



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Contaminant Hydrology 72 (2004) 165–188

JOURNAL OF

Contaminant
Hydrology

www.elsevier.com/locate/jconhyd

Nitrate in groundwater: an isotopic multi-tracer approach

David Widory^{a,*}, Wolfram Kloppmann^a, Laurence Chery^a,
Jacky Bonnin^b, Houda Rochdi^c, Jean-Luc Guinamant^d

^aBRGM, EAU/GRI 3, Avenue Claude Guillemin, 45060 Orléans Cedex, France

^bCOOPERL, ZI BP328, 22403 Lamballe Cedex, France

^cAINF, ZI rue Marcel Dassault, 59472 Seclin Cedex, France

^dANJOU RECHERCHE 1, place de Turenne, 94417 St. Maurice Cedex, France

Received 31 December 2002; received in revised form 13 October 2003; accepted 31 October 2003

Abstract

In spite of increasing efforts to reduce nitrogen inputs into groundwater from intensive agriculture, nitrate (NO₃) remains one of the major pollutants of drinking-water resources worldwide. Determining the source(s) of NO₃ contamination in groundwater is an important first step for improving groundwater quality by emission control, and it is with this aim that we investigated the viability of an isotopic multi-tracer approach ($\delta^{15}\text{N}$, $\delta^{11}\text{B}$, $^{87}\text{Sr}/^{86}\text{Sr}$), in addition to conventional hydrogeologic analysis, in two small catchments of the Arguenon watershed (Brittany, France). The main anthropogenic sources (fertilizer, sewage effluent, and hog, cattle and poultry manure) were first characterized by their specific B, N and Sr isotope signatures, and compared to those observed in the ground- and surface waters. Chemical and isotopic evidence shows that both denitrification and mixing within the watershed have the effect of buffering NO₃ contamination in the groundwater. Coupled $\delta^{11}\text{B}$, $\delta^{15}\text{N}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ results indicate that a large part of the NO₃ contamination in the Arguenon watershed originates from the spreading of animal manure, with hog manure being a major contributor. Point sources, such as sewage effluents, contribute to the NO₃ budget of the two watersheds.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Nitrate; Groundwater; Nitrogen isotopes; Strontium isotopes; Boron isotopes; Fingerprinting

* Corresponding author. Tel.: +33-2-38-64-47-72; fax: +33-2-38-64-34-46.

E-mail address: d.widory@brgm.fr (D. Widory).

1. Introduction

Nitrate (NO_3) is found naturally at moderate concentrations in many aquatic environments, but is often enriched to high levels by anthropogenic activities involving nitrogenous compounds such as mineral fertilizer and by-products of organic compounds from agriculture, septic systems, and poultry, hog or cattle manure (cf. Berger et al., 1976; Heaton et al., 1983; Mariotti et al., 1988; Ostrom et al., 1998; Williams et al., 1998). In spite of the increasing efforts at national and European (EC Directive 91/976/EEC) levels to reduce NO_3 inputs from intensive agriculture, NO_3 is still one of the major contaminants of groundwater resources.

The isotopic composition of the dissolved nitrogen (N) species has been used extensively to better constrain the sources and fate of N in groundwater (cf. Panno et al., 2001). The possibility of quantifying both origin and secondary processes affecting N concentrations by means of a single tracer appears more limited however. Nitrogen cannot be considered conservative because it is biologically modified through nitrification and denitrification reactions, both during infiltration of the water and in the groundwater body, causing isotopic fractionation that modifies the $\delta^{15}\text{N}$ signatures of the dissolved N species (Vogel et al., 1981; Mariotti et al., 1988; Böttcher et al., 1990; Smith et al., 1991; Feats et al., 1998; Aravena and Robertson, 1998; Pauwels et al., 2000). Discriminating multiple NO_3 sources by their N isotopic composition alone becomes impossible wherever heterogenic or autogenic denitrification occurs, thus there is a need for establishing co-migrating discriminators of NO_3 sources.

Due to its ubiquitous nature, boron (B) commonly exists in groundwater as a minor constituent (cf. Vengosh, 1998). The large range of B isotope ratios observed in nature implies significant contrasts between B sources in groundwater are possible. Previous studies of B isotopes as tracers of human impact on water resources focused on the identification of waste water and sewage dominated by synthetic B products (Bassett, 1990; Vengosh et al., 1994; Basset et al., 1995; Barth, 1998; Vengosh, 1998; Vengosh et al., 1999) as well as on the impact of fly ash leachate (Davidson and Basset, 1993). Basset et al. (1995) and Komor (1997) were the first to use B isotopes as a co-migrating tracer of NO_3 , but only Komor (1997) reports the B isotope signatures of inputs related to agriculture (e.g. hog manure, cattle feedlot runoff, synthetic fertilizers) and combines N and B isotopes in the aim of distinguishing NO_3 inputs to ground- and surface water.

Another potentially discriminating tracer is strontium (Sr). A prerequisite for the use of Sr isotopes as tracers for groundwater pollution is sufficient variability of $^{87}\text{Sr}/^{86}\text{Sr}$ signatures between the different end-members. Such variations have been observed between natural groundwater and human inputs (cf. Négrel and Deschamps, 1996; Horan and Bohlke, 1996; Négrel, 1999).

It is hypothesized that the combined use of geochemical and isotopic tracers (N, B and Sr) would provide a sensitive method for tracing sources of NO_3 in contaminated groundwater. The N isotopes, as an intrinsic tracer of the NO_3 molecule, will reflect both the sources and the fate (i.e. denitrification) of NO_3 in groundwater. The B isotopes, because they are not affected by denitrification, will bear the signature of the solute

sources, but may nevertheless fractionate through processes such as adsorption on clay minerals (Bassett, 1990). The Sr isotopes, in contrast to the N and B isotopes, will not fractionate through any natural process due to the low mass contrast between the ^{87}Sr and

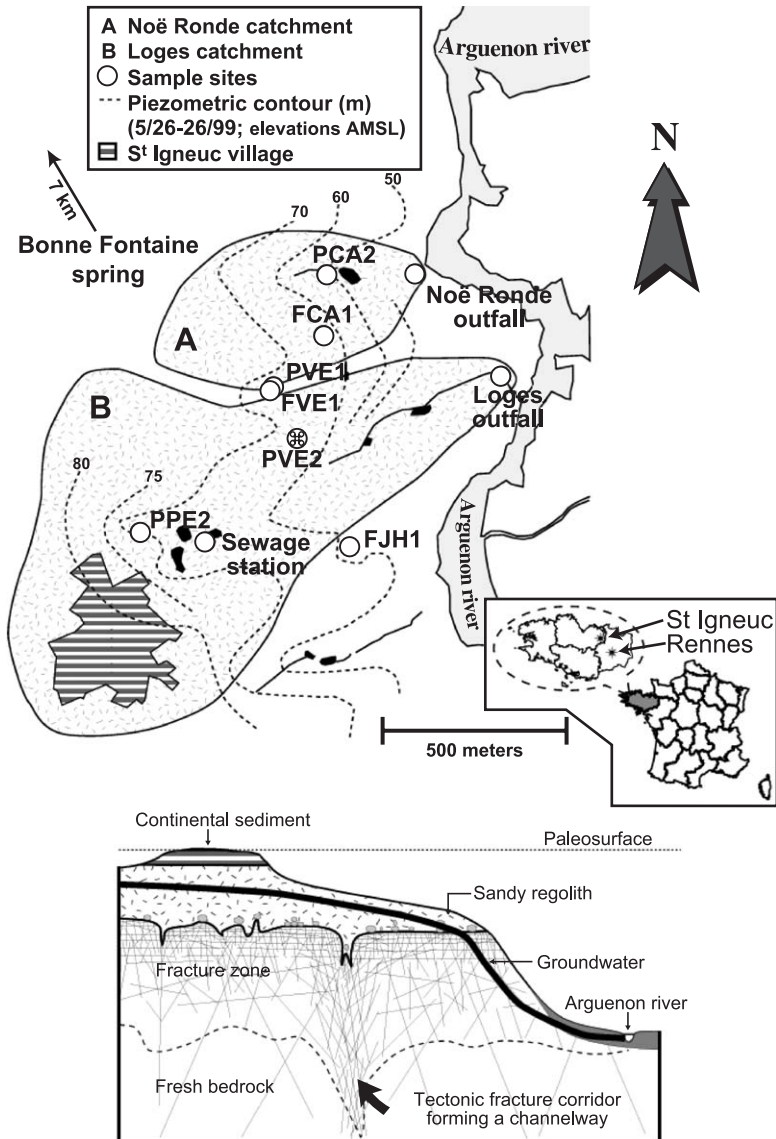


Fig. 1. Groundwater study site in Brittany (France), showing the location of the sampling sites. Watersheds and piezometric contours are also shown. The schematic cross section represents the typical hydrogeological context in Brittany with a thick weathered zone overlying the fractured crystalline basement and a piezometric level that closely follows the topography.

the ^{86}Sr isotopes; they will therefore essentially trace mixing processes, and also water–rock interaction within the aquifer.

The purpose of the present study of the Arguenon watershed (Brittany region, France), where NO_3 concentrations up to 250 mg l^{-1} are encountered, is to establish the isotope signatures of all potential pollution sources and to compare them with those of ground- and surface-water samples. This approach tests the capacity of N, B and Sr isotopes to appraise the respective contributions to the observed NO_3 contamination.

2. Brittany case study: hydrogeologic setting and land use

The highest NO_3 concentrations in French groundwater are observed in the Brittany region where they commonly exceed the 50 mg l^{-1} limit for drinking water (D.R.A.S.S., Bretagne, 1998). We have investigated two small catchments—Noë Ronde (33 ha) and Loges (125 ha)—located within the Arguenon watershed approximately 70 km northwest of Rennes in western Brittany (Fig. 1). The tectonic structure of the Arguenon watershed is dominated by the Cancale Fault (striking $\text{N}60^\circ\text{E}$) inherited from the Cadomian orogeny (580–540 Ma). The basement lithology is granitic gneiss to the north of the fault, and Brioverian mica schist to the south of the fault.

