

Boron isotope ratio ($\delta^{11}\text{B}$) measurements in Water Framework Directive monitoring programs: comparison between double focusing sector field ICP and thermal ionization mass spectrometry†

Kristof Tirez,^{*a} Wilfried Brusten,^a David Widory,^b Emmanuelle Petelet,^b Agnès Bregnot,^b Dongmei Xue,^c Pascal Boeckx^c and Jan Bronders^a

Received 27th January 2010, Accepted 26th March 2010

First published as an Advance Article on the web 27th April 2010

DOI: 10.1039/c001840f

The aim of our research was to compare $\delta^{11}\text{B}$ measurements performed with thermal ionization mass spectrometry (TIMS) and sector field-inductively coupled plasma-mass spectrometry (SF-ICP-MS) and evaluate the feasibility of implementing stable isotope methods in European water framework directive (WFD) monitoring programs. The comparison was based on $\delta^{11}\text{B}$ measurements of 192 ground- and surface water samples and 15 leachates of nitrate pollution source materials (organic and mineral fertilisers). The precision of $\delta^{11}\text{B}$ measurements attainable with SF-ICP-MS, $2\sigma = \pm 2.6\text{‰}$; ($n = 192$), is as expected lower than the precision achieved by TIMS, $2\sigma = \pm 0.3\text{‰}$ ($n = 183$). However the ease of use, rapidity and availability of SF-ICP-MS on one hand and the observed variability in $\delta^{11}\text{B}$ in ground- and surface water on the other (from -3.4 to $+37\text{‰}$), demonstrates that using SF-ICP-MS as an isotopic screening method would promote the use of isotopic methodology for WFD monitoring. Based on the results of the different case studies it is shown that retrieving precise information on the identification of pollution sources from $\delta^{11}\text{B}$ values requires reaching the best analytical precision and accuracy possible. Hence, the superior precision of TIMS advantages tracing of nitrate pollution sources. However for some cases, *e.g.* trying to decipher contributions between sources with really distinct $\delta^{11}\text{B}$ signatures (*e.g.* manure and sewage effluent), SF-ICP-MS results lead to the same conclusions and can therefore be used as a first approachable screening method for the determination of $\delta^{11}\text{B}$ in WFD monitoring programs.

Introduction

With the increasing precision of state-of-art mass spectrometry instruments in determining isotope ratios, interest in isotopic fingerprinting techniques for a variety of elements is increasing. The natural observed variations in isotope ratios can be used, among others, in i) identification of archaeological artefacts, ii) food authentication, iii) provenance studies and tracing of sources of contamination.

There is a considerable interest in determining variations of boron isotope ratios ($^{11}\text{B}/^{10}\text{B}$) in geochemistry because of the wide natural range of $^{11}\text{B}/^{10}\text{B}$ ratios in rocks, sediments and waters. Boron isotopes have been successfully used for tracing sources of anthropogenic input into ground- and surface water,^{1–5} rainwater and deposition,^{6–8} freshwater lakes,⁹ landfill percolates¹⁰ and even anthropogenic emissions in the atmosphere.¹¹

A variety of mass spectrometric techniques are used for isotope ratio measurements, depending on the demands of the specific application. The fundamentals and the use of plasma source mass spectrometry for isotope ratio measurements have been reviewed by several authors,^{12,13} especially since the introduction of multi collector ICP-MS.¹⁴

The classical method for measuring the boron isotopic composition, $\delta^{11}\text{B}$, is thermal ionization mass spectrometer (TIMS). It yields the highest degree of accuracy and precision ($\pm 0.3\text{‰}$). It is now well documented that various ICP-MS techniques are also widely used for measuring isotope ratios, with excellent results for multi-collector ICP-MS (MC-ICP-MS: $\delta^{11}\text{B} \pm 0.2\text{‰}$), satisfactory results for double focusing sector field ICP-MS (SF-ICP-MS: $\delta^{11}\text{B} \pm 2\text{‰}$) and poor results using quadrupole-based ICP-MS (Q-ICP-MS: $\delta^{11}\text{B} \pm 15\text{‰}$).^{15–24}

As boron isotope ratios are increasingly being applied in geochemistry, the comparison of isotopic measurements across different instrument types and techniques with respect to the demands of the application is of concern. Recently, an inter-laboratory comparison of boron isotope measurements was performed in order to address the correct reporting and comparison of isotopic measurements across different instrument types and techniques.¹⁵ Kasemann *et al.* reported a comparison of isotopic measurements with respect to boron isotope composition of marine carbonates to reconstruct seawater pH values and atmospheric $p\text{CO}_2$.¹⁶

^aFlemish Institute of Technological Research - Vito, Environmental analysis and technology, Boeretang 200, 2400 Mol, Belgium. E-mail: Kristof.tirez@vito.be; Fax: +32 14339472; Tel: +32 14335036

^bBureau de recherches géologiques et minières – BRGM, Avenue Claude Guillemin, BP 36009 45060 Orléans Cedex 2, France

^cGhent University, Faculty of Bioscience Engineering, Laboratory of Applied Physical Chemistry, Coupure 653, 9000 Gent, Belgium

† This article is part of a themed issue highlighting some of the most recent and significant developments in the area of Sector Field ICP-Mass Spectrometry.

To distinguish nitrate sources, trace them in water and quantify their respective contributions, research showed great added value of using a multi-isotopes approach including boron ($\delta^{15}\text{N}$ - NO_3 , $\delta^{18}\text{O}$ - NO_3 and $\delta^{11}\text{B}$).⁴ Nitrate contamination in water is a worldwide environmental problem and is of special concern in the European Water Framework Directive.²⁵ Mean nitrate concentrations in groundwaters in Europe are above background levels but do not exceed the limit of 50 mg L^{-1} as NO_3 . On average, groundwaters in western Europe have the highest nitrate concentration, due to the most intensive agricultural practices, twice as high as in eastern Europe, where agriculture is less intense. In the EU, it is estimated that mineral fertilisers account for almost 50% of nitrogen inputs into agricultural soils and manure for 40%. The rate of percolation is often slow and excess nitrogen levels may be the effect of pollution on the surface up to 40 years ago, depending on the hydrogeological conditions. There are also other sources of nitrate, including treated sewage effluents, which may also contribute to nitrate pollution in some rivers.

However chemical data alone, currently used in the different types of monitoring programs defined in the Water Framework Directive, do not permit to establish unambiguously the type, location and contribution of different sources of nitrate in a river basin. In particular, differentiating urban and agricultural origin is difficult, even by increasing the number of monitoring stations or samples. This information is nevertheless critical in defining correct measures to reduce the nitrate contamination.

Within the frame of the European Life ISONITRATE project, the aim of our research was to compare $\delta^{11}\text{B}$ measurements *via* TIMS and SF-ICP-MS for tracing nitrate sources and evaluate the feasibility of implementing stable isotope methods in European WFD monitoring programs.²⁶ Nitrate concentrations of more than 1000 groundwater monitoring stations across European Countries are reported to the European Environmental Agency.²⁵ However on a local scale, the frequency of quality monitoring of surface and groundwaters with respect to nutrients is much larger. In the Flanders region of Belgium alone, more than 2000 groundwater and 4000 surface monitoring stations control on a regular basis the nitrate content.²⁷ Because of these high frequency monitoring requirements, the WFD implementation has triggered the use of screening methodologies in particular for the detection of accidental pollution or the control of water bodies at risk.²⁸

For implementation and application of isotope techniques in WFD monitoring programs the ease and feasibility of measurement methods is of primary concern. The peculiar advantages of sector field based ICP-MS include high sample throughput, low analysis cost, instrument robustness, sensitivity and simple sample preparation. Moreover, these type of instruments are already available and implemented in WFD monitoring laboratories to analyse the content of different contaminants in ground- and surface water (Cd, Pb, ...). The more precise techniques (TIMS, MC-ICP-MS), on the other hand, often require labour-intensive sample preparation, such as chemical purification of the analyte and expensive equipment. The nitrate source tracking potential based on $\delta^{11}\text{B}$ measurements with TIMS and SF-ICP-MS was evaluated in four different cases.

Natural variations of $\delta^{11}\text{B}$

A synthesis of boron isotope variations in nature has been reported amongst others by Barth.²⁹ The ratio between the two stable isotopes of boron, ^{11}B and ^{10}B , is usually referred under the $\delta^{11}\text{B}$ notation, given by eqn (1):

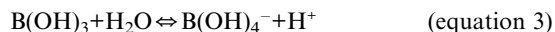
$$\delta^{11}\text{B} = \left[\frac{(^{11}\text{B}/^{10}\text{B})_{\text{sample}}}{(^{11}\text{B}/^{10}\text{B})_{\text{NIST951}}} - 1 \right] \cdot 10^3 \quad (\text{equation 1})$$

Where NIST SRM 951 (boric acid) is the accepted international reference material, with $^{11}\text{B}/^{10}\text{B} = 4.04362 \pm 0.00137$. The relative large mass difference between the two stable isotopes of boron leads to a wide range of boron isotope variations in natural samples.³⁰ Natural waters, such as seawater, river water, rainwater, groundwater, brines, geothermal fluids and fumaroles' condensates encompass a range of $\delta^{11}\text{B}$ of nearly 76‰.³ The lowest $\delta^{11}\text{B}$ values at -16‰ are reported for groundwater from the Artesian Basin in Australia, the most enriched reservoirs measured, to date, are saline groundwater in Israel and brines from the Dead Sea and Australian salt lakes with $\delta^{11}\text{B}$ values up to $+60\text{‰}$.

