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**Rates of hydroxyapatite formation and dissolution in a sandstone aquifer:
Implications for understanding dynamic phosphate behaviour within an agricultural
catchment**

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Abstract

Eutrophication, caused by excessive nutrient concentrations, is a major environmental issue and has significant impacts on both aquatic ecosystems and human health. Phosphorus (P) is a key element that contributes to this eutrophication response. As such, P concentrations are regulated under both the European Union Water Framework Directive (EU WFD) and Habitats Directive (EU HD). While P export to rivers from point sources is well-understood, diffuse sources, particularly that route through connected aquifer systems are less well-characterised. Based on data from a catchment in southern England where an Upper Greensand aquifer controls river baseflow, we hypothesise that dynamic precipitation and dissolution of phosphorus in the form of hydroxyapatite occurs along the groundwater flow path, affecting P storage and export. In addition, P may also occur as the less-reactive mineral fluorapatite or sorb onto, or substitute into, Fe-oxides, which also occur in the aquifer. To investigate hydroxyapatite kinetics in this context, batch experiments were conducted to precipitate the mineral onto sand grains, and then dissolved in a continuous-flow reactor under various pH and concentration conditions. The reactive transport of PO_4^{3-} along a 1D flow path was modelled to simulate hydroxyapatite precipitation and dissolution. Fe-oxides were modelled as sorbing surfaces for phosphate under chemical conditions representative of the aquifer.

Hydroxyapatite rapidly precipitated onto quartz sand grains from a solution that was supersaturated with respect to hydroxyapatite, thus demonstrating that an input of P to Ca-rich, alkaline porewaters can result in the precipitation of secondary hydroxyapatite. The dissolution rate of hydroxyapatite is strongly pH dependent, however within the aquifer porewaters, the solution is often close to equilibrium with respect to hydroxyapatite, which causes the dissolution rate to have a greater dependence on the PO_4^{3-} concentration. Within the range of measured pH and PO_4^{3-} concentrations, the dissolution rate ranges between $10^{-12.25}$ to $10^{-9.15}$ mol kg⁻¹ s⁻¹, contributing P to the catchment headwaters. Over a 1D flow path, there is dynamic precipitation and dissolution of hydroxyapatite, as well as PO_4^{3-} sorption and desorption, over relatively short timescales. These results indicate that hydroxyapatite is likely to precipitate within the pore space of the aquifer, but can then dissolve and re-precipitate, adsorb and desorb, under expected spatial and temporal variations in pH and water chemistry within the aquifer. Hydroxyapatite may therefore represent temporary pool of anthropogenic P, sourced from P-fertilisers, which represents a previously unrecognised pathway for anthropogenic P transfer between the soil surface and surface waters.

Keywords: Phosphate, apatite, hydroxyapatite, mineral dissolution rates, reactive transport, groundwater, eutrophication

1. Introduction

Globally, eutrophication is the primary problem that aquatic ecosystems face today (Smith & Schindler, 2009), and ultimately lowers water quality and aquatic biodiversity due to the excessive production of autotrophs caused by high phosphorus (P) and/or nitrogen (N) loading (Johnes, 1996; Correll, 1998; Torrent et al. 2007). In addition, the cost of environmental damage and mitigation responses to eutrophication of surface waters is between £75 and 115 million/yr in England and Wales (Pretty et al. 2003), while the environmental damage costs associated with P enrichment of UK waters has recently been

estimated by the UK Department for Environment, Food and Rural Affairs as £33 per kilogram of P exported from land to water, per year (Zhang et al. 2017). Eutrophication of surface waters and groundwaters also has implications for human health, and limits the use of water for drinking, fishing, recreation and industry (Carpenter et al. 1998). The sources of P to rivers can be divided into diffuse (agricultural run-off) and point sources (sewage facilities, from septic tanks and small packet sewage treatment works to large wastewater treatment works, and direct discharges from industry) that discharge a substantial nutrient load to waters of varying character, depending on the nature of the treatment process (Yates et al. 2019) either directly or via leakage (Goody et al. 2017). Some authors have argued that sewage effluent discharge of P to waters are a greater risk to river eutrophication than agricultural P (e.g. Jarvie et al. 2006), though there are many rural catchments where diffuse P loading is clearly shown to be the dominant source of P enrichment in the water body. Since 1991, the EU Urban Waste Water Treatment Directive (UWWTD; Council of the European Union, 1991) has led to an absolute reduction of P export to aquatic systems from all larger point sources serving a population equivalent in excess of 10,000, and for a selection of smaller systems where dilution capacity in the water body is low. In many rivers, this has reduced the relative contribution of point sources to P loading in the river, relative to diffuse loading from agricultural sources in their catchments (Yates & Johnes, 2013; Bowes et al. 2009; Kinniburgh & Barnett, 2010), though there remain systems where further P reduction in point source discharges in combination with a reduction in diffuse source P loading is still required to meet the European Union Water Framework Directive (EU WFD) and Habitats Directive (EU HD) targets. With regard to diffuse source P loading, while surface transfers of P via overland flow and throughflow from land surface to stream are relatively well characterised, the sources of natural and anthropogenic P loading from groundwater to surface water is poorly understood as a component of this flux. Differentiating between this complexity of P sources in catchments is particularly difficult, as the transport of P from source to receptor is likely to involve storage, release and chemical transformation along each of the flow pathways (George et al. 2018; Haygarth et al. 2005;

Johnes and Hodgkinson, 1998; Lloyd et al. 2009). The chemical form of P in transit ultimately affects its mobility and residence time within the receiving aquatic environment, and therefore its impact on the environment (Evans & Johnes, 2004; Noll et al. 2009; George et al. 2018).

Phosphorus in aquatic systems is controlled under the EU WFD for both surface waters (Council of the European Union, 2000) and groundwaters (Council of the European Union, 2006), and also under the EU HD (Council of the European Union, 1992) due to the environmental, ecological and economic implications of eutrophication. The EU WFD states that good ecological status in any water body represents a slight deviation from undisturbed conditions, which is calculated using alkalinity and altitude, as these are considered key geological and geographic features that determine the natural P concentration (Council of the European Union, 2000; UKTAG, 2013; Johnes, 2007). In the same context, the Common Standards Monitoring Guidance (CSMG) for Rivers (JNCC, 2016) use a similar approach to that of UKTAG (2013) for setting natural/background soluble reactive phosphorus (SRP) targets at EU HD designations, especially where precise local characterisation of natural/background concentrations is not available. The principal aim of the EU WFD is to “protect, enhance and restore all surface and groundwaters to promote a good ecological status with respect to the biodiversity within the river” (Tye et al. 2016; DEFRA, 2014), while the EU HD seeks to ensure the conservation of rare, threatened or endemic animal and plant species, including those in designated as Special Areas for Conservation (SAC) under the directive. The EU HD includes both terrestrial and aquatic environments. Under the EU HD, target riverine concentrations for P and other physico-chemical variables are established to define the favourable conditions needed to support ecosystem health within that particular habitat type.

Many rivers drain through landscapes that have a low baseflow index (BFI) and very low contribution of P to the river from groundwater or deep throughflow pathways. However, rivers draining permeable landscapes, those with a significant groundwater aquifer and high BFI, derive a significant portion of their flow through influent and effluent seepage linking the

aquifer to the river (Wheater et al. 2006). This seepage will vary spatially along the river and temporally over the seasons, as well as during extreme high or low flow periods (Headworth, 1972; Keery et al. 2007; Bloomfield, et al. 2009; Shand, et al. 2007). A holistic understanding of P delivery to rivers with a high BFI therefore requires a clear understanding of the nature and origins of P in groundwater, in addition to a conventional assessment of the diffuse agricultural and point source P export to the river along surface and throughflow pathways. Where groundwater flow drains through carbonate-rich rock matrices, such as Carboniferous limestone, Jurassic limestone and Cretaceous chalk, waters will have a high alkalinity. As calcium carbonate is abundant in such systems, P readily co-precipitates out of solution to form hydroxyapatite deposits (House, 1990; 2003). Phosphorus concentrations in such waters are typically lower than might be expected when assessing the rate of net P input from catchment sources (Neal et al. 2002; Prior and Johnes, 2002). A river with a high BFI, which sources a large fraction of its river flow from groundwater, may result in a high natural alkalinity, a low natural P concentration in the river and, in anthropogenically impacted waters, a lower P concentration relative to external P loading rates than would be seen in similarly farmed and populated low alkalinity waters (Tappin et al. 2018). In order to investigate the extent to which these processes control the nature and rates of P delivery to rivers from groundwaters in permeable catchments, the present study is focused on the Hampshire Avon catchment, in southern England, UK.

Little research has been conducted on the kinetics of hydroxyapatite precipitation or dissolution in the natural environment. Wright et al. (2011) demonstrated that the homogeneous precipitation of hydroxyapatite is thermodynamically possible from a synthetic groundwater, and it has been considered to be an important process in rivers and lakes where hydroxyapatite forms on the surface of plants and biofilms due to photosynthetic cycles which generate diurnal fluctuations in pH (Evans & Johnes, 2004; Neal et al. 2002; 2003; House, 1990; 2003). However, in general, the dissolution rates and weathering mechanisms of apatite minerals under the wide range of environmental variation that can occur in soils, groundwaters and rivers are not well known, and most previous work has

focused on fluorapatite, the fluoride endmember of the apatite group, due to its importance in marine phosphorus cycling (Guidry & Mackenzie, 2003; Chaïrat et al. 2007), as well as its high chemical stability and abundance in nature (Filippelli 2008; Tönsuaadu et al. 2012). The use of hydroxyapatite within permeable reactive barriers has led to some studies into its dissolution rate, but these are largely focused on ground particles of synthetic hydroxyapatite to remediate acid mine drainage (e.g. Oliva et al. 2012).

