

Phosphate immobilisation dynamics and interaction with arsenic sorption at redox transition zones in floodplain aquifers: insights from the Red River Delta, Vietnam

Author list: Harald Neidhardt^{1*}, Sebastian Rudischer¹, Elisabeth Eiche², Magnus Schneider², Emiliano Stopelli³, Vu T. Duyen⁴, Pham T.K. Trang⁴, Pham H. Viet⁴, Thomas Neumann⁵, and Michael Berg³

¹Geoecology, Eberhard Karls University Tübingen, 72070 Tübingen, Germany

²Institute of Applied Geosciences, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

³Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland

⁴Key Laboratory of Analytical Technology for Environmental Quality and Food Safety Control (KLATEFOS), VNU University of Science, Vietnam National University, Hanoi, Vietnam

⁵Applied Geochemistry, Technical University of Berlin, 10623 Berlin, Germany

*harald.neidhardt@uni-tuebingen.de, Rümelinstr. 19-21, Geoecology, Eberhard Karls University Tübingen, 72070 Tübingen, Germany

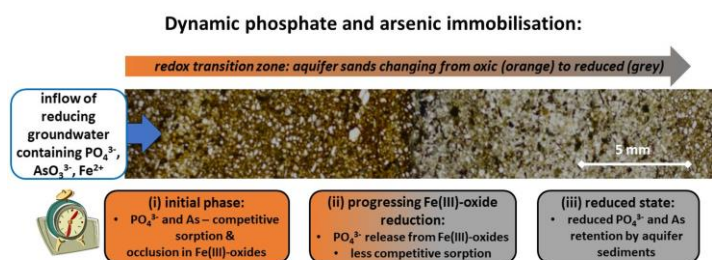
Keywords

1. arsenic
2. floodplain aquifer
3. groundwater
4. iron cycle
5. phosphate
6. redox transition

This document is the accepted manuscript version of the following article:
Neidhardt, H., Rudischer, S., Eiche, E., Schneider, M., Stopelli, E., Duyen, V. T., ... Berg, M. (2021). Phosphate immobilisation dynamics and interaction with arsenic sorption at redox transition zones in floodplain aquifers: insights from the Red River Delta, Vietnam. *Journal of Hazardous Materials*, 411, 125128 (13 pp.).
<https://doi.org/10.1016/j.jhazmat.2021.125128>

This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

Graphical abstract



Abbreviations

arsenic (As)

arsenate (AsO_4^{3-})

arsenite (AsO_3^{3-})

citrate-dithionite-bicarbonate (CDB) solution

continuous flow analyser (CFA)

electron probe microanalysis (EPMA)

high-density polyethylene (HDPE)

inductively coupled plasma optical emission spectrometry (ICP-OES)

inductively coupled plasma mass spectrometry (ICP-MS)

meters below the surface (m bls)

organic carbon (C_{org})

organic phosphorus (P_{org})

low-density polyethylene (PE-LD)

polyethylene terephthalate (PET)

phosphate (PO_4^{3-})

phosphorus (P)

redox potential (E_h)

reduced iron (Fe^{2+})

total arsenic (As_{tot})

total carbon (C_{tot})

total nitrogen (N_{tot})

total phosphorus (P_{tot})

wavelength dispersive X-ray fluorescence detector (WD-XRF)

Abstract

Although phosphate (PO_4^{3-}) may play a decisive role in enriching toxic arsenic (As) in the groundwater of many Asian deltas, knowledge gaps exist regarding its interactions with As. This study investigates the simultaneous immobilisation of PO_4^{3-} and As in aquifer sediments at a redox transition zone in the Red River Delta of Vietnam. The majority of PO_4^{3-} and As was found to be structurally bound in layers of Fe(III)-(oxyhydr)oxide precipitates, indicating that their formation represents a dominant immobilisation mechanism. This immobilisation was also closely linked to sorption. In the surface sorbed sediment pools, the molar ratios of total P to As were one order of magnitude higher than found in groundwater, reflecting a preferential sorption of PO_4^{3-} over As. However, this competitive sorption was largely dependent on the presence of Fe(III)-(oxyhydr)oxides. Ongoing contact of the aquifer sediments with iron-reducing groundwater resulted in the reductive dissolution of weakly crystalline Fe(III)-(oxyhydr)oxides, which was accompanied by decreased competition for sorption sites between PO_4^{3-} and As. Our results emphasise that, to be successful in the medium and long term, remediation approaches and management strategies need to consider competitive sorption between PO_4^{3-} and As and dynamics of the biogeochemical Fe-cycle.

1. Introduction

Phosphate (PO_4^{3-}) plays a decisive role in enriching toxic arsenic (As) in the groundwater of many Asian countries (e.g., Bangladesh, Cambodia, China, India, Vietnam) and elsewhere [1-4], but there are considerable knowledge gaps regarding its transport behaviour and interactions with As [5]. Remarkably high PO_4^{3-} and As concentrations occur in anoxic groundwater of floodplain aquifers in large Asian deltas, such as the Bengal Delta or the Red River Delta [5, 6], where the widespread enrichment of geogenic As in groundwater represents a major health threat to the local population, which often relies on groundwater for drinking and irrigation [7, 8]. While the presence of As in

groundwater has been thoroughly investigated over the past two decades, less is known about the simultaneous enrichment of PO_4^{3-} . In floodplain aquifers, PO_4^{3-} can be mobilised *in situ* through microbial mineralisation of natural organic matter that is embedded in the sedimentary deposits, thereby converting organic phosphorus (P_{org}) into PO_4^{3-} [9]. Microbial cycling of organic matter may also be coupled to the reductive dissolution of Fe(III)-(oxyhydr)oxides, which represent an important PO_4^{3-} host phase in aquifer and lake sediments [5, 10]. The reductive dissolution of Fe(III)-(oxyhydr)oxides is not only relevant for the geogenic release of As, but is also responsible for the mobilisation of PO_4^{3-} into groundwater of Asian floodplain aquifers [5, 11, 12].

After input or *in situ* mobilisation, subsequent biogeochemical processes and anthropogenic activities control the mobility of PO_4^{3-} and As in aquifers. For example, groundwater abstraction has a strong impact on the distribution of PO_4^{3-} and As in groundwater, especially in Asian floodplains [13, 14]. Here, groundwater represents not only the primary source for drinking water, but is also increasingly used for irrigation [15, 16]. Groundwater flow directions may change on local or regional scale because of extensive pumping activities causing anoxic PO_4^{3-} - and As-rich groundwater to migrate into less reducing aquifers as reported for large areas in the Bengal Delta and the Red River Delta [13, 17]. In redox transition zones, dissolved PO_4^{3-} and As can be efficiently immobilised in aquifer sediments, as observed at the Van Phuc field site in the Red River Delta [5, 18].

Valuable insight into the processes underlying PO_4^{3-} and As immobilisation can be gained from redox transition zones. Such knowledge can help facilitate effective remediation of contaminated aquifers, where PO_4^{3-} and As can remain mobile for decades or longer, substantially worsening the groundwater quality [13, 19-21]. Increased PO_4^{3-} concentrations in groundwater are also problematic because of the potential eutrophication of receiving surface water bodies [20, 22, 23]. To date, few studies have investigated PO_4^{3-} immobilisation mechanisms in aquifers [10, 20, 24-27]. Multiple immobilisation processes may control groundwater PO_4^{3-} concentrations, such as (co-)precipitation with secondary Ca- and Fe(II)-minerals (e.g. calcium phosphates, siderite, vivianite) and the sorption to surfaces of primary and secondary minerals (e.g. metal-(oxyhydr)oxides, clay minerals) [27, 28]. Robertson [25] and Harman et al. [29] investigated the movement of PO_4^{3-} plumes in sandy aquifers under anoxic conditions, and concluded that sorption processes were the only relevant PO_4^{3-} immobilisation mechanism at their study sites. Furthermore, PO_4^{3-} sorption can be partially reversible and strongly influenced by pH and competition with other oxyanions for sorption sites [20, 27]. In

particular, oxyanions of the toxic element As are competing species under iron-reducing conditions. In Asian Delta regions groundwater, dissolved As is often highly enriched in the form of inorganic arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) [30]. Surface complexation models suggested that dissolved As would entirely adsorb to the aquifer sediments in the absence of PO_4^{3-} [1, 2]. However, the interaction between PO_4^{3-} and As under natural conditions has not yet been studied in detail.

This study investigated the processes underlying PO_4^{3-} and As immobilisation at a pronounced redox transition zone at the Van Phuc field site in the Red River floodplain near Hanoi. Here, the aquifer sediments are subject to a change in colour from orange to grey, reflecting a transition in the redox properties owing to continuous contact with reducing groundwater that carries elevated PO_4^{3-} , As, and Fe^{2+} concentrations. This setting allowed us to investigate the influence of redox properties on the immobilization of PO_4^{3-} and As.

2. Study site

Our study site is located near the village of Van Phuc ($20^\circ 55' 7.00''\text{N}$, $105^\circ 53' 55.00''\text{E}$) in the floodplain of the Red River, about 15 km southeast of the Hanoi metropolitan area. Groundwater abstraction for the Hanoi drinking water supply changed the local groundwater flow direction most likely 50 to 60 years ago [31]. As a result, anoxic groundwater migrates laterally, currently about 40 m per year, from a reduced Holocene aquifer into an adjacent Pleistocene aquifer [31]. Migrating groundwater from the Holocene aquifer is characterised by a low redox potential (E_h of -5 to +118 mV), a near-neutral pH, and comparatively high concentrations of dissolved Fe^{2+} ($>0.10 \text{ mg L}^{-1}$), AsO_3^{3-} ($>0.10 \text{ mg L}^{-1}$), and PO_4^{3-} ($>1.50 \text{ mg L}^{-1}$) [5, 32]. Dissolved PO_4^{3-} represents the dominant, if not sole P species in groundwater.

The Pleistocene aquifer ranges to approximately 45 m below the surface (bfs) and is covered by a 15 to 22 m thick aquitard of clayey and silty deposits [33, 34]. Continuous contact with the anoxic groundwater has led to changed redox conditions in the Pleistocene aquifer within an approximately 120 m wide transition zone [31]. According to groundwater monitoring data, dissolved PO_4^{3-} and As concentrations sharply decline after traversing the redox transition zone [5]. Gradual colour transitions from orange over yellow-orange to grey in the sandy sediments of the Pleistocene aquifer reflect a pronounced change in the Fe-mineralogy, shifting from a dominance of Fe(III)-(oxyhydr)oxides to more reduced Fe(II)- and Fe(II,III)-mixed valence minerals [18]. These changes are further visible in

vertical depth profiles, where approximately 1 to 100 mm thick layers of orange and yellow-orange sediments alternate with grey-coloured sediments. Further details regarding the depositional history, hydrogeology, and biogeochemistry of the Van Phuc site is provided elsewhere [12, 18, 31, 34-36].

