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Assessing the source of nitrate pollution in water using stable N and O isotopes

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Abstract – We used the isotopic composition of nitrogen ($\delta^{15}\text{N}$) and oxygen ($\delta^{18}\text{O}$) in water nitrate (NO_3^-) to assess water pollution. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in drainage water nitrate of a conventionally managed field and the adjacent surface waters were measured for 6 weeks during the main discharge period of the hydrological year 2003/2004. We hypothesized that this approach could provide more information about the impact of drainage water containing high nitrate loads on the following surface water bodies than common measurements of concentrations. The nitrate concentrations ranged between 686 and 2040 μM in the tile drain outlets and were positively correlated to the tile drain discharge. The low $\delta^{18}\text{O}\text{-NO}_3^-$ values, from 1.8 to 4.3‰, indicated that most of the nitrate derived from the nitrification process in the agricultural soils. The high $\delta^{15}\text{N}\text{-NO}_3^-$ values, from 8.5 to 15.0‰, reflected the long-term fertilizing practice which was carried out for several years with inorganic as well as organic fertilizers. In the adjacent ditch and the brook nitrate concentrations were lower but showed a similar development to the tile drain outlet. The $\delta^{15}\text{N}\text{-NO}_3^-$ values (7.2–12.1‰) and $\delta^{18}\text{O}\text{-NO}_3^-$ values (2.4–9.1‰) in the ditch and the brook indicated that the nitrate from tile drain discharge is the major N source for the adjacent surface water bodies.

tile drainage / nitrate / eutrophication / $\delta^{15}\text{N}$ / $\delta^{18}\text{O}$

1. INTRODUCTION

Diffuse nitrogen inputs from agriculture are the major N source for river systems and aquifers in many areas of the world (Galloway and Cowling, 2002). Although only a small amount of nitrate is directly applied to the field, it is, amongst dissolved organic nitrogen (DON) forms, the dominant N form lost to aquatic environments (Addiscott et al., 1992). Mainly responsible for high nitrate losses are microbial processes in the soils. Mineralization of soil organic N followed by nitrification results in high nitrate concentrations, especially during autumn and winter, when crops are harvested and the soil is still warm enough for microbial activity (Kirchmann et al., 2002). The highly water-soluble nitrate is then shifted downwards with the soil water flow and reaches drainage systems and/or groundwater. Especially in artificially drained agricultural areas this is an efficient pathway because of the short residence times of the soil water in the biologically active unsaturated zone (Tomer et al., 2003). Several studies have shown that the concentration of nitrate is positively correlated to water discharge (Lammel, 1990; Göbel, 2000). From the drainage system NO_3^- is lost to rivers and reaches coastal areas, where it contributes to eutrophication (Addiscott et al., 1992; Galloway and Cowling, 2002).

A common method to trace diffuse nitrate inputs is the determination of stable isotope ratios of nitrogen and oxygen in nitrate (Amberger and Schmidt, 1987; Wassenaar, 1995; Spoelstra et al., 2001; Burns and Kendall, 2002; Campbell

et al., 2002; Chang et al., 2002; Mayer et al., 2002). Studies have shown that enhanced agricultural activity results in increased $\delta^{15}\text{N}$ values in nitrate of the adjacent surface waters, while nitrate in undisturbed watersheds shows $\delta^{15}\text{N}$ values below 4‰ (McClelland and Valiela, 1998). A positive correlation between the percentage of land used for agriculture and the $\delta^{15}\text{N}\text{-NO}_3^-$ values for 16 watersheds in the United States is reported by Mayer et al. (2002). The volatile loss of ammonia from organic and inorganic fertilizers, and denitrification in soils leads to higher $\delta^{15}\text{N}\text{-NO}_3^-$ values of nitrate in rivers receiving large amounts of N from agriculture, compared with natural watersheds (Flipse and Bonner, 1985; Mengis et al., 1999; Mayer et al., 2002; Frank et al., 2004). The stable isotope ratios of oxygen in nitrate were successfully applied to identifying microbial processes such as nitrification and denitrification (Böttcher et al., 1990; Mayer et al., 2001) and to identifying mixtures with rainwater nitrate, or nitrate from mineral fertilizers (Amberger and Schmidt, 1987; Durka et al., 1994; Campbell et al., 2002; Pardo et al., 2004; Piatek et al., 2005).