The Arguenon river flows from an elevation of 150 m down to an elevation of 25 m, with an average discharge of $0.9 \text{ m}^3 \text{ s}^{-1}$. The piezometric level for the greater part of the watershed follows the surface topography, which suggests a fairly low overall aquifer permeability as is common in hard-rock environments. Most of the sample wells are screened in the weathered zone or in both the weathered zone and the fresh basement rock. Well FJH1 is the only one that is exclusively screened in fractured crystalline bedrock (Chery et al., 2000; Widory et al., 2001).

The local agriculture includes a high level of indoor pig farming, poultry and cattle breeding, and cultivation for which the land is extensively fertilized. Domestic waste water is treated in a sewage station (direct discharge to infiltration ponds) downstream of St. Igneuc village.

3. Methods

3.1. Sampling

The selected sampling sites (Fig. 1) were a “non-polluted” spring (Bonne Fontaine) approximately 7 km northwest of the study site, two outfalls (Noë Ronde and Loges; stream point at the downstream end of the groundwater catchment), three boreholes (FCA1, FVE1, FJH1), three wells (PCA2, PPE2, PVE1) and one spring (PVE2) to give a total of 26 groundwater samples and 10 surface-water samples (Table 1). Each site, apart from the two non-polluted reference sites (borehole FJH1 and the Bonne Fontaine spring) and well PVE1, was sampled at least four times over the course of the July 1999 to November 2000 hydrologic cycle. The groundwater samples were taken after pumping a volume corresponding to three times that of the relevant well or borehole. They were then

filtered through a 0.45- μm membrane and stored at 4 °C for anion determination, or acidified to pH 2 with ultrapure HNO_3 for cation and trace-element determination. For the isotope measurements, the groundwater samples were collected in 1-l bottles (250 cm^3 filtered and acidified in the case of Sr) that were first rinsed several times with groundwater and then filled leaving no air space in the neck.

Rainwater was collected in a pluviometer during a 2-month period, from October to November 2000.

In order to characterize the chemical and isotopic compositions of the anthropogenic sources, we collected and analyzed chemical fertilizers, animal manure (cattle, hog and poultry) and raw sewage effluents from the field site. The chemical fertilizers were obtained directly from farmers in the investigated catchments, and the raw sewage effluents were sampled according to the groundwater-sampling procedure.

3.2. Analytical techniques

Two different procedures were adapted for collecting animal manure: (1) leaching, with 1 l of Milli-Q water, of 100 g of the dried solid samples collected in manure pits, and (2) using local rainwater to water impervious soil plots containing either sprinkled or buried manure (Martinez and Peu, 1999) and collecting the runoff.

Cation (Na, K, Ca, Mg) concentrations were determined by capillary electrophoresis (CIA Waters), and anion (NO_3 , NO_2 , Cl, SO_4) concentrations by ionic chromatography. Trace-element (B, Sr, Fe) concentrations were determined by ICP-MS. Total alkalinity was measured in the field by HCl titration according to Gran's method (Gran, 1952).

Tritium was measured on selected samples by liquid scintillation counting after electrolytic enrichment. Nitrate was reduced to NH_3 , and the mass spectrometry determination of $\delta^{15}\text{N}$ was performed on N_2 liberated by the reaction of NH_4Cl with LiOBr . For the $\delta^{11}\text{B}$ determination, B was analyzed from the ion Cs_2BO_2^+ (Spivack and Edmond, 1986; Mossadik, 1997) on a Finnigan MAT 261 mass spectrometer. The $^{11}\text{B}/^{10}\text{B}$ value obtained for the NBS951 boric acid standard after oxygen correction was 4.0467 ± 0.0022 (2σ , $n = 147$). The isotope ratios are reported as per mil deviation ($\delta^{15}\text{N}$ or $\delta^{11}\text{B}$) of the $^{15}\text{N}/^{14}\text{N}$ or $^{11}\text{B}/^{10}\text{B}$ ratios relative to air and NBS951 standards, according to the equations:

$$\delta^{15}\text{N} = \left[\frac{\left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{sample}}}{\left(\frac{^{15}\text{N}}{^{14}\text{N}}\right)_{\text{AIR}}} - 1 \right] \times 10^3 \quad \text{and} \quad \delta^{11}\text{B} = \left[\frac{\left(\frac{^{11}\text{B}}{^{10}\text{B}}\right)_{\text{sample}}}{\left(\frac{^{11}\text{B}}{^{10}\text{B}}\right)_{\text{NBS951}}} - 1 \right] \times 10^3 \quad (1)$$

Analytical precision on $\delta^{15}\text{N}$ and $\delta^{11}\text{B}$ was $\pm 0.2\text{‰}$ and $\pm 0.5\text{‰}$, respectively.

The Sr isotopic ratios were determined using a Finnigan MAT 26 2 mass spectrometer after chemical separation in a cation exchange column (Dowex AG50X8; HCl 2 N as the eluant). The total blank for Sr was less than 1 ng for the entire chemical procedure. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalized to an $^{88}\text{Sr}/^{86}\text{Sr}$ ratio of 0.1194. The reproducibility of the $^{87}\text{Sr}/^{86}\text{Sr}$ measurements was tested by duplicate analysis of the NBS 987 standard, with a mean value close to $0.710234 \pm 21 \times 10^{-6}$ (2σ ; $n = 99$).

Table 1
Chemical and isotopic characterization of the water samples

Sample	Date	Eh (mV)	Cond. (dS m ⁻¹)	Alk (meq l ⁻¹)	pH	$\delta^{15}\text{N}$ ($\pm 0.2\text{‰}$)	$\delta^{11}\text{B}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}^b$	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	NO ₃ (mg l ⁻¹)	Fe (mg l ⁻¹)	B ($\mu\text{g l}^{-1}$)	Sr (mg l ⁻¹)
Rainwater	10–11						30.0 \pm 0.2	0.71070 \pm 11	0.3	0.3	2.8	<0.3	4.5	1.5	1.6	<0.02	2.4	0.002
Rainwater	2000							0.70873 \pm 9	1.5	0.3	2	1.5	2.9	3.5	5.5	<0.02	7	0.002
Bonne Fontaine	06/99	405	195	0.30	5.7	6.7	38.5 \pm 0.4	0.715944 \pm 8	5.8	3.2	26.3	2.2	27.3	9.7	10.1	<0.02	11.0	
FJH1	11/00	388	267	1.11	5.8	–	40.5 \pm 0.4	0.719577 \pm 8	10.2	10.5	27.1	3.7	33.5	25	3.2	1.50	10.5	0.06
Noë Ronde	06/99	409	462	1.41	7.8	21.0	31.5 \pm 0.4		40.4	22.4	34.1	8.4	59.2	29.3	104.6	<0.02	32.0	
Noë Ronde	11/99	439	661	1.47	7.7	13.7	30.3 \pm 0.5		48.2	22.4	34.9	10.2	56.1	31.4	127.0	0.02	35.0	0.27
Noë Ronde	03/00	484	587	0.99	6.5	12.4	30.4 \pm 0.2	0.715569 \pm 9	41.3	20.1	30.9	8.3	47.7	30.8	131.0	0.2	23.0	0.24
Noë Ronde	06/00	396	403	1.23	7.6	14.9	31.6 \pm 0.3		38.6	19.8	30	8.6	45.7	29	106.5	<0.02	27.0	0.25
Noë Ronde	11/00	439	338	2.11	7.6	18.8	30.2 \pm 0.2		35.6	17.6	30.7	9.6	46.4	28.3	39.2	0.02	30.8	0.22
Loges	06/99	389	562	1.16	7.7	13.4	15.8 \pm 0.3		37.3	18.4	39.4	9.3	54.2	25.6	91.7	0.04	68.0	
Loges	11/99	439	582	1.05	7.4	9.8	18.5 \pm 0.4		36.1	15.9	32.9	8.1	52.5	30	90.2	0.04	51.0	0.19
Loges	03/00	466	531	0.88	6.2	10.8	17.8 \pm 0.3	0.714620 \pm 9	34.8	17.4	32.2	8.3	51.1	28.2	106.0	0.05	42.0	0.20
Loges	06/00	422	465	1.13	7.6	11.8	14.5 \pm 0.1		33.5	17.0	30.3	8.9	45.3	26.2	78.2	<0.02	55.0	0.21
Loges	11/00	464	289	1.16	7.2	11.3	17.4 \pm 0.1		28.5	11.4	30.2	8.2	40.6	26.8	44.9	0.11	46.0	0.14
FCA1	06/99	387	465	0.75	6.1	13.3	42.5 \pm 0.5		30.1	13.6	31.9	4.8	53.5	34.8	59.9	0.19	23.0	
FCA1	06/99	288	422	0.91	6.1	13.4	40.8 \pm 0.5		24.7	11.5	31.7	3.9	51.6	33.5	33.8	1.06	17.0	
FCA1	03/00	320	426	0.89	5.4	11.5	32.5 \pm 0.6	0.716724 \pm 1	24.9	11.5	32.6	4.8	49.6	35.1	35.7	0.58	16.0	0.08
FCA1	06/00	349	342	0.88	6.1	11.4	39.5 \pm 0.2		24.2	11.0	30.1	4.8	45.1	34	31.8	0.99	14.0	0.09

