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Using stable isotopes in tracing contaminant sources in an industrial area: A case study on the hydrological basin of the Olt River, Romania

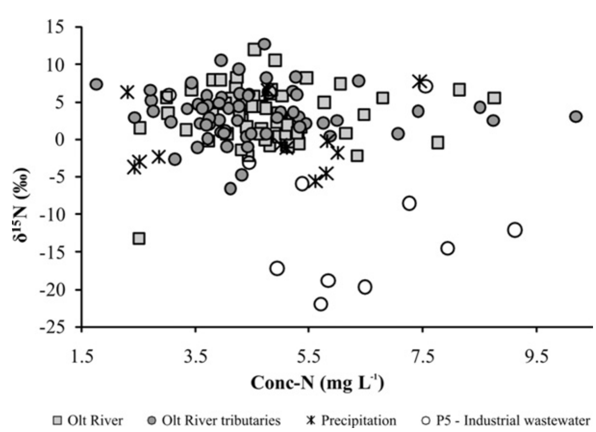
Raluca Popescu [a], Tanja Mimmo [b], Oana Romina Dinca [a], Calogero Capici [b], Diana Costinel [a], Claudia Sandru [a], Roxana Elena Ionete [a,*], Ioan Stefanescu [a], Damian Axente [c]

[a] National Research and Development Institute for Cryogenics and Isotopic Technologies, ICSI Ramnicu Valcea, 4 Uzinei Str, RO-240050 Ramnicu-Valcea, Romania
[b] Faculty of Science and Technology, Free University of Bozen-Bolzano, University Plaza no. 5, I-39100 Bolzano, Italy
[c] National Institute for Research and Development of Isotopic and Molecular Technologies, 65–103 Donath Str., RO-400293 Cluj-Napoca, Romania

HIGHLIGHTS

- The main source of nitrogen pollution was agriculture/residential.
- Anthropogenic additions of nitrogen were identified in the colder months.
- Industrial nitrogen source was differentiated from the agriculture/residential one.
- One industrial nitrogen release in the Olt River was observed during the study.

GRAPHICAL ABSTRACT



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ABSTRACT

Tracing pollution sources and transformation of nitrogen compounds in surface- and groundwater is an issue of great significance worldwide due to the increased human activity, translated in high demand of water resources and pollution. In this work, the hydrological basin of an important chemical industrial platform in Romania (Ramnicu Valcea industrial area) was characterized in terms of the physico-chemical and isotope composition of $\delta^{18}O$ and $\delta^{2}H$ in water samples and $\delta^{15}N$ of the inorganic nitrogen species. Throughout a period of one year, water samples from the Olt River and its more important tributaries were collected monthly in the industrial area, when the seasonal and spatial isotope patterns of the surface waters and the main sources of pollution were determined. Higher inorganic nitrogen concentrations (up to 10.2 mg N L^{-1}) were measured between November 2012 and April 2013, which were designated as anthropogenic additions using the mixing calculations. The main sources of pollution with inorganic nitrogen were agriculture and residential release. The inorganic nitrogen from the industrial waste water duct had a distinct $\delta^{15}N$ fingerprint (mean of −8.6‰). Also, one industrial release into the environment was identified for Olt River, at Ionesti site, in November 2012. The mean precipitation samples had the lowest inorganic nitrogen concentrations (less than 5.5 mg N L^{-1}) with a distinct $\delta^{15}N$ fingerprint compared to the surface and industrial waters.

* Corresponding author.
E-mail address: roxana.ionete@icsi.ro (R.E. Ionete).

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1. Introduction

The determination of nitrogen inorganic species in surface waters is usually an integral part of basic water quality assessment since their concentrations are often used as general indicators of the nutrient status and the degree of pollution of any affected water body. Nitrogen inorganic compounds like ammonium NH_4^+, nitrates NO_3^- and nitrites NO_2^- are essential plant nutrients, but in excess amounts they may cause significant water quality problems (Heaton, 1986; Battaglin et al., 2001). The natural level of ammonium or nitrate in surface water is usually less than 1 mg L^{-1}, but in the effluent of sewage treatment plants may have levels in excess, up to 30 mg L^{-1}. Often when nitrate concentrations are higher than 10 mg L^{-1}, hypoxia can appear and can become toxic to animals (Reinhardt et al., 2006). In natural surface waters, ammonium, which is a product of microbiological activity, is seen as indicative of sanitary pollution (Freney et al., 1983).

In surface water, inorganic nitrogen concentrations can increase for several reasons like upstream discharge of high nitrate or ammonium sewage effluents, leaching from agricultural land during high precipitation, discharge of farm or industrial effluents and/or seasonal effects (Ging et al., 1996). Identifying the source and biogeochemical transformations of the nitrogen is often of significant interest for water resource management (Segal-Rozenhaimer et al., 2004; Aggarwal et al., 2005; Hoefs, 2009), for proving suitable and safe water for human use and consumption. Isotope techniques have been proven a valuable tool in hydrology and monitoring water pollution sources. The isotopic composition of nitrogen ($\delta^{15}N$) from the water can provide information of different N sources, differentiating between the agricultural sources (synthetic fertilizers) and wastewaters from urban treatment plants. Nitrate derived from manure or sewage is usually characterized by $\delta^{15}N$ values between 7‰ and 20‰ (Heaton, 1986; Aravena et al., 1993; Wassenaar, 1995; Aravena and Robertson, 1998), nitrate and ammonium in rain have values between −15‰ and 2‰, and nitrate from synthetic fertilizers is around 0‰, due to their atmospheric origin (Heaton, 1986; Kendall, 1998). Additionally, spatial or temporal patterns of increasing and decreasing nitrogen concentrations together with changing isotope ratios may reveal biogeochemical processes governing its occurrence in aquatic systems (Battaglin et al., 2001; Aggarwal et al., 2005).

