

Accepted Manuscript

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PII: S0883-2927(18)30147-1

DOI: [10.1016/j.apgeochem.2018.05.025](https://doi.org/10.1016/j.apgeochem.2018.05.025)

Reference: AG 4102

To appear in: *Applied Geochemistry*

Received Date: 14 February 2018

Revised Date: 29 May 2018

Accepted Date: 31 May 2018

Please cite this article as: Goody, D.C., Bowes, M.J., Lapworth, D.J., Lamb, A.L., Williams, P.J., Newton, R.J., Davies, C.L., Surridge, B.W.J., Evaluating the stable isotopic composition of phosphate oxygen as a tracer of phosphorus from waste water treatment works, *Applied Geochemistry* (2018), doi: 10.1016/j.apgeochem.2018.05.025.

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1 **Evaluating the Stable Isotopic Composition of Phosphate Oxygen as a** 2 **Tracer of Phosphorus from Waste Water Treatment Works**

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14

15 **Abstract**

16 Eutrophication is a globally significant challenge facing freshwater ecosystems and is closely
17 associated with anthropogenic enrichment of phosphorus (P) in the aquatic environment. Phosphorus
18 inputs to rivers are usually dominated by diffuse sources related to farming activities and point
19 sources such as waste water treatment works (WwTW). The limited availability of inherent labels for
20 different P sources has constrained understanding of these triggers for eutrophication in natural
21 systems. There have been substantial recent advances in the use of phosphate oxygen isotopes
22 ($\delta^{18}\text{O}_{\text{PO}_4}$) as a way of understanding phosphate sources and processing. Results from all previous
23 studies of the $\delta^{18}\text{O}_{\text{PO}_4}$ composition of WwTW effluent and septic tanks are combined together with
24 significant new data from the UK to assess $\delta^{18}\text{O}_{\text{PO}_4}$ compositions in waste water sources. The overall
25 average $\delta^{18}\text{O}_{\text{PO}_4}$ value is 13.9‰, ranging from 8.4 to 19.7‰. Values measured in the USA are much
26 lower than those measured in Europe. A strong positive correlation exists between $\delta^{18}\text{O}_{\text{PO}_4}$ and
27 $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, suggesting biologically-mediated exchange between the water molecules and the phosphate

ions. A comparison of $\delta^{18}\text{O}_{\text{PO}_4}$ and the offset from isotopic equilibrium showed a strong positive linear correlation ($\rho = 0.94$) for the data from Europe but no relationship for the historic USA data which may be due to recent advances in the extraction procedure or to a relative paucity of data. This offset is most strongly controlled by the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ rather than temperature, with greater offsets occurring with lower $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. Time series data collected over 8-24 hours for three sites showed that, although there were significant changes in the phosphate concentration, for a given WwTW the $\delta^{18}\text{O}_{\text{PO}_4}$ stayed relatively constant. Two new studies that considered instream processing of $\delta^{18}\text{O}_{\text{PO}_4}$ downstream of WwTWs showed mixing of the upstream source with effluent water but no evidence of biological cycling 3 km downstream. It is suggested that $\delta^{18}\text{O}_{\text{PO}_4}$ can be an effective tool to trace P from WwTWs provided the source of the effluent is known and samples are collected within a day.

38

Keywords: Eutrophication; Phosphate oxygen isotopes; biogeochemical cycling; Waste water; Rivers

40

41

42 1. INTRODUCTION

43 Phosphorus (P) is the rate-limiting factor for microbial and primary producer communities in many
44 freshwater systems including rivers and streams (Smith, 1984). It is well established that high human
45 population densities and intensive agriculture can lead to the oversupply of P to freshwaters, resulting
46 in eutrophication and a variety of other problems for the environment and human society (Schindler,
47 2012). Phosphorus inputs to rivers in agricultural catchments are usually dominated by diffuse sources
48 related to various farming activities (Carpenter et al., 1998), but in more heavily populated
49 catchments, point sources such as waste water treatment works (WwTWs) are of great importance
50 (Howarth et al., 1996; Jordan et al., 1997; Jarvie et al., 2006; Palmer-Felgate et al., 2010). One
51 response to eutrophication has been the introduction of P consents on WwTWs leading to capital and
52 operating investment in P removal through tertiary treatment (Pretty et al., 2003) and other
53 technologies. The treatment of waste water is a billion pound industry in the UK (Bailey, 2003) and

54 some of these costs are directed towards the removal of an estimated 44,000 tonnes of P entering its
55 WwTWs annually (Comber et al., 2013).

56 Whilst there is evidence that P removal at WwTW can significantly reduce the concentration of P in
57 receiving waters (Kinniburgh and Barnett, 2010), there remains uncertainty over whether changes in
58 WwTW-derived P loads directly control the composition or functioning of river biota (Neal et al.,
59 2006). This is important since legislative drivers (e.g Water Framework Directive, 2000) for future
60 investment in P removal at WwTWs go beyond assessments solely of river chemical status to also
61 consider the biological status of receiving waters. Uncertainty regarding the relationship between
62 WwTW-derived P and river biological status can be explained by four key factors:

- 63 i) Despite P-removal through tertiary treatment at specific WwTWs, elevated P
64 concentrations may continue to be driven by the cumulative effect of upstream point
65 sources (Jarvie et al., 2006);
- 66 ii) Diffuse sources of P may be sufficiently large that elevated P concentrations are
67 maintained despite the investment in P removal at WwTWs (Goody et al, 2017);
- 68 iii) The structure and functioning of river biota may only be indirectly controlled by WwTW-
69 derived P, mediated by additional physical chemical or biological processes within a river
70 (Hilton et al., 2006).
- 71 iv) Despite huge reductions in P concentration, the P concentrations are still in excess for
72 algal growth, and so aquatic ecology is unaffected by these P reductions (Bowes et al.,
73 2012)

74 These issues reflect limitations in understanding the contribution of different sources, the degree of
75 biogeochemical cycling and biological impact of P within the environment. Traditional approaches to
76 quantifying the importance of different sources of P include those based on in-river assessments,
77 usually mass flux budgets or spatial and temporal analysis of P concentration (Bowes et al., 2014),
78 those based on export coefficient approaches (Johnes et al., 1996), and those based on indirect tracers
79 of source such as boron (Vengosh et al., 1994). However, none of these approaches provides an

80 inherent label for specific sources of P. As a result, none offers a direct means of tracing sources and
81 in-river transformations of P, and none can be used to assess cause-effect relationships between P
82 sources and the response of river biota.

