



Research papers

Non-domestic phosphorus release in rivers during low-flow: Mechanisms and implications for sources identification



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ABSTRACT

A common assumption in phosphorus (P) load apportionment studies is that P loads in rivers consist of flow independent point source emissions (mainly from domestic and industrial origins) and flow dependent diffuse source emissions (mainly from agricultural origin). Hence, rivers dominated by point sources will exhibit highest P concentration during low-flow, when flow dilution capacity is minimal, whereas rivers dominated by diffuse sources will exhibit highest P concentration during high-flow, when land-to-river hydrological connectivity is maximal. Here, we show that Soluble Reactive P (SRP) concentrations in three forested catchments free of point sources exhibited seasonal maxima during the summer low-flow period, i.e. a pattern expected in point source dominated areas. A load apportionment model (LAM) is used to show how point sources contribution may have been overestimated in previous studies, because of a biogeochemical process mimicking a point source signal. Almost twenty-two years (March 1995–September 2016) of monthly monitoring data of SRP, dissolved iron (Fe) and nitrate-N (NO₃) were used to investigate the underlying mechanisms: SRP and Fe exhibited similar seasonal patterns and opposite to that of NO₃. We hypothesise that Fe oxyhydroxide reductive dissolution might be the cause of SRP release during the summer period, and that NO₃ might act as a redox buffer, controlling the seasonality of SRP release. We conclude that LAMs may overestimate the contribution of P point sources, especially during the summer low-flow period, when eutrophication risk is maximal.

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1. Introduction

Phosphorus (P) concentration in freshwater bodies is an important controlling factor of eutrophication worldwide (Smith and Schindler, 2009). Hence, national and federal regulations, such as the European Water Framework Directive (Directive 2000/60/EC), attach much importance to the reduction of P emissions to streams and rivers. Cost-effective alleviation of P emissions requires precise estimation of the contribution of different P sources in catchments to prioritise management efforts (Bowes et al., 2014; Jarvie et al., 2013b; Withers et al., 2014b).

Point source emissions, mainly from domestic and industrial origins, consist of direct P delivery into the river system. Diffuse source emissions, mainly from agricultural origin, result from the

mobilisation of P sources distributed over the landscape and their delivery to rivers (Haygarth et al., 2005). In the case of point source emissions, P delivery from large waste water treatment plants can be monitored directly, but direct assessment of septic tanks leaking in rural areas requires detailed surveys or use of costly fingerprinting techniques (Arnscheidt et al., 2007; Neal et al., 2010; Richards et al., 2016). As an alternative, indirect methods have been developed to determine the relative contribution of point source and diffuse source emissions based on observed concentration-discharge relationships (Bowes et al., 2008, 2014; Greene et al., 2011; Jarvie et al., 2012). These load apportionment models (LAMs) can take different forms, but rely on the same assumptions: point emissions are assumed to be constant in time while diffuse emissions are assumed to increase with discharge, as a result of increasing P mobilisation and delivery during runoff events (Bowes et al., 2015). The point source contribution to P concentration is thus modelled as a linear function of the inverse of discharge (dilution effect) and several equations have been proposed to describe

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increasing diffuse P concentration during high flow. For example, [Bowes et al. \(2008\)](#) proposed a power function of discharge, and [Greene et al. \(2011\)](#) proposed a linear combination of discharge and the square of discharge. To account for the temporary retention of P during low-flow and its remobilisation during high flow, and not to attribute all the remobilised P to diffuse sources, [Jarvie et al. \(2012\)](#) proposed an improved version of LAMs using chloride as a conservative tracer of wastewater effluents. In summary, LAMs belong to a large family of empirical models used to fit water quality time series ([Minaudo et al., 2017](#); [Moatar et al., 2017](#); [Zhang and Ball, 2017](#)) with the characteristic that they make an explicit distinction between flow dependent and flow independent pollution emissions.

The estimated contribution of point and diffuse sources to annual P loads vary according to the area ([Jarvie et al., 2010](#)), but even in catchments where diffuse emissions dominate annual loads, it is common to observe that point source emissions dominate daily P loads during a majority of the time ([Greene et al., 2011](#); [Serrano et al., 2015](#); [Sharpley et al., 2009](#); [Shore et al., 2017](#)). Another consequence is that the summer low-flow season is assumed to be dominated by point emissions where they occur and are coincident to known point source pressures ([Jordan et al., 2007, 2012](#); [Withers et al., 2014a](#)). Also, because this season is when light and temperature conditions are favourable to eutrophication, river basin managers might decide to target point sources as a priority to mitigate river eutrophication problems in a cost-effective manner ([Jarvie et al., 2006](#); [Shore et al., 2017](#); [Stamm et al., 2014](#)).