The dominant boron species in aquatic systems are $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$, which are in isotopic equilibrium as shown in eqn (2):²



The calculated equilibrium constant for this reaction is 0.981 at 25 °C. This implies that ^{10}B is preferentially present in the tetrahedral species, while ^{11}B is enriched in the trigonal species. The $\text{B}(\text{OH})_4^-$ species are preferably adsorbed by soil and minerals, leading to an enrichment of ^{10}B in the solid phase (fractionated by 30–40‰) when boron is incorporated from aquatic systems by heterogeneous exchange, and a concomitant enrichment of ^{11}B in the residual fluids. In contrast, leaching of clay minerals (*e.g.* desorption) or extraction of fluid inclusions in crystalline rocks result in low $\delta^{11}\text{B}$ in the residual fluids. In aqueous solutions, the equilibrium between $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ is pH-dependent (eqn (3)):



At high pH values (pH > 11), $\text{B}(\text{OH})_4^-$ dominates, while $\text{B}(\text{OH})_3$ is the dominant form at pH < 7. An equilibrium isotope fractionation can, therefore, only be expected if the aquatic system has a pH between 7 and 11.

Anthropogenic influence of $\delta^{11}\text{B}$ in ground and surface water

With respect to nitrate groundwater contamination from intensive agriculture, the main sources to distinguish are mineral fertilizers, organic fertilizers (animal manure) and sewage. While Boron concentrations in natural groundwater and surface water are generally low ($< 0.05 \text{ mg L}^{-1}$), the contaminant sources are enriched in boron ($0.1\text{--}1.5 \text{ mg L}^{-1}$ in sewage effluent, $> 1 \text{ mg L}^{-1}$ in liquid manure, up to 22 mg L^{-1} in mineral fertilizer leachate).^{31,32} Consequently the boron isotope composition is sensitive to mixing of pristine and contaminated waters.

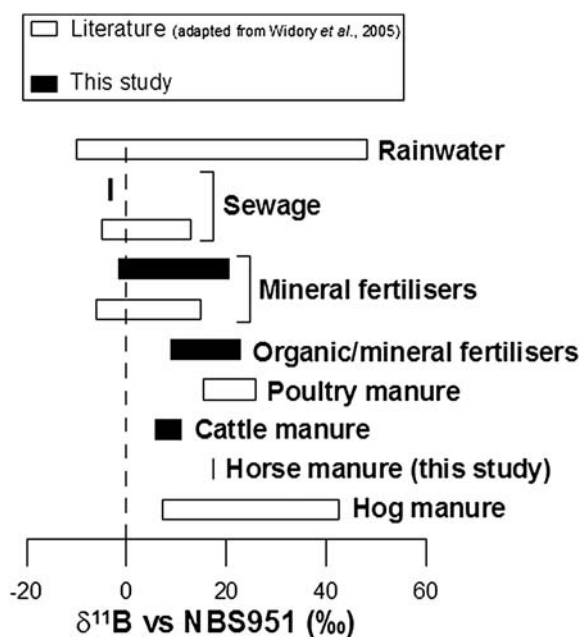


Fig. 1 Literature overview of $\delta^{11}\text{B}$ values of main NO_3 pollution sources in combination with data from the ISONITRATE project [4].

Moreover the isotopic composition of boron, as a nitrate co-migrant, is not affected by denitrification and can therefore be used as a conservative tracer of mixing processes.^{31,32} Fig. 1 summarizes the boron isotope composition ranges for the main anthropogenic sources. A synthesis of using coupled nitrogen and boron (measured with TIMS) isotopes for tracing the sources of nitrate in groundwater has been reported by Widory *et al.*⁴ A recent review of stable isotope methods for nitrate source identification ($\delta^{15}\text{N}\text{-NO}_3$, $\delta^{18}\text{O}\text{-NO}_3$) was presented by Xue *et al.*³³ In this paper it is shown that, especially in the case of differentiation between manure and sewage, the $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$ approach alone does not allow clear differentiation of the sources.

A summary of boron isotope ratios and concentration data for the main nitrate contaminant sources are given below.

Sewage water

The first studies of B isotopes as tracers of human impact on water resources have focused on the identification of wastewater and sewage dominated by synthetic B products. Sodium perborate (either monohydrate $\text{NaBO}_3\cdot\text{H}_2\text{O}$ or tetrahydrate $\text{NaBO}_3\cdot 4\text{H}_2\text{O}$) is widely used as a bleaching agent in a variety of domestic and industrial cleaning products. The raw materials are mainly from large non-marine evaporate deposits in the USA (*e.g.* Boron, Searles Lake) and western Turkey (*e.g.* Kirka) which account for almost 90% of world production of sodium perborate. During end use of perborate-enriched detergents and cleaning products, the anthropogenic water soluble boron compounds are discharged with domestic aqueous effluents into sewage treatment plants, where little or no boron is removed during conventional processing of the wastewater. Hence the anthropogenic boron load is almost entirely released into the aqueous environment by entering a receiving surface water

system where further dilution occurs. Boron concentrations in secondary effluents typically range from 0.1 to 1.5 mg L^{-1} . Covariations observed between B concentrations of freshwater and P concentrations or anionic detergent structures support the fact that sodium perborate is to be considered as the major anthropogenic source of boron. In natural borate minerals, $\delta^{11}\text{B}$ ranges from -5.4 to 10.2‰ for Na-borates, from -16 to -1.1‰ for Na/Ca borates and from -21.9 to -4.9‰ for Ca-borates. The rather narrow range in $\delta^{11}\text{B}$ of Na-borate minerals allows an isotope approach to distinguish a specific anthropogenic source of boron (mainly from industrial perborate, the dominant use of mined boron) in a given natural aquatic system, characterized by a distinct local background $\delta^{11}\text{B}$. The boron isotopic signature for a series of industrial sodium perborate monohydrate and tetrahydrate products manufactured in Europe (Germany) were reported by Barth.¹⁶ Sodium perborate monohydrate and tetrahydrate samples were characterized by $\delta^{11}\text{B}$ values ranging from -3.9 to $+0.9\text{‰}$ and -4.8 to $+0.5\text{‰}$, respectively. The total range in $\delta^{11}\text{B}$ values (-4.8 to $+0.9\text{‰}$) overlaps with the ranges of $\delta^{11}\text{B}$ reported for non-marine Na-borate minerals and commercial borax from the USA (-1.3 to $+10.2\text{‰}$) and Turkey (-5.4 to -1.7‰).

Fertilizers

Boron isotope signatures of inputs related to agriculture (*e.g.* hog manure, cattle feedlot runoff, synthetic fertilizers) and the combination of N and B isotopes were first used in 1997 to distinguish NO_3^- anthropogenic inputs to both ground- and surface water.³¹ For B to fulfil this role, however, manure and fertilizers must contain detectable B with distinctive isotopic compositions.

Komer *et al.* reported averaged boron concentrations in liquid hog manure of 2.9 mg L^{-1} ($n = 7$),³¹ for cattle manure and poultry manure concentrations of respectively 1.8 and 13.4 mg kg^{-1} were reported.³² In this study it was also shown that boron concentrations moderately correlated with potassium, a soluble element that occurs mostly in urine, but not with phosphorus, an element that is mostly in faeces. These correlations are consistent with boron residing mainly in the urine component of manure. Boron concentrations in fertilizers (on a dry weight basis) ranged from below detection limit for some brands of ammonium nitrate and urea up to 382 mg kg^{-1} in magnesium sulfate.³¹

However, the amounts of boron added to cultivated fields with fertilizers depend on the application rates of the specific fertilizer and its boron contents. As an example, it was calculated by Komer *et al.* that for typical liquid manure application rates a $0.28\text{--}0.42 \text{ kg B ha}^{-1}$ is added, while for N mineral fertilizers $0.05 \text{ kg B ha}^{-1}$ and in case of some brands of urea or ammonium nitrate no detectable boron was added.

In conclusion, boron isotopes can be used as tracers for discerning distinct solute sources in natural waters since (i) boron is highly soluble in aqueous solutions, and therefore a ubiquitous minor or trace constituent in nearly all water types, (ii) the boron isotopic composition is controlled by several known parameters among which the solute source compositions and isotope fractionation processes related to adsorption/desorption, mineral precipitation and dissolution, and volatilization are the most relevant and (iii) the relative large mass difference between the

two stable isotopes of boron leads to a wide range of variations of boron isotope compositions in the nature.

