Biogeochemical Phosphorus Cycling in Groundwater Ecosystems – Insights from South and Southeast Asian Floodplain and Delta Aquifers

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18 **Key words**

- 19 • aquatic phosphorus cycling
- 20 • groundwater
- 21 • Asian floodplain and delta regions
- 22 • phosphate
- 23 • reducing aquifers
- 24 • stable oxygen isotopic signature in phosphate

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Abstract

The biogeochemical cycling of phosphorus (P) in South and Southeast Asian floodplain and delta aquifers has received insufficient attention in research studies, even though dissolved orthophosphate (PO_4^{3-}) in this region is closely linked with the widespread contamination of groundwater with toxic arsenic (As). The overarching aim of this study was to characterize the enrichment of P in anoxic groundwater and to provide insight into the biogeochemical mechanisms underlying its mobilization, subsurface transport, and microbial cycling. Detailed groundwater analyses and *in situ* experiments were conducted that focused on three representative field sites located in the Red River Delta (RRD) of Vietnam and the Bengal Delta Plain (BDP) in West Bengal, India. The results showed that the total concentrations of dissolved P (TDP) ranged from 0.03 to 1.50 mg L⁻¹ in groundwater, with PO_4^{3-} being the dominant P species. The highest concentrations occurred in anoxic sandy Holocene aquifers where PO_4^{3-} was released into groundwater through the microbial degradation of organic carbon and the concomitant reductive dissolution of Fe(III)-(hydr)oxides. The mobilization of PO_4^{3-} may still constitute an active process within shallow Holocene sediments. Furthermore, a sudden supply of organic carbon may rapidly decrease the redox potential, which causes an increase in TDP concentrations in groundwater, as demonstrated by an *in situ* experiment. Considering the subsurface transport of PO_4^{3-} , Pleistocene aquifer sediments represented effective sinks; however, the enduring contact between oxic Pleistocene sediments and anoxic groundwater also changed the sediments PO_4^{3-} -sorption capacity over time. A stable isotope analysis of PO_4^{3-} -bound oxygen indicated the influences of intracellular microbial cycling as well as a specific PO_4^{3-} source with a distinct isotopically heavy signal. Consequently, porous aquifers in Asian floodplain and delta regions proved to be ideal natural laboratories to study the biogeochemical cycling of P and its behavior in groundwater environments.

1. Introduction: phosphorus in anoxic aquifers

Extensive research has been conducted in the Aquatic Sciences related to eutrophication and the biogeochemical cycling of phosphorus (P) in surface waters and marine environments (Conley et al. 2009, Reddy et al. 1999). In contrast, the behavior and occurrence of P in pristine aquifers has received little attention (Lewandowski et al. 2015). Previous research on P in groundwater has mainly focused on highly contaminated sites (Parkhurst et al. 2003, Robertson et al. 1998), and an increasing number of publications have only recently investigated the fate of P in pristine groundwater ecosystems. The biogeochemical cycling of P in aquifers is relevant because groundwater may serve as a potent source of P to surface waters, thereby increasing the risk of eutrophication (Holman et al. 2010, Lewandowski et al. 2015, Mellander et al. 2016). Furthermore, P is believed to play a key role in the enrichment of toxic arsenic (As) in the groundwater of the large floodplains and delta regions in South (S) and Southeast (SE) Asia (Ravenscroft et al. 2001).

To draw conclusions regarding cycling and potential sources, it is necessary to identify the P species present in groundwater. Dissolved inorganic phosphorus is considered the principle form of P in groundwater, which is predominantly present as orthophosphate anions (H_2PO_4^- and HPO_4^{2-}) under ambient conditions (Slomp and Van Cappellen 2004, Stumm and Morgan 2012). Dissolved orthophosphate (PO_4^{3-}) is routinely identified by analyzing filtered water samples (pore size: 0.2 or 0.45 μm) using Ion Chromatography (IC) or is photometrically measured using the molybdenum blue method (Murphy and Riley 1962, Nagul et al. 2015, Worsfold et al. 2016). In addition, the concentration of total dissolved P (TDP) is often measured from filtered samples using for example Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Mass Spectrometry (ICP-MS). Assuming that PO_4^{3-} represents the dominant species of P in groundwater, TDP measurements are considered a suitable proxy for a PO_4^{3-} analysis (McArthur et al. 2004); however, this assumption must be verified due to the presence of other forms of P in water (i.e., polyphosphates, pyrophosphates, reduced inorganic P species, and dissolved organic P compounds as well as complexes, colloids, and particles) that might be overlooked (Hanrahan et al. 2005, Scherrenberg et al. 2008, Spivakov et al. 1999). For example, there is evidence of the presence of sub-micrometer Fe-mineral particles and organic-colloids in the anoxic groundwater of West Bengal (India), causing a size-fractionation of different elements including As, which could also apply to PO_4^{3-} (Majumder et al. 2014). The P species composition in groundwater has a high relevance because it determines not only

the bioavailability but also the subsurface transport behavior of P (Baken et al. 2014, Gschwend and Reynolds 1987). A small number of groundwater contamination case studies have shown that PO_4^{3-} represents the dominant dissolved P species (Harman et al. 1996, Robertson et al. 1998); however, the groundwater in SE Asia has rarely been investigated (McArthur et al. 2004). Usually, PO_4^{3-} background concentrations in groundwater of pristine aquifers remain below $0.05 \text{ mg L}^{-1} \text{ PO}_4\text{-P}$ (Lewandowski et al. 2015); however, groundwater can receive and maintain high concentrations of PO_4^{3-} by leaching from arable land, or from leaking septic tanks and sewer pipes (Robertson et al. 1998, Roy and Bickerton 2014). For example, PO_4^{3-} concentrations exceeding $0.5 \text{ mg L}^{-1} \text{ PO}_4\text{-P}$ were reported for shallow sandy aquifers in the agricultural areas of the northern region of Germany (Kunkel 2004). Within the groundwater of the large delta areas of S and SE Asia, elevated concentrations of dissolved P (either determined as PO_4^{3-} or TDP) are especially widespread, as summarized in Fig. 1. Here, numerous groundwater quality studies were conducted due to the widespread occurrence of toxic dissolved As, which threatens the health of millions of residents (Charlet and Polya 2006, Nickson et al. 1998). The presence of PO_4^{3-} in groundwater is closely interrelated with the enrichment of dissolved arsenite (As^{3+} , present as H_3AsO_3) because both molecules specifically adsorb to Fe-(hydr)oxide surfaces via ligand exchange and thereby compete with each other for sorption sites (Ravenscroft et al. 2001). For example, sorption modeling conducted by von Brömssen et al. (2008) and Biswas et al. (2014b) for groundwater in Bangladesh indicated that dissolved As^{3+} would entirely adsorb to the aquifer sediments in the absence of PO_4^{3-} in the system.

location	unit	min.	25%	med.	75%	max.	avg.	std. dev.	n	r_s P,Fe	ref.
BDP, Bangladesh	TDP (mg L ⁻¹)	0.00	0.00	0.30	0.90	18.9	0.73	1.25	3530	0.56*	1
BDP, West Bengal, Nadia District	TDP (mg L ⁻¹)	0.00	0.05	0.41	1.13	3.20	0.63	0.65	181	0.85*	2
MD, Vietnam and Cambodia	PO ₄ ³⁻ (mg L ⁻¹ PO ₄ -P)	0.00	0.00	0.10	0.40	5.30	0.39	0.72	352	0.54*	3
RRD, Vietnam	PO ₄ ³⁻ (mg L ⁻¹ PO ₄ -P)	0.00	0.00	0.15	0.64	6.70	0.44	0.72	512	0.47*	4

Refs.: ¹BGS and DPHE (2001), ²Majumder et al. (2015), ³Buschmann et al. (2008), ⁴Winkel et al. (2011)

*significance: $p < 0.05$

Fig. 1: Overview compilation of dissolved P in groundwater (determined either as TDP or PO₄³⁻) in the Bengal Delta Plain (BDP) in Bangladesh (BGS and DPHE 2001) and the Nadia District located in West Bengal, India (Majumder et al. 2015), the Red River Delta (RRD) in Vietnam, and the Mekong Delta (MD) in Cambodia and Vietnam (Buschmann et al. 2008, Winkel et al. 2011).

Because the PO₄³⁻ concentrations in groundwater exceed 1 mg L⁻¹ PO₄-P in the aquifers of S and SE Asian floodplain and delta regions, it is important to identify the sources. Despite extensive research on the cycling of organic and inorganic P forms in marine and lake sediments, little is known regarding the cycling and transformation processes in porous aquifers. Groundwater with elevated TDP and PO₄³⁻ concentrations is mostly found between 20 to 60 m below the surface (bls) as illustrated in Fig. 1, where the aquifers are formed by sandy deposits of Holocene age (Tanabe et al. 2003, Umitsu 1993). Sedimentary organic carbon (SOC) and dissolved organic carbon (DOC) represent potential sources of P, which can release PO₄³⁻ during microbially mediated mineralization. Furthermore, reactive (i.e., easily degradable) DOC and SOC can fuel microbial respiration, which causes a rapid

depletion in the dissolved terminal electron acceptors (TEA). Once redox conditions are reached that are favorable for the reductive dissolution of Fe(III)-(hydr)oxides, adsorbed and/or occluded PO_4^{3-} is concomitantly released into ambient groundwater (Einsele and Vetter 1938, Stumm and Sulzberger 1992); however, there is little evidence that indicates that the PO_4^{3-} release into groundwater via the Fe(III) reduction pathway in the anoxic aquifers of SE Asia is still an active (i.e., recent, ongoing) process. In addition, other potential sources might contribute PO_4^{3-} to groundwater as well, especially anthropogenic activities (i.e., fertilizer application and sanitation) (Acharyya et al. 2000).