PCA2	06/99	441	773	0.24	5.7	12.5	32.9 ± 0.5		58.2	23.0	41.4	5.8	49.6	41.4	205.0	<0.02	40.0	
PCA2	11/99	440	744	0.71	5.9	11.2	31.4 ± 0.2		53.7	19.9	34.5	5.8	42.4	41.6	200.0	<0.02	39.0	0.27
PCA2	03/00	273	501	0.77	5.4	11.4	33.6 ± 0.1	0.714983 ± 8	41.5	16.4	26.6	5.2	31.1	41.3	124.0	<0.02	24.0	0.20
PCA2	06/00	425	428	1.11	5.7		33.0 ± 0.2		37.2	14.7	25.2	5.5	37.7	38.5	82.4	<0.02	30.0	0.20
PCA2	11/00	458	444	0.72	5.5	15.5	34.4 ± 0.1		36.6	14.9	30.3	5.3	40.6	34.8	104.0	<0.02	31.4	0.21
PPE2	06/99	271	480	1.40	6.4	20.8	34.0 ± 0.7		26.5	12.7	31.4	4.0	59.9	33.9	15.9	0.58	15.0	
PPE2	11/99	380	468	1.37	6.3	2.7	23.1 ± 0.2		29.7	14.4	38.8	6.6	55.8	53.8	25.1	0.03	22.0	0.11
PPE2	03/00	346	498	1.63	6.0	17	–		35.9	15.8	36	6.3	56.7	38.9	34.0	0.17	17.0	0.11
PPE2	06/00	413	435	2.20	6.3	19.4	20.6 ± 0.1		36.1	15.4	32.5	7.0	45.0	40.1	17.4	<0.02	23.0	0.13
PPE2	11/00	416	415	1.46	6.0	16.3	28.3 ± 0.2		30.8	14.3	40.6	5.5	55.6	52.3	16.3	0.06	18.4	0.12
FVE1	11/99	426	729	0.31	6.0				43.5	19.4	36.6	12.0	52.4	16.8	196.1	0.3	<0.5	
FVE1	11/99	434	630	0.37	5.8				41.8	18.7	35.5	11.8	52.5	16.3	192.7	0.2	<0.5	
FVE1	03/00	487	694	0.26	6.0	9.0	38.0 ± 0.3		43.4	19.8	36.3	11.5	57.8	17	225.0	0.14	13.0	0.20
FVE1	06/00	381	513	0.37	5.9	7.5	38.3 ± 0.2		38.8	16.9	32.8	11.0	45.3	19.4	172.2	0.5	60.0	0.17
PVE1	06/99	389	697	0.20	5.9	8.8	29.6 ± 0.4		43.0	21.6	26.5	17.1	46.7	40	198.0	<0.02	47.0	
PVE2	06/99	487	811	0.06	5.4	9.5	40.4 ± 0.4		26.5	12.7	31.4	4.0	62.6	15.5	245.0	<0.02	15.0	
PVE2	11/99	346	736	0.16	5.1	8.9	39.0 ± 0.2		29.7	14.4	38.8	6.6	59.4	15.6	230.0	<0.02	17.0	0.33
PVE2	03/00	393	677	0.13	4.8	9.4	38.9 ± 0.2	0.715398 ± 9	35.9	15.8	36.0	6.3	60.2	16.8	231.0	<0.02	13.0	0.33
PVE2	06/00	396	570	0.14	5.3	8.2	39.9 ± 0.1		36.1	15.4	32.5	7.0	46.7	15.4	213.4	<0.02	14.0	
PVE2	11/00	434	519	0.21	4.9	8.1	40.6 ± 0.4		30.8	14.3	40.6	5.5	58.6	14.1	229.0	<0.02	14.1	0.35

^a Maximum variability obtained by repeated measures of the sample.

^b Error is multiplied by 10⁶.

4. Results

4.1. Anthropogenic sources

Fig. 2 and Table 2 summarize the N, B and Sr isotope composition ranges for the main anthropogenic sources.

4.1.1. Mineral fertilizer

The NO_3 and NH_4^+ in fertilizers are usually synthesized through industrial fixation of atmospheric N_2 by quantitative processes that only slightly fractionate the isotope composition (Heaton, 1986), which is consistent with the measured $\delta^{15}\text{N}$ (-1.6‰). The B concentration of the mineral fertilizer sample was below the detection limit ($<0.1 \mu\text{g g}^{-1}$), so $\delta^{11}\text{B}$ could not be measured. Komor (1997) reports $\delta^{11}\text{B}$ values of -2‰ to 0.7‰ for ammonium nitrate and urea ($n=3$) and of 14.8‰ for phosphate fertilizer ($n=1$).

4.1.2. Sewage

The raw sewage $\delta^{15}\text{N}$ ($4.3\text{--}10.4\text{‰}$) is slightly lower than the values observed in other contexts (Bergé, 1983; Donville and Bergé, 1985; Aravena et al., 1993). The measured $\delta^{11}\text{B}$ values ($0.2 \leq \delta^{11}\text{B} \leq 0.8\text{‰}$) are in the lower range of those measured by other authors on sewage and non-marine evaporites, such as sodium borate (Fig. 2), which are generally between 0 and 10‰ (Barth, 1993; Vengosh et al., 1994, 1999; Mossadik, 1997). Sodium borate is widely used for the production of sodium perborate, a whitening agent found in most detergents.

4.1.3. Manures

Nitrogen in excreted waste is mainly in the form of urea, which is hydrolyzed to NH_3 and converted to NO_3 in the soil zone:



The hydrolysis of urea produces a temporary rise in pH, which favors the formation of ammonia, easily lost to the atmosphere. Both the kinetic fractionation associated with this hydrolysis and the equilibrium fractionation between ammonia (NH_3) and ammonium (NH_4^+) in solution result in a strong ^{15}N depletion of the NH_3 lost from the system, leaving the remaining NH_4^+ strongly enriched in ^{15}N . Most of this NH_4^+ is subsequently oxidized to ^{15}N -enriched NO_3 (Heaton, 1986). Following these processes, animal

Fig. 2. $\delta^{15}\text{N}$, $\delta^{11}\text{B}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ characterization of the NO_3 sources present in the watershed. Where possible, isotope compositions measured during this study (shadowed rectangles) are compared to values from the literature (open rectangles). For nitrogen isotopes data are compiled from Aravena et al. (1993), Bergé (1983), Berger et al. (1977), Donville and Bergé (1985), Feats et al. (1998), Freyer and Aly (1975), Girard and Hillaire-Marcel (1997), Heaton et al. (1983), Heaton (1986), Koba et al. (1997), Kreitler and Jones (1975), Mariotti et al. (1976), Mariotti (1984), Shearer et al. (1974) and Showers et al. (1990). For boron isotopes: Barth (1998), Bassett et al. (1995), Gellenbeck (1994), Komor (1997), Leenhouts et al. (1998), Scott (1996), and Vengosh et al. (1994, 1999). For strontium isotopes: Négrel and Deschamps (1996) and Négrel (1999).

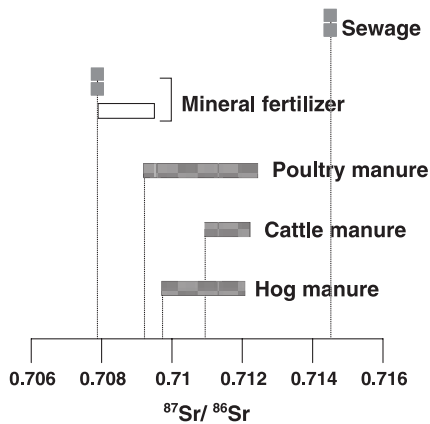
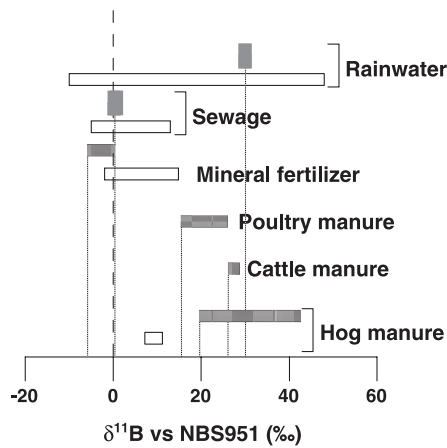
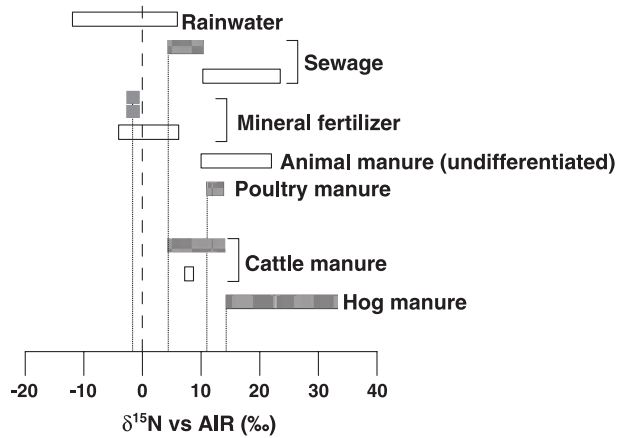


Table 2
Chemical and isotopic characterization of NO₃ sources

Sample	$\delta^{15}\text{N}$ ($\pm 0.2\%$) ^a	$\delta^{11}\text{B}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$ ^b	Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	NO ₃ (mg l ⁻¹)	NH ₄ (mg l ⁻¹)	Fe (mg l ⁻¹)	B ($\mu\text{g l}^{-1}$)	Sr (mg l ⁻¹)
<i>Sewage</i>														
	7.5	0.5 \pm 1.3	–	41.6	14.5	82.1	18.1	102.9	56.3	9.6	21.7	0.26	909	–
	8.7	0.2 \pm 0.4	–	28.4	15.6	28.2	17.3	43	31.9	92	<0.1	1.08	51	0.19
	9.7	0.5 \pm 0.6	0.71450 \pm 9	28.6	15.7	26.9	16	44.9	34	88.4	<0.1	0.29	38	0.18
	10.4	0.3 \pm 0.2	–	28.3	15.5	25.7	15.5	43.2	34.9	69.2	<0.1	0.2	38	0.20
	4.3	0.8 \pm 0.2	–	35.5	16.4	43.9	12.9	63.9	17.5	3	0.5	9.34	130	0.19
<i>Fertilizer</i>														
Ammonium NO ₃	–1.6	–	0.70788 \pm 8	–	–	–	–	–	–	–	–	–	<0.1 $\mu\text{g g}^{-1}$	<1 $\mu\text{g g}^{-1}$
				Ca (mg g ⁻¹)	Mg (mg g ⁻¹)	Na (mg g ⁻¹)	K (mg g ⁻¹)	Cl (mg g ⁻¹)	SO ₄ (mg g ⁻¹)	NO ₃ ($\mu\text{g g}^{-1}$)		Fe ($\mu\text{g g}^{-1}$)	B ($\mu\text{g g}^{-1}$)	Sr ($\mu\text{g g}^{-1}$)
<i>Leachate</i>														
Hog manure	–	19.5 \pm 0.1	0.70971 \pm 9	1.02	0.17	3.68	15.19	8.47	0.12	<0.1	1300	15.2	4.97	3.2
Cattle manure	–	28.6 \pm 0.2	0.71092 \pm 8	0.60	0.69	0.56	17.73	8.01	0.27	<0.1	71	63.9	1.84	17.9
Poultry manure	–	15.3 \pm 0.1	0.70920 \pm 10	1.86	1.64	3.08	16.65	7.07	3.95	<0.1	334	45.5	13.4	38.5
				Ca (mg l ⁻¹)	Mg (mg l ⁻¹)	Na (mg l ⁻¹)	K (mg l ⁻¹)	Cl (mg l ⁻¹)	SO ₄ (mg l ⁻¹)	NO ₃ (mg l ⁻¹)		Fe (mg l ⁻¹)	B ($\mu\text{g l}^{-1}$)	Sr (mg l ⁻¹)
<i>Experimental plots</i>														
Poultry (1999)	13.8	25.9 \pm 0.5	–	129	55.7	70.1	6.9	119	129	448	0.2	<0.02	46	–
Poultry (2000)	10.9	27.6 \pm 0.2	0.71206 \pm 10	77.2	33.7	73.3	7.7	119	137	206	0.2	<0.02	37.9	0.33
Cattle (1999)	14	26.0 \pm 0.6	–	99.1	46.7	76.1	7.7	152	161	203	0.1	0.02	47	–
Cattle (2000)	4.3	27.4 \pm 0.2	0.71220 \pm 9	15.1	6.9	10	1.4	18.4	40	15.5	<0.1	<0.02	7	0.06
Hog (1999)	33.2	42.1 \pm 0.5	–	76.9	24.6	51.5	85.5	101	205	268	<0.1	<0.02	28	–
Hog (2000)	14.1	19.5 \pm 0.3	0.71242 \pm 8	36.1	15.4	41.3	2.6	46.8	47.5	149	<0.1	<0.02	25.1	0.16

