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The oxygen isotopic composition of phosphate in river water and its potential sources in the Upper River Taw catchment, UK

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HIGHLIGHTS

- Can sources of aquatic PO_4 be traced using its stable oxygen isotope ratio?
- Various PO_4 sources within a catchment were analysed for their $\delta^{18}O_{PO4}$.
- River $\delta^{18}O_{PO4}$ indicated that rapid microbial cycling of PO_4 was occurring.
- This method appears inappropriate in systems where PO_4 cycling is rapid.

GRAPHICAL ABSTRACT
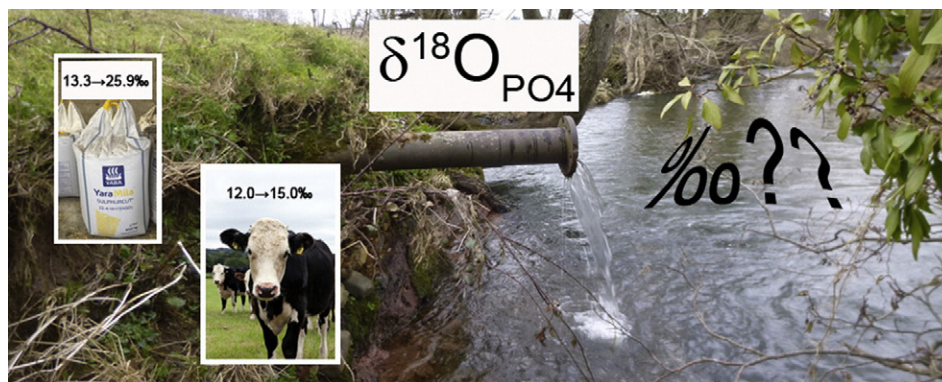
ARTICLE INFO

ABSTRACT

The need to reduce both point and diffuse phosphorus pollution to aquatic ecosystems is widely recognised and in order to achieve this, identification of the different pollutant sources is essential. Recently, a stable isotope approach using oxygen isotopes within phosphate ($\delta^{18}O_{PO4}$) has been used in phosphorus source tracing studies. This approach was applied in a one-off survey in September 2013 to the River Taw catchment in south-west England where elevated levels of phosphate have been reported. River water $\delta^{18}O_{PO4}$ along the main channel varied little, ranging from $+17.1$ to $+18.8$‰. This was no >0.3‰ different to that of the isotopic equilibrium with water ($E\delta^{18}O_{PO4}$). The $\delta^{18}O_{PO4}$ in the tributaries was more variable ($+17.1$ to $+18.8$‰), but only deviated from $E\delta^{18}O_{PO4}$ by between 0.4 and 0.9‰. Several potential phosphate sources within the catchment were sampled and most had a narrow range of $\delta^{18}O_{PO4}$ values similar to that of river $E\delta^{18}O_{PO4}$. Discharge from two waste water treatment plants had different and distinct $\delta^{18}O_{PO4}$ from one another ranging between $+16.4$ and $+19.6$‰ and similar values to that of a dairy factory final effluent ($+16.5$ to $+17.8$‰), mains tap water ($+17.8$ to $+18.4$‰), and that of the phosphate extracted from river channel bed sediment ($+16.7$ to $+17.6$‰). Inorganic fertilizers had a wide range of values ($+13.3$ to $+25.9$‰) while stored animal wastes were consistently lower ($+12.0$ to $+15.0$‰) than most other sources and $E\delta^{18}O_{PO4}$. The distinct signals from the waste water treatment plants were lost within the river over a short distance suggesting that rapid microbial cycling of phosphate was occurring, because microbial cycling shifts the isotopic signal towards $E\delta^{18}O_{PO4}$. This

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study has added to the global inventory of phosphate source $\delta^{18}O_{PO4}$ values, but also demonstrated the limitations of this approach to identifying phosphate sources, especially at times when microbial cycling is high.

1. Introduction

The need to reduce both point and diffuse source pollution to aquatic ecosystems has been widely recognised (Conley et al., 2009). The movement of potential pollutants such as sediment, faecal pathogens and nutrients into surface waters at above 'natural' levels has long been known to lead to their degradation. In particular, nutrients such as nitrogen and phosphorus (P) can lead to eutrophication through the proliferation of harmful algal blooms (Smith et al., 1999) as well as potentially direct toxic effects (Lewis and Morris, 1986). Surface waters are particularly sensitive to P because critical concentrations of only a few tens of μg available P l^{-1} can cause eutrophication, but are an order of magnitude lower than soil available P concentrations required for crop growth (Heathwaite and Dils, 2000).

Identifying the different pollutant source pressures on an impacted water body is critical to understanding the causes of degraded ecosystem health and has implications for matters such as point source consents, targeted remediation and habitat restoration. In the UK, water quality, which had been improving from the 1960s, had stalled by the 1980s. This had been blamed on a combination of increased emissions from both point and diffuse sources resulting from both a lack of investment in sewage treatment and an increase in pollution stemming from intensive farming practices (Heathwaite et al., 1996). In actuality, apportioning pollution to any given source or sources is fraught with difficulty (Bowes et al., 2008). However in recent years, several techniques have been developed such as sediment fingerprinting (Collins et al., 1997; Walling et al., 1999), natural fluorescence (Baker, 2002; Old et al., 2012) and the use of natural abundance stable isotope ratios particularly in relation to nitrate (Amberger and Schmidt, 1987; Granger et al., 2008). More recently, this stable isotope approach has been applied to soluble reactive phosphate (PO$_4$) as it is this form of P that is considered most biologically relevant and is a parameter that is routinely monitored to assess a water body's ecological status as defined by the EU Water Framework Directive (WFD) (EEC, 2000).

The PO$_4$ source tracing approach uses the stable oxygen (O) isotope ratio of $^{18}O/^{16}O$ within the PO$_4$ ($\delta^{18}O_{PO4}$). At normal surface water temperatures and pH, and in the absence of biological activity, the P—O bonds in PO$_4$ are stable and resistant to oxygen isotope exchange. Therefore, bonds are only broken through biological mediation, and in these cases PO$_4$ exchanges O with the ambient water in (Blake et al., 1997; Longinelli and Nuti, 1973; Paytan et al., 2002). The most influential biological process in the environment is considered to be that of inorganic pyrophosphatase the result of this enzymatic cycling is that the $\delta^{18}O_{PO4}$ moves towards a predictable equilibrium (E$\delta^{18}O_{PO4}$) with the isotopic ratio of the O in the water ($\delta^{18}O_{H2O}$) depending on its temperature (Chang and Blake, 2015; Longinelli and Nuti, 1973). In aquatic systems, where biological activity is limited by PO$_4$ concentrations (Bowes et al., 2014), it is assumed that rapid biological cycling of PO$_4$ leads to an over-writing of any original PO$_4$ source $\delta^{18}O_{PO4}$ signature (Tamburini et al., 2012) through a process described by (Cohn, 1958). However, where rates of biological uptake are low in comparison to PO$_4$ supply, measured $\delta^{18}O_{PO4}$ values should reflect the $\delta^{18}O_{PO4}$ of the original PO$_4$ source(s), or lie between source $\delta^{18}O_{PO4}$ values and the expected equilibrium value. In contrast, for any source tracing work to be successful, it is essential that a measurable and statistically robust isotopic difference must exist among the various PO$_4$ sources that are to be traced.

Gross et al. (2013) examined the $\delta^{18}O_{PO4}$ in dust and found that different source signatures from agricultural and natural soils prior to deposition in an aquatic environment could be determined. McLaughlin et al. (2006a, 2006b) and Elsbury et al. (2009) found that the $\delta^{18}O_{PO4}$

in lacustrine and coastal waters was not in equilibrium with the $\delta^{18}O_{H2O}$ suggesting that source $\delta^{18}O_{PO4}$ signatures were, in part, being preserved. However, data on the $\delta^{18}O_{PO4}$ of potential PO$_4$ sources remains limited. Gruau et al. (2005) found only small differences between the $\delta^{18}O_{PO4}$ of chemical P fertilizers and the PO$_4$ discharged from wastewater treatment plants. Young et al. (2009) then went on to publish the first collection of $\delta^{18}O_{PO4}$ source values reviewed from the literature and from their own studies. They found that there was a considerable range of $\delta^{18}O_{PO4}$ values (from 8.4 to 24.9‰) for different types of sources and, importantly, statistically significant differences were found between several of the individual source types. They concluded that the $\delta^{18}O_{PO4}$ tracing approach could be used for identifying PO$_4$ sources for aquatic systems. More recently reviews by Davies et al. (2014) and Tamburini et al. (2014) update the state of this embryonic application, the differing methodological approaches and set out research key new research areas. There remains, however, relatively little published information with regard to the $\delta^{18}O_{PO4}$ of different sources of PO$_4$ (Ayliffe et al., 1992; McLaughlin et al., 2006a), and although many sources have a high global $\delta^{18}O_{PO4}$ variability, locally, with a limited number of sources the range of $\delta^{18}O_{PO4}$ may be more restricted thereby increasing the opportunities for source discrimination.

