ASSESSMENT OF POTENTIAL NITRATE POLLUTION SOURCES IN THE MARANO LAGOON (ITALY) AND ITS CATCHMENT AREA USING A MULTI ISOTOPE APPROACH

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Abstract

The aims of this study were mainly: (i) the identification and differentiation of the main anthropogenic nitrogen sources in the Marano Lagoon (Italy) and its catchment area; and (ii) the assessment of the intra-lagoonal water circulation, the morphological development of the lagoon and its anthropogenic pressure by applying a combined approach of hydrochemical, isotopic and remote sensing techniques. To achieve the aforementioned targets analyses of the stable isotope signatures of nitrate, boron, water and sulphate have been used. Moreover,

the residence times of groundwater were determined by the tritium–helium dating method. To characterize the chemical composition of the different water types the concentrations of the major ions and nutrients as well as the physicochemical parameters have been measured. Remote sensing techniques have been applied to assess the spatial distribution of the most superficial algal flora, water temperature as well as the key environmental and morphological changes of the lagoon since the beginning of the 1970s.

1. INTRODUCTION AND METHODS

The present study represents a novel approach to the determination of potential nitrate sources in a lagoon environment, which, besides the traditional hydrochemical analyses (main ions and nutrients), introduces the isotope signature of nitrate ($\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$), boron ($\delta^{11}B$), water ($\delta^{2}H$ and $\delta^{18}O$), and sulphate ($\delta^{34}S$ and $\delta^{18}O$), the tritium/helium ($^{3}H/^{3}He$) isotopic method as well as remote sensing techniques. The stable isotopes in nitrate measured by the denitrifier method have been used to differentiate between different nitrate sources as described in [1] and [2]. Boron isotopes have been used to identify the impact of domestic wastewater to the aquatic system using the LA–MC–ICP–MS method [3]. Use of $\delta^{11}B$ coupled with $\delta^{15}N$ has proved to be an effective means for tracing agricultural nitrate sources (e.g., hog manure, cattle feedlot runoff and synthetic fertilizers) in surface and groundwaters [4, 6]. The stable isotopes in water have been used to calculate mixing ratios between sea and fresh water and to estimate the mean altitude of the recharge area of surface waters. The stable isotopes in sulphate have been adopted to determine both its origin and the marine and terrestrial contributions, while the tritium–helium isotopic method has been used to assess the mean residence time of groundwater (groundwater age). In order to characterize the chemical composition of the different water types, the concentration of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, NO_3^{-}, NO”, Cl^{-}, Br^{-}, SO_4^{2-}, PO’$^{-}$, HCO_3^{-}, total silicon, total phosphorus and total boron have been analysed. Moreover, the physicochemical parameters such as pH, electrical conductivity, dissolved oxygen, salinity and temperature have been measured. In order to identify the origin and the fate of nitrate, a water monitoring network was implemented in the Marano Lagoon and its catchment area. Monitoring involved the collection of water samples from the lagoon, tributary rivers, groundwater upwelling line, groundwater, sewer pipe and open sea on a quarterly interval from 2009 to 2010.

2. STUDY AREA

The Marano Lagoon is located in the Northern Adriatic Sea (north eastern Italy) and it is entirely included in the Province of Udine of the Friuli Venezia Giulia region as represented in Fig. 1.