^a Maximum variability obtained by repeated measures of the sample.

^b Error is multiplied by 10⁶.

manure is transformed into NO_3 with $\delta^{15}\text{N}$ values typically in the range of 10–20‰ (Kreitler, 1975, 1979). The range obtained in Brittany (5–35‰) is larger than previously observed (Kreitler and Jones, 1975; Kreitler, 1979; Heaton et al., 1983; Heaton, 1986; Showers et al., 1990) and may result from local environmental conditions (moisture, temperature, wind speed, etc.) influencing the volatilization of NH_3 and thus determining the degree of ^{15}N enrichment in the NO_3 (Heaton, 1986; Leenhouts et al., 1998).

The samples from the field experiments (i.e. manure spread on the experimental plots) contain no significant NH_4^+ (Table 2). The values are close to or below the detection limit, and so their $\delta^{15}\text{N}$ composition can be compared directly to the groundwater samples where nitrification of NH_4^+ has already taken place. Most of the analyzed sewage samples also have very low NH_4^+ . One sample with moderate NH_4^+ (20 ppm) plots in the isotopic range of the low NH_4^+ samples.

The $\delta^{11}\text{B}$ values in hog manure varied from 19.5‰ to 42.4‰, which is higher than those reported by Komor (1997). The observed difference between the USA values (i.e. Komor's study) and those in France may be explained by the fact that the B isotope composition reflects the animal's diet and physiology (Komor, 1997). The $\delta^{11}\text{B}$ of cattle and poultry manure (Fig. 2) cannot, to our knowledge, be compared to literature.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the anthropogenic sources vary from 0.70788 to 0.71450 (Fig. 2). Among these, mineral fertilizer and sewage represent the extreme values (0.70788 and 0.71450, respectively), with animal manure showing overlapping ranges (Fig. 2; Table 1) from 0.709 to 0.712.

4.2. Natural baseline end-member in the groundwater system

Two of the sampling sites, the Bonne Fontaine spring and borehole FJH1, were located in forested parts of the Arguenon watershed, away from any human influence, and were selected as characterizing the non-polluted watershed groundwater. Referred to as the “baseline” end-member, these groundwaters have low TDS values (195 and 267 dS m^{-1} , respectively; Table 1) and a sodium-chloride composition inherited from rainwater derived from the nearby ocean. Their chloride concentrations, $\approx 30 \text{ mg l}^{-1}$, are within the range of those generally observed in rainwater of the Brittany region (Faillat et al., 1999), but are higher than the two rainwater samples analyzed during this study (2.9–4.5 mg l^{-1}). However, Cl values in groundwater are expected to be higher in precipitation because of additional Cl in dry deposition and because of evapotranspiration enrichment. Borehole FJH1 is the only one that is filtered exclusively within the fresh granitic basement and not in the weathered zone. The tritium content for the chosen reference sample is close to detection limit (2 ± 1 TU) and can thus be considered as a “deep” baseflow end-member.

The $\delta^{15}\text{N}$ of Bonne Fontaine is $6.7 \pm 0.2\text{‰}$, consistent with values from the literature for unpolluted groundwater (Shearer et al., 1974; Rennie et al., 1976; Ben Halima, 1977; Mariotti, 1984; Heaton, 1986). As the NO_3 concentration at borehole FJH1 was equal to the required value for isotope analysis ($\approx 3 \text{ mg l}^{-1}$), its $\delta^{15}\text{N}$ could not be measured. The $\delta^{11}\text{B}$ values are comparable between the two sites ($38.5 \pm 0.4\text{‰}$ for Bonne Fontaine and $40.5 \pm 0.4\text{‰}$ for FJH1), which is consistent with the seawater value of 39.5‰ (Spivack

and Edmond, 1986), and thus with a marine origin. The $\delta^{11}\text{B}$ value (30‰) of the single analyzed rainwater sample (Table 2) is somewhat lower than that of the natural baseline groundwater, thus it is likely that the isotope composition of local rain is variable (Mather and Porteous, 2001). The measured groundwater sample is closer to the seawater value than are the rainfall values.

4.3. Ground- and surface water

Table 1 summarizes the chemical and isotopic characterization of the 26 groundwater and 10 surface-water samples. The NO_3 concentrations vary between 3.2 ± 0.2 and $245 \pm 12 \text{ mg l}^{-1}$, with a mean value of $106 \pm 78 \text{ mg l}^{-1}$ that is well above the 50 mg l^{-1} European drinking-water level. The corresponding $\delta^{15}\text{N}$ compositions vary between $2.7 \pm 0.2\text{‰}$ and $21 \pm 0.2\text{‰}$, within the range of $\delta^{15}\text{N}$ pollution sources (-1.6‰ to 33.2‰ ; Fig. 2 and Table 2). The $\delta^{15}\text{N}$ values of the most contaminated groundwater ($\text{NO}_3 > 200 \text{ mg l}^{-1}$), whose N isotope composition may be supposed to be closest to the initial values of the pollution sources, independently of subsequent mixing or denitrification, lie between 8.1‰ and 12.5‰ .

The $\delta^{11}\text{B}$ composition varies between 14.5‰ and 42.5‰ , matching the range of animal manure ($14.8\text{--}42.4\text{‰}$; Fig. 2).

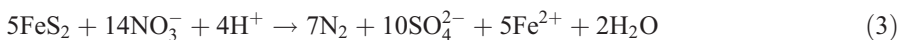
The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the groundwater samples varies from 0.71462 to 0.71958, with the most radiogenic (i.e. enriched in ^{87}Sr) values being observed for the “baseline” end-member FJH1. The contaminated samples show higher Sr concentrations and lower isotope ratios, but the overall $^{87}\text{Sr}/^{86}\text{Sr}$ variability of the groundwater samples is higher than that of the pollutants (0.70873–0.71450).

5. Discussion

5.1. Nitrogen isotopes

The main difficulty in using N isotopic signature as tracer of the NO_3 source lies in the interference between two processes that can lead to an isotopic shift: dilution of the polluted groundwater and natural denitrification (cf. Mariotti et al., 1988; Smith et al., 1991; Girard and Hillaire-Marcel, 1997; Aravena and Robertson, 1998).

Pauwels et al. (2000) showed that both autotrophic and heterotrophic denitrification occur in a geological setting similar to that studied here. As pyrite is present in the aquifer rock, the presence of Fe^{2+} (Fig. 3a) and a general tendency for the presence of SO_4^{2-} (Fig. 3b) in conjunction with a decrease in NO_3^- , hints at NO_3^- reduction coupled with pyrite oxidation in groundwater (autotrophic denitrification, Pauwels et al., 1998, 2001):



However, we see no clear individual trend of sulfate increase with decreasing NO_3 in Fig. 3, except perhaps for borehole FVE1 and well PPE2. Both the surface-water samples

