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# Identification and characterisation of potential sources of nitrate pollution in the Marano Lagoon (Italy) applying a multi-isotope approach

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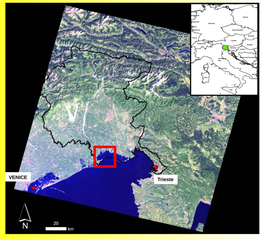
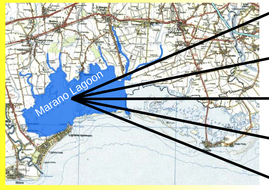
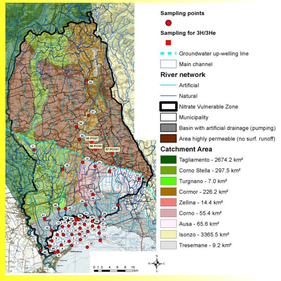
**Introduction.** The isotopic composition of nitrate ($\delta^{15}N$, $\delta^{18}O$ and $\Delta^{17}O$), boron ($\delta^{11}B$) and water ($\delta^{2}H$ and $\delta^{18}O$) were used to identify and characterize of multiple nitrate pollution sources in the Marano Lagoon (Italy) and part of its catchment area. The stable isotopes in nitrate measured by the denitrifier method have been adopted to differentiate among nitrate coming from agriculture (synthetic and natural fertilizers), airborne nitrate and nitrate from nitrification processes in soils. Boron isotopes have been used to identify the impact of domestic wastewaters to the aquatic system using the LA-MC-ICP-MS method. The combined use of $NO_3$ and B isotopes has proved to be an effective means in identifying multiple nitrate pollution sources because these isotopes co-migrate in many environmental settings, their isotopes are fractionated by different environmental processes, and because wastewater and fertilizers may have distinct isotopic signatures for N and B. The stable isotopes of water have been used to calculate mixing ratios between sea and fresh water as well as to estimate the mean altitude of the recharge area of surface waters. Additionally, the stable isotopes of sulphate ($\delta^{34}S$ and $\delta^{18}O$) have been adopted to trace natural and anthropogenic sources of sulphur in agricultural watersheds as well as in coastal systems. In order to characterize the chemical composition of the different water types the concentration of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, $K^{+}$, $NH_4^{+}$, $NO_3^{-}$, $NO_2^{-}$, $Cl^{-}$, $Br^{-}$, $SO_4^{2-}$, $HCO_3^{-}$, $PO_4^{3-}$, total phosphorus and total boron have been analyzed. Moreover, the physicochemical parameters such as pH, electrical conductivity, dissolved oxygen, salinity and temperature have been measured. To identify the origins and fate of nitrate a water monitoring program was implemented in the Marano lagoon and part of its catchment area. The water monitoring program involved the collection of 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.

## Study area




$\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$ $\Delta^{17}O_{NO3}$

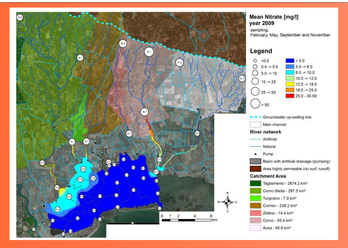
$\delta^{11}B$

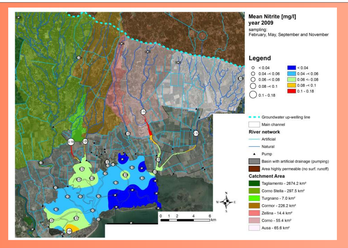
$\delta^{2}H_{H2O}$, $\delta^{18}O_{H2O}$

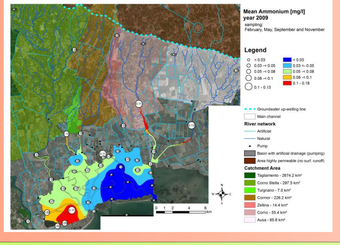
$\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$

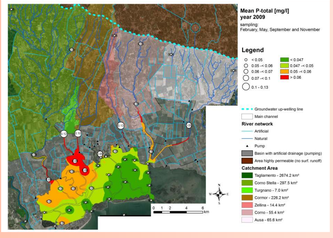
**Main ions and nutrients**

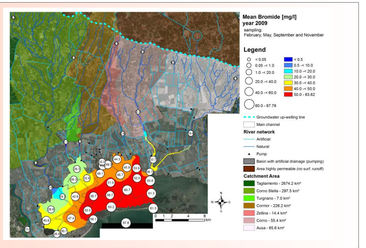
## Hydrochemistry



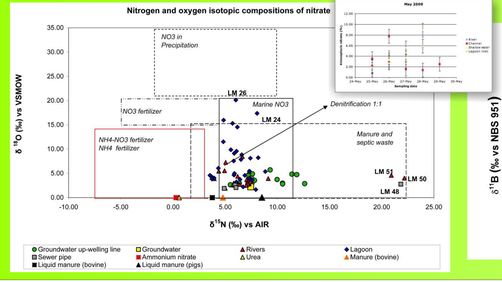



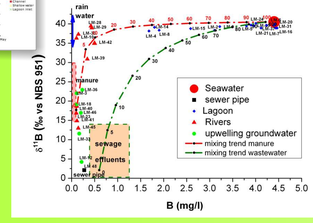



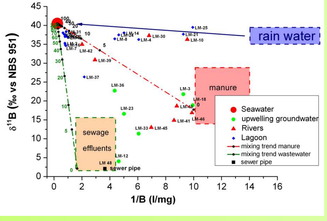



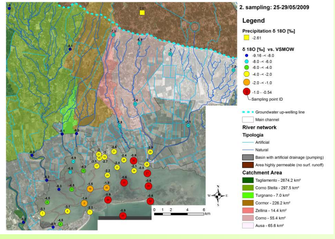



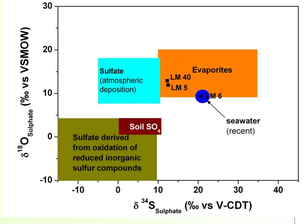

## Isotopes




**Conclusions.** 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 waste water as detected in some rivers like Cormor and Corno rivers. In the lagoon it was possible to identify 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 like urban waste water, 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 waste water and seawater were the three end-members used for this analysis. The distribution of $\delta^{11}B$ in the Marano Lagoon and its catchment area was resulting 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 waste water. 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 up-welling 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 up-welling line come from local groundwater. The isotopic signature of sulphate confirmed the influence of Tagliamento river in the western lagoon sector through the Bevazzana artificial channel.