GEOCHEMICAL AND ISOTOPIC ANALYSES ON THE PO DELTA WATER: INSIGHTS TO UNDERSTAND A COMPLEX RIVERINE ECOSYSTEM

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Key words: Po river; geochemistry; stable isotopes; hydro-archive; geochemical fluxes.

"This contribution is the written, peer-reviewed version of a paper presented at the XV Giornata Mondiale dell'Acqua "Grado di inquinamento naturale di acque e suoli in Italia", held at the Accademia Nazionale dei Lincei on March 20, 2015."

ABSTRACT

This contribution was preliminarily presented with an oral communication during the "Water Day 2015" conference organized in Rome the 20th of March 2015 by the Accademia Nazionale dei Lincei. It implements a recent paper that studied the Po river water from the Alpine springs toward the Adriatic Sea (Marchina *et al.* 2015; Environ. Sci. Pollut. Res. 22, 5184-5203), specifically focussing on its deltaic part. The new geochemical analyses are useful to evaluate the extent of salinization (due to mixing with sea-water) and to monitor the flux of nutrients that are conveyed by the river toward the coastal environment. The paper also contains oxygen/hydrogen water isotopes that represent a snapshot of the current climatic conditions to be compared with the literature data and with the future composition to set up a hydro-archive that should be updated to evaluate on-going climatic changes. Moreover, the paper reports preliminary nitrogen isotopes composition of Po river water that trace the impact of human activities, to be monitored in the future to understand possible on-going pollutions. We conclude that geochemical researches on Po river should consider with particular attention the delta because it is an extremely fragile ecosystem where biogeochemical variations are more relevant.

1. Introduction

This contribution implements a recent paper that studied the Po river water from the Alpine springs toward the Adriatic Sea (Marchina *et al.* 2015), specifically focussing on its deltaic part, where the river splits in six major distributaries: *Po di Goro*, *Po di Gnocca*, *Po di Tolle*, *Po di Venezia*, *Po di Maistra* and *Po di Levante* (the latter is artificially regulated and separated from the main course). In particular, we present geochemical analyses of major dissolved ions and some trace elements, as well as oxygen-hydrogen isotopic data carried out on 15 samples collected in the deltaic branches in August 2013, and more in general we review the available geochemical and isotopic data on waters that were monitored for 4 years (2010 – 2014), in order to compare geochemical and isotopic data obtained in different periods with different hydrological conditions. The original data are reported in Supplementary Table 1 that is included in the journal electronic repository. We also present preliminary results of an on-going project concerning the nitrogen isotopic composition of Po river water. On the whole, the data are useful to evidence mixing processes with seawater, as well as to investigate potential anthropogenic contributions that influence the riverine water in this complex and very sensitive system. The delta area, in fact, can be considered as a multicomponent sink that involves different biogeochemical processes, in turn influencing the adjoining North Adriatic sea which is affected by recurrent eutrophication episodes (Ventura et al., 2008).

2. Analytical methods

The new data have been carried out on water samples collected between the 8th and the 13th of August 2013. Electrical conductivity (EC), pH and temperature were directly measured in the field. Hydrogen and oxygen isotope ratios were determined using a CRDS Los Gatos LWIA 24-d isotopic analyser. Major cations and trace elements were detected by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo-Scientific X Series spectrometer and anions were determined by ion chromatography using a Dionex ICS-1000 instrument. Preliminary isotopic analyses of $\delta^{15}N$ and $\delta^{18}O_{(NO3)}$ have been carried out at Halle (Germany) in the Helmholtz Centre for Environmental Research by IRMS on the Dissolved Inorganic Nitrogen (DIN) using the bacteria denitrification method 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.

3. Results

The new isotopic analyses of oxygen and hydrogen on the water of Po river delta, properly expressed in δ units respect to the SMOW international standard, are reported together with those already existing in the literature in Fig. 1. The Po delta waters show $\delta^{18}O$ varying between -10.4‰ and -6.9‰ and δD varying from -71.0‰ to -48.0‰, i.e. values more variable (generally less negative) than those observed in the river part preceding the delta ($\delta^{18}O$ between -11.0‰ and -9.2‰; δD between -75.4‰ and -60.6‰) indicating variable extent of mixing with sea water and more effective evaporation processes. These mixing processes are transient because they are strictly related with *a)* discharge of the riverine system that varies seasonally and *b)* tide cycles that in turn influence the river flow into the sea. According to the presented data and mass balance calculations (see Bianchini et al., 2005), it can be envisaged up to 20% mixing with seawater in the Po di Venezia, that is the main branch of the Delta; and up to 50% mixing with seawater in the Po di Tolle (one of the peripheral branches).

Significant changes were also observed in the dissolved components as highlighted by the electrical conductivity (expressed in μS/cm) that resulted to be extremely variable in the distinct deltaic branches; the highest value recorded at the mouth of the main branch (Po di Venezia) was 6,200 μS/cm, but higher values were recorded in the peripheral branches, with the more extreme value (28,000 μS/cm) observed in August 2013 for a sample located at the Po di Tolle mouth. This observation is highlighted in the thematic maps of Fig. 2, which show that salinization become predominant in the outer branches respect to the main course where the discharge and the flow are more effective.

Accordingly, the TDS calculated as the sum of the major chemical is extremely variable revealing values up to 24,800 mg/L. The investigated deltaic waters, although generally displaying 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 and Langelier diagrams (Fig. 3) that corroborate the occurrence of mixing processes with saline waters.

