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# Decoupled water-sediment interactions restrict the phosphorus buffer mechanism in agricultural streams

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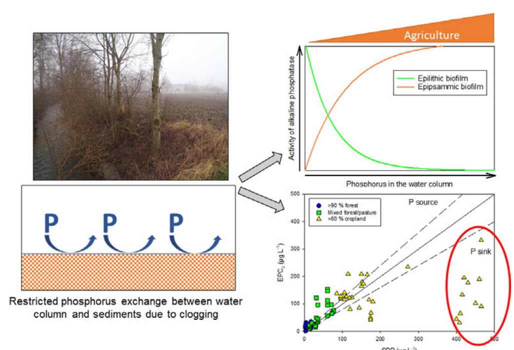
## HIGHLIGHTS

- Fine sediments and phosphorus concentrations increased with percent cropland.
- Sediments of polluted streams showed high potential for P adsorption.
- Phosphatase activity in epilithic biofilms decreased with increasing SRP in water.
- Phosphatase activity in epipsammic biofilms was highest in polluted streams.
- Fine sediments restrict P exchange between water column and sediments.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Our study aimed to explore the effects of agriculture on the phosphorus buffer capacity of 11 headwater streams in Austria. We used phosphorus adsorption curves and re-suspension experiments to determine both, the potential of the sediments to act as phosphorus source or sink and the actual phosphorus exchange between water and sediments. Additionally, we determined the alkaline phosphatase activity (APA) in epilithic and epipsammic biofilms as indicator for the phosphorus demand of the benthic and hyporheic community. We hypothesized that highly polluted streams will show decreased phosphorus buffer capacities, which were either due to saturation or restricted water-sediment interactions.

Our results support the second hypothesis. Fine sediment accumulations, organic matter content, and phosphorus concentrations in water and sediments increased with percent cropland in the catchment. Below SRP concentrations of 120 μg $L^{-1}$ in the stream water, sediments showed a high potential for phosphorus release, with zero equilibrium phosphorus concentrations ($EPC_0$) being more than twice as high as SRP concentrations. Above 150 μg $L^{-1}$, $EPC_0$ reached only 20–50% of SRP concentrations, indicating a high potential of the sediments to act as phosphorus sinks. These findings were confirmed by phosphorus uptake of these sediments during re-suspension. While APA in epilithic biofilms decreased with increasing SRP concentrations, APA in epipsammic biofilms showed the reverse pattern, indicating a restricted phosphorus supply of the hyporheic community despite phosphorus surplus in the water column.

Our study shows that inputs of fine sediments from agricultural sources may reduce the phosphorus buffering mechanism of stream sediments through restrictions of water-sediment interactions. Consequently, water

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column and sediment processes are increasingly decoupled and phosphorus-rich stream water will not effectively reach the reactive sites in the sediments responsible for uptake. Therefore, phosphorus mitigation measures in stream ecosystems must comprise sediment management in the catchment as well as in-stream measures for the rehabilitation of the hyporheic zone.



## 1. Introduction

The phosphorus (P) buffer mechanism describes the ability of sediments to regulate the concentrations of dissolved inorganic P in streams and rivers and keep them at almost constant levels over prolonged time periods (Froelich, 1988; Hoffman et al., 2009). The sedimentary buffer capacity originates from diverse geochemical and physical sorption processes, which lead to the fast and usually reversible P fixation to benthic and suspended sediment particles, thereby counterbalancing both P inputs to and outputs from the aquatic ecosystems (Haggard et al., 2004; Hoffman et al., 2009; Jarvie et al., 2005; Lottig and Stanley, 2007). In addition, biotic P uptake and release via assimilation and mineralization may substantially contribute to the buffering of P loads in streams and rivers (Dodds, 2003; Haggard et al., 1999; Lottig and Stanley, 2007; McDaniel et al., 2009). The P buffer mechanism results in increased in-stream retention of P imported from the terrestrial surroundings, thus providing a large pool of readily available P in the sediments and prolonging the time of P supply to the benthic community (McDowell, 2015; Palmer-Felgate et al., 2009). This P pool does not only represent a risk of internal eutrophication for the aquatic system, but it also increases its resistance to P mitigation measures (Froelich, 1988; Haggard et al., 2004; Hoffman et al., 2009; Sharpley et al., 2014; Stutter and Lumsdon, 2008).