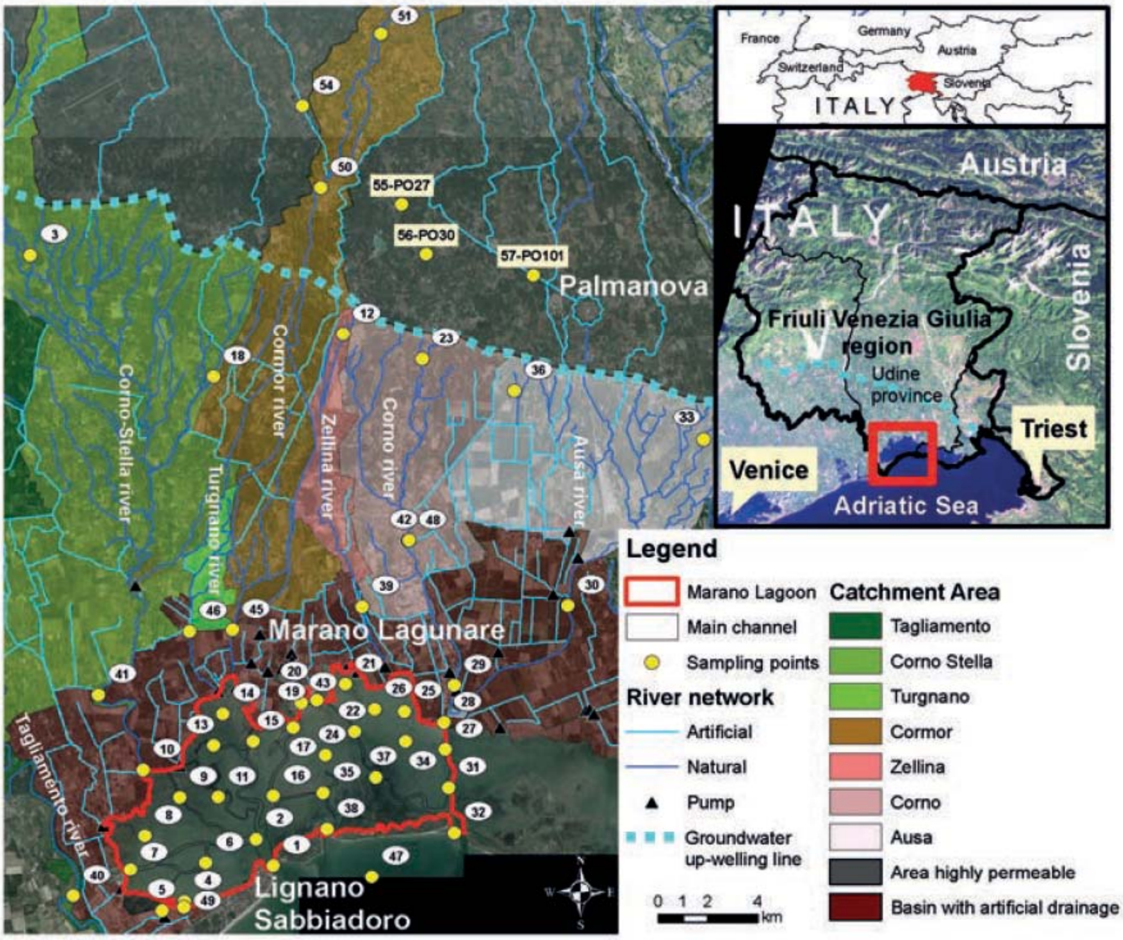

FIG. 1. Study area: Marano Lagoon (red line).

The lagoon has a surface of about 77 km², with a length of nearly 14 km and an average width of 5.5 km. The Marano Lagoon borders the Grado Lagoon to the east, 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). A total mean water exchange rate between the lagoon and the Adriatic Sea through the Porto Lignano and Porto Buso inlets are respectively on the order of 1750 and 1500 m³/s. The mean bathymetry in the shallow lagoon areas is around 0.8 m, while in the navigable channels is about 3.2 m. In the south west the lagoon is characterized by the urban and touristic areas of Lignano Sabbiadoro, which is one of the main summer resorts in northern Italy, and by the Aprilia Marittima resort. The artificial channel of Bevazzana is also located in this lagoon sector, and forms a connection between the Tagliamento river and the lagoon. The fishing community of Marano Lagunare is situated in the northern lagoon sector, which is, with its 2007 inhabitants, the main urban centre within the lagoon perimeter. This lagoon sector is also characterized by the discharge of freshwater from its tributary rivers: Stella, Turgnano, Cormor, Zellina, Corno and Ausa.

The groundwater upwelling line divides the Friulian Plain into two units, the Upper Friulian Plain and the Lower Friulian Plain. The mean discharge of the groundwater upwelling line in the left Tagliamento river side is about 80 m³/s which corresponds to a mean discharge per kilometre of about 1.3 m³/s·km^{-1}.

3. RESULTS

The isotopic composition of different anthropogenic and natural nitrate sources, as well as the values of measured samples, are reported in Fig. 2.

None of the samples fell into the isotopic range typically observed for nitrate originating from synthetic fertilizers. 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 $\delta^{15}N$ values can be much more enriched. This phenomenon has been detected in the Cormor river south of Udine city (sampling points: 50 and 51) and in the Corno river (sampling point 48 at sewer pipe). Moreover these isotopic values fit very well with the high concentration of nitrate, nitrite, ammonium and phosphate measured at the same sampling points. Since nitrite, ammonium and phosphate are typical indicators of local and direct anthropogenic pollution it could be concluded that, in this case, the main nitrate sources come from urban wastewater. Since water circulation in the lagoon is strongly influenced by the seawater (as confirmed by the analyses on the spatial distribution of bromide as well as by the isotopic composition of water)

