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Nitrate source identification using its isotopic ratios in combination with a Bayesian isotope mixing model in the Baltic Sea

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Abstract

Nitrate (NO_3^-) is the major nutrient responsible for coastal eutrophication worldwide and its production is related to intensive food production and fossil-fuel combustion. In the Baltic Sea NO_3^- inputs have increased four-fold over the last decades and now remain constantly high. NO_3^- source identification is therefore an important consideration in environmental management strategies. In this study focusing on the Baltic Sea, we used a method to estimate the proportional contributions of NO_3^- from atmospheric deposition, N_2 fixation, and runoff from pristine soils as well as from agricultural land. Our approach combines data on the dual isotopes of NO_3^- (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) in winter surface waters with a Bayesian isotope mixing model (Stable Isotope Analysis in R, SIAR). Based on data gathered from 46 sampling locations over the entire Baltic Sea, the majority of the NO_3^- in the southern Baltic was shown to derive from runoff from agricultural land (30–70 %), whereas in the northern Baltic, i.e., the Gulf of Bothnia, NO_3^- originates from nitrification in pristine soils (47–100 %). Atmospheric deposition accounts for only a small percentage of NO_3^- levels in the Baltic Sea, except for contributions from northern rivers, where the levels of atmospheric NO_3^- are higher. An additional important source in the central Baltic Sea is N_2 fixation by diazotrophs, which contributes 31–62 % of the overall NO_3^- pool at this site. The results obtained with this method are in good agreement with source estimates based upon δ^{15}N values in sediments and a three-dimensional ecosystem model, ERGOM. We suggest that this approach can be easily modified to determine NO_3^- sources in other marginal seas or larger near-coastal areas where NO_3^- is abundant in winter surface waters when fractionation processes are minor.

1 Introduction

Throughout the world, anthropogenic reactive N currently exceeds natural production (Galloway et al., 2003; Gruber and Galloway, 2008). Consequently, nitrogen (N) fluxes have doubled in recent years, which has strongly impacted the marine N cycle and ecosystem health, both at regional and global scales. In coastal ecosystems, the adverse effects of these excess N loads include eutrophication, hypoxia, loss of biodiversity, and habitat destruction (Galloway et al., 2003; Villnäs et al., 2013). For the shallow, brackish, semi-enclosed Baltic Sea, where intense anthropogenic nutrient loadings have been documented since the 1950s (Elmgren, 2001), riverine and atmospheric nutrient inputs are now at least four-fold higher than a century ago, when anthropogenic influences was low (Schernewski and Neumann, 2005; Stålnacke et al., 1999). Furthermore, cyanobacterial blooms, which can fix N_2, and thus add nutrients to the surface waters are regular large scale phenomenon each summer (Finni et al., 2001; Vahtera et al., 2007) and the overall increase in nutrient input has supported the expansion of hypoxic zones (Conley et al., 2009, 2011).

A main component of the N pool and the one most readily available is nitrate (NO_3^-) (Nestler et al., 2011; Vitousek et al., 1997), which derives from a wide variety of sources. These can be identified by analysis of the N and oxygen (O) isotopes (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) since the isotopic ratios of NO_3^- from different sources fall within distinct ranges (Kendall, 1998; Kendall et al., 2007). For example, NO_3^- inputs from forested catchments can be discriminated from those coming from agricultural runoff, and the NO_3^- signature of microbial nitrification differs from that of atmospheric deposition (Kendall, 1998; Kendall et al., 2007; Mayer et al., 2002). Source attribution is, however, complicated by N-transformation processes such as denitrification, nitrification, and assimilation, each of which gives rise to significant isotope fractionation. Since heavier isotopes are sequestered more slowly than lighter ones, the reaction product will be isotopically depleted compared to the original NO_3^- source (Kendall, 1998). Alterations of isotope values because of microbial fractionation processes can be minimized by collecting the samples in winter, when low water temperatures reduce microbial activity (Pfenning and McMahon, 1997).

Nonetheless, source attribution is still complicated when there are more than three sources but only two isotopes that describe them (Fry, 2013). SIAR (Stable Isotope

Analysis in R), a Bayesian isotope mixing model originally developed to infer diet composition from the stable isotope analysis of samples taken from consumers and their food sources (Moore and Semmens, 2008), was already successfully applied for NO_3^- source identification. Xue et al. (2012, 2013) were able to estimate the proportional contributions of five potential NO_3^- sources in a small watershed in Flanders (Belgium). Based on their determinations of the isotopes of nitrogen and oxygen they could show that manure and sewage were the major sources of NO_3^-.

The N cycle of the Baltic Sea follows the typical seasonal development of temperate oceans. Thus, the NO_3^- pool present in the surface waters in spring originates from the previous growth season and is consumed during the onset of the phytoplankton spring bloom, in February/March. In the central Baltic Sea, atmospheric deposition and N_2 fixation are the major N sources, whereas in coastal areas riverine discharge dominates (Radtke et al., 2012; Voss et al., 2011). Yet, to what extent the various NO_3^- sources add to the overall pool of NO_3^- in the Baltic as a whole is still a matter of debate. In this study, a source attribution for four major sources is presented. Taking the Baltic Sea as an example we will show, that the use of the isotopic composition of NO_3^- (δ^{15}N-NO_3^- and δ^{18}O-NO_3^-) in combination with SIAR can be used elsewhere for source identification on an ecosystem scale level.