83 The past few years have seen substantial advances in the use of phosphate $^{18}\text{O}/^{16}\text{O}$ analysis ($\delta^{18}\text{O}_{\text{PO}_4}$)
84 as a way of identifying sources of phosphate pollution and examining its biological and abiological
85 processing (Young et al., 2009; Jaisi et al., 2010; McLaughlin et al., 2013; Gooddy et al., 2015;
86 Gooddy et al., 2016; Granger et al., 2017). The basis to the use of $\delta^{18}\text{O}_{\text{PO}_4}$ in aquatic ecosystems has
87 recently been reviewed by Davies et al. (2014).

88 Briefly, because the P-O bonds in inorganic phosphate (P_i) are resistant to inorganic hydrolysis under
89 typical temperature, pressure and pH conditions in the Earth's surface water and groundwater
90 ecosystems (O'Neil et al., 2003). Under these conditions, $\delta^{18}\text{O}_{\text{PO}_4}$ may reflect the isotope composition
91 of P sources within an ecosystem. In contrast, enzyme-catalysed reactions cleave P-O bonds leading
92 to exchange between the isotopes of O in P_i and O in a surrounding fluid, either within a cell or within
93 the extracellular environment (Blake et al., 2005). Intracellular metabolism of P involving the
94 inorganic pyrophosphatase enzyme results in rapid, temperature-dependent equilibrium fractionation
95 between O in P_i and O within the intracellular fluid. The latter is expected to be identical in O-isotope
96 composition to water-O in the extracellular environment. Given sufficient intracellular-extracellular
97 exchange of P_i to maintain non-lethal intracellular P_i concentrations, a temperature-dependent
98 equilibrium will be established between $\delta^{18}\text{O}_{\text{PO}_4}$ and water-O in the extracellular environment.
99 Negligible O isotope exchange occurs between P_i and water within ecosystems without biological
100 mediation (Tudge, 1960; Blake et al., 1997). The equilibrium oxygen isotope fractionation between
101 dissolved P_i and water ($\alpha_{\text{PO}_4\text{-H}_2\text{O}}$) at surface temperatures has recently been determined (Chang and
102 Blake, 2015), using laboratory solutions catalyzed by the inorganic pyrophosphatase enzyme. These
103 authors derived the equation:

104

$$105 \quad 10^3 \ln \alpha_{\text{PO}_4\text{-H}_2\text{O}} = 14.43 \times (10^3/T) - 26.54 \quad (1)$$

106

107 where T is in degrees Kelvin. Since:

108

$$109 \quad \alpha_{PO_4-H_2O} = (\delta^{18}O_{PO_4} + 1000) / (\delta^{18}O_{H_2O} + 1000) \quad (2)$$

110

111 by combining 1 and 2 above, expected equilibrium $\delta^{18}O_{PO_4}$ values may be calculated from:

112

$$113 \quad \delta^{18}O_{PO_4} = (\delta^{18}O_{H_2O} + 1000) \times e^{[14.43 \times (10^3/T) - 26.54] / 1000} - 1000 \quad (3)$$

114

115 In this paper the currently limited existing global literature for WwTW final effluent source values is
 116 synthesized and augmented with additional data collected as part of this study. This larger data set is
 117 then evaluated to provide greater understanding of the major factors controlling on $\delta^{18}O_{PO_4}$ values in
 118 waste water relative to equilibrium calculations in order to determine whether there has been any
 119 biological processing of P_i. Seasonal and daily variation in the source term is assessed by combining
 120 published data with new data collected at a sub-daily time interval from WwTW's. Instream transects,
 121 up to 3 km downstream of a WwTW, are compared to equilibrium values to determine whether the
 122 source term is preserved or processed rapidly by in-stream microbial cycling. Lastly we summarise
 123 the current state of $\delta^{18}O_{PO_4}$ knowledge with respect to WwTW effluents and highlight key areas of
 124 future work.

125

126 2. METHODS

127 2.1 Spot Sampling of WwTW

128 Effluent samples were collected at the final outfall from 16 sites spanning a range of WwTW person
 129 equivalents, as well as those which employ a range of secondary, tertiary and other treatment
 130 technologies (Table 1). Sufficient sample (1- 10 L) was collected to enable the generation of ~1 mg of
 131 silver phosphate (Ag₃PO₄) which is required for isotopic analysis. Samples were filtered on site using

132 high volume 0.45 μ m filter cartridges and water temperature was measured immediately following
133 collection. A 5mL sub-sample from each site was also taken for analysis of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$.

134 **2.2 Sub-Daily Sampling of WwTW**

135 The composition of WwTW effluent may vary significantly over a daily cycle reflecting both the
136 nature and volume of waste water that is treated. To understand better this variation and the impact it
137 may have on the P_i concentration and $\delta^{18}\text{O}_{\text{PO}_4}$, studies were undertaken on the final effluent of three
138 different WwTW. All of the treatment works studied were in relatively rural settings and so it is
139 assumed there were minimal industrial effluents entering the WwTW and indeed the influent was
140 relatively similar between the three, being situated within 10km² of each other in Oxfordshire, UK. By
141 contrast, each of the sites had different treatment processes (See Table 1, sites 14, 15 and 16).

142 At site 14 an automated sampler was used to collect 400mL samples at hourly intervals starting at
143 9am and finishing at 6am the following day. These were then bulked into 3 hour blocks to provide
144 sufficient mass for extraction and analysis of P_i . A data logger was also used at this site to provide a
145 continuous measure of the effluent temperature. At site 15, 8 samples were collected manually every
146 hour from 9am until 4pm. At site 16, difficulties with filtration meant that sufficient sample volumes
147 were only obtained for three samples collected at 9am, 1pm and 4pm.

148 **2.3 Sampling Upstream and Downstream Transects**

149 Two WwTW (sites 1 and 18) and their associated river systems were selected to evaluate whether
150 downstream changes in $\delta^{18}\text{O}_{\text{PO}_4}$ occurred, and if so, to provide insight into the fate of WwTW-derived
151 P within the river. Samples were collected in September over a period of an hour from the thalweg of
152 the river at one sample point upstream of the effluent outfall and at several points downstream, up to 3
153 km at site 1 and 0.75 km at site 18. The transect at site 18 was much shorter due to the intersection of
154 another tributary 0.8 km downstream of the WwTW. Stream samples were processed in the same
155 manner as the WwTW detailed above.

