

A preliminary note on carbon and nitrogen elemental and isotopic composition of Po River suspended load

Luca Corazzari, Gianluca Bianchini, Paolo Billi, Chiara Marchina & Claudio Natali

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara

Abstract

We present a preliminary note on the carbon and nitrogen elemental and isotopic composition of the suspended load of the Po River, i.e., of the more important river of Italy, sampled in distinct hydrological periods. This paper explains thoroughly the sampling and the employed EA-IRMS analytical method. The results are discussed to (a) discriminate natural (geogenic) and anthropogenic components, (b) delineate geochemical fluxes transferred from the Po River to the Adriatic Sea. The analyses of total carbon (TC between 2.7 and 5.4 wt%; $\delta^{13}\text{C}$ between -16.1 and -7.5 ‰), properly speciated in its organic (OC between 1.0 and 2.2 wt%; $\delta^{13}\text{C}$ between -25.1 and -19.7 ‰) and inorganic (IC between 0.9 and 3.5 wt%; $\delta^{13}\text{C}$ between -0.2 and -3.3 ‰) components are useful to understand the provenance (Alps vs. Apennine) of the particles, whereas the analyses on nitrogen (TN between 0.1 and 0.6 wt%; $\delta^{15}\text{N}$ between 2.4 and 9.0 ‰) give insights on the pollution affecting the river. The data can be useful to constrain models that investigate the nutrient loads conveyed by the river toward the Adriatic coastal ecosystem that is affected by frequent eutrophication processes.

Introduction

The Po River is the most important fluvial system of Italy and its alluvial plain, the Padanian Plain, is densely taken up by urban settlements and industrial, agricultural and zootechnical activities, therefore, deserving accurate investigation and monitoring. In this light, the detailed and systematic geochemical investigation on the components dissolved in its water recently carried out by Marchina et al. (2015) has to be complemented with studies concerning the geochemical budget associated to the suspended load to quantify the geochemical fluxes delivered by the river into the Adriatic Sea. In particular, emphasis has to be given to the analysis of elements that act as “nutrients” such as carbon and nitrogen which are essential for biological processes (Pettine et al. 1998; Giani et al. 2009; Tesi et al. 2013 and references therein). For these reasons, this contribution specifically deals with the role of the suspended particles in the carbon and nitrogen riverine budgets. The investigation provides elemental and isotopic compositions (referred to samples collected from October 2013 to May 2015) that are useful to discriminate geogenic (i.e., natural) and anthropogenic (related to human activities) sources.

Sampling and analytical methods

This preliminary investigation has been based on data from the sampling station of Pontelagoscuro, which is located in the downstream reach of the river (close to the city of Ferrara), just upstream of the deltaic system. Sampling was repeated in distinct periods to evaluate the extent of geochemical variation in different hydrological conditions.

Different sampling modes were also used and compared. Samples were collected from a river pier and from a boat, taking water from the surface using a common 10-l bucket and by means of the US depth integrating DH-76 sampler (US Geological Survey) that integrates a water sample all along an individual vertical. Bottom sediments were also collected by a US BHM sampler.

Laboratory analyses were carried out at the Department of Physics and Earth Sciences of the University of Ferrara.

Samples were placed in Pyrex beakers and solid particles were isolated first by settling, subsequently removing the supernatant water and finally drying on hot plates; solid residuals were scratched off from the beaker bottom with a stainless steel spatula and then weighed.