2 Material and methods

2.1 Field sampling

Surface water samples from the Baltic Sea were collected in February 2008 ($n = 23$) and 2009 ($n = 17$) aboard the R/V *Alkor* and in November 2011 ($n = 1$) aboard the R/V *Meteor* using a Seabird CTD system with attached water bottles. Samples from the Nemunas River (55°18′5.5 N, 21°22′53.9 E; 55°41′25.6 N, 21°7′58.4 E; $n = 4$) and Kalix River (65°56′4.2 N, 22°53′9.2 E; $n = 1$) (Fig. 1) were taken between November 2009 and February 2010. Values for NO_3^- in which atmospheric deposition was the source were obtained from wet deposition samples collected at three stations around the Baltic Sea: Warnemünde, Germany (54°10′ N, 12°5′ E,); Majstre, Sweden (57°30′ N, 18°31′ E); and Sännen, Sweden (56°13′ N, 15°17′ E) from December 2009 until February 2010 (Table 2). In Warnemünde, precipitation was collected on an event basis using a sampler consisting of a plastic funnel (diameter: 24 cm) connected to a 1 L polyethylene bottle. At the two Swedish stations, rainwater was sampled monthly by the Swedish Environmental Research Institute (IVL) as part of the Swedish national long-term monitoring program. Here, the sampler consisted of a plastic funnel (diameter 20.3 cm) connected to an 8-L polyethylene bag. All samples were filtered through pre-combusted Whatman GF/F filters (4 h at 400 °C) and stored frozen until further analysis.

2.2 Nutrient concentrations and dual isotope analysis of NO_3^-

Samples were analyzed following a standard protocol for the determination of NO_3^- and nitrite (NO_2^-) (Grasshoff et al., 1983); the precision of the method is ±0.02 $\mu mol\,L^{-1}$. Dual isotope analysis of NO_3^- ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) was carried out using the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001), in which NO_3^- and NO_2^- are quantitatively converted to nitrous oxide (N_2O) by *Pseudomonas aureofaciens* (ATTC 13985), a bacterial strain that lacks N_2O reductase activity. In brief, N_2O is removed from the sample vials by purging with helium and then concentrated and purified in a GasBench II prior to analysis with a Delta Plus mass spectrometer (ThermoFinnigan). NO_2^- was not removed since its concentrations were always less than 2 % (Casciotti et al., 2007). N and O isotope measurements of roughly 30 % of the samples were replicated in separate batch analyses. Two international standards, IAEA-N3 ($\delta^{15}N = 4.7$ ‰ vs. N_2; $\delta^{18}O$ 25.6 ‰ vs. VSMOW) and USGS 34 ($\delta^{15}N - 1.8$ ‰ vs. N_2; $\delta^{18}O - 27.9$ ‰ vs. VSMOW) (Böhlke et al., 2003), were measured with each batch of samples. Samples with NO_3^-/NO_2^- concentrations as low as 1 $\mu mol\,L^{-1}$ were analyzed. The sample size for the actual stable isotope measurements was 20 nmol for samples with concentrations > 3.5 µmol L^{-1} and 10 nmol for those with concentrations < 3.5 µmol L^{-1}. Isotope values were corrected after Sigman et al. (2009) for δ^{18}O-NO_3^-; single point correction was referred to IAEA-N3 for δ^{15}N-NO_3^-. The precision was < 0.2 ‰ for δ^{15}N and < 0.6 ‰ for δ^{18}O. Together with the samples, a culture blank was analyzed to which no sample was added. The isotope ratios are reported using the delta notation in units of per mil (‰).

2.3 NO_3^- sources

To estimate the contribution of different NO_3^- sources, two isotopes δ^{15}N-NO_3^- and δ^{18}O-NO_3^- ($j = 2$) from the four major NO_3^- sources: (1) atmospheric deposition, (2) runoff from pristine soils, (3) runoff from agricultural land and (4) N_2 fixation were applied (Table 1). In this context, N_2 fixation was defined as NO_3^- originating from the degradation and remineralization of nitrogen fixers and therefore carried their low isotopic signal. Thus, for NO_3^- from N_2 fixation, δ^{15}N values of ~ −2 to 0 ‰ were assumed, since N_2 fixation produces organic material that is only slightly N depleted against air nitrogen (Carpenter et al., 1999, 1997; Montoya et al., 2002). The δ^{18}O values were estimated to be between −14.3 and −6.7 ‰, based on the assumption that newly produced NO_3^- should be 0.7–8.3 ‰ lower than the δ^{18}O of seawater (Buchwald and Casciotti, 2010), which according to Froehlich et al. (1988) is −6 ‰ for the central Baltic Sea.

To expand the dataset, we included NO_3^- isotope data from river water samples, ground water samples, and samples from tile drain outlets collected in 2003 and published in Deutsch et al. (2006). In that study, the Warnow River ($n = 2$) was sampled twice, in January and February 2003. These sources were likewise sampled in winter, since marked seasonal shifts in the isotopic composition of NO_3^- can occur due to shifts in the origins of the sources (Knapp et al., 2005). Samples from tile drain outlets were used to represent NO_3^- from agricultural runoff and were obtained from the catchment of the Warnow River, whose waters are strongly influenced by agricultural land use

(Pagenkopf, 2001). Groundwater samples were used as the source of NO_3^- from pristine land (Deutsch et al., 2006). Their δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values significantly differed from those of agricultural runoff ($p < 0.05$) but were similar to the values of other areas, such as Biscuit Brook (Burns et al., 2009) and the San River (Koszelnik and Gruca-Rokosz, 2013), where pristine soils were sampled. For these samples, dual isotopes of NO_3^- were analyzed according to Silva et al. (2000). In this method, NO_3^- is chemically converted via anion exchange resins to $AgNO_3^-$ and the δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values are measured via pyrolysis and isotopic ratio mass spectrometry (for a detailed description, see Deutsch et al., 2006). A normal distribution of the isotopic data from the four sources was confirmed by applying the Shapiro–Wilk normality test.

Six regions within the catchment of the Baltic Sea were investigated for their potential NO_3^- sources (Fig. 1). According to the topography of the Baltic Sea, the samples were assigned to four major areas: Western Baltic Sea, Baltic Proper, Gulf of Finland, and Gulf of Bothnia. Additionally, three rivers differing in their degree of anthropogenic impact were included in this study and divided into two groups: northern and southern rivers. Rivers with high nutrient loads drain mainly into the southern Baltic Proper and were represented here by the Nemunas and Warnow Rivers, whose NO_3^- concentrations in winter can be as high as 260 μmol L^{-1} (Deutsch et al., 2006; Pilkaityte and Razinkovas, 2006). The Gulf of Bothnia receives large amounts of fresh water from rivers represented by the Kalix River. These rivers drain mainly pristine, forested land and have maximum NO_3^- concentrations of around 20 μmol L^{-1} (Sferratore et al., 2008).