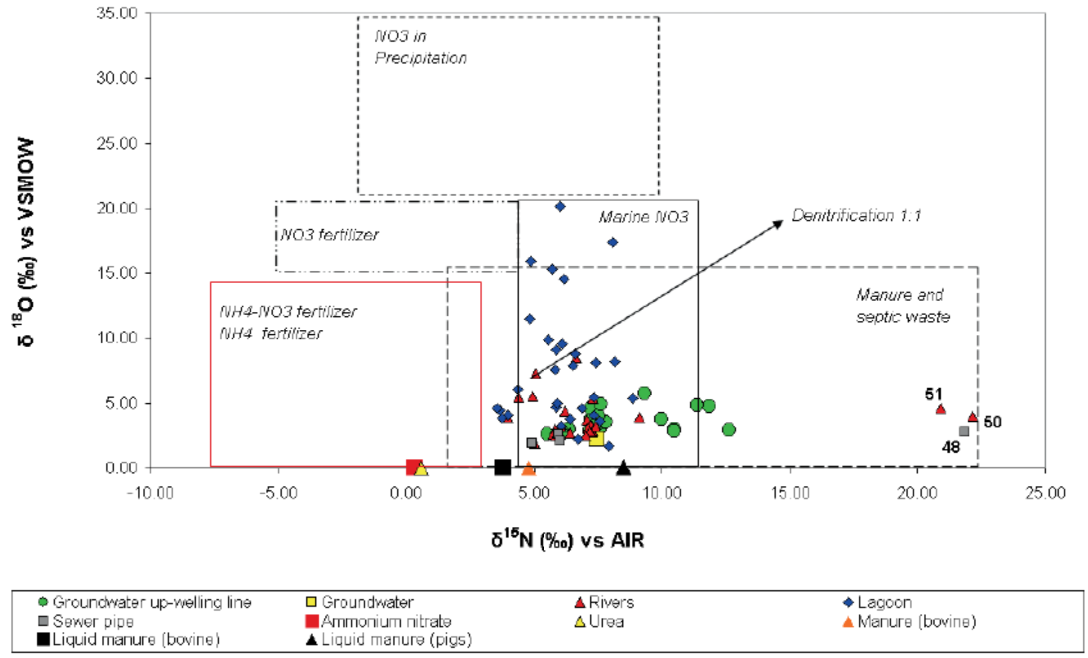

FIG. 2. Nitrogen and oxygen isotopic composition of nitrate (modified after [8]).

and since the $\delta^{18}O$ of seawater is higher than that of freshwater, the nitrate produced in the lagoon from nitrification of ammonium will have a higher $\delta^{18}O$ value. This may mean that nitrate with $\delta^{18}O > 8‰$ mainly originates from nitrification processes within the lagoon itself, especially since the small $\Delta^{17}O$ values (mean 0.65‰, maximum 3‰) indicate an atmospheric nitrate contribution of no more than 3% on average (but up to 10% locally). $\Delta^{17}O$ values of atmospheric nitrate fall in the range of 22 to 35‰, with the corresponding $\delta^{18}O$ values between 50 and 90‰. A contribution of 3% atmospheric nitrate would therefore increase the $\delta^{18}O$ of lagoon nitrate by only about 2‰.

Thus, the isotopic signatures of nitrates detected in the lagoon clearly showed that the nitrate load was not only derived from the agriculture activities but also from other sources such as urban wastewater and nitrification processes in the lagoon itself. To assess the impact of different boron sources in a catchment area an ‘endmember mixing model’ has been used. The most important pollution endmembers selected for this study were: manure, urban waste water and seawater. Manure has low boron concentrations (<0.1 mg/L and big variations in $\delta^{11}B$ values from 15 to 30‰. Upwelling groundwater is influenced from agriculture and characterized by relative low boron concentrations (0.11 to 0.23 mg/L). This is relatively close to natural background content (below 0.1 mg/L) in northern Italy [7]. The $\delta^{11}B$ values of the upwelling groundwater samples analysed in this study showed large variations from 4 to 22.7‰ (median value 17.7‰).

In contrast, urban wastewater has higher boron concentrations (0.46 to 1.1 mg/L) and lower $\delta^{11}B$ values from 0 to 12.9‰. No significant differences in boron contents and isotopic compositions have been found between raw and treated sewage. Therefore, boron isotope variations can be applied for tracing contamination of groundwater by both raw and treated sewage effluents. The sampled seawater in the Adriatic Sea at sampling point 47 was characterized by a boron content of 4.2 mg/L and a $\delta^{11}B$ value of 40.5‰. Most of the samples plotted within the range of these mixing curves can be explained by ternary mixing among the three endmembers. However, some of the river samples are above the mixing line. This group of data are characterized by low to moderate boron contents (0.1–0.45 mg/L) and high $\delta^{11}B$ values (36.2–39.6‰). From this it can be assumed that the mixing of river water boron with anthropogenic boron from manure and wastewater as well as with boron from seawater is the major factor which determines the distribution of $\delta^{11}B$ in the catchment of the lagoon and in the lagoon itself.

