OCCURRENCE AND SEASONAL VARIATION OF NITRATE IN NATURAL WATERS OF SARDINIA (ITALY)

Rosa Cidu and Riccardo Biddau

Dipartimento Scienze della Terra, Università di Cagliari, Italy
E-mail: cidur@unica.it

ABSTRACT

Nitrate in surface (187 samples) and ground (126 samples) waters collected in Sardinia (Italy) shows a large range of concentrations: from <1 to 249 mg/L. The highest median value of nitrate occurs in groundwater samples, especially in shallow wells, and spring waters circulating in granite environments. In surface waters, nitrate generally increases as flow increases following intense precipitation. Main sources of nitrate in the studied waters might derive from agriculture and farming.

Keywords: Nitrate, Surface water, Groundwater, Sardinia.

1. INTRODUCTION

Nitrate contamination often affects aquatic systems worldwide. Nitrate concentrations in water may increase due to natural and/or anthropogenic sources, such as waste materials, intensive animal operations, with nitrate from over-application of manure, irrigated and row crop agriculture, with nitrate from fertilizer-induced mineralization, septic tank systems and landfills (Canter, 1997). Nitrate derived from atmospheric deposition is generally taken by plants, but where vegetation is scanty, and/or input is so high, nitrate behaves as a mobile anion (Drever, 1997).
Under the EC Nitrate Directive (CEC, 1991) member states are required to identify any Nitrate Vulnerable Zone (NVZ) where the nitrate concentration in protected ground or surface waters is expected to rise above accepted limits. For areas that are designated, action plans to decrease nitrate losses must be undertaken.
Nitrate guidelines for drinking water established by the World Health Organization (WHO, 2006) are 50 mg/L for short-term exposure, and represent the reference values in the development of national standards. Italian legislation (GURI, 2003; 2006; 2009) also recommends 50 mg/L nitrate concentrations in drinking water. Primary health concern regarding nitrate intake is the so-called 'blue-baby syndrome': nitrate is reduced to nitrite in the stomach of infants, and nitrite is able to oxidize hemoglobin to methemoglobin, which is unable to transport oxygen around the body (Greer and Shannon, 2005). In Italy, a limit of 10 mg/L NO_3- has been recommended for drinking water destined to infants (GURI, 2003).
The aim of this study is to investigate the occurrence of nitrate in surface and ground waters in Sardinia (Italy). This region hosts intense agricultural activities and farming. Pasture-based livestock systems, mainly cattle and sheep (about 2 million sheep and goat), are more diffused than indoor systems, such as pigs and poultry.

2. STUDY AREA

Sardinia, an island located in the Mediterranean Sea between 38°40'N and 41°40'N and between 7°50'E and 9°40'E (Fig. 1), has variable climatic conditions. From 1922 to 1992, mean rainfall ranged from <500 mm/a in the plain and coastal areas to 1100 mm/a in the mountains, with a mean of <50 and 90 rainy days/a, respectively (R.A.S., 1998). Climate in the region is characterized by long periods of heat and drought interrupted by relatively short rainy periods, with occasional heavy rain events. Climate instability over the past decades implies that there is a changing pattern of the distribution of dry and wet periods. Accordingly, the flow of rivers and streams strongly depends on rainfall, and may vary by several orders of magnitude in a year, as well as from one year to another.

In Sardinia, surface waters constitute an important resource. The river water collected in artificial basins represents about 70% of the water supply for agricultural, industrial and domestic uses for a population of approximately 1.6 million people. The availability of groundwater is limited to small areas, but low flow (usually much less than 1 L/s) springs are widespread in the region. Spring waters are often used as drinking water by the local population.

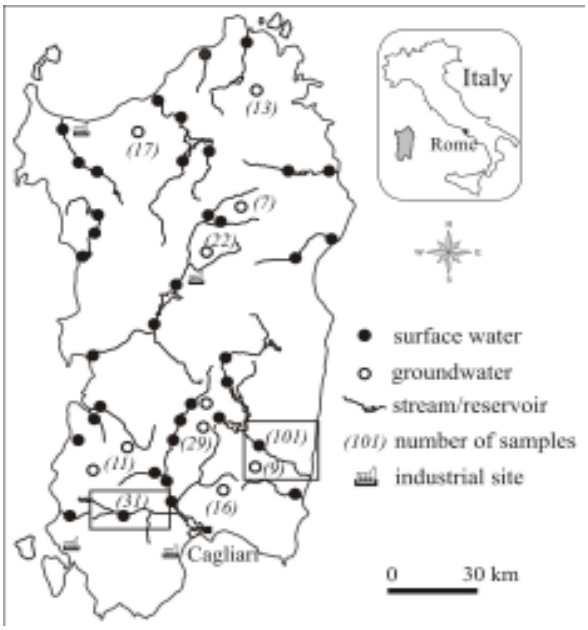

Figure 1. Map showing the location of water samples collected in Sardinia

3. ANALYTICAL METHODS

In this study, a total of 187 surface waters (95 streams with flow <100 L/s; 92 rivers with flow >100 L/s) and 126 ground waters collected in Sardinia are considered. Several water sampling campaigns were carried out since the 2001 to 2010. At selected sites, sampling of surface water was repeated under different seasonal conditions. Locations of water samples are shown in Figure 1.