156 2.4 Sample preparation and isotope analysis

157 The method used to isolate P_i from water samples and precipitate Ag_3PO_4 for isotope analysis has
158 already been presented in Gooddy et al. (2016) and is described in detail in Lapworth et al. (2014).
159 Samples were processed within 24 h of collection and were stored in the dark at 4 °C prior to
160 processing. In brief, the majority of dissolved organic matter is first removed by passing the sample
161 through an organic exchange resin and P_i is then isolated from the remaining matrix using an anion
162 exchange resin. Phosphate is eluted from the anion exchange resin and chromatographically separated
163 from competing anions using 0.3 M KCl. Eluted fractions containing phosphate are then processed
164 using a modified McLaughlin et al. (2004) method to produce a final Ag_3PO_4 precipitate for $\delta^{18}O_{PO_4}$
165 analysis. Any residual organic matter is removed by treating the Ag_3PO_4 with a solution of 15%
166 hydrogen peroxide prior to analysis. Combined with the organic exchange resin, this is a significant
167 advance over methods that use a repeated $CePO_4$ precipitation (e.g. Li et al., 2011).

168 $^{18}O/^{16}O$ ratios of Ag_3PO_4 were analysed by thermal conversion to CO gas at 1400 °C in a TC–EA on-
169 line to a Delta Plus XL mass spectrometer (ThermoFinnigan, Bremen, Germany). $\delta^{18}O$ values versus
170 Vienna Standard Mean Ocean Water (VSMOW) were calculated by comparison with an internally run
171 laboratory standard (Alfa Aesar silver phosphate 99%). In the absence of an international Ag_3PO_4
172 reference material, we derived the $\delta^{18}O$ value of the laboratory standard by comparison with the
173 Ag_3PO_4 standard ‘B2207’ (supplied by Elemental Microanalysis Ltd, Okehampton, England),
174 measured in an inter-laboratory comparison to have a certified $\delta^{18}O$ value of +21.7‰ versus
175 VSMOW. CO yields of the Ag_3PO_4 samples were always within $\pm 10\%$ of those of the laboratory
176 standard, and any organic contamination was deemed negligible on the basis that samples contained
177 <0.2% carbon (based on separate elemental analysis). Precision on the measurement are consistently
178 <0.2‰ and all less than 0.3‰. On this basis, we consider any difference of >0.3‰ as a reasonable
179 indicator that any two samples have a different isotopic composition for a reason other than analytical
180 error.

181

182 3. RESULTS AND DISCUSSION

183 3.1 Comparison of Global Data

184 A compilation of inorganic phosphate and $\delta^{18}\text{O}_{\text{PO}_4}$ values for all currently published data for effluent
185 from WwTW is presented in Table 2. Previous studies have been undertaken in France, Sweden, the
186 UK and the USA. The manuscript reports additional data from 16 new sites all from the UK. The data
187 contained within Table 2 is a mixture of spot samples taken once, seasonal samples taken during
188 spring, summer, autumn and winter, and a mean of time series data taken over the period of a day.
189 Four Swedish sites were from septic tank outflows and included in this study as they are considered to
190 be comparable as sources of human waste water. All other samples were from WwTW outflow
191 effluents. Most of these effluents underwent primary and secondary treatments but only a few
192 underwent any form of tertiary P treatment, where the intention is to achieve PO_4 concentrations in
193 the final effluent <1 mg/L. Phosphate concentrations in the effluent ranged from 0.16 to
194 25.2 mg PO_4/L , with a mean concentration of 9.5 mg PO_4/L (σ 7.0, median 9.0 mg PO_4/L).

195 These WwTWs serve between ~500-40,000 person equivalents (PE), and these data show no
196 relationship between PE and PO_4 concentration or $\delta^{18}\text{O}_{\text{PO}_4}$. Limited data are available for levels of
197 effluent treatment in published studies, although from the new work presented here there appears to
198 be no clear relationship between $\delta^{18}\text{O}_{\text{PO}_4}$ and secondary or tertiary treatment processes.

199 For all the data, the average $\delta^{18}\text{O}_{\text{PO}_4}$ value was 13.9‰ (σ 3.2‰, median 14.2‰), and a range of 8.4-
200 19.7‰. Figure 1 shows box-plots of the measured $\delta^{18}\text{O}_{\text{PO}_4}$ grouped by country. There do appear to be
201 some clear geographical differences, particularly between measured values in the USA and those in
202 Europe, although the sample size is still relatively small. Based on our calculations equilibrium values
203 ranged from 3.4 to 20.0‰ with a mean of 15.8‰ (σ 4.2‰, median 17.3‰) (Table 2). Where
204 temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ were available and calculations could be made, 78% of samples had
205 measured values lower than the equilibrium value. All measured values from the USA were higher
206 than the equilibrium calculated values. This may reflect higher $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values (values ~-2‰,
207 McLaughlin et al., 2006) as well as higher temperatures and greater evaporation of water during the
208 treatment process (Young et al., 2009).

209 If no microbial cycling of P_i occurs during the treatment process then the isotopic composition of the
210 outflow effluent should simply reflect the mixture of $\delta^{18}O_{PO_4}$ values of P_i sources received from
211 wastewater network. Pyrophosphatase mediated intracellular microbial cycling will shift the $\delta^{18}O_{PO_4}$
212 towards the calculated isotopic equilibrium which will be determined by the $\delta^{18}O_{H_2O}$ and temperature
213 of the water in the WwTW. Figure 2 shows the positive correlation ($\rho = 0.72$) between $\delta^{18}O_{PO_4}$ and
214 $\delta^{18}O_{H_2O}$, suggesting that there is biologically-mediated exchange occurring between the water
215 molecules and the PO_4 ions. This is consistent with the use of secondary biological treatment at each
216 of the WwTWs presented, in which the transformation of organic P compounds to inorganic P
217 through enzyme hydrolysis, alongside the uptake and intracellular cycling of P, results in exchange of
218 oxygen atoms between water and PO_4 . However, in all cases $\delta^{18}O_{PO_4}$ is not at the expected
219 pyrophosphatase equilibrium value which indicates incomplete intracellular cycling, and so is
220 consistent with the high concentrations of P in WwTW effluents.

221 3.2 Seasonal and Temperature Influences

222 Microbial reactions are commonly controlled by temperature with greater reaction rates occurring at
223 higher temperatures. For biological processing of $\delta^{18}O_{PO_4}$ it might be expected therefore that higher
224 temperatures are associated with $\delta^{18}O_{PO_4}$ values closer to equilibrium. Similarly therefore, for a given
225 site, samples taken in the summer may be closer to equilibrium than those taken in winter.