3. Materials and methods

3.1 Sampling

All samples were collected from a single drilling core that was drilled through the redox transition zone at Van Phuc in December 2018 (core RD54, 20°55'18.79"N, 105°53'38.30"E). This location was chosen based on previous drilling campaigns in the direct vicinity, allowing us to precisely target the redox transition zone. Coring was conducted with a 10 cm inner diameter rotary drill. The obtained core had an overall length of 43.5 m and reached to a depth of 46.5 m bls (note: the top 3 m were discarded because of disturbances from the drilling operation). Directly after drilling, drilling fluid remains were removed and each core section was described and photographed. The sediment colour was recorded based on the Munsell colour chart and the grain size was estimated manually by finger test. Then the core sections were divided lengthwise with a ceramic knife and samples were taken from the undisturbed centre of the core at intervals of 100 cm and more frequently if small-scale changes in colour or grain size were visible. The sample material was transferred into water- and air-tight zipper bags (PET/PE-LD/Aluminium stand-up pouches LamiZip, VWR), which were immediately flushed with N₂ before closing. The time of air contact was kept as short as possible (<1 min) to avoid oxidation reactions. Finally, all sample bags were sealed in larger air-tight bags (HDPE bags, Allpax) under N₂ atmosphere and kept frozen at -20°C until analysis. In total, 54 samples were collected.

The core samples were subdivided into different classes based on lithology and colour. Clayey silt samples mainly comprised the uppermost 19 m of the sediment core, but also a layer of unknown thickness encountered below the 43 m depth. Samples representing the Pleistocene aquifer comprised orange and yellow-orange (i.e. reflecting moderately reducing redox properties) and grey (i.e. representing a change towards strongly reducing redox properties) sandy sediments. Within the aquifer sands, redox interfaces with strong colour contrasts reflecting redox gradients are visible, especially at lithological boundaries (refer to note A.1 for further details on the sediment core). For sediments representing mixed redox properties, a clear separation based on the colour was not

possible owing to a very fine layering at the mm scale (see Fig. 1). For the statistical comparison, the aquifer sand samples were grouped into “orange sand” (n=17), “grey sand” (n=11), and “sand mixed redox” (n=6).

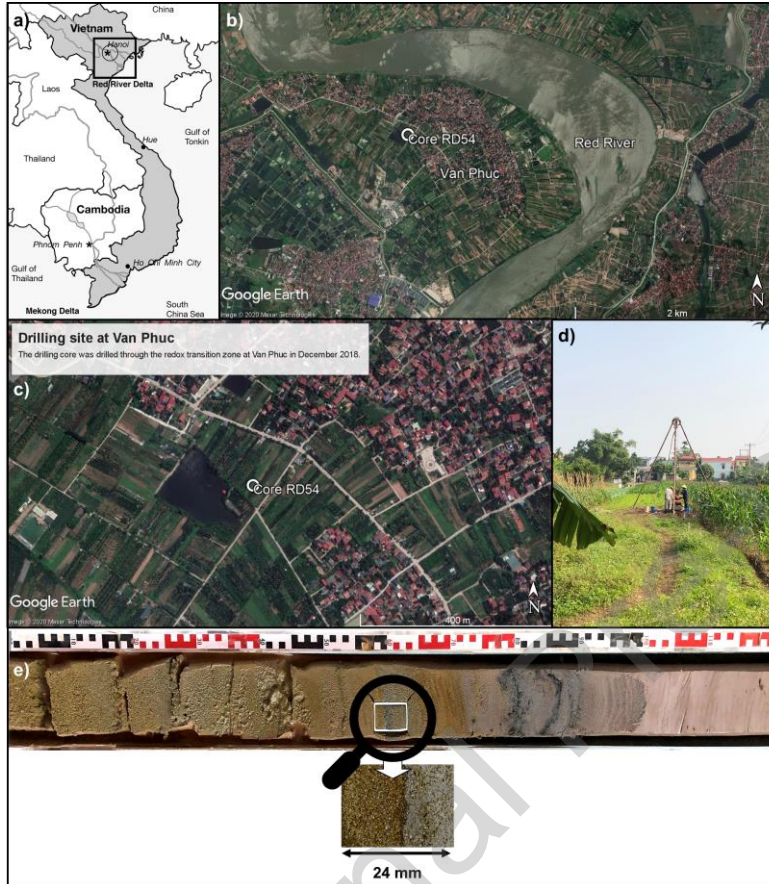


Fig. 1. Location of the study area in the Red River Delta close to Hanoi (a), and drilling site of core RD54 at a bend of the Red River in the Van Phuc village (b, c, d). Core section showing sandy aquifer sediments from 41.8 - 43.1 m bls (left to right) that exhibit different redox features (orange and grey sand) before transitioning into whitish clayey silt sediments (e). For an example of a redox transition refer to the white frame in the core middle (42.5 m bls) and the polished section prepared from it. Satellite images: Google 2020, Maxar Technologies.

3.2 Chemical analysis

All vials and storage devices were soaked in 1% HNO_3 and rinsed with Milli-Q water before use. For analytical detection limits refer to Table A.1. Total concentrations of P (P_{tot}), As (As_{tot}), and other major and trace elements were assessed with a microwave-assisted acid pressure digestion (method E701, MLS GmbH) of 0.5 g freeze-dried, pulverised, and homogenised sample material. Then, 5 mL Milli-Q water, 10 mL 65% HNO_3 (EMSURE, Merck), and 3 mL 37% HCl (ACS reagent, Sigma-Aldrich)

were added to the samples in polytetrafluoroethylene beakers before heating to 190 °C for 14 minutes in a laboratory microwave system (START 1500 Microwave Extractor, MLS GmbH). Digestion solutions were filtrated (Mn 619 G1/4, Macherey-Nagel) and analysed by inductively coupled plasma atomic emission spectroscopy (ICP-OES, Optima 5300 DV, PerkinElmer). The certified reference material Metals in Soil (SQC001-30G, lot LRAC3749, Sigma Aldrich) was used to check the accuracy and precision of the microwave-assisted acid pressure digestion. The average recovery rate was 122% for P_{tot} and 91% for As_{tot} , with relative standard deviations of <5 % (n=7).

Total C (C_{tot}) and N (N_{tot}) concentrations were measured from homogenised sample material with an Element Analyzer (EA, Vario EL III, Elementar Analysensysteme GmbH). Given the absence of detectable inorganic C (no reaction with 10% HCl), total C was considered to represent organic C (C_{org}). Samples originating from a parallel drilling core (RD42, located approximately 6 m next to RD54) were analysed by means of electron probe microanalysis (EPMA, JEOL, JXA-8530 F), which was equipped with a wavelength dispersive X-ray fluorescence detector (WD-XRF) allowing us to check the elemental composition of the samples at selected regions of interest (acceleration voltage: 15kV).

3.3 Sequential extraction

The P (comprising inorganic PO_4^{3-} and P_{org}) and As pool composition of the sediments was assessed using sequential extraction. We therefore combined different steps from sediment and soil extraction protocols to obtain an optimum combination for the aquifer sediments. Table 1 provides a summary of the five sequential extraction steps, including details regarding the targeted P and As pools and associated references. In the first step, 0.5 g of freshly thawed sediment was extracted with 0.25M $NaHCO_3$ ($\geq 99.5\%$, Sigma-Aldrich) at pH 8.5 on a rotary shaker. This processes aims to extract loosely bound, hence exchangeable PO_4^{3-} , P_{org} , and As, and was repeated three additional times to avoid carry-over effects [37]. Afterwards, samples were shaken with Milli-Q water as wash solution. Next, samples were extracted with 0.1M NaOH ($\geq 98\%$, Sigma-Aldrich) to release moderately labile P (represented by strongly bound PO_4^{3-} and P_{org}) and As sorbed to surfaces of metal-(oxyhydr)oxides, and PO_4^{3-} and As structurally bound in Al-(oxyhydr)oxides. The step was repeated for three more times, followed by a wash step with Milli-Q water. The third step was carried out with a citrate-dithionite-bicarbonate (CDB) solution targeting PO_4^{3-} and As that is structurally bound in weakly crystalline Mn(III,IV)- and Fe(III)-(oxyhydr)oxides. Afterwards, three repetitions with 0.5M $NaHCO_3$

solution and one wash with Milli-Q water were applied. For the fourth step, 37% HCl (ACS reagent, Sigma-Aldrich) was added to the sample material and heated for 30 minutes at 80°C. After cooling, Milli-Q water was added to the HCl solution, followed by three additional wash steps with Milli-Q water. Here, PO_4^{3-} and As were extracted from primary and secondary Ca- and Fe(II)-minerals as well as acid-hydrolysable P_{org} . Finally, residual P and As (i.e. structurally bound in stable minerals) and P_{org} in recalcitrant organic compounds were obtained after combustion at 550 °C followed by shaking with 0.5M H_2SO_4 (EMSURE Sulfuric, Merck) and three subsequent wash steps with Milli-Q water. Extraction solutions were degassed with N_2 before the respective extractions to simulate the contact of aquifer sediments at the field site with anoxic groundwater.

All extractions were centrifuged at 4500 rpm for 10 minutes before filtration (MN 619 G 1/4, Macherey-Nagel) and stored at 4°C. The solutions were analysed for total P, As, and other elements by ICP-OES. The NaHCO_3 , NaOH, and CDB extraction solutions were additionally analysed for PO_4^{3-} concentrations by the molybdenum blue method (DIN-EN-ISO-6878: 2004) using a spectrophotometer (Cary 100 UV/Vis, Agilent) and a continuous flow analyser (CFA, Seal Analytical). Because the NaHCO_3 solution is unstable, it was analysed within two weeks. Concentration values were corrected to dry-weight based on each sample's gravimetric water content (determined with a halogen moisture analyser). The concentration of P_{org} was calculated as the difference between P_{tot} and inorganic P (PO_4^{3-}) concentrations [38]. Note that no such distinction could be made for As species in the sequential extraction solutions. Therefore, As species in the respective sediment pools are referred to as "As" in the following. Because of low As concentrations, the aquifer sands extraction solutions were measured by inductively coupled plasma mass spectrometry (ICP-MS, 8900 series, Agilent). The same applied to Fe and Mn in the NaHCO_3 extracts.