Here we present an investigation of the kinetics of hydroxyapatite precipitation and dissolution and phosphate sorption, in the context of the Upper Greensand (UGS) aquifer underlying the Hampshire Avon catchment, using a combined experimental and modelling approach. We hypothesise that hydroxyapatite can both precipitate onto quartz sand and dissolve out of a sand matrix under UGS-relevant conditions, representing temporal and spatial variations in pH and PO_4^{3-} concentration. These parameters were also expected to control the rates of dissolution and precipitation of hydroxyapatite as well as sorption and desorption of PO_4^{3-} to/from UGS mineral surfaces.

2. Site Description

The Hampshire Avon is an agricultural catchment, with approximately 65% of the catchment used for arable and managed grazing (high intensity agriculture), and 22 – 30% used for grazing and woodland (low intensity agriculture; Jarvie et al. 2005; Whitehead et al. 2014). Phosphorus within the Hampshire Avon is of particular concern as the catchment is designated as a Special Area of Conservation (SAC) under the EU HD (Council of the European Union, 1992). Previous studies have identified high P concentrations in the Hampshire Avon, particularly at the headwaters of the Rivers Avon, Nadder and Wylfe, which likely reflects the use of P-fertilisers dating back to 1931 (Yates and Johnes, 2013; Whitehead et al. 2014; Lloyd et al. 2019). Research and catchment management has focused on P fate from agricultural land to surface waters due to overland or near surface quickflow (McGinley et al. 2016), and has used models such as FARMSOPER (Zhang et al. 2012; 2017), INCA (Whitehead et al. 2014) and PSYCHIC (Davison, et al., 2008), to

estimate the diffuse agricultural P load delivered to the river along these pathways. The PSYCHIC model underestimates the flow-weighted mean P concentration in the Hampshire Avon, particularly where the UGS outcrops at the headwaters of the river, perhaps reflecting that these models do not include the groundwater P flux (Strömqvist et al. 2008), which might be sourced from the dissolution of apatite group minerals in the aquifer matrix (Stuart & Lapworth, 2016).

Within the Hampshire Avon catchment, the geology is dominated by the Chalk group, which is underlain by the UGS formation (Allen et al. 2014). While the majority of flow in the Hampshire Avon derives from the chalk aquifer, the UGS provides baseflow to the headwaters of western tributaries such as the River Wylfe, and the northern headwaters of the Hampshire Avon in the Vale of Pewsey: the East Avon and West Avon (Soley et al. 2012; Allen et al. 2014). The UGS is typically a glauconitic and iron (hydr)oxide rich siltstone or sandstone, sometimes micaceous and clay rich, with some laterally continuous P-rich horizons, as well as lateral calcareous horizons of hard limestone or sandstone (Woods et al. 2008). In terms of its hydraulic properties, UGS permeability ranges from high to low depending on the level of cementation of its various horizons, whereas fracture flow can be important in the well cemented and hard horizons (Allen et al. 2014). Several mineral forms of P have been identified in the UGS, including various apatite phases such as hydroxyapatite $[\text{Ca}_5(\text{PO}_4)_3\text{OH}]$, fluorapatite $[\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})]$ and carbonate-fluorapatite/francolite $[\text{Ca}_5(\text{PO}_4)_3(\text{F},\text{OH})]$, as well as REE minerals such as monazite $[\text{LREE},\text{PO}_4]$ and xenotime $[(\text{Y},\text{HREE})\text{PO}_4]$ (data not shown). The cycle of dissolution and reprecipitation of mineral-bound P to porewaters may contribute a background, natural P signature to groundwaters draining to the Hampshire Avon from the aquifer. However, given the long-term agricultural land use of the catchment and the underlying lithology, we hypothesise that hydroxyapatite may have formed in the UGS matrix either through the reprecipitation of P released to the matrix through dissolution of primary minerals, or from fertiliser, septic tank, or manure P sources that have infiltrated from agricultural land and isolated dwellings overlying the UGS. The hydroxyapatite formed *in situ* from these sources

of P, may be considered an anthropogenic mineral source of P when it dissolves, contributing P to the Hampshire Avon via groundwater flow pathways. The methodology to calculate a robust P-threshold to protect river biodiversity under the EU HD, and support good ecological and chemical status for groundwaters under the EU WFD (Council of the European Union, 1992; 2000; 2006) needs to take into account these sources, separating P released through the weathering and dissolution of primary P minerals from that released from secondary, anthropogenically derived P minerals in the rock matrix. Clearly, there is a need to better understand these processes and the ways in which anthropogenic manipulation of the land surface, and flows into and out of the aquifer, impact secondary P mineral formation and dissolution in both the UGS and the neighbouring chalk aquifer if a complete picture is to be developed. This paper focuses on these processes within the UGS aquifer specifically, and in particular on hydroxyapatite formation, dissolution and reprecipitation processes within the aquifer.

3. Methodology

Hydroxyapatite was precipitated onto sand grains in batch experiments and then dissolved in a continuous flow reactor using an input solution pH range from 4 to 7, where the UGS pH varies from 6.5 to 8.4 (Butcher, 2013). The dissolution rate was estimated from the rate of PO_4^{3-} release and modelled using known mineral kinetics parameters. The precipitation and dissolution of hydroxyapatite during transport over a 1D flow path was also modelled. Further details on the methods used in each of these steps are given below.

3.1. Experimental precipitation of hydroxyapatite

The solutions used in the precipitation experiments included a high PO_4^{3-} concentration “simple solution” and a synthetic groundwater to represent the UGS porewaters (Table 1). The simple solution was prepared from H_3PO_4 and salts: $\text{Ca}(\text{OH})_2$ and NaOH . The pH was adjusted to 7.3 using KOH to represent the typical pH of UGS porewaters. To compliment the simple solution experiment, a synthetic groundwater was formulated to represent the

average chemical composition of the UGS groundwater within the Vale of Pewsey, but with PO_4^{3-} concentrations 4 orders of magnitude greater (1.57 mM; Table 2) to induce the precipitation over a shorter timescale and to represent periods of high P-fertiliser application (Agricultural Industries Confederation, 2017; Wolf et al. 2000). Triplicate batch experiments in 250 mL loosely capped beakers were set up with 100 mL of precipitating solution and 1 g of pure quartz, laboratory-grade sand (Fisher Scientific) and were conducted at 21°C over 24 hours and 7 days for the simple solution and the UGS synthetic groundwater, respectively. Batch experiments were conducted in beakers, which were manually agitated for one minute per day to represent flow within the UGS (Allen et al. 2014) and to prevent a concentration gradient developing within the precipitating solution (Brantley et al. 2008). Control experiments included pure sand with de-ionised water, and the precipitating solution without the sand grains, with the precipitate from the latter retained for dissolution experiments. The precipitation experiments were terminated at set intervals (1, 30, 60, 120, 240, 1440 minutes, and 24, 48, 72, 96, 120, 144, 168 hours, for the simple solution and UGS synthetic groundwater solution, respectively, chosen based on the results of preliminary experiments) by decanting the supernatant, which was then acidified to 1 vol% with 1.0 M HNO_3 and stored at 4°C to prevent further precipitation of calcium-phosphate minerals before the measurement of calcium and phosphate (as PO_4^{3-}) concentrations using ion chromatography (Dionex ICS-90 for calcium, Dionex IC25 for phosphate). The solid material (quartz sand and/or precipitate) from each experiment was dried for 24 hours at 30°C.

3.2. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS)

Dried, experimental solid samples were placed on carbon stubs and analysed without coating using a Hitachi S-3500N scanning electron microscope with energy-dispersive X-ray spectroscopy to observe the morphology of the hydroxyapatite precipitate and to determine its chemical composition. Beam voltage was set to 20 kV in a low vacuum mode (>200 Pa).

3.3. Experimental dissolution of hydroxyapatite

Additional hydroxyapatite was precipitated onto pure quartz sand as described above for the simple solution precipitation experiments. This “sand-bound” hydroxyapatite was used for the dissolution experiments to represent the mineral as present within the UGS aquifer matrix, and a pure hydroxyapatite precipitate (non-sand-bound) was used for comparison. Dissolution experiments were conducted using 0.42 g of hydroxyapatite (sand-bound or non-sand-bound) in a continuous flow reactor (Fig. 1; Bruno et al. 1991), which maintained complete mixing between the solid sample and solution and prevented the solution from rapidly reaching equilibrium. A thin layer of sand-bound hydroxyapatite (2 cm) was placed in a 2.5 cm diameter vessel, with 2.7 μm pore size filter paper, and a constant flow rate of 3 mL min^{-1} (Bruno et al. 1991; Ulrich et al. 2008; White & Brantley, 2003). A known PO_4^{3-} concentration and pH input solution was pumped into the reactor, which reacted with the solid sample, and these parameters were monitored in the output solution using ion chromatography (Dionex IC25) and a pH meter. The rate of reaction, r ($\text{mol m}^{-2} \text{s}^{-1}$), was calculated using the flow rate, Q ($\text{m}^3 \text{s}^{-1}$), the inlet and steady-state outlet concentrations, c_i and c_o (M), respectively, and normalised to the reactive surface area of the mineral, A ($\text{m}^2 \text{g}^{-1}$), and the mass of reactant, M (g) (Brantley, 2003):

$$r = \frac{Q(c_o - c_i)}{AM} \quad (1)$$

Dissolution reactions were run until c_o reached a steady-state concentration, which was followed by a decrease in concentration as the mass of reactant decreased.