In the above context, a study was therefore carried out within the River Taw catchment in south-west England within which elevated levels of PO$_4$ are one of the main reasons for failure to achieve 'good ecological status' under the EU WFD (EEC, 2000). The study was designed to answer three research questions: 1) What are the $\delta^{18}O_{PO4}$ values of different PO$_4$ sources within the study catchment? 2) Is the $\delta^{18}O_{PO4}$ within the study catchment at equilibrium with the river water?, and 3) If not at equilibrium, can the $\delta^{18}O_{PO4}$ of PO$_4$ sources be used to determine the origin of PO$_4$ within the river catchment?

2. Study catchment

The River Taw catchment is located in Devon, South West England, and is a predominantly rural catchment covering an area of 914 km^2 (Fig. 1a). The headwaters rise in the south on the Dartmoor granite plateau ca. 550 m above sea level. The river then flows northwards 72 km to the Taw/Torridge estuary, and the Bristol Channel. The soils of the catchment are predominantly agriculturally managed, typically poorly draining clay rich gley soils and typical brown earths, within which a narrow belt of well-drained, gritty reddish loams occur. The soils on Dartmoor granite consist of peat and podzols, some of low permeability.

Typical annual (1992–2014) rainfall averages 1601 mm on Dartmoor (50.703 N, −3.976 W), to <940 mm at the river mouth (51.089 N, −4.147 W).[1] The majority of the precipitation falls in the winter and the climate as a whole is typical of temperate Atlantic Britain (5–20 °C). River hydrology is dominated by surface water, reflecting the low permeability of the soils, sub-soils, and lithology and, as a result, river discharge (Q) responds rapidly to rainfall. Despite the low groundwater storage capacity of the underlying geology, water stored within rock fissures does continue to feed river Q and maintain base flow during extended dry periods.

This study focussed on the Upper River Taw catchment (Fig. 1a) which is 29.3 km in length and stretches from the source of the river to Taw Bridge. Aside from the unimproved semi-natural grass and heathlands of Dartmoor, the land-use is predominantly one of improved agricultural grassland. This supports beef, dairy and sheep production.

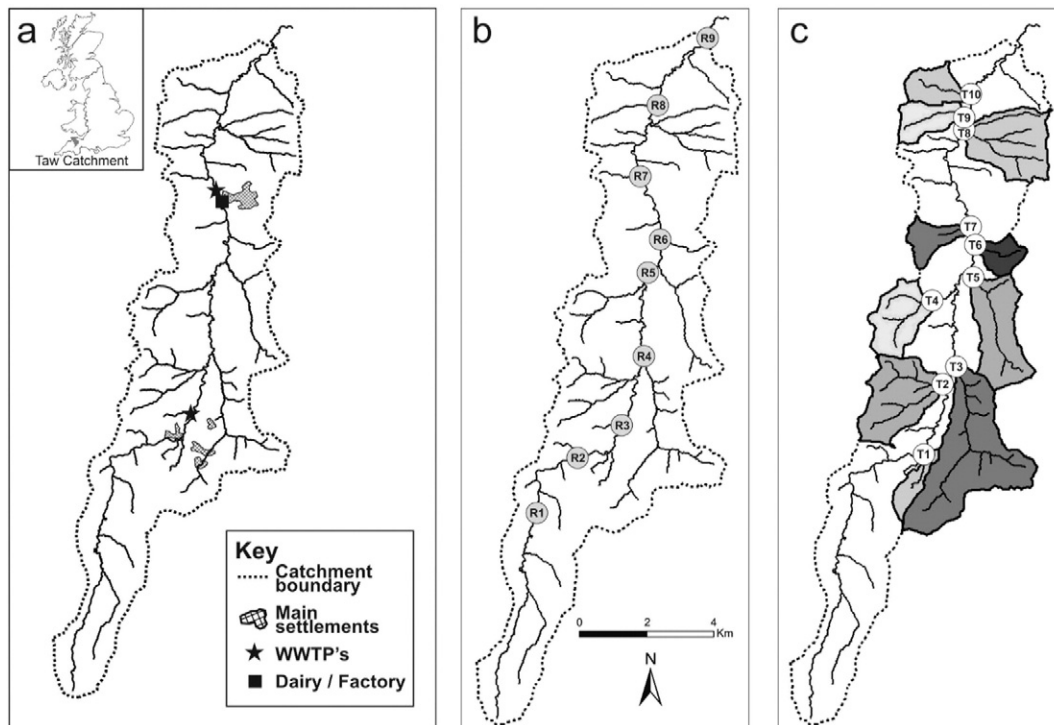[1] Data provided by the National Meteorological Archive.

Fig. 1. a) Location of the Upper Taw catchment within the United Kingdom, the catchment boundary and main settlements and point sources, b) the sample locations along the main river, and c) the sub-catchments sampled feeding the main river.

Cereals and fodder maize are also produced, particularly on the sandier, free-draining soils. Human settlement consists of scattered farmsteads and small rural towns and villages. The towns and villages tend to be served by small unmanned sewage treatment works while the more isolated rural dwellings have individual domestic septic systems.

At Taw Bridge, the river is subject to routine monthly monitoring for various water quality parameters by the Environment Agency (EA). The river is classified as a type 2n according to the UK Technical Advisory Group on the WFD (EEC, 2000) guidelines, with an altitude of >80 m and an alkalinity of <50 mg l^{-1} CaCO$_3$. The EA dataset reveals that unfiltered PO$_4$ concentrations exhibit a marked seasonal variation and can exceed 2000 μg P l^{-1} in the summer, with an annual mean concentration of 300 mg P l^{-1} (1990–2012). This is in contrast to the annual mean concentration for good ecological status being defined as <42 μg l^{-1} reactive P (United Kingdom Advisory Group (WFD-UKTAG), 2014).

Within the Upper River Taw catchment, nine approximately equidistant sampling sites were selected along the main river from R1, near the headwaters on Dartmoor, to R9 at Taw Bridge (Fig. 1b) to examine longitudinal spatial variations in unfiltered total reactive PO$_4$-P (TRP). Ten tributaries were also sampled at locations just prior to their confluence with the main river (Fig. 1c) to investigate how different areas of the catchment were influencing the river TRP variability.

3. Methodology

3.1. River water sample collection and preparation

A water sampling assay was carried out four times during 2013 (March, June, September and December). Sampling was timed to coincide with low flow for the time of year (i.e. non-storm flow) to minimise the variable impact of localised inputs due to rainwater runoff (Preedy et al., 2001; Granger et al., 2010) and to minimise spatial variation in catchment flow (Fig. 2). Conventional grab samples were collected mid-channel using a sampling boom and stored in acid washed 60 ml

HDPE bottles at 4 °C prior to analysis. The TRP analysis was performed within 24 h of sample collection, after which samples were refrigerated until determination of total P (TP).

During the September sampling assay, when historical EA data indicated RP concentrations might be highest, samples were collected at three locations along the river (R1, R4 and R9) and from three tributaries (T5, T6 and T7) for δ^{18}O$_{PO4}$ determination. At these locations when the samples were collected the temperature of the water was measured using a handheld digital thermometer. Two additional water samples were collected; i) a 25 ml sample bottle was completely filled and sealed, for the analysis of δ^{18}O$_{H2O}$, and ii) a sufficient volume to contain approximately 50 μmoles P, in acid washed HDPE barrels, typically between 25 and 50 l.
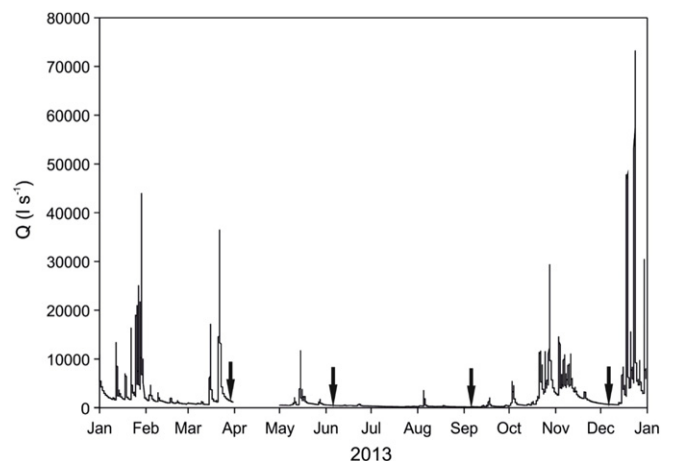

Fig. 2. The 2013 river discharge as monitored by the Environment Agency at Taw Bridge with sampling event times as indicated.

