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Assessing net-uptake of nitrate and natural dissolved organic matter fractions in a revitalized lowland stream reach

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ABSTRACT

Lowland streams are often revitalized by hydrologically reconnecting their surrounding terrestrial environment, which likely alters central ecosystem functions such as autotrophic and heterotrophic carbon and nutrient metabolism. However, such central ecosystem functions of stream reaches following revitalization have rarely been investigated. Here, we measured net-uptake of nitrate and of various dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) fractions (using size-exclusion chromatography, SEC), as well as fluorescence components (established by parallel factor analysis, PARAFAC) repeatedly along a revitalized 1.4 km reach of a Danish lowland stream during base flow conditions. Samples were taken at six stations every three hours for one day. We measured discharge at five of the six stations to calculate whole-stream net-uptake. Moreover, we continuously measured oxygen at the start and at the end of the reach to assess stream metabolism, and took piezometer samples from ten shallow groundwater sites to assess potential determinants of organic matter and nitrate metabolism. We found high metabolic activity within the stream reach with a gross-primary production of 4.8 and 3.6 g O₂ m⁻² day⁻¹ and a production to respiration ratio of 0.8 and 0.9 at the start and end of the reach, respectively. Nitrate exhibited relatively constant high net-uptake rates of 0.41–0.52 g N m⁻² d⁻¹, which varied little and were not related to the time of the day. Therefore, autotrophic nitrate uptake for was likely of minor importance, despite the apparently high primary production. In contrast, SEC DON and DOC fractions, as well as PARAFAC components did not suggest net-uptake or release. Instead, DOC and DON concentration were highly variable among the six stations and sampling times, a pattern that was not explainable by measurement errors but was likely related to the high variability of DOC and DON concentrations in the hyporheic zone and adjacent groundwater bodies. This pointed to a potentially high interaction with the hyporheic and riparian zone, underlining the strong linkage of DOM-related processes across the terrestrial-aquatic boundary. The high nitrate uptake points to the high retention potential of revitalized stream reaches, which, however, would need to be corroborated by further studies with reference reaches.

1. Introduction

Arable farming covers a significant percentage of the world's landmasses (Alexandratos and Bruinsma, 2012) and it is recognized as an important diffuse source of nutrients, especially nitrate (Kronvang et al., 2008). Moreover, recent studies point to the importance of arable farming for changes in river dissolved organic matter (DOM) and dissolved organic carbon (DOC) composition (Graeber et al., 2012b) and especially dissolved organic nitrogen (DON) amount (Graeber et al.,

2015a,b; Heinz et al., 2015).

Human-induced changes of DOM composition can affect DOC uptake in streams and lakes and may influence food webs in those systems (Tranvik, 1992; Kamjunke et al., 2015). Moreover, changes in DOM concentration and composition affect greenhouse gas emissions from streams (Bodmer et al., 2016) and lakes (Tranvik et al., 2009). This has led to the idea that, in terms of solute export, stream and landscape restoration should not only encompass reductions in nutrient export to fresh waters but also reductions in DOM export (Stanley et al., 2012).

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However, to our knowledge, terrestrial-aquatic DOM transfer and DOM processing have not yet been investigated under revitalized stream conditions and, hence, remain speculative so far.

Nutrient and DOM processing of revitalized stream reaches is likely higher than those of degraded reaches due to a higher hydrological connectivity to the riparian zone, a longer residence time, and a higher physico-chemical diversity (Craig et al., 2008; Klocker et al., 2009; Stanley et al., 2012). Here, autotrophic uptake may play an important role: For nitrate, autotrophic uptake may be considerable, especially in lowland streams with long water residence time and high light irradiation (Mulholland et al., 2006; Heffernan et al., 2010). For DON, there are indications of autotrophic uptake from laboratory experiments with lake algae (Fiedler et al., 2015), but potential autotrophic and heterotrophic uptake of DON in streams has never been compared.

A potential approach to assess nutrient and DOM behaviour within revitalized stream reaches would be the usage of net-uptake measurements. It has been proposed to adapt the nutrient spiraling method to measure net-uptake with the natural concentrations of reactive (e.g. DOM) and conservative tracers (e.g. Cl^-) (von Schiller et al., 2011, 2015). This is different from the classical nutrient spiraling approach where those tracers are added in addition to the natural concentration to measure uptake and release separately (Newbold et al., 1981; Gücker and Boëchat, 2004). However, the application of the nutrient spiraling approach to measure net-retention clearly borrows from the classical approach and clearly differs from the classical mass-balance approach to measure net-uptake (von Schiller et al., 2011): The nutrient spiraling method has a number of advantages (von Schiller et al., 2011) compared to the more commonly used mass balance method (e.g. Roberts and Mulholland, 2007) and other alternative methods (e.g. Heffernan and Cohen, 2010). First, the nutrient spiraling method is based on a 1st-order reaction model, which is likely to be more representative of in-stream nutrient dynamics. In addition, the spiraling method is based on a whole-reach integrative measure of a consistent concentration trend across several sampling points. Moreover, uptake estimates with the spiraling method are based on changes in nutrient concentration rather than on changes in nutrient mass; thus, the spiraling method minimizes the influence of either groundwater inputs or stream-water losses on the calculation compared to the mass-balance method. Groundwater nutrient concentrations and fluxes are not required when applying the spiraling method, but relatively small groundwater inputs and similar concentrations between groundwater and surface water are the two conditions that must be fulfilled to obtain reliable measurements with this approach (von Schiller et al., 2011, 2015). The spiraling method to assess net-uptake has been shown to work for nitrate, phosphate and to some extent for ammonium, but only in Mediterranean streams (von Schiller et al., 2011; Bernal et al., 2012, 2015). Moreover, in contrast to the classical nutrient spiraling approach with tracer addition (e.g. Newbold et al., 1982), the net-uptake nutrient spiraling approach has never been applied to DOC and DON concentrations or fractions of DOM composition.