At the sampling site, water samples were filtered through 0.4 μm pore-size filters into new polyethylene bottles, and taken refrigerated till analysis (storage time was usually <10 days). Water pH by glass electrode, redox potential, alkalinity and conductivity were measured on site. The redox potential (Eh) measured by a Pt electrode was corrected against the Zobell's solution (Nordstrom, 1977). Alkalinity was determined by acidimetric titration using the indicator methyl orange; because the hydrogen ion concentration in most studied waters was low, alkalinity was assumed to correspond

to the bicarbonate ion (HCO_3-). Nitrate was determined by ion chromatography (Dionex DX-120). Ultrapure water (Millipore, Milli-Q, 16MΩ cm) was used in sample dilution and standard preparation.

4. RESULTS

The studied waters show large variations in physical-chemical parameters, salinity and chemical composition, but generally occur under oxidizing conditions (median value of Eh = 0.45 V). Table 1 summarize nitrate concentrations in the Sardinian waters, together with pH and conductivity values. A large range of values can be observed. Median values of pH and conductivity in surface water and groundwater are similar, but the median nitrate in groundwater (15.5 mg/L) is significantly higher than the median value in surface water (0.9 mg/L).

Table 1. Statistic values of pH, conductivity and nitrate in surface and ground waters collected in Sardinia (SD = standard deviation)

	surface water samples			groundwater samples			stream	river	granite
Points	187			126			95	92	39
	pH	Cond mS/cm	NO_3^- mg/L	pH	Cond mS/cm	NO_3^- mg/L	NO_3^- mg/L	NO_3^- mg/L	NO_3^- mg/L
Minimum	6.5	0.15	0.1	5.7	0.18	0.1	0.08	0.1	0.1
Maximum	9.0	2.85	31.2	9.5	4.28	249	31.2	29.2	249
Median	7.8	0.52	**0.9**	7.1	0.73	**15.5**	**0.1**	**3.1**	**18.8**
Mean	7.8	0.61	5.4	7.1	0.87	26.5	4.0	6.9	38.1
SD	0.4	0.43	8.3	0.6	0.68	40.3	7.9	8.4	54.3

Nitrate concentrations in surface and ground waters appear unrelated to pH. Figure 2 shows dissolved nitrate versus conductivity and potassium concentrations in the Sardinian surface waters. Positive correlations occur although large scattering is observed, especially in the stream waters. The positive correlation between nitrate and potassium might indicate a common source from agricultural practices via the use of fertilizers and from farming.

The main Sardinian river waters were sampled in 2003 under different seasonal conditions (Cidu et al., 2007). It was observed that relatively high nitrate concentrations occurred more frequently in January under high-flow condition, when a significant rainwater component was present; relatively high concentrations were measured in waters draining cultivated and farmed areas and were associated to relatively high K contents.

These observations suggest that nitrate flushing via rainwater allows nitrate transport in surface water, as well as potential infiltration in groundwater. Indeed, peak winter values exceeding 100 mg/L NO3- concentrations have been observed in other rivers draining intensively farmed areas, such as East Anglia in the UK (Alloway and Ayres, 1997). Also, in the River Thames nitrate concentration was higher under high flow compared to low flow (Neal et al., 2000). Moreover, rainwater itself might carry dissolved nitrate; mean values of 2 mg/L NO_3- have been reported in Sardinian rain samples (Caboi et al., 1992).

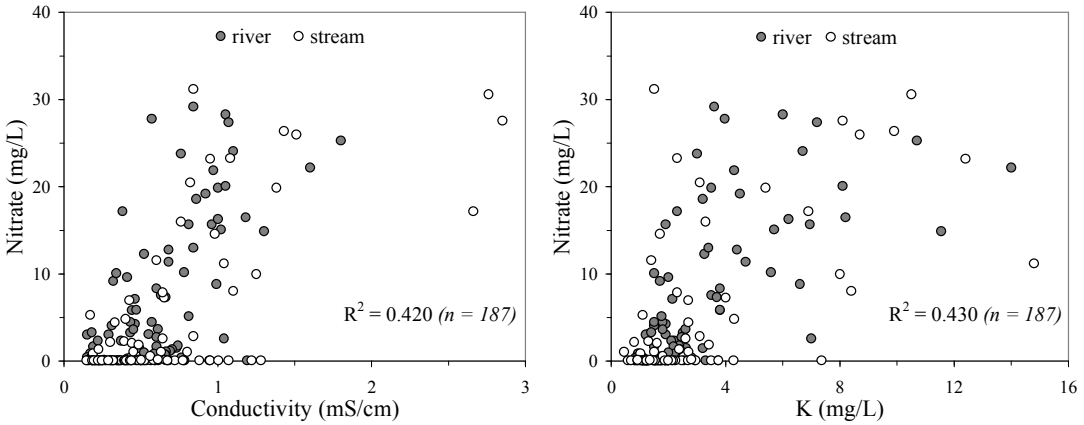

Figure 2. Plots showing nitrate concentrations versus conductivity and potassium in river (92 samples) and stream (95 samples) waters collected in Sardinia

In Figure 3, dissolved nitrate in the Sardinian ground water samples does not show significant correlation with conductivity and potassium. The highest nitrate concentrations were observed in groundwater circulating in granite rocks, where water circulation occurs close to surface.