3.4. Upper Greensand groundwater chemistry

Groundwater samples from boreholes are taken by Wessex Water as part of its statutory undertaking and are analysed at Saltford Scientific Centre accredited under ISO17027:2017 and prior to 2017 ISO17027:2014. Water quality concentration data from boreholes in the Vale of Pewsey Wilshire, taken between 2010 and 2018 were provided by Wessex Water for calcium, pH and orthophosphate. Calcium and pH were analysed using Standing Committee

of Analysts (SCA) methodologies (1977 and 1978, respectively). Orthophosphate was analysed using a Wessex Water in-house method based on spectrophotometry where orthophosphate ions react with a solution containing molybdic acid, ascorbic acid and antimony (II) ions in the presence of acid, to form a 12-molybdophosphoric acid. This is reduced in situ to a blue heteropoly compound (phosphomolybdenum blue) in which antimony is incorporated. The absorbance of the compound is measured spectrophotometrically at 880 nm and related to the orthophosphate concentration in the sample by means of a calibration curve.

3.5. Geochemical modelling

3.5.1. Mineral kinetics

The Geochemist's Workbench® Professional v.12 (GWB12; Bethke et al. 2018) with the Thermo database (Daveler & Wolery, 1992) was used to calculate the thermodynamic favourability of hydroxyapatite dissolution or precipitation under different scenarios and to determine the rate at which these processes could occur. Here, the forward reaction represents the dissolution of hydroxyapatite, and the backward reaction represents its precipitation:

The saturation index, Ω (dimensionless), with respect to a mineral, was calculated as:

$$\Omega = \text{IAP}/K_{\text{sp}} \quad (3)$$

Where IAP is the ion activity product (M), calculated from solution composition (Ca , PO_4^{3-} , and OH^-), and K_{sp} (M) is the solubility product of the mineral. The saturation index is proportional to the rate of reaction, R ($\text{mol m}^{-2} \text{g}^{-1}$) (Lasaga, 1998), according to:

$$R = A m k (1 - \Omega)^n \quad (4)$$

where A is the initial reactive surface area ($\text{m}^2 \text{g}^{-1}$), m is the mineral mass (g), k is the rate constant ($\text{mol m}^{-2} \text{s}^{-1}$) and n is the reaction order. The initial reactive surface area, $A = 0.16$

$\text{m}^2 \text{g}^{-1}$ was estimated using the relationship between the geometric surface area and the BET surface area (White & Brantley, 2003):

$$A = \frac{6\lambda}{\rho D} \quad (5)$$

assuming that particles are spherical, where λ is the surface roughness (1.7 for unweathered hydroxyapatite; López et al. 2013), ρ is the mineral density (3.16 g cm^{-3}), and D is the average grain diameter ($20 \mu\text{m}$, determined from SEM images). Using Equations 4 and 5, the dissolution/precipitation rate was modelled using a range of input parameters (Ca , PO_4^{3-} , OH^-) to examine the controls on the hydroxyapatite reaction rates.

3.5.2. Sorption/desorption modelling

Iron(III)-(hydr)oxides, which are present in the UGS, are well known sorbents of phosphate, often accounting for a substantial fraction of the total or available phosphate in soils and sediments (e.g. Zhang et al. 2001). In addition to Fe(III)-(hydr)oxides, the UGS is also abundant in glauconite (Woods et al. 2008), and phosphate may also adsorb to this phase. However, we were unable to find sorption data for PO_4^{3-} onto glauconite in the literature and therefore model sorption of PO_4^{3-} in the UGS with respect to Fe(III)-(hydr)oxides only (simplified here as Fe-oxides), recognising that sorption onto glauconite may also occur. The mineral abundance, surface properties, surface reactions and their associated equilibrium constants for Fe-oxide are summarised in Table 2 (Dzombak & Morel, 1990). These parameters were input to GWB12 and used to model the effect of pH, phosphate concentration and Fe-oxide abundance on PO_4^{3-} sorption and desorption.

3.5.3. One-dimensional reactive transport modelling

One-dimensional reactive transport models of porewater PO_4^{3-} concentration along a 1D flow path were constructed using GWB12, combining the mass transport of solutes within a porous medium with the kinetics of hydroxyapatite precipitation and dissolution, and phosphate sorption. Mass transport within saturated groundwater flow is defined using the

groundwater advection, diffusion and hydrodynamic dispersion equation. These fundamental mass transport equations (Bethke et al. 2018; Brantley et al. 2008) are therefore combined with the mineral kinetic equations and sorption kinetics introduced above, to model dynamic PO_4^{3-} behaviour over a 1D flow path. The modelled domain had a 1.0 wt% abundance of hydroxyapatite, 1.0 wt% Fe-oxide throughout a 5 m profile, which had a 30% porosity and a groundwater velocity of 200 m yr^{-1} , which represents flow within the UGS (Allen et al. 2014). The initial calcium and phosphate concentrations, and pH were close to saturation with respect to hydroxyapatite, and input solutions to the model were either saturated or undersaturated (Table 3), to encourage precipitation or dissolution at the surface. Reactive transport was modelled for 100 days over 25 time steps.

4. Results

4.1.1. Experimental precipitation of hydroxyapatite onto sand

The concentrations of Ca^{2+} and PO_4^{3-} in the simple solution decreased rapidly over 24 hours (Fig. 2a-c) and the solution became semi-opaque. In the synthetic groundwater experiment, the concentrations of Ca^{2+} and PO_4^{3-} initially decreased as did pH over ~4 days, after which Ca^{2+} increased over ~24 hours and PO_4^{3-} and pH increased over ~48 hours before a steady-state was achieved (Fig. 2d-f). The simple solution produced a greater mass of precipitate than the synthetic groundwater, which had a lower saturation index ($\Omega = 5.6$) than the simple solution ($\Omega = 11$).

4.1.2. SEM/EDS

Backscattered Electron (BSE) SEM images of the solid phase material collected from the simple solution and synthetic groundwater precipitation experiments reveal a fine-grained precipitate with a microcrystalline and spherical morphology on the quartz sand grains (Figs. 3a,c). The precipitate covers a larger proportion of the sand grains from the simple solution compared to the synthetic groundwater solution. The microcrystalline and spherical morphology is consistent with hydroxyapatite precipitates (Joseph et al. 2002; Wright et al.

2011). The EDS analysis of the precipitate from both experiments indicated a Ca-P phase with the stoichiometry of apatite, identified as hydroxyapatite based on the morphology and lack of F or Cl (Figs. 3b,d; Deer et al. 2013).

4.2. Dissolution of sand-bound hydroxyapatite

4.2.1. Experimental dissolution of hydroxyapatite

Dissolution of sand-bound hydroxyapatite occurred in two steps, starting with a rapid increase in pH and PO_4^{3-} concentration in the output solution from the continuous flow-through reactor in the first 1 – 10 minutes of reaction (Fig. 5). After this initial peak in concentration, PO_4^{3-} then decreased until about $t = 50$ minutes, after which the PO_4^{3-} concentration again increased until steady-state was achieved. At steady-state, a gradual decrease in PO_4^{3-} concentration is observed in the output solution as the abundance of hydroxyapatite decreases. The two-step dissolution of hydroxyapatite was only observed when using sand-bound hydroxyapatite in the continuous flow reactor. The dissolution of hydroxyapatite crystals without the presence of sand, resulted in the outlet PO_4^{3-} concentration increasing until steady state was achieved (Fig. 6b). The time until steady-state was achieved, and the concentration at steady-state, varied with the pH of the input solution, where a lower pH resulted in a shorter time to steady-state and a higher steady-state PO_4^{3-} concentration. However, the relationship between pH and the dissolution rate of hydroxyapatite is not linear, as the pH dependence on the dissolution rate is considerably greater at $\text{pH} < 6$, compared to $\text{pH} > 6$ (Fig. 5). This relationship is consistent with fluorapatite dissolution kinetics, which similarly exhibit a log-linear relationship between dissolution rate and solution pH (at approx. pH 4 - 5.5; Chaïrat et al. 2007).