226 Samples 18 to 21 (Table 2) have all been sampled in at least two seasons and so provide a comparison
227 to test the hypothesis that there is a relationship between P processing and season/temperature. Site 18
228 (WwTP in the River Beult catchment, UK) showed consistent $\delta^{18}O_{PO_4}$ values of around 16.2 ‰ from
229 January 2014 to September 2015 although is ~1.5‰ lower in September 2013. Between September
230 2013 and March 2015 the final effluent remained a fairly constant -1.2‰ away from equilibrium, but
231 this fell to -0.6‰ in September 2015. Samples from WwTW sites 19 and 20 (in the River Taw
232 catchment, UK) sampled at the same time showed markedly different values between the WwTW of
233 around 3‰. In terms of seasonal variation, site 19 was furthest from equilibrium in June but closer to
234 calculated equilibrium in December. By contrast, site 20 was furthest from equilibrium in December
235 but closer to calculated equilibrium in September. Samples taken from site 21 (California Bay, USA)

236 showed a difference of ~3‰ between sampling in October and January, although the sample taken in
237 January was closer to the calculated equilibrium value by more than 1‰.

238 In all of the cases from the UK there was some ~10°C variation in the temperatures observed during
239 sampling (site 18 a range of 8.8 to 20.3°C; site 19 a range of 9.5 to 18.0°C; and site 20 a range of
240 10.5 to 19.8 °C). For $\delta^{18}\text{O}_{\text{H}_2\text{O}}$, seasonal differences of around 0.6-0.9‰ were also observed at each of
241 the sites (site 18 a range of -7.32 to -6.84‰; site 19 a range of -5.57 to -6.35‰; and site 20 a range of
242 -5.62 to -6.31‰).

243 As temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ are the two variables in the equilibrium calculation, a comparison was
244 been made across the full data set to see if any relationship can be discerned between measured and
245 equilibrium $\delta^{18}\text{O}_{\text{PO}_4}$ values. Figure 3 shows the relationships between measured $\delta^{18}\text{O}_{\text{PO}_4}$ and the offset
246 from isotopic equilibrium of $\delta^{18}\text{O}_{\text{PO}_4}$ in terms of a) sample temperature and b) sample $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. For
247 data from Europe the goodness of fit for the difference between measured and offset from equilibrium
248 calculated $\delta^{18}\text{O}_{\text{PO}_4}$ is very strong ($\rho = 0.94$) suggesting there is a relationship between the source term
249 and the equilibrium. Data from the US however does not seem to show any clear relationship
250 ($\rho = 0.41$) which possibly reflects the use of an older analytical method for P_i extraction that is less
251 effective at removing organic carbon (see McLaughlin et al., 2006 and Goody et al., 2015).

252 For the samples from Europe, Figure 3a shows no convincing trend for a relationship between sample
253 temperature and the distance from equilibrium i.e. temperature of the effluent water alone is not a
254 good indicator that the $\delta^{18}\text{O}_{\text{PO}_4}$ will be closer or further from equilibrium. Figure 3b however does
255 show some quite strong clustering of the data, whereby samples with the more negative $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ are
256 further from equilibrium while the samples with more positive $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ fall closer to equilibrium. This
257 implies that, for this limited data set, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is a better predictor of how close the measured $\delta^{18}\text{O}_{\text{PO}_4}$
258 will be to the calculated equilibrium. Since rainfall values of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ are quite predictable due to
259 weather patterns and orography (Darling et al. 2003) this suggests the geographical location of the
260 WwTW could determine how close the measured $\delta^{18}\text{O}_{\text{PO}_4}$ is to the equilibrium value.

261 3.3 Diurnal changes in phosphate, $\delta^{18}\text{O}_{\text{PO}_4}$ and $\text{E}\delta^{18}\text{O}_{\text{PO}_4}$

262 Figure 4 shows time series data for three WwTWs from SE England. As reflected by the varying
263 degrees of treatment, and the presence or absence of chemical PO_4 stripping (Table 1), concentrations
264 varied from 2.35 mg PO_4 /L at site 14, to 0.35 mg PO_4 /L at Site 15 and 0.15 mg PO_4 /L at Site 16.
265 Each of the WwTWs showed a significant change in P_i concentrations over the sampling interval.
266 Over 24 hours at site 14 there was a 20% increase in P_i , at site 15 there is a 25% decrease over 7 hours
267 and at site 16 there was a 12% decrease also over 7 hours.

268 In contrast to the P_i concentration, $\delta^{18}\text{O}_{\text{PO}_4}$ values stayed relative constant over the sampling intervals.
269 For site 14 the mean $\delta^{18}\text{O}_{\text{PO}_4}$ was 14.5‰ (σ 0.3 ‰), at site 15 the mean was 16.5‰ (σ 0.2 ‰), and at
270 site 16 the mean was 11.5‰ (σ 0.3 ‰). Similarly, for equilibrium values at site 14 the mean $\delta^{18}\text{O}_{\text{PO}_4}$
271 was 16.9‰ (σ 0.05 ‰), at site 15 the mean was 16.5‰ (σ 0.1 ‰), and at site 16 the mean was 17.3‰
272 (σ 0.05 ‰).

273 One implication of this finding is that the treatment type appears to have an impact on the $\delta^{18}\text{O}_{\text{PO}_4}$
274 value, for example where chemical PO_4 stripping was employed (Site 16) $\delta^{18}\text{O}_{\text{PO}_4}$ was much lower. If
275 this was sorption of P to FeCl_2 or Al_2SO_4 , higher $\delta^{18}\text{O}_{\text{PO}_4}$ values would be expected in this system as
276 the isotopically lighter P^{16}O_4 is preferentially incorporated into sorbed/solid phases (Jaisi et al., 2010).
277 Clearly the kinetics of the reaction are important and require further investigation to fully understand.
278 However, it is also worth noting that for the UK sites in Table 1 there was no clear relationship
279 between treatment type and $\delta^{18}\text{O}_{\text{PO}_4}$ values, i.e. with chemical PO_4 stripping, lower $\delta^{18}\text{O}_{\text{PO}_4}$ values
280 were not necessarily observed. This strongly suggests that the P outflow from a WwTW is highly
281 dependent on the treatment technologies and conditions at the plant, although over a relatively short
282 period, the $\delta^{18}\text{O}_{\text{PO}_4}$ values remain constant even though the PO_4 concentrations change. This is in
283 contrast to the seasonal data where changes are seen, possibly due to a change in dominant P source
284 throughout the year. In terms of understanding WwTW as a source this is a positive finding as it
285 suggests over a normal daily sampling interval there is unlikely to be a significant change in the
286 $\delta^{18}\text{O}_{\text{PO}_4}$ value. The data suggest that WwTW effluent needs to be characterised locally for any

287 particular study (i.e. a global/regional mean cannot be assumed) and that at least seasonal temporal
288 characterisation is required.