In this study the variations in the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of nitrate in drainage water and an adjacent ditch and brook were measured during the main discharge period of the hydrological year 2003/2004, to assess the impact of the tile drainage nitrate to the following surface waters. Sampling took place from the end of January to the middle of March at a high temporal resolution in a small, predominantly rural catchment near Rostock in northeastern Germany.

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Table I. Drained area, soil types and land use for the tile drain outlet, ditch and brook.

Sampling location	Drained area (km ²)	Soils	Land use
Tile drain outlet	0.042	Mineral	cropland, conventionally treated, 100% drained
Ditch	1.8	Mineral	cropland, conventionally treated, 80% drained
Brook	16	Mineral/Organic	48% cropland, 28% pasture, 14% forest

Figure 1. Map of the investigation area; the sampled stations are marked with triangles and letters (A tile drain outlet; B adjacent ditch, and C brook). Redrawn from Kahle et al. (2005).

2. MATERIALS AND METHODS

Water samples were taken in the catchment area of the brook Zarnow 15 km southeast of the city of Rostock (Mecklenburg-Vorpommern, Germany) from January 30th, 2004 to March 13th, 2004. Sampling stations for discharge measurements and water sampling were located at the drain outlet of a tile-drained field site (0.042 km²), at an adjacent ditch draining around 1.8 km² used for crop production by conventional farming and the brook Zarnow with a catchment of about 16 km² (Fig. 1, Tab. I).

At the tile drain outlet, the water level was recorded in a Venturi flume at 15-minute intervals, while an automatic sampler (ISCO) took samples every three hours, which were then merged into 22 daily composite samples. At the other stations, manual sampling was carried out daily or twice a week, depending on meteorological conditions. Here, 10 samples were selected for isotopic analysis. All samples were collected in 1-L preacidified PE bottles and frozen at -20 °C until further preparation. Analysis for nitrate was carried out by ion chromatography. Further investigations included a soil survey,

measurements of flow rates and solute concentrations of different relevant anions and cations, and the operation of a weather station, described in more detail by Kahle et al. (2005). Cultivated crops on the tile-drained field site were corn in 2003 and winter wheat in 2004. Application of fertilizers was carried out in organic and inorganic forms: altogether 240 kg N ha⁻¹ in 2003. In 2004 the first N application was carried out on February 23rd in the form of liquid manure (23 m³ ha⁻¹) and the mineral fertilizer ammonium sulfate saltpeter (ASS; 230 kg ha⁻¹).

For isotope analysis the nitrate of the water samples was converted into AgNO₃ using the method of Silva et al. (2000). After the sample had passed through a cation exchange column (5 mL AG 50-W40, H⁺ form; Biorad), the nitrate of the sample was enriched using an anion exchange column (AG 1-X8, Cl⁻ form; Biorad). The nitrate was eluted from the column with 15 mL HCl (3M), and neutralized with Ag₂O until a pH of 5.5–6.0. Precipitated AgCl and remaining Ag₂O were removed by filtration through a 0.45-μm membrane filter. To remove the other O-bearing anions SO₄²⁻ and PO₄³⁻, 1 mL of a 1M BaCl₂ solution was added. BaSO₄ and Ba₃(PO₄)₂ were again removed by filtration. Then, the sample was passed through a second cation exchange column (5 mL AG 50-W40, H⁺ form; Biorad) to eliminate the excess Ba⁺. Afterwards the sample was neutralized with Ag₂O, and the AgCl was removed by filtration using a 0.2-μm nylon membrane filter. Finally, the solution was freeze-dried, and the resulting solid AgNO₃ weighed into silver caps for the determination of the δ¹⁵N and δ¹⁸O values.

The analysis of the stable isotope ratios was carried out using a Thermo Finnigan Delta Plus IRMS via open split. The samples were measured in duplicate. For the determination of the δ¹⁵N values, combustion in a Flash EA was carried out at 1020 °C; δ¹⁸O values were determined after pyrolysis in a Thermo Finnigan TC/EA at 1350 °C. The reference substances for δ¹⁵N and δ¹⁸O were atmospheric N₂ and VSMOW, respectively. International reference materials used for calibration of the N₂ gas were IAEA-N1 (δ¹⁵N = (0.4 ± 0.07)‰) and IAEA-N2 (δ¹⁵N = (20.3 ± 0.1)‰). The internally used standards were acetanilide (δ¹⁵N = (-1.7 ± 0.2)‰; n = 244), peptone (δ¹⁵N = (5.8 ± 0.2)‰; n = 245) and KNO₃ from Merck (lot No. A286463; δ¹⁵N = (-0.4 ± 0.16)‰; n = 20).