Furthermore, recovery rates were calculated by comparing the sum of extractable and total element concentrations as determined by acid pressure digestion [39]. Considering the sum of PO_4^{3-} and P_{tot} in the individual samples compared to respective P_{tot} concentrations, the average recovery rate reached $97.6 \pm 25.4\%$ ($n=58$, Fig. A.3). As an additional quality control, the certified P reference material River Sediment (BCR[®]-684, Institute for Reference Materials and Measurements) was extracted. The sum of extractable P concentrations in all extraction steps were consistent with the certified values for total PO_4^{3-} , P_{org} , and P_{tot} , reaching recovery rates of 97.4, 92.3, and 92.9%, respectively.

The average recovery rate for As in the samples was $61.7 \pm 17.5\%$ ($n=34$). This moderate underestimation for As was attributed to the presence of non-extractable As in stable minerals and the generally low As_{tot} concentrations. For the reference material Metals in Soil, the sum of extractable As compared to the certified As_{tot} concentration yielded a recovery rate of 114%. For further technical details and a critical evaluation of the extraction scheme see Note A.2, Figs. A.1, A.2, and Tables A.2 and A.3.

Table 1. Sequential extraction scheme used for the characterisation of the phosphorus (comprising inorganic phosphate, PO_4^{3-} , and organic phosphorus, P_{org}) and arsenic (As) pools.

Extractant	Targeted pools	Extraction details	Mechanism(s)	Ref.
$NaHCO_3$	exchangeable PO_4^{3-} , P_{org} , and As	20 mL of 0.25M $NaHCO_3$ (pH 8.5) for 30 min, followed by three repetitions, and one wash with 25 mL Milli-Q water for 30 min	desorption of PO_4^{3-} , P_{org} , and As through HCO_3^{3-} , CO_3^{2-} and pH increase	a, b
$NaOH$	PO_4^{3-} , P_{org} , and As strongly surface sorbed to metal-(oxyhydr)oxides and PO_4^{3-} and As structurally bound in Al-(oxyhydr)oxides	30 mL of 0.1M $NaOH$ for 16h, followed by three repetitions for 30min, and one wash with 25 mL Milli-Q water for 30 min	desorption of strongly bound PO_4^{3-} , P_{org} , and As by OH^- ions and pH increase, dissolution of Al-(oxyhydr)oxides	c, d, e
CDB	PO_4^{3-} and As structurally bound in Fe(III)- and Mn(III,IV)-(oxyhydr)oxides	45 mL of 0.3 M Na_3 -citrate and 1M $NaHCO_3$ solution and 1.125 g Na-dithionite (pH 7.4) for 16h, followed by three extractions with 20 ml 0.5m $NaHCO_3$ for 30min, and one wash with 25 mL Milli-Q water for 30 min	release of structurally bound PO_4^{3-} and As from reductive dissolution of Fe(III)- and Mn(III,IV)-(oxyhydr)oxides	f
HCl	PO_4^{3-} and As in Ca- and Fe(II)-minerals, acid-soluble P_{org}	5 mL 37% HCL heated for 30 Minutes at 80°C and adding 25 ml Milli-Q water during cool down, followed by three washes with 25 mL Milli-Q for 30 min	release of PO_4^{3-} and As from dissolution of Ca- and Fe(II)-minerals, hydrolysis of P_{org}	c, e, g
H_2SO_4	Chemically stable and insoluble PO_4^{3-} and As, recalcitrant P_{org}	Drying at 105°C overnight and incineration of sample remains at 550°C for 1h, followed by addition of 20 mL 0.5M H_2SO_4 and 16h of shaking, followed by three washes with 25 mL Milli-Q water for 30 min	dissolution of residual forms of P and As	h, i

^a Mattingly [40], ^b Hiemstra et al. [41], ^c Thiessen and Moir [42], ^d Psenner et al. [43], ^e Shiowatana et al. [44], ^f Ruttenberg [45], ^g Hupfer et al. [46], ^h Ivanoff et al. [47], ⁱ Walker and Adams [48]

3.4 Statistical analysis

Statistical analysis was carried out with Microsoft Excel 2016 and IBM SPSS Statistics (Vers. 24). Concentration values below the detection limit were set to half of the respective detection limit. The contribution of the respective P pools was included as a percentage of the sum of extractable PO_4^{3-} (for the $NaHCO_3$ and CDB extracts) and P_{tot} (for the $NaOH$, HCl and H_2SO_4 extracts).

The confidence interval for all tests was 95%, and p values ≤ 0.05 were considered statistically significant. The data was tested for normal distribution with the Shapiro-Wilk test. Group comparisons

for P and As concentrations were conducted with the non-parametric Kruskal-Wallis 1-way ANOVA on ranks and a pair-wise post-hoc test with significance values adjusted using the Bonferroni correction for multiple tests. The Spearman rank correlation test (two-tailed) was used to explore relationships between measured sediment sample variables.

4. Results and discussion

4.1 Sedimentary P pools

Depth distribution of P_{tot} : The depth distribution of P_{tot} varied widely within the sediment core with concentrations ranging from 61 up to 1025 mg kg^{-1} (median: 167 mg kg^{-1} , $n=58$). The highest P_{tot} concentrations were found in the clayey silt sediments and in the orange aquifer sediments (e.g. at 22.3 and 30.6 m bls, see Fig. 2). This concentration range for P_{tot} is consistent with previously analysed aquifer sediments from Van Phuc (reduced Holocene aquifer: 44 to 305 mg kg^{-1} , Pleistocene aquifer: 44 to 284 mg kg^{-1}) [5]. Similar values were reported for aquifer sediments from floodplains in the Bengal Delta, with two field sites located in West Bengal, India (P_{tot} of 223 to 620 mg kg^{-1}) and one site in Bangladesh (P_{tot} 170 to 780 mg kg^{-1}) [5, 49]. The P_{tot} distribution in the sediments was positively correlated with As_{tot} , Ca_{tot} , Fe_{tot} , Al_{tot} , Mn_{tot} , and C_{org} (all had $p<0.01$). The correlation was strongest between P_{tot} and Fe_{tot} (Spearman's Rho $r=0.90$, $p<0.01$), which was consistent with previous sediment analyses at Van Phuc by Neidhardt et al. [5]. This result was a first indication of the prominent role of Fe-minerals as P host phases. A detailed description of the sediment core lithology and redox properties is provided in note A.1.

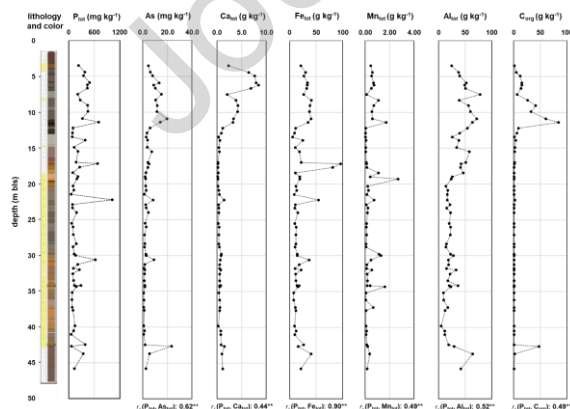


Fig. 2. Lithology and depth distribution of total element concentrations in core RD54. Correlations with P_{tot} concentrations are indicated at the bottom of each plot, with significant correlations highlighted by asterisks

(Spearman's Rho, $**p<0.01$). The yellow shading in the lithology plot (left) indicates the aquifer sediments, the grey shading indicates clayey silt sections.

P pool composition: The positive correlation between P_{tot} and C_{org} (Spearman's Rho $r=0.49$, $p<0.01$, Fig. 2) could suggest the presence of P_{org} in the sediments. However, the proportion of P_{org} remained below 5% relative to total extractable P in the respective pools (average NaHCO_3 -extractable P_{org} proportion: 0.1%, NaOH -extractable: 2.6%, CDB-extractable: 0.1%). Because sedimentary P pools were dominated by inorganic PO_4^{3-} , the NaHCO_3 -extractable pool is referred to as “exchangeable PO_4^{3-} ” and the NaOH -extractable pool as “strongly sorbed PO_4^{3-} ” in the following. Considering the high concentration of Fe and the comparatively low Mn and Al concentrations that were CDB-extractable (Table A.2), we concluded that Al- and Mn(III,IV)-(oxyhydr)oxides are of only minor importance. Thus, the majority of CDB-extractable P is represented by PO_4^{3-} that is structurally bound in weakly crystalline Fe(III)-(oxyhydr)oxides. In HCl- and H_2SO_4 -extractable P, it was not possible to differentiate between PO_4^{3-} and P_{org} due to methodological reasons (i.e. acid-hydrolysis of P_{org} during the extraction). Therefore, the HCl pool may comprise PO_4^{3-} in the form of primary and secondary Ca- and Fe(II)-phosphate minerals, and acid-soluble P_{org} . The H_2SO_4 pool is generally considered to contain non-extractable mineral PO_4^{3-} and P_{org} in the form of recalcitrant C_{org} compounds. Thus, this pool is referred to as “residual P” in the following. For a detailed overview of the P pools, refer to Fig. 3a.

A comparison of our results to previous research is limited, because this is the first time that P pools in floodplain aquifer sediments have been characterised in such detail. While sequential extractions were frequently used for characterising As pools, this has not been applied to P pools. A parallel assessment of As and P is not common because surface adsorbed As is normally assessed by extraction with a concentrated PO_4^{3-} -solution. However, a few studies conducted single-step extractions or leaching experiments to estimate the amounts of surface adsorbed or Fe(III)-associated PO_4^{3-} in floodplain aquifer sediments. For example, the amount of PO_4^{3-} that is leachable from reductive dissolution of Fe(III)-(oxyhydr)oxides (via ascorbic acid at pH3) and from proton induced dissolution (with 1mM HCl at pH3) was determined with oxic and reduced aquifer sediments from a study site in the Red River Delta, located about 20 km north of our site [50]. Here, leachable PO_4^{3-} concentrations for both extractions ranged up to $3.1 \text{ mg PO}_4\text{-P kg}^{-1}$. This range is comparable to the

exchangeable P pool in this study; however, comparison is limited because our values are from an extraction and Postma et al.'s values originated from leaching experiments. Oxalate-extractable P was previously determined in floodplain sediments at three sites in Bangladesh (Bengal Delta) by BGS and DPHE [9]. That single-step oxalate extraction comprised surface sorbed and PO_4^{3-} structurally bound in weakly crystalline metal-(oxyhydr)oxides with concentrations of up to 400 mg kg^{-1} . This is similar to the present study's sum of exchangeable, strongly bound, and Fe(III)-(oxyhydr)oxide structurally bound PO_4^{3-} . Another study conducted in Bangladesh identified adsorbed PO_4^{3-} in aquifer sediments of the Bengal Delta with a single-step extraction at pH 2 [51]. Here, concentrations of Holocene aquifer sediments were clearly higher (57 to 528 mg kg^{-1}) than in underlying Pleistocene aquifer sediments (28 to 66 mg kg^{-1}) [51]. The range of these values is similar to the sum of exchangeable and strongly bound PO_4^{3-} in Van Phuc (9 to $195 \text{ mg PO}_4\text{-P kg}^{-1}$, see Fig. A.4).

