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Water Rock Interaction [WRI 14]

Determination of nitrate pollution sources in the Marano Lagoon (Italy) by using a combined approach of hydrochemical and isotopic techniques

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Abstract

Due to increased pollution by nitrate from intensive agricultural and other anthropogenic activities the Marano lagoon (northeast Italy) and part of its catchment area have been investigated, applying a combined approach of hydrochemical and isotopic techniques. Thus, to identify and characterize the potential multiple-sources of nitrate pollution the isotopic compositions of nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$), boron ($\delta^{11}\text{B}$), water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$), and sulphate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$), as well as the chemical composition of different water types have been determined. In the monitoring program water samples from the lagoon, its tributary rivers, the groundwater upwelling line, groundwater, sewage, and open sea on a quarterly interval from 2009 to 2010 have been collected and analyzed. Coupling isotopic and hydrochemical results indicate that the nitrate load in the lagoon was not only derived from agriculture activities but also from other sources such as urban wastewaters, in situ nitrification, and atmospheric deposition. However, none of the samples showed the isotopic characteristics of synthetic fertilizers.

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Keywords: nitrate; lagoon; pollution; N, O, H, B, S isotopes; hydrochemistry; atmospheric deposition; groundwater upwelling line.

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1. Introduction and study area description

Stable isotope data of NO_3 ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and B ($\delta^{11}\text{B}$) have been frequently used for nitrate source identification in surface and groundwater (e.g. [1], [2], [3]). Isotope approaches have already been used in lagoon and coastal environments for characterization of salinization (e.g. [1], [4]) or for determination of organic matter sources [5]. However, a combined use of N, B, S, O and H isotopes for studying the origin and fate of nitrate in lagoon environments has not been often applied. Therefore, the present study represents a novel approach on the identification and characterization of potential multiple sources of nitrate pollution in a lagoon environment, which, beside the traditional hydrochemical analyses (major ions and nutrients), introduces the whole suite of stable isotopes of nitrate ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}$), the isotopic signature of boron ($\delta^{11}\text{B}$), the stable isotopes in water ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) and the stable isotopes in sulphate ($\delta^{34}\text{S}$ and $\delta^{18}\text{O}$). Thus, to identify and characterize multiple-sources of nitrate pollution of agricultural and other anthropogenic origins, a water monitoring network in the Marano lagoon and parts of its catchment area was set-up. In the monitoring program water samples from the lagoon, its tributary rivers, the groundwater up-welling line, groundwater, sewer pipe and open sea on a quarterly interval from 2009 to 2010 were collected and analyzed. The Marano Lagoon is located in the Northern Adriatic Sea (North-eastern Italy) and it has a surface of about 77 km². The Marano Lagoon borders to the east to the Grado Lagoon, which is the second part of the whole Grado-Marano Lagoon system. In the south the Marano Lagoon communicates to the Adriatic Sea through three lagoon inlets (Porto Lignano, S. Andrea and Porto Buso). In the southwest the lagoon is characterized by the urban and touristic areas of Lignano Sabbiadoro city, and by the Aprilia Marittima resort. The artificial channel of Bevazzana is also located in this lagoon sector, which is responsible of the connection between the Tagliamento River and the lagoon. The fishing community of Marano Lagunare is situated in the northern lagoon sector. This lagoon sector is also characterized by the discharge of freshwater from its tributary rivers: Corno-Stella, Turgnano, Cormor, Zellina, Corno and Ausa. The groundwater up-welling line divides the Friulian Plain into two units, the Upper Friulian Plain and the Lower Friulian Plain. The mean discharge of the groundwater up-welling line in the left Tagliamento River side is about 80 m³/s.

2. Analytical methods and results

For the chemical characterization of the different water types their chemical compositions have been determined applying the following methods: (i) in-situ chemical analysis and measurement of the physicochemical parameters; (ii) post-sampling analyses in the laboratories. The in-situ chemical analysis and measurement of the physicochemical parameters included the following activities: (i) measurement of pH, water temperature, electrical conductivity, dissolved oxygen and salinity; (ii) measurement of nitrate, nitrite, and ammonium concentration using a portable spectrophotometer “WTW FC photoFlex/Turb 430 LED”; (iii) measurement of orthophosphate concentration using a second portable spectrophotometer “Merck SQ 118”; and (iv) storage of all collected water samples for the later analyses in the laboratories. Dissolved cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (Cl^- , Br^- , SO_4^{2-}) were analyzed by ion chromatography (Dionex ICS-3000). Alkalinity was measured by titration and total phosphorus was determined photometrically in the laboratory after digestion of deep frozen water samples. Deuterium ($\delta^2\text{H}$) was measured with a Finnigan DELTA^{plus} XP continuous flow stable isotope ratio mass spectrometer by chromium reduction using a ceramic reactor. The oxygen isotopic composition ($\delta^{18}\text{O}$) of water was measured by the classic $\text{CO}_2\text{-H}_2\text{O}$ equilibrium technique with a fully automated device coupled to a Finnigan DELTA^{plus} mass spectrometer. The nitrate nitrogen and oxygen-18 isotopic compositions were analyzed using the denitrifying bacteria procedures (denitrifier method) described in [6], [7], [8] and have been used to differentiate among nitrate coming from agriculture (synthetic and

natural fertilizers), airborne nitrate and nitrate from nitrification processes in soils. The measurements of boron isotopes were performed on a Thermo Fisher AXIOM MC-ICP-MS equipped with an ESI New Wave Research LFC [9]. Stable sulphur isotope measurements were carried out with a Thermo Finnigan MAT 253 gas mass spectrometer that was connected to via a Thermo Electron ConFlo IV open split interface to a Thermo Scientific Flash 2000 elemental analyzer, while, $\delta^{18}\text{O}$ of sulphate were carried out with a Thermo Finnigan DELTA^{plus} gas mass spectrometer after conversion in a Thermo Quest TC/EA preparation system. The isotopic composition of different anthropogenic and natural nitrate sources as well as the values of measured samples are reported in Figure 1.