Calibration of the reference gas, CO, was done with IAEA-KNO₃ (δ¹⁸O = (25.1 ± 0.6)‰; n = 51), USGS 34 (δ¹⁸O = (-27.9 ± 0.75)‰; n = 61), and IAEA-C3-Cellulose (δ¹⁸O = (32.2 ± 0.2)‰; n = 38). The internal standard was Merck KNO₃ (lot No. A286463; δ¹⁸O = (24.6 ± 0.7)‰; n = 52). Standard samples, which contained Merck KNO₃, were converted into AgNO₃ to determine the accuracy and precision of the sample preparation. The δ¹⁸O values of the resulting AgNO₃ were (23.4 ± 0.7)‰ (n = 16) and δ¹⁵N = (-0.43 ± 0.2)‰ (n = 16). The isotope values of the prepared samples were not corrected

Figure 2. Amount of precipitation and drain discharge for the tile drain outlet (A), as well as concentration (B) and isotope values (B) of the drainage water nitrate.

for the observed difference between Merck KNO_3 and the Ag NO_3 .

3. RESULTS AND DISCUSSION

On January 30th the nitrate concentration in the tile drain outlet was $686 \mu\text{M}$ (Fig. 2B) and then increased to the maximum value of $2040 \mu\text{M}$ with the increased drain discharge (Fig. 2A). After February 7th concentrations decreased to $874 \mu\text{M}$ until the end of the sampling period. During the whole sampling period high discharge rates corresponded to high nitrate concentrations. Between the tile drain discharge and the nitrate concentration, a positive linear relationship ($r^2 = 0.84$; $P < 0.001$, Kahle et al., 2005) was observed. The $\delta^{15}\text{N-NO}_3^-$ values varied between 8.5 and 15‰, indicating a long-term application of organic N (Amberger and Schmidt, 1987; Kendall, 1998). The values started at 15‰, dropped to 9.2‰ within the first five days and then fluctuated between 8.5 and 11.8‰ (Fig. 2B).

A similar pattern was observed for the $\delta^{18}\text{O-NO}_3^-$ values. At the start of the sampling period the value was 4.3‰ and decreased within five days to 1.8‰, then the values fluctuated between 1.8 and 4.2‰ (Fig. 2B). Considering that the sampling was carried out during the main discharge period within the hydrological winter 2003/2004, it was assumed that the nitrate

in the drainage water derived from the nitrification of soil organic N during autumn and winter (Göbel, 2000; Kirchmann et al., 2002). This can be proved by means of the $\delta^{18}\text{O-NO}_3^-$ values, which are in the range for nitrification (−2 to 15‰) reported from other agricultural and forested soils (Amberger and Schmidt, 1987; Kendall, 1998; Mayer et al., 2001). The significant decrease in the $\delta^{15}\text{N-NO}_3^-$ values and the moderate decrease in the $\delta^{18}\text{O-NO}_3^-$ values might be a result of a mixture of nitrate originating from different sources. Nitrate in the top-soil horizon mainly originates from the nitrification process in autumn and spring, and thus has lower $\delta^{15}\text{N-}$ and $\delta^{18}\text{O-NO}_3^-$ values. In the deeper, temporarily waterlogged soil horizons denitrification leads to low nitrate concentrations with high $\delta^{15}\text{N-}$ and $\delta^{18}\text{O-NO}_3^-$ values. Whereas soil water from deeper horizons is discharged during base flow conditions, heavy rainfall events, as observed at the beginning of the sampling period, increase the downward water flow, and nitrate from the topsoil horizon is shifted downwards to the drainage system. This would result in an increase in nitrate concentration and a decrease in $\delta^{15}\text{N-}$ and $\delta^{18}\text{O-NO}_3^-$.