Following the reductive dissolution of Fe(III)-(hydr)oxides, subsequent abiotic and biotic processes influence the PO_4^{3-} concentration in groundwater. Under reducing conditions, the concentration of PO_4^{3-} is considered to mainly be constrained by surface adsorption and co-precipitation with reduced mineral phases, such as vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) and siderite (FeCO_3) (Barber 2002, Parkhurst et al. 2003, Robertson et al. 1998); however, limited field data are available regarding the adsorption and mineral precipitation processes that determine the mobility and concentrations of PO_4^{3-} in groundwater (Spiteri et al. 2007). Furthermore, the extensive abstraction of groundwater may greatly alter groundwater flow paths and therefore trigger different responses in the aquifer. Floodplain and delta sediments usually behave as one large hydraulically interconnected aquifer system and the migration of anoxic groundwater into less reducing aquifer zones was reported for large parts of the Red River Delta (RRD) and the Bengal Delta Plain (BDP) (Michael and Khan 2016, Winkel et al. 2011). Nevertheless, the impact of groundwater abstraction on the spatial distribution of PO_4^{3-} has rarely been addressed thus far. For example, Neidhardt et al. (2013a) simulated repeated cycles of groundwater abstraction during the dry season in the Bengal Delta Plain. The outcomes of this field experiment suggested that pumping can desorb loosely bound PO_4^{3-} from the sandy aquifer sediments solely by increasing the local groundwater flow velocity. In addition, this experiment affected the partitioning of PO_4^{3-} between groundwater and the aquifer sediments thereafter for several months. Furthermore, due to intensive groundwater abstraction, reactive DOC may be transported into OM-depleted aquifer sections and may potentially trigger subsequent biogeochemical reactions, such as microbial Fe(III) reduction, as was suggested at the field site located in Van Phuc in the RRD of Vietnam (van Geen et al. 2013).

Despite the detailed hydrochemical and geochemical data sets available for aquifers in Asian deltas and floodplains, no specific attempt has been made to systematically analyse the mechanisms underlying the mobilization and enrichment of PO_4^{3-} in the groundwater of these regions. There is also

a general lack of studies that utilized mechanistic approaches to investigate P cycling in groundwater ecosystems. Such knowledge, especially regarding immobilization pathways, can be highly valuable regarding the remediation of anthropogenically influenced aquifer systems, which represent a considerable issue in agricultural areas. Therefore, in this study, groundwater monitoring data, sediment analyses and *in situ* experimental data from the field sites in the Bengal Delta and the RRD were combined to address the following questions:

- (i) Is PO_4^{3-} the dominant P species in the groundwater of anoxic aquifers of S and SE Asia?
- (ii) What are the sources of dissolved PO_4^{3-} in anoxic groundwater?
- (iii) Is Fe(III) reduction the principal PO_4^{3-} mobilization mechanism and is this still an active process?
- (iv) What abiotic and biotic processes occur during the subsurface transport of PO_4^{3-} ?

2. Methods

2.1 Study sites

The primary study area was located in the RRD near the metropolitan area of Hanoi. The RRD is located in the NW–SE-orientated Basin of the Sông Hồng (Red River) and covers an area of 14,300 km² (Luu et al. 2010). Details regarding the sedimentation history and hydrogeology of the RRD are provided elsewhere (Berg et al. 2007, Tanabe et al. 2003). The village of Van Phuc (20°55'7.00"N, 105°53'55.00"E) is located in the floodplain of the Red River and represents an ideal natural laboratory to study the cycling and transport of P in the groundwater of two contrasting aquifer systems (Fig. S1). The natural flow direction of groundwater was reversed due to extensive groundwater abstraction in the vicinity of Hanoi (van Geen et al. 2013). Consequently, anoxic groundwater characterized by a low redox potential laterally migrates from greyish Holocene aquifer sediments into adjacent orange-colored Pleistocene sand deposits that are characterized by a high content of Fe(III)-(hydr)oxides (Eiche et al. 2008). Long-term contact with reducing groundwater strongly altered the Pleistocene aquifer sediments and changed the groundwater composition along an approximately 120 m wide transition zone (van Geen et al. 2013). The aquifers are covered by a confining layer of clayey and silty deposits, which represent a common feature of the RRD and prevent a direct infiltration of surface water (Tanabe et al. 2003). The groundwater of the Pleistocene aquifer is usually characterized by a near-neutral pH and low Fe^{2+} , As^{3+} , and TDP concentrations, whereas the groundwater of the transition zone and the Holocene aquifer are characterized by elevated total concentrations of Fe^{2+} , Mn^{2+} , As^{3+} , and TDP (Neidhardt et al. 2018). Detailed descriptions of the sedimentation history and

groundwater evolution at Van Phuc have been presented in previous publications (Berg et al. 2008, Eiche et al. 2017, Eiche et al. 2008, van Geen et al. 2013).

Two additional study sites were included for comparison purposes, which were located in the Nadia District in West Bengal, India. This region is located in the western part of the central floodplain area of the Bengal Basin, which is often referred to as the Ganges-Brahmaputra-Meghna delta and floodplain or simply as the BDP (Umitsu 1993). Further details regarding the geology of the BDP are provided elsewhere (Goodbred Jr et al. 2003). A hydrochemical survey was conducted in the Nadia District between 2007 and 2008 to obtain a detailed picture of the local and regional composition of the groundwater (Majumder et al. 2015). Based on the outcomes of this survey, two field sites with a representative groundwater composition were selected for the installation of five multi-level monitoring wells (screenings located between 12 to 45 m bls as described in Biswas et al. (2011) and Neidhardt et al. (2014)). The two sites were located in the villages of Sahispur (N23°40'15.5", E88°36'33.5") and Chakudanga (N22°04'58.2", E88°38'13.1"), which are located 3.1 km apart from each other (Fig. S2). Sandy aquifer sediments were confined towards the surface by a ~3 m thick aquitard that represented young (Holocene) clayey and silty overbank deposits of the nearby Hooghly River. Down to 45 m bls, gray-colored aquifer sediments occurred that were primarily composed of fine- to medium-grained sand with varying proportions of silt, representing channel infill sands of Holocene age (Neidhardt et al. 2013b). Below this layer, Pleistocene sand was found that dated back to the last glacial maximum (Biswas et al. 2014a). The setup of the two study sites in the BDP provided ideal conditions to study the vertical distribution of P in groundwater. Further information regarding the groundwater and sedimentation history of the study sites in the Nadia District is provided elsewhere (Biswas et al. 2014b, Biswas et al. 2014c, Majumder et al. 2015, Neidhardt et al. 2013a, Neidhardt et al. 2014, Neidhardt et al. 2013b).

2.2 Sampling, field analysis and experiments

Groundwater sampling in the RRD: At the field site in Van Phuc, 12 groundwater monitoring wells were sampled using a submersible electric pump. The majority of the wells was situated along a 3.5 km long transect in the NW direction following the local groundwater flow direction (see Fig. S1). Groundwater samples were collected in 2006, 2009, 2013, 2014, and 2015, either during April (end of the dry season) or October (after the rainy season). A multi meter (WTW, since 2014 Hach) was used to record pH, water temperature, electrical conductivity (EC), oxidation reduction potential (ORP, which was converted into E_h according to the manufacturer's manual) and dissolved oxygen (O_2)

contents. A flow through cell was used for O₂ and ORP measurements. Once the values for water temperature, pH, and EC stabilized, sampling was carried out. In addition, total alkalinity (TA) was determined on-site by titration as HCO₃⁻ mg/L at the given groundwater pH values (alkalinity test kit, Merck). Samples for the analysis of major and trace elements were immediately filtered (0.45 µm cellulose acetate filter, Sartorius), acidified (1% v/v with 65% HNO₃; Merck, suprapure) and stored in acid-washed, pre-conditioned PE flasks. Samples for DOC analysis with a high TOC analyzer (Elementar, Hanau) were filtered, acidified (1% v/v with 30% HCl; Merck, suprapure) and stored in acid-washed, pre-conditioned brown glass bottles. Anion and stable oxygen isotope samples (δ¹⁸O_{H₂O}) were filtered and stored in 60 and 5 mL, pre-conditioned PE bottles. All samples were kept at 4°C until analysis. To determine the presence of particulate P forms, a series of groundwater samples were taken in 2013 without filtration and following filtration through filters of decreasing pore size, each pore size representing one individual sample (0.45 µm: nylon membrane filters; 0.20 µm and 0.10 µm cellulose nitrate membrane filters; Whatman). Afterwards, sample aliquots were acidified and treated as samples for major and trace element analyses.

Two aeration tests were also performed at Van Phuc in 2013 and 2015 to determine the amount of TDP that could be removed from groundwater samples via the co-precipitation of Fe(III)-(hydr)oxides. This was a necessary pre-step for the stable O isotope analysis of PO₄³⁻ (see 2.3). In brief, 1 L of fresh groundwater was collected into acid-washed and pre-conditioned 1.5 L PE bottles and then regularly aerated within the following 24 hours by opening the bottles and shaking them. Afterwards, oxidized samples were carefully filtered by vacuum-filtration (0.2 µm filter in 2013 and 0.45 µm filter in 2015) and the precipitate was air-dried on the filters. Subsamples were collected from the filtered aliquot to determine the amount of dissolved Fe²⁺, PO₄³⁻, and DOC that could be removed by aeration and precipitation in comparison to filtered (0.45 µm) and acidified subsamples of fresh groundwater that were taken during the sample collection in the field.