The first nitrogen isotope ratio measurements on water samples were reported in the 1950s, but they were used more widely in hydrological studies starting in the 1970s (Aggarwal et al., 2005). Current research focuses mainly on identifying pollution sources and determining the contributions of these sources (Peterson et al., 2001; Setzinger et al., 2002; Master et al., 2003; Segal-Rozenhaimer et al., 2004; Reinhardt et al., 2006; Nestler et al., 2011; Kanduc et al., 2012; Widory et al., 2013). As for isotopic investigations on the rivers in Romania, there are several published studies (Cuna et al., 2001; Costinel et al., 2009; Vremera et al., 2011; Butiuc-Keul et al., 2012), some with emphasis on the use of tritium as a tracer in the environment (Varlam et al., 2010; Faurescu et al., 2011), only few regarding the Olt River (Dinu et al., 2000; Popescu et al., 2014) and none on the subject of pollution source identification using the $\delta^{15}N$ fingerprint. For this reason, the paper investigates the sources and transformations of inorganic nitrogen compounds (nitrate, nitrite and ammonium) in the middle Olt River basin, near the industrial area of Ramnicu Valcea, by applying a combination of physico-chemical and isotopic techniques, to determine if there are major industrial nitrogen releases in the environment.

2. Study area

The study area is the Olt River basin in the residential and industrial area of Ramnicu Valcea town, comprising Olt River along 50 km and 6 tributaries, draining an area of approximately 2500 km^2 (Fig. 1). The Olt River has in the study area an approximate width of 70–100 m and up to 500 m at the accumulation dams and a depth of 1–3 m and up to 6 m at the dams. The basin is located between 44°49′08″ and 45°14′21″ N latitude, 20°20′36″ and 24°15′01″E longitude and at 200 m altitude.

The hydrological basin has residential, chemical industry platform and agricultural usage. In the study area resides a population of 170,000 dispersed in Ramnicu Valcea town and ten smaller localities. The chemical industry platform produces hundreds of thousands tons per year of salt, soda ash and organic derivates. The water in the industrial platform is used for chemical processing, discharge of wastes and electricity production. The industrial waste water is continuously monitored, when overflows of inorganic nitrogen contaminants are registered at high production.

The maximum volume of water flow of the Olt River is registered in May and the minimum in September. The lowest flows occur both in the summer and autumn, due to the small quantities of precipitation and high temperatures during August–September (Ujvari, 1971). The average annual temperature was 11.3 °C in the area. The relative air humidity reached average values between 60 and 80%. Precipitation falls mainly in spring and in autumn, with an average annual rainfall of less than 1000 mm/year (Ielenicz and Patru, 2005). The precipitation amount and mean temperature for the study area from November 2012 to October 2013 were measured at the GNIP monitoring station, located on the industrial platform, on the ICSI Ramnicu Valcea site. The precipitation amount varied between 11.2 mm in July 2013 and 112.0 mm in September 2013, while the mean temperature between −0.6 °C in December 2012 and 22.9 °C in August 2013 (Supplementary material).

3. Sampling and analysis

Analysis were carried out on surface water samples collected from 11 locations in the residential and industrial area of Ramnicu Valcea town, on Olt River and its main tributaries (Fig. 1, Table 1), for physico-chemical and isotopic characterization ($\delta^{18}O$ and δ^2H of the water samples and $\delta^{15}N$ of the dissolved inorganic nitrogen (nitrate, nitrite and ammonium)). The sampling was done monthly from November 2012 to October 2013. The environmental temperature and the temperature and pH of the water samples were measured on site.

Another set of samples were represented by the monthly mean precipitation for the sampling area, characterized in the same manner. Precipitation samples were collected using a rain gauge connected with a mesh-protected funnel to a 1 L polyethylene bottle and the environmental conditions (temperature and quantity of precipitation) were recorded. The bottles were gathered right after the event so that the isotope ratio would not be altered by evaporation processes within the container. The individual events in a month were used to make a weighted mean precipitation sample.

All water samples were filtered through 0.45 μm PTFE membranes and were refrigerated (4–8 °C) in 500 ml glass dark containers right after sampling. A second sample of 50 ml was kept at ambient temperature for the $\delta^{18}O$ and δ^2H analyses. No chemicals were added to the water. Each bottle was clearly identified with batch code, location, date, hour and temperature.

Within two days after sampling, the nitrate, nitrite and ammonium concentrations were measured from the samples kept at 4–8 °C temperature. For the $\delta^{15}N$ analysis of the inorganic nitrogen species, the water samples that were analyzed in a period of 2 weeks after sampling were refrigerated at 4–8 °C, while the ones analyzed within 6 weeks from sampling were kept frozen (−20 to −18 °C).

The nitrate, nitrite and ammonium concentrations were determined by the colorimetric method, according to standard methods (ISO 7890-3, 2000; ISO 7150-1, 2001; SR EN 26777, 2002), using a SPECORD 250 UV–VIS spectrophotometer (Analytik Jena AG, Germany). The quality control analysis has been tested using certified reference materials. Measurement reproducibility of duplicates was better than 8% of the measured value. All the results, for ammonium, nitrite and nitrate concentration are expressed in mg L^{-1}.