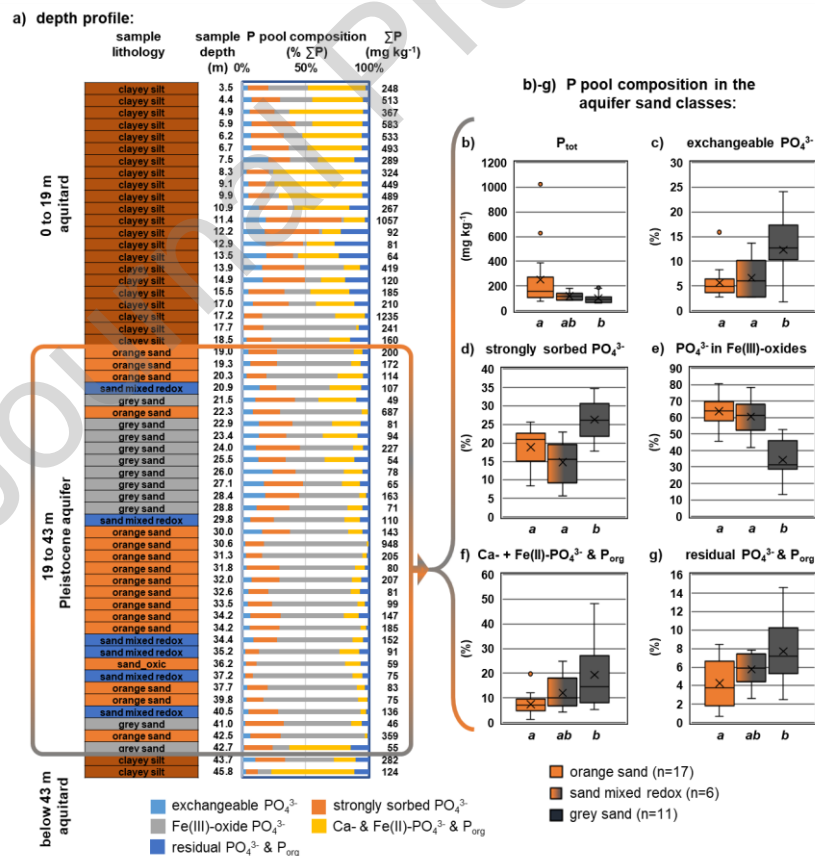


Fig. 3. Relative composition of the P pools along the vertical depth profile (a) including the sum of extractable P (ΣP). The sample classification is based on sediment colour and lithology. The boxplots summarize the

distribution of P_{tot} concentrations in the three aquifer sediment classes (b), and the proportion of extractable P in the five sequential extraction steps (c-g). Different lower-case letters (i.e. a, b) below the bars indicate significant differences between the respective aquifer sand classes (pair-wise post-hoc test, $p < 0.05$).

Aquifer sediments: The following section focusses on the sandy aquifer sediments, where PO_4^{3-} is actively immobilised from migrating groundwater (note: dissolved PO_4^{3-} concentrations in groundwater sharply drop from up to 1.30 to below 0.18 mg L⁻¹ along the flow path at the redox transition zone [5]). Here, the concentration of P_{tot} was strongly linked to the redox conditions as represented by the three aquifer sand classes (Fig. 3b). The mean P_{tot} concentration was highest in the orange aquifer sand, representing mildly to moderately reducing redox properties (median: 159 mg kg⁻¹), while it was significantly ($p < 0.01$) lower in the strongly reduced grey aquifer sand (median: 89.5 mg kg⁻¹). For sand with mixed redox properties, P_{tot} (median: 119 mg kg⁻¹) did not differ significantly from the two other classes ($p > 0.05$). Note that P_{tot} concentrations in the orange sand showed high variations (spanning from 78 to 1025 mg kg⁻¹).

Pronounced differences were also visible in the extracted P pools (Fig. 3c-g). Compared to the orange and mixed redox state sand, the grey sand was characterised by significantly higher median proportions of exchangeable PO_4^{3-} (12.7% versus 5.0% and 6.0%, $p < 0.05$, Fig. 3c) and strongly sorbed PO_4^{3-} (26.0% versus 21.0% and 15.6%, $p < 0.01$, Fig. 3d). The mean proportion of Fe(III)-(oxyhydr)oxide structurally bound PO_4^{3-} was almost twice as high for the orange and mixed redox state sand than for the grey sand (median values of 64.1% and 61.4% versus 31.5%, $p < 0.05$, Fig. 3e). Conversely, the proportion of HCl-extractable P (i.e. Ca- and Fe(II)- PO_4^{3-} and acid-soluble P_{org}) was almost two times higher in the grey sand than in the orange sand (median of 14.6% versus 7.1%, $p < 0.01$, Fig. 3f). The same was true for residual P (median: 7.2% versus 3.8%, $p < 0.05$, Fig. 3g). For a summary of absolute P concentrations in the respective pools refer to Fig. A.4. In the following, the P pool composition of the three sand classes is interpreted in terms of the processes that most likely caused these differences.

Orange aquifer sand: Comparatively high P_{tot} concentrations (from 78 up to 1025 mg kg⁻¹, Fig. 3b) occurred in the orange aquifer sand. Interestingly, these concentrations were considerably higher than those in corresponding orange-coloured aquifer sand located 200 m downstream from the redox transition zone, which was not yet influenced by the advection of reducing groundwater (66 to 109 mg kg⁻¹, $n=7$, [34]). Therefore, we assume that the relatively high P_{tot} concentrations in the orange

sediments at the redox transition zone already included considerable amounts of migrating PO_4^{3-} , which was immobilised in the aquifer sediments. This immobilisation of dissolved PO_4^{3-} at the redox transition zone is closely linked to Fe(III)-(oxyhydr)oxides, as reflected in the P pool composition of the orange aquifer sand. Here, the highest proportion of extractable P was found to be PO_4^{3-} structurally bound in weakly crystalline Fe(III)-(oxyhydr)oxides, followed by strongly sorbed PO_4^{3-} (median proportion of 64% and 21%, respectively, Fig. 3c-e). Despite the continuous contact with reducing groundwater ($E_h < 20$ mV, [18]), Fe(III)-(oxyhydr)oxides are still present in the sediments as indicated by the orange colour and the considerable concentrations of CDB- and HCl-extractable Fe (Table A.2). This could be directly linked with the sorption of PO_4^{3-} , which has been shown to stabilise Fe(III)-(oxyhydr)oxides by providing protection from reductive dissolution [52]. According to previous investigations by Eiche et al. [34], Fe(III)-(oxyhydr)oxides in the Pleistocene aquifer sediments of Van Phuc are represented by hematite, goethite, and weakly ordered phases such as ferrihydrite. In general, Fe(III)-(oxyhydr)oxides can not only adsorb large quantities of PO_4^{3-} on their surfaces, they can also incorporate PO_4^{3-} during their formation [53]. Element mappings further confirmed the presence of Fe(III)-(oxyhydr)oxide precipitates in the form of cementations and coatings in the redox transition zone aquifer sediments (Fig. A.5). Such precipitates were found at sub-cm thick redox interfaces in a parallel drilling core located approximately 6 m next to the present core. The formation of Fe(III)-(oxyhydr)oxide dominated precipitates (composed of amorphous Fe(III)-(oxyhydr)oxides, hematite, goethite, and magnetite; [54]) is considered to result from an abiotic and/or microbially mediated oxidation of dissolved Fe^{2+} coupled with the reduction of sedimentary Mn(III,IV)-(oxyhydr)oxides [18]. The spatial distribution of P in these secondary precipitates (see element mapping in Fig. A.5) further suggests that initially surface sorbed PO_4^{3-} became structurally incorporated through the growth of the precipitate layers.

The combination of sorption and incorporation into newly formed Fe(III)-(oxyhydr)oxide precipitates appears to be a highly effective immobilization mechanism for dissolved PO_4^{3-} , which, to the best of our knowledge, has not been accounted for in previous studies, where surface sorption is considered the dominant PO_4^{3-} immobilisation in aquifers [19, 20].

Influence of redox state on P pools: On average, the P_{tot} concentration in the grey aquifer sand was 150 mg kg^{-1} lower than in the orange sand (101 versus 251 mg kg^{-1} , Fig. 3b). This P_{tot} net concentration difference was almost entirely reflected in PO_4^{3-} structurally bound in weakly crystalline

Fe(III)-(oxyhydr)oxides, which was the only P pool that was largely lower in the grey than in the orange sand (average concentration of 33 versus 152 mg kg⁻¹, Fig. 3e). Hence, the most pronounced characteristic of the grey aquifer sand was the reductive dissolution of weakly crystalline Fe(III)-(oxyhydr)oxides. This was not only reflected by the colour change, but also by a significantly lower content of weakly crystalline Fe(III)-(oxyhydr)oxides in the grey sand than in the orange sand (median: 3,020 versus 7,440 mg kg⁻¹ CDB-extractable Fe, $p < 0.01$). The reductive dissolution of weakly ordered Fe(III)-(oxyhydr)oxides and a concomitant loss of previously sorbed PO₄³⁻ is an active process at the study site as revealed by a six month long *in situ* sorption experiment using orange-coloured Pleistocene sand from Van Phuc as well as synthetic ferrihydrite [5, 32]. Interestingly, the loss of weakly ordered Fe(III)-(oxyhydr)oxides and associated sorption sites was not reflected in the two surface sorbed pools of the sediments (Fig. 3c,d), where the respective relative proportions were significantly higher in the grey sand than in the orange sand ($p < 0.05$).

The relative proportion of HCl-extractable P was also significantly higher in the grey sand (Fig. 3f). Given the generally low absolute P concentrations and missing differences between the orange and grey sand, there was no indication that migrating PO₄³⁻ was immobilised by secondary Ca-, Fe(II)-, Mn(II)-carbonates and phosphates.