***In situ* adsorption experiments:** To test the PO₄³⁻ sorption properties of the aquifer material, a series of *in situ* sorption experiments were carried out at Van Phuc between April and October 2013. In brief, original sediment material from the Pleistocene aquifer from 27.4 to 27.7 m bls was used. Further details, such as the detailed geochemical analyses of the sediment sample, are provided elsewhere (Eiche 2009, Eiche et al. 2008). The sample material was collected as a bulk sample and was kept frozen before it was freeze-dried and sieved to a 0.2-0.5 mm grain size for the adsorption experiments. In addition, quartz sand of a 0.2 to 0.4 mm grain size (cristobalite, Sigma-Aldrich p.a.) was coated with

pure synthetic Fe(III)-(hydr)oxides following the procedure described by Schwertmann and Cornell (2008). This grain size spectrum corresponded to the dominant sediment grain size in the Pleistocene aquifer of Van Phuc. Three different Fe(III)-(hydr)oxides were selected - ferrihydrite, goethite, and hematite - which served as model minerals and represented Fe-minerals typically found in aquifer sediments of delta and floodplains such as the RRD and the BDP (Mai et al. 2014). All samples were exposed to six different anoxic groundwater wells for seven days (April 2013), 28 days (October 2013), and 182 days (April to October 2013), respectively. Pleistocene sediment and Fe(III)-(hydr)oxide coated quartz sands were inserted into the monitoring wells using a custom-made sample carrier system covered with 0.2 mm nylon mesh, which was placed directly in range of the respective well screens. Triplicate samples were generated for all 182 days of exposure and Pleistocene sediment samples, while duplicates were used for the remaining samples. Further experimental details are described by Neidhardt et al. (2018).

Groundwater investigations in the BDP: Groundwater sampling at the nested monitoring of the two field sites in the BDP was regularly carried out at a bi-weekly interval between December 2008 to August 2010, as described by Biswas et al. (2014c). To obtain insight into the influence of microbially controlled reactions on groundwater composition, an *in situ* biostimulation experiment was carried out at the Chakudanga field site, as described by Neidhardt et al. (2014). In brief, dissolved sucrose representing reactive DOC was injected into four of five nested monitoring wells. The resulting changes in the groundwater composition were closely monitored by collecting groundwater samples every second day for a period of two weeks, followed by a two-week sampling interval for the following seven months. The shallowest well, well A, was solely used for extracting groundwater to circulate dissolved sucrose within the aquifer. The sucrose was previously dissolved in 30 L of groundwater (wells B and C received 2 kg of sucrose, wells D and E received 4 kg) and was then inserted into wells B to E. Subsequently, groundwater was pumped from well A into the four surrounding wells for about 18 min at a rate of 70 L min⁻¹ (distance to well A: 2.5 m for wells B and C, 5.75 m for D and E, respectively). The outcomes of the experiment were then reevaluated with a specific focus on previously unpublished P data.

Sediment samples: At Van Phuc, two 55 m-long sediment cores were recovered by rotary drilling from two sites representing the Pleistocene and the Holocene aquifers (see Fig. S1), as described by Eiche et al. (2008). In the BDP, continuous sediment cores were collected with a combination of rotary

drilling and hammer drilling using a split-spoon core barrel lined with a PVC tube as a core catcher during the installation of the nested monitoring wells (Neidhardt et al. 2013b).

2.3 Chemical analysis

Groundwater analyses: Concentrations of dissolved major and trace elements (including P as TDP) in groundwater samples from the field site at Van Phuc were measured by ICP-MS (Agilent 7500 series, limit of quantification (LOQ) for TDP: $6.4 \mu\text{g L}^{-1}$). An additional set of groundwater samples was previously analyzed for PO_4^{3-} photometrically using the molybdenum blue method (Varian Cary 100 UV/Vis spectrophotometer; LOQ: $5 \mu\text{g L}^{-1}$) in addition to TDP. Anions were determined via an IC (Dionex), while DOC was measured using a High-TOC analyzer (Shimadzu). Furthermore, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was analyzed via a WS-CRDS-based liquid water isotope analyzer (type L1102-I, Picarro) with δ values reported in ‰ relative to the Vienna Standard Mean Ocean Water (VSMOW) standard. Samples from the BDP were analyzed for TDP (LOQ: $0.27 \mu\text{g L}^{-1}$) and other major and trace elements by HR-ICP-MS as described elsewhere (Neidhardt et al. 2013a, Neidhardt et al. 2014). Groundwater data were used to calculate the saturation indices (SI) for mineral phases that might serve as a sink or source for PO_4^{3-} at the field sites using the geochemical modeling program PHREEQC (Vers.3) and the wateq4f database (Parkhurst and Appelo 1999).

Sediment analysis: For all field sites, bulk total P (TP) and Fe contents in sediment samples were determined. For samples from Van Phuc, TP contents were analyzed using a wavelength dispersive X-ray fluorescence analysis (WDXRF, SRS 303, Siemens) and Fe contents were analyzed using ICP-OES (Spectro Ciros CCD, Kleve, Germany) after acid digestion following the Environmental Protection Agency (EPA) 3050B method. The contents of TP and Fe in sediment samples from the two BDP sites were determined from acid pressure digestion solutions using a high resolution-inductively coupled plasma mass spectrometer (HR-ICP-MS; AXIOM, VG Elemental). Further details regarding the sediment analyses are described by Eiche et al. (2008) and Neidhardt (2012). The contents of TP in sediments (mg kg^{-1}) were combined with corresponding TDP groundwater concentrations (mg L^{-1}) to calculate the distribution coefficients (K_d values, L kg^{-1}). Although K_d values are usually obtained from laboratory experiments and aim to specifically assess the sorption of a contaminant to surfaces of aquifer minerals (Limousin et al. 2007), this parameter was used to compare the partitioning of PO_4^{3-} between the solid and the aqueous phase at the study sites.

In situ adsorption experiment: After exposure, the sample material was freeze-dried and analyzed for TP and Fe contents from microwave-assisted acid digestions (ultraCLAVE IV A, MLS GmbH),

following the EPA methods 3050B and 3051A. Digestion solutions were analyzed for P by HR-ICP-MS (Element 2, Thermo Fisher) with a methodical LOQ of 0.32 mg kg⁻¹ for a sample weight of 50 mg. Fe was determined from the digestions by ICP-MS (ICP-MS 7500 series, Agilent).

Stable oxygen isotope ratio analysis of PO₄³⁻: A stable oxygen isotope ratio analysis of PO₄³⁻ (δ¹⁸O_{PO4}) was carried out using groundwater samples from Van Phuc. The values of δ¹⁸O_{PO4} are reported in ‰ relative to VSMOW standard. Although this method has been applied to apatite samples in paleoenvironmental studies for some time, the δ¹⁸O_{PO4} analysis offers a relatively new possibility to obtain insights into the microbial cycling and behaviour of PO₄³⁻ in different terrestrial and aquatic environments (Davies et al. 2014, Tamburini et al. 2014). This was made possible by improvements and adaptations, both in the sample preparation process and the analytical methods (see methodological details provided in the SI). In brief, the principle is based on the stability of the P-O bond in PO₄³⁻, which is resistant to inorganic hydrolysis under ambient conditions (Winter et al. 1940); later confirmed by others, e.g., Blake et al. (1997). Furthermore, abiotic reactions such as adsorption and desorption to Fe-(hydr)oxides as well as the dissolution and precipitation of apatite only produce negligible fractionations in δ¹⁸O_{PO4} in solutions over prolonged reaction time scales (Jaisi et al. 2010, Liang and Blake 2007). In contrast to abiotic reactions, enzymatic processes involved in the microbial cycling of P can cause significant modifications in the δ¹⁸O_{PO4} signal. For example, during the regeneration of PO₄³⁻ from organic matter (OM) via specific enzymes (e.g., alkaline phosphatases), a kinetic fractionation occurs through the incorporation of one or more O atoms from ambient water (Liang and Blake 2006, Tamburini et al. 2014). Another process, presumably more relevant in groundwater systems characterized by high concentrations of bioavailable PO₄³⁻, is the intracellular equilibrium isotope exchange by pyrophosphatases, which involves all four P-bound O atoms and produces a temperature-dependent fractionation with ambient water (Blake et al. 1998, Longinelli and Nuti 1973). The resulting expected equilibrium value of δ¹⁸O_{PO4} in the case of a complete intracellular enzymatic turnover can be calculated for known temperatures and δ¹⁸O_{H2O} values of ambient water according to Chang and Blake (2015):

$$1000\ln \alpha_{(P-H_2O)} = \frac{14.43 * 1000}{T[K]} - 26.54 \quad (1)$$

For an initial pilot study, sample duplicates previously obtained from five wells during the aeration test at the Van Phuc site were used. Dissolved PO₄³⁻ was successfully separated from groundwater by coprecipitation with Fe(III)-(hydr)oxides (see sections 2.2 and 3.1). After filtration, the samples were air-

dried and transported to Tübingen. Detailed information regarding the sample preparation as well as precautionary measures to prevent errors during preparation is provided in the SI and Fig. S3. In brief, the samples were subsequently processed over several dissolution, precipitation, and resin steps to ultimately convert PO_4^{3-} extracted from groundwater into silver phosphate (Ag_3PO_4). These steps were necessary to purify the sample from other possibly O-bearing compounds and constituents that would interfere with a quantitative conversion of PO_4^{3-} into Ag_3PO_4 . The procedure represents a combination and modification of existing protocols that were developed by Gruau et al. (2005), McLaughlin et al. (2004) and Tamburini et al. (2010) for the $\delta^{18}\text{O}_\text{P}$ analysis of surface waters and liquid extractions. The samples were then measured as Ag_3PO_4 with a TC/EA-IRMS (HekaTech HTO; Isoprime GV IRMS). The measurements were calibrated using the international VSMOW ($\delta^{18}\text{O} = 0.00 \pm 0.30\text{‰}$, $n = 5$) and GISP ($\delta^{18}\text{O} = -24.76 \pm 0.16\text{‰}$, $n = 4$) reference standards as well as an in-house Ag_3PO_4 standard ($\delta^{18}\text{O}_{\text{PO}_4} = 20.68 \pm 0.20\text{‰}$, $n = 14$).