The obtained analyses were also compared to past analyses retrieved from the literature, i.e. historical chemical analyses that are available for Po river since the end of the years fifties when human impacts were less effective. The comparison highlights that the concentration of most dissolved elements remained constant over the last decades of years, with the notable exception of nitrate which drastically increases from less than 2 mg/L to the average value of ca 9 mg/L (Fig. 4). In particular literature data are provided by Gherardelli and Canali (1960) and Fossato (1971), that report temperature, HCO_3^-, Ca^{2+}, Mg^{2+} and NO_3^- values for Po river water collected in the Province of Rovigo (just before the delta inception) for the years 1959 and 1968 – 1969. We noted that the values of conductivity, HCO_3^-, Ca^{2+} and Mg^{2+} (and Mg/Ca ratio) were comparable with those recorded nowadays, whereas NO_3^- concentration showed marked temporal variations. NO_3^- had an average value of 2 mg/L in the fifties and 4 mg/L in the sixties, reaching concentrations higher than those recorded nowadays in the eighties (up to 10 mg/L, according to a data-set provided by Arpa-Veneto), and then declining to the current values. This historical series highlights a significant temporal increase of NO_3^- attesting a progressive intensification of the anthropogenic inputs that reached a culmination in the eighties in connection with massive development of urban settlements and a phenomenal growth in the agriculture and zootechnical activities. The slight decrease of NO_3^- in Po river water recorded after the eighties possibly reflects the effects of environmental policy and governance (e.g. nitrates directive 91/676/CEE) which imposed the treatment of waste water (*s.l.*) and a more sustainable (i.e. limited) use of fertilizers. In this light the preliminary isotopic analyses of $\delta^{15}N$ and $\delta^{18}O_{(NO3)}$ reported in Fig. 5 can be useful to investigate the origin of this component and its evolution. It can be observed that the isotopic signature of Po river water conforms to a mixing of anthropogenic pollutants (Clark and Fritz, 1997; Natali and Bianchini, 2015), also suggesting an incipient denitrification trend that seems to be more effective in the deltaic waters.

Although denitrification is scarcely documented in riverine systems, it has to be noted that analogous trends were also observed in Oglio river study in Bartoli et al. (2012). Accordingly during denitrification the $\delta^{15}N$ and $\delta^{18}O$ values of the remaining nitrate increase; coherently, in the delta water samples 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 (Sacchi *et al.* 2013). Attention has to be paid also to the concentration of phosphorous, which represents an additional nutrient critical for the development of eutrophication processes; in the presented analyses we recorded by ICP-MS phosphorous concentrations ranging between 0.03 and 0.09 mg/l (average and median 0.05 and 0.06 mg/l, respectively) which can be compared with those recorded in the literature. The concentration of this element increased drastically in the period between 1960 and 1990 (Fossato, 1971; Marchetti et al., 1989; Degobbis and Gilmartin, 1990; Ludwig et al., 2009) and then reached background values similar to those envisaged by the presented data in the period between the years 2003 and 2007 (Naldi et al., 2008). From the above, we can state that some elements still maintain a geogenic signature (i.e. they are mainly influenced by weathering and dissolution of litologies), whereas some others have been significantly overprinted by human activities.

4. Conclusions

We conclude emphasizing that the presented data give geochemical backgrounds useful for an environmental monitoring. The presented analyses of conservative elements (e.g. chlorine, sulphates, sodium, boron) give indication on the interface between river water and sea water that are variously mixing in the distinct deltaic branches, whereas the analyses of nutrients (e.g. nitrogen and phosphorous) provide an indication useful to calculate the critical loads that potentially trigger eutrophication processes. Coherently, the concentration of the mentioned nutrients has an important influence on the trophic condition of the Po river as demonstrated on a recent study on the phytoplankton contained in its water (Zonneveld et al., 2012).

Moreover, the presented oxygen/hydrogen isotopes represent 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 nitrogen isotopes, on the other hand, trace the impact of human activities and have to be monitored also in the future to understand possible on-going pollutions. Future geochemical researches on Po river should consider with particular attention the delta because it is an extremely fragile ecosystem where biogeochemical variations are more relevant.

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.

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Captions

Figure 1. $\delta^{18}O$ – δD isotopic composition of the Po Delta waters collected in August 2010 compared with those available in the literature (Marchina et al., 2015). The global meteoric water line (GMWL; Craig 1961) and the local meteoric water line (LMWL) defined for Northern Italy (Longinelli and Selmo 2003) are also reported.

Figure 2. Thematic map showing spatial variation of (a) electric conductivity (µS/cm) and (b) dissolved chloride (mg/l) in the water of the Po river delta during August 2013, obtained by the Geostatistical Analysis tool ArcGis 9.3. For a better interpretation refers to the coloured web version of the paper.

Figure 3: Composition of Po Delta waters, a) Gibbs diagram (TDS vs [Na^+/(Na^++Ca^{2+})]) reported in mg/L for the Po river water; b) Ludwig – Langelier classification diagram.

Figure 4: Temporal variation of nitrates dissolved in the terminal part of Po River water occurred during the last fifties years (historical data from Gherardelli and Canali 1960; Fossato,1971; Arpa-Veneto).

Figure 5: $\delta^{15}N$ - $\delta^{18}O_{(NO3)}$ of the Po river waters collected in the entire course of river (from Monviso to the deltaic area) together with the potential sources of nitrate (Clark and Fritz 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.