003; Longinelli et al. 2006). Samples from UP collected in different periods registered an isotopic composition that reflects the influence of meteoric precipitations (rain, snow, glacier, snow melting) in the drainage zone; whereas the MP samples become quite homogeneous and remain similar throughout the riverine course (average value for the MP ≈ -12,5 ‰), varying only in the terminal part as observed for the chemical composition.

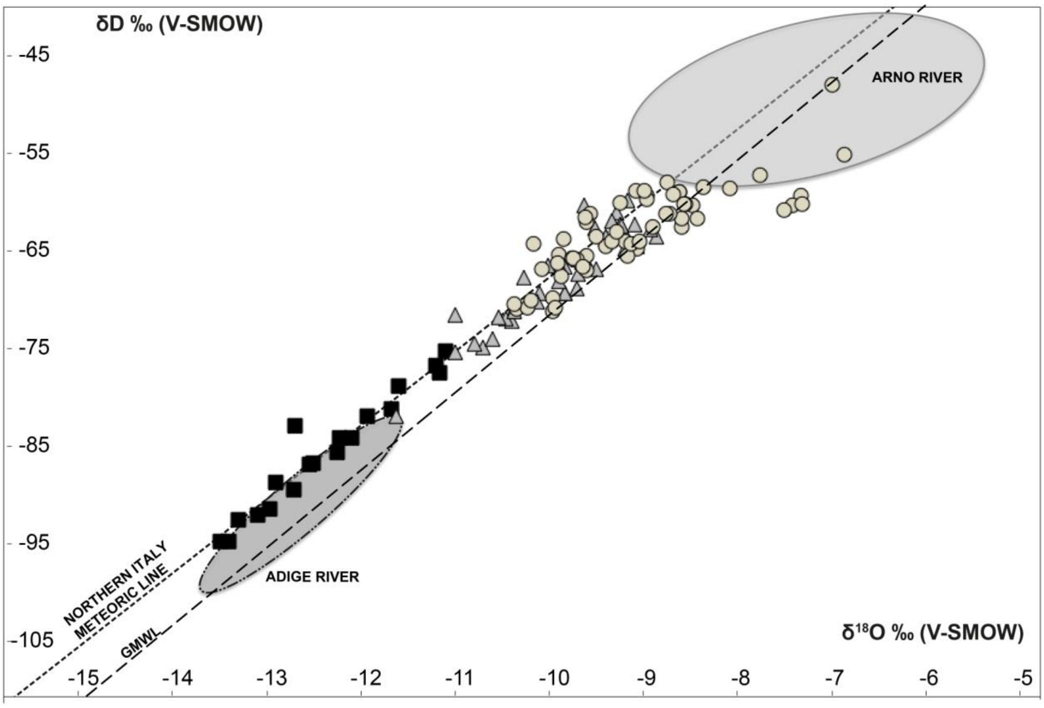

Figure 3: $\delta^{18}O$ – δD isotopic composition of Po river waters together with compositional field of Adige river and Arno river (Nisi et al. 2008). Meteoric water line are also reported for comparison: the dashed line represents the Local Meteoric Water Line, define for Northern Italy (LMWL; Longinelii and Selmo, 2003); the dotted line represent the Global Meteoric Water Line (GMWL; Craig,1961).

The data of the Po River are also compared with those of other important Italian Rivers. For example, I report a comparison with another important fluvial system, that is Adige river that, as mentioned, has been studied within the framework of a undergraduate thesis that I am co-supervising. Isotopic composition of these two riverine systems could be a useful tool in order understand processes in river with different characteristics. In particular Adige river is known as the second longest Italian river, showing an extremely differentiated stream flow which develops from the Alpine Italian/Austrian administrative boundary, through the eastern alps down to its flows into the Adriatic Sea. The differences and the extent of the morphoclimatic characteristics of the Adige river flowing path, represent therefore an ideal situation for the application of water isotope in hydrological studies, beside that a systematic geochemical and isotopic characterizations were never reported for the whole basin.