Statistical analysis: All statistical analyses were conducted using Statistica 13 (Statsoft) and Microsoft Excel 2010. Because no normal distributions were met for the distribution of TDP and PO_4^{3-} concentrations in groundwater (Shapiro-Wilk test), paired data sets were tested for significant differences by carrying out a non-parametric Wilcoxon test. In addition, a Spearman's correlation two-tail test was used to identify significant correlations between different elements.

3. Results and Discussion

3.1 P species in the groundwater of anoxic aquifers in and SE Asia

At the field site of Van Phuc in Vietnam, TDP concentrations in the groundwater of the Pleistocene aquifer remained at comparatively low concentrations $<0.1 \text{ mg L}^{-1}$ (see wells AMS-2 und AMS-4). In contrast, the highest concentrations of up to 1.50 mg L^{-1} were observed in the shallow groundwater of the adjacent Holocene aquifer (Table 1). Information regarding the dissolved P species in groundwater was obtained from a set of groundwater samples, which were analyzed for both TDP and PO_4^{3-} concentrations (see Table 2). On average, DIP accounted for 103% of the corresponding TDP concentrations, and no significant difference was found between the two measurements ($p = 0.05$), suggesting that PO_4^{3-} represented the predominating and most likely sole P species in groundwater. In addition, the filtration of the groundwater samples through filters of decreasing pore sizes showed statistically significant differences ($p < 0.03$), but the differences regarding the TDP concentrations as

compared to non-filtrated groundwater samples were negligible (average difference: 6%, see Fig. 2). This indicated that “truly dissolved” PO_4^{3-} was dominant in the groundwater and that no P-containing particles or colloids $\geq 0.1 \mu\text{m}$ occurred.

Two additional sets of aeration tests were performed using fresh groundwater samples collected from various monitoring wells at Van Phuc in 2013 and 2015, respectively. The initial TDP concentrations determined from the fresh water samples ranged from 0.03 to 1.69 mg L^{-1} and dropped to values below the detection limit for nearly all samples after filtration following 24 hours of aeration (Table S1). The same applied to dissolved Fe^{2+} , indicating PO_4^{3-} removal from the solution via co-precipitation with Fe(III)-(hydr)oxides. The removal efficiencies for PO_4^{3-} ranged from 98 to 100%, except for one groundwater sample (AMS-5, 2013) that initially contained extremely high Fe^{2+} concentrations and whose oxidation appeared to be incomplete. Aeration also removed at an average 23% of the DOC. In sum, the removal efficiencies for the TDP further supported the assumption that PO_4^{3-} represented the sole species of P in the groundwater. Hence, the TDP measurements were considered a reliable proxy for PO_4^{3-} concentrations in groundwater samples from Van Phuc.

At the two focus sites in the BDP, Sahispur and Chakudanga, the concentrations of TDP observed in the groundwater were similar to those at Van Phuc (Table 1). The variation in TDP concentrations at the different depth intervals of the nested monitoring wells was less pronounced at Sahispur (0.83 - 0.97 mg L^{-1}) compared to Chakudanga (0.35 – 1.07 mg L^{-1}). Generally, the concentration ranges for TDP and the general composition of groundwater at the study sites were representative of shallow aquifers in Asian floodplain and delta regions, as summarized by Majumder et al. (2015) for the Nadia District in the BDP; BGS and DPHE (2001) for the entire BDP in Bangladesh; Elumalai et al. (2017) for the Cauvery River Delta in South India; and Buschmann et al. (2008) and Winkel et al. (2011) for the Mekong Delta and the RRD in Vietnam and Cambodia. Interestingly, if the groundwater was not largely contaminated with high concentrations of dissolved As, often clearly exceeding 100 $\mu\text{g L}^{-1}$ (Table 1), groundwater irrigation could noticeably reduce the P fertilizer requirement. For instance, irrigation with 500 mm of groundwater containing 1.0 $\text{mg/L PO}_4\text{-P}$ during the dry season translates to an annual P input of 5 kg ha^{-1} (note: the average annual P fertilizer application in Asia currently ranges at 28 kg ha^{-1} , Sattari et al. (2012); however, regular irrigation with groundwater would also cause a subsequent accumulation of As within the topsoil, increasing the risk of a loss of the yield and transfer of As into the food chain (Neidhardt et al. 2012, Norra et al. 2005).

Table 1: Composition of groundwater at the study sites in Van Phuc (RRD) and the two field sites Sahispur and Chakudanga (BDP). Dissolved O₂ and E_h were measured at Van Phuc during a previous field campaign in Oct. 2013 (O₂ was <0.18 mg L⁻¹, and E_h ranged from -5 to +151 mV in all monitoring wells). At Sahispur and Chakudanga, O₂ concentrations were <0.5 mg L⁻¹. Included in the table header are the thermodynamically dominant species according to the PHREEQC calculations.

well ID	screen interval	aquifer geology	pH	TA HCO ₃ ⁻	DOC	NO ₃ ⁻	SO ₄ ²⁻	TDP H ₂ PO ₄ ⁻ / HPO ₄ ²⁻	Mn Mn ²⁺	Fe Fe ²⁺	As H ₃ AsO ₃
	m bls			mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	mg L ⁻¹	µg L ⁻¹
Van Phuc*											
AMS-1 ^a	24-25	P	7.2	616	11.9	<0.25	<0.2	0.84	0.26	10.0	502
AMS-2 ^b	24-25	P	7.1	488	<0.50	<0.25	0.9	0.03	0.41	0.07	<0.07
AMS-3 ^a	24-25	P	7.2	645	5.62	<0.25	nd	0.55	0.33	15.9	558
AMS-4 ^b	37-38	P	7.0	586	0.76	<0.25	<0.2	0.06	1.32	0.13	0.5
AMS-5 ^b	23-24	H	6.9	751	8.95	<0.25	3.8	1.30	0.20	10.7	404
VPNS-5 ^b	30-31	H	7.0	592	2.04	<0.25	<0.2	0.73	0.14	12.6	337
AMS-7 ^b	37-38	H	7.1	534	2.68	<0.25	<0.2	1.03	0.35	6.13	208
VPNS-9 ^b	25-26	H	6.8	564	2.07	<0.25	<0.2	1.50	0.23	16.1	63.8
AMS-11 ^b	24-25	P	7.0	610	2.90	<0.25	<0.2	0.26	0.27	10.1	375
AMS-12 ^b	24-25	H	6.9	603	4.63	<0.25	0.6	0.25	0.77	6.57	124
AMS-15 ^b	27-28	H	7.0	nd	1.12	<0.25	0.7	0.03	1.25	0.71	17.6
AMS-32 ^b	24-25	P	7.1	567	1.86	<0.25	<0.2	0.51	3.65	7.59	123
Red River (surface water)			nd	nd	2.47	0.46	8.5	<0.01	0.02	0.11	3.7
Nadia District											
Sahispur ^c											
A	12-21	H	6.9	586	3.02	<0.88	7.78	0.83	0.92	7.77	98.0
B	22-25	H	6.9	610	4.52	<0.88	10.7	0.95	0.74	8.96	100
C	26-29	H	7.2	482	2.55	<0.88	<0.85	0.80	0.85	1.09	296
D	30-33	H	7.1	500	1.53	0.97	<0.85	0.97	0.37	4.76	262
E	34-37	H	7.0	513	1.32	<0.88	<0.85	0.90	0.47	4.80	158
Chakudanga ^c											
A	12-21	H	7.1	415	7.47	<0.88	<0.85	0.75	0.77	4.34	49.1
B	24-27	H	7.2	482	6.68	<0.88	<0.85	1.07	0.47	3.76	155
C	30-33	H	7.2	451	5.10	<0.88	<0.85	0.35	0.41	5.57	135
D	36-39	H	7.2	464	4.73	<0.88	<0.85	0.69	0.42	2.86	132
E	42-45	H	7.1	445	6.67	<0.88	<0.85	0.61	0.60	2.15	133

sampling date: ^aOct. 2013, ^bApr. 2015, ^cDec. 2009 (Neidhardt et al. 2013a, Neidhardt et al. 2014)
nd: not determined

Fig. 2: Distribution of TDP in water samples originating from the Holocene aquifer in Van Phuc that were percolated through filters of different pore sizes. The results indicated that dissolved P was dominant in groundwater, while no P-containing particles $\geq 0.1 \mu\text{m}$ were present.