2.4 SIAR mixing model

The applied mixing model is described by the following equations:

$$X_{ij} = \sum_{k=1}^{K} p_k (s_{jk} + c_{jk}) + \varepsilon_{ij} \tag{1}$$

$$s_{jk} \sim N(\mu_{jk}, \varpi^2_{jk}) \tag{2}$$

$$c_{jk} \sim N(\lambda_{jk}, \tau^2_{jk}) \tag{3}$$

$$\varepsilon_{ij} \sim N(0, \sigma^2_j) \tag{4}$$

where X_{ij} is the observed isotope value j of the mixture i; $i = 1,2,3,\ldots,I$ are individual observations; and $j = 1,2,3,\ldots,J$ are isotopes. s_{jk} is the source value k of isotope j ($k = 1,2,3,\ldots,K$) and is normally distributed, with a mean of μ_{jk} and a standard deviation of ϖ_{jk}. p_k is the proportion of source k that needs to be estimated by the model. c_{jk} is the fractionation factor for isotope j on source k and is normally distributed, with a mean of λ_{jk} and a standard deviation of τ_{jk}. ε_{ij} is the residual error representing additional unquantified variations between mixtures and is normally distributed, with a mean of 0 and a standard deviation of σ_j. Detailed descriptions of the model can be found in Jackson et al. (2009), Moore and Semmens (2008), and Parnell et al. (2010). As noted above, by collecting samples between November and February we minimized the influence of fractionation processes such as assimilation and denitrification that can alter the isotopic signal of NO_3^-. Therefore in Eq. (1) we assumed that $c_{jk} = 0$.

Two different runs of the SIAR model were performed. In the first, for the Western Baltic Sea, Baltic Proper, and Gulf of Finland, all four sources were included in the calculation. In the second, for the Gulf of Bothnia, the southern rivers, and the northern rivers, N_2 fixation as a potential NO_3^- source was excluded since in these areas there is no N_2 fixation by diazotrophs because the Gulf of Bothnia is phosphorus limited, in contrast to the Baltic Proper (Graneli et al., 1990).

3 Results and discussion

3.1 NO_3^- in the Baltic Sea

Winter (November–February) surface NO_3^- concentrations ranged from a minimum of 2.6 µmol L^{-1} in the open Baltic Sea to a maximum of 259 µmol L^{-1} close to the estuaries of the most nutrient-rich rivers, i.e., the Nemunas and Warnow Rivers (Fig. 2). These concentrations are typical for eutrophied systems and similar amounts have been reported from the Chesapeake Bay and the coastal areas of the North Sea (Dähnke et al., 2010; Francis et al., 2013). The concentrations of nutrients in the subbasins of the Baltic Sea reflect the densities of the human populations in the vicinity of the adjacent sub-catchments. Thus, in the near-coastal area of the southern Baltic Proper, NO_3^- concentrations were higher than in the northern parts, since the catchment areas of Germany, Poland, and the Baltic States are much more densely populated ($>$ 500 inhabitants km^{-2}) and the land is intensively used for agricultural purposes. The northern regions are dominated by boreal forests and less populated ($<$ 10 inhabitants km^{-2}) (Lääne et al., 2005; Stepanauskas et al., 2002; Voss et al., 2011). Consequently, for the southern Baltic Proper a relationship between fluvial NO_3^- loads and NO_3^- concentrations in coastal waters could be established that indicates a direct impact of riverine nutrients on coastal waters (Voss et al., 2011; HELCOM, 2009). However, there was no similar correlation between riverine N loads and nutrient concentrations either for the coastal areas of the Gulf of Bothnia or for the open waters of the Baltic Proper (Voss et al., 2011). The Gulf of Bothnia is the only sub-basin in which the effects of eutrophication are so far minor, although Lundberg et al. (2009) and Conley et al. (2011) reported a degradation in the water quality from north to south and from the outer to the inner coastal area of the Gulf, with seasonal hypoxia at many sites. Trends of increasing nutrient levels should be interpreted as a warning signal for the future and highlight the need for management approaches based on sound knowledge of the many potential sources of NO_3^-.

In most basins of the Baltic Sea, the NO_3^- concentrations in winter were almost identical, with the exception of the Gulf of Finland, where concentrations were about two-fold higher ($7.6 \pm 0.9\,\mu mol\,L^{-1}$; Fig. 2). This sub-basin is regarded as the most heavily eutrophied sub-basin of the Baltic Sea, a consequence of it receiving nutrient loads from the Neva River and the city of St. Petersburg (Lundberg et al., 2005). By contrast, NO_3^- concentrations in the western Baltic Sea, the Baltic Proper, and the Gulf of Bothnia were much lower (3.3 ± 0.6, 3.4 ± 0.8, and $3.7 \pm 0.4\,\mu mol\,L^{-1}$, respectively). These data clearly show that NO_3^- concentrations alone cannot be used to identify NO_3^- sources for the sub-basins; rather, stable NO_3^- isotopes values allow for accurate source determination, as we will show in the following sections.

3.2 Sources of NO_3^-

The use of NO_3^- stable isotopes for source identification is complicated when the mixing of multiple N sources with overlapping isotopic ranges occurs together with microbial processes such as nitrification, assimilation, and denitrification (Kendall, 1998; Wankel et al., 2006). In this study, we assumed that the effects of fractionation by microbial processes were negligible because all our samples were collected in winter, when microbial activity is low (Pfenning and McMahon, 1997), as confirmed in the study of Jäntti et al. (2011). Those authors showed that in the Gulf of Finland although nitrification potentials may be high during cold months, in situ nitrification is undetectable whereas the rate increases progressively towards the summer.