Total carbon (TC), total nitrogen (TN), and the relative isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively) of the particles suspended in the Po River water were investigated with the Elemental Vario Micro Cube elemental analyser in line with an ISOPRIME 100 Isotopic Ratio Mass Spectrometer operating in continuous-flow mode. Powdered samples were placed in tin capsules that were wrapped and weighed by an AND high-precision balance (accuracy up to 10 μg); these capsules, which can contain as much as 40 mg of sample, were then inserted in the Vario Micro Cube autosampler and analyzed. Flash combustion at 950 °C took place in a sealed quartz tube filled with copper oxide grains (padded with corundum balls and quartz wool) which acted as catalyst, in excess of high purity (6 grade purity) O_2 gas. Freed gaseous species were transferred through a reduction quartz tube (at 550 °C) filled with metallic copper wires that reduced the nitrogen oxides (NO_x) to N_2 . The formed analyte gases (N_2 , H_2O and CO_2), carried by dry He (5 grade purity) gas, passed through a water-trap filled with sicapent to ensure complete removal of moisture; they are sequentially separated by a temperature programmable desorption column (TPD) and quantitatively determined on a thermo-conductivity detector (TCD). Sample N_2 was sent directly to the interfaced IRMS for isotopic composition determination, while CO_2 was held by the TPD column, kept at room temperatures of 20–25 °C. When N_2 isotopic analysis was over, CO_2 was desorbed from the TPD column raising the temperature to 210 °C, and finally reached the IRMS compartment for the determination of carbon isotopic ratios. The detection of the distinct isotopic masses of the sample was sandwiched between those of reference N_2 and CO_2 (5 grade purity) gases, which were 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 isotope ratios were 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. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were characterized by an average standard deviation of ± 0.1 and ± 0.2 ‰, defined by repeated analyses of the above-mentioned standards.

As concerns carbon, further insights on the studied samples were obtained on a thermal basis using the analytical protocol defined by Natali and Bianchini (2014, 2015) by which is possible to discriminate the amount of organic (OC) and inorganic (IC) fractions forming the total carbon budget (TC). According to this analytical protocol:

- Total carbon (and TN) was carried out by EA-IRMS combusting the bulk sample at 950 °C;
- Organic carbon was carried out by EA-IRMS combusting the bulk sample at 470 °C;
- Inorganic carbon was carried out by EA-IRMS combusting at 950 °C the sample deprived of organic matter, i.e., preliminary burnt in a muffle furnace at 470 °C for 12 h; the relative gravimetric loss (LOI) is also determined to correct the elemental concentration of the IC fraction.

The resulting wt% and $\delta^{13}\text{C}$ (‰) of the OC and IC fractions allow a mass balance to calculate a theoretical TC fingerprint which is compared with that directly measured ($\delta^{13}\text{C}_{\text{TC}}$ measured).

$$\delta^{13}\text{C}_{\text{TCTheoretical}} = \delta^{13}\text{C}_{\text{OC}} \times X_{\text{OC}} + \delta^{13}\text{C}_{\text{IC}} \times X_{\text{IC}}$$

where $X_{\text{OC}} + X_{\text{IC}} = 1$ and represent the organic and inorganic fractions, respectively.

Results

During the field investigation period (fall 2013–spring 2015), the amount of suspended particles was observed to vary from 45 mg/l during low water stage (summer time), to 70–80 mg/l measured with intermediate base flow conditions, and progressively increases during higher flow rates. However, the increase of suspended load in the Po River is not well correlated with the increase in discharge, because it is also strongly influenced by the relative sediment supply from distinct tributaries. Extreme values up to 1720 mg/l have been observed during a high flow discharge (October 2014) generated by a large rainstorm centered on the Northern Apennine sector of the river catchment (Table 1). In this particular circumstance, high rainfall intensities caused extreme floods in the Apennine tributaries such as the Baganza River which broke its banks and inundated the city of Parma in which a thick layer of mud and debris were deposited.

On the whole, the analyses of the suspended particles show carbon concentration varying from 2.7 to 5.4 wt% coupled with an isotopic $\delta^{13}\text{C}$ signature ranging from -16.1 to -7.5 ‰, and nitrogen concentration varying from 0.1 to 0.6 wt% coupled with $\delta^{15}\text{N}$ isotopic signature $\delta^{15}\text{N}$ ranging from 2.4 to 9.0 ‰. All the available data on the suspended particles display a marked difference with respect to the sandy bottom sediments that are comparatively depleted in carbon and nitrogen contents (0.8 and <0.1 wt%, respectively) and characterized by totally distinct isotopic ratios ($\delta^{13}\text{C}$ -1.6 ‰; $\delta^{15}\text{N}$ 0.3 ‰).