4.2.2. Modelled dissolution of hydroxyapatite

The modelled dissolution of hydroxyapatite revealed an increase in phosphate concentration, until steady-state was reached, followed by a decline in concentration due to the transport of solutes in the models. These models do not simulate the two-step dissolution

process, but they do accurately model the steady-state concentration (Fig. 4 & 5). Curve fitting between the model and experimental data was used to determine the rate constant (Bandstra & Brantley, 2008), which was used to calculate the dissolution rate (Eq. 3). The estimated rate constant is $2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, and is slightly lower than the average rate constant for fluorapatite dissolution of $7.22 \times 10^{-7} (\pm 3.57 \times 10^{-7}) \text{ mol m}^{-2} \text{ s}^{-1}$ (Brantley et al. 2008), however the solubility product of hydroxyapatite is greater than that of fluorapatite ($10^{-11.5} \text{ mol m}^{-2} \text{ s}^{-1}$ and $10^{-33.4} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively; Bethke et al. 2018; Wolery, 1992). The fit between the measured dissolution rate and the predicted rate (from the model; $k = 2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $A = 0.16 \text{ m}^2 \text{ g}^{-1}$) between pH 4 and 7 represents a good fit (Fig. 7; $r^2 = 0.957$, $n = 21$).

Changing the phosphate concentration in the modelled input solution results in a log-linear relationship between phosphate concentration and rate when the solution is far from equilibrium (i.e. $< 1 \times 10^{-10} \text{ mol PO}_4^{3-} \text{ L}^{-1}$). When the solution is close to equilibrium ($> 1 \times 10^{-8} \text{ mol PO}_4^{3-} \text{ L}^{-1}$), a change in phosphate concentration has a significant effect on the modelled dissolution rate, where a small increase in concentration can result in a decrease in rate by 2 to 2.5 orders of magnitude (Fig. 8). The model results represent a large range in hydroxyapatite dissolution rates across the range of UGS porewater conditions, typically between 1×10^{-8} and $4 \times 10^{-5} \text{ M}$ of PO_4^{3-} and a pH range of 6.5 - 8 (Butcher, 2013).

4.3. Modelling of phosphate sorption

Using a relatively high concentration of phosphate ($4 \times 10^{-5} \text{ M}$), and a range in abundance of adsorbing surfaces (Fe-oxide; 0.1 – 5 wt%), the sorption of phosphate is greatest at pH 5 (Fig. 9). This trend is comparable to other clay and Fe-oxide minerals that have been studied (Bai et al. 2017). An increase in the wt% of adsorbing surfaces also resulted in an increase in the sorption of phosphate. Within the UGS, the solution pH ranges from 6.1 to 7.8, which is typically where the modelling results show the most significant change in phosphate sorption. Within this pH range, the solution is likely to be close to equilibrium with respect to hydroxyapatite, and some solutions within this range will be able to dissolve

hydroxyapatite, and others would be able to precipitate hydroxyapatite (note equilibrium line on Fig. 9).

4.4. 1D Reactive Transport Models

The reactive transport of PO_4^{3-} along a 1D flow path was modelled using three input solutions, summarised in Table 3, to cover the likely range of input solutions to the UGS. In the first scenario, over 20 and 60 day model runs, hydroxyapatite dissolved in the upper 1 to 4 m of the vertical profile, and precipitates below (Fig. 11a). There is also an increase in the sorption of phosphate to mineral surfaces in the upper 0.5m of the profile over the model run (Fig. 11b & d). Below approximately 0.5 m depth, phosphate desorbs from mineral surfaces (Fig. 11b), but with less desorption after 20 days, particularly at depth (> 2 m). Over a longer timescale of 100 days, dissolution occurs at both the surface of the profile (0.1 m), and at depth (4.9 m). The sorption of phosphate continues at the surface until almost 100% of porewater phosphate is adsorbed, and at depth, there continues to be desorption.

In the second scenario, the modelled input solution has a positive saturation index with respect to hydroxyapatite, resulting in precipitation of hydroxyapatite near the top of the profile, and dissolution at depth over the first 40 days of reactive transport. After 40 days, however, the entire 5 m profile precipitates hydroxyapatite (Fig. 12a). In addition, when the input solution is applied, there is rapid desorption of phosphate from Fe-oxide surfaces from the whole profile (Fig. 12d).

In the third modelled scenario, after 20 days, hydroxyapatite abundance (wt%) of the profile is unchanged, but decreases below 0.1 m depth. After 60 days, there is precipitation of hydroxyapatite at the top 1.5 m of the profile, with dissolution below (Fig. 13a). Over longer timescales, there is continued precipitation at the profile surface and dissolution at depth, but between 40 and 100 days there is precipitation throughout the profile (Fig. 13c). Again, there is rapid desorption of phosphate from mineral surfaces after the input solution is applied (Fig. 13b and d).

4.5 Spatial and temporal variability in hydroxyapatite behaviour across the catchment

The saturation index, with respect to hydroxyapatite, varies spatially and temporally in groundwater wells across the catchment, with the majority of sample points reflecting the chemical conditions that would favour the dissolution of hydroxyapatite (Fig. 10). The saturation indices also vary over time in these wells, reflecting temporally variable P behaviour. In some wells, the groundwater switches between undersaturated and supersaturated with respect to hydroxyapatite at different times of the year.

5. Discussion

5.1. Hydroxyapatite precipitation: Implications for the Upper Greensand aquifer

Hydroxyapatite precipitated within seconds from a solution that was saturated with respect to the mineral (Fig. 2a-c). When the solution is substantially supersaturated (i.e. $\Omega \geq 11$), much of the precipitation is via homogeneous nucleation as precipitation occurs within the solution, resulting in the solution becoming semi-opaque. According to Liu (2000), when the solution is closer to equilibrium, but still has a positive saturation index, such as the experiment using a UGS synthetic groundwater (Fig. 2d-f), most of the precipitation was via heterogeneous nucleation onto the surface of the sand grain. In an alkaline solution, the surface attracts negatively charged OH^- ions, which are able to attract Ca cations, which ultimately increases the saturation index at the surface and triggers the precipitation of hydroxyapatite (Zhu & Koumoto, 2004).

In the laboratory samples, the hydroxyapatite precipitate occurs on and between grains and typically has a spherical, microcrystalline morphology with a rough texture (Fig. 3). The average conditions within the UGS groundwater (pH, calcium, phosphate) are thermodynamically favourable for hydroxyapatite dissolution ($\Omega < 0$), although the conditions within the groundwater change spatially and temporally (Table 1; Fig. 10) such that precipitation would occur ($\Omega > 0$) instead of dissolution in some locations and at some points in time.

The UGS is overlain by the Chalk group, which when weathered, releases Ca, resulting in high concentrations of Ca in UGS porewaters (Gallois, 2005; Chenini et al. 2010). Calcium is therefore unlikely to be the limiting species for the precipitation of hydroxyapatite within the UGS, as the PO_4^{3-} concentration would have to be ≥ 1.8 mM for Ca to be limiting, assuming an average Ca concentration of 2.9 mM and a hydroxyapatite mineral stoichiometry of $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. Phosphate is therefore likely to always be the limiting species due to the Chalk unit overlying the UGS in the catchment, which likely produces Ca concentrations that are approximately 2 orders of magnitude greater than phosphate concentrations that are observed in the UGS.

When there is a neutral to alkaline solution pH and an input of PO_4^{3-} , precipitation of hydroxyapatite into pore spaces is likely to be rapid. The solution entering the UGS from the overlying soil is slightly acidic (pH 6.5) (Butcher, 2013), favouring dissolution of hydroxyapatite. The depth at which the precipitation of hydroxyapatite onto sand surfaces is thermodynamically favoured occurs when the solution pH becomes more neutral/alkaline. As hydroxyapatite dissolves near the surface of the profile, OH^- is released (Eq. 1) into downward infiltrating porewaters, which would raise the pH deeper in the profile. If porewater PO_4^{3-} in the UGS is sourced from the application of fertilisers to overlying agricultural fields, this input is likely to change seasonally and vary with land use. Land use in the Vale of Pewsey is mostly agricultural, with 48.5% arable, 22.5% grassland, and 10.5% rough grazing, all of which have P applied as inorganic fertilisers and manures (Strömqvist et al. 2008). Typical P application rates to UK agricultural land ranges from 8 kg P ha⁻¹ yr⁻¹ on grassland to 30 kg P ha⁻¹ yr⁻¹, and an average of 18 kg P ha⁻¹ yr⁻¹ in 2017 (DEFRA, 2018; Cooper & Carliell-Marquet, 2013).

Application of P-rich fertiliser to the fields overlying the UGS is likely to increase the saturation index with respect to hydroxyapatite in the porewaters. As the rate of hydroxyapatite precipitation is proportional to the saturation index (Eq. 3), fertiliser application may increase the hydroxyapatite precipitation rate, potentially leading to a greater mass of hydroxyapatite mineral forming in the sandstone pore space. Indeed, our

experiments precipitated a greater mass of hydroxyapatite when the experimental saturation index was more positive. Groundwater chemistry data from across the catchment indicates that porewater within the UGS is able to precipitate hydroxyapatite, reflected by a positive saturation index, at certain locations and times across the Hampshire Avon catchment (Fig. 10). However, the dissolution of hydroxyapatite within the UGS is favoured at more locations and times across the catchment.