We are aware that the variability of the source signals must be taken into account in source attributions. Both Xue et al. (2012, 2013) and Yang et al. (2013) showed that SIAR can be applied in NO_3^- source identification, although the resolution of this model is largely determined by the uncertainty of the isotopic composition of the sources. In the studies of both groups, the means and variances of the sources were calculated mostly from literature values, which were not obtained in the investigation areas, nevertheless they received consistent results. In contrast, in our study, the isotopic composition of the sources, except NO_3^- from N_2 fixation, was determined from samples obtained within the study area. In our calculations we considered the impact of the variability of the sources and report not only mean values and error estimates but also minimum and maximum contributions, as suggested by Fry (2013) (Table 3).

3.2.1 NO_3^- from agricultural runoff

The isotopic values of riverine NO_3^- were previously shown to be enriched when agricultural land is the source of inputs (Johannsen et al., 2008; Mayer et al., 2002; Voss et al., 2006). Catchments with high percentages of agricultural and/or urban land use export NO_3^- with δ^{15}N-NO_3^- values of around 7 ‰. In the same study, the oxygen isotope ratios of NO_3^- were almost uniformly 13 ± 1 ‰ (Mayer et al., 2002). Johannsen et al. (2008) measured δ^{15}N-NO_3^- values of 11.3 ‰ in highly eutrophied rivers draining into the North Sea, whereas the highest δ^{18}O-NO_3^- value was 2.2 ‰. Our measurements for the Warnow and Nemunas Rivers fall in the expected range, with a mean δ^{15}N-NO_3^- of 9.2 ‰ and a mean δ^{18}O-NO_3^- of 3.1 ‰, and are consistent with the high percentages of agricultural land in the river catchment areas: 50 % for the Warnow River (Pagenkopf, 2001) and 50 % for the Nemunas River (Christoph Humborg, personal communication, 2011) (Fig. 2). For both, SIAR calculations indicated that 75.7–100 % (mean 93.5 ± 4.1 %) of the NO_3^- pool is from agricultural runoff (Fig. 1, Table 3). NO_3^- with this signature seems to be transported to the central Baltic Sea, since SIAR-based estimates showed significant percentages of agriculturally derived NO_3^- in the Western Baltic Sea (37.1–67.0 %; mean: 52.8 ± 3.7 %), the Baltic Proper (29.4–48.4 %; mean: 39.5 ± 2.3 %), and the Gulf of Finland (42.1–69.8 %; mean: 56.1 ± 3.4 %) (Table 3). However, high percentages were only expected for the Gulf of Finland and the Western Baltic Sea, where large N loads from agricultural land have been documented (Hong et al., 2012). Indeed, for the Baltic Proper, the sizeable contribution of agricultural NO_3^- (39.5 ± 2.3 %) was surprising and contrasted with previous findings that nearly excluded riverine NO_3^- as a major nutrient source for the central Baltic Sea (Voss et al., 2005, 2011). However, Neuman (2000) estimated that 13 % of the N input of the Oder River is transported to the central Baltic Sea, while Radtke et al. (2012) could show, using the three-dimensional ecosystem model ERGOM, that at least a part of the dissolved inorganic nitrogen (DIN) load from the Vistula River, the main NO_3^- contributor to the Baltic Sea (Wulff et al., 2009), enters the Baltic Proper.

Another explanation for the high estimated agricultural influence in our study could be the intrusion of water containing NO_3^- with similar NO_3^- isotope values as our agricultural NO_3^- source during mixing/advection from below the halocline. Deep-water NO_3^- in the Baltic Sea has a $\delta^{15}N$ of about 7 ‰ (Frey et al. unpubl. data), which is higher than the average deep-water ocean NO_3^- signature of 5 ‰ (Sigman et al., 2000). This elevated $\delta^{15}N$ in NO_3^- mainly comes from water column denitrification in the oxic-anoxic interface in water at a depth of about 100 m (Dalsgaard et al., 2013). However, the year-to-year variations in DIN due to vertical mixing and advection from below the halocline are sensitive to hydrographic conditions. When the halocline is weak and well ventilated, oxygen conditions improve, resulting in higher DIN concentrations in deep waters and greater advection and/or mixing (Vahtera et al., 2007) such that the NO_3^- contribution from below the halocline is difficult to estimate. Overall, the range of 29.4–48.4 % (mean: 39.5 ± 2.3 %) determined for NO_3^- presumably originating from agricultural runoff has to be considered with caution, because the former imprint of deep water column denitrification and mixing/advection of this isotopically enriched NO_3^- from below the halocline with the residual winter surface NO_3^- pool could have resulted in an overestimation of the percentage of NO_3^- from agricultural runoff in the Baltic Proper.

3.2.2 NO_3^- from N_2 fixation

The average $\delta^{15}N$-NO_3^- value of 3.6 ‰ for the Baltic Proper (Fig. 2) is significantly lower than the ocean average of around 5 % (Sigman et al., 2000) and presumably reflects the influence of N_2 fixation. This is because the $\delta^{15}N$ of newly fixed N is between −2 and 0 ‰ such that NO_3^- has slightly lower $\delta^{15}N$ values, around 3.9 ‰ (Knapp et al., 2005; Liu et al., 1996). The δ^{18}O-NO_3^- value of −0.5 ‰ in the Baltic Proper (Fig. 2) is also slightly lower than the ocean average of 1.5 ‰ although our theoretical considerations support a value of −9.8 ‰, assuming an ambient δ^{18}O of Baltic Sea seawater of −6 ‰ (Froehlich et al., 1988) and a δ^{18}O of newly produced NO_3^- that is 0.7–8.3 ‰ lower (Buchwald and Casciotti, 2010), resulting in a δ^{18}O-NO_3^- value of −9.8 ± 3.8 ‰ during the degradation and remineralization of N_2 fixers.