It is worth noticing that the prevalent $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic compositions recorded in the suspended load of the Po River evidence a remarkable similarity with the isotopic fingerprint of the dissolved components measured in the Po River water (Marchina 2015; Fig. 1), thus suggesting that they are influenced by similar sources and processes. Distinct carbon end-members are represented by the samples recorded in fall 2014 (C 3.2–5.4 wt%, $\delta^{13}\text{C}$ between -10.3 and -7.5 ‰) and those from spring 2015 (C 2.7 wt%, $\delta^{13}\text{C} = -16.1$ ‰). These end-members are plausibly characterized by a different origin of the suspended load, which was mainly of Apennine provenance in fall 2014,

and of Alpine provenance in spring 2015, as evidenced by the relative contribution of the main tributaries to the Po River flow.

Further insights into the carbon budget were obtained—from a samples subset—investigating the distinct elemental contribution of OC and IC to the TC, as well as their specific isotopic composition (Table 2; Fig. 2). It is interesting to point out that the IC fraction records the significant difference delineated by TC between fall 2014 and spring 2015. However, if we consider the IC/TC ratio it can be observed that the real outlier is represented by the sample of spring 2015. This sample, in fact, is the only one with a IC/TC ratio lower than 0.5. In this light, we tentatively propose that low IC/TC mark minor Apennine contributions, in agreement with the relative water discharge that in this period mainly originates from Alpine snow melt. On the other hand, it is important to emphasize the content (and isotopic composition) of the OC fraction, which is more reactive and potentially promote oxygen consumption and eutrophication. In the investigated samples OC varies between 1.0 and 2.2 wt% with a peak value recorded in spring 2015, when OC is nearly 70 % of TC. The isotopic composition of OC is variable, with $\delta^{13}\text{C}$ ranging between -25.1 and -19.7 ‰, thus conforming to values typical of organic matter dominated by a C3 photosynthetic pathway (De Niro and Epstein 1978). It is interesting to note that less negative values are generally measured during low Po River discharge, suggesting for these periods a more intense organic matter (OM) microbial degradation as observed in other river systems (e.g., Bernardes et al. 2004). On the other hand, during peak discharge a trend is observed toward more negative isotopic values of the OC fraction probably as a result of more effective take in charge of fresh OM that during high flow conditions is preserved by degradation.

On the whole, the recorded carbon isotopic signature can be considered geogenic (i.e., natural) and derived by a mixture of carbonate lithologies outcropping in the basin and organic matter that in the area is dominated by a C3-type signature. On the contrary, the nitrogen isotopic signature reflects the involvement of multiple anthropogenic sources including synthetic fertilizers, zootechnical manure and sewage wastewater (Clark and Fritz 1997), which seems to increase during low flow discharge periods. In this light, it is important to note that we obtained nitrogen concentration (and isotopic values) slightly higher than those reported by Tesi et al. (2013) thus suggesting a persistent (not decreasing) anthropogenic effect in the investigated fluvial system. This is confirmed by the positive correlation between N (wt%) and $\delta^{15}\text{N}$ ‰ observed in Fig. 3.

Conclusions

Elemental composition of carbon and nitrogen in the suspended matter is useful to assess the geochemical fluxes toward the Adriatic Sea. These predictions are extremely important to understand the eutrophication processes that are affecting the Adriatic coastal ecosystems. Considering an average discharge of $1500\text{ m}^3/\text{s}$ and a consequent volume of 47.3 km^3 , it is possible to calculate the mass of “suspended” carbon and nitrogen transferred from the Po River to the Adriatic Sea (195,000 and 14,000 t/yr for carbon and nitrogen, respectively). These estimates are in the same order of magnitude of those reported by Pettine et al. (1998) and Cozzi and Giani (2011) and can be used to implement data on the dissolved load to calculate nitrogen and carbon balances at basin scale.