5.2. The dissolution of hydroxyapatite

The steady-state dissolution of hydroxyapatite was achieved over short experimental timescales. However, the trend in phosphate concentration in the output solution does not follow a typical mineral dissolution curve where solute concentrations increase until steady-state dissolution is reached. When dissolving sand-bound hydroxyapatite, there is a two-step dissolution process, with an initial rapid release of phosphate, followed by a slower release until steady-state is achieved. The surfaces of homogeneously precipitated hydroxyapatite appear to be smooth in SEM images (Fig. 6a), and the bulk mineral dissolves and releases phosphate to solution until steady state is achieved (Fig. 6b). In contrast, hydroxyapatite that has precipitated heterogeneously onto the sand grains, has a rough surface texture (Fig. 6c) of fine grained particles, that are expected to have a large surface area and would therefore rapidly dissolve (Beckingham et al. 2016; Israeli & Emmanuel, 2018), producing the first stage of dissolution observed in our experiments. Alternatively, hydroxyapatite not bound to sand grains (i.e. precipitated between sand grains) may dissolve faster than hydroxyapatite attached to the sand grains. Larger hydroxyapatite grains and/or those directly attached to sand grains or located in a less accessible part of the sandy matrix may dissolve later and more slowly, producing the second stage of dissolution observed in our experiments (Figs. 4 and 6d). Our experiments suggest that the dissolution of hydroxyapatite within the UGS may involve a sequence of dissolution reactions at different rates, governed by the reactive and accessible surface area of the mineral. Other factors that would affect the mineral dissolution

rate in the field include the speed at which groundwater can transport dissolution products away, and the accessibility of the mineral to dissolving pore fluids.

5.2.1. Controls on the rate of hydroxyapatite dissolution

The dissolution of sand-bound hydroxyapatite has a log-linear rate dependence on the input solution pH, decreasing with increasing pH between pH 4 and 6 (Fig. 5). Between pH 6 and 7, the dissolution rate appears to be less dependent on pH, which has also been shown in similar studies using fluorapatite (Guidry & Mackenzie, 2003; Chairat et al. 2007). Within our experimental pH range (4 - 7), the dissolution rate of sand-bound hydroxyapatite varied between 4.52×10^{-6} and $2.60 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, and reflects a dissolution rate that is approximately 2-4 orders of magnitude faster than those in the literature for fluorapatite (Guidry & Mackenzie, 2003; Valsami-Jones et al. 1998; Welch et al. 2002). These authors used open flow through and closed batch reactors to dissolve natural fluorapatite samples, and report dissolution rates at $4 \leq \text{pH} \leq 7.3$ between 1.7×10^{-9} and $5.0 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1}$. The difference in dissolution rates between hydroxyapatite and fluorapatite may represent the greater solubility product and reactive surface area of sand-bound hydroxyapatite compared to fluorapatite (Chairat et al. 2007).

Lowering pH increases the concentration of H^+ at the expense of OH^- , shifting the equilibrium of the dissolution reaction (Eq. 2) to the right. The pH dependence of the dissolution rate indicates proton-promoted dissolution in which protons bond to oxygen ions of orthophosphate and hydroxide groups of the apatite mineral (Dorozhkin, 2012), resulting in the hydrolysis of the Ca-O bond (Dorozhkin, 1997; Chairat et al. 2007), followed by the detachment of phosphate (Dorozhkin, 2012). According to a model by Wu et al. (1991), apatite surfaces become protonated at $5 \leq \text{pH} \leq 7$, and become fully protonated at $\text{pH} < 5$, which reflects the increase in dissolution rate at a more acidic pH. Following the hydrolysis of the Ca-O bond, the Ca cation diffuses through the Nernst layer into the bulk solution (Dorozhkin, 2012). The removal of Ca from the mineral lattice weakens its attraction to the nearest phosphate group (PO_4^{3-}). Following the detachment of all (or almost all) of the Ca

cations, the phosphate group will detach due to a reduction in attraction between PO_4^{3-} and the mineral lattice (Zhang & Nancollas, 1992). Whilst this acidic dissolution mechanism was proposed for fluorapatite, the mechanism is independent of the anion (F^- , Cl^- , OH^-) in the apatite structure, and is therefore applicable to fluorapatite, chlorapatite and hydroxyapatite. Previous studies have proposed an alkaline dissolution mechanism for apatite minerals (Chaïrat et al. 2007), which was not investigated in the present study because at an alkaline pH, the precipitation of hydroxyapatite, as opposed to dissolution, would likely be favoured thermodynamically as the UGS porewaters are typically high in calcium and phosphate. The alkaline dissolution mechanism involves the breaking of the Ca-O bond during the hydration of surface calcium ions, which lose a proton in alkaline solutions, and is followed by the detachment of PO_4^{3-} , as per the acidic dissolution mechanism (Chaïrat, et al., 2007).

The influence of the phosphate concentration on the dissolution rate of hydroxyapatite depends on how close the solution is to equilibrium (Fig. 8). When the solution is close to equilibrium with hydroxyapatite, the phosphate concentration has a significant impact on the dissolution rate, where, for example, at pH 6.5, an increase in phosphate concentration from 1×10^{-7} to 4.4×10^{-7} M results in a decrease in dissolution rate by approximately two orders of magnitude (Fig. 8). The initial phosphate concentration therefore has a greater effect than pH on the dissolution rate, which across a pH range from 4 to 7, decreased by approximately 1.2 orders of magnitude in our experiments. However, when the solution is far from equilibrium, i.e. when the phosphate is $\leq 1 \times 10^{-10}$ M, a change in this concentration does not have a significant effect on the dissolution rate. A similar trend between solute concentration and dissolution rate has been identified for silicate minerals, such as quartz, gibbsite and kaolinite (Arvidson & Luttge, 2010; Lasaga & Luttge, 2001; Dove et al. 2005), as well as for fluorapatite (Guidry & Mackenzie, 2003), and has been termed a dissolution plateau. Mathematically, this trend is a result of the logarithmic function used to calculate the saturation index (Eq. 2), but chemically, it may represent a change in dissolution mechanism in a solution far from equilibrium (Dove & Han, 2007).

5.3. Dissolution of hydroxyapatite within the Upper Greensand

The phosphate concentration within the UGS ranges from approximately 1×10^{-8} to 4×10^{-5} M, with a pH range between 6.5 and 8. However, it is important to note that this data represents part of the UGS that is overlain by chalk, which would likely sequester (as hydroxyapatite) much of the P that may be applied to overlying fields due to the abundance of Ca^{2+} and the alkaline pH. In parts of the UGS that are not overlain by the chalk unit, and may have high rates of P-rich fertiliser application, such as in the Vale of Pewsey, it is likely that the phosphate concentration within the porewaters is greater than in the UGS porewaters underlying chalk. Within this range in phosphate concentration, and at a pH above 7, the saturation index with respect to hydroxyapatite is positive and therefore precipitation is favoured. However, at $\text{pH} < 7.5$, within the phosphate concentration range, dissolution of hydroxyapatite is favoured, and PO_4^{3-} would be released to porewaters. Within the UGS porewaters, and typically in natural groundwaters (Brantley et al. 2008; Jalali, 2009), the solution is close to equilibrium, particularly within the pH range of 6.5 - 8, and the phosphate concentration would therefore have a significant effect on the dissolution rate of hydroxyapatite (Fig. 8). Within the pH and phosphate concentration range of the UGS porewaters, the dissolution rate can vary from $10^{-12.25}$ to $10^{-9.15} \text{ mol kg}^{-1} \text{ s}^{-1}$, a range of ~3 orders of magnitude. Within a 5 m^3 profile of sandstone with 30% porosity and 1 wt% of hydroxyapatite, hydroxyapatite dissolution within the UGS pH and PO_4^{3-} concentration range would produce a flux between 4.5×10^{-11} and $5.7 \times 10^{-8} \text{ mol PO}_4^{3-} \text{ s}^{-1}$. This represents a significant release of PO_4^{3-} to porewaters, especially as the UGS has a high BFI to the headwaters of the Hampshire Avon.

Many of the borehole locations within the UGS are able to dissolve hydroxyapatite (Fig. 10), and as such, the UGS provides a high groundwater contribution to the headwaters of the Hampshire Avon (BFI: 0.84 for the East Avon at Upavon, and 0.87 for the West Avon at Upavon, both draining the Vale of Pewsey; National River Flow Archive, UK), and therefore, the release of PO_4^{3-} to porewaters due to the rapid dissolution of hydroxyapatite may represent a major source of P to headwaters from the UGS. However, due to spatial

and temporal variations in the saturation index across the catchment, the flux of P to headwaters from the dissolution of hydroxyapatite will be spatially and temporally variable. This weathering flux of secondary mineral P is likely contributing to the elevated concentrations of P in the two tributaries draining Pewsey Vale, the East Avon and West Avon, and in the Nadder River catchment where the UGS also outcrops. These concentrations, as reported by Jarvie et al. (2005) for the period 1993-2000, are 0.21-0.32 mg P L⁻¹ as total reactive P (TRP) in the West Avon, 0.31 – 0.42 mg P L⁻¹ as TRP in the East Avon, and 0.1 – 0.21 mg P L⁻¹ in the River Nadder at Wilton. Lloyd et al. (2019) similarly report a range of daily frequency phosphate (measured as PO₄³⁻P) concentrations over two water years (730 days) averaging 0.15 – 0.17 mg P L⁻¹ in the headwaters of the River Nadder at Priors Farm, and 0.03-0.04 mg P L⁻¹ at the adjacent tributary sampled at Cool's Cottage under the Defra Demonstration Test Catchments programme. Each of these represent locations where the WFD chemical status for P is currently classified as poor or moderate. As discussed above, the P in this mineral may represent an anthropogenic origin, and therefore an anthropogenic flux of P from ground- to surface waters, which needs to be quantified to meet the EU WFD (Council of the European Union, 2000).