However considering the concentration ratio of nitrate and boron in the different nitrate sources, boron isotopes are mainly useful for tracing or discerning organic fertilizer (manure) and sewage effluent (washing detergents). This is especially relevant considering the impossibility to clearly differentiate between these two sources with the $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ approach alone.

Experimental

Instrumentation

Two distinct types of mass spectrometers were used to measure and compare $\delta^{11}\text{B}$ values:

1. a single collector double focusing SF-ICP-MS (ELEMENT II, ThermoFisher, Germany)
2. a single collector thermal ionization mass spectrometer TIMS (MAT261, Finnigan®, Germany)

Water samples

The ISONITRATE demonstration project relied upon a survey of 12 sampling campaigns over a 15 month period (October 2007–December 2008).²⁶ The pilot site is located in the Alsace region (France), it is part of the Upper Rhine basin between the German-French-Swiss border near Basel in the south and the mouth of the river Nahe near Bingen in the north. The site is flanked by the low mountain ranges of the Vosges and the Pfälzerwald in the west as well as of the Blackforest and the Odenwald in the east.

Because of an intensive agricultural land use, viticulture and the presence of industries and mining activities in the Upper Rhine Valley, water on this pilot site is strongly impacted by anthropogenic inputs. The average nitrate concentration of the groundwater in the Upper Rhine Valley is just under 30 mg L^{-1} nitrate and herewith indicates a substantial pollution of the groundwater.

Table 1 Description of ground - and surface water samples. Four different environmental contexts: single source of NO_3 , “unpolluted” water, multiple sources of NO_3 , natural denitrification

	Code	Type
Single source of NO_3	A1	Surface water
	A2	Surface water
	A3	Groundwater
	A4	Groundwater
Unpolluted water	B1	Surface water
	B2	Groundwater
Multiple sources of NO_3	C1	Surface water
	C2	Surface water
	C3	Groundwater
	C4	Groundwater
	C5	Groundwater
Natural Denitrification	D1	Groundwater
	D2	Groundwater
	D3	Groundwater
	D4	Groundwater
	D5	Groundwater

Within the Alsace aquifer four distinct scenarios were selected:
(i) Natural case (B1-2, boron corresponding to the local, natural recharge);

(ii) Simple case (A1-4, the source of anthropogenic boron is unique);

(iii) Complex case (C1-5, multiple distinct sources of boron involved);

(iv) Denitrification case (D1-5, nitrate is reduced but should not affect the boron isotopic budget).

The description of the collected water samples is given in Table 1. All samples for $\delta^{11}\text{B}$ measurement were collected in polyethylene (PE) bottles and stored at about $5\text{ }^\circ\text{C}$ in a refrigerator until they were analysed. Other parameters that were monitored are pH, Eh, EC, O_2 , T° , NO_3 , NH_4 , P, TOC, Ca, Mg, Cl, Zn, B, and alkalinity.

Source material samples

After identification, local sources of anthropogenic inputs were sampled from farms or farming cooperative and sewage stations. For the natural case, no pollution sources were sampled as this site represents the natural/uncontaminated reference. For the simple case, which was supposed to be impacted by a single pollution source consisting of mineral fertilizers used for viticulture, the sampling of the main fertilizers was done in a local agricultural marketing cooperative (Pfaffenheim, France). The fertilizers sampled are representative for usage in this specific basin. It thus appears that even if mineral fertilizers are the dominant products, there is also a non negligible use of organic fertilizers. The complex case is located in the eastern part of the Sundgau in an area dominated by farming (cows, horses), agriculture (maize, wheat, sugar beet, rape), direct waste water inputs to surface water were also identified from detached houses which are not connected to a water treatment plant. Most of the waste water from this area is collected and treated in the waste water treatment plant of Sierentz located a few km south-east from the basin. The effluents of this waste water treatment plant were sampled in February 2008. The solid residues of the water treatment are dried in the Sierentz station to be used as fertilizers (dried mud) and were also sampled in February 2008. The main livestock farming consists of cows and horses. Three samples of manures were sampled directly from farms of this basin (April 2008) as well as a dunghill liquid effluent. Sampling of the main fertilizers was done in a local agricultural marketing cooperative (Sierentz). The sampled fertilizers are representative of the products used in this specific basin. The denitrification case is located in the German part of the Alsace plain, the site mainly consists of vineyards. The main mineral fertilizers used in this region were sampled in a local agricultural marketing cooperative (2 samples). A dunghill located nearby the D5 piezometer was also sampled.

The source materials were extracted with milli-Q water ($L/S = 10$) and the $\delta^{11}\text{B}$ measurements were performed on the filtrated leachates.

Reagents and standard solutions

Boron standard solutions were prepared from a 10 g L^{-1} commercially available standard (Spex CertiPrep Inc.,

Metuchen, NJ). De-ionised water was purified by a Millipore Milli-Q system. The $\delta^{11}\text{B}$ values were calculated based on standard reference material NIST 951a Boric acid. All solutions were gravimetrically prepared in polypropylene bottles.

Optimisation SF-ICP-MS

Many factors may affect precision and accuracy of isotope ratio determination by SF-ICP-MS, including sensitivity, spectroscopic interferences, mass discrimination and dead time correction.

Sensitivity. Using the instrument settings given in Table 2, a sensitivity of 100,000 counts per second (cps) per $\mu\text{g B L}^{-1}$ for ^{11}B was obtained using Ni cones. In order to achieve better precision on the isotope ratio, samples containing boron concentrations $> 25 \mu\text{g L}^{-1}$ were diluted so that both isotopes were measured in counting mode. The instrument is equipped with a perfluoroalkoxy copolymer resin (PFA) nebulizer and spray chamber in order to reduce background level. For pure water, a reading of $\sim 10,000$ cps on ^{11}B was obtained ($\sim 0.1 \mu\text{g B L}^{-1}$). Washing periods of 1 h are insufficient to reduce the memory effect below 1%, even when using a range of different solvents (mannitol, ammonia).²³ In our study, the signal on ^{11}B in natural surface and groundwater samples are typically at least more than 50 times higher than the blank. The blank can, thus, be considered as negligible.

Spectroscopic interferences. In order to reduce the spectroscopic interference of $^{40}\text{Ar}^{4+}$ on the $^{10}\text{B}^+$ peak, the radio frequency power setting was reduced and the auxiliary and nebuliser gas flow optimised.¹ The use of a magnetic sector ICP-MS at a low resolution mode yields flat topped peaks. Higher signal intensity coupled to the flat tops of the peaks at lower resolution is used

Table 2 Optimised instrument settings for measurement of $\delta^{11}\text{B}$ with SF-ICP-MS

Nebulizer type	PFA micro flow
Spray chamber	PFA Scott type
RF power/W	1050
Cooling gas flow rate/L min ⁻¹	15
Auxiliary gas flow rate/L min ⁻¹	1
Nebulizer gas flow rate/L min ⁻¹	0.95
Solution uptake rate/ml min ⁻¹	0.7
Ion extraction lens/V	-2000
Focus lens/V	-1140
Mass resolution (m/ Δ m)	300 (low)
Uptake time	4 min
Analysis time	4 min 15 s
Rinsing time	4 min
Scan type	E-scan
Detection mode	Counting
Mass range	10.012–10.013 (^{10}B) 11.008–11.010 (^{11}B)
Mass window (%)	5
Settling time/s	0.001
Sample time/s	0.02 (^{10}B) 0.005 (^{11}B)
Samples per peak	100
Runs	10
passes	200
Integration type	Average
Dead time/ns	10

for precise isotope ratio measurements.³⁴ In the low resolution mode, the peak width (located at 5% peak height) for ^{10}B is 0.033 a.m.u. (9.979–10.046 a.m.u.), and the instrument is set to divide this peak into 100 measurement samples. The mass window for precise isotopic ratio measurement is set to a narrow range of 5%, meaning that the scanning range of the instrument around the boron peak represents $\pm 2.5\%$ peak width of the accurate mass and is centred in the flat top region 10.012–10.013.

Mass discrimination. The space charge effect is assumed to have the strongest influence on the total mass discrimination in an ICP-MS.¹³ After the positively charged ion beam leaves the skimmer cone, the mutual repulsion of ion limits the total number of ions which are transmitted by the optics. If an ion beam consists of light and heavy ions, the light ions are deflected more extensively than the heavy ions, whereas the heavy ions preferably remain in the central ion beam. The total mass bias can be experimentally determined by the mass discrimination factor f_{MD} :

$$f_{\text{MD}} = R_{\text{true}}/R_{\text{measured}} \quad (\text{equation 4})$$

where R is the isotope ratio of the light over the heavy isotope.