289 **3.4 Instream Processing of WwTW Source**

290 Having established that over an 8-24 hour period that the $\delta^{18}\text{O}_{\text{PO}_4}$ value of final effluent from a
291 WwTW does not vary significantly, additional work was undertaken to determine whether or not this
292 source term is preserved downstream of the effluent input to the river. Figure 5 shows 2 transects
293 taken from different sites, including samples taken upstream and downstream of WwTWs. In both
294 cases it can be observed that there is a significant spike in P_i concentrations resulting from the input of
295 effluent from the WwTW although it is also important to note that both streams have significant
296 upstream concentrations of P_i (~0.4-0.5 mg PO_4/L) suggesting the river is not P limited.

297 At site 1, P_i had an upstream concentration of 0.38 mg PO_4/L . Effluent from the WwTW entered at
298 7.65 mg PO_4/L and this then decreased to 0.59 ± 0.04 mg PO_4/L in the downstream reach. There was
299 clearly significant dilution of the P_i emanating for the WwTW by the upstream river water. The
300 calculated equilibrium value 18.4‰ changes very little from upstream to downstream. The Effluent
301 water had a higher temperature (~2.5°C) and a higher $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (0.3‰) which when combined
302 produced a similar equilibrium value to the rest of the stream. Upstream, $\delta^{18}\text{O}_{\text{PO}_4}$ was 14.0‰ (-4.4‰
303 from equilibrium) which decreased to 11.1‰ (-7.2‰ from equilibrium) when the effluent water
304 entered the stream. As the effluent moved downstream the $\delta^{18}\text{O}_{\text{PO}_4}$ value increased slightly to an
305 average of 12.3 ± 0.3 ‰ (-6.2 ± 0.3 ‰ from equilibrium) but with no observed shift towards
306 equilibrium 3 km downstream of the WwTW.

307 At site 18, P_i had an upstream concentration of 0.47 mg PO_4/L . Effluent from the WwTW entered at
308 1.80 mg PO_4/L and this then stayed fairly constant at to 1.77 ± 0.01 mg PO_4/L in the downstream
309 reach. The small decrease in concentration reflected the large volume of the WwTW effluent relative
310 to the upstream flow. The calculated equilibrium value for upstream was 16.5‰. The calculated
311 equilibrium value for the effluent was 16.8‰ and further downstream this increased slightly to 17.0‰
312 The effluent water had a lower temperature (~2.9°C) and a higher $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (0.2‰). The slightly higher
313 equilibrium value further downstream resulted from a lower water temperature. Upstream, $\delta^{18}\text{O}_{\text{PO}_4}$

314 was 17.0‰ (+0.6‰ from equilibrium) which decreased to 16.1‰ (-0.6‰ from equilibrium) when the
315 effluent water entered the stream. As the effluent moved downstream the $\delta^{18}\text{O}_{\text{PO}_4}$ value increased very
316 slightly to an average of $16.2 \pm 0.1\text{‰}$ ($-0.6 \pm 0.1\text{‰}$ from equilibrium) but with no shift towards
317 equilibrium 0.75 km downstream of the WwTW.

318 In both cases river water $\delta^{18}\text{O}_{\text{PO}_4}$ samples were not at equilibrium. The $\delta^{18}\text{O}_{\text{PO}_4}$ values upstream also
319 strongly suggested there is a different source of P_i to the WwTW at the point of measurement.
320 Importantly, downstream of the WwTWs there was no significant shift towards the equilibrium value.
321 This indicates that there was no rapid or significant microbial processing of the P and the source term,
322 allowing for mechanical mixing, was therefore retained. This enabled tracing of the effluent down to
323 distances of 3 km, and quite possibly further depending on the river network pattern and flow,
324 microbial activity, as well as downstream inputs of additional sources of P. These data are consistent
325 with the conclusion that the concentration of P_i upstream of the WwTWs was already in excess of
326 metabolic requirements, meaning that WwTW-derived P was not closely coupled to the metabolism
327 of in-river biota. However, recent experimental work (Chang et al., 2015) suggests microbial reaction
328 $t_{1/2}$ times are of the order of several hours depending on temperature which would be equivalent to
329 more than 10 km downstream from a WwTW discharging into a moderately flowing river. Hence
330 little or no metabolism of P would be observed.

331

332 4 CONCLUSIONS

333 This study has shown there can be considerable variability between the $\delta^{18}\text{O}_{\text{PO}_4}$ values in the effluent
334 of different WwTWs. This does not appear to be related to treatment type or population equivalents.
335 There are also significant differences in $\delta^{18}\text{O}_{\text{PO}_4}$ observed for a given WwTW between seasons,
336 although this study suggests the dominant control on difference between measured $\delta^{18}\text{O}_{\text{PO}_4}$ and
337 isotopic equilibrium is the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ rather than temperature although more data is need to confirm this.
338 Studies examining diurnal cycles suggested that, although the P_i concentration of the effluent water
339 changed markedly, there was no comparable variation in the $\delta^{18}\text{O}_{\text{PO}_4}$ values. As such the $\delta^{18}\text{O}_{\text{PO}_4}$ value

340 from an effluent recorded in the morning could be assumed to be the same as the value recorded
341 throughout the day. When $\delta^{18}\text{O}_{\text{PO}_4}$ is monitored downstream of a WwTW, there is no evidence of
342 processing of P up to a distance of at least 3 km and the measured value is a reflection of the upstream
343 P source mixing with the effluent. This is due to the system having an excess of P (i.e. not P limited)
344 but also due to the reaction times required for biotic cycling.

345 This study builds significantly on the earlier work of Gruau et al. (2005), who cast doubt on the use of
346 $\delta^{18}\text{O}_{\text{PO}_4}$ as a tracer as a means to differentiate between fertilisers and effluents due to the overlap in
347 isotopic source values. Based on this study and using a much improved extraction method for
348 Ag_3PO_4 , which is better suited to processing effluents compared with the previous studies of both
349 Gruau et al (2005) and Young et (2009), it is considered that $\delta^{18}\text{O}_{\text{PO}_4}$ can be used to both trace
350 WwTW effluents and to also understand the metabolism of WwTW-derived P in waters. For this, you
351 simply need a difference between effluent $\delta^{18}\text{O}_{\text{PO}_4}$ and river $\delta^{18}\text{O}_{\text{PO}_4}$ immediately upstream. From the
352 work presented here, it is recommended that the effluent sampling and tracing downstream are carried
353 out on the same day due to both seasonal variations and the range of values obtained from different
354 WwTWs.