Differing from the Po river, the Adige waters are characterized by strong seasonal variation. The samples collected in August are more negative than samples collected in May. The average composition of δD in the UP is 90.2‰ and -88.2‰ for August 2013 and May 2014 respectively, and $\delta^{18}O$ average composition is -12.6‰ and -12.4‰ for August 2013 and May 2014; for comparable periods in Po river; the average composition of δD in the MP is -86.0‰ and -84.1‰ for August 2013 and May 2014 respectively, and $\delta^{18}O$ average composition is -12,1‰ and -11,8‰ for August 2013 and May 2014. These results for the Adige river indicate a more significant contribution of snowmelt and glacier melting that becomes evident due to the discharge of the river during the two different periods (in August $Q_m \approx$ 172 m^3/s) and the relative contribution of the main tributaries of the river. It is important to take into account that most of the tributaries of the Adige river are located in the alpine catchment and the small riverine system are strongly influenced by the seasonal variation.

Geochemical data of the Adige river exhibit a limited variation compared to the Po river along the whole path and generally reflects the interaction with the rocks of upper part of the basin. Adige and Po river waters display a similar Ca–HCO_3 hydrochemical facies, maintaining these geochemical features for most of the river stream, only varying in the terminal part where they approach the Adriatic sea mixing with saline water, as evidenced by slightly higher TDS and chloride content.

If we consider rivers as natural regional-scale pluviometers the data of these two important rivers could be used to define un updated meteoric water line valid for northern Italy.

Additional data could be taken from the literature for another important river, e.g. Arno which has been systematically studied within the framework of another PhD thesis (Nisi et al. 2008). This extended rivers dataset could be used to define some geochemical maps, referred as isotopic landscape in the literature (Bowen et al., 2003; Nisi et al. 2013) that can highlight ongoing environmental variations.

In other words, as a synthesis of this thesis, I propose that the multi-proxies geochemical analysis of rivers coexisting in the same region is a key to monitor the environment and understand on-going natural and anthropogenic processes.

APPENDIX A

ETG RISORSE E TECNOLOGIA srl

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Training Certificate

Claudio Natali (Assegnista Lab. Terra&Acqua Tech)
Chiara Marchina (Tesista Laurea Specialistica)
Gianluca Bianchini (Ricercatore - Dip. Scienze della Terra)
Tassinari Renzo (Tecnico di Laboratorio - Dip. Scienze della Terra)
Colombani Nicolo (Assegnista Lab. Terra&Acqua Tech)
Mastrocicco Micol (Ricercatore TD Lab. Terra&Acqua Tech)

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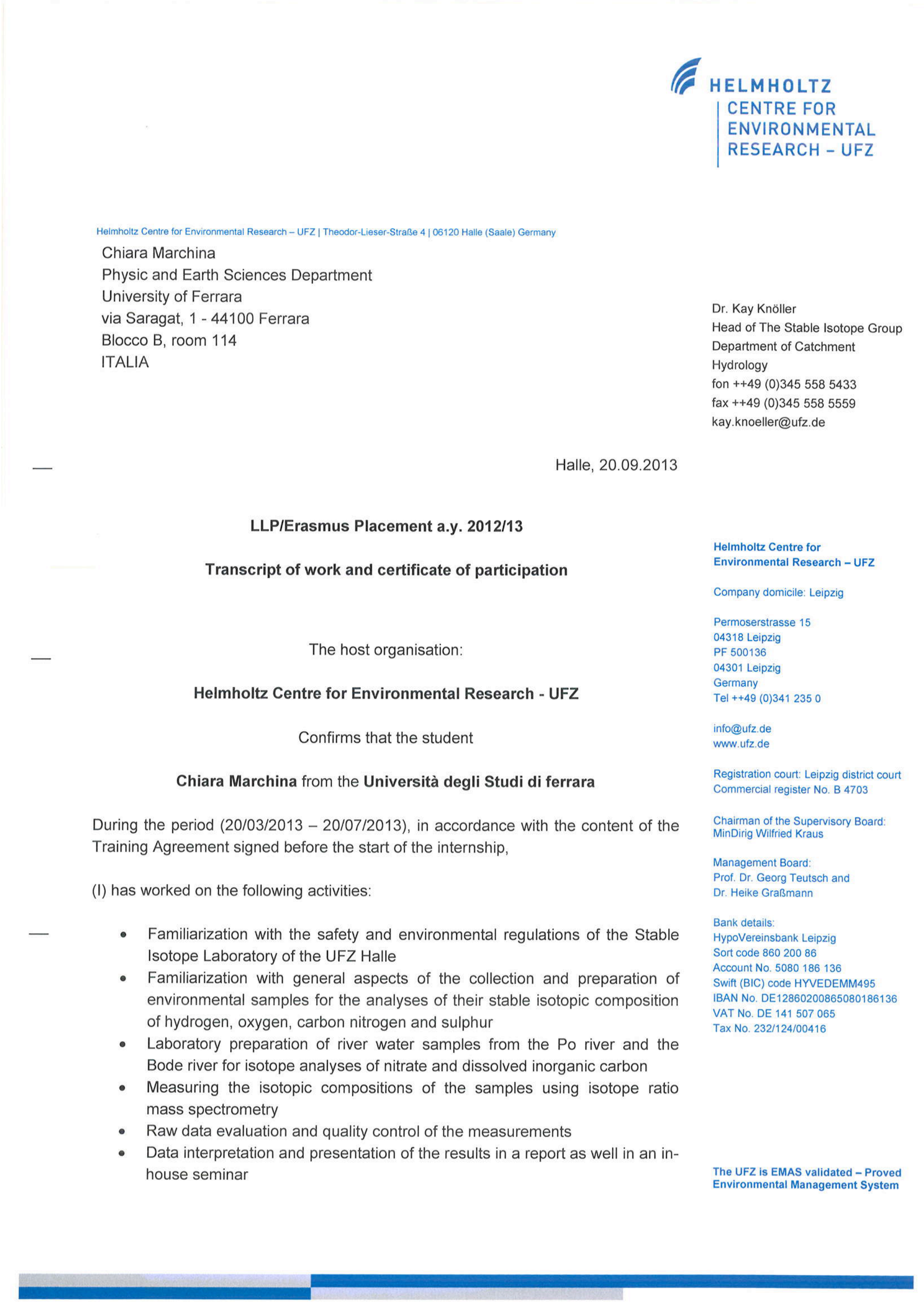
Montiglio M.to, 2011 / 05 / 12-13