Due to the large percentage mass difference between the two stable boron isotopes and the relatively low degree of ionization of boron in the argon plasma of an ICP-MS instrument, the mass discrimination is significant. Based on the alternate NIST SRM 951 measurements during the measurement run, the range of mass discrimination per mass unit, MD, ranged between 7.5 and 10.5%. Correction for mass discrimination is performed by bracketing samples with NIST SRM 951, the average $^{11}\text{B}/^{10}\text{B}$ ratio of NIST SRM 951 measured before and after each sample is used to calculate the $\delta^{11}\text{B}$ value of the bracketed sample, which is the recommended routine procedure for $\delta^{11}\text{B}$ analysis.¹⁵ The correction for matrix-induced mass discrimination was also investigated by Gäbler *et al.* by analyzing seawater. They found, with instrumental settings similar to ours, comparable results for $\delta^{11}\text{B}$ measurements by both SF-ICP-MS and NTIMS.¹

Dead time. Boron isotope ratios were calculated from dead-time corrected intensities. Because of the 4 fold difference in natural abundance of B isotopes, a dead time correction in counting mode is necessary to obtain concentration-independent and accurate values of $\delta^{11}\text{B}$. The dead time is iteratively deduced from the measurement of the $^{235}\text{U}/^{238}\text{U}$ isotopic ratio in 0.4, 0.6, 0.8 and $1 \mu\text{g U L}^{-1}$ standard solutions according to the manufacturer instructions. The optimized dead time obtained was 10 ns.

In conclusion, using the typical optimized instrumental settings as summarized in Table 2, single $\delta^{11}\text{B}$ measurement with SF-ICP-MS can be performed without sample pre-treatment within 12 min (before starting a series of boron measurements, rinsing the SF-ICP-MS instrument with Milli-Q water is recommended). For the routine measurement of $\delta^{11}\text{B}$ with SF-ICP-MS, the following procedure was used on a set of 16 samples per campaign.

(1.) The instrument is tuned to maximum sensitivity for boron (NIST SRM 951 solution of $25 \mu\text{g L}^{-1}$), by tuning ion lenses and adjusting the nebulizer gas flow rate. Subsequently, in order to

reduce the spectroscopic interference of $^{40}\text{Ar}^{4+}$ on the $^{10}\text{B}^+$ peak, the auxiliary and nebuliser gas flow are further optimised.

(2.) samples are analysed by bracketing with NIST SRM 951 standards, the average $^{11}\text{B}/^{10}\text{B}$ ratio of NIST SRM 951 measured before and after each sample is used to calculate the $\delta^{11}\text{B}$ value of the bracketed sample, which is the recommended routine procedure for $\delta^{11}\text{B}$ analysis.¹⁵

Boron concentration measurements. When using SF-ICP-MS an advantage, compared to TIMS, is that in one single analysis both boron concentrations and its isotope composition can be obtained simultaneously. For the determination of the boron concentration in the water samples, an external calibration line where Be was added on-line as internal standard was used. In the frame of this project it was evaluated if the SF-ICP-MS method optimised for isotopic analysis can be used for the quantification of the concentration. In this case, the average of the ^{11}B signal (cps) of NIST SRM 951 before and after the measurement of the ^{11}B signal (cps) of the sample was used to calculate the B concentration of the sample. The concentration of Boron in the prepared NIST SRM 951 standard amounted $27.5 \mu\text{g L}^{-1}$.

Optimisation TIMS

For Boron isotope compositions ($\delta^{11}\text{B}$) in water, sample volume is determined to ultimately yield a quantity of 6 to $10 \mu\text{g}$ of boron. Samples then undergo a two-step chemical purification using Amberlite IRA-743 selective resin (method adapted from Gaillardet *et al.*).³⁵ First, the sample (pH ~ 7) is loaded on a Teflon PFA[®] column filled with 1 ml resin, previously cleaned with ultrapure water and 2N ultrapure NaOH. After cleaning again the resin with water and NaOH, the purified boron is collected with 15 ml of sub-boiled HCl 2N. After neutralisation of the HCl by Superpur NH_4OH (20%), the purified boron is loaded again on a small 100 μl resin Teflon PFA[®] column. Boron is collected with 2 ml of HCl 2N. An aliquot corresponding to 2 μg of boron is then evaporated below 70°C with mannitol in order to avoid boron loss during evaporation.³⁶ The dry sample is loaded onto a tantalum (Ta) single filament with graphite (C), mannitol ($\text{C}_6\text{H}_8(\text{OH})_6$) and caesium (Cs). $\delta^{11}\text{B}$ are then determined by measuring the Cs_2BO_2^+ ion.^{37,38} The analysis is run in dynamic mode by switching between masses 308 and 309. Each analysis corresponds to 10 blocks of 10 ratios. Samples are always run twice. Total boron blank is less than 10 ng corresponding to a maximum contribution of 0.2%, which is negligible. Seawater (IAEA-B1) is purified regularly in the same way in order to check for a possible chemical fractionation due to an uncompleted recovery of boron, and to evaluate the accuracy and reproducibility of the overall procedure.^{39–41} Reproducibility was obtained by repeated measurements of the NBS951, accuracy and reproducibility are controlled with the analysis of the IAEA-B1 seawater standard.

Statistical evaluation

The Bland-Altman technique was used to assess agreement between two measurement methods. This technique was conducted in this study to compare results obtained *via* the TIMS and SF-ICP-MS for the determination of $\delta^{11}\text{B}$. The average (\bar{d})

and standard deviation (s_d) of the difference (d) between the measurement results of two methods on the samples were computed. If the differences are normally distributed, and 95% of the differences lie between $\bar{d} - 1.96 s_d$ and $\bar{d} + 1.96 s_d$ (termed “95% limits of agreement”), the two analytical methods can be used interchangeably.

Results and discussion

The implementation of $\delta^{11}\text{B}$ and boron concentration measurements in large scale WFD monitoring programs requires high sample throughput. The discussion on the nitrate source tracking potential is therefore focused on the attainable analytical performances of $\delta^{11}\text{B}$ measurement with a SF-ICP-MS instrument operating without additional sample pretreatment on the one hand *versus* a TIMS instrument including labour intensive matrix separation on the other. The interpretation on the use of the multi-isotopes approach ($\delta^{15}\text{N}\text{-NO}_3$, $\delta^{18}\text{O}\text{-NO}_3$ and $\delta^{11}\text{B}$) to distinguish nitrate sources will be presented elsewhere.²⁶

Boron concentration levels

An overview of the measured concentrations of boron and nitrate over the different locations is given in Fig. 2 and Table 3. The Nitrate Directive (91/676/EEC) aims to control nitrogen pollution and requires Member States to identify groundwaters that contain more than 50 mg L^{-1} nitrate or could contain more than 50 mg L^{-1} nitrate if preventative measures are not taken. Ground waters A4, D2 and C3 are well above the current limit of nitrate, A3, C4, D3 and 5 are around the limit and C5, D1 and B1 are below the limit.

The average B concentration for the 16 sites ranged from 3 to $70 \mu\text{g L}^{-1}$ (Table 4). The variability during the 15 months sampling campaign per location ranged from ± 2 (B1) to ± 32 (C3) $\mu\text{g B L}^{-1}$ (2σ , $n = 12$). For the natural case, the average concentration was $3.8 \pm 1 \mu\text{g B L}^{-1}$ (2σ , $n = 12$).

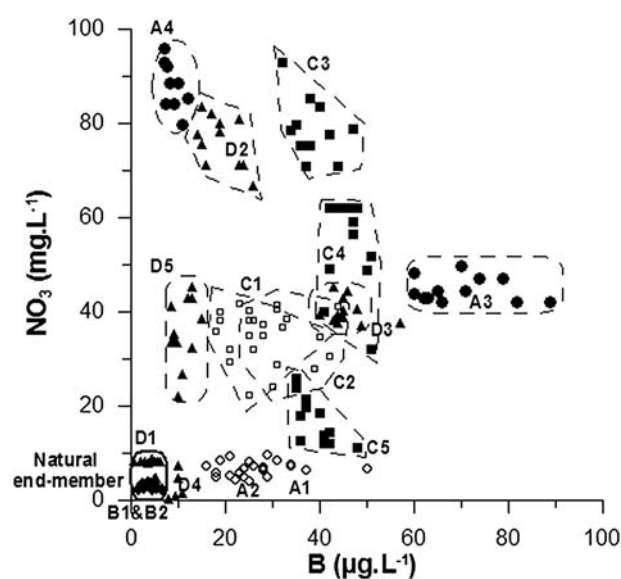


Fig. 2 General overview of the coupled variations of nitrate and boron concentrations for the different case studies. Empty symbols represent surface water samples.