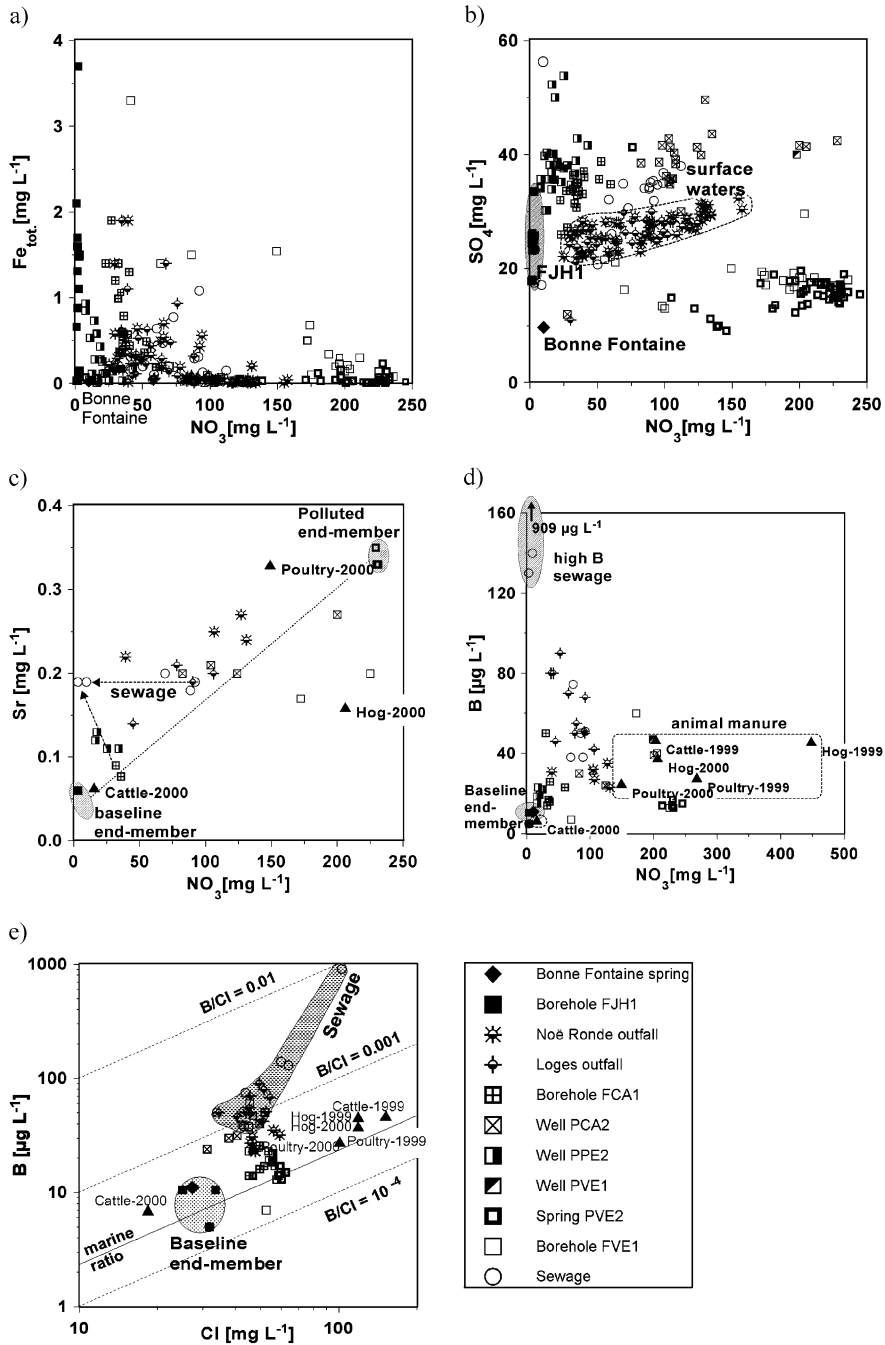
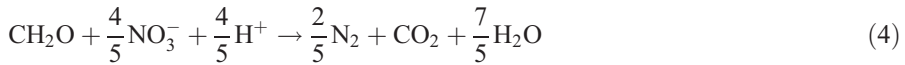


Fig. 3. Binary chemical covariations within the groundwater samples. (a) Fe–NO₃. (b) SO₄–NO₃. (c) Sr–NO₃. (d) B–NO₃. (e) B–Cl.

from the Noë Rone and Loges outfalls and the groundwater from well PCA2 show a fairly simultaneous decrease of SO_4 and NO_3 that can be interpreted as dilution of the contaminated water with a non-contaminant end-member (close to FJH1 and Bonne Fontaine). Well PCA2 shows a similar dilution trend for Cl concentrations.

Heterotrophic denitrification (oxidation of organic matter catalyzed by heterotrophic bacteria) contributes to the production of CO_2 without increasing SO_4 as follows:



where CH_2O is a simplified formula for organic matter.

Both autotrophic and heterotrophic reactions are accompanied by fractionation inducing a ^{15}N enrichment of the residual NO_3 (cf. Mariotti, 1982; Pauwels et al., 1998) that is described by the classic Rayleigh distillation law:

$$\delta - \delta_0 = \varepsilon \ln \frac{C}{C_0} \quad (5)$$

where δ is the $\delta^{15}\text{N}$ of the residual NO_3 , δ_0 the $\delta^{15}\text{N}$ of the initial NO_3 (i.e. before denitrification), C the NO_3 concentration; C_0 the initial NO_3 concentration and ε the isotopic enrichment factor.

We observe a rough linear trend of increasing $\delta^{15}\text{N}$ with the decreasing logarithm of the NO_3 concentrations ($r=0.77$; Fig. 4). The slope of the relation yields an approximate enrichment factor of $\varepsilon = -3.1 \pm 0.5\%$, consistent with the value of -4% estimated for the nearby site of the Coët–Dan catchment on altered Paleozoic basement (Pauwels et al., 2000), and compatible with denitrification occurring with rapid kinetics (Vogel et al., 1981; Mariotti, 1994).

Fig. 4 shows the enrichment of ^{15}N as NO_3 concentrations decrease, in agreement with natural denitrification. The Bonne Fontaine sample, which represents the unpolluted end-member, lies outside this tendency with a low NO_3 concentration and a low $\delta^{15}\text{N}$. The domestic effluents show a tendency of decreasing $\delta^{15}\text{N}$ with decreasing NO_3 concentrations that indicate dilution with a low NO_3 end-member. Fig. 4 also shows modeled denitrification curves relative to the various pollution sources. For each pollution source, the initial NO_3 concentration, C_0 in Eq. (5), is arbitrarily set at 300 mg l^{-1} (higher than the most concentrated groundwater measured), and the enrichment factor at -3.1% as previously determined. The following conclusions can be drawn from the $\delta^{15}\text{N}$ vs. NO_3 diagram (Fig. 4):

1. The isotopic composition of the most concentrated samples which are assumed to be close to their NO_3 source(s) composition (flat part of the denitrification curve) lies in the domain of animal manure (poultry and cattle and the lowermost range of hog) and also of sewage water (but at higher concentrations).
2. Most of the samples plot within the range of animal manure influenced by nitrification. Fertilizers seem to have a negligible effect.
3. All samples values can be rationalized by considering both mixing (dilution) and denitrification. The highest $\delta^{15}\text{N}$ values for hog manure exceed the maximum values

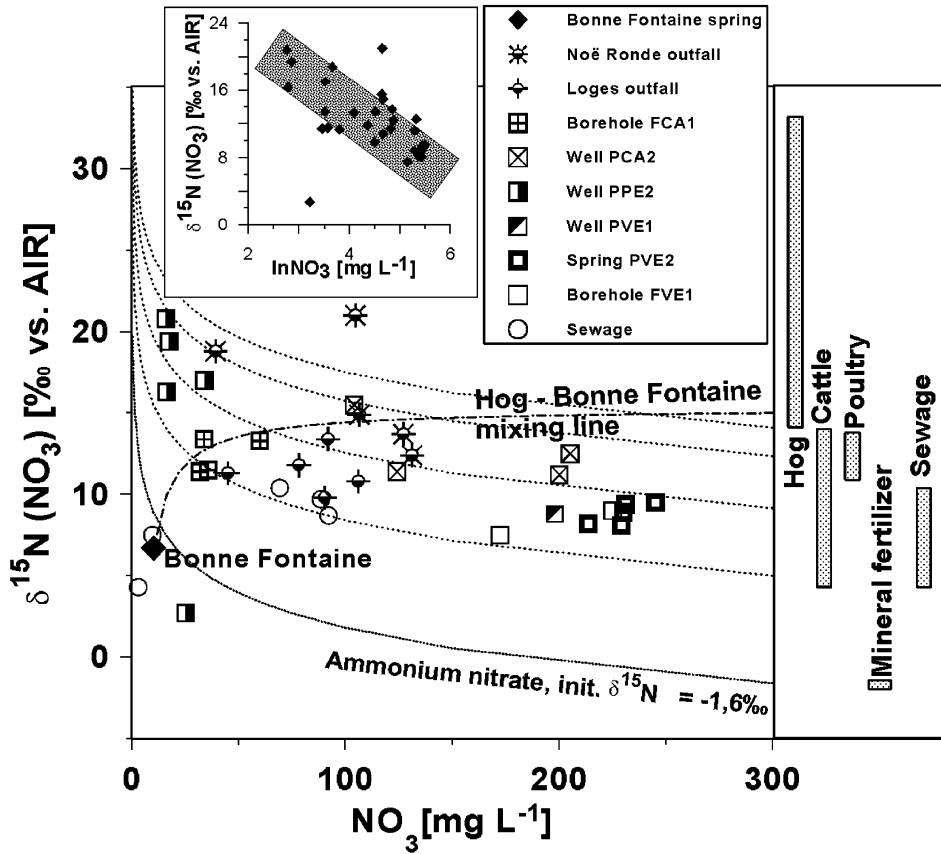


Fig. 4. $\delta^{15}\text{N}(\text{NO}_3)\text{--NO}_3$ concentrations covariations in groundwater samples. Also shown are specific theoretical denitrification and pollution (i.e. binary mixing) models. The Raleigh distillation calculations for denitrification take into account an ϵ value of -3.1% and an initial NO_3 concentration C_0 of 300 mg l^{-1} . The insert shows linear relationships between $\delta^{15}\text{N}$ and $\ln \text{NO}_3$ typical for denitrification reactions.

observed in groundwater (mixing line in Fig. 4), thus dilution (i.e. mixing) is also an important process.

- The domestic wastewaters do not undergo significant denitrification, but seem to be diluted by the uncontaminated end-member.

5.2. Strontium isotopes

We observe a clear positive correlation ($r=0.84$) between Sr concentrations and NO_3 contents that can be explained by a simple mixing between a contaminated end-member and the baseline end-member (Fig. 3c). Sewage samples have near-constant Sr concentrations around 0.2 mg l^{-1} for varying NO_3 contents. A slight contribution of the low NO_3 sewage end-member would explain some of the dispersion of the correlation. Low Sr concentrations at high NO_3 can be explained by a contribution of Hog-2000-type drainage.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the groundwater samples confirm the binary mixing trend: they correlate linearly with the reciprocal value of Sr concentrations ($r^2=0.82$; Fig. 5). The dilute reference end-member (here represented by borehole FJH1) is characterized by radiogenic Sr isotope ratios. It is interesting to note that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the drainage from the experimental plots are systematically more radiogenic than the corresponding leachate samples. This may indicate mixing with dilute, but highly radiogenic, waters (type FJH1) that underwent water–soil interaction during the drainage of the experimental plots. The highly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the reference source (borehole FJH1; $^{87}\text{Sr}/^{86}\text{Sr}=0.71958$) is consistent with the drainage of Brioverian gneiss and mica schist (e.g. Probst et al., 2000). The isotopic contrast between borehole FJH1 groundwater and rainwater ($^{87}\text{Sr}/^{86}\text{Sr}=0.70873\text{--}0.71070$ for rainwater) reflects the interaction of infiltrating rainwater with the soil and rock matrix. The measured Sr concentrations of the drainage water from plots spread with animal manure are close to those of the most polluted groundwater (up to 0.33 mg l^{-1}). Animal manure can thus be considered as a major Sr source in the groundwater system.