Ing. Fabrizio Manassero, Chief Project Engineer

APPENDIX B



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Helmholtz Centre for Environmental Research – UFZ | Theodor-Lieser-Straße 4 | 06120 Halle (Saale) Germany

Chiara Marchina
Physic and Earth Sciences Department
University of Ferrara
via Saragat, 1 - 44100 Ferrara
Blocco B, room 114
ITALIA

Dr. Kay Knöller
Head of The Stable Isotope Group
Department of Catchment
Hydrology
fon ++49 (0)345 558 5433
fax ++49 (0)345 558 5559
kay.knoeller@ufz.de

Halle, 20.09.2013

LLP/Erasmus Placement a.y. 2012/13

Transcript of work and certificate of participation

The host organisation:

Helmholtz Centre for Environmental Research - UFZ

Confirms that the student

Chiara Marchina from the **Università degli Studi di ferrara**

During the period (20/03/2013 – 20/07/2013), in accordance with the content of the Training Agreement signed before the start of the internship,

(I) has worked on the following activities:

- Familiarization with the safety and environmental regulations of the Stable Isotope Laboratory of the UFZ Halle
- Familiarization with general aspects of the collection and preparation of environmental samples for the analyses of their stable isotopic composition of hydrogen, oxygen, carbon nitrogen and sulphur
- Laboratory preparation of river water samples from the Po river and the Bode river for isotope analyses of nitrate and dissolved inorganic carbon
- Measuring the isotopic compositions of the samples using isotope ratio mass spectrometry
- Raw data evaluation and quality control of the measurements
- Data interpretation and presentation of the results in a report as well in an in-house seminar

Helmholtz Centre for Environmental Research – UFZ

Company domicile: Leipzig

Permoserstrasse 15
04318 Leipzig
PF 500136
04301 Leipzig
Germany
Tel ++49 (0)341 235 0