However, the higher boron concentrations in the seawater endmember result in non-linear (hyperbolic) boron concentration versus $\delta^{11}B$ mixing curves. That complicates the identification of the other pollution sources especially in the lagoon itself. Therefore, $\delta^{11}B$ values have been normalized using the bromide concentration in the water as a second tracer for the admixing of seawater. The data plotted in Fig. 3 indicates that most of the samples were influenced by both agriculture and urban waste water pollution sources. Moreover, the data show that in some areas

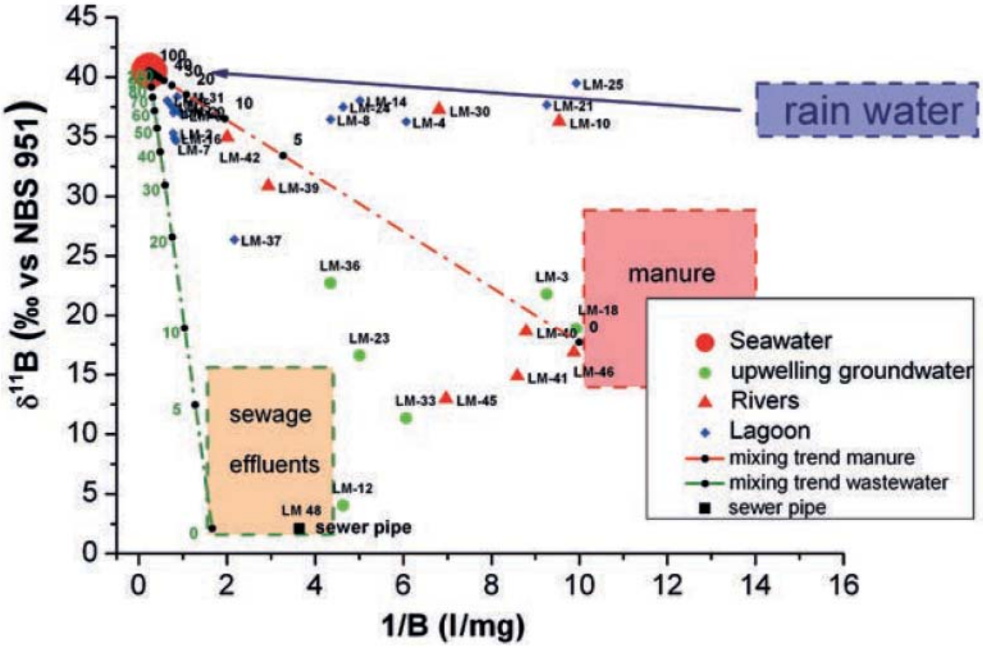

FIG. 3. $\delta^{11}B$ vs 1/B diagram showing normalized boron concentrations and $\delta^{11}B$ values.

of the lagoon the waters are less affected by these pollution sources. This identifies rainwater as an additional mixing endmember.

Sulphate in aquatic ecosystems can be from atmospheric, pedospheric and lithospheric origins. Moreover, sulphur compounds in industrial waste products are an additional source of sulphate. The different sulphates are introduced to the aquatic ecosystem by groundwater discharge to rivers (atmospheric, pedospheric and lithospheric sulphate) and direct mixing with seawater and precipitation (marine and atmospheric sulphate). Therefore sulphur isotopes can be used to trace natural and anthropogenic sources of sulphur in agricultural watersheds as well as in coastal aquifers.

The measured $\delta^{34}S$ and $\delta^{18}O$ values for sulphate at the sampling points 40 (Tagliamento river) were 12.3‰ and 12.9‰ respectively, while at the sampling point 5 (Bevazzana channel) they were 12.5‰ and 11.9‰ respectively, most likely indicating a lithogenic origin, e.g. from the dissolution of Permian evaporites [9]. This is in agreement with ion balance calculations of the dissolved components found at these sites. In contrast, dissolved sulphate at sampling point 6 (lagoon) shows $\delta^{34}S$ and $\delta^{18}O$ (20.6‰ vs V–CDT and 9.3‰ vs V–SMOW, respectively) that are typical for Mediterranean Seawater without indication for net sulphate reduction or an intense reduction–oxidation cycle. The sulphur and oxygen isotope analyses confirm that the waters of the southwestern lagoon sector are influenced by the Tagliamento river. Since 2008 the entire catchment area of the Marano Lagoon has been defined as a nitrate vulnerable zone (NVZ), where an action programme on the reduction of nitrate leaching has been launched. In order to assess the time necessary to expect the effects of the action programme in the NVZ an additional sampling campaign

