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Phosphorus fractions in discharges from artificially drained lowland catchments (Warnow River, Baltic Sea)

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ABSTRACT

Understanding phosphorus (P) dynamics, from inland sources to the sea, is essential for developing strategies to reduce P loads. In this study, we examined concentrations, fractions, and association of P with other elements at a tile-drain outlet, the adjacent ditch and brook, further downstream from the brook, and in the river itself. The study was conducted in a sub-basin of the Warnow River catchment from 1 November 2013 to 30 April 2014 covering a mild and dry winter. Total phosphorus (TP) concentrations were lowest at the tile-drain effluent and increased in the ditch and brook, as a result of elevated dissolved reactive phosphorus (DRP), particulate reactive (PRP) and organic (POP) phosphorus. Dissolved organic phosphorus (DOP) concentrations remained constant. Further increase of TP along the brook and in the river reflected the increase in DRP + DOP along the first 2.5 km and the doubling of PRP along the 6.5 km thereafter. In the river, phytoplankton growth transformed P into POP in early spring. Total loads of DRP, PRP + POP, and DOP emitted during the study period were 4.3–5.6, 3–7, and 1–2 g ha^{-1} respectively, with an increasing tendency downstream. Despite their low P content (0.7–3.9%), clay minerals and Fe(hydr)oxides particles were the most important carriers because they formed 68–90% of all P-containing particles. A shift from Ca-phosphate to Fe-phosphate occurred from winter to spring and there was a variation in composition of P-containing particles along the flow course. Our results underline the importance of particulate P in discharge and show that the brook Zarnow following the drain outlet and the ditch is a location of P-enrichment and modification probably due to other inputs. The entire flow course has to be considered to assess nutrient inputs from agricultural land because P-composition and loads are changing in time and space.

1. Introduction

Eutrophication caused by anthropogenic nutrient input is a major concern in freshwater and marine coastal systems globally (GIWA, 2003; Nixon, 1995; Powers et al., 2016; Smil, 2000). Among its effects are changes in diversity of organisms and biogeochemical cycles, both have important economic and social consequences. Eutrophication is also the most serious environmental threat to the Baltic Sea (HELCOM, 2009, 2010, 2014). Nutrient discharge into the Baltic increased throughout the 20th century, reaching a peak in the 1980s. It was accompanied by a change in the sea's trophic status from oligotrophic to eutrophic (Andersen et al., 2011; Gustaffson et al., 2012; Larsson et al., 1985). Following the adoption of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area (Helsinki Convention)" by riparian countries, a wide-ranging series of measures aimed at reducing nutrient discharges were implemented. According to the latest "Pollution Load Compilation" (HELCOM, 2015), inputs into the whole Baltic Sea drainage basin in 2010 consisted of 758 000 t of nitrogen (N) and 36 200 t of phosphorus (P). Based on normalized runoff data, these values reflect reductions of 17% and 20%, respectively, for the period between 1994 and 2010 (HELCOM, 2015).

In the German catchment area, riverine P-input to the Baltic Sea was reduced by 61% within the period from 1986/1990 until 2004/2008 (Nausch, 2011). This was mainly due to P-removal in sewage treatment plants, which reduced P discharges by as much as 98%. However, despite improvements in the eutrophication status

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of the Baltic Sea, coastal regions are still eutrophic (HELCOM, 2009, 2014). Accordingly, the Baltic Sea Action Plan called for further reductions (HELCOM, 2007, 2013) via measures to be implemented nationally. In the German catchment area, the P-reduction target needed to achieve a “good ecological status” by 2021 is 170 t year^{-1} (HELCOM, 2013). Since P inputs from point sources have already been eliminated to a substantial extent (Nausch, 2011), current nutrient loadings can mainly be attributed to diffuse sources, with agriculture contributing roughly 60%.

A full understanding of the spatial and temporal dynamics of P in the catchment is essential if appropriate management strategies are to be successfully implemented to fulfill the ambitious reduction targets. This requires that all P sources, their composition, and their changes along the flow path in streams and rivers are accounted for. Beside traditionally measured dissolved reactive phosphorus (DRP) and total phosphorus (TP) concentrations, P determinations must include particulate phosphorus (PP) as well as dissolved organic phosphorus (DOP), given that all P fractions can be transformed into each other and back. DOP can supply P for phytoplankton to support their growth, which also contributes to eutrophication.

In Mecklenburg West Pomerania (northeastern Germany), the Warnow River catchment area is the second largest discharging into the Baltic Sea (Behrendt and Bachor, 1998). Its ~3300 km^2 are sparsely populated (25–50 inhabitants km^{-2}) and consists largely of countryside, with little industry. Agriculture accounts for 75% of the land use (with 60% as arable land and 15% grassland). Further uses are 19% forests, 2% open water and 4% urban area (Koch et al., 2017). Classical tile-drains and ditches systematically drain ~65% of the agricultural land, thus shortening the residence time of nutrients in the soil (Koch et al., 2010; Tiemeyer et al., 2006) by enhancing their transport from topsoil (Ulen et al., 2008). These artificial drainage systems are an important pathway for nutrient flows from agricultural land to surface waters in Mecklenburg West Pomerania (Kahle and Mehl, 2014). In fact, their contribution to the total nutrient load is of the same order of magnitude as inputs from groundwater and erosion (Behrendt and Bachor, 1998; Kunkel et al., 2016). However, subsequent processes in brooks and rivers are often not considered in catchment management, even though they influence nutrient transport from the sources to the sea (Withers and Jarvie, 2008).