3.2. Phosphate source sampling

The main potential sources of PO_4 in the Upper River Taw catchment were identified and sampled during the course of the study. These were; 1) waste water treatment plant (WWTP) final effluent, 2) a dairy factory final effluent, 3) mains tap water, 4) agricultural inorganic fertilizers and animal wastes, 5) domestic septic tanks, and 6) river channel bed sediment.

3.2.1. Wastewater treatment plants and dairy factory final effluent

Two WWTPs discharge their final effluents directly into the River Taw within the Upper Taw catchment (Fig. 1a). WWTP1 serves a resident population of approximately 1350 and discharges into the River Taw just below sample location R3, while WWTP2 has a resident population of approximately 2000 and discharges into the River Taw between sample locations R6 and R7. The dairy factory also discharges into the river between R6 and R7, upstream of WWTP2. Samples of the WWTP final effluent were collected in June, September and December, while samples of dairy factory final effluent were collected in September, November and December.

3.2.2. Mains tap water

Three samples of mains tap water were collected from within the Upper Taw catchment in December. The water originates from a reservoir on Dartmoor and, as part of its treatment before supply to customers, has PO_4 added in the form of phosphoric acid. This is a standard treatment across a large part of the UK and relates to reducing the propensity of many waters to be plumbo-solvent. Samples were collected after the tap had been left to run for 1 min.

3.2.3. Agricultural inorganic fertilizers and animal wastes

In the UK phosphate fertilizers are applied to land to increase agricultural production and to support high stocking densities. Furthermore, high stocking densities can generate large quantities of animal waste (Chadwick and Chen, 2002). Which aside from direct returns to land during grazing, is directly applied to land in the spring after being stored over the winter period as 'slurry'. Samples of inorganic P fertilizer and slurry were collected from five representative farms within the Upper Taw catchment. Samples of fertilizer were ground to a powder to homogenise them, while the animal wastes were frozen and freeze dried before being ground to a powder. Phosphate was extracted from each sample by adding 0.5 g of material to 100 ml of de-ionised water, and shaking overnight. The resultant solution was then filtered through GF/F filters.

3.2.4. Domestic septic systems

In rural areas, where direct connections to local sewerage and WWTP are not possible, residential properties are often served by domestic septic systems. These systems treat domestic waste which typically consists of excreta and various washing water with associated chemicals. They may discharge either directly or indirectly to water courses, and because they contain human excreta and P bearing chemicals such as detergents, domestic septic systems can represent key distributed 'point sources' across the landscape, especially if they are poorly maintained or managed (Withers et al., 2014). Samples were collected from the main tank from two septic systems on three occasions in March and April 2013. Samples were oven dried at 30 °C before PO_4 was extracted by adding between 1 and 5 g of material to 100 ml of de-ionised water, and shaking overnight. The resultant solution was then filtered through GF/F filters.

3.2.5. River channel bed sediment

Bed sediment from the river channel was sampled at seven locations in August 2013 along the main river, just downstream of R1, R2, R4, just upstream of R6, at Yeobridge between R7 and R8, and R8 and R9 (see Fig. 1b and Table S1). Samples of surface and ingressed material were collected using a modified version (Collins et al., 2012) of the method described by Lambert and Walling (1988) and Collins and Walling (2007). This resuspension procedure has been shown to generate reliable samples of bed sediment material (Duerdoth et al., 2015). Briefly, a large plastic open-ended drum was pressed into the river bed at three locations across the channel. The water and bed sediment within it was strongly agitated using a battery powered drill with stirrer attachment and, after allowing 5 s for the coarser material to settle out; a sample of the sediment rich water was collected. In total, approximately 5 l of water/sediment was collected across the channel at each location. Samples were then wet sieved through a 63 μm sieve to remove sand-sized particles before the remaining sediment was allowed to settle overnight in a refrigerated environment. The majority of the water was then discarded and the residual sediment/water was centrifuged down to a volume of 250 ml, frozen and freeze dried.

Due to the low sample mass collected and previous experience of low concentrations of water extractable TRP, a 1 M HCl acid was used as the extracting media to maximise TRP concentration for isotopic analysis (Tamburini et al., 2010). Between 0.6 and 8.4 g of bed sediment was added to 100 ml of acid and shaken overnight. The resultant solution was then filtered through Whatman GF/F filters before being analysed for RP and converted to Ag_3PO_4. Water extractable RP was determined by adding sediment to de-ionised water at a ratio of 1:5 which was shaken for 30 min at 20 °C before filtration through a Whatman GF/F filter paper.

3.3. Sample analysis

In water samples that were to have PO_4 analysed for $\delta^{18}O_{PO4}$ the PO_4-P was quantitatively removed from solution through a process of co-precipitation with magnesium hydroxide otherwise known as brucite (Karl and Tien, 1992) and is a process that has been used successfully in other freshwater studies (e.g. Elsbury et al. (2009)). About 20 ml of 3 M $MgCl_2$ was added for every 1 l of sample and mixed, followed by 5 ml of 1 M NaOH per litre of sample to induce brucite formation. The precipitate was allowed to settle overnight in a refrigerated environment to minimise microbial activity, before the supernatant was discarded and the brucite collected and centrifuged. The resultant solids were then dissolved in a minimal quantity of 1 M HNO_3. If the resultant solution was > 200 ml in volume the process was repeated by increasing the pH to 10–11 using 1 M NaOH, and re-precipitating, centrifuging and dissolving the brucite. The solution was then filtered through Whatman GF/F filters.

Reactive P concentrations for all samples/extracts were determined colourimetrically on an Aquachem 250 analyser using a molybdenum blue reaction (Murphy and Riley, 1962), while TP in water samples was analysed on the same equipment following oxidation with acidified potassium persulphate. The value of unreactive P (UP) was taken as the difference between TP and TRP. When samples were in a 1 M HCl solution they were diluted by at least 1/10 to avoid acid interference with the molybdenum chemistry. Bed sediment samples were analysed for TP using an ICP-MS after an aqua-regia digestion.

Any PO_4 bearing extractions that were to be analysed for $\delta^{18}O_{PO4}$ were converted to silver phosphate (Ag_3PO_4) using the purification protocol described by Tamburini et al. (2010), subject to minor modification. The process utilizes a series of dissolution and precipitation reactions to isolate and purify dissolved PO_4. The PO_4 is precipitated firstly as ammonium phospho-molybdate before it is dissolved and re-precipitated as magnesium ammonium phosphate. Excess magnesium and chloride is removed through the addition of a cation resin and a small dose of silver nitrate crystals respectively. The resultant PO_4 in solution is then converted to Ag_3PO_4 though the addition of an Ag-ammine solution and subsequent adjustment of the pH down to between 7 and 8. The solution is then placed in an oven for two days at 50 °C. Although the Tamburini protocol uses a DAX-8 resin early in the extraction its use is not necessary unless organic contamination is present in

the subsequent Ag_3PO_4 (Tamburini pers. Comm.). Where samples were extracted using 1 M HCl, additional duplicate samples were also extracted using ^{18}O-labelled 1 M HCl to test that no RP was being released through the hydrolysis of organic matter as described in the Tamburini et al. (2010) protocol.

For analysis of $^{18}O/^{16}O$ ratios, about 400 µg of Ag_3PO_4 wrapped in a silver capsule is dropped into a thermal conversion elemental analyser at 1400 °C, and the resultant carbon monoxide carried in a flow of helium through a GC column into a Delta + XL mass spectrometer (ThermoFinnigan, Germany). The $^{18}O/^{16}O$ values are calculated by comparing the abundance ratios of mass 30 ($^{12}C^{18}O^{16}O$) over mass 28 ($^{12}C^{16}O^{16}O$) to those of an internally run Ag_3PO_4 laboratory standard ('ALFA-1'). The $\delta^{18}O$ values versus SMOW are calculated by assigning a $\delta^{18}O_{SMOW}$ value of $+14.2‰$ to ALFA-1. In the absence of an international Ag_3PO_4 reference material we derived this value for ALFA-1 by comparison to the Ag_3PO_4 standard 'B2207' (Elemental Microanalysis Ltd., England) which has been measured in an inter-laboratory comparison study to have a $\delta^{18}O$ value of $+21.7‰$ versus VSMOW. All samples were run in triplicate, with a typical precision $\sigma \le 0.3‰$. Sample purity was assessed by determining the CO yield compared with the yield of Ag_3PO_4 standards, and rejecting samples where this differed by >10%. Samples were also analysed for their %C by separate elemental analysis; this was usually below 1%C. Samples extracted in duplicate were found to have differences in $\delta^{18}O_{PO4}$ of between 0.3 and 0.4‰.