N_2 fixers are abundant in summer, reflecting the stimulation of their growth by the low N/P ratios. N in the cyanobacterial biomass is remineralized over the winter months and the resulting NO_3^- remains in the water masses down to the halocline. Our results show that the contribution of N_2 fixation by diazotrophs to the NO_3^- pool is 30.9–61.8 % (mean 48.8 ± 5.1 %) (Fig. 1, Table 3). This is in agreement with Wasmund et al. (2001), who estimated that 39 % (370 kt yr^{-1}) of a total input of 955 kt N yr^{-1} (HELCOM, 2002) stems from N_2 fixations in the central Baltic Sea. Both Radtke et al. (2012) and Voss et al. (2005) concluded that N_2 fixation was the main NO_3^- source in the Baltic Proper. Using an independent approach, we were able to confirm the contribution of N_2 fixation in this area. In addition, we found that N_2 fixation is also a major source of NO_3^- in the Western Baltic Sea and the Gulf of Finland (respectively, 4.9–50.5 %, mean 31.4±6.5 % and 24.5–52.9 %, mean 39.2 ± 3.7 %; Fig. 1, Table 3). This finding is consistent with our current understanding of N_2 fixation in the Gulf of Finland (Vahtera et al., 2005) whereas the western Baltic Sea is rather perceived as an area with no N_2 Fixation activity (Stal et al., 2003). In summary, our results provide important evidence that N_2 fixation by cyanobacteria is a significant N source not only in the Baltic Proper but also in the Western Baltic Sea and Gulf of Finland.

3.2.3 NO_3^- from atmospheric deposition

NO_3^- from atmospheric deposition is generally heavily enriched in ^{18}O (> 60 ‰) because of reactions involving ozone (O_3), which is anomalously enriched in heavy oxygen isotopes (Durka et al., 1994; Kendall et al., 2007). This is consistent with the δ^{18}O measurements at the three stations around the Baltic Sea, where the averaged isotope value in winter was 77 ‰ (Table 2).

Our results show that atmospheric deposition contributes significantly less NO_3^- than all other sources. Indeed, among all basins of the Baltic Sea (Fig. 1), the maximum mean contribution was in the Western Baltic Sea (2.1 ± 0.8 %; 0–5.7 %; Fig. 1, Table 3). Moreover, using a dataset from Michaels et al. (1993), Duce et al. (2008) estimated that even an extremely rare and large atmospheric deposition event distributed over a 25 m mixed-layer depth would increase the reactive N concentration only by around 0.045 $\mu mol\,L^{-1}$. A study in the Kattegat estimated an input of 52 $kt\,N\,yr^{-1}$ from atmospheric deposition, which implied rather limited nutritional support for phytoplankton (Spokes et al., 2006). Taking into account that in the open Baltic Sea in winter the mixed-layer depth is 80–100 m and that the residual NO_3^- pool, with a concentration of 3.6 $\mu mol\,L^{-1}$, has a $\delta^{18}O\text{-}NO_3^-$ of −0.5 ‰, a comparable rain event with a $\delta^{18}O$ of 76.7 ‰ (Table 1) would increase the $\delta^{18}O\text{-}NO_3^-$ of the residual NO_3^- pool only by 0.2–0.3 ‰, which is within our analytical error. Even though several rain events typically occur during winter, their influence seems to be too low to leave a detectable isotopic imprint. Additionally, the NO_3^- from atmospheric deposition is presumably intensively cycled through the organic N pool in spring and summer such that after several mineralization cycles its origin is difficult to recognize isotopically (Mayer et al., 2002).

In the Kalix River, $\delta^{18}O\text{-}NO_3^-$ was clearly enriched (10.6 ‰) compared to the values determined for the Baltic Sea. We calculated that in this river up to 17.6 % (mean 12.1 ± 1.1 %) of the NO_3^- originates from atmospheric deposition (Fig. 1, Table 3). Mayer et al. (2002) compared the isotopic NO_3^- signature of 16 watersheds in the USA and were able to show that riverine NO_3^- derived from atmospheric NO_3^- deposition and not from nitrification in soils is the dominant N input in predominantly forested watersheds, when riverine NO_3^- concentrations are generally low. Therefore only in the Kalix River, where up to 97 % of the catchment is covered by forests and NO_3^- concentrations are low during winter (Voss et al., 2011), was the imprint of NO_3^- from atmospheric deposition visible; by contrast, in the southern Baltic Sea and the rivers draining into it, the anthropogenic influence due to agriculture is very high and therefore masks atmospheric contributions. However, NO_3^- loads to the northern Baltic Sea from the Kalix River and other, comparable boreal rivers are small, comprising only about 20 % of the sea's total N load (Voss et al., 2011). Thus, overall, we assume that atmospheric deposition is a very minor source of NO_3^- in the Baltic Sea.

3.2.4 NO_3^- from pristine soils

In general, in rivers such as the Kalix River, whose catchments include pristine vegetation, δ^{15}N-NO_3^- values are low while those of δ^{18}O-NO_3^- are high (Voss et al., 2006). This finding was confirmed in the present study, in which δ^{18}O-NO_3^- and δ^{15}N-NO_3^- values of 10.6 ‰ and 1.6 ‰, respectively, were determined (Fig. 2). In the Kalix River, the NO_3^- contribution from the runoff of pristine soils as determined by SIAR is 47.3–90.5 % (mean 73.6 ± 6.9 %). The high percentage of NO_3^- derived from nitrification in soils is in agreement with previous studies of small catchments, where much of the NO_3^- was shown to be of microbial origin (Campbell et al., 2002; Kendall et al., 2007; Mayer et al., 2002). Similar δ^{15}N-NO_3^- values were reported for areas where pristine soils were also sampled. For example, δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values of 1.9 and 2.8 ‰ were determined for Biscuit Bay (Burns et al., 2009) and 2.9 and 2.8 ‰ for the San River (Koszelnik and Gruca-Rokosz, 2013), respectively. The higher δ^{18}O-NO_3^- values of the Kalix River can, as discussed above, be attributed to atmospheric deposition.