Table 3 Average boron (B) and nitrate (NO₃) concentrations

	[B] µg L ⁻¹	2σ	Min	Max	[NO ₃] mg N L ⁻¹	2σ	Min	Max	NO ₃ /B
A1	30	15	22	50	1.5	0.5	0.9	1.8	50
A2	23	10	16	31	1.5	0.9	0.9	2.2	70
A3	70	19	60	89	10.1	1.2	9.5	11.2	140
A4	8.7	3.2	7	12	20.0	2.2	18.0	21.6	2300
B1	4.4	2.0	3	7	0.65	0.2	0.49	0.86	150
B2	3.3	2.2	2	5	0.70	0.2	0.50	0.86	210
C1	25	12	18	40	7.8	2.5	5.0	9.4	320
C2	32	13	25	44	8.0	2.6	5.4	9.3	250
C3	43	32	32	92	17.3	4.4	12.0	21.0	400
C4	46	7	41	51	12.2	4.5	7.2	14.0	260
C5	39	8	35	48	3.8	2.3	2.5	5.8	100
D1	3.7	3.4	1	6	1.8	0.2	1.6	1.9	480
D2	19	8	14	26	17.0	2.4	15.0	18.8	900
D3	46	8	40	57	9.0	1.2	8.3	10.1	200
D4	8.2	4.8	5	11	0.7	0.9	0.1	1.6	80
D5	11	4	9	15	8.0	3.1	4.9	10.1	720

A comparison between the B concentration in 72 water samples measured with SF-ICP-MS using an external calibration line on one hand and the bracketed NIST SRM 951 on the other hand showed a correlation coefficient of 0.99 ($y = 1.02x + 0.12$). The average measurement difference of boron concentration was 0.4 µg L⁻¹ and the 95% limits of agreement according to the Bland-Altman technique amounted -3.4 and 4.3 µg L⁻¹.

The large variation in boron concentration levels observed between the different collected samples in combination with (in most cases) low variability per sample makes it possible to use the data for interpretation. However, there is no general correlation between the boron and nitrate concentrations, e.g. the most contaminated nitrate groundwater A4 has a concentration in boron similar to the natural background. This is in line with the remarks by Komer *et al.* that the amounts of boron added to cultivated fields with fertilizers depend on the application rates of the specific fertilizer and its boron contents.³¹

When using boron as a co-migrant tracer of nitrate, it is important to consider the extracted N_{total}/B concentration ratio

from the different pollution sources. In general the following order in the N_{total}/B ratio can be derived (Table 5): mineral fertilizer (ammonium nitrate, urea): 1/10⁶; mineral fertilizer (NPK): 1/10³; organic fertilizer: 1/10²; sewage effluent: 1/10. In the case of A4, high nitrate concentration in combination with low boron concentration could indicate the use of mineral fertilizers.

Comparison of δ¹¹B measurement by SF-ICP-MS and TIMS on water samples

The average δ¹¹B values varied over the 16 sampling sites from -3.4 (C5) to 37‰ (D2) (Table 7). The δ¹¹B variability during the 15 months sampling campaign per location ranged from ± 1.0 to ± 15‰ (2σ, $n = 12$). These data show that single sampling and analysis will not lead in all cases to a correct interpretation of the isotope ratios and this has to be considered when implementing in monitoring programs. On the other hand, the observed large variation in δ¹¹B values allows clear discernible distinction between samples.

An estimate of the analytical performance characteristics of the δ¹¹B measurement by SF-ICP-MS was derived based on the measurements of the bracketed NIST SRM 951 samples. In a typical measurement run the 16 samples of the sampling campaign were bracketed in between the measurement of 17 NIST SRM 951 samples. Per measurement run 15 δ¹¹B values of NIST SRM 951 were derived, e.g. δ¹¹B of NIST SRM 951 (3rd position) was calculated using the average ¹¹B/¹⁰B ratio from NIST SRM 951 (2nd position) and NIST SRM 951 (4th position). The average of the calculated δ¹¹B values of NIST SRM 951 (theoretical value = 0) in the course of the project amounted to -0.096 ± 2.6‰ (2σ, $n = 192$). The analytical performance is in agreement with previous reported precision values of δ¹¹B measured by SF-ICP-MS.^{1,15}

For TIMS measurement, reproducibility was obtained by repeated measurements of the NBS951 and the accuracy was controlled with the analysis of the IAEA-B1 seawater standard (δ¹¹B = 38.6 ± 1.7‰). The ¹¹B/¹⁰B ratio of replicate analyses of the NBS951 boric acid standard (after oxygen correction) was

Table 4 Boron concentrations measured by SF-ICP-MS

[B] µg L ⁻¹	Time of sampling (month/year)												Mean µg L ⁻¹	2*σ
	10/07	11/07	12/07	01/08	02/08	03/08	04/08	06/08	08/08	10/08	11/08	12/08		
A1	22	26	28	28	24	29	25	37	28	50	34	34	30	15
A2	23	21	21	19	18	18	16	28	24	25	31	29	23	10
A3	70	71	63	66	60	62	60	65	79	82	74	89	70	19
A4	7.7	8.3	7.5	9	7.2	7	7.1	8.6	12	9.9	8.5	11	8.7	3.2
B1	5.2	4.2	4.6	4.5	4.4	4.6	2.7	4.8	4.3	6.5	3.2	3.5	4.4	2.0
B2	3.7	5	4.3	3.7	3.4	3.8	1.5	2.4	2.1	4.7	2.5	2.3	3.3	2.2
C1	19	25	25	21	18	21	19	23	26	31	28	40	25	12
C2	31	42	30	26	25	28	25	31	44	39	33	32	32	13
C3	34	35	32	37	36	38	38	40	42	44	47	92	43	32
C4	42	44	42	46	45	48	47	41	51	50	47	51	46	7
C5	37	41	36	41	42	42	40	35	35	37	36	48	39	8
D1	4.5		6.2	5.7	5.1	4.7	0.6	2.6	2.1	3.6	3.1	2.9	3.7	3.4
D2	15	23	26	16	15	16	14	19	17	19	23	24	19	8
D3	43	45	40	44	44	45	43	45	48	49	46	57	46	8
D4	9.4	8.1	5.3	10	5.2	5.1	5	9.4	11	11	9.5	9.9	8.2	4.8
D5	11	10	9.2	8.5	9.6	9.3	8.7	12	13	13	13	15	11	4

Table 5 Chemical characterisation of the extracts of collected nitrate pollution sources ($L\ S^{-1} = 10$, the WWTP effluent was measured directly)

Name	Source Type	Sampling location	NH ₄ mg N L ⁻¹	NO ₃ mg N L ⁻¹	NO ₂ mg N L ⁻¹	N _{tot} mg N L ⁻¹	B μg L ⁻¹	N _{tot} /B
NPK 14-7-17	Mineral fertilizer	Single source of NO ₃	7600	5800	<0.15	13000	13900	940
NPK 15-5-20	Mineral fertilizer		10000	6300	<0.15	15000	14400	1040
Fumeterre	Organic/mineral fertilizer	Multiple sources of NO ₃	20	45	0.8	160	380	420
Orgaveg	Organic/mineral fertilizer		270	0.005	—	630	1300	490
Ammonium nitrate 27%	Mineral fertilizer		14000	5300	<0.15	24000	20	1200000
NPK 13-13-21	Mineral fertilizer		—	—	—	—	—	—
NPK 18-46	Mineral fertilizer		—	—	—	—	—	—
Urea 46%	Mineral fertilizer	Natural Denitrification	220	3.9	—	43000	70	614000
Cow manure	Organic fertilizer		12	1.5	0.8	44	150	300
Cow manure	Organic fertilizer		16	1.3	74	120	290	410
Cow manure-liquid	Organic fertilizer		0.5	2.5	<0.15	11	130	80
Horse manure	Organic fertilizer		0.5	0.23	<0.15	30	220	140
WWTP-dry mud	WWTP-dry mud		5.4	230	<0.15	810	220	3700
WWTP effluent	WWTP-effluent		0.9	1.4	<0.15	1.5	130	12
Ammonium nitrate 27%	Mineral fertilizer		17000	13000	<0.15	27000	30	900000
NPK 14-8-13	Mineral fertilizer		9800	3500	—	13000	2700	4800
Cow manure	Organic fertilizer		1.1	2.5	0.2	60	410	150

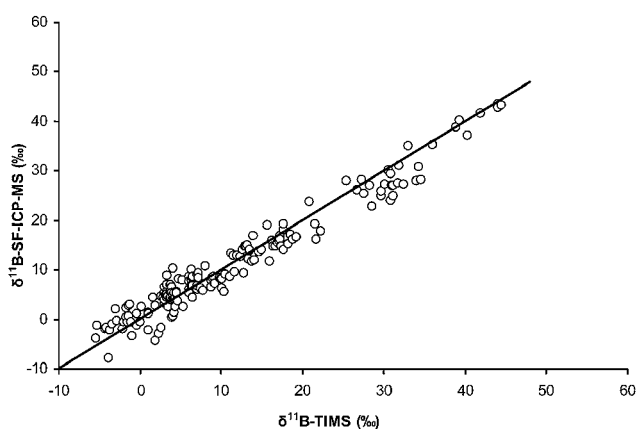


Fig. 3 Relation between $\delta^{11}\text{B}$ determined by both TIMS and SF-ICP-MS for all water samples. The solid line represents the 1 : 1 line ($y = x$), the calculated linear regression equation is $y = 0.90x + 0.86$ ($r = 0.98$, $n = 176$).

4.05045 ± 0.00130 (2σ , $n = 183$). The reproducibility of the $\delta^{11}\text{B}$ determination was $\pm 0.32\%$ (2σ). The mean value obtained on $\delta^{11}\text{B}$ of seawater was $39.21 \pm 0.31\%$ (2σ) ($n = 20$).

