Isotopic Characterization of Nitrate Sources in Karstic Springs in the Basin of Paris

[1]Mathieu SEBILO [1,2] Jihane EL GAOUZI

[1] Université Pierre et Marie Curie, UMR BIOEMCO, 4 Place Jussieu, 75252 Paris cedex 05, France
[2] Eau de Paris, Unité Sud, 3 route de Morêt, 77690 Montigny sur Loing

Groundwater resource protection is the vital concern of water suppliers (Liu et al., 2006) especially for big cities such as Paris (France). The resource protection became a primary task since contaminants were found in groundwater at concentrations sometimes exceeding the allowed thresholds. The increasing contents are linked to the intensive use of fertilizers since the beginning of the fifties in France and in the Paris basin (Ledoux et al., 2007). The attendance of nitrate in groundwater is the result of the increasing anthropogenic activities especially crops and disposal of wastewater).

During the rainfall season, contaminants are leached and then stored in the aquifer or transported to other points of the watershed. Pollution transport, from sources to the aquifer and then to the tapped springs, depends on many factors such as the hydrology and the geology of the system.

Many protective areas were then delineated in the watersheds where springs used in drinking water are embedded.

The problem is more underlined when the concerned system is karstic because of the vulnerability of these geologic formations. Owing to the high heterogeneity of karst aquifer and the quantity of the conduits almost always unknown, the understanding of these kinds of geologic areas remains difficult (Mahler et al. 2008).

In the basin of Paris, weathering is important and some springs take place within karstic system in chalk formations. Numerous underground bypasses and pipes allow rapid water transfers to the springs. These conduits assure also connecting neighboring watersheds and enable rapid transport of contaminants as nitrate in the aquifer (Brian et al., 2004; Mahler et al., 2008). The two groups of springs studied in the present work are located in the Lunain watershed.

The karst Lunain watershed is studied using chemical measurements and associated nitrate nitrogen isotopic composition. Two groups of springs, Sp1 (Villeron) and Sp2 (Villemer), located in this basin, are used in Paris drinking water supply. They have special characteristics because of the rapid variations of nitrate concentrations, bacteriology and phytosanitary products. For Sp1, nitrate concentrations are ranged between 30 and 50 mg/L, turbidity vary between 0.2 and 2.5 NTU, and peaks of phytosanitary products are observed with a minimum value of 0 µg/L and maximum value of 0.5 µg/L. Likewise, at Sp2, nitrate concentration is about 47 mg/L and can reach 55mg/L. Phytosanitary products vary between a minimum of 0.01 and a maximum of 0.2 µg/L but there is no turbidity in this site.

Prior studies and especially tracing experiences have shown the existence of rapid flow between the stream sinking zone and springs (Souchet, 2000).

To better understand the springs functioning and to explain the differences between them, it is important to study the links that could exist between the sinking surface water (Lunain River) and the springs and to understand the effect of seasonal variations on water supply of the springs.

For this reason, isotopic measurements ($\delta^{15}N$ and $\delta^{18}O$ of nitrate) were carried out in springs and surface waters for different seasons.

In the purpose of distinguishing nitrate sources in the springs, stable isotopic measurement of nitrate nitrogen is a suitable tool. Natural stable isotope composition of nitrate has been extensively used as perfect nitrate contamination marker in many studies (Mariotti, 1982; Sebilo et al., 2006). It provides informations on nitrate origins and its transformations in the hydrosphere depending on the environmental characteristics.

Nitrogen is present as various forms in the environment because of the reactions that step in the nature (Panno et al. 2001). Manure and inorganic fertilizers input in soils are at first responsible for groundwater nitrate contaminations. Other potential origins are sewage effluents, livestock waste and atmospheric precipitation. Each source is distinguished by producing nitrate with specific isotopic composition (Mariotti, 1982; Ostrom et al., 1998 and Liu et al., 2006).

Isotopes tracing used for different season in the study site have shown that :

- Denitrification occurs in the upstream sector of the Lunain river and that downstream sector is dominated by chalk groundwater.

- Villeron Site (SP1): the springs are supplied by groundwater in low and high water flows and they are affected by an additional contribution of agricultural water in the high flow period.

- Villemer spring (SP2): may be resulting from a supply of the Lunain river to groundwater during low flow period and from in addition to groundwater and Lunain river, we assume that this spring receives agricultural water and domestic waste water in the high flow period.

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