info@ufz.de
www.ufz.de

Registration court: Leipzig district court
Commercial register No. B 4703

Chairman of the Supervisory Board:
MinDirig Wilfried Kraus

Management Board:
Prof. Dr. Georg Teutsch and
Dr. Heike Graßmann

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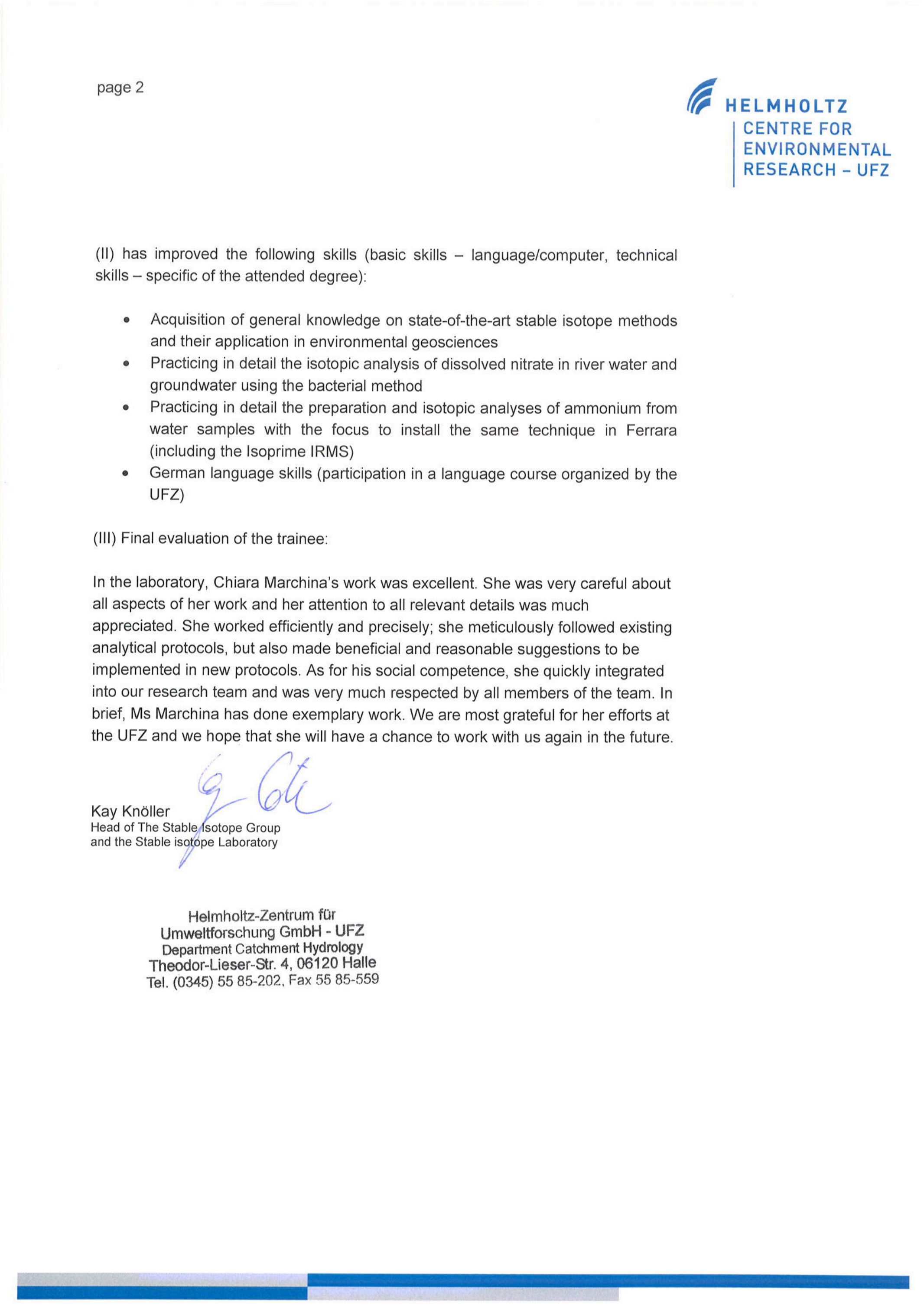
APPENDIX C



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(II) has improved the following skills (basic skills – language/computer, technical skills – specific of the attended degree):

- Acquisition of general knowledge on state-of-the-art stable isotope methods and their application in environmental geosciences
- Practicing in detail the isotopic analysis of dissolved nitrate in river water and groundwater using the bacterial method
- Practicing in detail the preparation and isotopic analyses of ammonium from water samples with the focus to install the same technique in Ferrara (including the Isoprime IRMS)
- German language skills (participation in a language course organized by the UFZ)