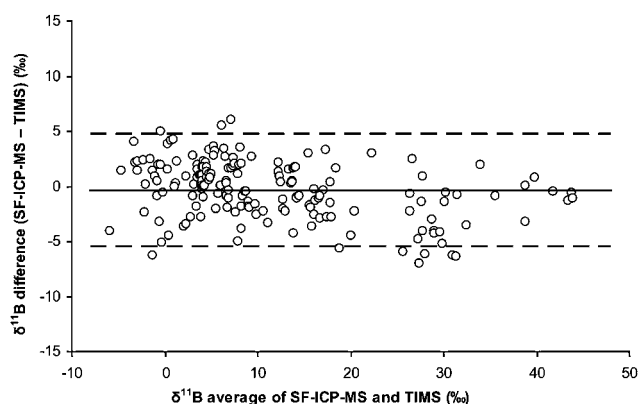


Fig. 4 Bland-Altman comparison of the TIMS and SF-ICP-MS $\delta^{11}\text{B}$ determinations of water samples collected during the ISONITRATE project. The solid line represents the average difference between both methods, while the dashed lines represent the 95% limits of agreement.

The individual $\delta^{11}\text{B}$ values measured with SF-ICP-MS and TIMS on the water samples are summarized in Table 6 and Table 7 respectively. There is a positive linear relationship between the

Table 6 $\delta^{11}\text{B}$ values (in ‰ vs. NBS951) measured with SF-ICP-MS during ISONITRATE sampling campaign

$\delta^{11}\text{B}$	10/07	11/07	12/07	01/08	02/08	03/08	04/08	06/08	08/08	10/08	11/08	12/08	Mean	$2^*\sigma$
A1	6.6	5.4	5	4.3	3.9	3.3	4.5	0.8	6.4	0.6	4.8	4.4	4.2	3.8
A2	4.4	4.4	8.3	7.9	7.7	5.4	7.9	3.4	2.6	2.5	8.6	6.4	5.8	4.6
A3	14.8	14.7	16	18.1	16.9	16.3	19.3	18.5	19	14	15.6	17.3	17	3.5
A4	8.5	7.9	10.7	6.5	7.3	8.3	8.4	9.6	9	8.2	9	9.5	8.6	2.2
B1	12.7	15.3	17	16.1	16.6	19.3	16	14.3	12.8	16.1	17.8	18	16	4.0
B2	22.7	24.9	27.6	26.9	27	24.9	25	30.8	31	27.9	28.2	25.1	27	5.0
C1	-1.2	4.3	4.4	4.9	1	2.8	-2.2	-0.9	1.3	3.7	4.5	3	2.1	5.0
C2	3.9	5.4	5.5	7.1	4.5	3.9	8.9	4.2	5.1	2.4	5.3	6.7	5.2	3.4
C3	4.1	7	4.1	5.3	5.5	4.9	10.2	5.9	8.1	6.1	9.9	10.6	6.8	4.7
C4	3	2.3	-0.6	0.3	0.5	-1.9	-0.6	3.6	2.7	-0.5	2.5	0.7	1.0	3.5
C5	-0.3	-1.1	-2.3	-1.8	-2	-3.9	-1.3	-3.9	2	-3.4	-0.5	0.9	-1.5	3.7
D1	27.2	—	25.3	26	25.7	27.3	27.9	29.4	29.5	26.9	27.3	31.7	28	3.8
D2	41.5	28.3	23.8	38.9	37.2	35.2	40.2	45.4	42.8	43.4	35	39.7	38	12.6
D3	12.1	14.9	13.9	15	14.6	13.7	14	14.8	17	13.8	14	14.4	14	2.3
D4	6.9	8.5	13.6	14.2	13.4	9.5	12.9	10.2	8.1	9.4	11.8	12.9	11	4.9
D5	8.6	4.5	6.8	6.7	6.1	6.8	9.3	8.3	8.4	5.8	6.4	9.4	7.3	3.0

Table 7 $\delta^{11}\text{B}$ values (in ‰ vs. NBS951) measured with TIMS during ISONITRATE sampling campaign

$\delta^{11}\text{B}$	10/07	11/07	12/07	01/08	02/08	03/08	04/08	06/08	08/08	10/08	11/08	Mean	$2*\sigma$
A1	3.9	3.3	3.3	3.8	3.1	3.1	1.6	2.3	3.1	4.0	3.9	3.2	1.4
A2	3.4	4.3	6.4	6.3	6.1	6.1	5.2	3.9	3.4	5.3	6.1	5.1	2.4
A3	16.7	16.4	16.3	17.7	17.2	17.2	17.7	17.4	15.6	17.7	16.9	17	1.3
A4	9.0	8.8	8.0	8.8	9.2	9.8	8.9	10.1	7.1	10.1	10.6	9.1	2.0
B1	12.4	18.2	18.6	18.8	19.3	21.5	17.2	16.0	11.9	21.7	22.3	18	6.9
B2	28.6	30.9	31.7	28.3	31.0	29.7	31.1	34.3	31.9	34.1	34.6	32	4.3
C1	-0.4	3.3	2.9	3.2	1.1	1.9	1.0	1.9	1.1	4.7	3.6	2.2	2.9
C2	4.1	4.6	3.7	3.4	2.6	3.8	3.4	2.6	4.5	4.3	3.0	3.6	1.4
C3	4.2	3.8	4.0	4.2	4.5	4.1	4.1	4.2	4.7	6.0	6.4	4.6	1.7
C4	-1.3	-1.6	-1.5	-1.7	-1.4	-2.1	-2.0	-0.4	-1.4	0.1	0.2	-1.2	1.6
C5	-2.8	-3.4	-3.7	-4.1	-4.2	-5.3	-5.3	-3.9	-3.0	-1.0	-1.1	-3.4	2.9
D1	—	—	27.5	26.7	29.8	30.2	25.4	30.6	30.9	31.2	32.4	29	4.7
D2	42.0	27.4	20.8	38.9	40.4	36.1	39.4	44.1	44.1	44.5	33.1	37	15.1
D3	13.3	13.2	13.5	13.3	13.0	13.5	13.5	13.8	14.0	14.7	14.9	14	1.2
D4	—	11.2	14.7	12.6	11.2	11.7	11.6	10.4	9.9	12.8	14.1	12	3.1
D5	6.5	6.5	6.4	7.1	7.1	6.6	7.2	7.7	7.3	7.8	7.5	7.1	1.0

$\delta^{11}\text{B}$ values measured by the two methods (Fig. 3, $y = 0.90x + 0.86$) with a high correlation coefficient ($r = 0.98$). The average difference in $\delta^{11}\text{B}$ values measured by TIMS and SF-ICP-MS is -0.3‰ (Fig. 4) and there is no tendency for the difference to vary with variation of isotope ratios. The Kolmogorov-Smirnov normality test showed that differences of the $\delta^{11}\text{B}$ as determined by TIMS and SF-ICP-MS ($p = 0.23$) were normally distributed. The limits of agreement within which 95% of the differences expected are calculated according to the Bland-Altman technique as -5.4 and $+4.8\text{‰}$.

The consequences of the difference in analytical precision of $\delta^{11}\text{B}$ measurements with TIMS and SF-ICP-MS with respect to the interpretation to distinguish nitrate sources, is discussed for the complex case (C1–C5) and the denitrification case (D1–D5).

Complex case. In Fig. 5A, the $\delta^{11}\text{B}$ values measured with TIMS versus $1/\text{B}$ for the water samples collected at the complex case are compared to the ranges measured for local nitrate pollution sources. Based on the TIMS results, surface waters (C1 and C2) together with groundwater C3 yield similar $\delta^{11}\text{B}$ values, slightly positive ($\delta^{11}\text{B} = 2$ to 6‰), whereas both C4 and C5 (groundwaters)

were depleted in $\delta^{11}\text{B}$. When plotting $\delta^{11}\text{B}$ versus $1/\text{B}$, three different scenarios appear: (i) samples C1, C2 and C3 define a negative trend according to $\delta^{11}\text{B} = -129.8 * (1/\text{B}) + 7.9$ ($n = 33$, $R^2 = 0.75$). This trend characterises potentially the input of an organic fertilizer (with a $\delta^{11}\text{B}$ around 8‰), in agreement with the local measured manures and the $\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$ data;²⁶ (ii) C4 samples present a very homogeneous signature over the hydrological cycle. This sampling site is affected by mineral fertilizer/wastewater, with wastewater being probably more realistic considering the depleted $\delta^{11}\text{B}$ of the pollution source ($\delta^{11}\text{B} \sim -6\text{‰}$) and the characterization of the local sources (Table 8); (iii) C5 samples present the most negative $\delta^{11}\text{B}$ signatures, in agreement with the signatures of the WWTP effluents (locally identified).⁴

Based on the SF-ICP-MS measurements as shown in Fig. 5 B a negative trend according to $\delta^{11}\text{B} = -195.8 * (1/\text{B}) + 10.8$ ($n = 33$) with a worse correlation ($R^2 = 0.34$) is found. The results are visually more scattered and there is overlap between the C3, C4 and C5 measurement areas. In contrast to the TIMS data, no trend to a distinct potential nitrate pollution source can be characterized.