Table 2: Comparison of dissolved P concentrations in the groundwater of Van Phuc measured by ICP-MS (TDP) and the molybdenum blue method (PO_4^{3-}).

well ID	well depth (m bls)	TDP (mg L ⁻¹)	PO_4^{3-} (mg L ⁻¹ $\text{PO}_4\text{-P}$)	% ratio $\text{PO}_4\text{-P}$ related to TDP
AMS-2	27	0.01	0.01	85
AMS-5	25	1.82	2.21	121
VPNS-5	31	0.83	0.93	111
AMS-7	38	1.27	1.22	96
VPNS-9	26	2.02	1.79	89
AMS-11	25	0.69	0.71	103
AMS-12	25	1.00	1.02	102
AMS-15	28	0.08	0.09	116

3.2 Potential sources of dissolved PO_4^{3-} in groundwater

Sedimentary P pools: Considering the pronounced enrichment of PO_4^{3-} in shallow groundwater at the study sites and elsewhere in Asian floodplain and delta regions, the origin should be investigated. The aquifer sediments represent one plausible source, which is comprised of PO_4^{3-} associated with buried OM as well as primary and secondary minerals in which it is either directly incorporated into the mineral structure or is sorbed to the mineral surface. Total P contents in sediments of Van Phuc ranged from 44 to 305 mg kg⁻¹ (core from the Holocene aquifer site) and 44 to 284 mg kg⁻¹ (Pleistocene aquifer site) (Table S2). At the two sites in the BDP, the TP contents were higher, reaching up to 620 mg kg⁻¹; however, the TP content represents only a sum parameter and is only a

weak indicator of the amount of PO_4^{3-} that could actually be released into groundwater through biogeochemical weathering and desorption. Nevertheless, K_d values ranging from 113 to 1104 L kg^{-1} at the Holocene site of Van Phuc and the two sites in the Nadia District (Table 3) indicated that a considerable amount of PO_4^{3-} was enriched within the aqueous phase compared to the sediment. In contrast, values for the Pleistocene aquifer at Van Phuc exceeded 2180 L kg^{-1} . This pronounced difference in the K_d values was either linked to a high sorption capacity of the Pleistocene aquifer material or the mobilization and enrichment of PO_4^{3-} in groundwater was confined to the Holocene aquifers, which is further explored in the following sections.

Table 3: Sediment TP contents, corresponding groundwater TDP concentrations and K_d values for the study sites in the Nadia District and Van Phuc.

depth (m bls)	TP (mg kg^{-1})	well screening (m bls)	TDP (mg L^{-1})	K_d (L kg^{-1})
Van Phuc, Holocene aquifer				
16.6	240	16-17	0.69	349
20.8	109	20-21	0.62	176
27.3	109	26-27	0.20	543
32.0	87.3	33-34	0.18	477
36.1	43.6	35-36	0.39	113
41.6	109	40-41	0.46	240
44.8	87.3	44-45	0.37	235
Van Phuc, Pleistocene aquifer				
23.8	109	23-24	0.03	3637
27.5	65.5	26-27	0.03	2338
32.4	65.5	32-33	0.03	2182
38.8	65.5	38-39	0.01	10910
47.3	109	44-45	0.02	5455
Nadia District, Chakudanga				
13.0	418	12-21	0.75	558
20.1	432	12-21	0.75	577
25.3	337	24-27	1.07	315
30.5	386	30-33	0.35	1104
38.3	234	36-39	0.69	339
45.5	371	42-45	0.61	608
Nadia District, Sahispur				
12.4	620	12-21	0.83	747
23.5	223	22-25	0.95	235
29.4	304	26-29	0.80	380
30.7	375	30-33	0.97	386
30.7	354	30-33	0.97	365
38.5	507	34-37	0.90	564

Furthermore, TP contents were positively correlated with Fe in the sediments ($p < 0.05$, except for Chakudanga) indicating that Fe-minerals, like Fe(III)-(hydr)oxides, represented an important PO_4^{3-} pool (see Fig. 3 and Table S2). In general, Fe(III)-(hydr)oxides are either able to incorporate PO_4^{3-} during the moment of formation, or to adsorb it on the mineral surface via surface complexation, which could eventually be released to groundwater (Borch and Fendorf 2007). The mineralogy of the aquifer sediments was not specifically determined for this study, but based on previous investigations, traces of Fe(III)-(hydr)oxides (i.e., hematite, goethite) and weakly ordered Fe-(hydr)oxides were still present at both study sites (Eiche et al. 2008, Neidhardt et al. 2013a, Neidhardt et al. 2013b). Hence, PO_4^{3-} could have been mobilized via microbial Fe(III) reduction, as suggested by BGS and DPHE (2001) for Bangladesh. BGS and DPHE (2001) also estimated that the decomposition of OM could have released sufficient PO_4^{3-} to increase the concentration in groundwater to around $1.5 \text{ mg L}^{-1} \text{ PO}_4\text{-P}$; however, PO_4^{3-} released via the mineralization of OM was likely readily re-adsorbed onto surfaces of Fe-(hydr)oxides of ambient aquifer sediments, as indicated by high contents of oxalate-extractable P (up to 400 mg/kg) in the sediments of three study sites located along a North-South transect across Bangladesh (BGS and DPHE 2001). Because the microbial degradation of OM and microbial Fe(III) reduction are partially intertwined, it is challenging to distinguish between these two PO_4^{3-} mobilization pathways using field-based research.

Fig. 3: Bivariate plot of bulk TP and Fe contents in the aquifer sediments of the field sites in Van Phuc, Chakudanga and Sahispur. The relationships were almost linear in the Holocene sediments of Van Phuc and also pronounced in the Nadia District as well as in the Pleistocene aquifer of Van Phuc.

Mobilization of PO_4^{3-} from aquifer sediments by Fe(III) reduction: Hydrochemical monitoring data were used to further explore potential PO_4^{3-} mobilization pathways at the sites. Groundwater at the Holocene aquifer at Van Phuc was depleted in dissolved O_2 ($<0.20 \text{ mg L}^{-1}$), NO_3^- ($<0.25 \text{ mg L}^{-1}$) and SO_4^{2-} ($<3.8 \text{ mg L}^{-1}$), whereas TA, dissolved Fe^{2+} and Mn^{2+} exceeded 500, 0.10 and 0.05 mg L^{-1} , respectively (Table 1). The groundwater at the two field sites in the BDP showed similar hydrochemical features. This groundwater composition typically reflects influences of microbial cycling of SOC and DOC, resulting in anoxic conditions with mildly to strongly reducing redox conditions (Holocene aquifer at Van Phuc: E_h of -5 to +118 mV, and TA values $>500 \text{ mg L}^{-1} \text{ HCO}_3^-$). Elevated Fe^{2+} concentrations thus suggested a mobilization of PO_4^{3-} via the Fe(III) reduction pathway, as has been previously proposed for the mobilization of As from Holocene sediment deposits in the BDP and RRD (Berg et al. 2008, McArthur et al. 2001, Nickson et al. 1998, Postma et al. 2016). The mobilization of PO_4^{3-} into shallow groundwater in riparian floodplains via Fe(III) reduction has also been described elsewhere (Carlyle and Hill 2001). Indeed, the reductive dissolution of weakly ordered Fe(III)-(hydr)oxides (i.e., amorphous phases such as ferrihydrite) is possible from a thermodynamic point of view as indicated by the negative SI values calculated for respective groundwater compositions at the study sites (see Table S3). This is further supported by a significant positive correlation between Fe^{2+} and TDP ($r_s = +0.73$, $p < 0.05$; $n = 12$) in the groundwater at Van Phuc. A significant positive correlation between Fe^{2+} and TDP ($r_s = +0.85$, $p < 0.05$; $n = 181$) also occurred in the groundwater of the surrounding area of the two monitoring sites at Sahispur and Chakudanga in the Nadia District of the BDP, which was observed during the groundwater survey (Fig. 1). The same applies to the other three groundwater data sets summarized in Fig.1. In the Nadia District, increased TDP concentrations were also closely coupled with the prevailing redox state and increased once respective groundwater samples showed a chemical composition indicative for Fe(III) reduction (Fig. 4). This was also described by Winkel et al. (2011) for groundwater across the entire RRD. Fe(III) reduction is thus considered a potential key mechanism underlying the enrichment of PO_4^{3-} in the groundwater of the study sites. Hence, it is important to determine whether PO_4^{3-} release via Fe(III) reduction still represents still an active process.

Fig. 4: Distribution of TDP in the groundwater of the Nadia District (West Bengal). The results depict a close relation between the TDP concentration and the predominating redox state. Redox state classification was done following Jurgens et al. (2009). *Note: 13 wells with missing depth information were excluded.

Release of PO₄³⁻ via Fe(III) reduction as an active process: The active release of PO₄³⁻ into groundwater could be determined by a steady concentration increase observed during regular monitoring. At Van Phuc, groundwater samples were repeatedly collected between 2006 and 2015 (see Table S4). The results revealed a mixed outcome; while TDP concentrations in the majority of the wells remained constant, one well (AMS-5) was characterized by highly varying concentrations that shifted between 1.00 to 2.02 mg L⁻¹. In addition, TDP concentrations dropped along with Fe²⁺ in water samples collected from four wells (AMS-11, AMS-12, AMS-15, and AMS-32) during the final sampling campaign in April 2015. This sharp decline was attributed to an unusually dry year in 2015, which resulted in a drop-off in the water level and a subsequent aeration of the upper aquifer sediments, likely causing the precipitation of Fe(III)-(hydr)oxides and a concomitant removal of Fe²⁺ and PO₄³⁻ from groundwater. Although it was not possible to draw a definite conclusion regarding a potential active PO₄³⁻ release at Van Phuc, the monitoring data demonstrated that strong concentrations may change in shallow groundwater over time.