However, the low-flow period also corresponds to the warm summer season in catchments of the temperate zone, and it is well known that the biogeochemical processes influencing the P cycle in soils and river sediments are temperature dependent ([Withers and Jarvie, 2008](#)). In this paper, we hypothesised that temperature dependent biogeochemical processes could lead to P release to rivers during the summer low-flow period and that this release might be unduly attributed to point source emissions in load apportionment studies. To test this hypothesis, three rivers draining small forested catchments free of any point sources were investigated over a 22-year period to: i) quantify the seasonal variability of Soluble Reactive P (SRP) concentration and other solutes, ii) determine if previous P LAMs can be misrepresented by the seasonal dynamics observed, and iii) identify the controlling factors of this seasonal dynamics in order to improve future LAMs.

2. Materials and methods

2.1. Study area

The Carlsfeld reservoir is located in eastern Germany, in the federal state of Saxony ([Fig. 1](#)). Its catchment area is 5 km² and spans both sides of the German – Czech border. Climate is temperate continental, with mean \pm standard deviations of annual precipitation and temperature of 1237.0 \pm 273.0 mm and 5.7 \pm 1.0 °C, respectively (1995–2015). Mean monthly temperature varies from -3.0 ± 4.4 °C in January to 14.4 ± 3.8 °C in July (1995–2015). The catchment is located in a low-mountain range, the Ore Mountains, with elevations ranging from 904 to 971 m. The geology is dominated by granite capped by podsolis (classified as “well drained”) in the upslope domain and organic gleysols (classified as “poorly drained”) in valley-bottoms. Both dominant soil types were classified as “very acidic” (pH < 5), according to the German soil classification (DBK Sachsen, 1:50,000).

Three independent sub-catchments were selected for this study: Carlsfeld 1, 1.8 km²; Carlsfeld 2, 0.6 km² and Carlsfeld 3, 0.6 km² ([Fig. 1](#)). Their topography is gentle with an average slope

of 3° in each of the sub-catchments. The percentage of organic gleysols was 58.2% in Carlsfeld 1, 44.4% in Carlsfeld 2 and 50.2% in Carlsfeld 3. Land use was 100% forest (spruce) without any agriculture or human dwellings. Hence, the three study sub-catchments are free of any point source emissions to the streams and any fertiliser application on the land surface.

2.2. Hydro chemical monitoring

The total discharge into the Carlsfeld reservoir was estimated daily from a mass balance calculation involving 15 min record of the reservoir water level (aggregated on a daily basis) and daily record of outflowing discharge. It was assumed that all three sub-catchments had the same specific discharge (in mm d⁻¹), equal to the specific discharge estimated for the whole catchment area of the reservoir. This assumption was considered acceptable because the total catchment area was small, with similar topography and the same land use over the sub-catchments. Discharge data were available for the whole study period (March 1995 to September 2016) except from June 1997 to November 1999 ([Fig. 2](#)).

Grab samples were collected monthly from March 1995 to September 2016, at the outlet of the three sub-catchments, between 8:00 am and 12:00 pm local time, and analysed for Soluble Reactive Phosphorus (SRP), nitrate-N (NO₃) and dissolved Fe after 0.45 μ m filtration ([Fig. 2](#)). Chemical analyses of water samples were performed using standard protocols (Wasserchemische Gesellschaft, 2014). SRP was determined colorimetrically by reaction with ammonium molybdate (UV-VIS Specord 200); NO₃ was determined as N by ionic chromatography (ICS-1100 Dionex); Fe was determined by atomic absorption spectrometry (AAS Solaar M5, Thermo).

The three studied catchments have been previously included in two multi-site biogeochemical studies ([Musolff et al., 2016](#); [Sucker et al., 2011](#)). A shorter time series of Carlsfeld 1 has also been selected for a showcase analysis of long-term Dissolved Organic Carbon (DOC) and SRP trends in [Musolff et al. \(2016\)](#), and in a DOC load uncertainty evaluation study ([Buettner and Tittel, 2013](#)). In contrast to the previously published biogeochemical studies, the present paper focuses on seasonal SRP variations and their implications for LAM.

2.3. Data analysis

The data analysis was threefold.

- The seasonal component of concentration and discharge time series was extracted from a long term trend component using Generalised Additive Models (GAM). GAM are generalized linear models in which the linear form is replaced by a sum of smooth functions ([Hastie and Tibshirani, 1987](#)). Technically, the year (1995–2016) and the month (1–12) for each data point were used as predictor variables to estimate the long term non-linear trend and a seasonal component, respectively. The R package *mgcv* ([Wood, 2006](#)) was used for this purpose, with cyclic cubic spline to avoid discontinuities at the end points of the spline (in other words, no discontinuity between December and January) and a correction for autocorrelation (autoregressive-moving-average model).
- The significance of trends was quantified by the slope of a linear regression model of annual mean concentration and discharge values as a function of the year. Although the GAM long term trend was not perfectly linear (see results), analysis of residuals showed that a linear model was acceptable to quantify a mean percentage increase or decrease during the study period and whether this increase or decrease was significant ($p < 0.05$).

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