Water $^{18}O/^{16}O$ ratios were determined on CO_2 equilibrated with water samples in an Isoprime Aquaprep coupled to an Isoprime 100 dual-inlet mass spectrometer (Isoprime Ltd., Cheadle, England). The isotope ratios are reported as $\delta^{18}O_{H2O}$ values versus VSMOW, based on comparison with laboratory standards calibrated against IAEA standards VSMOW and SLAP, with analytical precision typically $\sigma < 0.05‰$.

3.4. Data analysis

Data summaries and Hierarchical Cluster Analysis were undertaken using Genstat 16 software (VSN International, 2013).

The $\delta^{18}O_{PO4}$ values expected for temperature dependant isotopic equilibrium with the waters measured $\delta^{18}O_{H2O}$ were calculated using the following equation defined by (Chang and Blake, 2015) based on a rigorous and controlled laboratory calibration of the temperature-dependence of equilibrium PO_4 and water, catalyzed by inorganic pyrophosphatase, over typical environmental temperatures:

$E\delta^{18}O_{PO4} = -0.18T + 26.3 + \delta^{18}O_{H2O}$ where $E\delta^{18}O_{PO4}$ is the stable oxygen isotope ratio of PO_4 at equilibrium in ‰, T is the temperature in degrees Celsius and $\delta^{18}O_{H2O}$ is the stable oxygen isotope ratio of H_2O in ‰.

This equation updates the traditionally used formula defined by Longinelli and Nuti (1973) and gives values typically 0.9 to 2.5‰ higher.

4. Results

4.1. Phosphorus sources

4.1.1. WWTP and dairy factory final effluents

Data from these two sources are presented in Table 1. The TRP concentration in the final effluent from WWTP1 ranged between 3053 and 6450 µg P l^{-1} and overall comprised >83% of the TP. From WWTP2, the corresponding concentrations were higher ranging between 6438 and 10,100 µg P l^{-1} and again TRP was the dominant form of P, comprising >89% of TP. The TRP in the dairy factory final effluent ranged from 1737 to 8100 µg P l^{-1} and comprised between 57 and 96% of the TP.

The $\delta^{18}O_{PO4}$ of the final effluent from WWTP1 had a mean of $+19.2‰$ ($\sigma = 0.8$) and decreased from $+19.7‰$ in June to $+18.2‰$ in December. Values of $\delta^{18}O_{PO4}$ at WWTP2 were lower than those at WWTP1 and less variable with a mean of $+16.7‰$ ($\sigma = 0.3$) and ranged from $+16.4‰$ in June to $+16.9‰$ in December. The calculated $E\delta^{18}O_{PO4}$ for both WWTPs was similar and rose from $+17‰$ in June to $+18.5‰$ in December. This increase was predominantly due to a marked drop in the effluent temperature caused by the onset of cooler winter temperatures. The $\delta^{18}O_{PO4}$ of WWTP1 had the greatest difference from $E\delta^{18}O_{PO4}$ being 2.6‰ higher in June and 2.1‰ higher in September but dropping to near $E\delta^{18}O_{PO4}$ in December. At WWTP2 the measured $\delta^{18}O_{PO4}$ was lower than $E\delta^{18}O_{PO4}$ by 0.5, 0.2, and 1.6‰ in June, September and December respectively. The $\delta^{18}O_{PO4}$ of the dairy factory final effluent ranged between $+16.5‰$ in September and $+17.8‰$ in November with a mean value of $+17.1‰$ ($\sigma = 0.7$). As with the $\delta^{18}O_{PO4}$ values from WWTP2, the dairy factory final effluent $\delta^{18}O_{PO4}$ were all lower than $E\delta^{18}O_{PO4}$ by between 0.7 and 2.2‰ with a mean of 1.5‰ ($\sigma = 0.8$).

4.1.2. Mains tap water

The TRP concentration of three mains tap water samples were similar, with a mean of 976 µg P l^{-1} ($\sigma = 19$), which comprised between 95 and 97% of the TP. The measured $\delta^{18}O_{PO4}$ was found to range between $+17.8$ and $+18.4‰$ ($\bar{x} = +18.2‰$, $\sigma = 0.3$) while the $E\delta^{18}O_{PO4}$ ranged between $+18.4$ and $+18.8‰$ ($\bar{x} = +18.7‰$, $\sigma = 0.2$) with measured $\delta^{18}O_{PO4}$ values being just between 0.4 and 0.6‰ lower than $E\delta^{18}O_{PO4}$.

4.1.3. Agricultural inorganic fertilizers and animal wastes

All five inorganic fertilizers were compound fertilizers, containing P with differing combinations of N, K and S, although three of the five were from the same supplier referred to as A, B and C in (Table 2). The P content was expected to range between 1.7 and 10.5% on the basis of the formulation supplied by the manufacturer and values of $\delta^{18}O_{PO4}$ measured for the fertilizers ranged between $+13.3$ and $+25.9‰$ ($\bar{x} = +20.9‰$, $\sigma = 5.6$) and were not related to the amount of P present nor the manufacturer.

The five dairy farm slurries contained water extractable TRP concentrations ranging from 961 to 3502 µg P g^{-1} ($\bar{x} = 2364$ mg P g^{-1}, $\sigma = 1.1$) while their $\delta^{18}O_{PO4}$ ranged between $+12.0$ and $+15.0‰$ ($\bar{x} = +13.5‰$, $\sigma = 1.2$) and were also not related to TRP content.

4.1.4. Domestic septic systems

The TRP concentration in the septic system waste differed between the two tanks sampled although did not change greatly within the tank over the time period sampled (Table 3). The mean TRP concentration in Tank A was 289 µg P g^{-1} ($\sigma = 0.08$) while in Tank B it was 34 µg P g^{-1} ($\sigma = 0.03$). Due to the low TRP concentration of the sample from Tank B it was not possible to extract sufficient Ag_3PO_4 to analyse for $\delta^{18}O_{PO4}$. A lack of sample from Tank A for the March assay also meant that no $\delta^{18}O_{PO4}$ value could be determined; however sufficient

Table 1
Data parameters measured in the waste water treatment plants (WWTP) and dairy factory final effluents.

	WWTP1			WWTP2			Dairy factory final effluent		
	June	Sept	Dec	June	Sept	Dec	Sept	Nov	Dec
TRP (µg P l^{-1})	6298	6450	3053	10,100	9832	6438	8100	1737	477
TP (µg P l^{-1})	7581	6959	3697	11,351	10,021	6952	8862	1803	833
Effluent Temp (°C)	16.0	18.0	9.5	17.2	19.8	10.5	20.6	11.7	12.3
$\delta^{18}O_{H2O}$ (‰)	−6.35	−5.57	−6.11	−6.31	−5.62	−5.88	−4.46	−5.70	−5.00
$E\delta^{18}O_{PO4}$ (‰)	+17.1	+17.5	+18.5	+16.9	+17.1	+18.5	+18.1	+18.5	+19.1
Measured $\delta^{18}O_{PO4}$ (‰)	+19.7	+19.6	+18.2	+16.4	+16.9	+16.9	+16.5	+17.8	+16.9
Deviation from $E\delta^{18}O_{PO4}$ (‰)	2.6	2.1	−0.3	−0.5	−0.2	−1.6	−1.6	−0.7	−2.2

Table 2
Properties of inorganic fertilizers sampled from farms in the Upper Taw catchment.

Manufacturer	Compound	$\delta^{18}O_{PO4}$ (‰)
A	N (27): P (5): K (5): S (7.5)	+13.3
A	N (16): P (16): K(16)	+25.5
A	N (0): P (24): K(24)	+16.9
B	N (0): P (16): K(36)	+22.8
C	N (23): P (4): K(13): S (7)	+25.9

PO₄ was extracted from the April samples. The $\delta^{18}O_{PO4}$ value of the PO₄ in Tank A was found to be consistent in April and ranged from +20.5 to +21.1‰.

4.1.5. River channel bed sediment

The TP of the <63 μm fraction of the river channel bed sediment generally increased along the river, from a minimum at R1 of 1001 mg TP kg⁻¹ to a maximum at R8 of 2444 mg TP kg⁻¹ (Table 4). Concentrations of 1 M HCl extractable TRP followed similar trends to that of the TP. The proportion of TP extracted using 1 M HCl was significantly ($r_5 = 0.9156$; $p < 0.01$) related to the TP of the bed sediment and increased in a positive and non-linear trend, ranging from 40.1 and 61.8% of the TP. The $\delta^{18}O_{PO4}$ values of the 1 M HCl bed sediment extractions showed little variation along the length of the channel and ranged between +16.7 to +17.5‰ ($\bar{x} = +17.3$‰, $\sigma = 0.3$).

