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Limnologica 38 (2008) 126–138
LIMNOLOGICA
www.elsevier.de/limno

Variation in riverine phosphorus between 1994 and 2003 as affected by land-use and loading reductions in six medium-sized to large German rivers

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Received 29 September 2006; received in revised form 21 September 2007; accepted 18 October 2007

Abstract

Land use and in-stream transformation exert great influence on concentrations and loads of phosphorus (P) in rivers. We aimed to display differences in the courses of total P (TP) and soluble reactive P (SRP) concentrations and loads in six medium-sized to large rivers in the central region of Germany, and to identify the reasons for different long-term trends. Therefore, we applied multivariate statistics to 10-year-time series (1994–2003) of TP, SRP, discharge (Q), water temperature (T), pH, dissolved organic carbon (DOC), total organic carbon (TOC), dissolved oxygen (DO), total iron (Fe), and total manganese (Mn). Statistical results were related to land use in the catchments of the rivers. TP concentrations ranged between 0.02 and 0.78 $\mathrm{mg\,l^{-1}}$, and SRP concentrations ranged between 0.01 and 0.44 $\mathrm{mg\,l^{-1}}$. Q correlated negatively with TP and SRP concentrations over the entire year. Furthermore, Fe correlated significantly and positively to TP and SRP and therefore, ferric hydroxides likely were the major P sorption sites. DOC showed significant positive correlation to SRP particularly in spring, indicating manure exposure in early spring as a major source of both, DOC and SRP. Significant negative correlations between DO and SRP in summer hint at internal P loading in rivers or in flushed lakes. Different forms of land use were the reasons of enhanced or retarded recovering from previous increases in P concentrations. High portions of arable land within some of the catchments impeded the process of decreases since 1996 because of remaining high-diffuse emissions from fertilized soils. Agricultural practices, exposing fertilizer to soils within the river catchments and high Q in early spring caused high TP and SRP loads to downstream systems, and evoked risks for downstream river reaches.

Keywords: Phosphorus; Emissions; Imissions; Catchment characteristics; Multivariate statistics

Introduction

Worldwide, the increased loading of rivers with phosphorus (P) has been a severe problem starting in the 1960s (Dodds, 2006). Increases in concentrations of P were caused by point and diffuse emissions from the river catchments such as wastewater inlets and agriculture intensely using fertilizers and manure (Jensen et al., 2006). P has mostly been the limiting nutrient in streams and rivers, and excessive supply caused increases in phytoplankton biomass and thus temporary deficits in concentrations of dissolved oxygen (DO), which in turn had negative impact on the riverine biotic community (Alexander and Smith, 2006).

However, increases in P concentrations did not occur equally in all rivers. For example, River Main, located in

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0075-9511/$ - see front matter
doi:10.1016/j.limno.2007.10.002

central Germany, experienced intense increases in P concentrations, while other rivers, such as River Fulda, were less degraded by increased P emissions in their upper and middle courses. These differences reflect differences in land use within the catchments (Jensen et al., 2006), but also the capability of rivers to retain and transform P (Heidenwag et al., 2001), and the catchment-specific background concentrations (Robinson et al., 2003).

P retention is evoked by benthic structures, such as macrophytes (Schulz et al., 2003), mussels (Wanner and Pusch, 2001), wood debris (Valett et al., 2002), and microphytobenthos (Romaní et al., 2004). However, P retention is permanent only in part, because high waters might resuspend sediments and biofilms, rich in particulate P (PP), and macrophyte biomass might be decomposed and transported downstream at the end of the vegetation period (Kronvang et al., 1999). Schulz and Köhler (2006) evidenced high P retention in spring and summer and P releases in autumn and winter in a German lowland river, which was attributed to the presence of submerged macrophytes. The six rivers considered in our study are scarcely settled by macrophytes, but other benthic biota might evoke similar courses in P retention, concentrations, and loads (Logue et al., 2004). Permanent retention occurs when riparian areas of the lower course of a river becomes inundated during high waters and PP is exported and settled in meadows adjacent to the river (Kronvang et al., 1999).

In addition, diffuse P sources in the catchments reflect seasonally different agricultural practices (Kronvang et al., 2001). For example, manure is mainly exposed in spring, and plant coverage is generally low in autumn and winter, thus exposing soils to surface erosion. Overall in rivers, particulate and dissolved P forms are prone to both, intrinsic and extrinsic mechanisms, which cause differences in P concentrations and loads.

Organic seston rich in P, correlates to total organic carbon (TOC) (Schulz et al., 2003). Phosphate as determined as soluble reactive P (SRP) may also become sorbed to sestonic particles, such as ferrihydrites, and dissolved organic carbon (DOC), which to a large portion consists of humic substances (Kozerski and Kleeberg, 1998). However, the sorption of SRP to DOC is only relevant if humic compounds and SRP polymerize, as it was discussed for a brackish estuary by Forsgren and Jansson (1992). Sorption and desorption again are subdued to changes in pH (Aminot and Andrieux, 1996) and DO (Driescher and Gelbrecht, 1993), and P sorption in rivers can be affected by the availability of potential sorption sites.

Our study aimed to exhibit changes of total P (TP) and SRP concentrations and loads in six medium-sized to large rivers in the central part of Germany. Therefore, we used monitoring data of a 10-year-time series of these rivers comprising TP, SRP, discharge (Q), and physico-chemical parameters. We conducted multivariate statistics to analyse TP and SRP for temporal and spatial differences, and to correlate TP and SRP to physico-chemical parameters and Q. In addition, land use data were applied to identify major P sources in the catchments. In turn, the knowledge of the influence of land use on TP and SRP concentrations and loads in rivers may serve to support further decreases in P loads by adapting agricultural practice to potential risks in downstream lakes and rivers.

Materials and methods

Study sites

Six medium-sized to large rivers in central Germany, i.e., Rivers Main, Fulda, Lahn, Werra, Nidda, and Kinzig were investigated between 1994 and 2003. The monitoring stations were situated at the lower part of the rivers in planar to hilly areas. Fig. 1 illustrates the river courses, their catchments, and monitoring stations. Table 1 provides an overview of land use in the catchments, which is based on Coordination of Information on the Environment (CORINE) land-use data for the year 2000. The mapping of the land cover and land use was performed on the basis of satellite remote sensing images on a scale of 1:100,000.

River Main is the largest river investigated with a catchment comprising 27,292 km^2. The White and Red River Main originate in the northern mountains of Bavaria, SE Germany. Downstream of their confluence, River Main flows for 524 km mostly through Mesozoic rock formations, before entering into River Rhine. River Main experienced severe pollution and increases in P concentrations during the 1960s and 1970s by intense agriculture and poorly developed wastewater treatment, but recovered significantly thereafter. Q of River Main as Q of all rivers investigated is regularly lowest in summer and highest in early spring (Table 2).

River Fulda is a medium-sized to large river, originating in the Rhön Mountains and flowing for 218 km through Triassic sandstone. The catchment of River Fulda comprises 6932 km^2.

River Lahn originates in the Rothaar Mountains in the western part of Germany and passes for 242 km diverse Paleozoic and Mesozoic rocks, before entering into River Rhine. The catchment area amounts to 5964 km^2 and covers mostly forested regions. In 1999, River Lahn was chemically and biologically categorized as close to a natural state.

River Werra originates in the Federal State of Thuringia, East Germany, and flows for 292 km through Paleozoic and Mesozoic rock formations, before flowing into River Fulda. The catchment of River Werra covers 5496 km^2 of forested and agricultural regions with little industry.