



# Photochemical degradation of dissolved organic matter reduces the availability of phosphorus for aquatic primary producers

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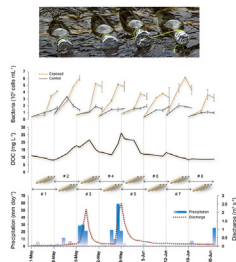
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## HIGHLIGHTS

- In situ photochemical experiments demonstrated a decline in dissolved phosphorus concentrations.
- Abiotic and biotic mechanisms are responsible for the reduction of dissolved phosphorus in headwater streams.
- DOM quantity and quality affect the proportion of biotic and abiotic processes in dissolved phosphorus immobilization.

## GRAPHICAL ABSTRACT



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## ABSTRACT

*In situ* experiments were done to determine the effects of the photochemical degradation of dissolved organic matter (DOM) and subsequent formation of particulate matter on dissolved phosphorus (P) concentrations in surface waters. Filtered (1.2 or 0.4  $\mu\text{m}$ ) headwaters (DOM of 8.1–26  $\text{mg L}^{-1}$ ; P of 22–43  $\mu\text{g L}^{-1}$ ) were exposed to solar radiation in quartz bottles located 5 cm below the water surface for 7–10 days. Dark controls were wrapped in aluminum foil. After incubation, particulate organic carbon (POC) and particulate phosphorus (PP) were determined in both the filtrate and newly formed particles. The results revealed increasing concentrations of PP and POC in exposed samples with increasing exposure time (cumulative irradiation energy). At the end of experiments, PP concentrations were from 5 to 20  $\mu\text{g L}^{-1}$  in the exposed samples. Based on an enumeration of bacteria in the samples, we estimated the contribution of biotic and abiotic processes to the PP production. The abiotic PP formation ranged from 56 to 83% and 50–95% of the total PP in the exposed and control samples, respectively. The remainder was assumed to be bacterial P uptake. Despite the overlapping intervals, biotic and abiotic PP productions were usually higher in exposed samples than in controls. The PP and POC production was affected by the properties of DOM, such as its humic content and freshness index. We hypothesize that the observed immobilization of dissolved P in bacteria and on photochemically-formed particles can contribute to a P limitation of primary production in headwater environments that receive waters rich in soil DOM.

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## 1. Introduction

The main process affecting the net photochemically-induced formation of particulate organic matter (POC) is the

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### Abbreviations

DOM	dissolved organic matter
DOC	dissolved organic carbon
DIC	dissolved inorganic carbon
POC	particulate organic matter
DP	dissolved phosphorus
SRP	soluble reactive phosphorus

photochemically-induced release of organically bound metals (Porcal et al., 2013) and photodissolution of POC (Estapa et al., 2012). Aluminum (Al) and iron (Fe) are quantitatively the most abundant organically bound metals in natural freshwaters. Their hydrolysis, following photochemical liberation, results in the formation of poorly soluble hydroxides in circum-neutral (and in the case of Fe also oxygenated) surface waters (Stumm and Morgan, 1996).

The specific surface area of freshly precipitated (mostly colloidal) Fe and Al hydroxides is large, which together with positively charged surfaces in acidic and circum-neutral conditions enables them to strongly bind phosphate (as well as organic acid anions) (Hingston et al., 1972; Detenbeck and Brezonik, 1991; Pullin et al., 2004).

Alternatively, positively charged metal species can bind to anionic sites of DOM, thus neutralizing its negative charge, and causing DOM coagulation to POC, similar to the process used in the removal of DOM from drinking water (Hocking, 1998). This mechanism probably dominates in the formation of POC-metal particles under acidic conditions (Porcal et al., 2013), where the formation of colloidal Al and Fe hydroxides is thermodynamically less favorable, and soluble cationic forms dominate the metal species (Stumm and Morgan, 1996). The co-precipitation of DOM with liberated metals (i.e., the simultaneous precipitation of soluble organic C with Al and Fe (hydr)oxides) forms mixed precipitates. The result is an increasing production of POC in solution during and after irradiation (von Wachenfeldt et al., 2008; Porcal et al., 2009, 2013), which contributes to an overall decrease in DOM concentrations, predominantly caused by photo-oxidation to CO and CO<sub>2</sub> and cleavage to low molecular weight organic species that are mineralized by microbial processes (Miller and Zepp, 1995; Graneli et al., 1996; Bertilsson and Tranvik, 2000).

