Photochemical cleaving of allochthonous organic-metal complexes contributes to phosphorus immobilization in surface waters

Petr Porcal [a, b, *], Kristýna Frejlachová [b], Jiří Kopáček [a], Jiří Nedoma [a], Tereza Šavrdová [b]

[a] Biology Centre of the Czech Academy of Sciences, v.v.i, Institute of Hydrobiology and Soil & Water Research Infrastructure, Na Sadkach 7, Ceske Budejovice, 370 05, Czech Republic
[b] University of South Bohemia in Ceske Budejovice, Faculty of Science, Branisovska 1760, 370 05, Czech Republic

HIGHLIGHTS

- Photochemical degradation of dissolved organic matter affects metal complexation.
- Photochemically formed metal particles support phosphorus sorption.
- This process reduces the phosphate mobility and bio-availability in waters.

ARTICLE INFO

ABSTRACT

The photochemical transformation of terrestrial dissolved organic carbon (DOC) in surface waters exposed to UV radiation causes the precipitation of metal (Al and Fe) bearing complexes with high phosphorus sorption capacities. To better elucidate this process, a series of laboratory experiments was performed with stream and river waters with pH range from 3.5 to 8.2 and concentrations of dissolved reactive phosphorus from 2 to 142 $\mu g\,L^{-1}$. Samples were filtered (0.4 μm) and UV (350 nm) irradiated for 24 h at 68 $W\,m^{-2}$, i.e. under conditions equivalent to ~2 summer days of natural solar radiation. Irradiated samples and dark controls were then spiked with ^{33}P-phosphate and the kinetics of P adsorption on freshly formed particles was determined after separation by ultracentrifugation. Up to 68% of the added P was removed from the solution within 48 h of the spike. The P sorption was pH dependent, with the maximum sorption ability at pHs of 6–7. We hypothesize that this process can importantly contribute to the immobilization and lower bioavailability of P in the inlet areas of (especially circum-neutral) lakes due to the intensive photochemical degradation of allochthonous DOC-metal complexes.

1. Introduction

Photochemical transformation of allochthonous dissolved organic matter (DOM) in surface waters results in the production of several different photoproducts, including low molecular weight (labile and easily bio-available) compounds (Kieber et al., 1989; Bertilsson and Tranvik, 2000) and dissolved inorganic carbon (Miller and Zepp, 1995; Graneli et al., 1996), as well as the liberation of organically bound metals (e.g. Kelton et al., 2007; Kopacek et al., 2005; Shiller et al., 2006). Of the released metals, iron (Fe) and aluminum (Al) are usually most quantitatively important. Both these metals hydrolyze and (depending on the water pH) form poorly soluble hydroxides that precipitate (Stumm and Morgan, 1996). The specific surface area of these 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 and other anions including organic molecules (Kingston et al., 1972; Detenbeck and Brezonik, 1991; Pullin et al., 2004). The adsorption of DOM on these Fe and Al hydroxides is an additional mechanism decreasing DOM concentrations during (and after) irradiation, resulting in the production of particulate organic C (POC) (Porcal et al., 2009, 2013). Alternatively, positively charged metal species can bind to anionic

sites of dissolved organic carbon (DOC), thus neutralizing its negative charge, and causing DOC coagulation to POC, similar to the process used in the removal of DOC 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 Al and Fe hydroxides is negligible and soluble cationic forms dominate the metal species (Stumm and Morgan, 1996).

Photochemical transformations of DOM can also lead to the release of inorganic nutrients such as P and N (Francko and Heath, 1982), (Vähätalo et al., 2003; Vähätalo, 1996; Mostofa et al., 2011). Solar UV radiation affects P cycling by the photodegradation of enzymes such as alkaline phosphatase (Zepp et al., 2003) or by the photolysis of phosphatase-humic complexes in the aquatic environment (Boavida and Wetzel, 1998; Espeland and Wetzel, 2001; He et al., 2009). Another important photochemical source of phosphate is its release from humic substances by the UV mediated transformation of iron complexes that bind humic substances and phosphate together (Francko and Heath, 1982). Acidic forest soils with elevated concentrations of Fe and Al and humic (and fulvic) acids in soil solutions are potential sources of such soluble DOC-Fe(Al)-phosphate complexes (Gerke, 2010). During photochemical cleaving of these complexes in surface waters, phosphate is first liberated, but then bound by Fe and Al hydroxides resulting from hydrolyzes of ionic metal forms also liberated during irradiation (Kopacek et al., 2005; Porcal et al., 2009; Roy et al., 1999; Kopacek et al., 2001, 2006). This process may cause a decreasing availability of orthophosphate for phytoplankton (Nalewajko and Paul, 1985).

This study was aimed at elucidating the effect of the photodegradation of autochthonous DOM on the fate of soluble reactive phosphorus in surface waters. A collection of water samples from different sources was used to test the hypothesis that the photochemically induced formation of particles such as aluminum and iron hydroxides can reduce the availability of soluble reactive phosphorus in surface waters.