To unequivocally trace active releases of PO_4^{3-} , monitoring data with a higher temporal resolution are required, which was available at the two sites in the BDP (Biswas et al. 2014c). Pronounced temporal variations occurred in TDP concentrations of the shallowest wells (screening situated between 12-21 m bls). At both sites, TDP concentrations gradually increased over a period of 20 months (Sahispur: from 0.38 mg L^{-1} to 1.05 mg L^{-1} , Chakudanga: 0.22 mg L^{-1} to 0.79 mg L^{-1}) along with dissolved Fe^{2+} (Fig. 5). This clearly indicates that active Fe(III) reduction was the underlying PO_4^{3-} mobilization mechanism, which was also observed at a shallow aquifer in Bangladesh (Cheng et al. 2005, Dhar et al. 2008).

Fig. 5: Groundwater data from the shallowest monitoring wells at the two study sites, Sahispur and Chakudanga, in West Bengal (Biswas et al. 2014c). Blue highlighted areas are temporary influences of field experiments, which caused short-term perturbations due to pumping measures. Baseline concentrations of TDP and Fe^{2+} (determined during July at the end of the monsoon season) gradually increased in the groundwater at Chakudanga in 2009 and 2010 (see table below).

Microbial activity linked to P mobilization– outcomes of an *in situ* biostimulation experiment: In contrast to the two shallowest monitoring wells, there was no evidence of an active Fe(III) reduction or accompanying PO_4^{3-} mobilization for the deeper wells (screening situated below 25 m bls) at the two sites in the BDP (Biswas et al. 2014c); however, the system quickly reacted when a reactive DOC source was provided in the frame of an *in situ* biostimulation experiment at the Chakudanga site. An injection of dissolved sucrose resulted in a rapid stimulation of anaerobic microbes that decomposed the sucrose stepwise into intermediate catabolic products (e.g., acetic acid). and eventually to

CO₂/HCO₃⁻ (Neidhardt et al. 2014). Consequently, the pH and redox potential temporarily declined, causing Ca-carbonate dissolution and the release of considerable amounts of dissolved Fe²⁺. Respective TDP concentrations increased in all five nested monitoring wells and peaked after four to ten days, reaching maximum concentrations that were two to four times higher than the initial baseline values (Fig. S4a). In well A, TDP concentrations increased from 0.75 to a maximum of 1.82 mg L⁻¹, in well B from 1.07 to 2.72 mg L⁻¹, in well C from 1.12 to 2.68 mg L⁻¹, in well D from 0.69 to 2.36 mg L⁻¹, and in well E from 0.61 to 2.58 mg L⁻¹.

This sharp increase in TDP could be attributed to several partially overlapping processes. First, the release of PO₄³⁻ was coupled to the reductive dissolution of weakly crystalline Fe(III)-(hydr)oxides, which was the main source of released Fe²⁺ (Rawson et al. 2017). As mentioned, Fe(III)-(hydr)oxides represented an important potential pool for PO₄³⁻ at the study sites; thus, Fe(III) reduction would also release adsorbed and co-precipitated PO₄³⁻. Second, the temporary decrease in pH values might have resulted in a shift from HPO₄²⁻ to H₂PO₄⁻ and the surface charge of Fe-minerals, both affecting PO₄³⁻ sorption equilibria (Parkhurst et al. 2003). In addition, a decreasing pH might have caused PO₄³⁻ release via the dissolution of carbonate minerals (Golterman 2001).

Nevertheless, the timing of the TDP increase is intriguing because it predated the observed increase in Fe²⁺ and Ca²⁺ concentrations for most of the five wells (i.e., C, D and E), and the reason for this is still unclear. TDP increased in well A as well, which received only minor amounts of sucrose when dissolved sucrose added to the other four wells was distributed within the aquifer. Consequently, groundwater from this well showed no release of Fe²⁺ or Ca²⁺ (Fig. S4a) or other signs of microbial activity, such as an increase in TA and fatty acids or a decrease in the pH (Neidhardt et al. 2014). This dynamic behavior calls for further exploration regarding potential PO₄³⁻ pools and mobilization mechanisms. Perturbations caused by pumping during the sucrose injection may have resulted in an initial desorption of weakly adsorbed PO₄³⁻. A strong increase in TDP concentrations at the second field site (Sahispur) due to strong pumping was previously observed, which was attributed to the desorption of loosely bound PO₄³⁻ from the sandy sediments (Neidhardt et al. 2014); however, the reason this would affect the groundwater at the monitoring wells with a temporal delay of three days is unclear.

To check for possible mixing and desorption influences on respective TDP concentrations resulting from the injection of the sucrose, concentration changes were compared to Cl⁻. Due to a pronounced initial concentration difference between well A (7.9 mg L⁻¹) and the four deeper wells (<2.6 mg L⁻¹),

inert Cl^- represented an ideal internal tracer to monitor the influence of mixing on groundwater composition. TDP/ Cl^- mol ratios depicted the same courses as TDP concentrations in all wells with their peaks reached at three to six days after the sucrose injection (Fig. S4a). Hence, the sharp increases in TDP were clearly the result of a PO_4^{3-} mobilization from the aquifer sediments. While the exact mechanisms underlying the *in situ* biostimulation experiment remained vague, it definitely caused a pronounced increase in TDP concentrations. The rapid response to the injection of sucrose also suggested that microbial activity within the aquifer was previously limited by the availability of reactive OM. Laboratory incubation experiments using aquifer sediments from the study sites also supported this observation because Fe(III) reduction occurred once reactive DOC sources were added (Freikowski et al. 2013).

After the depletion of the sucrose, microbial-mediated responses declined, and the system slowly returned to the initial baseline conditions, as revealed by subsequent groundwater monitoring data (Fig. S4b). Considering the temporary strongly reducing conditions, high bicarbonate and dissolved Fe^{2+} concentrations, siderite and vivianite were likely precipitated, thereby removing PO_4^{3-} from the solution by adsorption and incorporation (Barber 2002, Rothe et al. 2016). In addition, dilution with slowly inflowing pristine groundwater occurred. Based on the temporal changes in conservative Cl^- , the natural groundwater flow velocities in the respective aquifer layers were estimated at 1.3 to 5.1 m a^{-1} (Rawson et al. 2017). Hence, the dilution effects were less important compared to the removal of PO_4^{3-} via adsorption and mineral precipitation; however, the TDP concentrations remained at elevated levels in four of the five wells until the end of the groundwater monitoring campaign in August 2010, with a relative increase of +5 to +23% compared to the initial baseline values in December 2009. In sum, the injection of a reactive DOC source resulted in a pronounced temporary disturbance of the partitioning of PO_4^{3-} between the aqueous and the solid phases, which was closely linked with the microbial cycling of Fe.

Other potential PO_4^{3-} sources: When investigating potential sources for PO_4^{3-} in groundwater, it is also necessary to consider external sources. For example, shallow groundwater at Van Phuc is recharged by water from the Red River (van Geen et al. 2013); however, the TDP concentration in the Red River was below 0.01 mg L^{-1} , which would dilute the concentrations in groundwater. Furthermore, some studies argued that land use patterns (e.g., sanitation facilities and agriculture) directly influenced groundwater properties in shallow aquifers of the BDP and the RRD (Majumder et al. 2016, McArthur et al. 2012). The leaching and transport of PO_4^{3-} from the soil to groundwater was previously

observed in other areas of intensive agricultural use (McDowell et al. 2015); however, a downward transport of PO_4^{3-} was also shown to be mostly associated with well-drained soils and sediments to be restricted to shallow depths of <2 m bls only (Domagalski and Johnson 2011, Mabilde et al. 2017, McDowell et al. 2015, McGinley et al. 2016, Robertson 2008). In contrast, the TDP concentrations at the study sites and elsewhere in groundwater of the RRD, BDP, and Mekong delta usually peak between 20 to 60 m bls (see Fig. 1). In addition, topmost Holocene sediment layers in the RRD and BDP consist of clayey and silty deposits that are several meters thick, which represent a characteristic feature of the floodplain and delta regions of S and SE Asia and constitute a barrier towards the direct infiltration of surface water (Eiche et al. 2008, Goodbred Jr et al. 2003, Neidhardt et al. 2013b, Tanabe et al. 2003). Hence, while the possibility that agriculture and waste water locally contributed PO_4^{3-} to groundwater at the study areas is not excluded, the possibility that these represent its main sources has been ruled out.