4.2. Upper River Taw

4.2.1. Seasonal variability in catchment discharge

Although samples were collected at 'low Q', i.e. between storm events (Fig. 2), Q was higher in the winter than the summer. This difference is important to take into account when examining RP concentration data. Flow was gauged by the EA at R2 and R9 within the Upper River Taw catchment (Table 5) with the highest Q at both sites occurring in March, and the lowest in September. The Q at R9 was positively related ($r_2 = 0.9995$; $p < 0.001$) to the Q at R2 at the time of sample collection and increased exponentially. As sampling occurred during low, stable flows, it is assumed that tributary Q reflects that of the main river (i.e. Q being lowest in September and highest in March).

4.2.2. Upper River Taw TRP concentrations

The TRP concentrations measured in the Upper River Taw ranged between 1 and 2286 μg P l⁻¹ (Table 5). The TRP concentrations showed a seasonal trend at each sample location, increasing from March when they were at their lowest, through to September when they were highest, and declining again in December. This pattern mirrors that of the river Q and may well reflect changes in TRP dilution within the water column. During each sample period, it was notable also that the TRP concentrations showed a spatial variability, with lowest concentrations between R1–3, increasing downstream. This was especially pronounced during the June and September sampling assays. The TRP component of TP also increased below R3 and was generally >50% of TP.

Regression analysis of the TRP concentrations in the main channel showed that they were not linear and could be divided into groups. Hierarchical cluster analysis of the TRP concentrations found that sample sites R1–3 and R4–6 were grouped at the 99% confidence level, while

Table 3
The TRP content and $\delta^{18}O_{PO4}$ of two domestic septic systems sampled in March and April 2013.

	Sample event	μg TRP g⁻¹	$\delta^{18}O_{PO4}$ (‰)
Tank A	March	377	–
Tank A	April a	250	+20.5
Tank A	April b	241	+21.1
Tank B	March	10	–
Tank B	April a	58	–

sites R7–9 were grouped at the 93% level. For sites R1–3, TRP concentrations were low. Sample site R1 had the lowest recorded concentrations ($\bar{x} = 2.75$ μg P l⁻¹, $\sigma = 1.0$), while the highest concentrations typically occurred at R2 ($\bar{x} = 4.70$ μg P l⁻¹, $\sigma = 3.4$). The predominant form of P in the river in the upper section was UP, with TRP comprising between 5 and 47%. Sites R4–6 had TRP concentrations an order of magnitude higher than R1–3, with RP comprising between 24 and 92% of TP. Finally, from R7–9, the TRP concentrations were higher again although this increase was very pronounced in June and September when they ranged from 398 to 529 μg P l⁻¹, and 1611 to 2286 μg P l⁻¹, respectively. The predominant form of P between R7 and R9 was always TRP comprising between 79 and 100% TP.

4.2.3. Upper River Taw $\delta^{18}O_{PO4}$

Although samples of river water were collected from R1, the TRP concentration was too low for successful Ag₃PO₄ precipitation. At R4 and R9, during the September sampling assay, TRP had similar $\delta^{18}O_{PO4}$ values of +17.7 and +17.8‰, respectively. The calculated E$\delta^{18}O_{PO4}$ values for R4 and R9 were also very similar at +17.4 and +17.7‰, indicating that the river water $\delta^{18}O_{PO4}$ was 0.3 and 0.1‰ higher than E$\delta^{18}O_{PO4}$.

4.3. Tributary TRP concentrations

The TRP concentrations measured in the tributaries ranged between 2 and 154 μg P l⁻¹ (Table 5). Concentrations were, in general, lower than those seen along the main river. In most tributaries, RP comprised <50% TP, with the exceptions of T6, T7, T9 and T10. The form of P was also variable between the tributaries with most having UP as the dominant form, while in T6, 7, 9 and 10 the reverse was true with RP predominating. Total RP concentrations did not display the same consistent seasonal trend that was observed in the main river. Hierarchical cluster analysis of the RP concentrations in the tributaries revealed that T1–5 and T8 were similar and could be grouped at the 97% similarity level. Sample sites T7, 9 and 10 were grouped at the 87% similarity level whilst T6 joined this second group at the 73% level. On the basis of this analysis, the tributaries could be divided into two groups; Group 1, consisting of sites T1–5 and 8, and Group 2 consisting of T6, 7, 9 and 10.

The TRP concentrations in Group 1 were always lower than those in Group 2 for any given sampling assay, often by an order of magnitude or more. They ranged between 2 and 26 μg TRP l⁻¹ which in most cases comprised <50% TP. Some tributaries had slight increases in RP with decreasing Q (e.g. T3 and 8), others were unaffected by Q (e.g. T2), while again others actually showed a slight decreased in concentration with decreasing Q (e.g. T4 and 5).

Concentrations of TRP in Group 2 tributaries ranged between 21 and 154 μg P l⁻¹ with highest concentrations always occurring in T6. Unlike Group 1 tributaries, Group 2 displayed a pronounced seasonality in concentration being highest in June and September when Q was lowest. Unlike Group 1 tributaries TRP comprised >50% TP in most cases. At both T6 and 10 TRP was always the predominant form of P ranging between 58 and 100% of TP while at T9 RP was only <50% on one occasion. Sample site T7 was an exception to the rule where TRP only >50% on one occasion.

4.3.1. Tributary $\delta^{18}O_{PO4}$

The $\delta^{18}O_{PO4}$ of the TRP in the Upper Taw catchment tributaries were +18.8, +17.1 and +17.7‰ for sample sites T5, 6 and 7, respectively. The water temperature at these locations was consistent, ranging between 15.0 and 15.6 °C which was similar to that measured in the main river close to these locations (R4 = 15.1 °C). While the $\delta^{18}O_{H2O}$ within the river appeared similar along its length, more variability was observed in the tributary $\delta^{18}O_{H2O}$. At T6 and T7, values were similar to the main river at −5.58 and −6.26‰, at T5 the $\delta^{18}O_{H2O}$ was >1‰ lower at −4.44‰ This value is unusual as meteoric waters in this area typically have values of between −5.5 and −6.3‰ and this range is consistent with those $\delta^{18}O_{H2O}$ measured at T6 and 7 and within the

Table 4
The concentrations of different forms of extractable P in the channel bed sediment of the Upper River Taw, and its $\delta^{18}O_{PO4}$ when extracted using 1 M HCl.

| Sample location | Extractant | | | | | |
| | Aqua-regia | 1 M HCl | | | De-ionised water | |
	(mg TP kg^{-1})	(mg TRP kg^{-1})	% of TP	$\delta^{18}O_{PO4}$ (‰)	(mg TRP kg^{-1})	% of 1 M HCl extractable
Sheepfold	1001	402	40.1	–	–	–
Skaigh (R2)	1070	542	50.6	+17.3	–	–
Taw Green (R4)	1631	793	48.6	+17.6	–	–
Newlands (R6)	1278	559	43.7	+16.7	0.42	0.08
Yeobridge	2328	1438	61.8	+17.5	4.52	0.31
Bondleigh (R8)	2444	1496	61.2	+17.3	7.27	0.49
Taw Bridge (R9)	2155	1251	58.0	+17.5	2.94	0.24

main river stem. These data gave $E\delta^{18}O_{PO4}$ of +19.2, +18.0 and +17.2‰ respectively meaning that at T5 and 6 measured $\delta^{18}O_{PO4}$ were 0.4 and 0.9 lower than their respective $E\delta^{18}O_{PO4}$, while at T7 $\delta^{18}O_{PO4}$ was 0.5 higher than $E\delta^{18}O_{PO4}$.

5. Discussion

5.1. Phosphorus sources

The $\delta^{18}O_{PO4}$ data collected from the various P sources within the Upper River Taw catchment are summarised in Fig. 3. From this it can be seen that considerable variation in $\delta^{18}O_{PO4}$ occurs both between sources, and within sources. The TRP of these sources and their $\delta^{18}O_{PO4}$ are discussed in greater detail within the following sections.

5.1.1. WWTP and dairy factory final effluents

The concentrations of TRP in the discharge from WWTP2 were always higher than those from WWTP1, however without information on discharge from the two WWTPs and the dairy factory final effluent it is difficult to interpret their impact on the TRP concentrations in the river. Discharge from WWTPs is not only affected by precipitation, but also by patterns of human behaviour and processes within the WWTP as well permitted discharge limits (Bowes et al., 2012).

Table 5
Main river and tributary TRP concentrations and % TP for the four sampling assays. Measured Q values for sample sites R2 and R9 are included for reference.