355 However, based on the variations observed both between and within countries, further work is
356 required to determine if variation in final effluent $\delta^{18}\text{O}_{\text{PO}_4}$ reflects differences in sources and loads of
357 P to individual WwTWs, and hence differences in $\delta^{18}\text{O}_{\text{PO}_4}$ within influent P sources. Differences in
358 antecedent weather conditions and hence WwTW residence time is also an important consideration
359 that needs to be addressed to improve understanding. Lastly, further fundamental work is required to
360 understand the isotopic fractionation that is potentially imposed by different treatments within a
361 WwTW and whether $\delta^{18}\text{O}_{\text{PO}_4}$ can be used to optimise these processes.

362

363 **Acknowledgements**

364 The research was funded by the UKs Natural Environment Research Council (NERC) National
365 Capability resources devolved to the British Geological Survey and through the NERC Isotope

366 Geoscience Facility Grant IP-1522-0515. The authors are grateful to the two anonymous reviewers
367 whose comments have significantly improved the manuscript. This paper is published with permission
368 of the Executive Director, British Geological Survey (NERC).

369

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Table 1. Details of WwTWs sampled in the UK

Site	Person Equivalents		Treatments		
			Secondary	Tertiary	Other
1	512	Filters		Drum filters	
2	2449	Activated Sludge		None	
3	1015	Filters		Tertiary filters	
4	5318	Activated Sludge		None	
5	40665	Activated Sludge		Tertiary filters	
6	11413	Filters		Sand filters	
7	1168	Filters		None	
8	23759	Filters		Sand filters	Iron chloride
9	4291	Filters		None	
10	889	Filters		None	
11	20985	Filters		None	
12	1537	Filters		Tertiary Filters	
13	13028	Filters		None	
14	20822	Filters		Disk Filters	
15	4790	Filters		Disk Filters	Iron chloride
16	7177	Filters		Disk Filters	Aluminium sulphate

Table 2. Synthesis of global data for sewage treatment works (1-33) and septic tank outflows (34-37). Sites 14-16 multiple samples have been taken over a day (14 n = 8; 15 n = 8; 16 n = 3) and mean values are presented. Sites 18-21 samples have been taken from the same site over a several seasons (RB = River Beult, RT = River Taw, CB = California Bay).

Site	Country	PO ₄ mg/L	$\delta^{18}\text{O}_{\text{PO}_4}$ ‰	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ‰	T °C	$\text{E}\delta^{18}\text{O}_{\text{PO}_4}$ ‰	Measured- $\text{E}\delta^{18}\text{O}_{\text{PO}_4}$ ‰	Data Source
1	UK	7.65	11.1	-6.13	10.6	18.3	-7.2	this study
2	UK	15.7	8.7	-7.97	9.2	16.7	-8.0	this study
3	UK	15.0	10.9	-8.36	8.8	16.4	-5.5	this study
4	UK	11.9	15.1	-6.57	10.2	18.0	-2.9	this study
5	UK	14.3	14.2	-7.50	11.3	16.8	-2.6	this study
6	UK	25.2	11.6	-7.82	10.8	16.6	-5.0	this study
7	UK	14.0	11.4	-7.41	8.0	17.5	-6.1	this study
8	UK	19.1	12.9	-6.74	9.6	17.9	-5.0	this study
9	UK	2.50	15.8	-6.68	8.4	18.2	-2.4	this study
10	UK	17.1	9.4	-7.63	8.7	17.1	-7.7	this study
11	UK	20.7	14.1	-6.52	10.9	17.9	-3.8	this study
12	UK	21.2	11.5	-7.65	8.1	17.2	-5.7	this study
13	UK	17.1	14.3	-8.16	8.6	16.6	-2.3	this study
14	UK	2.35	14.5	-6.88	14.5	16.9	-2.4	this study
15	UK	0.35	14.0	-7.00	15.8	16.5	-2.5	this study
16	UK	0.16	11.5	-6.59	13.6	17.3	-5.8	this study
17	UK	1.10	15.8	-6.53	12.7	17.5	-1.8	Davies 2016
18(Sep2013)	UK,RB	0.92	14.7	-6.84	20.3	15.9	-1.2	Goody et al. 2016
18(Jan2014)	UK,RB	1.26	16.2	-7.32	9.6	17.3	-1.1	Goody et al. 2016
18(Mar2015)	UK,RB	1.19	16.2	-7.32	8.8	17.4	-1.3	Davies 2016
18(Sep2015)	UK,RB	1.80	16.1	-6.87	15.2	16.8	-0.6	Davies 2016
19(Jun2013)	UK,RT	7.58	19.7	-6.35	16.0	17.1	2.6	Granger et al. 2017
19(Sep2013)	UK,RT	6.96	19.6	-5.57	18.0	17.6	2.0	Granger et al. 2017
19(Dec2013)	UK,RT	3.70	18.2	-6.11	9.5	18.6	-0.4	Granger et al. 2017
20(Jun2013)	UK,RT	11.4	16.4	-6.31	17.2	17.0	-0.6	Granger et al. 2017
20(Sep2013)	UK,RT	10.0	16.9	-5.62	19.8	17.2	-0.3	Granger et al. 2017
20(Dec2013)	UK,RT	6.95	16.9	-5.88	10.5	18.6	-1.7	Granger et al. 2017
21(Oct2005)	USA,CB		9.1			7.3	1.8	Young et al. 2009
21(Jan2005)	USA,CB		12.3			11.6	0.7	Young et al. 2009
22	USA		8.4					McLaughlin et al. 2006
23	USA		11.1					McLaughlin et al. 2006
24	USA		8.4			7.3	1.1	Young et al. 2009
25	USA		11.1			8.4	2.7	Young et al. 2009
26	USA		8.7			3.4	5.3	Young et al. 2009
27	USA		9.0			3.5	5.5	Young et al. 2009
28	USA		13.6			11.5	2.1	Young et al. 2009
29	France	10.8	18.4	-4.3	12.0	20.0	-1.6	Gruau et al. 2005
30	France	9.13	16.6	-6.0	11.0	18.4	-1.8	Gruau et al. 2005
31	France	8.16	17.7	-4.2	12.7	19.9	-2.2	Gruau et al. 2005
32	France	10.8	18.0	-5.0	11.0	19.4	-1.4	Gruau et al. 2005
33	France	8.81	17.6	-4.3	13.8	19.6	-2.0	Gruau et al. 2005
34	Sweden		13.7					Tonderski et al. 2017
35	Sweden		16.2					Tonderski et al. 2017
36	Sweden		13.2					Tonderski et al. 2017
37	Sweden		14.5					Tonderski et al. 2017