The mixed redox state aquifer sand sample class comprised orange sand mixed with grey sand at the sub-cm scale (see section in Fig. 1). The P_{tot} concentration and the P pool composition of the mixed redox state sand was similar to the orange sand (Fig. 3). Because some grains were still orange while others were already bleached, the continuous contact with anoxic groundwater resulted in a partial, but not fully reductive dissolution of weakly crystalline Fe(III)-(oxyhydr)oxides. Hence, Fe(III)-(oxyhydr)oxide structurally bound PO₄³⁻ still represents the dominant P pool (Fig. 3e, Fig. A.4d).

Basing conclusion on sequential extraction data for past and present processes requires caution. However, comparing aquifer sediments that are transitioning from a moderately to a strongly reduced redox state allows indirect insight into the biogeochemical processes underlying the dynamic immobilisation of PO₄³⁻ along redox transition zones. In summary, the immobilisation of PO₄³⁻ at redox transition zones is a highly dynamic process closely linked to several biogeochemical cycles, where the redox cycle of Fe is central. These processes can significantly alter sedimentary P pools over time and result in the re-release of previously immobilised PO₄³⁻.

4.2 As pools in the aquifer sediments

Depth distribution and As pool composition: For As_{tot} , the depth distribution in the aquifer sand was similar to P_{tot} (Fig. 2), although concentrations were considerably lower, ranging from 0.7 up to 23.5 mg kg⁻¹ (median: 2.7 mg kg⁻¹, $n=58$). This concentration range is characteristic of aquifer sediments in Asian floodplains such as the Red River Delta [55], the Mekong Delta [56], or the Bengal Delta [9, 49, 51, 57, 58], where As_{tot} concentrations are usually in a range of 0.25 to about 25 mg kg⁻¹. Similar to PO_4^{3-} , dissolved As is largely immobilised at the redox transition zone, where As concentrations in groundwater sharply drop from up to 393 to below of 10 ug L⁻¹ along the flow path [18]. A strong positive correlation between As_{tot} and P_{tot} concentrations (Spearman's Rho $r=0.62$, $p<0.01$) indicates that both elements are controlled by similar processes, with sorption to Fe(III)-(oxyhydr)oxides being the most likely one [4]. The important role of Fe-minerals as primary sorbents for As is further supported by a significant correlation between As_{tot} and Fe_{tot} (Spearman's Rho $r=0.72$, $p<0.01$), and is consistent with a previous study that analysed aquifer sediments in the vicinity of the redox transition zone [59]. This finding is also in line with other As-contaminated aquifers in Vietnam and elsewhere in South and Southeast Asia, where sedimentary Fe(III)-(hydr)oxides were identified as important sorbents for As [3, 21, 60, 61]. Dissolved As in groundwater is predominantly present as reduced oxyanion AsO_3^{3-} , with minor proportions of AsO_4^{3-} [32]. Both inorganic As species show a similar sorption behaviour to Fe(III)-(oxyhydr)oxides at circum-neutral pH values [62].

Sorption is further reflected in the composition of the As pools. Compared to the amount of total extractable As, the proportion of exchangeable As was low (median: 3.9%), while strongly sorbed As had a higher proportion (median: 12.8%, see Fig. 4c,d). The surface adsorbed pools are of particular relevance, because As sorption in Asian aquifers represents a partially reversible process [32, 60, 63]. Significant amounts of As could be re-released into groundwater from aquifer sediments of the redox transition zone when inflowing groundwater As concentrations decline.

Similar to PO_4^{3-} , most As was found to be structurally bound in Fe(III)-(oxyhydr)oxides (median: 49%, see Figs. 4e and A.5). About one third of the total extractable As was related to the remaining two pools (HCl-extractable and residual As, Fig. 4e,f).

The results of the sequential extraction are consistent with outcomes from previous sequential extractions from the Holocene and Pleistocene aquifer in Van Phuc [59], as well as other As-troubled regions, such as the Bengal Delta [51, 58, 64, 65]. Although the applied sequential extraction

schemes in these studies partially differed from our protocol and from each other, most of the As was generally found to be strongly sorbed and structurally bound in weakly ordered and/or well-crystalline Fe(III)-(oxyhydr)oxides. The proportion of surface adsorbed As we observed at the redox transition zone in Van Phuc is generally lower than reported by the aforementioned studies, which we attribute to the formation of Fe(III)-(oxyhydr)oxide coatings that subsequently convert surface sorbed As into structurally incorporated As. The formation of As-sulphides as another potential As immobilisation process [66] could be excluded, given the absence of S species in groundwater [67].

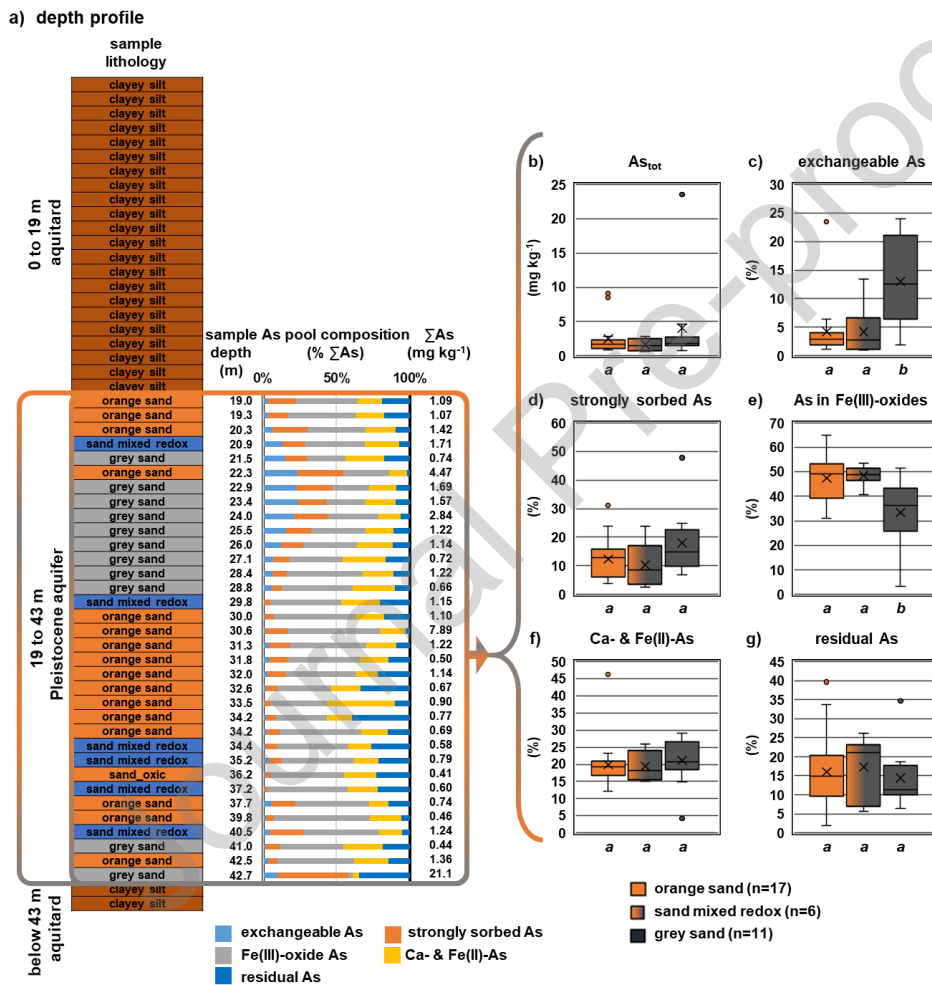


Fig. 4. Relative composition of the As pools in the aquifer sands along the vertical depth profile (a) including the sum of extractable As (ΣAs). The boxplots summarize the distribution of As_{tot} concentrations in the three aquifer sediment classes (b), and the proportion of extractable As in the five sequential extraction steps (c-g). Different lower-case letters (i.e. a, b) below the bars indicate significant differences between the respective aquifer sand classes (pair-wise post-hoc test, $p < 0.05$).

Influence of redox state on As pools: In contrast to the P pools, differences in the As pools were less pronounced between the orange, grey, and mixed redox state sand (Fig. 4). Compared to the orange and mixed redox state sand, the grey sand was characterised by significantly higher median proportions of exchangeable As (12.6% versus 2.9% and 2.8%, $p < 0.01$, Fig. 4c). This corresponded to absolute median concentrations of 0.14 mg kg^{-1} , 0.03 mg kg^{-1} , and 0.02 mg kg^{-1} , respectively. The mean relative proportion of Fe(III)-(oxyhydr)oxide structurally bound As was significantly lower in the grey sand than for the orange and mixed redox state sand (median value of 36.3% versus 49.1% and 48.8%, $p < 0.01$, Fig. 4e). However, the absolute As concentrations in this pool did not significantly differ for the three classes (median concentrations of 0.41 mg kg^{-1} , 0.46 mg kg^{-1} , and 0.47 mg kg^{-1} , respectively, $p > 0.05$, Fig. A.6). In contrast to PO_4^{3-} , a re-release of As through the reductive dissolution of Fe(III)-(oxyhydr)oxides was not visible in our data. Considering the previously described PO_4^{3-} behaviour and what is known from field observations [32], forced redox state microcosm experiments [68, 69], and hydrogeochemical modelling [21], one would expect a considerable release of As via the reductive dissolution of Fe(III)-(oxyhydr)oxides. This deviant As behaviour in the grey aquifer sand could be related to incorporation of As in more crystalline secondary Fe(III)-(oxyhydr)oxides such as hematite and goethite, which are stable under moderately reducing redox conditions (see [32]), whereas PO_4^{3-} was also incorporated into less crystalline phases such as ferrihydrite, which became rapidly liberated through the change in redox state. Alternatively, the observed concentration difference for Fe(III)-(oxyhydr)oxide structurally bound As was too low to be statistically significant but might further increase with ongoing interaction of the aquifer sediment with reducing groundwater.

For the other three As pools, relative proportions as well as absolute concentrations did not differ between the three sand classes ($p > 0.05$).

Considering the composition of the As pools in the aquifer sediments of the transition zone, we concluded that the As immobilisation is controlled by the same processes as PO_4^{3-} , which comprises sorption and the subsequent incorporation into secondary Fe(III)-(oxyhydr)oxides. In contrast to PO_4^{3-} , a change in the redox state has only minor effects on the sedimentary As pools, but increases the proportion of exchangeable As.