3.3 Abiotic and biotic processes influencing the subsurface transport of PO_4^{3-}

Subsurface transport of PO_4^{3-} : The monitoring well network at Van Phuc allowed for studying the transport behavior of PO_4^{3-} in aquifers. As described, PO_4^{3-} -enriched groundwater currently migrates from reducing Holocene aquifer sediments into an adjacent Pleistocene aquifer. Monitoring data revealed that PO_4^{3-} in migrating groundwater was efficiently retarded as indicated by a rapid drop in TDP concentrations from 1.30 mg L⁻¹ (well AMS-5) to below 0.06 mg L⁻¹ (wells AMS-2 and AMS-4, see Table 1). This retardation is primarily attributed to the presence of Fe(III)-(hydr)oxides in the Pleistocene aquifer sediments, which are characterized by a high adsorption affinity for PO_4^{3-} (Borggaard 1983). Laboratory batch experiments confirmed this high PO_4^{3-} sorption capacity for Pleistocene sediment material from Van Phuc (Rathi et al. 2017).

Nevertheless, the sorption potential of the Pleistocene sediments directly adjacent to the Holocene aquifer appeared limited, as indicated by TDP concentrations exceeding 0.26 mg L⁻¹ in groundwater (see monitoring wells AMS-1, AMS-3, AMS-11, and AMS-32, Table 1). The gradual exhaustion of available binding sites resulted in a plume of PO_4^{3-} that extended into the Pleistocene aquifer, as recently described by van Geen et al. (2013) for dissolved As. A similar transport behavior was reported by Robertson (2008) and Harman et al. (1996), who investigated the movement of PO_4^{3-} -plumes in sandy aquifers under anoxic conditions. They considered adsorption processes to be the

only attenuation mechanism in operation, with the exhaustion of available adsorption sites resulting in PO_4^{3-} concentrations of up to $1.5 \text{ mg L}^{-1} \text{ PO}_4\text{-P}$.

Retention of PO_4^{3-} by Pleistocene sediments and Fe(III)-minerals: Further insight into the transport behavior of PO_4^{3-} at Van Phuc was obtained through the *in situ* sorption experiments. Original Pleistocene aquifer sediment as well as synthetic Fe(III)-minerals that served as complementary controls were used. The resulting TP contents of the experimental samples after 28 days of exposure to groundwater in five different wells with different TDP concentrations (ranging from 0.05 to 1.93 mg L^{-1}) are presented in Fig. 6. The net increases in the TP contents of the Pleistocene sediment (calculated as the difference between the initial and resulting TP content after the 28 days of *in situ* exposure) yielded similar results (3.2 to 14.2 mg kg^{-1}) compared to a laboratory batch sorption experiment previously conducted by Rathi et al. (2017) at pH values of 6.1 to 7.9 using the same Pleistocene sediment material. Among the synthetic Fe(III)-(hydr)oxides, hematite-coated sand showed the highest TP contents after exposure (up to 13.1 mg kg^{-1}), which is consistent with values reported by Colombo et al. (1994) for laboratory batch sorption experiments at pH 6. In contrast, the amounts of TP in goethite-coated sand resulting from *in situ* exposure were one order in magnitude lower than what has been obtained for goethite-sand by batch experiments at neutral pH values (Strauss et al. 1997). The reduced PO_4^{3-} sorption under field conditions is attributed to the competition with other anions for sorption sites (i.e., HCO_3^- , H_3AsO_3). For example, this was suggested by hydrogeochemical modeling calculations performed for the field sites in the BDP in which goethite and ferrihydrite served as model minerals for the underlying surface complexation calculations (Biswas et al. 2014b).

In contrast to the synthetic Fe-minerals, the TP contents of the Pleistocene sediment did not show large net increases during the *in situ* exposures. The initial TP content of the Pleistocene sediment was $28.1 \pm 5.4 \text{ mg kg}^{-1}$, indicating that some of the available sorption sites were already preoccupied with PO_4^{3-} (note: the TDP concentration of corresponding groundwater at the sediments' depth of origin (26-27 m bls) was 0.03 mg L^{-1}). Also, some of the detected initial TP resembled occluded P that became liberated by the acid-pressure digestion; however, TP contents consistently increased from 31.3 to 42.3 mg kg^{-1} during the experiment, although there was no clear relation to the TDP concentration in the groundwater observed (Fig. 6).

Continuous contact with anoxic groundwater (E_h ranging from -5 to $+118 \text{ mV}$, see Table S5) further altered the PO_4^{3-} sorption behavior of the synthetic Fe(III)-minerals and the Pleistocene sediment as

suggested by the net changes in TP contents over time. After seven days of exposure, synthetic Fe(III)-mineral coated sand samples contained considerable amounts of TP (ferrihydrite: 8.6 to 14.2 mg kg⁻¹, goethite: 4.2 to 8.2 mg kg⁻¹, hematite: 12.2 to 14.2 mg kg⁻¹) depending on the TDP concentrations in groundwater (see Table S5). After 28 and 182 days, the TP contents of ferrihydrite-coated sand largely declined, reaching values below the LOQ after 182 days in wells AMS-1 and AMS-12. This decrease was accompanied by a pronounced loss in the total Fe content (-94 % and -100 %, respectively), which indicated a reductive dissolution of the ferrihydrite coating and a concomitant loss of PO₄³⁻ sorption sites. This observation further supports the previous assumption that Fe(III) reduction represents an important PO₄³⁻ release pathway in anoxic aquifers.

In contrast, goethite-coated sand sorbed most of the PO₄³⁻ in the seven days of exposure, although TP contents further increased after 182 days (well AMS-1: from 5.3 to 6.1 mg kg⁻¹; AMS-12: 4.2 to 7.0 mg kg⁻¹). A similar behavior was observed for goethite-coated sand in a batch sorption experiment conducted by Strauss et al. (1997), in which the sorption equilibrium with PO₄³⁻ was reached after three weeks due to slow diffusion effects. Furthermore, the precipitation of P-containing, cubic secondary minerals on the goethite-coating was observed after the *in situ* exposure to the groundwater of well AMS-1 (E_h of +45 mV) for seven and 182 days, respectively (see Fig. S5). These mineral crystals contained traces of Ca and P in addition to Fe, which was revealed by electron microscopic images and a coupled energy-dispersive X-ray spectroscopy analysis (Neidhardt et al. 2018). This is in agreement with laboratory experiments that showed the formation of authigenic Fe-PO₄³⁻ minerals such as vivianite, in Fe-rich sediments with a low S²⁻ production (Rothe et al. 2016), which was the case at the study sites. The saturation indices calculated for AMS-1 further indicated that reducing groundwater was supersaturated regarding several mineral phases (e.g., magnetite, siderite and vivianite, see Table S3), which can immobilize PO₄³⁻ by (co-)precipitation and/or adsorption (Barber 2002, Lewandowski et al. 2015, Ptacek 1998). In addition, vivianite and siderite were previously verified in the aquifer sediments of Van Phuc (Eiche et al. 2008). Hematite-coated sand sorbed PO₄³⁻ readily during the first days of exposure and the TP contents remained nearly stable thereafter (e.g., in well AMS-1, TP contents reached 12.2 mg kg⁻¹ after 7 days, 12.4 mg kg⁻¹ after 28 days and 12.5 mg kg⁻¹ after 182 days, respectively). The observed differences in the temporal sorption behavior of hematite and goethite indicated different underlying sorption kinetics and mechanisms, which has been suggested by researches such as Persson et al. (1996).

Considering the Pleistocene sediment, the TP contents either slightly decreased (well AMS-12: -5%, AMS-5: -11%) or increased (well AMS-1: + 9%) after seven days of *in situ* exposure compared to the initial TP content. Similar to goethite-coated sand, TP contents consistently increased (+11 to +50%, n= 5) after 28 days in relation to the initial content; however, after 182 days, the TP contents were again close to the initial TP content baseline (-6 to +3%, n= 3). These dynamic changes in the TP contents of the Pleistocene sediment were likely caused by a combination of slow adsorption and the formation of secondary minerals (see goethite-coated sand), followed by a loss of sorption sites due to mineral changes induced by the prolonged contact with reducing groundwater during the 182 days of exposure (see ferrihydrite-coated sand).

In sum, the *in situ* sorption experiments indicated that PO_4^{3-} sorption in aquifers may undergo pronounced temporal changes especially when different Fe(III)-minerals are involved and redox gradients occur, such as at the transition zone in Van Phuc. When anoxic groundwater migrates into Pleistocene aquifer sediments, adsorption by Fe(III)-(hydr)oxides rapidly removes PO_4^{3-} from the solution; however, PO_4^{3-} will slowly continue to migrate once available adsorption sites are saturated. Due to a decline in E_h , weakly ordered Fe(III)-minerals will further undergo reductive dissolution, resulting in a re-release of previously immobilized PO_4^{3-} in the mid-term (months). Thereafter, secondary mineral phases gain an increasing importance in constraining PO_4^{3-} concentrations in the mid- to long-term, although mineral precipitation might be kinetically very slow.

An overview summary of potential sources and mobilization and immobilization processes that control PO_4^{3-} concentrations in the groundwater of porous aquifers in S and SE Asian floodplain aquifers and

similar settings is provided in Table 4.

Fig. 6: Amount of TP sorbed to experimental samples after 28 days of *in situ* exposure in relation to ambient TDP

concentrations of the respective wells (see Table S5 for further details). Note: while the initial TP content of the synthetic Fe(III)-(hydr)oxides was below the LOQ of 0.32 mg kg⁻¹, the Pleistocene sediment samples contained 28.1 ±5.4 mg kg⁻¹ before the experiments.

Table 4: Overview of potential sources and mobilization and immobilization processes that control PO₄³⁻ concentrations in the groundwater of porous and partially anoxic aquifers (Hartland et al. 2015, Lewandowski et al. 2015, Parkhurst et al. 2003, Robertson et al. 1998, Stollenwerk 1996). The sources and processes that predominate at the study sites (representing Asian delta and floodplain aquifers) are highlighted in bold.