TABLE 1. RESULTS OF THE ANALYSIS FOR TRITIUM (^3H) AND HELIUM ISOTOPES FOR GROUNDWATER DATING

Sample ID	^3H (TU)	Excess Ne (%)	^4He rad. (ccSTP/kg) Error: 0.2 E–6	$^3He_{tri}$ (TU)	Age (years)
55-PO27	4.95±0.1	48	0.0 E–6	0.4	1.3±0.5
56-PO30	5.1±0.1	44	0.0 E–6	0.4	1.4±0.5
57-PO101	4.85±0.1	34	0.0 E–6	1.2	4.0±1.0

Note: The derived data were calculated with assumed infiltration temperature of 10°C, altitude 0 masl and scaled to the sampling date of June 15th 2010.

to estimate the mean groundwater residence time has been carried out in June 2010. Groundwater in the Upper Friulian Plain was sampled at three irrigation wells (Fig. 1: 55–PO27, 56–PO30 and 57–PO101) for ^3H–^3He dating. The dating method utilized for these analyses is described e.g. by Ref. [10]. The results of the measurements of tritium (^3H) and helium isotopes for dating groundwater are reported in Table 1. Ages were calculated with the assumption of piston flow conditions in the aquifer. None of the samples show ^4He from radiogenic sources, which is used as an indicator for waters with ages much above 50 years. The concentration of ^3H and tritiogenic ^3He ($^3He_{tri}$) in the samples match the concentration of ^3H in precipitation quite well. The portion of excess Ne — compared to solubility equilibrium concentration — is rather high, namely in the order of 34–48% of the equilibrium value. This indicates that a recent equilibration of the dissolved gases in the water with the atmosphere could be excluded. Hence, the low concentration of $^3He_{tri}$ and the derived young ages are a reliable feature of the aquifer.

To explain the groundwater age differences between the first two sampling points (55–PO27 and 56–PO30) and the point 57–PO101 it must be noted that before sampling groundwater at point 57–PO101, the two pumps installed in the irrigation well were running. Therefore, mixed waters between upper groundwater and deeper groundwater layers (older groundwater) have been sampled. In the other two irrigation wells (55–PO27 and 56–PO30) the pumps were out of order for many days, therefore the sampled waters from these two wells were not mixed with deeper water as in the first case.

4. 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 Marano Lagoon and its catchment area have been measured. Nitrates detected in groundwater and along the groundwater upwelling line are mainly related to the use of manure (both liquid and solid), while other nitrate sources come from urban wastewater as detected in some rivers such as the Cormor and Corno rivers. In the lagoon, the characterization of the origin and fate of nitrate was in general much more difficult to achieve because of complex mixing processes among different water types such as seawater, riverwater and rainwater. However, it was possible to confirm that nitrate can be formed in the lagoon itself by nitrification processes of ammonium coming from both anthropogenic sources as well as from remineralization. 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 such as urban wastewater, nitrification processes in the lagoon itself as well as from atmospheric deposition. Due to the fact that boron represents a co-migrant of nitrate in anthropogenic pollution sources, boron isotopes have been used as an additional tracer to identify different human impacts on aquatic ecosystems. Manure, urban wastewater and seawater were the three endmembers used for this analysis. From the concentration values and from the isotopic signature of boron found in the sampled waters it can be concluded that the distribution of $\delta^{11}B$ in the Marano Lagoon and its catchment area resulted from mixing of anthropogenic boron from urban wastewater and manure (liquid and solid) as well as from boron in seawater. The measured data indicate that most of the samples were influenced by both pollution sources: agriculture and urban wastewater.

Moreover, the data are showing that in some parts of the lagoon the water is less affected by these two pollution sources. Few samples along the groundwater upwelling line could not be explained with the use of the endmember mixing model. Therefore, these samples may be affected by the contamination of a different anthropogenic boron source such as landfill. The isotopic compositions in 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 upwelling line. Additionally the water isotopes were used to identify mixing processes between freshwater and seawater within the lagoon. From these results it was possible to confirm that the sampled water along the groundwater upwelling line comes from local groundwater. The isotopic signature of sulphate confirmed the influence of the Tagliamento river in the western lagoon sector through the Bevazzana artificial channel. Moreover, the analysis conducted in three groundwater irrigation wells in the Upper Friulian Plain has shown that the groundwater age is very young in the range between 1.3 and 4.0 a.

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