The binary mixing model gives a first approximation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the mean Sr source at the scale of the watershed. The intercept of the regression line yields an

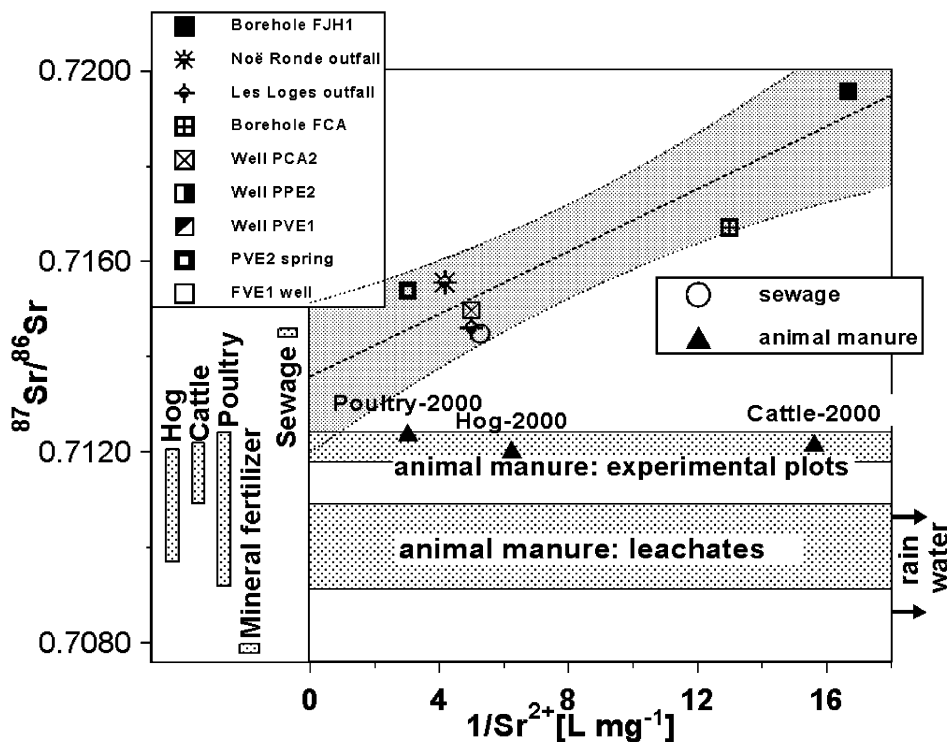


Fig. 5. $^{87}\text{Sr}/^{86}\text{Sr}$ values plotted against the reciprocal of Sr content in groundwater. Data are fitted by a linear regression, indicating that Sr in the groundwater is governed by a binary relation of mixing between a reference end-member (FJH1) and a pollution end-member.

$^{87}\text{Sr}/^{86}\text{Sr}$ between 0.712 and 0.715, corresponding to the 95% confidence interval. The lower limit of this interval is compatible with the $^{87}\text{Sr}/^{86}\text{Sr}$ values for the drainage water from the experimental plots. The Sr isotope signature may be slightly altered by water–rock interaction, leading to more radiogenic values within the groundwater body. The narrow $^{87}\text{Sr}/^{86}\text{Sr}$ range (0.71095 to 0.71242; Fig. 2) of all types of animal manure makes a differentiation of individual sources on the basis of Sr isotopes impossible. Mineral fertilizers are characterized by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios lower than those of animal manure (0.70788 for ammonium nitrate), comparable to those reported by Négrel (1999), but their influence seems to be negligible in groundwater samples.

5.3. Boron isotopes

The isotopic composition of B as a co-migrating tracer is not affected by the denitrification process (Vengosh et al., 1994; Bernard et al., 1996; Leenhouts et al., 1998) and can be used as an indicator of mixing processes. Interaction with the aquifer matrix with dissolution of B-bearing silicates, or adsorption–desorption processes on clays or ferrihydroxides, may nevertheless affect the isotopic composition and concentration of dissolved B (Palmer et al., 1987; Yingkai and Lan, 2001).

The B vs. NO_3 diagram (Fig. 3d) indicates at least a ternary mixing system with the following end-members:

1. Animal manure with high NO_3 (150–450 mg l^{-1}) and intermediate B concentrations (around 40 $\mu\text{g l}^{-1}$).
2. Unpolluted ground- and rainwater with low B and NO_3 .
3. Two types of sewage: one with high B that can be related to washing detergents and low NO_3 , and the other one with intermediate NO_3 and B contents comparable to the animal end-member that might be related to human excrement. The differences in the concentrations correspond to different sampling dates and indicate temporal variations in the character of the wastewater inputs.

This interpretation is supported by the isotope data (Fig. 6). The dilute end-member is clearly identified by the Bonne Fontaine/FJH1 samples ($\delta^{11}\text{B} \approx 40\text{‰}$). With increasing B concentration, the isotope compositions diverge and fall within a triangle defined by the dilute end-member, the extreme values of high-B sewage ($\delta^{11}\text{B}$ near 0‰), and the Hog-1999 runoff (42.4‰). Mixing tendencies are rather well defined for the individual observation points. This is especially true for well PPE2 whose groundwater tends towards the high-B/low- $\delta^{11}\text{B}$ sewage end-member (with a typical washing powder $\delta^{11}\text{B}$; Vengosh et al., 1999), which is compatible with the local situation: the pollution origin is either the scavenger well located on the plot, or contamination from the nearby village of St. Igneuc. The isotope composition of the other groundwater samples can be explained by B input from animal manure or type-2 sewage (moderate B and NO_3 concentrations). A certain number of samples (in particular the samples from wells PVE2 and PCA2 and borehole FVE1) are too enriched in ^{11}B to be explained by any input other than hog manure; moreover, their

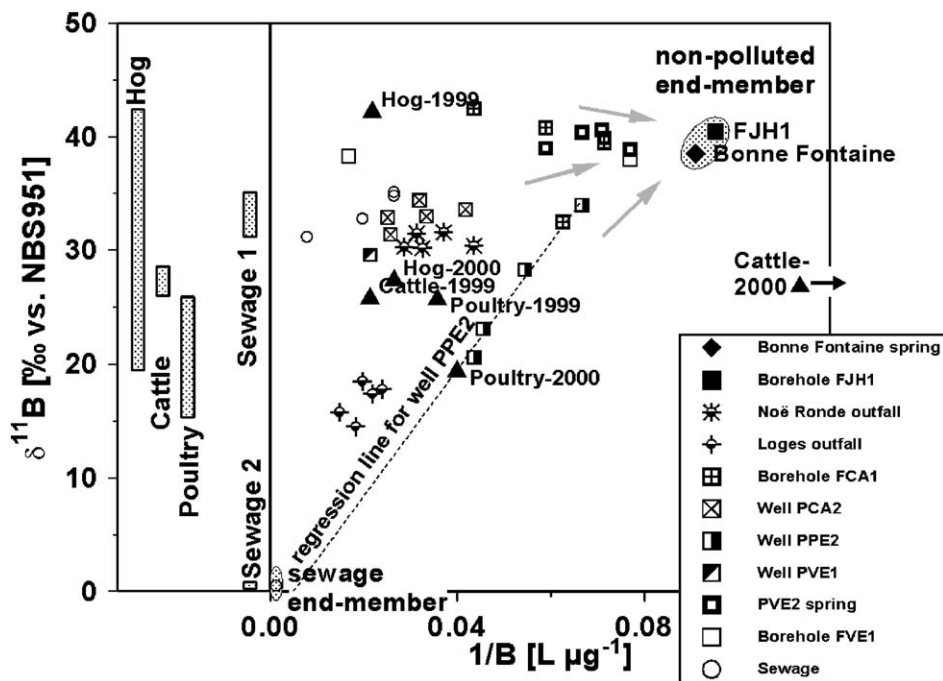


Fig. 6. $\delta^{11}\text{B}$ vs. $1/B$ diagram for groundwaters and pollution sources.

NO_3 concentrations ($>200 \text{ mg l}^{-1}$) are too high to be explained by sewage input ($\text{NO}_3 < 100 \text{ mg l}^{-1}$).

The surface waters from the two catchments are clearly differentiated. That from the Noë Ronde outfall is compatible with the groundwater of the catchment bearing an animal-manure signature, whereas that from the Loges outfall plots near the tendency defined by well PPE2 that lies within this catchment and seems to be dominated by the high-B sewage end-member.

The fact that borehole FJH1, which is clearly marked by water–rock interaction (high F, Li, Fe concentrations), shows low B concentrations and high $\delta^{11}\text{B}$ values close to those of the Bonne Fontaine spring, as well as a marine signature, suggests against significant B input from silicate dissolution. This further adds to the usefulness of B as a source tracer in this flowsystem. If B was derived from the rock matrix we would expect $\delta^{11}\text{B}$ values close to the range for groundwater from crystalline rocks (close to 0‰ or negative; Spivack et al., 1987). For the case of B loss by adsorption onto clay minerals, we would expect a systematic ^{11}B enrichment with decreasing B, which is not the case for most of the observation points. Moreover, B adsorption is not favored at the observed acid pH range of these groundwaters (4.8 to 6.4) where undissociated boric acid is the dominant species, because the sorption affinity of clay for $\text{B}(\text{OH})_3$ is relatively weak (Palmer et al., 1987). Moreover, if significant B adsorption occurred, we would expect to find decreased B/Cl ratios below the potential source values, which is not the case (Fig.

3e). Most of the animal manures (with the exception of the poultry and cattle manure leachates), the baseline end-member, and most of the groundwater samples have B/Cl ratios near or above the seawater value (Fig. 3e). The highest B enrichment with respect to Cl is observed for the B-rich sewage end-member and for the Loges outfall. Consequently, we can argue that the behavior of B in our system is relatively conservative and reflects essentially mixing.

