



Nitrogen and sulphur cycling in the saline coastal aquifer of Ferrara, Italy. A multi-isotope approach[☆]



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ABSTRACT

The origin of high ammonium and sulphate concentrations, characterizing the saline groundwater of the Po River floodplain coastal aquifer, are documented. A detailed understanding of the hydrogeochemical conceptual model is built up using a hydrochemical (major ions, DOC, DIC and methane) and isotopic ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{15}\text{N}_{\text{NH}_4}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{13}\text{C}_{\text{DIC}}$) approach. Based on previous hydrogeological investigations, two boreholes located in contrasting environments (urban and agricultural) have been sampled at high vertical resolution.

Groundwater is mostly under reducing conditions, characterized by high DOC and DIC concentrations but low to moderate methane content. Dissolved ammonium, as high as 87.8 mgL^{-1} , derives by the mineralization of N-organic rich fine sediments, as indicated by its N isotopic signatures ($1\div 3\%$). Attenuation processes of ammonium are ruled by dilution and by partial nitrification, supported by the enrichment in $\delta^{15}\text{N}_{\text{NH}_4}$ ($\sim +7\%$). Apart from dilution/oxidation processes, the positive correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ agreed with the occurrence of denitrification in the shallow part of the aquifer. $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ data highlight that oxidation of pyrite occurs but is not necessarily linked to nitrate removal. The isotope data showed that sulphate ($>2500 \text{ mgL}^{-1}$) is of marine origin. In the deeper part of the aquifer, sulphur and oxygen isotopes enrichment patterns, demonstrated that sulphate reduction (SR) occurs in the aquifer and it is also possible that SR occurred in the underlying clay units. $\delta^{13}\text{C}_{\text{DIC}}$ pattern toward depleted $\delta^{13}\text{C}_{\text{DIC}}$ values even as low as -40.4% documented the occurrence of SR mediated by organic carbon and SR coupled to oxidation of methane (AOM) are involved in the sulphur and carbon cycles. The present study shows the advantage of using stable isotopes complemented with geochemical data to characterize the solutes' origins, both natural and anthropogenic, and giving insights on biogeochemical transformations involving nitrogen, sulphur and carbon in coastal sediments.

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1. Introduction

Hydrogeochemical investigations, worldwide, highlight that saline and brackish groundwater constitute one of the most common issues in many reclaimed coastal aquifers (Da Lio et al., 2015; Wang and Jiao, 2012; Werner et al., 2013). Additional attention to these environments is driven by natural and anthropogenic contributions, such as evaporation, transpiration and dissolution of salt deposits, flood events, vertical seepage from

deeper aquifers and paleo-seawater intrusion (Akouvi et al., 2008; Barlow and Reichard, 2009; Cary et al., 2015; Cheikh et al., 2012). Especially if related to overexploitation and extensive agricultural practices, high saline groundwater still represents a pervasive source of degradation (Grassi et al., 2007; Jørgensen et al., 2008; Sola et al., 2013). Multiple factors regulate the chemical nature of coastal aquifers: e.g., the depositional sequence, water-rock interactions processes as well as anthropogenic activities, which in turn can modify aquifers' media (Jayasingha et al., 2014). While saline and brackish environments have been extensively documented, studies on the impact of other sources of major ions on a coastal aquifer, e.g. biogenic ammonium (NH_4^+) derived by sediments with an elevated content of organic matter (Jiao et al., 2010;

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Wang and Jiao, 2012), are still far from being completed. As NH_4^+ , many other chemical compounds like sulphate (SO_4^{2-}) can represent a threat for groundwater quality (Bouzourra et al., 2015; Ortega-Guerrero, 2003), potentially causing a large and hitherto unappreciated deterioration effect on surface waters. Coastal aquifers act as a terrestrial-marine buffer system where mixing and attenuation processes usually overlap (Slomp and Van Cappellen, 2004); this complicates the identification of the factors that contribute to their hydrochemical groundwater composition, and even more the distinction between natural processes and the ones deriving from human activities. Constraining the role of the hydrogeological processes is essential to assess the degree of fragility and/or turnover of these complex systems (Han et al., 2015; Kazakis et al., 2016). The identification of detrimental chemical species and their fate in groundwater leads to a correct water resources management, particularly at those areas where intensive agriculture and lowland reclamation activities periodically change the hydrological flow patterns (Castaldelli et al., 2013a; Petitta et al., 2009). Potential attenuation processes, which can naturally contain anthropogenic or natural pollutants, are of high importance; their characterization also play a key-role for robust water resource management plans, future actions and regulations (Rügner et al., 2006).