4.3 Interactions between PO_4^{3-} and As

Competitive sorption of As and PO_4^{3-} : Compared to P_{tot} , the As_{tot} concentrations were lower in the aquifer sediments, resulting in total P/As molar ratios of 1 to 85 (median: 23, Fig. 5a). To characterise the competitive sorption between PO_4^{3-} and As at the redox transition zone, we first looked at P/As molar ratios in the different pools of the orange aquifer sand. Although a considerable proportion of As was exchangeable and strongly sorbed, a preferential sorption of PO_4^{3-} resulted in mean P/As ratios of >100 in both pools of the orange aquifer sand (median values: 121 and 101, respectively, Fig. 5b,c). These ratios are about one order of magnitude higher than that of the migrating groundwater, where the P/As molar ratio ranges between 3 to 16 [18, 32]. This preferential sorption of PO_4^{3-} has important consequences regarding the mobility of dissolved As. Currently, a plume of dissolved As migrates into the Pleistocene aquifer sediments at the redox transition zone at Van Phuc. Van Geen et al. [31] estimated that there is a 16 to 20-fold retardation for dissolved As relative to the average lateral groundwater advection (some 40 m per year). Possible reasons include changes in the mineralogy of the aquifer sediments (altering their sorption properties) in combination with competitive sorption with PO_4^{3-} . Competition of PO_4^{3-} and As for sorption sites was observed by Rathi et al. [3] in laboratory sorption experiments using orange-coloured aquifer sediment from Van Phuc. Competitive sorption has also been investigated in other laboratory sorption experiments using synthetic metal-oxides or natural aquifer sediments [60, 70], and in surface complexation models [1, 2, 4], but the present study represents, to the best of our knowledge, the first detailed verification in a natural aquifer system.

Similar to PO_4^{3-} , the most of As was structurally bound in Fe(III)-(oxyhydr)oxides. For this fraction, the P/As ratio in the orange aquifer sand was clearly lower than the ratios measured in the two surface sorbed pools (median value of 84), indicating that the effect of competition for sorption sites decreases when As and PO_4^{3-} become structurally bound in Fe(III)-(oxyhydr)oxides. The important role of Fe(III)-(oxyhydr)oxides raises a further question regarding how changing redox conditions influence the competitive sorption and therefore immobilisation of As and PO_4^{3-} , which is discussed in the following section.

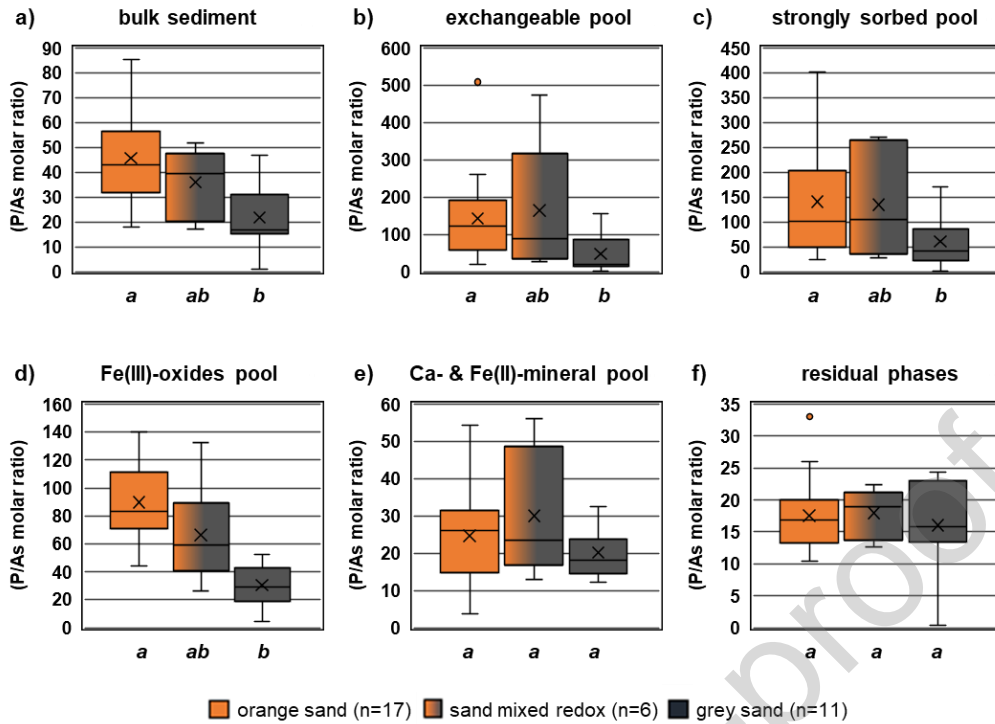


Fig. 5. Boxplots illustrating the P_{tot}/As_{tot} molar ratios in the sediment samples (a) as well as in the five sequential extraction pools (b-f) of the three aquifer sand classes. Different lower-case letters (i.e. a, b) below the bars indicate significant differences between the respective aquifer sand classes (pair-wise post-hoc test, $p < 0.05$).

Influence of redox conditions on P/As ratios: To assess the impact of the redox conditions on competitive sorption of PO_4^{3-} and As, we compared their ratios in the pools from the orange and grey aquifer sand and found that the mean total P/As ratio in the grey aquifer sand was less than half of the orange sand (17 versus 43, $p < 0.01$, Fig. 5a). This difference was also visible in the exchangeable, strongly sorbed, and Fe(III)-(oxyhydr)oxide structurally bound pools ($p < 0.05$, Fig. 5b-d). Furthermore, P/As ratios in these three pools of the grey sand (median of 18 to 42) were closer to the ratio in migrating groundwater (3 to 16) as compared to respective ratios of the orange sand (median of 84 to 121). Thus, competitive sorption of PO_4^{3-} and As largely depends on the presence of Fe(III)-(oxyhydr)oxides and becomes significantly less pronounced with their partial reductive dissolution and the associated loss of sorption sites.

Similar to the P pools, P/As ratios in the mixed redox state sand fell between the orange and grey sand values, representing a transition between these two endmembers (Fig. 5b-f).

About one third of the total extractable As was related to the remaining two pools (HCl-extractable and residual), where the median P/As ratios did not differ by the redox state of the aquifer sands ($p > 0.05$, Fig. 5e,f). We consider the comparatively low P/As ratios (median values of 16 to 18) in these mineral pools to represent the general background P/As ratio in the sediments, because both pools are stable considering the prevailing conditions (i.e. not susceptible to changes in redox conditions) [59].

In summary, the preferential sorption of PO_4^{3-} over As at the redox transition zone was clearly reflected in the surface sorbed pools, which showed considerably wider P/As ratios than found in migrating groundwater. These results support hydrogeochemical models, which assumed a strong competition between PO_4^{3-} and dissolved inorganic As in form of AsO_3^{3-} and AsO_4^{3-} [1, 2]. Our results further reveal that the competition for sorption sites largely depends on the presence of Fe(III)-(oxyhydr)oxides, and becomes less pronounced with their dissolution and the associated loss of sorption sites. Considering the importance of competitive sorption between PO_4^{3-} and As and the associated influence of redox changes, these processes should be considered in reactive transport models that aim to predict the movement of As in aquifers.

5. Conclusions

The observed differences in the P and As pools at the redox transition zone reflected a cascade of biogeochemical processes resulting from the ongoing contact of the aquifer sediments with reducing groundwater, which contains elevated concentrations of dissolved PO_4^{3-} , inorganic As (mainly AsO_3^{3-}), and Fe^{2+} . We suggest the following conceptual model to summarise these processes:

- (i) Initial contact phase: Dissolved As is first immobilised along with PO_4^{3-} by sorption and becomes subsequently incorporated into secondary precipitates dominated by weakly ordered Fe(III)-(oxyhydr)oxides despite the anoxic conditions. The first step comprises weak (i.e. exchangeable) and strong sorption to surfaces of Fe(III)-(oxyhydr)oxides. This further results in competition between PO_4^{3-} and As for sorption sites, which increases the P/As molar ratios in the sorbed pools by one order of magnitude compared to migrating groundwater.
- (ii) Redox transformation phase: Over time, prolonged contact with the anoxic groundwater results in the partial reductive dissolution of weakly ordered Fe(III)-(oxyhydr)oxides. As a consequence, the PO_4^{3-} immobilisation potential of the aquifer sands decreases and more than half of the previously

immobilised PO_4^{3-} is liberated. At the same time, the proportion of exchangeable As increases, generating a pool of As that is easily (re-)mobilisable. Furthermore, the competition between PO_4^{3-} and As becomes less pronounced with the progressive loss of Fe(III)-(oxyhydr)oxides.

- (iii) Reduced state: After aquifer sediments have reached a strongly reduced redox state over the years, the immobilisation capacity for PO_4^{3-} and As is largely depleted and groundwater with increased PO_4^{3-} and As concentrations further advances in flow direction. Here, the competitive sorption results in an increasing spatial separation of the dissolved PO_4^{3-} and As plumes.

Our study confirmed the decisive influence of PO_4^{3-} on the immobilisation of As for a natural aquifer system, which was previously only described in sorption experiments and predicted by numerical models. We further found that the immobilisation of PO_4^{3-} and As at a redox transition zone was not only governed by sorption but was also closely linked to subsequent incorporation into Fe(III)-oxyhydroxides. The fixation of PO_4^{3-} and As via the occlusion in Fe(III)-(oxyhydr)oxide precipitates appears to be a highly effective immobilisation mechanism in oxic or mildly reducing aquifers. The underlying biogeochemical processes could also be useful when considering remediation of contaminated aquifers, where *in situ* remediation approaches should focus on the Fe-cycle. Remediation measures and reactive transport modelling predictions should consider the competition between PO_4^{3-} and As for sorption sites, because this has a pronounced effect on the mobility of toxic As.

Competing interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to thank the German Research Foundation (DFG) and Swiss National Science Foundation (SNF) funded D-A-CH project "AdvectAs" for support of the drilling campaign (DFG grant number 320059499, SNF grant number 167821). The authors thank all AdvectAs project members for their collaboration and support. Special thanks to Reto Britt, Vi Mai Lan, Nguyen Van Thanh, Lang The Anh, Tran T. Mai, and Dao Viet Nga for assistance during the field campaign. We further thank

the villagers of Van Phuc for their support, as well as Caroline Stengel, Sabine Flaiz, Rita Mögenburg, Christiane Nagel, Wen Shao, Li Yao, and Annelie Papsdorf for their analytical support.

Author contributions statement

Harald Neidhardt: Conceptualization, Visualization, Methodology, Writing- Original draft, Writing- Reviewing and Editing, Supervision. **Sebastian Rudischer:** Formal analysis, Investigation, Writing- Original draft. **Elisabeth Eiche:** Writing- Reviewing and Editing, Funding acquisition. **Magnus Schneider:** Investigation. **Emiliano Stopelli:** Writing- Reviewing and Editing. **Vu T. Duyen:** Investigation. **P.T.K. Trang:** Project administration. **Pham H. Viet:** Project administration, Funding acquisition. **Thomas Neumann:** Writing- Reviewing and Editing, Project administration, Funding acquisition. **Michael Berg:** Resources, Writing- Reviewing and Editing, Project administration, Funding acquisition.