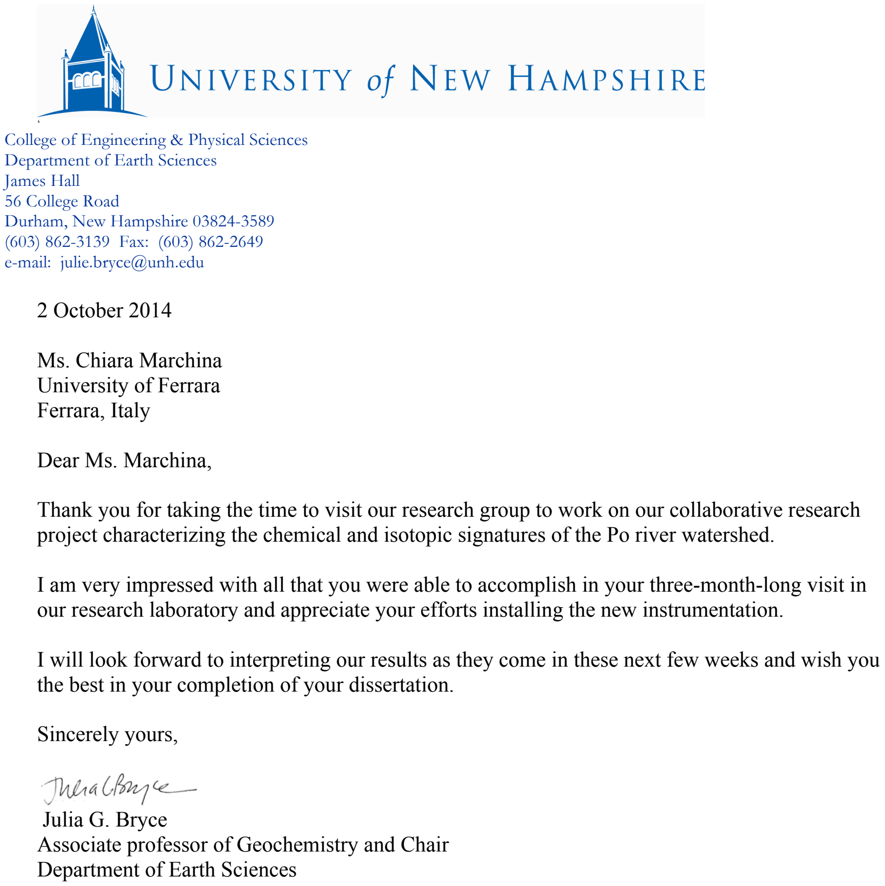
(III) Final evaluation of the trainee:

In the laboratory, Chiara Marchina's work was excellent. She was very careful about all aspects of her work and her attention to all relevant details was much appreciated. She worked efficiently and precisely; she meticulously followed existing analytical protocols, but also made beneficial and reasonable suggestions to be implemented in new protocols. As for his social competence, she quickly integrated into our research team and was very much respected by all members of the team. In brief, Ms Marchina has done exemplary work. We are most grateful for her efforts at the UFZ and we hope that she will have a chance to work with us again in the future.

Kay Knöller
Head of The Stable Isotope Group
and the Stable isotope Laboratory

Helmholtz-Zentrum für
Umweltforschung GmbH - UFZ
Department Catchment Hydrology
Theodor-Lieser-Str. 4, 06120 Halle
Tel. (0345) 55 85-202, Fax 55 85-559

APPENDIX D



UNIVERSITY of NEW HAMPSHIRE
College of Engineering & Physical Sciences
Department of Earth Sciences
James Hall
56 College Road
Durham, New Hampshire 03824-3589
(603) 862-3139 Fax: (603) 862-2649
e-mail: julie.bryce@unh.edu

2 October 2014

Ms. Chiara Marchina
University of Ferrara
Ferrara, Italy

Dear Ms. Marchina,

Thank you for taking the time to visit our research group to work on our collaborative research project characterizing the chemical and isotopic signatures of the Po river watershed.

I am very impressed with all that you were able to accomplish in your three-month-long visit in our research laboratory and appreciate your efforts installing the new instrumentation.

I will look forward to interpreting our results as they come in these next few weeks and wish you the best in your completion of your dissertation.

Sincerely yours,

Julia G. Bryce
Associate professor of Geochemistry and Chair
Department of Earth Sciences

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