Our aim was to assess nitrate and DOM net-uptake in a previously revitalized reach of a Danish lowland stream situated in an area dominated by sandy, relatively coarse soils (Audet et al., 2013). We measured DOC and DON composition by size-exclusion chromatography (SEC) and DOM composition by fluorescence combined with parallel factor analysis (PARAFAC). Furthermore, we assessed stream ecosystem metabolism to link it to potential net-uptake or net-release of nitrate or DOM within the investigated stream. For our experiment, we hypothesized that:

1. Considerable nitrate and DOM uptake occurs due to their lability and the high uptake potential of the investigated stream reach.
2. The day-time net-uptake of nitrate is higher than the night-time uptake since the autotrophic uptake adds to the heterotrophic uptake.
3. Uptake differs among DOM fractions since labile, less complex

fractions should be taken up faster than refractory, complex fractions.

2. Materials and methods

2.1. Study site and design

Odderbæk stream (Jutland, Denmark) is a second-order stream that drains a 27.6-km² catchment dominated by agriculture (68%), forested areas (31%) and other land uses (1%; Audet et al., 2013) and is situated in an area dominated by sandy soils (Højberg et al., 2015). The present study was conducted in a 2-km long stream reach that was revitalized in 2010–2011 and reverted from arable farming into a dry and wet meadow extensively used for cattle farming. In detail, a 2-km long channelized segment of the river was restored by recreating meanders, raising the stream bed by 0.5–1.0 m and disconnecting tile drains (Audet et al., 2013). Furthermore, gravel was inserted to create spawning grounds for trout (see Levesen, 2014 for details on the project).

To assess diurnal changes in net-uptake of nitrate and DOM, we took samples at six stations every three hours during a whole diel cycle. The experiment was conducted from 10th July 2014 at 09:00 to the 11th July 2014 at 06:00, with samplings at the 10th at 09:00, 12:00, 15:00, 18:00 and 21:00 and the 11th at 00:00, 03:00 and 06:00. The stations were situated at 0, 227, 575, 802, 1158 and 1362 m downstream the start of the experimental stream reach (Fig. 1). Sunset was at 22:04 and sunrise was at 04:52, hence samples taken from 00:00–03:00 are night-time samples. In addition, samples of ground water were taken at the 10th July between 10:00 and 14:00 from 10 piezometers that were positioned between 101 and 47 cm depth, with a screen length of 47–53 cm. The piezometers were situated at 1–2 m from the stream bank, and distributed between the stream water stations (Fig. 1). Furthermore, three small inflows ($< 1 \text{ L s}^{-1}$) were found along the investigated stream reach (Fig. 1). Water samples of these inflows were taken around 12:00 on the 10th July.

2.2. Stream hydraulics and metabolism

Baseflow conditions were assessed by measurements of water level every three hours (to the nearest cm) and by a pressure transducer every 15 min (to the nearest mm). Both types of measurements were conducted at the end of the experimental stream reach.

Discharge measurements were carried out at the all stations along the stream reach. Point water velocities were measured with an OTT C2 propeller instrument (OTT Hydromet, Sheffield, UK) and discharge was calculated by the depth-velocity integration method (Hersch, 1978). Each discharge measurement was based on point velocities measured in vertical profiles with a lateral distance of 20 cm between them. In each vertical, velocity was measured for each 5–10 cm depth. Due to instrumental failure, the current velocity data for the discharge measurement at station 2 was lost. Hence, discharge data is only available for five of the six stations (station 1, 3–6, Fig. 1).

Stream widths were measured every 20 m with a metering tape along the entire length of the experimental stream reach (overall 70 measurements). The distance between each width measurement as well as the distance between the sampling sites, the position of the piezometers and the entire reach length was measured by GPS (Leica Viva, Leica Geosystems, Munich, Germany).

To estimate stream ecosystem metabolism, dissolved oxygen (DO) saturation and water temperature were measured and logged every 10 min during the 24-h period in the river thalweg at approximately half depth at station 1 and station 6 (Fig. 1) with an optical ProODO probe (YSI Inc., YellowSprings, Ohio, USA). Beforehand, the optical DO sensor was calibrated to the DO content of air with 100% water saturation. As our measurement period was too short to adjust measurements for travel time between the two stations ($> 5 \text{ h}$), we could not

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