References

- [1] A. Biswas, J.P. Gustafsson, H. Neidhardt, D. Halder, A.K. Kundu, D. Chatterjee, Z. Berner, P. Bhattacharya, Role of competing ions in the mobilization of arsenic in groundwater of Bengal Basin: Insight from surface complexation modeling, *Water Res.*, 55 (2014) 30-39.
- [2] M. von Brömssen, S. Häller Larsson, P. Bhattacharya, M.A. Hasan, K.M. Ahmed, M. Jakariya, M.A. Sikder, O. Sracek, A. Bivén, B. Doušová, C. Patriarca, R. Thunvik, G. Jacks, Geochemical characterisation of shallow aquifer sediments of Matlab Upazila, Southeastern Bangladesh — Implications for targeting low-As aquifers, *J. Contam. Hydrol.*, 99 (2008) 137-149.
- [3] B. Rathi, H. Neidhardt, M. Berg, A. Siade, H. Prommer, Processes governing arsenic retardation on Pleistocene sediments: Adsorption experiments and model-based analysis, *Water Resour. Res.*, 53 (2017) 4344-4360.
- [4] K.G. Stollenwerk, G.N. Breit, A.H. Welch, J.C. Yount, J.W. Whitney, A.L. Foster, M.N. Uddin, R.K. Majumder, N. Ahmed, Arsenic attenuation by oxidized aquifer sediments in Bangladesh, *Sci. Total Environ.*, 379 (2007) 133-150.
- [5] H. Neidhardt, D. Schoeckle, A. Schleinitz, E. Eiche, Z. Berner, P.T.K. Tram, V.M. Lan, P.H. Viet, A. Biswas, S. Majumder, D. Chatterjee, Y. Oelmann, M. Berg, Biogeochemical phosphorus cycling in groundwater ecosystems – Insights from South and Southeast Asian floodplain and delta aquifers, *Sci. Total Environ.*, 644 (2018) 1357-1370.
- [6] J. Podgorski, M. Berg, Global threat of arsenic in groundwater, *Science*, 368 (2020) 845-850.

- [7] E.C. Gillispie, T.D. Sowers, O.W. Duckworth, M.L. Polizzotto, Soil pollution due to irrigation with arsenic-contaminated groundwater: Current state of science, *Current Pollution Reports*, 1 (2015) 1-12.
- [8] D. Polya, L. Charlet, Environmental science: Rising arsenic risk?, *Nature Geosci*, 2 (2009) 383-384.
- [9] BGS, DPHE, Arsenic contamination of groundwater in Bangladesh. Vol. 2: Final report. BGS Technical report WC/00/19, Vol. 2., in, 2001.
- [10] J. Lewandowski, G. Nützmann, Nutrient retention and release in a floodplain's aquifer and in the hyporheic zone of a lowland river, *Ecol. Eng.*, 36 (2010) 1156-1166.
- [11] R. Nickson, J. McArthur, W. Burgess, K.M. Ahmed, P. Ravenscroft, M. Rahmann, Arsenic poisoning of Bangladesh groundwater, *Nature*, 395 (1998) 338-338.
- [12] I. Wallis, H. Prommer, M. Berg, A.J. Siade, J. Sun, R. Kipfer, The river-groundwater interface as a hotspot for arsenic release, *Nature Geoscience*, 13 (2020) 288-295.
- [13] L.H.E. Winkel, P.T.K. Trang, V.M. Lan, C. Stengel, M. Amini, N.T. Ha, P.H. Viet, M. Berg, Arsenic pollution of groundwater in Vietnam exacerbated by deep aquifer exploitation for more than a century, *PNAS*, 108 (2011) 1246-1251.
- [14] M.O. Stahl, Groundwater pumping is a significant unrecognized contributor to global anthropogenic element cycles, *Groundwater*, 57 (2019) 455-464.
- [15] H. Neidhardt, S. Norra, X. Tang, H. Guo, D. Stüben, Impact of irrigation with high arsenic burdened groundwater on the soil-plant system: Results from a case study in the Inner Mongolia, China, *Environ. Pollut.*, 163 (2012) 8-13.
- [16] S. Siebert, J. Burke, J.-M. Faures, K. Frenken, J. Hoogeveen, P. Döll, F.T. Portmann, Groundwater use for irrigation—a global inventory, *Hydrol. Earth Syst. Sc.*, 14 (2010) 1863-1880.
- [17] H.A. Michael, M.R. Khan, Impacts of physical and chemical aquifer heterogeneity on basin-scale solute transport: Vulnerability of deep groundwater to arsenic contamination in Bangladesh, *Adv. Water Resour.*, 98 (2016) 147-158.
- [18] E. Stopelli, V.T. Duyen, T.T. Mai, P.T.K. Trang, P.H. Viet, A. Lightfoot, R. Kipfer, M. Schneider, E. Eiche, A. Kontny, T. Neumann, M. Glodowska, M. Patzner, A. Kappler, S. Kleindienst, B. Rath, O. Cirpka, B. Bostick, H. Prommer, L.H.E. Winkel, M. Berg, Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: Interplay of mobilisation and retardation processes, *Sci. Total Environ.*, 717 (2020) 137143.
- [19] W. Robertson, S. Schiff, C. Ptacek, Review of phosphate mobility and persistence in 10 septic system plumes, *Groundwater*, 36 (1998) 1000-1010.
- [20] D.L. Parkhurst, K.G. Stollenwerk, J.A. Colman, Reactive-Transport Simulation of Phosphorus in the Sewage Plume at the Massachusetts Military Reservation, Cape Cod, Massachusetts, in, USGS, 2003.
- [21] D. Postma, T.K.T. Pham, H.U. Sørensen, M.L. Vi, T.T. Nguyen, F. Larsen, H.V. Pham, R. Jakobsen, A model for the evolution in water chemistry of an arsenic contaminated aquifer over the last 6000 years, Red River floodplain, Vietnam, *Geochim. Cosmochim. Acta*, 195 (2016) 277-292.
- [22] J. Lewandowski, K. Meinikmann, G. Nützmann, D.O. Rosenberry, Groundwater – the disregarded component in lake water and nutrient budgets. Part 2: effects of groundwater on nutrients, *Hydrol. Process.*, 29 (2015) 2922-2955.
- [23] J. Kazmierczak, D. Postma, S. Müller, S. Jessen, B. Nilsson, J. Czekaj, P. Engesgaard, Groundwater-controlled phosphorus release and transport from sandy aquifer into lake, *Limnol. Oceanogr.*, 9999 (2020) 1-17.

- [24] T.D. McCobb, D.R. LeBlanc, A.J. Massey, Monitoring the removal of phosphate from ground water discharging through a Pond-Bottom permeable reactive barrier, *Groundwater Monitoring & Remediation*, 29 (2009) 43-55.
- [25] W.D. Robertson, Irreversible Phosphorus Sorption in Septic System Plumes?, *Groundwater*, 46 (2008) 51-60.
- [26] C. Spiteri, C.P. Slomp, P. Regnier, C. Meile, P. Van Cappellen, Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems, *J. Contam. Hydrol.*, 92 (2007) 87-108.
- [27] K.G. Stollenwerk, Simulation of phosphate transport in sewage-contaminated groundwater, Cape Cod, Massachusetts, *Appl. Geochem.*, 11 (1996) 317-324.
- [28] M. Rothe, A. Kleeberg, M. Hupfer, The occurrence, identification and environmental relevance of vivianite in waterlogged soils and aquatic sediments, *Earth-Sci. Rev.*, 158 (2016) 51-64.
- [29] J. Harman, W.D. Robertson, J.A. Cherry, L. Zanini, Impacts on a Sand Aquifer from an Old Septic System: Nitrate and Phosphate, *Ground Water*, 34 (1996) 1105-1114.
- [30] M. Berg, C. Stengel, P. Trang, P. Hungviet, M. Sampson, M. Leng, S. Samreth, D. Fredericks, Magnitude of arsenic pollution in the Mekong and Red River Deltas — Cambodia and Vietnam, *Sci. Total Environ.*, 372 (2007) 413-425.
- [31] A. van Geen, B.C. Bostick, P. Thi Kim Trang, V.M. Lan, N.-N. Mai, P.D. Manh, P.H. Viet, K. Radloff, Z. Aziz, J.L. Mey, M.O. Stahl, C.F. Harvey, P. Oates, B. Weinman, C. Stengel, F. Frei, R. Kipfer, M. Berg, Retardation of arsenic transport through a Pleistocene aquifer, *Nature*, 501 (2013) 204-207.
- [32] H. Neidhardt, L.H.E. Winkel, R. Kaegi, C. Stengel, P.T.K. Trang, V.M. Lan, P.H. Viet, M. Berg, Insights into arsenic retention dynamics of Pleistocene aquifer sediments by in situ sorption experiments, *Water Res.*, 129 (2018) 123-132.
- [33] E. Eiche, M. Berg, S.-M. Hönig, T. Neumann, V.M. Lan, T.K.T. Pham, H.V. Pham, Origin and availability of organic matter leading to arsenic mobilisation in aquifers of the Red River Delta, Vietnam, *Appl. Geochem.*, 77 (2017) 184-193.
- [34] E. Eiche, T. Neumann, M. Berg, B. Weinman, A. van Geen, S. Norra, Z. Berner, P.T.K. Trang, P.H. Viet, D. Stüben, Geochemical processes underlying a sharp contrast in groundwater arsenic concentrations in a village on the Red River delta, Vietnam, *Appl. Geochem.*, 23 (2008) 3143-3154.
- [35] M. Glodowska, E. Stopelli, M. Schneider, A. Lightfoot, B. Rath, D. Straub, M. Patzner, V. Duyen, A.T. Members, M. Berg, Role of in Situ Natural Organic Matter in Mobilizing As during Microbial Reduction of FeIII-Mineral-Bearing Aquifer Sediments from Hanoi (Vietnam), *Environ. Sci. Technol.*, (2020).
- [36] M. Berg, P.T.K. Trang, C. Stengel, J. Buschmann, P.H. Viet, N. Van Dan, W. Giger, D. Stüben, Hydrological and sedimentary controls leading to arsenic contamination of groundwater in the Hanoi area, Vietnam: The impact of iron-arsenic ratios, peat, river bank deposits, and excessive groundwater abstraction, *Chem. Geol.*, 249 (2008) 91-112.
- [37] D.S. Baldwin, The phosphorus composition of a diverse series of Australian sediments, *Hydrobiologia*, 335 (1996) 63-73.
- [38] G.S. Toor, S. Hunger, J.D. Peak, J.T. Sims, D.L. Sparks, Advances in the characterization of phosphorus in organic wastes: Environmental and agronomic applications, *Advances in agronomy*, 89 (2006) 1-72.
- [39] A.K. Mensah, B. Marschner, S.M. Shaheen, J. Wang, S.-L. Wang, J. Rinklebe, Arsenic contamination in abandoned and active gold mine spoils in Ghana: Geochemical

fractionation, speciation, and assessment of the potential human health risk, *Environ. Pollut.*, 261 (2020) 114116.