For the Gulf of Bothnia, where the catchment is dominated by forests (50 %) and shrub areas (20 %), NO_3^- from pristine soils contributes 90.4–100 % (98.5 ± 1.2 %) (Fig. 1, Table 3). However, the NO_3^- derived from nitrification is very low in concentrations and remain in the Gulf because of the cyclonic circulation in the Bothnian Sea and Bothnian Bay (Humborg et al., 2003). The high residence time of the water (7.4 years) results in a rather slow exchange with the Baltic Sea (Myrberg and Andrejev, 2006). Thus, for the Baltic Proper the NO_3^- contribution from pristine soils is negligible.

3.3 Comparison of isotope patterns in the water column and sediments

The $\delta^{15}N$ values from surface water correlated significantly with those from surface sediments, as reported in Voss et al. (2005) ($p < 0.001$; Figs. 3 and 4). Similar correlations were noted in the Cariaco Basin (Thunell et al., 2004), Guaymas Basin, Monterey Bay, and San Pedro Basin (Altabet et al., 1999). In the Baltic Proper, the $\delta^{15}N$ of the surface water of was indistinguishable from that of the sediment surface (3.6 ± 1.0 ‰ and 3.5 ± 0.6 ‰, respectively; Fig. 3), as occurs when NO_3^- in the surface mixed layer is fully consumed. This is the case in the Baltic Proper during the spring bloom, when the only significant loss comes from the sinking of particulate nitrogen (Altabet et al., 1999). Moreover, high organic matter preservation seems to stimulate the similarity in the $\delta^{15}N$ in the surface water and sediments as seen in other depositional environments (Thunell et al., 2004).

In the near-coastal areas of the Baltic Proper and the Gulf of Finland, the $\delta^{15}N$ of surface water NO_3^- was 7.9 ± 1.8 ‰, slightly higher than the surface sediment value for the same area of 7.3±2.1 ‰ (data in Voss et al., 2005). This might be due to the fact that in the coastal strip NO_3^- is only partially consumed by primary producers (Korth et al., 2013). Consequently, the $\delta^{15}N$ of the surface sediment incorporating this incompletely utilized NO_3^- would be lower than that of NO_3^- in the overlying water (Francois et al., 1992). Overall, a comparison with the sediment data set from Voss et al. (2005) shows that the isotopic signature of NO_3^- in the euphotic layer of the central Baltic Sea is directly transferred to the particulate organic nitrogen pool and is subsequently found in the sediment surface as detritus, thus conserving information about the origin of this NO_3^- source.

4 Conclusions

By combining dual isotope data of winter NO_3^- ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^-) in surface waters with a Bayesian isotope mixing model (SIAR), we estimated the contribution of four major NO_3^- sources for the different basins of the Baltic Sea. A clear shift in the source of NO_3^- inputs, from agricultural sources in the south to runoff from pristine soils in the north, was identified. However, we could not fully determine how much of the agriculturally derived NO_3^- entering the Baltic Sea finally ends up in the open waters of its central region, where the addition of deep-water NO_3^- with similar isotope values might falsely indicate a higher contribution. However, we were able to show that N_2 fixation is an important NO_3^- source in the central Baltic Sea while the contribution of NO_3^- from atmospheric deposition is only a minor one.

Because they are particularly sensitive to human pressure and global climate change, marginal seas, including the Baltic Sea, will no doubt be affected by the increases in temperature and precipitation predicted for the near future (BACC, 2008). Indeed, increasing atmospheric depositions of NO_3^- in the world's oceans have already been reported, by Duce et al. (2008) and Kim et al. (2011) and, may impact ocean areas to a larger extent. For surface waters that are oligotrophic and/or perennially or seasonally NO_3^- depleted, additional NO_3^- may alter their biogeochemical cycles. Additionally, in coastal waters under increasing eutrophication pressure the efficiency of NO_3^- removal was shown to be reduced (Lunau et al., 2013; Mulholland et al., 2008). Therefore, the identification of NO_3^- sources, especially as anticipated in response to global climate change, is important for future environmental management strategies for the Baltic Sea and other marine environments. We suggest that with an adaption of the potential sources the approach used in this study can easily be applied in other environments where NO_3^- is a major N contributor.

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Table 1. Means and standard deviations of the δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values of the NO_3^- sources used in the SIAR mixing model. For further details, see Material and Methods, SIAR mixing model.

Source	δ^{15}N-NO_3^- (mean ± SD)	δ^{18}O-NO_3^- (mean ± SD)	*n*	Origin
NO_3^- from atmospheric deposition	0.3 ± 1.4	76.7 ± 6.8	10	Warnemünde (Germany), and Sännen and Majstre (Sweden)
NO_3^- from pristine soils	1.3 ± 1.4	1.5 ± 0.9	5	Groundwater
NO_3^- from agricultural runoff	9.9 ± 1.5	4.6 ± 1.0	21	Tile-drain outlets, Warnow River
NO_3^- from N_2 fixation	−1.0 ± 1.0	−9.8 ± 3.8	0	Estimated

Table 2. NO_3^- concentrations and $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values of wet atmospheric deposition. Data are from Warnemünde (Germany), Sännen (Sweden), and Majstre (Sweden).

Location	Date	NO_3^- ($\mu mol\,L^{-1}$)	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)
Warnemünde	21 Dec 2009	52.7	2.1	75.6
Warnemünde	4 Jan 2010	51.2	1.1	68.3
Warnemünde	19 Jan 2010	104.4	0.2	84.6
Warnemünde	1 Feb 2010	50.8	0.8	65.8
Warnemünde	19 Feb 2010	94.4	0.6	79.5
Warnemünde	22 Feb 2010	106.8	2.1	81.8
Sännen	Dec 2009	12.1	−0.3	69.2
Sännen	Jan 2010	60.4	−1.1	81.8
Sännen	Feb 2010	69.3	−2.1	77.0
Majstre	Dec 2009	30.7	−0.8	83.8

Table 3. Source attribution results: mean, standard deviation, and minimum and maximum values for the potential contributions of four potential NO_3^- sources for the areas Western Baltic Sea, Baltic Proper, Gulf of Finland, Gulf of Bothnia, southern rivers, and northern rivers.