On such purpose, the use of stable isotopes definitely help constraining the origin of dissolved species in groundwater. Vitòria et al. (2004) proved the usefulness of multi-isotopic analyses to trace fertilizers contaminations; Mayer and Krouse (2004) among others, extensively reported how sulphur and oxygen isotopic compositions give insights on SO_4^{2-} sources; Urresti-Estala et al. (2015) applied the isotopic approach to Guadalhorce River Basin (southern Spain) to characterize SO_4^{2-} and nitrate (NO_3^-) sources, and to quantify natural background levels in groundwater bodies. Moreover, multi-isotopic approaches coupled to hydrochemistry play a major role in understanding biogeochemical reactions in aquifers and surface water systems. Several research studies support the use of environmental isotopes to evaluate processes affecting NO_3^- , NH_4^+ and SO_4^{2-} concentrations in groundwater (Aravena and Mayer, 2010; Kendall et al., 2007). The use of combined $\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{13}\text{C}_{\text{DIC}}$ for natural aquifer systems has been proposed to identify the occurrence of denitrification processes in many case studies (Hosono et al., 2014a,b; Otero et al., 2009; Petitta et al., 2009). Furthermore, Robertson et al. (2012) demonstrated the occurrence of N removal by anaerobic NH_4^+ oxidation (anammox) measuring both $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{15}\text{N}_{\text{NH}_4}$. Vitòria et al. (2008) showed the effectiveness of the multi-isotopic approach in marking N processes: both nitrification and denitrification coupled with pyrite oxidation were estimated. Jurado et al. (2013) proposed a multi-isotope data application to quantify redox processes in urban groundwater (e.g. SO_4^{2-} reduction).

The present study proposes a geochemical investigation of the unconfined coastal aquifer in the Po River floodplain, northern Italy. The elevated saline content of this unconfined aquifer has been previously documented (Colombani et al., 2016; Giambastiani et al., 2013), suggesting a seepage from the under-lying hypersaline aquitard as the proposed hydrogeochemical conceptual model for aquifer salinization, especially in back barrier sedimentary environments (Caschetto et al., 2016). The long lasting land reclamation is the main cause of the basal saline and hypersaline groundwater upconing, allowing the upward migration of saline groundwater characterized by high concentrations of NH_4^+ , SO_4^{2-} , Cl^- and Na^+ into the unconfined aquifer (Giambastiani et al., 2013; Mastrocicco et al., 2013; Mollema et al., 2012). The concurrent potential inputs from agriculture and urbanized areas in this region make difficult to distinguish among natural and anthropogenic sources of species, as NO_3^- , NH_4^+ and SO_4^{2-} . In order to validate and refine the

biogeochemical conceptual model of the study area, a high-resolution multi-level sampling technique together with the use of stable isotopes were adopted in two contrasting environments (urban and agricultural). The focus of the study was to evaluate sources of NH_4^+ and SO_4^{2-} and processes that affect their concentrations in the aquifer.

2. Site description

The study was carried out in the coastal floodplain of the Po River (Fig. 1), a recently reclaimed land with flat topography (from 5 to -11 m a.s.l.), where a large-scale deforestation, the establishment of intensive agriculture and a widespread urbanization have led to a progressive modification of the natural configuration of the territory (Amorosi et al., 2016). The main consequences are the tangling up of the hydrological network and the loss of many coastal wetlands. Nowadays the surface water system consists of the main watercourses (Po di Goro, Po di Volano, Canale Navigabile and Reno River), a reclamation network extending for more than 1850 km and what remains of the widespread brackish coastal lagoons (Valle Bertuzzi and Valli di Comacchio; Fig. 1). From a stratigraphic point of view, the area is characterized by the Holocene transgressive-regressive depositional cycle with an average depth of 25–30 m, bounded at the bottom by Pleistocene alluvial facies (Amorosi et al., 1999). From east to west, the sedimentary units are composed by a variable thickness wedge of shallow marine sandy sediments, coastal sands formed in the foreshore and in the adjacent beaches, and sand dune systems (Curzi et al., 2006).

The studied coastal aquifer is predominantly situated in littoral sandy units and shallow marine wedge deposits and its average thickness ranges between 16 and 22 m. The aquifer hydraulic conductivity is variable, depending on the sorting of aquifer materials, and ranges from 1×10^{-6} ms^{-1} in depressed areas to 1×10^{-3} ms^{-1} in the coastal dunes (Giambastiani et al., 2013). The average horizontal hydraulic gradient is 0.5‰ and the horizontal flow velocity is generally very low (about 7–10 $\text{m} \text{y}^{-1}$). The aquifer is characterized by elevated salinity, and is mainly under anoxic conditions (Giambastiani et al., 2013).

Of the 40 monitoring wells present in the studied coastal aquifer, P5 and P34 have been chosen as representative of two contrasting environments, an urban and an agricultural setting, respectively (Fig. 1). For a comprehensive geochemical description of the coastal aquifer see Colombani et al. (2016) while for the hydrogeological representativeness of the selected monitoring wells see Caschetto et al. (2016). P5 is located in a small village characterized by impermeable surfaces (streets and buildings) while P34 is located in an agricultural landscape along a country trail flanked on both sides by reclamation ditches, part of the reclamation network.

3. Materials and methods

To characterize the distribution of dissolved species concentration, namely major ions, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and methane (CH_4), and stable isotopes composition ($\delta^{15}\text{N}_{\text{NO}_3}$, $\delta^{15}\text{N}_{\text{NH}_4}$, $\delta^{18}\text{O}_{\text{NO}_3}$, $\delta^{34}\text{S}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^{13}\text{C}_{\text{DIC}}$) groundwater samples were collected along two representative profiles selected within the unconfined aquifer (Fig. 1). The groundwater samples were collected every meter using an 800 L straddle packers system (Solinst, Canada). Samples were collected via low-flow technique by mean of an inertial pump after measuring the groundwater static level and purging the sample window.

Temperature, oxidation-reduction potential (ORP), pH and electrical conductivity (EC) were measured in situ using an Oxi

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