[40] G. Mattingly, Labile phosphate in soils, *Soil Science*, 119 (1975) 369-375.

[41] T. Hiemstra, J. Antelo, R. Rahnemaie, W.H. van Riemsdijk, Nanoparticles in natural systems I: The effective reactive surface area of the natural oxide fraction in field samples, *Geochim. Cosmochim. Acta*, 74 (2010) 41-58.

[42] H. Thiessen, J.O. Moir, Characterization of Available P by Sequential Extraction, in: *Soil Sampling and Methods of Analysis*, Canadian Society of Soil Science, New York, 2008.

[43] R. Psenner, R. Pucsko, M. Sager, Die Fraktionierung organischer und anorganischer Phosphorverbindungen von Sedimenten–Versuch einer Definition ökologisch wichtiger Fraktionen, *J Arch. Hydrobiol. Suppl*, 70 (1984).

[44] J. Shiowatana, R.G. McLaren, N. Chanmekha, A. Samphao, Fractionation of arsenic in soil by a continuous-flow sequential extraction method, *J. Environ. Qual.*, 30 (2001) 1940-1949.

[45] K.C. Ruttenberg, Development of a sequential extraction method for different forms of phosphorous in marine sediments, *Limnology and Oceanography*, 37 (1992) 1460-1482.

[46] M. Hupfer, D. Zak, R. Roßberg, C. Herzog, R. Pöthig, Evaluation of a well-established sequential phosphorus fractionation technique for use in calcite-rich lake sediments: identification and prevention of artifacts due to apatite formation, *Limnol. Oceanogr. Methods*, 7 (2009) 399-410.

[47] D.B. Ivanoff, K.R. Reddy, S. Robinson, Chemical Fractionation of Organic Phosphorus in Selected Histosols, *Soil Science*, 163 (1998) 36-45.

[48] T.W. Walker, F.R. Adams, Studies on Soil oranic Matter: I. Influence of Phosphorus Content of Parent Materials On Accumulations of Carbon, Nitrogen, Sulfur, And Organic Phoshorus in Grassland Soils, *Canterbury Agricultural College*, (1958).

[49] M. Shamsudduha, A. Uddin, J. Saunders, M.-K. Lee, Quaternary stratigraphy, sediment characteristics and geochemistry of arsenic-contaminated alluvial aquifers in the Ganges–Brahmaputra floodplain in central Bangladesh, *J. Contam. Hydrol.*, 99 (2008) 112-136.

[50] D. Postma, S. Jessen, N.T.M. Hue, M.T. Duc, C.B. Koch, P.H. Viet, P.Q. Nhan, F. Larsen, Mobilization of arsenic and iron from Red River floodplain sediments, Vietnam, *Geochim. Cosmochim. Acta*, 74 (2010) 3367-3381.

[51] C.H. Swartz, N.K. Blute, B. Badruzzman, A. Ali, D. Brabander, J. Jay, J. Besancon, S. Islam, H.F. Hemond, C.F. Harvey, Mobility of arsenic in a Bangladesh aquifer: Inferences from geochemical profiles, leaching data, and mineralogical characterization, *Geochim. Cosmochim. Acta*, 68 (2004).

[52] T. Borch, Y. Masue, R.K. Kukkadapu, S. Fendorf, Phosphate imposed limitations on biological reduction and alteration of ferrihydrite, *Environ. Sci. Technol.*, 41 (2007) 166-172.

[53] O. Borggaard, Effects of surface area and mineralogy of iron oxides on their surface charge and anion-adsorption properties, *Clays Clay Miner.*, 31 (1983) 230-232.

[54] M. Schneider, M. Glodowska, E. Stopelli, A. Lightfoot, B. Rath, E. Eiche, A. Kontny, M. Berg, L.H. Winkel, A. Kappler, Iron Mineralogy along Redox Gradients in an Arsenic Contaminated Aquifer in Van Phuc, Vietnam, in: *Goldschmidt Conference 2019*, 2019.

[55] D. Postma, F. Larsen, N.T.M. Hue, M.T. Duc, P.H. Viet, P.Q. Nhan, S. Jessen, Arsenic in groundwater of the Red River floodplain, Vietnam: controlling geochemical processes and reactive transport modeling, *Geochim. Cosmochim. Acta*, 71 (2007) 5054-5071.

[56] T.H. Hoang, S. Bang, K.-W. Kim, M.H. Nguyen, D.M. Dang, Arsenic in groundwater and sediment in the Mekong River delta, Vietnam, *Environ. Pollut.*, 158 (2010) 2648-2658.

- [57] T. Pal, P. Mukherjee, S. Sengupta, A. Bhattacharyya, S. Shome, Arsenic pollution in groundwater of West Bengal, India-an insight into the problem by subsurface sediment analysis, *Gondwana Research*, 5 (2002) 501-512.
- [58] M. Sankar, M. Vega, P. Defoe, M. Kibria, S. Ford, K. Telfeyan, A. Neal, T. Mohajerin, G. Hettiarachchi, S. Barua, Elevated arsenic and manganese in groundwaters of Murshidabad, West Bengal, India, *Sci. Total Environ.*, 488 (2014) 570-579.
- [59] E. Eiche, U. Kramar, M. Berg, Z. Berner, S. Norra, T. Neumann, Geochemical changes in individual sediment grains during sequential arsenic extractions, *Water Res.*, 44 (2010) 5545-5555.
- [60] N.T.H. Mai, D. Postma, P.T.K. Trang, S. Jessen, P.H. Viet, F. Larsen, Adsorption and desorption of arsenic to aquifer sediment on the Red River floodplain at Nam Du, Vietnam, *Geochim. Cosmochim. Acta*, 142 (2014) 587-600.
- [61] A. Biswas, P. Bhattacharya, A. Mukherjee, B. Nath, H. Alexanderson, A.K. Kundu, D. Chatterjee, G. Jacks, Shallow hydrostratigraphy in an arsenic affected region of Bengal Basin: Implication for targeting safe aquifers for drinking water supply, *Sci. Total Environ.*, 485 (2014) 12-22.
- [62] S. Dixit, J.G. Hering, Comparison of Arsenic(V) and Arsenic(III) Sorption onto Iron Oxide Minerals: Implications for Arsenic Mobility, *Environ. Sci. Technol.*, 37 (2003) 4182-4189.
- [63] K.A. Radloff, Y. Zheng, M. Stute, B. Weinman, B. Bostick, I. Mihajlov, M. Bounds, M.M. Rahman, M.R. Huq, K.M. Ahmed, P. Schlosser, A. van Geen, Reversible adsorption and flushing of arsenic in a shallow, Holocene aquifer of Bangladesh, *Appl. Geochem.*, 77 (2017) 142-157.
- [64] H. Neidhardt, Z.A. Berner, D. Freikowski, A. Biswas, S. Majumder, J. Winter, C. Gallert, D. Chatterjee, S. Norra, Organic carbon induced mobilization of iron and manganese in a West Bengal aquifer and the muted response of groundwater arsenic concentrations, *Chem. Geol.*, 367 (2014) 51-62.
- [65] H. Neidhardt, Z. Berner, D. Freikowski, A. Biswas, J. Winter, D. Chatterjee, S. Norra, Influences of groundwater extraction on the distribution of dissolved As in shallow aquifers of West Bengal, India, *J. Hazard. Mater.*, 262 (2013) 941-950.
- [66] G. Du Laing, S. Chapagain, M. Dewispelaere, E. Meers, F. Kazama, F. Tack, J. Rinklebe, M. Verloo, Presence and mobility of arsenic in estuarine wetland soils of the Scheldt estuary (Belgium), *J. Environ. Monit.*, 11 (2009) 873-881.
- [67] E. Stopelli, V.T. Duyen, T.T. Mai, P.T. Trang, P.H. Viet, A. Lightfoot, R. Kipfer, M. Schneider, E. Eiche, A. Kontny, Spatial and temporal evolution of groundwater arsenic contamination in the Red River delta, Vietnam: Interplay of mobilisation and retardation processes, *Sci. Total Environ.*, (2020) 137143.
- [68] J.J. LeMonte, J.W. Stuckey, J.Z. Sanchez, R. Tappero, J.r. Rinklebe, D.L. Sparks, Sea level rise induced arsenic release from historically contaminated coastal soils, *Environ. Sci. Technol.*, 51 (2017) 5913-5922.
- [69] T. Frohne, J. Rinklebe, R.A. Diaz-Bone, G. Du Laing, Controlled variation of redox conditions in a floodplain soil: impact on metal mobilization and biomethylation of arsenic and antimony, *Geoderma*, 160 (2011) 414-424.
- [70] C. Tiberg, C. Sjöstedt, A.K. Eriksson, W. Klysubun, J.P. Gustafsson, Phosphate competition with arsenate on poorly crystalline iron and aluminum (hydr) oxide mixtures, *Chemosphere*, (2020) 126937.

Author contributions statement

Harald Neidhardt: Conceptualization, Visualization, Methodology, Writing- Original draft, Writing- Reviewing and Editing, Supervision. **Sebastian Rudischer:** Formal analysis, Investigation, Writing- Original draft. **Elisabeth Eiche:** Writing- Reviewing and Editing, Funding acquisition. **Magnus Schneider:** Investigation. **Emiliano Stopelli:** Writing- Reviewing and Editing. **Vu T. Duyen:** Investigation. **P.T.K. Trang:** Project administration. **Pham H. Viet:** Project administration, Funding acquisition. **Thomas Neumann:** Writing- Reviewing and Editing, Project administration, Funding acquisition. **Michael Berg:** Resources, Writing- Reviewing and Editing, Project administration, Funding acquisition.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

--

Highlights

- PO_4^{3-} and As retention in aquifer sediments controlled by redox properties
- competition between PO_4^{3-} and As for sorption sites reflected in P/As ratios
- PO_4^{3-} and As retention by sorption and subsequent incorporation in Fe-oxides
- changing sedimentary P and As pools due to influence of Fe-reducing groundwater
- Fe-reduction lowers sorption sites and competitive sorption of PO_4^{3-} and As