We may therefore attempt to backtrack the source isotopic composition by a simple binary mixing model implying the sample and the baseline end-member. Each end-member (baseline and pollutant) is characterized by its B concentration (B) and

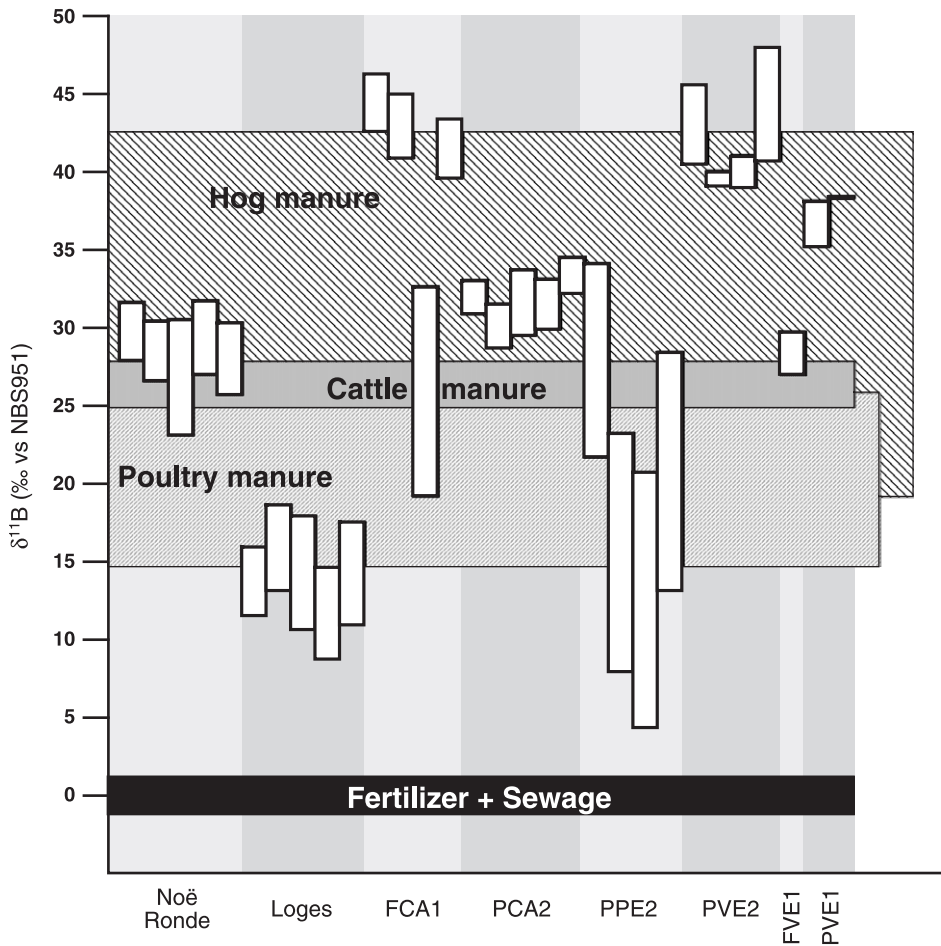


Fig. 7. Determination of the B isotope composition of the main pollution source ($\delta^{11}B_p$) for each sampling site based on the mixing model given in Eq. (6). For each site, several samples were taken during the hydrological cycle. They are plotted in chronological order for each site, allowing the monitoring of pollution-source variations along the hydrological cycle.

corresponding B isotope composition ($\delta^{11}\text{B}$), as described by the following mixing equation system:

$$\begin{cases} B_r \times f + B_p \times (1 - f) = B \\ B_r \times f \times \delta^{11}B_r + B_p \times (1 - f) \times \delta^{11}B_p = B \times \delta^{11}B \end{cases} \quad (6)$$

where r and p refer to the reference and pollution end-members, respectively, and f represents the proportion ($0 \leq f \leq 1$) of the reference end-member in the mixing.

To be consistent with the N isotope systematics, the reference end-member values taken into consideration are those of the Bonne Fontaine spring.

Not knowing the real B concentration of the pollutant (B_p), we can only calculate the $\delta^{11}\text{B}$ range of the pollution source responsible for the B excess (compared to non polluted groundwater) of each sample. B_p necessarily varies between the measured concentration of the polluted sample ($f=0$, no dilution) and infinity. The $\delta^{11}\text{B}$ values calculated for these two extreme values give the potential range for the pollutant, provided that only two components participate in the mixing and that no other processes affect the B geochemistry.

Calculated $\delta^{11}B_p$ values obtained from the several samples taken from each site during a hydrological cycle vary from $4.2 \pm 0.1\%$ to $47.9 \pm 0.4\%$ —the results are given in Fig. 7. This large range is compatible with almost all types of pollution sources. The calculated ranges agree with animal manure as the main vector of NO_3 in the groundwater of the Arguenon watershed, which is consistent with the conclusions based on N isotopes. Among them, hog manure seems to be a major contributor at borehole and well sites FCA1, PCA2, PVE2 and PVE1, and to a lesser extent at the Noë Ronde outfall. Two of the samples (Loges outfall and well PPE2) indicate that the contribution of the high-B/low- $\delta^{11}\text{B}$ sewage end-member is more significant, particularly because both the N and Sr isotopes exclude mineral fertilizer as a major pollution source. In the case of the Loges outfall, the incrimination of sewage is reinforced by a slight enrichment in phosphate. For well PPE2, the pollution origin is either the scavenger well located on the plot, or contamination from the nearby village of St. Igneuc.

Monitoring shows that NO_3 sources are almost constant through the hydrological cycle, except for two samples: one at site FCA1, which shows the contribution of a low- $\delta^{11}\text{B}$ source, and the other at site PPE2 with a varying contribution of sewage effluent.

6. Conclusions

The combination of inherent (N) and co-migrating (Sr, B) isotopic tracers of NO_3 pollution in a small watershed on crystalline basement gives an insight into sources and processes affecting NO_3 under conditions of intensive stock breeding and crop cultivation. NO_3 concentrations, while exceeding the drinking water limit by a factor of 4, decrease downstream in the aquifer.

1. The ^{15}N enrichment accompanying this decrease may indicate that, to some extent, denitrification takes place in the system. However, it is impossible, on the basis of water

chemistry and N isotopes alone, to distinguish the denitrification processes from dilution by unpolluted groundwater. Nitrogen isotopes cannot be considered as conservative, which limits the identification of sources. Isotope signatures of the most contaminated waters however confirm the dominance of animal manure and indicate that mineral fertilizer is not a significant NO_3 source.

2. Strontium isotopes suggest a binary mixing between a dilute end-member that is marked by water–rock interaction and a polluted end-member that is similar to the drainage waters on the experimental plot with hog manure. A differentiation between the different pollutants (hog, poultry and cattle manure, and sewage) is not possible using Sr alone due to the similarity of the isotope signatures. Furthermore, highly radiogenic Sr may be entering the groundwater flow system from the aquifer matrix and alter the isotopic signature. Mineral fertilizer can be excluded on the basis of both Sr and N isotope ratios.
3. Boron isotopes show a significant contrast for the different input sources and the polluted groundwater, and provide the most discriminating source indicator. We have at least a ternary mixing system with hog-manure drainage, sewage, and the natural groundwater background as extreme end-members. The B isotopes distinguish two types of sewage: a high-B/low- NO_3 /low- $\delta^{11}\text{B}$ type that is derived from washing powders, and a moderate-B/moderate- NO_3 type with an isotopic signature close to animal manure (probably human excrement). Water–rock interaction does not seem to play a significant role in the B budget, and thus B appears to be a relatively conservative tracer. A semi-quantitative mixing model approach suggests a predominance of hog manure for almost half the observation sites.

All three tracers demonstrate the major role of animal manure in the NO_3 budget, as opposed to mineral fertilizer, which is negligible. Only B isotopes enable a differentiation between the different types of animal manure and sewage. The applied multi-isotope approach seems to be promising in terms of source identification, but has to be strengthened by a more extensive characterization of potential NO_3 source terms that are largely influenced by local or regional factors such as animal nutrition.

Acknowledgements

This study was supported financially by Cooperl-Hunaudaye, Vivendi Environment, the AINF and BRGM. We are grateful to Matthew Landon and an anonymous reviewer for their constructive remarks that helped us improve the manuscript. We wish to thank Patrick Skipwith for his detailed editing of both language and form.

References

- Aravena, R., Robertson, W.D., 1998. Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic system plume. *Ground Water* 36, 975–982.
- Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in sources identification of nitrate from septic systems. *Ground Water* 31, 180–186.