2. Methods

2.1. Locations

The samples used in this study were collected at several locations (streams, rivers, bog and lake) in Central Europe, mostly in the Czech Republic (Supplementary information, SI; Figure SI1, Table SI1). The selection of particular locations was based on the following chemical parameters: pH, DOC concentration, and aluminum and iron concentrations, to cover wide ranges of these parameters. Table SI2 shows the selected locations, sampling dates, and initial chemical parameters.

2.2. Sampling and sample preparation

Samples were collected into 18 L polyethylene terephthalate bottles previously acid washed and thoroughly rinsed with demineralized water. Additionally, each bottle was rinsed with sample water prior to sampling. Closed sampling bottles were wrapped in aluminum foil to prevent solar irradiation after sampling and during their transport to the laboratory (<12 h). In the laboratory, samples were immediately filtered through a 0.4 μm pore size glass fiber filter (MN-5, Macherey Nagel, Germany) and stored in the dark at 4 °C before irradiation experiments (<12 h).

2.3. Irradiation experiments

Filtered samples were divided into four aliquots (triplicates plus a dark control) and irradiated for 24 h in quartz tubes (25 cm length, 5 cm in diameter, total volume of ~0.5 L, tightly closed with a ground glass stopper) in an UV irradiation chamber (Rayonet RPR-200, The Southern New England Ultraviolet Company, USA). The UV irradiation chamber was equipped with sixteen UV lamps (Rayonet RPR-3500, The Southern New England Ultraviolet Company, USA) emitting radiation in the UV-A range with maximum at 350 nm (24 h of exposure to the artificial UV radiation in the laboratory corresponded to ~2 days of natural solar radiation in May 2012) (Porcal et al., 2014b). The temperature inside the irradiation chamber was regulated by a fan; temperature of the irradiated samples did not exceed 30 °C, which was approximately 5 °C above ambient laboratory temperature. Dark controls were wrapped in aluminum foil and kept at the same temperature for the same time as irradiated samples.

After irradiation, samples were split into two parts. One part (45 mL) was not further filtered and was used in ^{33}P sorption experiments. The rest was filtered again through the 0.4 μm glass fiber filters to characterize chemical changes in water composition and particulate matter that originated during irradiation. Filters with retained particles were used for the determination of POC, and particulate Al (Al_{part}) and Fe (Fe_{part}) concentrations. The filtrate was used to determine pH and concentrations of DOC, dissolved Al (Al_d) and Fe (Fe_d), and reactive phosphorus concentrations.

2.4. Analyses

POC was determined by catalytic oxidation at 900 °C (SSM 5000A module in combination with a TOC 5000A analyzer, Shimadzu, Japan) with a detection limit of ~9 μmol L^{-1}. DOC was analyzed by catalytic combustion at 680 °C (TOC 5000A, Shimadzu, Japan) with a detection limit of ~8 μmol L^{-1}.

Non-labile, mostly organically bound, Fe (Fe_o) and Al (Al_o) species were determined according to Porcal et al. (2009), with the filtered samples promptly passed through a column filled with strong cation-exchange resin (DOWEX 50WX8, 2% in H$^+$ and 98% in Na$^+$ form) to remove ionic and labile forms of metals from the solution. Concentrations of Al_{part} and Fe_{part} were determined after nitric acid digestion ($\geq$99.999% trace metals basis, Sigma-Aldrich) of the filters at 25 °C for 24 h. Concentrations of Al and Fe in water samples and digests were determined by atomic absorption spectrophotometry (Varian AA240Z with a GTA 120 graphite tube atomizer) with a detection limit of ~0.05 μmol L^{-1}.

Dissolved reactive phosphorus (DRP) was determined by a molybdate method according to Murphy and Riley (1962).

2.5. ^{33}P sorption experiment

Adsorption of P on particles (either original <0.4 μm, or formed during irradiation) was tested using the ^{33}P radionuclide added as H$_3$PO$_4$ (American Radiolabeled Chemicals, Inc., St. Louis, U.S.A.), and determining its activity in solution after particle removal by centrifugation. From 10 to 20 μL of the stock ^{33}P solution was added to centrifuge tubes with 45 mL of dark controls and unfiltered irradiated samples to reach the same initial ^{33}P activity of 2 mCi mL^{-1}. The volume of added stock solution depended on its actual activity (^{33}P half-live is 25.3 days), determined before each experiment. We suppose that the possible competition for adsorption sites between DRP and added ^{33}P was negligible due to an order of magnitude difference in their concentrations.

During the adsorption experiment, samples were stored at laboratory temperature in closed centrifuge tubes in the dark, and were occasionally flipped over carefully so that to mix the contents, but not to damage particles. After adsorption times of 0, 1, 2, 4, 8, 24, 48 h, 1.3 mL of sample was collected and centrifuged for 10 min at 17,530 relative centrifugal force to separate particles (Hettich Mikro