Sampling time										
	Location	March		June		Sept				Dec	
Q (l s^{-1}) =	R2	480		193		128				278	
	R9	2531		447		167				805	
		µg TRP l^{-1}	% TP	µg TRP l^{-1}	% TP	µg TRP l^{-1}	$\delta^{18}O_{PO4}$ (‰)	% TP		µg TRP l^{-1}	% TP
	R1	3	31	4	12	1			5	3	29
	R2	4	47	4	13	1			6	10	28
	R3	4	43	4	13	4			18	4	31
	R4	8	24	55	86	68	+17.7	74		30	85
	R5	11	85	50	92	107		74		21	74
	R6	8	43	53	90	66		68		24	73
	R7	33	100	398	89	1611		89		62	93
	R8	32	100	500	100	1659		82		91	95
	R9	25	94	529	100	2286	+17.8	79		55	91
	T1	5	57	11	30	11			18	10	49
	T2	4	26	4	12	3			6	4	31
	T3	5	14	6	19	8			26	4	31
	T4	8	25	8	15	2			2	5	28
	T5	16	31	13	22	7	+18.8		8	41	
	T6	36	100	105	62	154	+17.1	67		101	66
	T7	24	45	38	65	85	+17.7	16		32	34
	T8	9	31	12	30	10			12	6	28
	T9	24	49	73	81	70			59	27	76
	T10	21	100	102	93	152			78	22	58

Where the TRP proportion of TP is >50% it has been highlighted in bold text.

The measured $\delta^{18}O_{PO4}$ values in the WWTP final effluents were generally out of equilibrium with their water and indicated that initial source $\delta^{18}O_{PO4}$ values could be, in part, preserved within the effluent. Given the high TRP concentrations present, it would seem unlikely that all of the PO_4 would have been completely cycled thus removing any original source values. The two WWTPs also had distinct $\delta^{18}O_{PO4}$ signatures from each other (Fig. 3) although what caused this difference is unclear. In Fig. 4 it can be seen that the measured values from WWTP2 were similar to those of the river water into which it discharged, while the $\delta^{18}O_{PO4}$ of WWTP1 was greater than that of the river potentially enabling its signature to be identified.

The $\delta^{18}O_{PO4}$ reported here for WWTP final effluents (+16.4 to +19.7‰) were similar to those reported elsewhere, although those values do vary greatly. Gruau et al. (2005) reported a range of +16.6 to +18‰ for samples from three WWTPs in France which were at or very near $E\delta^{18}O_{PO4}$. Young et al. (2009) examined many effluents, both within and at the outlets, from three geographically distinct WWTPs in the USA and found $\delta^{18}O_{PO4}$ values of between +8.4 to +14.2‰. Young et al. (2009) concluded that the $\delta^{18}O_{PO4}$ of WWTP effluent can vary considerably both within, and between, different WWTPs and sometimes may not be in isotopic equilibrium with the WWTP water. This was due to a combination of factors including variability in source $\delta^{18}O_{PO4}$, changes during treatment, or changes in $\delta^{18}O_{H2O}$, temperature, and residence time within the treatment plant. Therefore, the $\delta^{18}O_{PO4}$ value of WWTP effluent must be directly measured for each study area where $\delta^{18}O_{PO4}$ measurements are being used to track source inputs.

The measured $\delta^{18}O_{PO4}$ of the dairy effluent was always lower than the $E\delta^{18}O_{PO4}$ for their water when sampled but without information on what P sources enter the dairy factory (e.g. milk, process chemicals, etc.) and what processes the effluent undergoes prior to discharge (e.g. temperatures) it is impossible to comment further on the $\delta^{18}O_{PO4}$ other than to confirm its values are indistinguishable from those

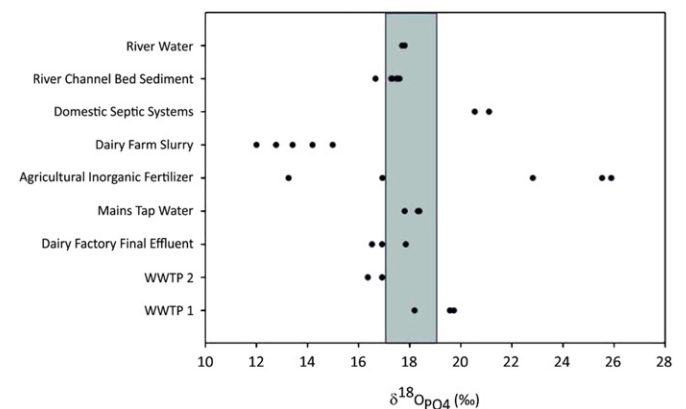**Fig. 3.** Summary of $\delta^{18}O_{PO4}$ values for various PO_4 sources within the Upper Taw catchment and the values measured within the river itself. All values are for water soluble/extractable TRP except for the River Channel Bed Sediment which is a 1 M HCL extraction. Range of $E\delta^{18}O_{PO4}$ for the river is indicated by the grey area.

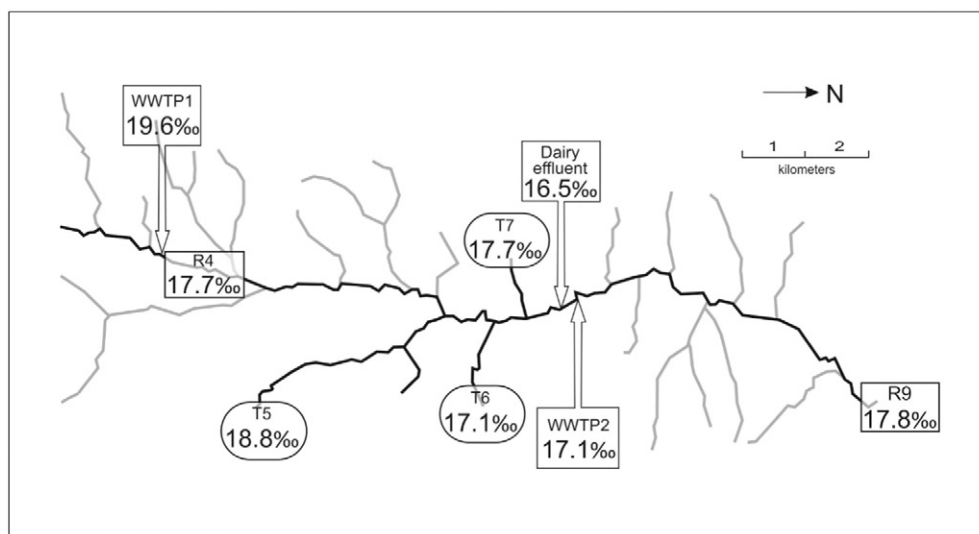**Fig. 4.** The Upper Taw catchment $\delta^{18}O_{PO4}$ riverine values and $\delta^{18}O_{PO4}$ values of other relevant TRP sources. The E$\delta^{18}O_{PO4}$ for the main river channel was $+17.4$ (R4) and $+17.7$‰ (R9), and the distance between WWTP1 and R4 was 2 km.

expected for PO_4 in equilibrium with river water (Fig. 3). Thus, in this case, the $\delta^{18}O_{PO4}$ cannot be used to distinguish this specific catchment source.

5.1.2. Mains tap water

It is not unsurprising that the TRP concentrations of the tap water samples and their $\delta^{18}O_{PO4}$ are similar given they share a common source. The $\delta^{18}O_{H2O}$ was also similar between the samples ($\bar{x} = -5.89$, $\sigma = 0.0$), and again it was variation in temperature (8.7 to 11.2 °C) that caused any variation in the E$\delta^{18}O_{PO4}$ for the mains tap water which ranged between $+17.4$ and $+18.0$‰ The $\delta^{18}O_{PO4}$ of tap water was similar to the E$\delta^{18}O_{PO4}$ for both the tap water itself and the river water (Fig. 3) and similar to other reported standard PO_4 sources (Young et al., 2009). Gooddy et al. (2015) report that while there may be some isotopic effects associated with biotic and abiotic cycling of PO_4 which could affect $\delta^{18}O_{PO4}$, it is primarily the orthophosphoric dosing acid that determines the $\delta^{18}O_{PO4}$. Their study indicated that within the region of our study, dosing acid 'B' was used with a mean $\delta^{18}O_{PO4}$ of $+19.7$‰, and that the mains waters in the region had a slightly lower value of $+18.8$ and $+19.3$‰ (which were 0.7 and 1.8‰ higher than the mains tap water E$\delta^{18}O_{PO4}$). The mains tap water samples in our study, although with a slightly lower $\delta^{18}O_{PO4}$ than reported in Gooddy et al. (2015), fit well with the national and regional picture they describe, and are higher than the $\delta^{18}O_{PO4}$ of the measured river water meaning mains tap water entering the river could potentially be distinguished as a source.

5.1.3. Agricultural inorganic fertilizers and animal wastes

Chemical fertilizers are derived from the mining and processing of phosphorite rocks which primarily originate from marine deposits. Only a small number of $\delta^{18}O_{PO4}$ fertilizer values are available in the published literature and have been summarised by Young et al. (2009). Both Gruau et al. (2005) and McLaughlin et al. (2006a) reported a narrow range of values of between 19.4 and 23.1‰ while Young et al. (2009) reported a more widely distributed set of $\delta^{18}O_{PO4}$ values of between 15.5 and 22.3‰. In this study, the $\delta^{18}O_{PO4}$ of chemical fertilizers had a wider range of values ranging from $+13.3$ to $+25.9$‰ (Fig. 3).