- Barth, S., 1993. Boron isotope variations in nature: a synthesis. *Geol. Rundsch.* 82, 640–651.
- Barth, S., 1998. Application of boron isotopes for tracing sources of anthropogenic contamination in groundwater. *Water Res.* 32, 685–690.
- Bassett, R.L., 1990. A critical evaluation of the available measurements for the stable isotopes of boron. *Appl. Geochem.* 5, 541–554.
- Basset, R.L., Buszka, P.M., Davidson, G.R., Chong-Diaz, D., 1995. Identification of groundwater solute sources using boron isotopic composition. *Environ. Sci. Technol.* 29, 2915–2922.
- Ben Halima, A., 1977. Apport de la géochimie isotopique de l'azote à la connaissance des sources de pollution azotées des eaux par les nitrates sur l'exemple de la Brie. Doctoral thesis, University of Paris 6, France.
- Bergé, P., 1983. Détection par le traçage isotopique de l'origine des pollutions azotées d'un aquifère alluvial de la vallée de la Garonne. Doctoral thesis, University Paul Sabatier, Toulouse, France.
- Berger, G., Bosch, B., Letolle, R., Marcé, A., Mariotti, A., Megnien, C., 1976. Recherches sur l'origine des nitrates dans les eaux souterraines de la Beauce. BRGM Report 76 SGN 444 BDP.
- Bernard, D., Blin, F., Leclercq, S., Ouddane, B., Maillot, H., 1996. Apport du traçage naturel du bore dans l'évaluation de la pollution des eaux souterraines: cas de la nappe de la craie dans le bassin Artois-Picardie. Premiers résultats. *Tech. Sci. Méthodes* 6, 401–407.
- Böttcher, J., Strebel, O., Voerkelius, S., Schmidt, H.L., 1990. Using stable isotope fractionation of nitrate–nitrogen and nitrate–oxygen for evaluation of microbial denitrification in a sandy aquifer. *J. Hydrol.* 114, 413–424.
- Bretagne, D.R.A.S.S., 1998. Nitrates et eau potable en Bretagne: situation en 1997. Report III1780 LB.
- Chery, L., Talbo, H., Jegou, J.P., Brach, M., Bonin, J., Plancard, D., Rochdi-Ghandour, H., 2000. Apport de l'hydrogéochimie isotopique à la connaissance des sources de pollution azotée sur un site du bassin versant de l'Arguenon (Côtes d'Armor). BRGM Report RP 40911-FR.
- Davidson, G.R., Basset, R.L., 1993. Application of boron isotopes for identifying contaminants such as fly ash leachate in groundwater. *Environ. Sci. Technol.* 27, 172–176.
- Donville, B., Bergé, P., 1985. Impact de l'assainissement individuel sur les teneurs en nitrates des eaux souterraines. *Sci. Tech. Eau* 18, 159–163.
- Faillat, J.P., Corre, S., Sicard, T., Somlette, L., 1999. Influence de l'hydrogéologie et des bactéries dans l'élimination du nitrate des nappes de fissure en Finistère. *Pollutions Diffuses: du Bassin Versant au Littoral*. Ifremer Ed. ALT, Brest, France, pp. 179–197.
- Feats, N.A., Hiscock, K.M., Dennis, P.F., Andrews, J.N., 1998. Nitrogen isotope hydrochemistry and denitrification within the Chalk aquifer system of north Norfolk. *J. Hydrol.* UK 211, 233–252.
- Freyer, H.D., Aly, A.I.M., 1975. Nitrogen-15 variations in fertilizer nitrogen. *J. Environ. Qual.* 3, 405–406.
- Gellenbeck, D.J., 1994. Isotopic compositions and sources of nitrate in ground water from western salt river valley, Arizona. *U.S. Geol. Surv. Water Res. Invest.*, 94–4063.
- Girard, P., Hillaire-Marcel, C., 1997. Determining the source of nitrate pollution in the Niger discontinuous aquifers using the natural $^{15}\text{N}/^{14}\text{N}$ ratios. *J. Hydrol.* 199, 239–251.
- Gran, G., 1952. Determination of the equivalence point in potentiometric titrations. *Analyst* 77 (Part II), 661–671.
- Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: a review. *Chem. Geol.* 59, 87–102.
- Heaton, T.H.E., Talma, A.S., Vogel, J.C., 1983. Origin and history of nitrate in confined groundwater in the western Kalahari. *J. Hydrol.* 62, 243–262.
- Horan, M.F., Bohlke, J.M., 1996. Isotopic composition of strontium in agriculture ground waters, Locust Grove Maryland. *Am. Geoph. Union Spring Meeting* S-102.
- Koba, K., Tokuchi, N., Wada, E., Nakajima, T., Iwatsubo, G., 1997. Intermittent denitrification: the application of a ^{15}N natural abundance method to a forested ecosystem. *Geochim. Cosmochim. Acta* 61, 5043–5050.
- Komor, S.C., 1997. Boron contents and isotopic compositions of hog manure, selected fertilizers, and water in Minnesota. *J. Environ. Qual.* 26, 1212–1222.
- Kreitler, C.W., 1975. Determining the sources of nitrate in groundwater by nitrogen isotope studies. Doctoral thesis, University of Texas, Austin.
- Kreitler, C.W., 1979. Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas. *J. Hydrol.* 42, 147–170.

- Kreitler, C.W., Jones, D.C., 1975. Natural soil nitrate: the cause of the nitrate contamination of ground water in runnels county, Texas. *Ground Water* 13, 53–61.
- Leenhouts, J.M., Bassett, R.L., Maddock III, T., 1998. Utilization of intrinsic boron isotopes as co-migrating tracers for identifying potential nitrate contamination sources. *Ground Water* 36, 240–250.
- Mariotti, A., 1982. Apports de la géochimie organique à la connaissance du cycle de l'azote. Doctoral thesis, University Pierre et Marie Curie, France.
- Mariotti, A., 1984. Utilisation des variations naturelles d'abondance isotopique en ^{15}N pour tracer l'origine des pollutions des aquifères par les nitrates. *International Isotope Hydrology Symposium*, pp. 605–633. Vienna.
- Mariotti, A., 1994. Dénitrification in situ dans les eaux souterraines, processus naturels ou provoqués: une revue. *Hydrogéologie* 3, 43–68.
- Mariotti, A., Ben Halima, A., Berger, G., 1976. Apport de l'étude isotopique de l'azote à la connaissance de la pollution des aquifères souterrains par les nitrates en milieu agricole (Brie, Beauce-France). *Rev. Géogr. Phys. Géol. Dyn.* 18, 375–384.
- Mariotti, A., Landreau, A., Simon, B., 1988. ^{15}N isotope biogeochemistry and natural denitrification process in groundwater: application to the chalk aquifer of northern France. *Geochim. Cosmochim. Acta* 52, 1869–1878.
- Martinez, J., Peu, P., 1999. Étude de suivi d'un dispositif expérimental (biologique et physico-chimique) de surépandage de lisiers de porcs ($1000 \text{ m}^3 \cdot \text{ha}^{-1} \cdot \text{an}^{-1}$). Cemagref Report.
- Mather, J.D., Porteous, N.C., 2001. The geochemistry of boron and its isotopes in groundwaters from marine and non-marine sandstone aquifers. *Appl. Geochem.* 16, 821–834.
- Mossadik, H., 1997. Les isotopes du bore, traceurs naturels dans les eaux: mise au point de l'analyse en spectrométrie de masse à source solide et applications à différents environnements. Doctoral thesis. University of Orléans, France.
- Négrel, P., 1999. Geochemical study of a granitic area—The Margeride Mountains, France: chemical element behaviour and $^{87}\text{Sr}/^{86}\text{Sr}$ constraints. *Aquat. Geochem.* 5, 125–165.
- Négrel, P., Deschamps, P., 1996. Natural and anthropogenic budgets of a small watershed in the Massif Central (France): chemical and strontium isotopic characterization of water and sediments. *Aquat. Geochem.* 2, 1–27.
- Ostrom, N.E., Knoke, K.E., Hedin, L.O., Robertson, G.P., Smucker, A.J.M., 1998. Temporal trends in nitrogen isotope values of nitrate leaching from an agricultural soil. *Chem. Geol.* 146, 219–227.
- Palmer, M.R., Spivack, A.J., Edmond, J.M., 1987. Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay. *Geochim. Cosmochim. Acta* 51, 2319–2323.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Kelly, W.R., 2001. Determination of the sources of nitrate contamination in karst springs using isotopic and chemical indicators. *Chem. Geol.* 179, 113–128.
- Pauwels, H., Kloppmann, W., Foucher, J.C., Martelat, A., Fritsche, V., 1998. Field tracer test for denitrification in a pyrite-bearing schist aquifer. *Appl. Geochem.* 13, 767–778.
- Pauwels, H., Foucher, J.C., Kloppmann, W., 2000. Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes. *Chem. Geol.* 168, 307–324.
- Pauwels, H., Lachassagne, P., Bordenave, P., Foucher, J.C., Martelat, A., 2001. Temporal variability of nitrate concentration in a schist aquifer and transfer to surface waters. *Appl. Geochem.* 16, 583–596.
- Probst, A., El Gh'mari, A., Aubert, D., Fritz, B., McNutt, R., 2000. Strontium as a tracer of weathering processes in a silicate catchment polluted by acid atmospheric inputs, Strengbach, France. *Chem. Geol.* 170, 203–219.
- Rennie, D.A., Paul, E.A., Johns, L.E., 1976. Natural nitrogen-15 abundance of soil and plant samples. *Can. J. Soil Sci.* 56, 43–50.
- Scott, P.S., 1996. Effluent recharge to the upper Santa Cruz River flow plain aquifer, Santa Cruz County, Arizona. Doctoral thesis. University of Arizona, Tucson, Arizona.
- Shearer, G.B., Kohl, D.H., Commoner, B., 1974. The precision of determination of the natural abundance of nitrogen-15 in soils, fertilizers, and shelf chemicals. *Soil Sci.* 118, 308–316.
- Showers, W.J., Eisenstein, D.M., Paerl, H.W., Rudek, J., 1990. Stable isotope tracers of nitrogen sources to the Neuse river, NC. UNC Water Resources Research Institute Report.
- Smith, R.L., Howes, B.L., Duff, J.H., 1991. Denitrification in nitrate-contaminated groundwater: occurrence in steep vertical geochemical gradients. *Geochim. Cosmochim. Acta* 55, 1815–1825.
- Spivack, A.J., Edmond, J.M., 1986. Determination of boron isotope ratios by thermal ionization mass spectrometry of the dicesium metaborate cation. *Anal. Chem.* 58, 31–35.

- Spivack, A.J., Palmer, M.R., Edmond, J.M., 1987. The sedimentary cycle of the boron isotopes. *Geochim. Cosmochim. Acta* 51, 1939–1949.
- Vengosh, A., 1998. Boron isotopes and groundwater pollution. *Water Environ. News* 3, 15–16.
- Vengosh, A., Heumann, K.G., Juraske, S., Kasher, R., 1994. Boron isotope application for tracing sources of contamination in groundwater. *Environ. Sci. Technol.* 28, 1968–1974.
- Vengosh, A., Barth, S., Heumann, K.G., Eisenhut, S., 1999. Boron isotopic composition of freshwater lakes from Central Europe and possible contamination sources. *Acta Hydrochim. Hydrobiol.* 27, 416–421.
- Vogel, J.C., Talma, A.S., Heaton, T.H.E., 1981. Gaseous nitrogen as evidence for denitrification in groundwater. *J. Hydrol.* 50, 191–200.
- Widory, D., Chery, L., Mougin, B., Talbo, H., Bonnin, J., Plancard, D., Rochdi-Ghandour, H., 2001. Traçage isotopique des sources de nitrates dans les eaux souterraines: cas du bassin de l'Arguenon. BRGM Report RP-51091-FR.
- Williams, A.E., Lund, L.J., Johnson, J.A., Kabala, Z.J., 1998. Natural and anthropogenic nitrate contamination of groundwater in a rural community, California. *Environ. Sci. Technol.* 32, 32–39.
- Yingkai, X., Lan, W., 2001. The effect of pH and temperature on the isotopic fractionation of boron between saline brine and sediments. *Chem. Geol.* 171, 253–261.