P sources	P mobilization	P immobilization
<ul style="list-style-type: none"> • SOC and DOC • primary and secondary minerals within the aquifer (e.g., apatite, Al-, Mn-, Fe-(hydr)oxides, clay minerals) • agriculture (pore water leaching from arable land; with manure, synthetic fertilizers, and pesticides) • infiltrating eutrophic water from contamination plumes (pit latrines, leaking sewage canals or septic tanks) • groundwater recharge from eutrophic streams and rivers 	<ul style="list-style-type: none"> • biotic mineralization of OM • passive mobilization via reductive dissolution and/or diagenetic changes of metal (hydr)oxides • biogeochemical weathering of primary and secondary mineral phases (e.g., carbonate dissolution) • desorption from aquifer material via local disequilibrium controlled by prevailing hydro-chemistry (e.g., pH, ion exchange) 	<ul style="list-style-type: none"> • sorption to primary and secondary minerals (carbonates, Al-, Mn-, Fe-(hydr)oxides, 3-layer clay minerals), dispersed SOC and DOC, living microorganisms (biosorption) • co-precipitation with secondary mineral phases such as carbonates (calcium phosphates, siderite) or Fe-phosphates (vivianite) • assimilation and storage by biota (free-floating microbial cells, biofilms)

Microbial P cycling during transport: Another uncertainty closely intertwined with the fate of P is whether microbes actively participate in the cycling of PO₄³⁻ within the aquifer during transport. Thus, the δ¹⁸O_{PO4} analysis was carried out to characterize PO₄³⁻ in the groundwater of the study site in Van Phuc. Because the underlying preparations for the δ¹⁸O_{PO4} analysis are generally elaborate and its specific application to anoxic groundwater characterized by high contents of dissolved Fe²⁺ represents a novel and challenging approach, only a small sample set could be processed during the pilot study. The δ¹⁸O_{PO4} values obtained from the four sampled wells ranged between 14.60 and 16.78 ‰, with a good reproducibility of external sample replicates (Fig. S6, Table S6). The duplicate measurements and simultaneously processed KH₂PO₄ standards indicated a good reproducibility of the method adaption. Furthermore, a quality assessment based on a discussion of the potential alterations and contaminating factors indicated a complete, loss-free transfer of PO₄³⁻ from groundwater samples to Ag₃PO₄ and a minor contamination with As (refer to Tables S6 and S7 and the SI for further details). To date, few studies have reported δ¹⁸O_{PO4} values for groundwater, and only values for regions in the US and Great Britain have been reported (Blake et al. 2001, Davies 2016, McLaughlin et al. 2006, Young et al. 2009), resulting in a highly limited dataset. The range of δ¹⁸O_{PO4} in the groundwater of all

previously conducted studies, as summarized by Davies (2016), was slightly higher (+15.1 to +22.4 ‰, n= 24) compared to the values obtained for the field site in Van Phuc. Given the small spatial resolution of the study site, the range of $\delta^{18}\text{O}_{\text{PO}_4}$ values spanning over 2.18 ‰ was still surprisingly high.

Theoretical equilibrium values of $\delta^{18}\text{O}_{\text{PO}_4}$ calculated for ambient groundwater (temperatures of 25.3 to 26.7 °C and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of -6.55 to -7.64 ‰) according to Chang and Blake (2015) were expected to be in the range of 14.1 to 15.1 ‰ (see Fig. 7). One of the measured $\delta^{18}\text{O}_{\text{PO}_4}$ values was in this range (AMS-11), indicating a potential incorporation of O into PO_4^{3-} from ambient water via intracellular enzymatic microbial cycling (Blake et al. 2001). The remaining three samples were 0.5 to 1.4 ‰ higher than the expected equilibrium value (Fig. 7). If Ag_3AsO_4 , which could have contaminated the final Ag_3PO_4 precipitates, is taken into account, the deviation from the expected equilibrium values would be even higher for the measured samples (see Table S7). This mostly positive deviation from the expected equilibrium value is consistent with observations made by Blake et al. (2001) and Davies (2016) and would allow for interpretations extending beyond a simple intracellular equilibration of PO_4^{3-} with ambient groundwater. Blake et al. (2001) and Young et al. (2009) suggested that the source signal of PO_4^{3-} in aquatic environments would not be completely overprinted by intracellular enzymatic turnover if PO_4^{3-} were present in excess and/or DOC concentrations were low. Furthermore, the extracellular release from OM would result in isotopic signals of PO_4^{3-} even further below the expected equilibrium values considering the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of ambient water in the study area (Blake et al. 2005). Hence, the values of positive disequilibrium could indicate a specific source with a distinct isotopically heavier $\delta^{18}\text{O}_{\text{PO}_4}$ signal.

In sum, the pilot study constituted a successful proof of concept for the application of the $\delta^{18}\text{O}_{\text{PO}_4}$ analysis to obtain insight into the cycling of P in anoxic aquifers. The high Fe^{2+} and PO_4^{3-} concentrations in the groundwater facilitated the analytical procedure. While fine tuning is likely still needed to exclude As in the final Ag_3PO_4 precipitates, this approach could serve as a solid basis for further investigations, which should specifically target potential source signals. In addition, carefully selected vertical and horizontal sampling transects along small-scale hydrological gradients allow for obtaining information regarding the intracellular microbial cycling of P and its regeneration from OM, thereby further improving the understanding of P cycling in Asian floodplain and delta aquifers.

Fig. 7: Measured $\delta^{18}\text{O}_{\text{PO}_4}$ values in groundwater and corresponding $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values of ambient water determined from the groundwater samples collected at Van Phuc. Solid lines depict the range of expected equilibrium $\delta^{18}\text{O}_{\text{PO}_4}$ values after Chang and Blake (2015) covering the measured temperature range in groundwater of the study site (25.3 to 29.5°C). Dashed lines depict the range of expected equilibrium values for the equation provided by Longinelli and Nuti (1973), which showed a higher degree of disequilibrium to the measured $\delta^{18}\text{O}_{\text{PO}_4}$ values of the samples.

4. Conclusion

- Porous aquifers in the S and SE Asian floodplain and delta regions represent remarkable environments that are characterized by an unusual enrichment of P in the form of dissolved PO_4^{3-} in groundwater. They therefore represent ideal natural laboratories to study the biogeochemical cycling and behavior of PO_4^{3-} in groundwater environments, which should also be valid for many other floodplain and delta regions of Asia and beyond.
- Field observations and *in situ* experiments at three representative field sites in the RRD and the BDP provided valuable insights into the mobilization and enrichment of PO_4^{3-} in groundwater. While the possibility that external sources (e.g., agriculture and sanitation) may locally influence PO_4^{3-} concentrations has not been ruled out, the widespread occurrence of elevated PO_4^{3-} concentrations in groundwater is considered the natural geogenic background level. Ultimately, the pronounced enrichment of PO_4^{3-} results from biogeochemical processes, which are based on the microbial degradation of reactive OM coupled with the reductive dissolution of Fe(III)-(hydr)oxides.

- It was also observed that the release of PO_4^{3-} into groundwater could constitute an active process within shallow sediments of Holocene age under reducing redox conditions, which was controlled by the availability of biodegradable OM. In aquifer sections that are depleted in OM, a sudden supply of organic carbon (i.e., caused by a drawdown of DOC due to excessive pumping) may rapidly stimulate indigenous microorganisms and cause an increase in PO_4^{3-} concentrations in groundwater.
- After its mobilization, PO_4^{3-} is subsequently controlled by multiple and superimposed processes, which ultimately result in distinctive spatiotemporal distribution patterns in groundwater. While Holocene aquifer sediments are closely linked to mobilization and increased PO_4^{3-} concentrations in groundwater, sediments of Pleistocene age represent effective scavengers for migrating PO_4^{3-} . In this case, PO_4^{3-} is efficiently immobilized by (co-)precipitation with secondary mineral phases and the adsorption to mineral surfaces until available adsorption sites are exhausted. Furthermore, the PO_4^{3-} sorption capacity of aquifer sediments may slowly change over time due to alterations in the mineral composition. The $\delta^{18}\text{O}_{\text{PO}_4}$ analysis indicated influences of intracellular microbial cycling as well as a specific source of PO_4^{3-} with a distinct isotopically heavy $\delta^{18}\text{O}_{\text{PO}_4}$ signal.
- Considering the numerous complex processes involved and the little attention this topic has received thus far in groundwater studies, a better understanding of P cycling in groundwater ecosystems is needed. Future research should aim to (i) further distinguish PO_4^{3-} release from OM and Fe(III) reduction; (ii) determine the local contribution of anthropogenic derived PO_4^{3-} ; (iii) characterize the dynamics of the immobilization of PO_4^{3-} in Holocene aquifer sediments; and (iv) characterize P species not only in groundwater but also within the aquifer sediments.

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Highlights

- Consistent high PO_4^{3-} conc. in groundwater of the Red River and the Bengal Delta
- PO_4^{3-} represented the dominant P species in anoxic groundwater reaching 1.5 mg L^{-1}
- PO_4^{3-} release via reductive dissolution of Fe-oxides coupled with OM mineralization
- PO_4^{3-} is subject to microbial cycling, subsurface transport, and immobilization
- Stable O isotope analysis in PO_4^{3-} as tool to unravel P cycling and its sources

Graphical abstract