Table 8 Comparison of $\delta^{11}\text{B}$ (in ‰ vs. NBS951) values measured by both TIMS and SF-ICP-MS on leachates from NO_3 sources

Name	Type	Sampling location	B $\mu\text{g L}^{-1}$	$\delta^{11}\text{B}$ (TIMS) ‰	$\delta^{11}\text{B}$ (SF-ICP-MS) ‰
NPK 14-7-17	Mineral fertilizer	Single source of NO_3	13900	0.2	0.8
NPK 15-5-20	Mineral fertilizer		14400	0.4	1.6
Fumeterre	Organic/mineral fertilizer		380	9	13.6
Orgaveg	Organic/mineral fertilizer	Multiple sources of NO_3	1300	22.6	20.8
Ammonium nitrate 27%	Mineral fertilizer		20	-1.4	-1
NPK 13-13-21	Mineral fertilizer		—	24.6	—
NPK 18-46	Mineral fertilizer		—	14.1	—
Urea 46%	Mineral fertilizer		70	20.6	20.6
Cow manure	Organic fertilizer		150	10.9	11.1
Cow manure	Organic fertilizer		290	6.2	7.8
Cow manure-liquid	Organic fertilizer	130	5.8	5.7	
Horse manure	Organic fertilizer	220	17.4	14	
WWTP-dry mud	WWTP-dry mud	220	-3.5	-4.2	
WWTP effluent	WWTP-effluent	130	-2.8	-0.3	
Ammonium nitrate 27%	Mineral fertilizer	Natural Denitrification	30	—	-2.7
NPK 14-8-13	Mineral fertilizer		2700	—	7.2
Cow manure	Organic fertilizer		410	8	8.2

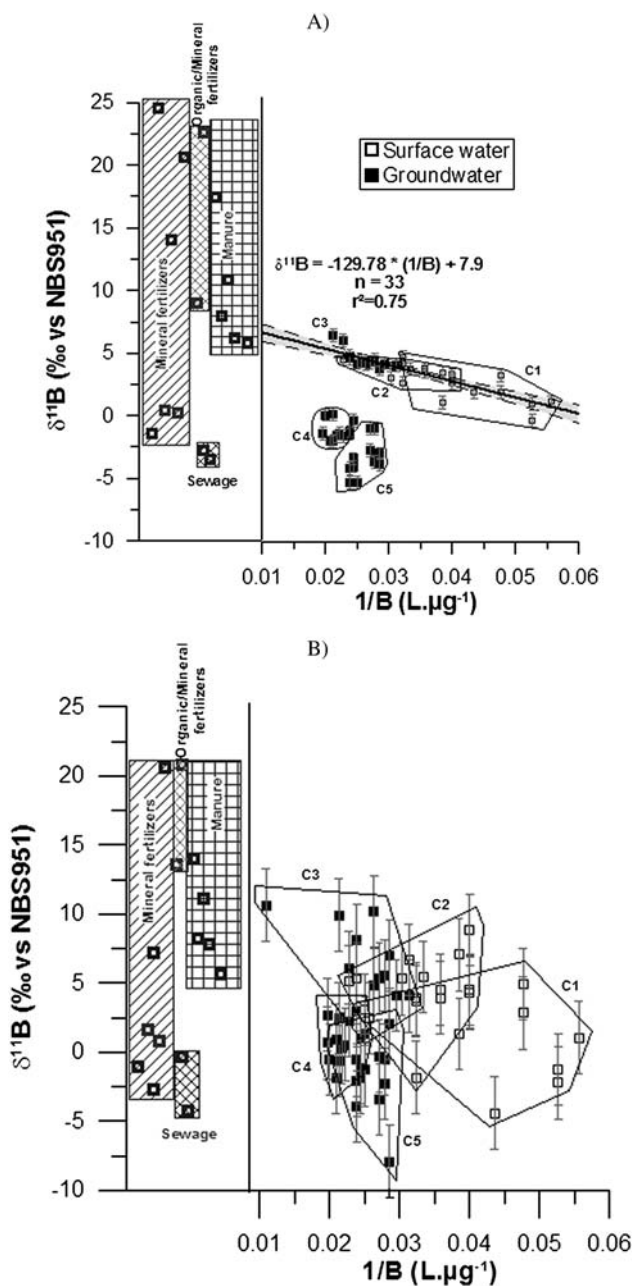


Fig. 5 Comparison of the identification of sources of nitrate pollution by coupling the reciprocal of B content and $\delta^{11}\text{B}$ values of the water samples from the multiple sources case study. The boxes on the left represent the range of the measured $\delta^{11}\text{B}$ values of the different nitrate pollution sources. $\delta^{11}\text{B}$ values are determined by A) TIMS and B) SF-ICP-MS (error bars represent the 95% confidence limits).

These findings illustrate that end-users have to keep in mind that retrieving precise information on the identification of pollution sources from $\delta^{11}\text{B}$ values requires reaching the best precision and accuracy possible.

Denitrification case. On the other hand, as presented in Fig. 6 A and B for the denitrification case, both analytical methods come to a same conclusion when trying to decipher contributions between sources with really distinct $\delta^{11}\text{B}$ signatures: (i) the

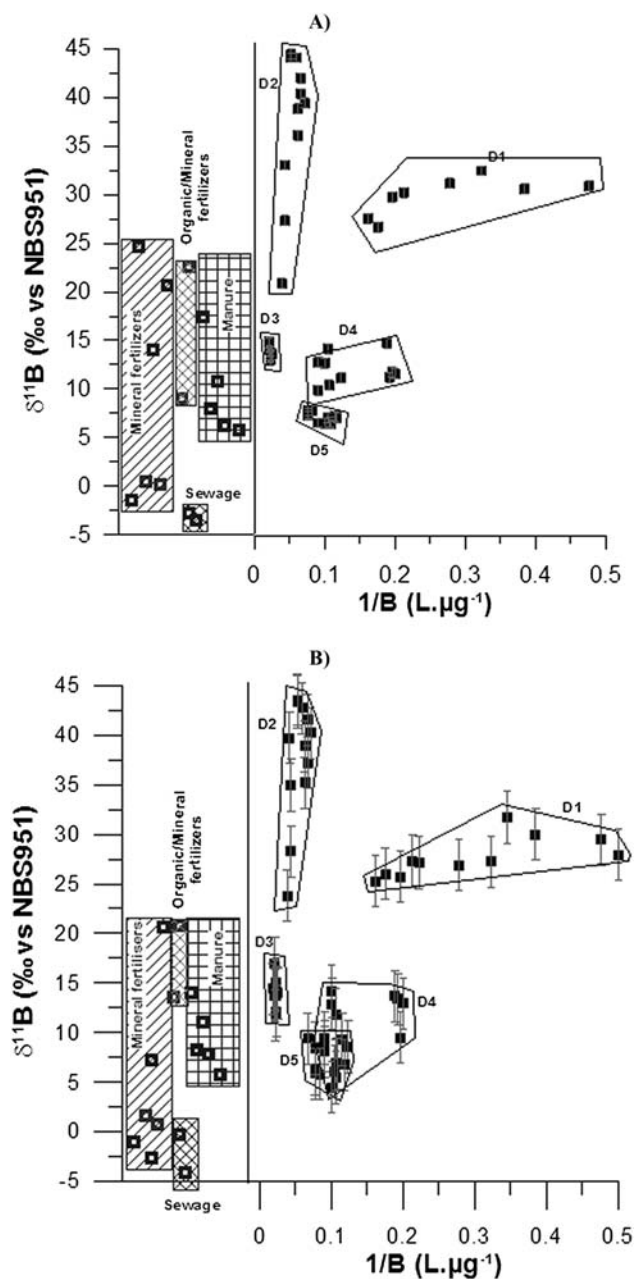


Fig. 6 Comparison of the identification of sources of nitrate pollution by coupling the reciprocal of B content and $\delta^{11}\text{B}$ values of the water samples from the natural denitrification case study. The boxes on the left represent the range of the measured $\delta^{11}\text{B}$ values of the different nitrate pollution sources. $\delta^{11}\text{B}$ values are determined by A) TIMS and B) SF-ICP-MS (error bars represent the 95% confidence limits).

signature of D1: values centred around 30‰, close to the value expected for boron from natural rainwater origin; (ii) D2 (*i.e.* the samples with the highest NO_3 concentrations, presumed to represent the closest agreement with the input of pollution source), displays large $\delta^{11}\text{B}$ variations (from 20 to more than 40‰) together with a large variation of boron concentrations (14 to $27 \mu\text{g L}^{-1}$). D2 reaches values that are higher (>40‰) than all the measured pollution sources. In light of the available results it is not possible to conclude if other nitrate sources are present or

other processes occur (*i.e.* interactions with clay minerals); (iii) D3 to D5 display intermediate boron isotopic compositions ($5 < \delta^{11}\text{B} < 15\%$) that may correspond to the mixing of different pollution sources including mineral fertilizer, manure and sewage.