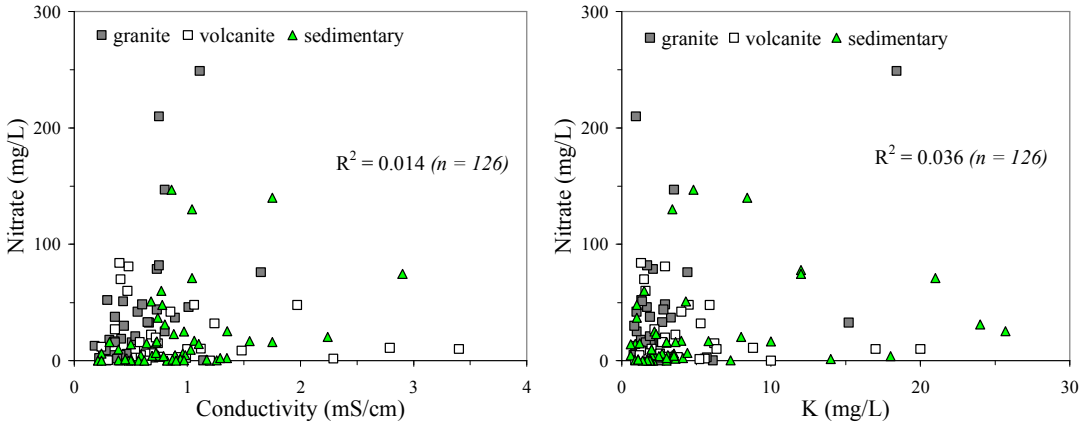

Figure 3. Plots showing nitrate concentrations versus conductivity and potassium in groundwater samples collected in Sardinia. Water samples are distinguished on the basis of dominant rocks at the sampling site

Among the investigated waters, about 56% of groundwater samples and 22% of surface water samples showed concentrations of NO_3- > 10 mg/L. Taking into account that many of these waters are used as drinking water, their regular consume may pose a health hazard, especially to infants.

At sites where high nitrate water is only available, an alternative could be the use of bottled water. Indeed, the consume of bottled water in Sardinia is high. However, an investigation aimed to compare the quality of bottled water available in the market and Italian tap water showed several samples with NO_3- concentrations higher than 10 mg/L (Cidu et al., 2011). Figure 4 shows a median value of NO_3- in tap waters (6 mg/L) slightly higher than that observed in bottled waters (4 mg/L). Concentrations of NO_3- ≥ 10 mg/L occurred in 14% and 20% of bottled and tap water samples, respectively.

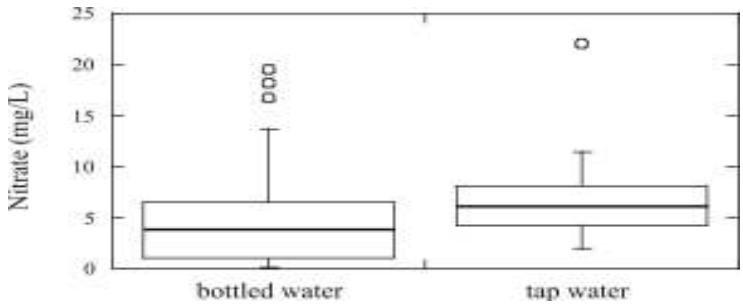

Figure 4. Box-plot showing nitrate concentrations in bottled (37 samples) and tap (15 samples) waters (Cidu et al., 2011). Each box includes the 25th and 75th percentiles with the median displayed as a thick line; bottom and upper whiskers respectively show the smallest and largest values within the fences; circles indicate extreme values (outliers).

5. CONCLUSIONS

The regular consumption of drinking water with high concentrations of nitrate may pose health hazards, especially to infants. In Sardinia, nitrate concentrations in natural waters vary from 0.1 to about 250 mg/L. Higher concentration of nitrate occur in waters draining cultivated and farming areas; in these waters, nitrate is likely to derive mostly from agricultural and farming practices.

Appropriate management of livestock wastes, and rational use of fertilisers appear therefore necessary for controlling nitrate accumulation in the soil, which in turn will help reducing its transport by leaching. Most drainage from agricultural land in most European and North American regions occurs during autumn and winter. Any nitrate remaining in the soil profile after the end of growing season, which coincides with the beginning of the leaching season, is susceptible to leaching because of little opportunity for nitrate removal by plant uptake. Applying fertilisers based on soil testing and strictly according to the plant requirement, and evolving strategies that minimise the residence time of nitrate in soil can help mitigate the nitrate leaching problem (Hooda et al., 2000).

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