5.4. Phosphate sorption within the Upper Greensand

The precipitation and dissolution of hydroxyapatite is likely to contribute to the porewater PO₄³⁻ concentration, and ultimately the P flux from groundwaters to surface waters in the UGS. However, along the flow paths through the UGS, adsorption and desorption are also likely to affect PO₄³⁻ (Spiteri et al. 2007; Lapworth et al. 2011), particularly in catchments dominated by agriculture (Gustafsson et al. 2012; Gérard, 2016). Fe(III)-(hydr)oxides within the Upper Greensand provide sorption sites for phosphate (Woods et al. 2008; Woods, 2012). The sorption of phosphate to mineral surfaces is most likely controlled by solution pH, which affects surface charge by protonation and deprotonation of surface sites (Fig. 9). Between pH 5 and 7, aqueous phosphate is mainly present as H₂PO₄⁻ and HPO₄⁻, which can adsorb to positively charged Fe-oxide surface sites at an acidic pH (Bolland et al. 1980). At a

more alkaline pH, phosphate desorbs as negatively charged surface sites increase, repulsing the negatively charged phosphate species (Zeng et al. 2004; Bai et al. 2017).

Within the UGS, the sorption potential is likely to vary with solution pH, the abundance of Fe-oxides, and the concentration of competing anions. However, using these scenarios (Fe-oxide 0.1 – 5wt%, pH 4 – 8), mineral surfaces are able to adsorb between 6% and 80% of the dissolved phosphate (Fig. 9). The presence of Fe-oxides within this sandstone aquifer can therefore release or retain phosphate to or from porewaters, and ultimately act as a source or sink of phosphate. However, due to the relatively high calcium concentrations within the porewaters of the UGS, sourced from the weathering of the surrounding Chalk group (Gallois, 2005), and the neutral to alkaline pH, the precipitation of hydroxyapatite introduces an added complexity. The modelled porewater solution (1×10^{-5} mol $\text{PO}_4^{3-} \text{ L}^{-1}$) is in equilibrium with hydroxyapatite (i.e. $\Omega = 0$) at pH 6.2, and therefore, above this pH, phosphate is able to precipitate out of solution as hydroxyapatite, which is likely to be accompanied by the desorption of phosphate from Fe-oxide surfaces. Below this pH, the saturation index with respect to hydroxyapatite is negative, resulting in the release of phosphate to porewaters from the dissolution of hydroxyapatite, but is then more likely to adsorb to mineral surfaces due to the acidic pH.

These models suggest that Fe-oxide surfaces are able to adsorb considerably more phosphate at a lower pH. However, at a more acidic pH, the rate of PO_4^{3-} release from the dissolution of hydroxyapatite would be faster, which may then adsorb to the Fe-oxide surfaces, until the surface sites become saturated with phosphate, which is dependent on the abundance of these minerals, their reactive surface areas within the UGS, and competition for surface sites from other anions. The modelled sorption of phosphate within the UGS pH range indicates that the sorption to mineral surfaces is likely to be an important process in governing the overall P flux to headwaters.

5.5. Dynamic PO_4^{3-} behaviour within the UGS along a 1D flow path

Previous models focusing on phosphorus dynamics between groundwater, soil, stream beds and sediments that have dominant inputs of P from agricultural activity (INCA-P model; Wade et al. 2002; Crossman et al. 2013), identified sorption and desorption of phosphate within the aquifer matrix as the dominant control on groundwater phosphate concentrations (Whitehead et al. 2014). However, as discussed above, the precipitation of hydroxyapatite onto sand, and its dissolution, are both rapid processes, and result in the removal or release of Ca^{2+} , PO_4^{3-} and OH^- ions from/to porewaters. Therefore, along a one-dimensional flow path, which could represent a vertical profile from the ground surface into the UGS aquifer, we would expect dynamic PO_4^{3-} behaviour, involving hydroxyapatite precipitation and dissolution and phosphate sorption and desorption due to spatial and temporal variation in pH, and phosphate concentration (Fig. 10).

Here we present three reactive transport model scenarios over a 1D flow path to understand PO_4^{3-} behaviour due to hydroxyapatite precipitation/dissolution and phosphate adsorption/desorption. The input solutions to the model reflect a slightly acidic solution with a low phosphate concentration, an average UGS pH with a high phosphate concentration, and a slightly acidic pH with a high phosphate concentration, to represent the range of expected processes within the UGS.

5.5.1. Dynamic PO_4^{3-} behaviour after rainwater recharge

Firstly, we used a reactive transport model to simulate the application of a slightly acidic input solution (pH 6.5), reflecting shallow porewater mixed with rainwater (Edmunds & Kinniburgh, 1986; Stuart & Smedley, 2009), and having a low phosphate concentration (1×10^{-7} M) recharging the UGS aquifer to a sandstone with a 1 wt% abundance of hydroxyapatite, and a 0.5 wt% abundance of Fe-oxide. Over a 1D flow path, we observed dynamic PO_4^{3-} behaviour with depth and over time (Fig. 11). In the upper 1 to 4 m of the profile (depending on the time scale of the model run), there is dissolution of hydroxyapatite which releases Ca^{2+} , PO_4^{3-} and OH^- ions to the porewaters. Due to the slightly acidic pH, phosphate is able to adsorb to Fe-oxide surfaces within the upper horizon of the model.

Vertical groundwater flow, and the mass transport of ions through the porous medium, results in the downward movement of the dissolution products deeper into the 1D profile. Therefore, at depth, hydroxyapatite is able to precipitate onto the sand grains (e.g. Fig. 2), and represents a sink of PO_4^{3-} . An increase in pH at this depth due to the overlying release of OH^- from the dissolution of hydroxyapatite, would also cause the desorption of phosphate from mineral surfaces, which would contribute to the elevated phosphate concentration here, and therefore result in a greater mass of hydroxyapatite precipitated. This dynamic PO_4^{3-} behaviour with dissolution and sorption in the upper part of the profile, and precipitation and desorption at depth may represent a point in time, but spatial and temporal variations in the input pH and phosphate concentration would result in the changes to these processes that control porewater P (Fig. 10). Under this scenario, precipitation at depth due to dissolution near the surface of the profile, continues for 66 days. Dissolution then slows, reducing the concentrations of Ca^{2+} , PO_4^{3-} , and OH^- that are transported downwards until dissolution, instead of precipitation, is favoured at depth ($\Omega < 0$). Over time, phosphate continues to adsorb to mineral surfaces in the upper part of the profile (where pH is lower) until the surface sites become saturated such that no additional phosphate can be adsorbed. After 18 days, there is rapid desorption of phosphate, reflecting an increase in pH due to the overlying dissolution of hydroxyapatite.

5.5.2. Dynamic PO_4^{3-} behaviour after high phosphate recharge under agricultural land, at near neutral pH

In the second scenario, we used a high PO_4^{3-} concentration of 5.0×10^{-5} M to reflect arable and grassland farming, which makes up 48.5% of land use within the Hampshire Avon catchment (Strömqvist et al. 2008) and are typically applied with high rates of P-fertiliser (Agricultural Industries Confederation, 2017; Johnes, et al., 2007) that ultimately results in a high porewater PO_4^{3-} concentration beneath arable and grassland sites (Jordan et al. 2012). Using this input PO_4^{3-} concentration with an average porewater pH for the UGS of 7.3 (Butcher, 2013), we observe a reversal of the scenario described above: hydroxyapatite

precipitates in the upper part of the profile, which removes Ca^{2+} , PO_4^{3-} and OH^- from solution, lowering the pH and saturation index of the water that infiltrates such that dissolution is favoured at depth (Fig. 12). However, after approximately 50 days, hydroxyapatite precipitation occurs at depth because the pH and saturation index rises due to the accumulation of Ca^{2+} , PO_4^{3-} and OH^- that was released by dissolution over the first 50 days. The slightly alkaline (pH 7.3) input solution also results in the desorption of phosphate from mineral surfaces, which contributes to the mass of hydroxyapatite that is able to precipitate in the upper part of the profile. Due to this precipitation and the mass transport of solution downwards, the pH at depth is more acidic (Eq. 1), which encourages more phosphate sorption for the first 40 days of the model run.

5.5.3. Dynamic PO_4^{3-} behaviour after slightly acidic, high phosphate recharge beneath agricultural land

In a third scenario, we again used a slightly acidic input solution (pH 6.5) to recharge our modelled UGS, but this time with agricultural fields that have high P fertiliser application rates, consistent with those in the Vale of Pewsey (8 – 30 kg P ha⁻¹ yr⁻¹; DEFRA, 2018; Strömqvist et al. 2008), which results in high concentrations of PO_4^{3-} infiltrating into the UGS (5×10^{-5} M; Fig. 13). Due to the acidic pH, dissolution is initially favoured in the upper part of the profile, until a positive saturation index with respect to hydroxyapatite is achieved due to the accumulation of Ca^{2+} , PO_4^{3-} and OH^- in the porewaters. At depth, there has been a greater mass of hydroxyapatite dissolved after 20 days compared to the surface of the profile, reflecting a faster rate of dissolution at depth compared to the surface, therefore resulting in a hydroxyapatite abundance of ~1 wt%. After 60 days, there is precipitation near the profile surface, which removes Ca^{2+} , PO_4^{3-} and OH^- from porewaters, leading to slightly acidic, undersaturated ($\Omega < 0$) solutions infiltrating downwards causing dissolution beneath the shallow precipitation zone. However, despite an initial period of hydroxyapatite dissolution, there would always be precipitation after some time due to the high P loading of the input solution. The high P input causes the percentage of phosphate adsorbed to mineral

surfaces relative to phosphate in solution to decrease, as the sorption sites are likely to be occupied and no more phosphate is able to adsorb. A period of dissolution at the start of the model run also results in an increase in the pH, which reduces the anion sorption capacity of mineral surfaces within the model. The influence of phosphate sorption under this high P-input scenario is therefore likely to be negligible. The UGS itself may have localised zones with a greater glauconite or iron oxide content (Woods et al. 2008), which may increase the sorption capacity for PO_4^{3-} , and therefore have a greater influence on the PO_4^{3-} behaviour within the UGS.