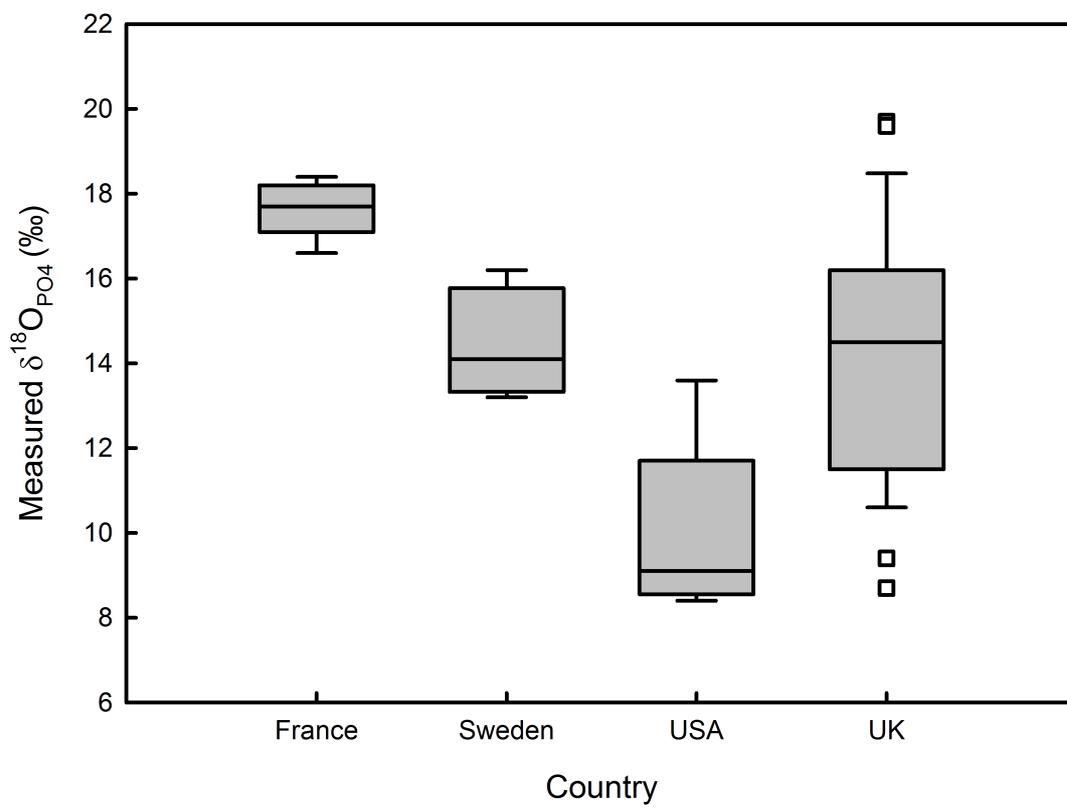


Figure 1. Measured $\delta^{18}\text{O}_{\text{PO}_4}$ values for effluent from each of the countries studied. France $n = 5$; Sweden $n = 4$; USA $n = 9$; UK $n = 27$.

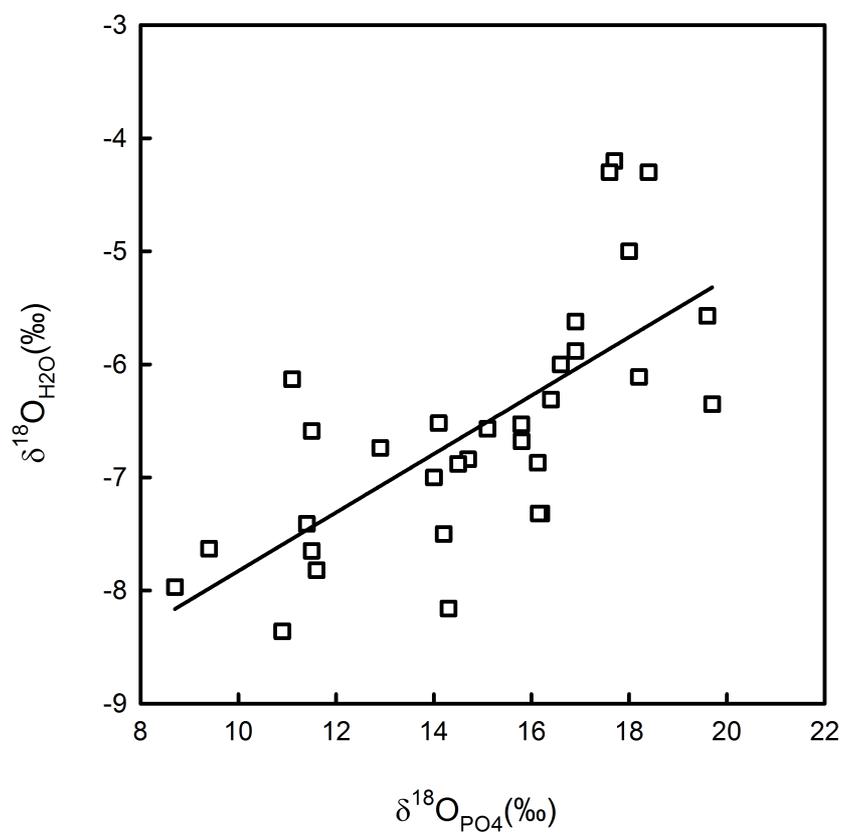


Figure 2. Cross plot of $\delta^{18}\text{O}_{\text{PO}_4}$ and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ for all effluent samples