The photochemically-mediated degradation of DOM is an important source of phosphorus (P) through the transformation of iron complexes that bind humic substances and phosphate together (Francko and Heath, 1982). During this process in surface waters, phosphate is first liberated, but then bound by Fe and Al hydroxides, also resulting from photochemical cleaving of metal-DOM complexes e.g., (Kopáček et al., 2005; Porcal et al., 2009). Most studies have suggested that phosphate adsorption on metal hydroxides is chemisorption, where phosphate ions replace hydroxide ions e.g., (Lijklema, 1980; Lueddecke et al., 1989). The adsorption of phosphate onto the surface of crystalline oxides such as goethite (α-FeOOH) e.g., (Hiemstra and VanRiemsdijk, 1996; Weng et al., 2012) or freshly formed hydrous ferric oxides (Conidi and Parker, 2015) has been well characterized. Freshly formed amorphous Fe and Al (hydr)oxides have a higher adsorption capacity in comparison to aged, crystalline forms (Jan et al., 2013; Conidi and Parker, 2015). Phosphate adsorption on their surfaces or co-precipitation together with POC may cause a decreasing availability for phytoplankton (Nalewajko and Paul, 1985). Baken et al. (2016) showed that the biological availability of bound P is

affected by the type of binding, with phosphate adsorbed on the surface of oxyhydroxides being more available to biota than co-precipitated P.

The adsorption of phosphate on different types of Al and Fe (hydr)oxides has been widely studied in soils and under laboratory conditions e.g., (SanClements et al., 2010; Jan et al., 2013; Porcal et al., 2017). Photochemically-induced P adsorption on freshly formed Al and Fe (hydr)oxides and their co-precipitates with POC has not been, however, thoroughly studied in natural aquatic ecosystems. The potential of formation of Al and Fe (hydr)oxides in streams has been documented by Porcal et al. (2009), who demonstrated that 17% and 51% of organically bound Al and Fe, respectively, can be released to stream water within 8 h of a day around summer solstice from fulvic acids, while it is lower for humic acids (4–7% for Al and 24–48% for Fe). Here, we present results of *in situ* photochemical experiments conducted to quantify the effect of the photochemically induced changes of DOM by solar radiation to the subsequent formation of particulate matter and the immobilization of dissolved P in a headwater stream.

## 2. Methods

### 2.1. Locations

All experiments were done with samples from the main tributary to the Jiřícká Pond (48.6189N, 14.6731E), situated in the southern part of the Czech Republic close to the border with Austria at an elevation of 892 m a. s. l. The Jiřícká Pond watershed (12.5 km<sup>2</sup>) is covered with forest (76%), pastures (23%) and peat bogs (1%), with very little human influence.

### 2.2. Exposure experiments

A series of *in situ* irradiation experiments with water from the freshwater headstream was done in late spring and the early summer months. Hydrological conditions during the experiments ranged from base flow to extreme flow events (Fig. 1), and covered a wide range of temperature and solar insolation intensity. Experiments #1–8 were done in May and June 2014, and experiment #9 was done in June and July 2013. Samples were collected into polyethylene-terephthalate bottles covered in aluminum foil. Samples were immediately transported to the laboratory and filtered through glass fiber filters (experiments #1–8, pore size 1.2 μm, GF/C, Whatman, U.S.A.; experiment #9, pore size 0.4 μm, MN-GF5, Macherey Nagel, Germany). Aliquots of filtered samples were placed in quartz flasks (length 30 cm, diameter 5 cm, closed with grounded glass stopper) and in borosilicate glass bottles (volume 500 mL) wrapped in aluminum foil as a control. Prefiltered samples were placed back into the tributary (48.6127N, 14.6826E) and exposed to natural solar radiation for 7–10 days. Quartz flasks were placed horizontally in a wooden (not shading) holder, ensuring stability and a constant mean submersion depth of 5 cm. Control samples were also submerged into the tributary (mean depth was 10 cm due to the shape of the bottles). Exposed and control samples were collected regularly (at least 4-times) during the course of the experiments and immediately processed as described below. All sampling was done in duplicate.

### 2.3. Chemical analysis

Measured volumes of exposed and control samples were filtered through 0.4 μm glass fiber filter (MN-GF5, Macherey Nagel, Germany) and 0.45 μm membrane filter (mixed cellulose ester, Millipore, U.S.A.). Material retained on glass filters was analyzed for POC, and on membrane filters for concentrations of particulate

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