5.5.4. Dynamic PO_4^{3-} behaviour in the UGS due to changing conditions

The depth at which these processes occur is likely to be changing over time and influenced by the fluctuating water seasonal table within the UGS (Soley et al. 2012), as well as the input solution chemistry (with a characteristic pH and phosphate concentration), and the duration of application. The mineralogical heterogeneity of the UGS (Woods, 2012) would also affect PO_4^{3-} behaviour along a flow path, and ultimately the overall flux of P from the UGS to the Hampshire Avon. The porosity and connectivity of pore space within the aquifer matrix affects solute transport and in a heterogeneous aquifer would likely result in a highly differentiated fluid velocity (Hornberger et al. 1990). In turn, the fluid velocity influences the PO_4^{3-} controlling processes, particularly the dissolution of hydroxyapatite, as this requires the removal of dissolution products (Maher, 2010).

We predict that the precipitation and dissolution of hydroxyapatite along a vertical flow path largely controls the porewater concentration of PO_4^{3-} , and ultimately the flux of P from the UGS to the Hampshire Avon. The chemical conditions within the UGS porewaters, which have a high concentration of Ca due to the overlying Chalk unit (Butcher, 2013; Woods et al. 2008) and a high P loading due to the agricultural nature of the catchment (Jordan et al. 2012; Strömqvist et al. 2008), and a slightly acidic input solution (Stuart & Smedley, 2009), encourages dynamic PO_4^{3-} behaviour over a 1D flowpath. The porewater chemistry of the UGS varies spatially and temporally across the Hampshire Avon catchment

(Fig. 10), which ultimately results in dynamic PO_4^{3-} behaviour throughout the UGS. Therefore, aqueous P doesn't simply flow through groundwater and out to rivers, which can be modelled using a simple mass transport model, but is affected by precipitation and dissolution of hydroxyapatite and by phosphate sorption and desorption along a flow path. The adsorption or desorption of phosphate to/from mineral surfaces within the UGS also affects the residence time of phosphate within the UGS. However, the dissolution of secondary (probably anthropogenic) hydroxyapatite is likely to contribute anthropogenic phosphate from groundwaters to surface waters. The dynamic processes that this anthropogenic P can undergo due to spatial and temporal variability in pH and phosphate concentration are clearly complex, but when it eventually discharges into the Hampshire Avon, it will contribute to the anthropogenic P loading, and would therefore have to be reduced according to the EU WFD (Council of the European Union, 2000).

6. Conclusions

In this study, we investigated PO_4^{3-} behaviour using experiments and models representing a sandstone aquifer underlying an agricultural catchment. Hydroxyapatite was precipitated onto sand, and then dissolved, under a range of chemical conditions to determine the kinetics of hydroxyapatite precipitation and dissolution in the presence of sand. We used 1D reactive transport models to demonstrate the potential for dynamic PO_4^{3-} behaviour in a sandstone aquifer (UGS), through the precipitation and dissolution of hydroxyapatite and the sorption and desorption of phosphate.

Rapid precipitation of hydroxyapatite onto sand grains from supersaturated groundwater solutions was observed over time-series experiments, demonstrating that an elevated porewater PO_4^{3-} concentration (e.g. from fertiliser application) can induce the rapid precipitation of hydroxyapatite under field-typical conditions. Experimental precipitates have a similar morphology to hydroxyapatite within the UGS, consistent with formation of UGS hydroxyapatite as a secondary mineral precipitate of anthropogenic porewater phosphate. The dissolution of sand-bound hydroxyapatite in a continuous flow-through reactor released

phosphate from hydroxyapatite until steady-state was reached. The release of phosphate occurred in two stages at different rates, likely reflecting the variability in reactive and accessible surface area of hydroxyapatite formed on and between sand grains. The dissolution of hydroxyapatite is strongly pH dependent, particularly at an acidic pH, which likely reflects the acidic dissolution of hydroxyapatite. Changing the pH, within the UGS range, and with no change in initial phosphate concentration, the hydroxyapatite dissolution rate only changes by approximately $10^{-0.1} \text{ mol kg}^{-1} \text{ s}^{-1}$. However, when the solution is close to equilibrium, as we observe in the UGS, the rate is more strongly dependant on the phosphate concentration than on pH. However, it is important to note that a neutral to acidic pH is required for dissolution to be thermodynamically favourable, within the phosphate concentration range we can expect in UGS porewaters. The dissolution rate within the pH and phosphate concentration range of the UGS is between $10^{-12.25}$ and $10^{-9.15} \text{ mol kg}^{-1} \text{ s}^{-1}$, and as the headwaters of the Hampshire Avon (where the UGS outcrops) has a BFI of 0.7 to 0.91, we can expect a high rate of P release from the UGS to the Hampshire Avon if there is hydroxyapatite in the pore space and the porewater chemistry reflects a negative saturation index with respect to the mineral.

Sorption and desorption of PO_4^{3-} onto Fe-oxide surfaces were shown to be important processes in influencing P transport through a sandstone aquifer. However, the reactions with hydroxyapatite within the UGS are likely to be controlling the PO_4^{3-} contribution from the UGS to the Hampshire Avon, particularly due to the high agricultural P loading within the catchment.

We demonstrated dynamic and complex PO_4^{3-} behaviour along a 1D flow path using reactive transport models and UGS-realistic conditions. Some fraction of this PO_4^{3-} is likely to be anthropogenic in origin, due to the agricultural nature of the catchment, which can then be stored within the pore space of the UGS as hydroxyapatite. The presence of hydroxyapatite and Fe-oxides within the UGS can result in dynamic dissolution/precipitation and sorption/desorption, but the anthropogenic P will eventually be released to surface water bodies. In the context of the EU WFD, these processes and occurrence of anthropogenic

hydroxyapatite represent a potentially significant source of anthropogenic P from groundwaters to surface waters.

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847 9. Tables

848 Table 1: UGS synthetic groundwater^a and simple solution compositions

Species	UGS synthetic groundwater concentrations (mM)	Simple solution concentrations (mM)
Ca ²⁺	2.62	23
PO ₄ ³⁻	1.57	13.8
NO ₃ ⁻	0.29	
Mg ²⁺	0.11	
K ⁺	0.06	
Na ⁺	2.43	1.0
SO ₄ ²⁻	0.38	
Cl ⁻	0.42	
HCO ₃ ^{-b}	0.19	0.19

849 ^aData from Wessex Water, averages taken from 14 boreholes across the Hampshire Avon
850 catchment

851 ^bBicarbonate concentration estimated from the solution pH

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853 Table 2: Surface properties and reactions (log K) for phosphate with kaolinite (Devau et al.
854 2011; Devau et al. 2009) and hematite surfaces (Dzombak & Morel, 1990)

	Kaolinite	Hematite
<i>Surface properties</i>		
Concentration (wt%)	0.1 – 5	0.1 – 5
Specific surface area (m ² g ⁻¹)	23.6	600
Site density (site nm ⁻²)	0.62	0.40
<i>Surface reactions</i>		
≡SOH + 1H ⁺ + 1PO ₄ ³⁻ ⇌ ≡SOPO ₃ ^{-2.5} + H ₂ O	25.1	17.72
≡SOH + 2H ⁺ + 1PO ₄ ³⁻ ⇌ ≡SO ₂ PO ₂ ⁻² + 2H ₂ O	28.3	25.39

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856 Table 3: Initial and input solution chemistry for the 1D reactive transport model

Parameter	Initial	Scenario 1	Scenario 2	Scenario 3
Ca (M)	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}
PO_4^{3-} (M)	1.5×10^{-5}	1×10^{-7}	5×10^{-5}	5×10^{-5}
pH	7.3	6.5	7.3	6.5

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10. Figure Captions

Figure 1: Experimental set-up of the 2.5 cm diameter continuous flow-through reactor used to dissolve sand-bound hydroxyapatite (HAP) on 3 μm filter paper (Fisher Scientific, Grade 55 Ashless Hardened quantitative filter paper). A constant flow rate was maintained using pumps. Solution samples were collected over a time series for pH and phosphate measurement. Solid samples were retrieved from the filter at the end of the experiments only.

Figure 2: Precipitation of hydroxyapatite from the simple solution (a-c), as shown by the decrease in a) calcium concentration, b) phosphate concentration, and c) pH over 24 hours to reach steady state. A cycle of precipitation, dissolution and precipitation from a synthetic groundwater (d-f) is shown by a decrease, increase and then decrease in d) Ca concentration, e) phosphate concentration, and f) pH. Error bars represent 1 standard deviation of triplicate experiments.