Area	NO_3^- from atmospheric deposition		NO_3^- from pristine soils		NO_3^- from agricultural runoff		NO_3^- from N_2 fixation	
	Mean ± SD	Min-max	Mean ± SD	Min-max	Mean ± SD	Min-max	Mean ± SD	Min-max
Western Baltic Sea	2.1 ± 0.8	0–5.7	13.7 ± 8.7	0–55	52.8 ± 3.7	37.1–67.0	31.4 ± 6.5	4.9–50.5
Baltic Proper	0.4 ± 0.3	0–2.8	11.4 ± 6.8	0–36.1	39.5 ± 2.3	29.4–48.4	48.8 ± 5.1	30.9–61.8
Gulf of Finland	0.5 ± 0.4	0–3.6	4.3 ± 3.7	0–27.2	56.1 ± 3.4	42.1–69.8	39.2 ± 3.7	24.5–52.9
Gulf of Bothnia	0.1 ± 0.1	0–0.6	98.5 ± 1.2	90.4–100	1.4 ± 1.2	0–9.5	–	–
Southern rivers	0.2 ± 0.1	0–1.2	6.3 ± 4.1	0–24.4	93.5 ± 4.1	75.7–100	–	–
Northern rivers	12.1 ± 1.1	8.3–17.6	73.6 ± 6.9	47.3–90.5	14.4 ± 7.1	0–42.4	–	–

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Table 4. Comparison of δ^{15}N-NO$_3^-$ values from surface water samples and δ^{15}N values from sediments samples in sub-regions of the Baltic Sea.

	Baltic southern coastal areas/ Gulf of Finland	Central Baltic Proper	
δ^{15}N sediments (‰)	7.3 ± 2.1	3.5 ± 0.6	Voss et al. (2005)
δ^{15}N-NO$_3^-$ surface water column (‰)	7.9 ± 1.8	3.6 ± 1.0	This study

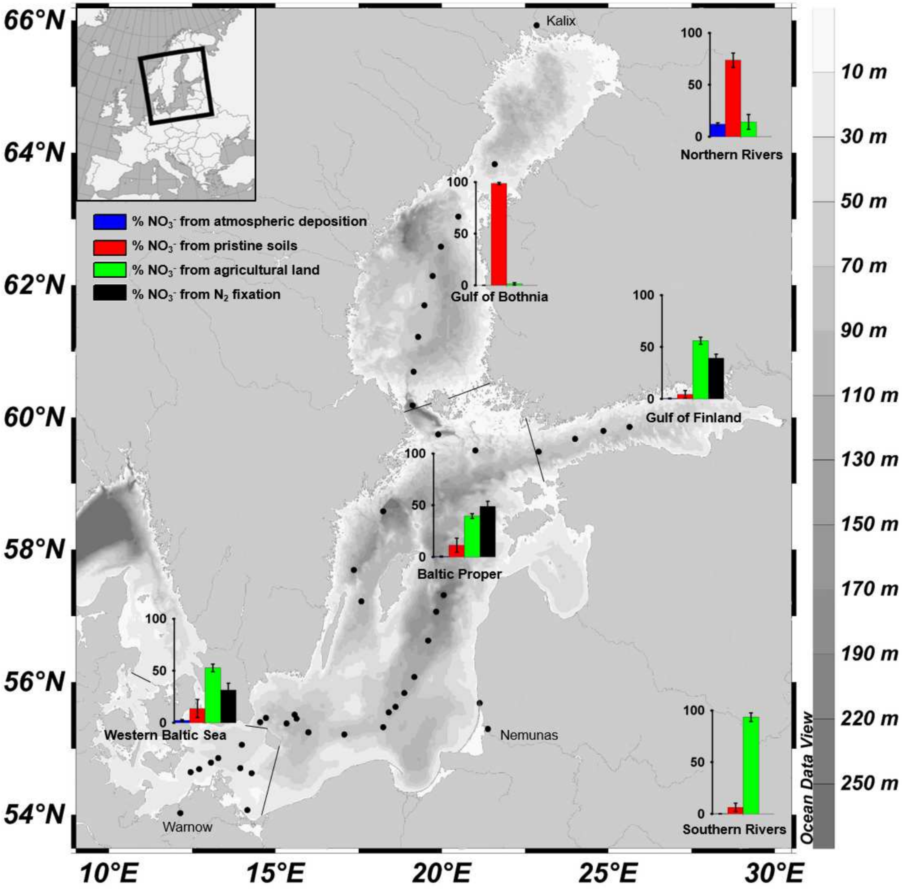

Fig. 1. Station Map of the Baltic Sea and percent contribution of the four nitrate sources, NO_3^- from atmospheric deposition (blue), pristine soils (red), agricultural runoff (green), and N_2 fixation (black), for the Western Baltic Sea, Baltic Proper, Gulf of Finland, Gulf of Bothnia, southern rivers, and northern rivers. Stations are indicated as black dots.

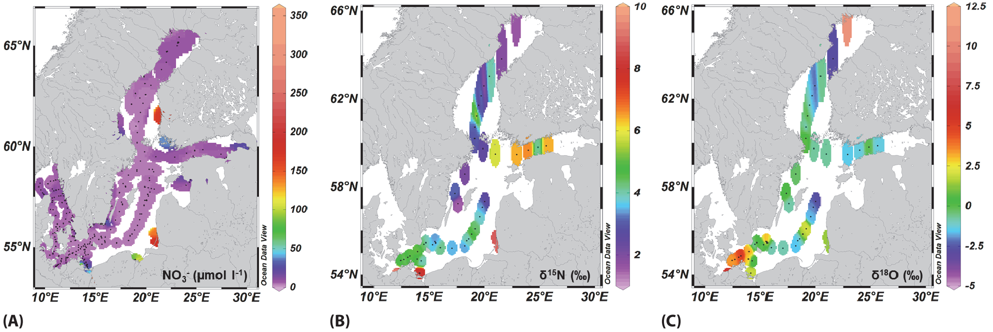

Fig. 2. Surface water column NO_3^- concentrations **(A)**, δ^{15}N-NO_3^- values **(B)**, and δ^{18}O-NO_3^- values **(C)** for the Baltic Sea. Stations are indicated as black dots. Additional NO_3^- concentrations were obtained from the Data Assimilation System (DAS) (http://nest.su.se/das/) in winter (November–February) of the years 2000 to 2012.