The fertilizer application carried out on February 23rd, 2004 had no direct influence on the nitrate concentration and on the stable isotope ratios of nitrate. This was expected because of the low $\text{NO}_3\text{-N}$ percentage of the applied ASS fertilizer (7%) and negligible $\text{NO}_3\text{-N}$ in manure, the low temperatures (mean air temperature in the period from February 23rd to March 13th, 2004: 0°C ; Kahle et al., submitted) and the absence of heavy rainfall events (Fig. 2A).

The parallel curves of the nitrate concentrations in the tile drain outlet, the ditch and the brook suggest that drainage water is the dominant N source for the adjacent surface waters. In the ditch, nitrate varied between 574 and $1652 \mu\text{M}$, whereas the brook had concentrations between 312 and $947 \mu\text{M}$ (Fig. 3A, C). The time lag between the highest nitrate concentration in the tile and the maximum concentrations in the ditch and the brook was 5 days. The $\delta^{15}\text{N-NO}_3^-$ values ranged between 7.2 and 11.0‰ in the ditch, and between 7.5 and 12.1‰ in the brook (Fig. 3B, D). The values started low and increased during the sampling period. A close similarity was indicated by a linear correlation between the $\delta^{15}\text{N-NO}_3^-$ values from the ditch and the brook ($r^2 = 0.74$; $P < 0.01$; $y = 1.15x - 0.73$).

For the ditch, $\delta^{18}\text{O-NO}_3^-$ values were in a range of 2.3 to 4.1‰, and showed an increase until the end of the sampling period. The $\delta^{18}\text{O-NO}_3^-$ values for the brook varied between 2.6 and 9.1‰, and also showed an increase over time (Fig. 3B, D). The simultaneous increase in the $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ values in the brook and the ditch at the end of the sampling period might be an indicator of a fractionation process such as denitrification or phytoplankton NO_3^- uptake (Mariotti et al., 1988; Böttcher et al., 1990; Kendall, 1998), but seems unlikely because of the low temperatures during this period. Mixture with nitrate from another source seems more plausible. A comparison of the isotope values of all samples from February 2nd to March 13th (the period where samples from all three waters are available) reveals significant differences in the $\delta^{15}\text{N-}$ as well as $\delta^{18}\text{O-NO}_3^-$ values (ANOVA; $P = 0.05$).

The $\delta^{15}\text{N-NO}_3^-$ values were significantly different between samples from the tile drain outlet, and samples from the ditch and the brook. In the $\delta^{18}\text{O-NO}_3^-$ values significant differences

Figure 3. Nitrate concentrations and nitrate stable isotope values for the ditch (A, B) and the brook (C, D).

were measured between samples from the tile drain outlet and the ditch, and the samples in the brook (Fig. 4A, B). Possible other nitrate sources could be nitrate leaching from cropland less treated with organic fertilizer, pasture and forested soils. None of these nitrate sources were tested for their $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values during this study. Nevertheless, some general statements which additional sources can be considered can be given. Since it is known that the ditch also drains cropland, the significant difference in the $\delta^{15}\text{N}$ values between nitrate from the tile drain outlet and the ditch might be a result of differences in the fertilizing practice among the arable fields. This has also been reported by Kellman (2005). Differences in the average $\delta^{15}\text{N-NO}_3^-$ values of up to 10‰ were measured in tile drain nitrate beneath cropland treated only with mineral fertilizers and cropland treated with both mineral and organic fertilizers. Besides cropland, the brook also drains pasture and forested areas, which can all be sources of nitrate with a different isotopic composition. Unless all of these sources have an influence on the isotope values of the nitrate in the brook, the close similarity between the nitrate stable isotope values of the tile drain outlet, the ditch and the brook indicate that the drainage water nitrate strongly influences the adjacent surface waters.

Figure 4. Box-Whisker plots of the $\delta^{15}\text{N}$ (A) and $\delta^{18}\text{O}$ values (B) for nitrate from the tile drain outlet, ditch and brook. The boxes represent the lower and upper quartiles, the line shows the median, and the caps at the end of each box indicate the maximum and minimum values.

4. CONCLUSION

Although the $\delta^{15}\text{N-}$ and $\delta^{18}\text{O-NO}_3^-$ values of the tile drainage nitrate were not reflected exactly in the nitrate of the ditch and the brook, in combination with the concentration measurements it was shown that nitrate from tile drainage is a major N source for the adjacent surface waters. For an exact quantification of the nitrate inputs via tile drainage a mixing model should be applied. However, for this approach it is necessary to sample the other possible sources as well.

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