Phosphorus delivered to streams in dissolved form can either be adsorbed by sediment particles or assimilated by the autotrophic and heterotrophic benthic and hyporheic community (House, 2003; Mainstone and Parr, 2002; Reddy et al., 1999; Withers and Jarvie, 2008). In both cases, the imported P is temporarily stored in the sediments. Under stable hydrological conditions, a balance between soluble reactive phosphorus (SRP) in the water column and loosely bound P in the sediments will develop (Lottig and Stanley, 2007; McDaniel et al., 2009). Imbalance between water column and sediments may result from restricted surface-subsurface water exchange, recent inputs of sediments or soil from the surroundings, or variable SRP concentrations from point-sources (Haggard et al., 1999; McDowell, 2015; Stutter and Lumsdon, 2008). As the surface of particles available for sorption is limited, the adsorption process is expected to tend towards saturation at high P concentrations, equally causing P disequilibrium between water and sediments (House et al., 1995; Stutter and Lumsdon, 2008). While benthic and hyporheic communities are the main beneficiaries of the sedimentary P pool, they are also key components of the P buffer system (Dodds, 2003; House, 2003; Haggard et al., 1999; Lottig and Stanley, 2007). The buffer capacity of bacteria and algae stems from their ability to generate P from the mineralization of organic matter with the help of alkaline phosphatase (Rier et al., 2011; Romani and Sabater, 2000). While phosphatase is mainly produced under P-limiting conditions (Davies and Bothwell, 2012; Rier et al., 2014; Sabater et al., 2011), bacteria and algae can store excess P during periods of elevated P availability (Khoshmanesh et al., 2002; Mateo et al., 2006). Hence, bacteria and algae can switch between internal and external P sources depending on the supply of bio-available P in their immediate surroundings. As biotic uptake is influenced by the ratio of P supply to demand, it should equally become saturated at high P concentrations (Covino et al., 2010; Haggard et al., 2004; Niyogi et al., 2004).

Agriculture affects the P buffer capacity of sediments in two ways: by increasing the overall P supply of the system and by changing the sediment structure (Allan, 2004; Gordon et al., 2008; Hancock, 2002; Palmer-Felgate et al., 2009). Numerous studies have shown that agricultural streams are exposed to elevated P inputs from the surroundings, resulting in increased P concentrations in both the water column and the sediments (Haggard et al., 2007; Hoffman et al., 2009; Palmer-Felgate et al., 2009). According to the concept of saturation, increased P loading should lead to decreased buffer capacities as long as the sediment structure remains unchanged (Haggard et al., 2004; Withers and Jarvie, 2008). However, agriculture also impacts stream ecosystems through the export of eroded, mostly fine and organic-rich soil particles, which are deposited on the channel bed or in the hyporheic zone (Hancock, 2002; Hoffman et al., 2009; Stutter and Lumsdon, 2008; Teufl et al., 2013). As abiotic adsorption is highest in clay and silt, the overall sorption capacity of stream sediments should increase with increasing clay and silt proportions (Agudelo et al., 2011; Lottig and Stanley, 2007; McDaniel et al., 2009), thus moving the threshold of saturation towards higher P concentrations. However, most soil particles entering streams may already be loaded with P (Agudelo et al., 2011; Ekholm et al., 1997; Stutter and Lumsdon, 2008). Furthermore, fine sediment particles may clog the interstices and reduce the exchange between surface water and sediments (Hancock, 2002; Teufl et al., 2013; Wood and Armitage, 1997). Consequently, sediments in agricultural streams may not be able to exploit their full P buffer capacity.

In our study, we explored the question of how agriculture affects the P buffer capacity of sediments in headwater streams. Specifically, we were interested in whether we could detect any signs of decreased buffer capacities in highly impacted stream sediments and, if so, whether such effects were due to P saturation or to a restricted surface-subsurface water exchange. We used the zero phosphorus equilibrium concentration ($EPC_0$) obtained from batch equilibrium experiments as a measure for the potential of sediments to act as P source or sink for the water column (Froelich, 1988; House, 2003; Jarvie et al., 2005; Reddy et al., 1995). In addition, we performed re-suspension experiments with phosphorus-poor and in-situ water to determine a) maximum P release rates and b) release or uptake rates under ambient P conditions, thus mimicking resuspension during floods. We determined the alkaline phosphatase activity (APA) in both epipsammic (attached to fine sediment particles) and epilithic (attached to stones) biofilms as indicator for the P demand of the benthic and the (surficial) hyporheic community. We hypothesized that $EPC_0$ will increase with increasing P (and fine sediment) loading of our study streams (Fig. 1a). However, we also expected that this increase would follow some kind of saturation curve (i.e. $EPC_0$ lying distinctly below stream water concentrations at high P loads), indicating decreased P buffer capacities of sediments in highly polluted streams. If such a water-sediment imbalance were caused by saturation (Fig. 1b), P net exchange between water and sediments should be negligible under ambient P concentrations and APA in both epilithic and epipsammic biofilms should decrease with increasing SRP concentrations in the stream water. However, if this water-sediment imbalance were caused by restricted surface-subsurface water exchange (Fig. 1c), we expected APA in epilithic biofilms to decrease with increasing SRP in the stream water, while APA in epipsammic biofilms increased, thus reflecting the limited P supply of the hyporheic communities. Likewise, we expected sediments to function as P sink when suspended in stream water.