Comparison $\delta^{11}\text{B}$ measurement SF-ICP-MS and TIMS on source material

Table 8 shows comparable results between $\delta^{11}\text{B}$ values measured with TIMS and SF-ICP-MS on the leachates of the different pollution sources (correlation coefficient of 0.96, $y = 0.88x + 1.10$; due to limited results ($n = 13$) no further Bland-Altman statistics were performed). The extracted boron and nitrate contents (Table 5) are in line with previous reported results on manure and mineral fertilizers.^{31,32} These results show the method robustness and the ease of using one single SF-ICP-MS method for $\delta^{11}\text{B}$ measurements of both water samples and leachates of the source materials.

An overview of literature data of $\delta^{11}\text{B}$ in combination with the data of source materials collected during the ISONITRATE project are summarised in Fig. 1. The measured $\delta^{11}\text{B}$ values are in agreement with previous published data, but it should be stressed that for interpretation of the multi-isotopic approach accurate and precise $\delta^{11}\text{B}$ data of local source materials need to be included in the monitoring program. As an example the mineral fertiliser NPK 13-13-21, collected in the multiple sources of nitrate case, showed based on literature unexpected high $\delta^{11}\text{B}$ value (NPK 13-13-21: $\delta^{11}\text{B} = +24.6\%$; Table 8). This may indicate that the origin of boron in this specific mineral fertiliser material is different than previously measured mineral fertilisers.

Conclusions

During the last decade, the number of isotope systems currently being explored in new investigations and (routine) application fields has exploded. As both the number of techniques being developed and the number of laboratories making these measurements increases, it is important to evaluate the fit-for-purpose of measurement techniques for (routine) application.

An evaluation of boron isotope compositions measured in parallel by both SF-ICP-MS and TIMS was performed in the ISONITRATE project. Based on the results of the different case studies it is shown that end-users have to keep in mind that retrieving precise information on the identification of pollution sources from $\delta^{11}\text{B}$ values requires reaching the best analytical precision and accuracy possible. However for some cases, *e.g.* trying to decipher contributions between sources with really distinct $\delta^{11}\text{B}$ signatures, SF-ICP-MS has shown to come to the same conclusions. The ease of use, rapidity and availability of SF-ICP-MS on one hand and the observed variability in $\delta^{11}\text{B}$ in ground- and surface water on the other, demonstrates that using SF-ICP-MS as an isotopic screening method would promote the use of isotopic methodology in WFD monitoring programs.

Acknowledgements

This work is supported by the EU LIFE Project (Number LIFE06 ENV/F/000158).

References

- 1 H. E. Gäbler and A. Bahr, *Chem. Geol.*, 1999, **156**, 323.
- 2 S. Eisenhut, K. G. Heumann and A. Vengosh, *Fresenius J. Anal. Chem.*, 1996, **354**, 903.
- 3 S. Barth, *Water Res.*, 1998, **32**, 685.
- 4 D. Widory, E. Petelet-Giraud, P. Négrel and R. Ladouche, *Environ. Sci. Technol.*, 2005, **39**, 539.
- 5 B. Chetelat and J. Gaillardet, *Environ. Sci. Technol.*, 2005, **39**, 2486.
- 6 J. D. Mather and N. C. Porteous, *Appl. Geochem.*, 2001, **16**, 821.
- 7 R. L. Bassett, P. M. Buszka, G. R. Davidson and D. Chong-Diaz, *Environ. Sci. Technol.*, 1995, **29**, 2915.
- 8 N. Demuth and K. G. Heumann, *J. Anal. At. Spectrom.*, 1999, **14**, 1449.
- 9 A. Vengosh, S. Barth, K. G. Heumann and S. Eisenhut, *Acta Hydrochim. Hydrobiol.*, 1999, **27**, 416.
- 10 S. Eisenhut and K. G. Heumann, *Fresenius J. Anal. Chem.*, 1997, **359**, 375.
- 11 B. Chetelat, J. Gaillardet and R. Freyrier, *Appl. Geochem.*, 2009, **24**, 810.
- 12 F. Vanhaecke, L. Balcaen, P. Taylor, *Inductively Coupled plasma spectrometry and its application*, second edition, 2006, 160–215.
- 13 K. G. Heumann, S. M. Gallus, G. Rädlinger and J. Vogl, *J. Anal. At. Spectrom.*, 1998, **13**, 1001.
- 14 M. E. Weiser and J. B. Schwieters, *Int. J. Mass Spectrom.*, 2005, **242**, 97.
- 15 J. Aggarwal and et al, *J. Anal. At. Spectrom.*, 2009, **24**, 825.
- 16 S. A. Kasemann, D. N. Schmidt, J. Bijma and G. L. Foster, *Chem. Geol.*, 2009, **260**, 138.
- 17 J. R. Encinar, J. I. Garcia Alonso, A. Sanz-Medel, S. Main and P. J. Turner, *J. Anal. At. Spectrom.*, 2001, **16**, 315.
- 18 S. F. Boulyga, I. Segal, T. I. Platzner, L. Halicz and J. S. Becker, *Int. J. Mass Spectrom.*, 2002, **218**, 245.
- 19 D. C. Gregoire, *Anal. Chem.*, 1987, **59**, 2479.
- 20 D. C. Gregoire, *J. Anal. At. Spectrom.*, 1990, **5**, 623.
- 21 A. Al-Ammar, E. Reitznerova and R. M. Barnes, *Spectrochim. Acta, Part B*, 2000, **55**, 1861.
- 22 P. P. Coetzee and F. Vanhaecke, *Anal. Bioanal. Chem.*, 2005, **383**, 977.
- 23 J. K. Aggarwal, D. Sheppard, K. Mezger and E. Pernicka, *Chem. Geol.*, 2003, **199**, 331.
- 24 J. K. Aggarwal, K. Mezger, E. Pernicka and A. Meixner, *Int. J. Mass Spectrom.*, 2004, **232**, 259.
- 25 <http://www.eea.europa.eu/themes/water/status-and-monitoring/water-framework-directive-and-monitoring>.
- 26 ISONITRATE, <http://isonitrate.brgm.fr/index.htm>.
- 27 <http://www.vmm.be/water/toestand-watersystemen/waar-meten-wehet-water>.
- 28 I. J. Allan, G. A. Mills, B. Vrana, J. Knutsson, A. Holmberg, N. Guiges, S. Laschi, A. M. Fouillac and R. Greenwood, *TrAC, Trends Anal. Chem.*, 2006, **25**, 704.
- 29 S. Barth, *Geol. Rundsch.*, 1993, **82**, 640.
- 30 T. B. Coplen and et al, *Pure Appl. Chem.*, 2002, **74**, 1987.
- 31 S. C. Komor, *J. Environ. Qual.*, 1997, **26**, 1212.
- 32 D. Widory, W. Kloppmann, L. Chery, J. Bonnin, H. Rochdi and J. L. Guinamant, *J. Contam. Hydrol.*, 2004, **72**, 165.
- 33 D. Xue, J. Botte, B. de Baets, F. Accoe, A. Nestler, P. Taylor, O. Van Cleemput, M. Berglund and P. Boeckx, *Water Res.*, 2009, **43**, 1159.
- 34 F. Vanhaecke, L. Moens and R. Dams, *Anal. Chem.*, 1996, **68**, 567.
- 35 J. Gaillardet and C. J. Allègre, *Earth Planet. Sci. Lett.*, 1995, **136**, 665.
- 36 T. Ishikawa and E. Nakamura, *Anal. Chem.*, 1990, **62**, 2612.
- 37 A. J. Spivack and J. M. Edmond, *Anal. Chem.*, 1986, **58**, 31.
- 38 A. J. Spivack, M. R. Palmer and J. M. Edmond, *Geochim. Cosmochim. Acta*, 1987, **51**, 1939.
- 39 R. Gonfiantini, S. Tonarini, M. Gröning, A. Adorni-Braccesi, A. S. Ammar, M. Astner, S. Bächler, R. M. Barnes, R. L. Bassett, A. Cocherie, A. Deyhle, A. Dini, G. Ferrara, J. Gaillardet, J. Grimm, C. Guerrot, U. Krähnenbühl, G. Layne, D. Lemarchand, A. Meixner, D. J. Northington, M. Pennisi, E. Reitznerová, I. Rodushkin, N. Sugiura, R. Surberg, S. Tonn, M. Wiedenbeck, S. Wunderli, Y. Xiao and T. Zack, *Geostand. Geoanal. Res.*, 2003, **27**, 41.
- 40 S. Tonarini, M. Pennisi, A. Adorni-Braccesi, A. Dini, G. Ferrara, R. Gonfiantini, M. Wiedenbeck and M. Gröning, *Geostand. Geoanal. Res.*, 2003, **27**, 421.
- 41 D. Lemarchand, J. Gaillardet, C. Göpel and G. Manhès, *Chem. Geol.*, 2002, **182**, 232.