Figure 3: SEM-BSE images from the precipitation experiment using a) the simple solution, and c) the synthetic groundwater. EDS spectra for the points marked on the accompanying SEM-BSE images represent b) Point 1 in the simple solution, and d) Point 2 in the synthetic groundwater solution. Peaks in Ca and P indicate a Ca-P phase consistent with hydroxyapatite in both samples.

Figure 4: Output phosphate concentrations (μM) from the dissolution of sand-bound hydroxyapatite in a continuous flow dissolution reactor (symbols) and models (lines) at a pH range from 4 to 7. Error bars represent 1 standard deviation of triplicate experiments. When the input pH is more acidic, the steady-state concentration is higher, reflecting a faster dissolution rate. At steady-state, the phosphate concentration decreases as it is flushed out

of the reactor and the abundance of hydroxyapatite decreases. There is a good agreement between initial dissolution and steady-state concentrations (except for pH 4), but the models do not capture the dip in output phosphate concentration that occurs within the first approx. 50 minutes. Please note the difference in scale on the y-axis.

Figure 5: Relationship between input solution pH and hydroxyapatite dissolution rate ($\text{mol kg}^{-1} \text{ s}^{-1}$), where the dissolution rate is more pH dependent at $\text{pH} < 6$, compared to $\text{pH} > 6$. As also demonstrated in Figure 4, there is a good fit between the model (line) and experimental (symbols) results, except at pH 4.

Figure 6: a) BSE-SEM image of a large, platy hydroxyapatite crystal before it was dissolved in a continuous-flow reactor. b) Output phosphate concentration of pure hydroxyapatite dissolved in the continuous-flow reactor reached a peak at steady-state, then decreased as phosphate was flushed out of the reactor and the abundance of hydroxyapatite decreases. c) BSE-SEM image of hydroxyapatite that has precipitated onto a sand particle and has a rough and amorphous texture. d) Sand-bound hydroxyapatite results in a two-step dissolution process, producing an initial pulse of phosphate that is flushed through the reactor before a second stage of dissolution occurs, which reaches a peak concentration at steady-state.

Figure 7: The modelled dissolution rate is a good fit ($r^2 = 0.957$, $n = 21$) to the and experimental dissolution rate of sand-bound hydroxyapatite at an input pH range from 4 to 7. The model rate was calculated in GWB12 using Eq. 3 (where $k = 2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, $A = 0.16 \text{ m}^2 \text{ g}^{-1}$, $m = 0.42\text{g}$).

Figure 8: Modelled effect of initial phosphate concentration on the dissolution rate of hydroxyapatite at pH 6.5 and 7. The initial phosphate concentration has a significant impact on the dissolution rate when the solution is close to equilibrium, which is representative of

the phosphate range within the UGS (shaded green area). Precipitation of hydroxyapatite is favoured when the phosphate concentration is within the yellow shaded area, which indicates where the solution is in equilibrium with respect to hydroxyapatite (i.e. $\Omega = 0$).

Figure 9: Sorption of phosphate to Fe-oxide surfaces at a range of mineral abundances (wt%) with a high initial phosphate concentration of 4×10^{-5} M. The vertical black line represents where the solution is in equilibrium with respect to hydroxyapatite, and therefore, at higher pH, there would be precipitation and removal of P from porewaters, and at lower pH, there would be dissolution, and release of P to porewaters.

Figure 10: The saturation index (SI) with respect to hydroxyapatite (HAP), calculated using Wessex Water time-series data (Table 1) from wells drilled into the UGS across the Hampshire Avon catchment. Different colours represent different wells. The majority of points indicate undersaturation with respect to hydroxyapatite ($\Omega < 0$, Eq. 2), which would favour dissolution.

Figure 11: 1D reactive transport model of Scenario 1 (Table 3), in which a slightly acidic (pH 6.5) input solution with a low phosphate concentration (1×10^{-7} M) was applied to the surface of a 5 m deep profile for 100 days. Time $t = \text{day } 0$ indicates equilibration of initial solution (Table 3). a) Hydroxyapatite abundance with depth changes over time, where <1 wt% indicates net dissolution at the surface and >1 wt% indicates net precipitation at depth. b) The percentage of phosphate sorbed to Fe-oxide minerals increases at the top of the profile after $t=0$, but decreases below, indicating desorption. c) pH changes over depth due to the input pH and the dissolution/precipitation of hydroxyapatite. Distinct differences at the surface (0.1 m) and at depth (4.9 m) are seen in d) hydroxyapatite abundance, e) phosphate sorption, and f) modelled pH over the 100 day duration, with dissolution and sorption observed at the surface and precipitation and desorption at depth.

Figure 12: 1D reactive transport model of Scenario 2 (Table 3), in which an average UGS pH (pH 7.3) input solution with a high phosphate concentration (5×10^{-5} M) was applied to the surface of a 5 m deep profile for 100 days. Time, $t = \text{day } 0$ indicates equilibration of initial solution (Table 3). a) Hydroxyapatite abundance with depth changes over time, where >1 wt% indicates net precipitation at the surface and <1 wt% indicates net dissolution at depth. b) The percentage of phosphate sorbed to Fe-oxide minerals decreases at the top of the profile after $t=0$, indicating desorption. c) pH changes over depth due to the input pH and the dissolution/precipitation of hydroxyapatite. Distinct differences at the surface (0.1 m) and at depth (4.9 m) are seen in d) hydroxyapatite abundance, e) phosphate sorption, and f) modelled pH over the 100 day duration, with precipitation observed at the surface, dissolution observed at depth and desorption observed throughout the profile, but at a slower rate at depth.

Figure 13: 1D reactive transport model of Scenario 3 (Table 3), in which a slightly acidic (pH 6.5) input solution with a high phosphate concentration (5×10^{-5} M) was applied to the surface of a 5 m deep profile for 100 days. Time, $t = \text{day } 0$ indicates equilibration of initial solution (Table 3). a) Hydroxyapatite abundance with depth changes over time, where >1 wt% indicates net precipitation at the surface and <1 wt% indicates net dissolution at depth. b) The percentage of phosphate sorbed to Fe-oxide minerals decreases at the top of the profile after $t=0$, indicating desorption. c) pH changes over depth due to the input pH and the dissolution/precipitation of hydroxyapatite. Distinct differences at the surface (0.1 m) and at depth (4.9 m) are seen in d) hydroxyapatite abundance, e) phosphate sorption, and f) modelled pH over the 100 day duration, with dissolution observed at the surface and at depth for the first 6 and 42 minutes respectively, which was then followed by precipitation. Desorption was observed throughout the profile, but at a slower rate at depth.

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Figure 12: 1D reactive transport model of Scenario 2 (Table 3), in which an average UGS pH (pH 7.3) input solution with a high phosphate concentration (5×10^{-5} M) was applied to the surface of a 5 m deep profile for 100 days. Time, $t = \text{day } 0$ indicates equilibration of initial solution (Table 3). a) Hydroxyapatite abundance with depth changes over time, where >1 wt% indicates net precipitation at the surface and <1 wt% indicates net dissolution at depth. b) The percentage of phosphate sorbed to Fe-oxide minerals decreases at the top of the profile after $t=0$, indicating desorption. c) pH changes over depth due to the input pH and the dissolution/precipitation of hydroxyapatite. Distinct differences at the surface (0.1 m) and at depth (4.9 m) are seen in d) hydroxyapatite abundance, e) phosphate sorption, and f) modelled pH over the 100 day duration, with precipitation observed at the surface, dissolution observed at depth and desorption observed throughout the profile, but at a slower rate at depth.

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43 Figure 13: 1D reactive transport model of Scenario 3 (Table 3), in which a slightly acidic (pH
44 6.5) input solution with a high phosphate concentration (5×10^{-5} M) was applied to the
45 surface of a 5 m deep profile for 100 days. Time, $t = \text{day } 0$ indicates equilibration of initial
46 solution (Table 3). a) Hydroxyapatite abundance with depth changes over time, where >1
47 wt% indicates net precipitation at the surface and $<1\text{wt}\%$ indicates net dissolution at depth.
48 b) The percentage of phosphate sorbed to Fe-oxide minerals decreases at the top of the
49 profile after $t=0$, indicating desorption. c) pH changes over depth due to the input pH and the
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51 depth (4.9 m) are seen in d) hydroxyapatite abundance, e) phosphate sorption, and f)
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53 depth for the first 6 and 42 minutes respectively, which was then followed by precipitation.
54 Desorption was observed throughout the profile, but at a slower rate at depth.

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Highlights

APGEO-D-19-00567-R1: Rates of hydroxyapatite formation and dissolution in a sandstone aquifer:
Implications for understanding dynamic phosphate behaviour within an agricultural catchment

Bingham ST, Buss HL, Mouchos EM, Johnes PJ, Goody DC, Bagnall JP

- Input of P to Ca-rich, alkaline porewaters can precipitate secondary hydroxyapatite
- Near equilibrium, hydroxyapatite dissolution controlled by P concentration not pH
- Hydroxyapatite can form, dissolve, and re-precipitate dynamically in an aquifer
- Hydroxyapatite may be a temporary pool of anthropogenic P in aquifers

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:

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