The main objective of this study was to characterize the P composition of effluents from artificially drained agricultural land and its modification along the flow path. The work described herein reflects our interest in P dynamics within the Warnow River catchment as a basis for the development of management strategies aimed at achieving further reductions in P loads. This includes a determination if and how P composition varies from the tile-drain outlet to the river, whether DRP transformation into POP is coupled with phytoplankton development, and the identification of the forms of bound P that occur in PRP.

2. Material and methods

2.1. Study site and sampling

The study site was located ~15 km southeast of the city of Rostock, in the catchment (49.6 km^2) of the brook Zarnow, a tributary of the Warnow River (Fig. 1). This area is part of the Pleistocene lowlands of northeastern Germany and is a typical rural area of Mecklenburg West Pomerania, with 65% arable land, 22% grasslands, and 8% forests (Koch et al., 2017). The catchment is characterized by gentle slopes with maximum elevation differences of 30–50 m.

Long-term mean annual precipitation is 689 mm, reference crop evapotranspiration is 490 mm, and the mean temperature is 8.3 °C. Predominant soil units according to the WRB classifications (FAO, 1998) are Luvisols (43%), Cambisols (19%), Stagnosols (19%), Gleysols (2%) under arable use, while grassland and forests are typically situated on degraded Histosols (16%). The particle size distribution of the mineral soils is characterized by 55–88% sand, 9–35% silt and 4–16% clay. A schematic description of the land use areas in the Zarnow catchment is shown in Fig. 1.

About 88% of the Zarnow catchment area is artificially drained by tile drainage systems. Drainage pipes are located at a depth of 1 m, with a spacing of 8–20 m (Tiemeyer et al., 2009); the 2.5-m deep ditch is part of the artificial drainage system receiving the effluent of the collector tile-drain. The drain discharge occurs mainly during the winter period from December to April, because of a precipitation surplus caused by lower temperatures and low evapotranspiration rates. During the growth period in summer, generally only small and infrequent flow events take place and smaller ditches frequently fall dry (Tiemeyer et al., 2006).

Crop rotation includes winter wheat (*Triticum aestivum* L.), oilseed rape (*Brassica napus*), winter barley (*Hordeum vulgare*), and corn (*Zea mays*). In the tile-drain catchment, winter wheat was grown in 2013. Fertilizer was applied here in organic and inorganic forms, amounting to 171–226 kg ha^{-1} N supplied in February and March 2014. Additionally 10 kg ha^{-1} P was applied as digested residues in February 2014. In the area of the drainage ditch, cultivation of winter rape and silage maize dominated in the year 2013, and winter corn and winter barley in 2014 with fertilizer application of 132–185 kg ha^{-1} N applied in March, April and June 2013, and 145–227 kg ha^{-1} N applied in February, two times in March and April 2014. Determined by double lactate extraction, the P nutrition status in the top soils of 50–80 mg kg^{-1} plant available P can be described as optimal according to the German nutrient classes (very low, low, optimal, high and very high (Vdlufa, 1997). Therefore, no additional P-fertilization was necessary.

The sampling design followed the flow direction, starting from the tile-drain outlet, with a contributing area of 4.2 ha, to the receiving ditch and the subsequent brook (Za-D), with catchment areas of 179 and 1550 ha, respectively (Table 1) (Tiemeyer et al., 2009; Zimmer et al., 2016). Samples were also collected along the flow path of the brook, 2.5 km (Za-P) and 6.5 km (Za-R) downstream of station Za-D. Another station (Wa-K) was located in the Warnow River, ~3.5 km south of Rostock.

The study period lasted from the beginning of November 2013 until the end of April 2014 and covered the principal discharge period. Starting on 7 November 2013, water samples were taken on a weekly basis, except at Christmas and New Year’s Eve, when the sampling interval was 17 days. The collected water samples were stored in a cooling box, transported to the laboratory, and immediately processed to avoid alterations of the various P fractions.

Concurrent with sampling, the air and water temperature were measured using a laboratory thermometer.

2.2. Analytical methods

2.2.1. Precipitation and discharge

Data on precipitation (Seba Hydrometrie GmbH, Kaufbeuren, Germany) were directly recorded at the field site.

The discharge at the collector drain outlet was measured with a Venturi flume (Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands). The sampling station at the ditch and the brook were equipped with an ultrasonic water level measurement device (Teledyne Isco, Inc., Lincoln, NE). Discharge gauging with an inductive flowmeter (Flo-MateTM, Marsh-McBirney, Inc., Frederick, MD) was conducted weekly to develop rating curves. For the remaining