Previous work has reported P concentrations in European dairy slurries ranging from 28 to 910 mg TP l^{-1} and that the TP, in most cattle and pig slurries, is largely insoluble (Scotford et al., 1998). However, 83% of the water extractable TP in fresh dairy faeces has been shown to be PO_4 (Chapuis-Lardy et al., 2004). A limited number of $\delta^{18}O_{PO4}$ values have been published for animal wastes, and to the author's knowledge, none on stored agricultural wastes. Ayliffe et al. (1992) reported values

of between $+19.8$ to $+23.1$‰ for modern guano from several different species of seabirds, while Young et al. (2009) reported water extractable $\delta^{18}O_{PO4}$ values of $+15.7$‰ and $+18.3$‰ for dog and goose faeces, respectively. Agricultural slurries tend to be variable in their composition (e.g. dry matter content) and very difficult to sample representatively (Chadwick and Chen, 2002). Given the variable nature of the material, the resulting $\delta^{18}O_{PO4}$ values were surprisingly consistent and notably lower than, not only the existing data for animal wastes, but also most other materials reported by Young et al. (2009). These source values are the lowest found in this study, and are below E$\delta^{18}O_{PO4}$ values expected for river water (Fig. 3). The slurry PO_4 is most likely to be mainly sourced from animal excreta, which contains approximately 70 to 80% of the P ingested by the animal (Parr et al., 1998). The slurry $\delta^{18}O_{PO4}$ will therefore be a function of the animals feed, but most probably, the animal's internal temperature, $\delta^{18}O_{H2O}$ and metabolic processes that most strongly affect the $\delta^{18}O_{PO4}$ of the excreted PO_4. While the mineralization of organic matter by phosphatases and other enzymes can lead to lower $\delta^{18}O_{PO4}$ it can be calculated that the animals internal E$\delta^{18}O_{PO4}$ is also low. Assuming the animals' internal temperature is 38 °C, and that its body water is similar to local meteoric waters (-5.5‰) then E$\delta^{18}O_{PO4}$ would be around $+14$‰. It is also possible that further cycling of PO_4 occurs within the slurry during storage.

5.1.4. Domestic septic systems

Little information exists on the P content and contribution of domestic septic systems to water quality (Beal et al., 2005; Withers et al., 2011). This is perhaps unsurprising given the number of systems operating and their variability in age, type of discharge, treatment process and distance to receiving waters (Withers et al., 2012).

To the best of our knowledge, there are no reported $\delta^{18}O_{PO4}$ values for such waste material to date. The mean value of $+20.8$‰ (Tank A) is higher than the few $\delta^{18}O_{PO4}$ values reported for 'animal wastes'. The $\delta^{18}O_{PO4}$ value is, however, one of the few TRP sources that was isotopically distinct from the calculated E$\delta^{18}O_{PO4}$ for river water in the study catchment (Fig. 3). More data are needed if these point sources are to be better understood as potential sources of PO_4 pollution on the basis of their $\delta^{18}O_{PO4}$ signal.

5.1.5. River channel bed sediment

The TP concentration in bed sediment generally increased downstream with concentrations of around 1000 mg P kg^{-1} in the upper reaches, with peaks at Taw Green (R4) and Yeobridge of 1631 and 2328 mg P kg^{-1}, respectively. The reason for this increase is uncertain;

but likely to be related to the WWTPs and dairy factory which represent significant point sources of TRP directly upstream from them. This relationship between high TP concentrations in bed sediment and significant sources of TRP has been reported by Jarvie et al. (2005). This could also explain the increased percentage of acid and water extractable TRP from the bed sediment along the river.

At all sites, the acid extractable TRP from bed sediment samples had very similar $\delta^{18}O_{PO4}$ values with a mean of $+17.3‰$ ($\sigma = 0.3$). If the increasing P content of the bed sediment reflects the increasing contribution of one of more TRP sources being adsorbed onto the deposited sediment, those sources must either have similar initial $\delta^{18}O_{PO4}$ values, as fractionation due to abiotic processes like precipitation of P minerals is rather small (around 1‰) (Jaisi, 2013; Jaisi et al., 2010; Liang and Blake, 2007), or that any distinct $\delta^{18}O_{PO4}$ source values were lost through biogeochemical cycling of the PO$_4$. The latter is the most likely explanation as the acid extractable $\delta^{18}O_{PO4}$ of the bed sediment samples is very similar to $E\delta^{18}O_{PO4}$ of the river water (Fig. 3). It is also possible that the 1 M HCl extraction $\delta^{18}O_{PO4}$ values do not reflect water soluble TRP source values sufficiently given that the acid extraction integrates all forms of TRP from loosely bound PO$_4$ through to P associated with Ca minerals and detrital apatite (Tamburini et al., 2010). The $\delta^{18}O_{PO4}$ of water soluble TRP contained within these bed sediment samples may also be over-ridden by the $\delta^{18}O_{PO4}$ of any mineral PO$_4$ given that <0.49% of the acid extractable TRP was water extractable. To establish whether different P forms in the channel bed sediment samples have different $\delta^{18}O_{PO4}$ signatures, further studies using sequential extraction media are required to separate potential adsorbed PO$_4$ from catchment sources from truly mineral PO$_4$ forms (Cross and Schlesinger, 1995). Joshi et al. (2015) extracted sediment samples from the Chesapeake Bay in the USA and found that the $\delta^{18}O_{PO4}$ values of the ferric iron-bound and authigenic P pools were in a rather narrow range. However, the authors do not report isotope values for the other extracted P pools, i.e. the exchangeable and detrital P pools. Furthermore, a method for the determination of the $\delta^{18}O_{PO4}$ of organic P extracted from sediments or soils is still lacking.

5.2. The Upper Taw catchment

5.2.1. Upper Taw tributaries

5.2.1.1. TRP concentrations. The fact that no tributaries had TRP concentrations as great as those in the lowest reach of the main river suggests that there were no major point sources located within their catchments. However, statistical analysis of the tributaries show they can be split into 2 groups based on the change in their seasonal TRP concentrations and the predominant form of P. From these temporal concentration dynamics, it is possible to infer what the main sources of P might be within each group. Group 1 tributaries were generally located within the upper and middle reaches of the catchment, had no distinct seasonal relationship with Q, and were dominated by UP.

This implies that Group 1 tributaries had no significant P point sources and are not strongly influenced by any major diffuse inputs. Where slight seasonal patterns are observed it is probably as a result of domestic septic systems (Jarvie et al., 2008) or unregistered sources (Edwards et al., 2008). Group 2 tributaries, generally were located in the lower reaches of the catchment, had higher P concentrations than Group 1 and were TRP dominated. These catchments had a strong seasonality in TRP concentration with higher concentrations measured during the lower Q of the summer period suggesting that point sources were strongly affecting their water quality (Edwards and Withers, 2007; Jarvie et al., 2006). However, the prevalence of domestic septic systems within these tributary catchments was no different to those comprising Group 1. This highlights the complexity of P transport and delivery in such catchments, making interpreting spatial and temporal TRP patterns extremely difficult (Haygarth et al., 2005).

Tributary T7 differs slightly from the other Group 2 tributaries in that generally UP was the dominant P form. This is noteworthy as this tributary has no domestic septic systems registered within it, but it does however drain a series of lakes and ponds which are managed as fisheries, which might explain why organic forms of P are more prevalent and further highlights the complexity of these smaller point sources in affecting the P dynamics within some rural watersheds.

5.2.1.2. $\delta^{18}O_{PO4}$ isotopic characterisation of tributaries. Of the three tributaries sampled for $\delta^{18}O_{PO4}$, one was a Group 1 tributary (T5) and the others were Group 2 (T6 and T7). The seasonal TRP/Q dynamics of T5 indicated it was not affected by point sources, and that in fact it might be subject to TRP turnover and net immobilisation by the time of sampling and analysis for $\delta^{18}O_{PO4}$. It had the highest value of $+18.8‰$ measured in the Upper Taw catchment, and the $E\delta^{18}O_{PO4}$ here was also the highest within the catchment and this was because of the higher than typical $\delta^{18}O_{H2O}$ of $-4.44‰$ when compared to other surface waters sampled at that time (ranging between -6.26 to $-5.00‰$). This anomalous $\delta^{18}O_{H2O}$ value is explained by the fact that at the time of sampling, the Q in T5 was extremely low and it is possible that the very slow moving water was subject to considerable evaporative fractionation leading to an enrichment in ^{18}O. The fact that the $\delta^{18}O_{PO4}$ is elevated and similar to that of the elevated $E\delta^{18}O_{PO4}$ indicates that within this tributary the PO$_4$ was being biologically cycled having picked up the evaporative enrichment $\delta^{18}O_{H2O}$ signature. Tributary T6 was considered to be strongly P impacted due to its seasonal variation and high %TRP; however, its $\delta^{18}O_{PO4}$ was just 0.9‰ lower than $E\delta^{18}O_{PO4}$ although this was the greatest difference measured in the catchment. Although not a large difference it suggests that a source signal(s) may be present. The Group 2 tributary T7 had characteristics of both T5 and T6 (i.e. high seasonal TRP variability but low %TRP) and this unusual combination of variables was put down to the presence of a small fish farm discharging into the tributary further upstream, although this potential source was not examined further. The measured $\delta^{18}O_{PO4}$ in September was found to be just 0.5‰ higher than $E\delta^{18}O_{PO4}$, so again no conclusions could be drawn on the potential sources of the PO$_4$ in the tributary.