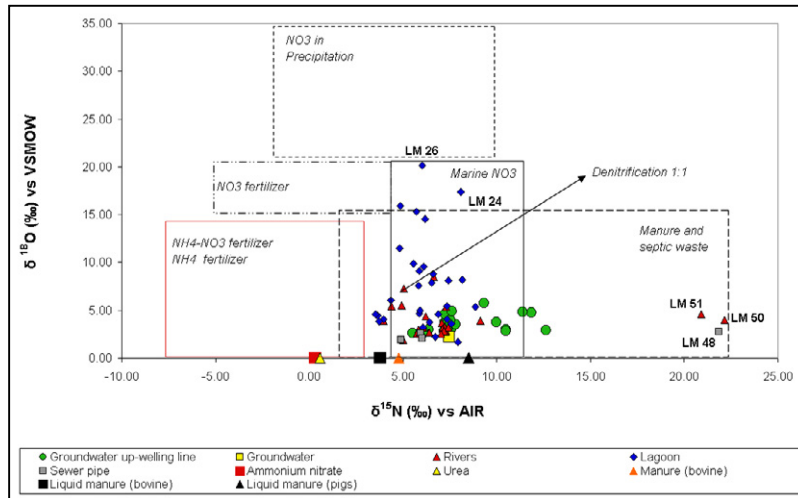


Figure 1: Nitrogen and oxygen isotopic composition of nitrate (modified after [3]).

None of the samples fell into the isotopic range typically observed for nitrate originating from synthetic fertilizers. This result indicates that synthetic fertilizers have not entered the lagoon directly or, if present, have undergone additional biological processing. The isotopic composition of nitrate measured in the rivers was in the typical range of animal manure and urban sewage water but in the case that urban sewage water flows directly into the river system the $\delta^{15}\text{N}$ values can be much more enriched. This phenomenon has been detected in the Cormor River and in the Corno River. Moreover, these isotopic values fit very well with the high concentrations of nitrate, nitrite, ammonium and phosphates measured at the same sampling points. Since nitrite, ammonium and phosphates are typical indicators of local and direct anthropogenic pollution it could be concluded that, in this case, the main nitrate sources come from urban wastewaters. Denitrification processes have not been identified due to the oxic conditions of the study area. Since water circulation in the lagoon is strongly influenced by seawater, the nitrate directly produced in the lagoon from nitrification of ammonium coming from both anthropogenic sources as well as from mineralization of local dead biomass will have a higher $\delta^{18}\text{O}$ value. This may mean that nitrate with $\delta^{18}\text{O}$ greater than 8 ‰ mainly originated from nitrification processes within the lagoon itself, especially since the small $\Delta^{17}\text{O}$ values (mean 0.65 ‰) indicate an atmospheric nitrate contribution of no more than 3% on average (but up to 10% locally). To assess the impact of different boron sources in a catchment area an “end-member mixing model” has to be used. The most important pollution end-members selected for this study were: manure, urban wastewater and seawater. This indicates that most of the samples were affected by both agriculture (manure) and urban wastewater (sewage) pollution sources. The isotopic compositions of water have been used to characterize the mean altitude of the recharge area of the freshwater samples as well as to identify the origin of groundwater along the groundwater up-

welling line. From these results it was possible to confirm that the sampled water along the groundwater up-welling line comes from local groundwater. The sulphur isotope results indicate that pyrite oxidation in aquifers or at the sediment-water interface of the lagoon that could be induced by oxidants like, nitrate or oxygen can be neglected as a significant sulphate source. Moreover, the stable isotope analyses of sulphate confirm that the water of the southwestern lagoon sector is dominated by Adriatic seawater during most of the seasons.

3. Conclusions

The isotopic compositions of different anthropogenic and natural nitrate sources as well as the isotopic signatures of nitrate in numerous water samples collected in the catchment area of the lagoon and in the lagoon itself were measured. None of the samples fell into the isotopic range typically observed for nitrate originating from synthetic fertilizers. Nitrates detected in groundwater and along the groundwater up-welling line are mainly related to the use of manure (both liquid and solid), while other nitrate sources come from urban wastewaters as detected in some rivers. In the lagoon the characterization of the origins and fate of nitrate was in general much more difficult to achieve because of complex mixing processes among different water types like seawater, river water and rainwater. However, it was possible to identify that nitrate can be formed in the lagoon by nitrification processes of ammonium coming from both anthropogenic sources as well as from remineralization. Moreover, the concentration values and the isotopic signatures of boron found in the sampled waters also indicate that the majority of water samples were influenced by two main pollution sources, i.e. manure discharges and sewage effluents. Therefore, it can be concluded that the nitrate load in the lagoon, as detected during the monitoring period 2009-2010, was not only derived from agriculture activities but also from other sources like urban wastewaters, nitrification processes in the lagoon as well as from atmospheric deposition.

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