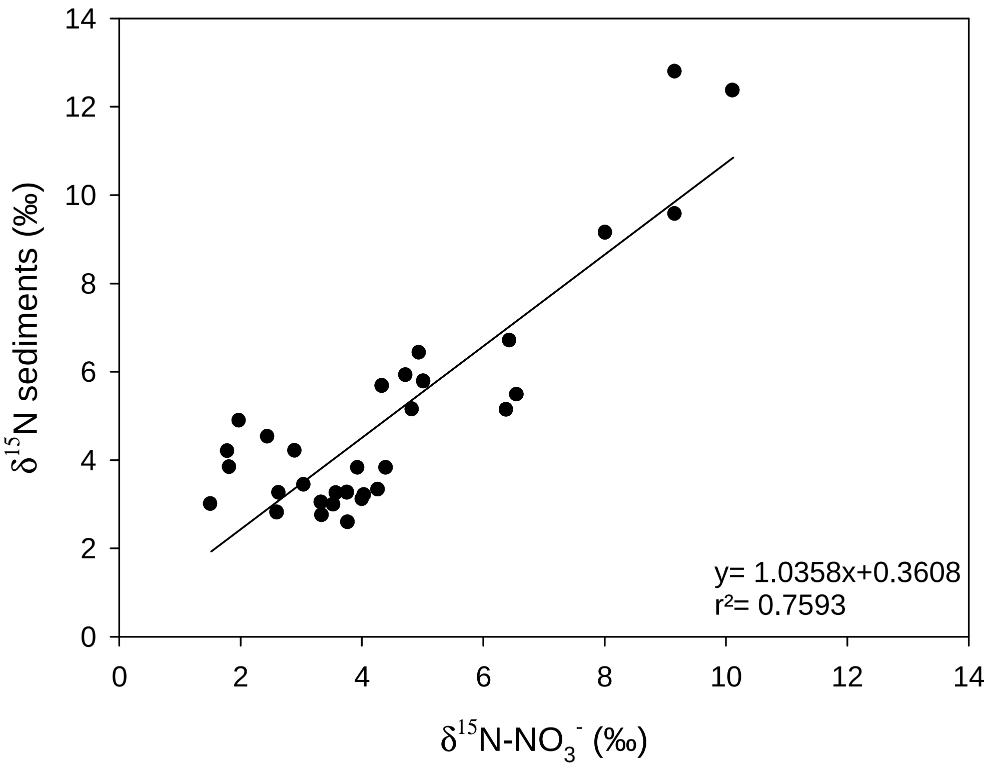

Fig. 3. δ^{15}N from sediment samples vs. δ^{15}N-NO$_3^-$ from surface water samples. δ^{15}N values from sediments were taken from Voss et al. (2005). The positive slope suggests a tight coupling between δ^{15}N-NO$_3^-$ in surface waters and δ^{15}N in sediment samples.

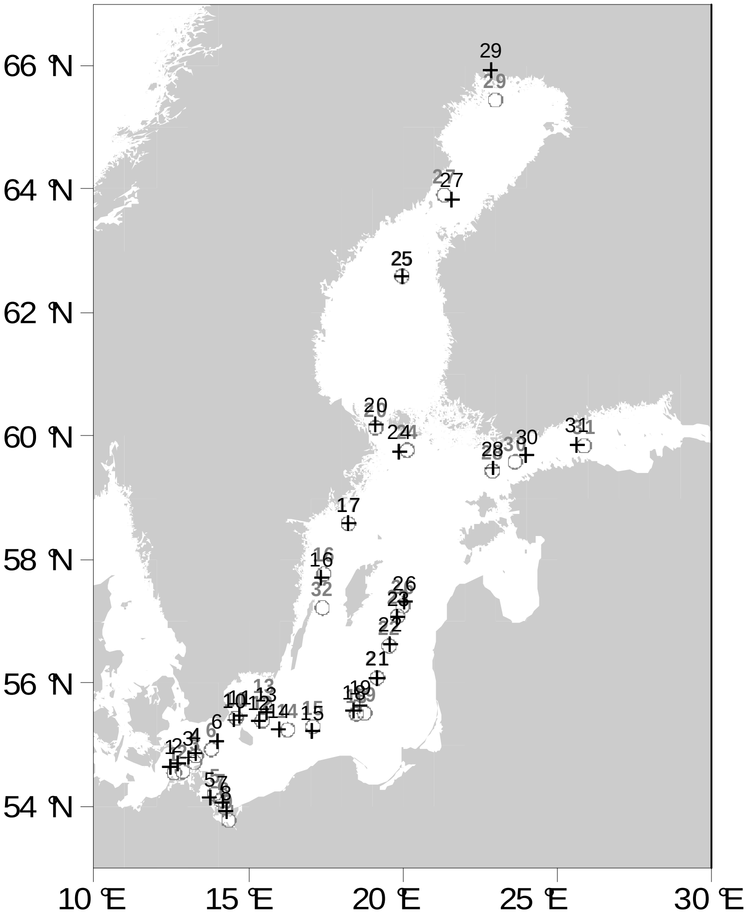

Fig. 4. Station map for the comparison of isotope patterns in the water column and sediments. Gray circles are the stations referred to in Voss et al. (2005) and black crosses are those from this study. Isotope values were compared at stations with the same number.