The monitoring and analysis will be continued to provide better constraints on the relationships between geochemical fingerprint and hydrological parameters, and the out coming data will contribute to define an hydro-archive useful to delineate geochemical backgrounds and to understand the on-going hydro- and geochemical processes. Considering that the activity of the dissolved carbon species is strictly related to the temperature and the atmospheric CO_2 content, the

data presented in this study represent a snapshot of the current environmental condition and can be taken into account by future investigations to evaluate possible changes. Moreover, these data (in particular those of nitrogen) are important because they are also proxies of the human activities that can—at various extent—overprint the geogenic geochemical signature in the river catchment, in its delta (where fish and shellfish farming has great socio-economic impact) and also in the Adriatic sea that is its final receptor (Viaroli et al. [2015](#)).

References

1. Bernardes MC, Martinelli LA, Krusche AV, Gudeman J, Moreira M, Victoria RL, Ometto JPHB, Ballester MVR, Aufdenkampe AK, Richey JE, Hedges JI (2004) Riverine organic matter composition as a function of land use changes, southwest Amazon. *Ecol Appl* 14:S263–S279
 2. Clark ID, Fritz P (1997) *Environmental isotopes in hydrogeology*. Lewis Publishers, New York
 3. Cozzi S, Giani M (2011) River water and nutrient discharges in the Northern Adriatic Sea: current importance and long term changes. *Cont Shelf Res* 31:1881–1893
 4. DeNiro MJ, Epstein S (1978) Influence of diet on the distribution of carbon isotopes in animals. *Geochim Cosmochim Acta* 42:495–506
 5. Giani M, Berto D, Rampazzo F, Savelli F, Alvisi F, Giordano P, Ravaioli M, Frascari F (2009) Origin of sedimentary organic matter in the north-western Adriatic Sea. *Estuar Coast Shelf Sci* 84:573–583
 6. Marchina C (2015) *Geochemical and isotopic investigation on the Po river waters from Monviso sources to its delta: natural and anthropogenic components*. Unpublished Ph.D. thesis, University of Ferrara
 7. Marchina C, Bianchini G, Natali C, Pennisi M, Colombani N, Tassinari R, Knoeller K (2015) The Po river water from the Alps to the Adriatic Sea (Italy): new insights from geochemical and isotopic ($\delta^{18}\text{O}$ - δD) data. *Environ Sci Pollut Res* 22:5184–5203
 8. Natali C, Bianchini G (2014) Understanding the carbon isotopic signature in complex environmental matrices. *EQA-Environ Qual* 14:11–18
 9. Natali C, Bianchini G (2015) Thermally based isotopic speciation of carbon in complex matrices: a tool for environmental investigation. *Environ Sci Pollut Res* 22:12162–12173
 10. Pettine M, Patrolecco L, Camusso M, Crescenzo S (1998) Transport of carbon and nitrogen to the northern Adriatic sea by the Po river. *Estuar Coast Shelf Sci* 46:127–142
 11. Tesi T, Miserocchi S, Acri F, Langone L, Boldrin A, Hatten JA, Albertazzi S (2013) Flood-driven transport of sediment, particulate organic matter, and nutrients from the Po River watershed to the Mediterranean Sea. *J Hydrol* 498:144–152
 12. Viaroli P, Nizzoli D, Pinardi M, Soana E, Bartoli M (2015) Eutrophication of the Mediterranean Sea: a watershed-cascading aquatic filter approach. *Rendiconti Lincei, Scienze Fisiche E Naturali* 26:13–23
-

Acknowledgments

The authors gratefully acknowledge the anonymous referees and the editor for their constructive comments that helped to improve earlier versions of the manuscript. The study was funded in part by the European Fund of Regional Development (POR FESR 2007-2013), Terra&AcquaTech Labs., Technopole of Ferrara.