5.2.2. Main river

5.2.2.1. TRP concentrations. Statistical analysis of the main river TRP concentrations divided the river into three sections. The Upper section (R1–3) had low TRP concentrations ($<10\,\mu g\,P\,l^{-1}$) with little or no pronounced seasonal variation. This is typical of a drainage system in a low intensity agriculture and semi-natural grassland system with no major P point sources, and where the main form of P was UP sourced from the peat moorlands of Dartmoor and in-stream autochthonous sources (Edwards et al., 2000; Turner et al., 2003). The middle river section (R4–6) had TRP concentrations greater than upstream, was predominantly TRP, and demonstrated strong seasonal variation in TRP concentration and Q. This section of the river would therefore appear to be dominated by point sources (Jarvie et al., 2006) and most likely that of WWTP1. Downstream of R7, in the lower reach of the main river, TRP comprised nearly all the TP and concentrations were higher still again particularly in June and September when Q was at its lowest. As with the middle reach of the river, these trends are most likely to be controlled by the major TRP point source inputs from WWTP2 and the dairy factory final effluent. Without Q data from these two point sources it is not possible to assess the effect of their mixing with the river water, but what is clear is that the combined effect of these two significant point sources is probably leading to the large increases and seasonal patterns in TRP concentration in the lower reach. What is not clear is what is causing the large increase in TRP between R7 and R9 in June and September. This increase occurs without any further significant point sources of TRP. There are no further significant point sources between these sampling locations and the TRP concentrations in the tributaries feeding this lower reach are still much lower than those in the main river and should be causing dilution of TRP within the river. We speculate that this is most likely the result of some in-channel processes,

possibly mineralization of UP sourced within the final effluents from WWTP2 and dairy factory final effluent. However, if this were the case it might be expected that the %TRP in the main river would also be increasing and in September this is not the case. Furthermore, given that the vast majority of P in the two effluents is already in TRP form it doesn't seem possible that there is sufficient UP to cause such a large increase in TRP. Channel bed sediment TRP release may also explain this effect but it is unclear whether such sediment is a TRP source or sink. Jarvie et al. (2005) reported that in rivers with high SRP concentrations at low flows linked to WWTP discharges, bed sediments consistently acted as net sinks. Further work is needed to understand the TRP dynamics in this lower reach and what is driving the spatial increase in TRP concentrations.

5.2.2.2. Isotopic characterisation of river PO₄. The two samples collected in September for $\delta^{18}O_{PO4}$ characterisation were taken from R4 and R9 (Fig. 4). Sample site R4 was downstream of WWTP1, but upstream of WWTP2 and the dairy factory, while R9 is at the catchment outlet downstream of all sources within the Upper River Taw catchment. The measured $\delta^{18}O_{PO4}$ values were virtually identical to $E\delta^{18}O_{PO4}$ (only 0.3 and 0.1‰ higher, respectively). At R4 WWTP1 was most likely the main point source contributor for TRP in the river. This assumption is based on the observed jump in TRP concentration between R3 and R4, the very high concentration of TRP in WWTP1's effluent, that no other point sources are present between R3 and R4, and that T2 was also low in TRP. However, despite the $\delta^{18}O_{PO4}$ signature of the final effluent from WWTP1 being 2.2‰ higher than the river $E\delta^{18}O_{PO4}$ it was not detectable some 2 km downstream where the measured $\delta^{18}O_{PO4}$ was just 0.3‰ higher than $E\delta^{18}O_{PO4}$. Given this it would seem as though over this distance the WWTP1 effluent $\delta^{18}O_{PO4}$ signature had become completely cycled (e.g. Goldhammer et al., 2011; Stout et al., 2014).

At R9 the river $\delta^{18}O_{PO4}$ is similar to that at R4 (0.1‰ higher). At R9 the river TRP dynamics are far more complicated than at R4, with two other point sources contributing in addition to WWTP1 as well as a larger catchment area. The $\delta^{18}O_{PO4}$ of both the dairy final effluent and WWTP2 are similar, but lower than WWTP1. Their values are however, much closer to that of the river $E\delta^{18}O_{PO4}$, meaning that their signals are indistinguishable from $E\delta^{18}O_{PO4}$. Given these values it is perhaps unsurprising that at R9 the river $\delta^{18}O_{PO4}$ is again almost the same as $E\delta^{18}O_{PO4}$ (0.1‰ higher). It seems likely that the high concentrations of TRP in the river at R9 are derived from the main point sources, but as seen in the spatial TRP concentration variability of this lower river stretch, some dynamics are occurring that are as yet undefined.

6. Conclusions

This study increases the current published information on the $\delta^{18}O_{PO4}$ of various P sources and $\delta^{18}O_{PO4}$ values within a river catchment which had an $E\delta^{18}O_{PO4}$ of between +17.2 and +19.2‰. In answer to our first research question, our specific findings were:

- Two WWTPs appeared to have different and distinct $\delta^{18}O_{PO4}$ ranging between +16.4 and +19.6‰ with, on average, a 2.4‰ difference between them
- A dairy factory final effluent had $\delta^{18}O_{PO4}$ values ranging between +16.5 and +17.8‰
- Inorganic fertilizers had a very wide range of $\delta^{18}O_{PO4}$ ranging between +13.3 and +25.9‰
- Dairy farm animal waste slurries were consistently low, with a mean $\delta^{18}O_{PO4}$ of +13.5‰
- Domestic septic systems may have elevated $\delta^{18}O_{PO4}$ (>20‰) when compared to $E\delta^{18}O_{PO4}$ (and WWTPs), although more data is needed
- River channel bed sediment were found to have acid extractable $\delta^{18}O_{PO4}$ very similar to $E\delta^{18}O_{PO4}$ and along the channel network (+16.7 to +17.6‰)

In general, sources were often found to have a narrow range of $\delta^{18}O_{PO4}$ values very similar to the $E\delta^{18}O_{PO4}$ calculated for the river network, although a great deal of variability did occur within some sources. In response to our second research question, the $\delta^{18}O_{PO4}$ values measured within the river network show that:

- The $\delta^{18}O_{PO4}$ within the river network were all very similar ranging from +17.1 to +18.8‰
- The $\delta^{18}O_{PO4}$ within the main river stem was found to be no >0.3‰ different to that of $E\delta^{18}O_{PO4}$
- The $\delta^{18}O_{PO4}$ in the tributaries showed more variability and deviation from $E\delta^{18}O_{PO4}$, but only by between 0.4 and 0.9‰
- Rapid microbial cycling would appear to be occurring within the river network as demonstrated by the loss of the WWTP1 $\delta^{18}O_{PO4}$ signal over just a 2 km river stretch and through the transference of the enriched $\delta^{18}O_{H2O}$ signal in T4 into the TRP.

From this work it was not possible to draw any definitive conclusions using the $\delta^{18}O_{PO4}$ signature of P sources. In the study river, through either, or a combination of, the observations, we conclude that a) the majority of sources did not have suitably distinct $\delta^{18}O_{PO4}$ signatures from each other or $E\delta^{18}O_{PO4}$, or b) that within-river microbial cycling was rapidly removing any original source $\delta^{18}O_{PO4}$ values. While this tool may yet prove useful in examining riverine P sources and dynamics, more work is needed in the following critical areas:

1. Better source characterisation. It is fundamental that potential sources are characterised by higher between-, rather than within-source variation – and on the basis of this dataset, that poses some challenges as individual sources can be characterised by quite a range of tracer values. Further, many sources remain relatively uncharacterised, such as managed and unmanaged animal wastes, aquaculture, and channel bed sediment.
2. Better spatial characterisation. The dynamics of within-channel TRP are still poorly understood, let alone the $\delta^{18}O_{PO4}$ signals. If rapid cycling in rivers is occurring then it should be detectable, but higher spatial and temporal sampling resolutions are needed to resolve this uncertainty.

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