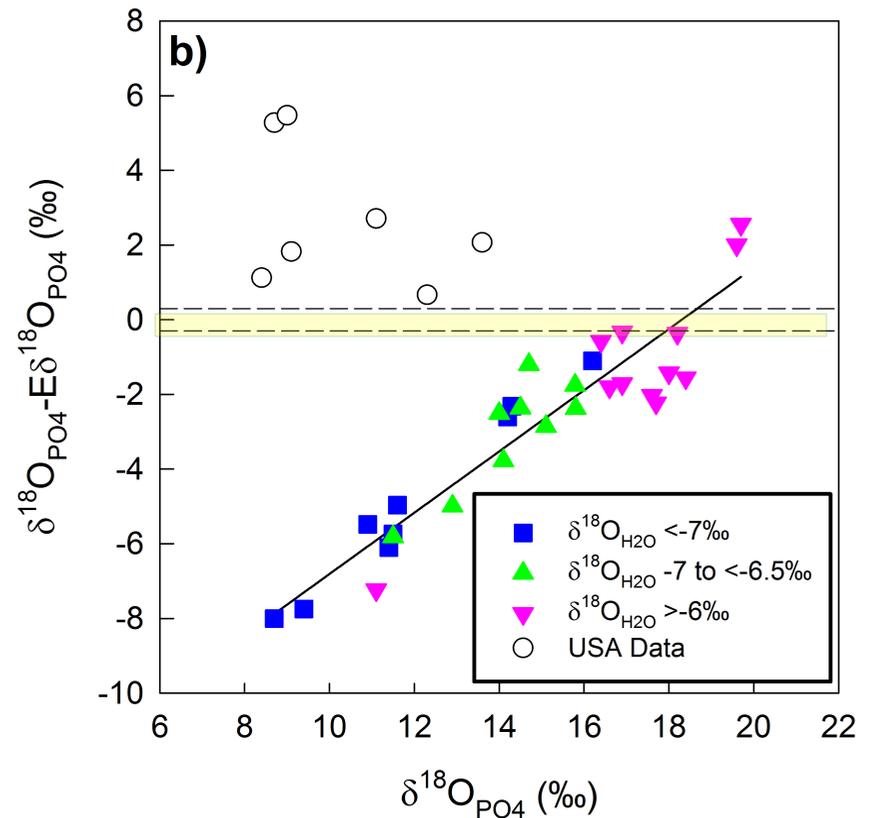
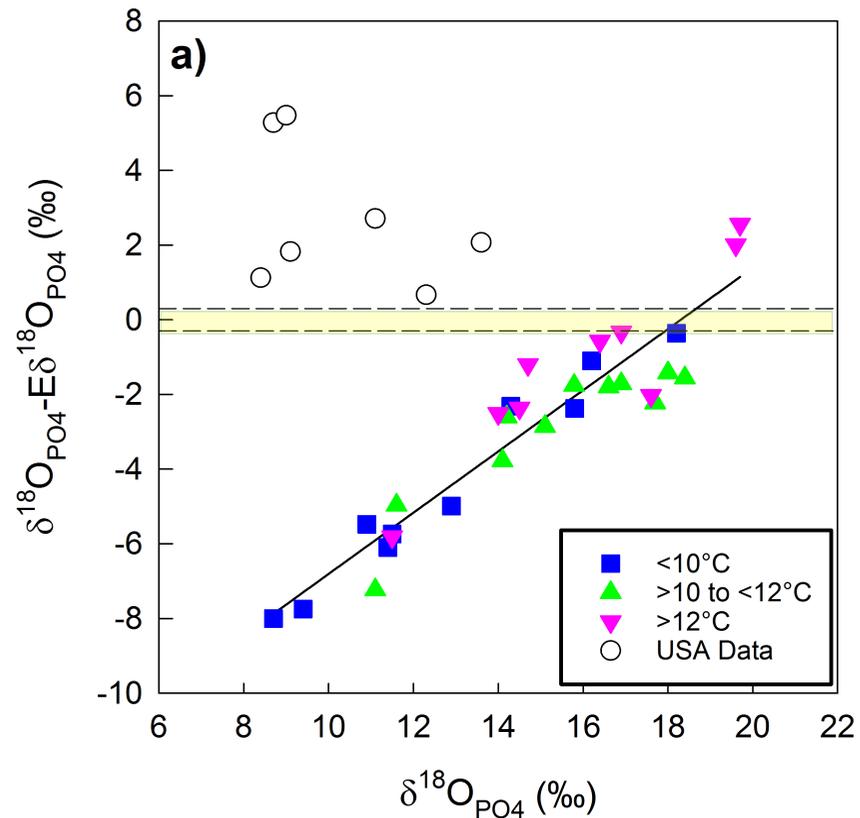


Figure 3 a) the offset from isotopic equilibrium ($E\delta^{18}\text{O}_{\text{PO}_4}$) of $\delta^{18}\text{O}_{\text{PO}_4}$ with the data displayed in three temperature ranges b) the offset from isotopic equilibrium ($E\delta^{18}\text{O}_{\text{PO}_4}$) of $\delta^{18}\text{O}_{\text{PO}_4}$ with the data displayed in three ranges of $\delta^{18}\text{O}_{\text{H}_2\text{O}}$

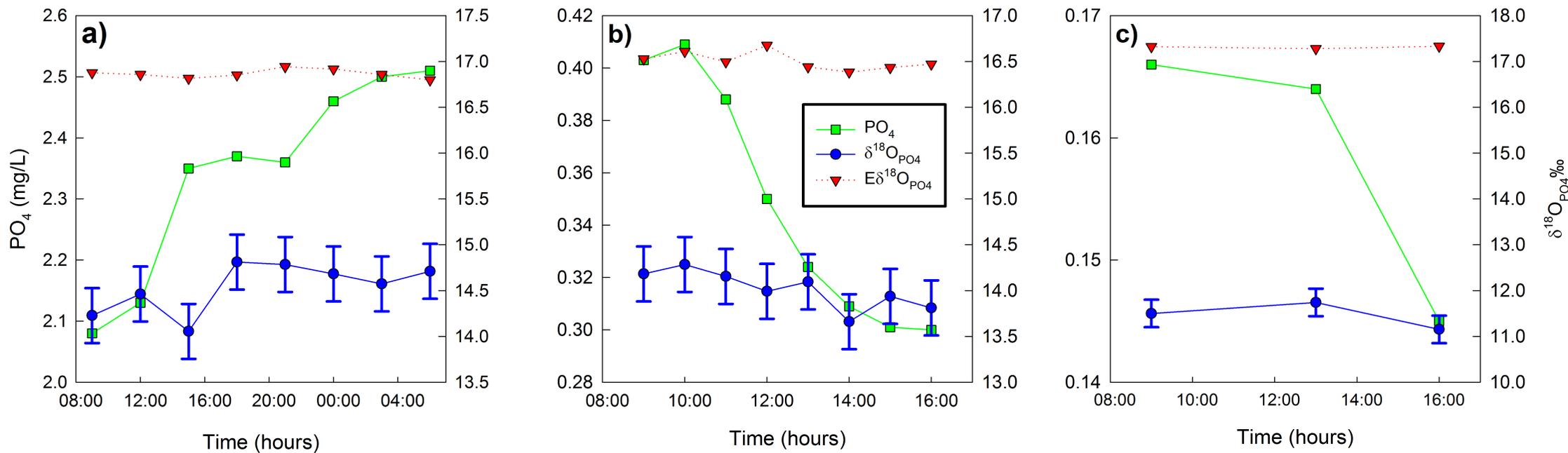


Figure 4. Time series data for PO_4 , $\delta^{18}\text{O}_{\text{PO}_4}$ and equilibrium ($E\delta^{18}\text{O}_{\text{PO}_4}$) at 3 sites where different treatment technologies have been employed. (a) Site 14 disk filters only; (b) Site 15 disk filters and iron chloride; (c) Site 16 disk filters and aluminium sulphate

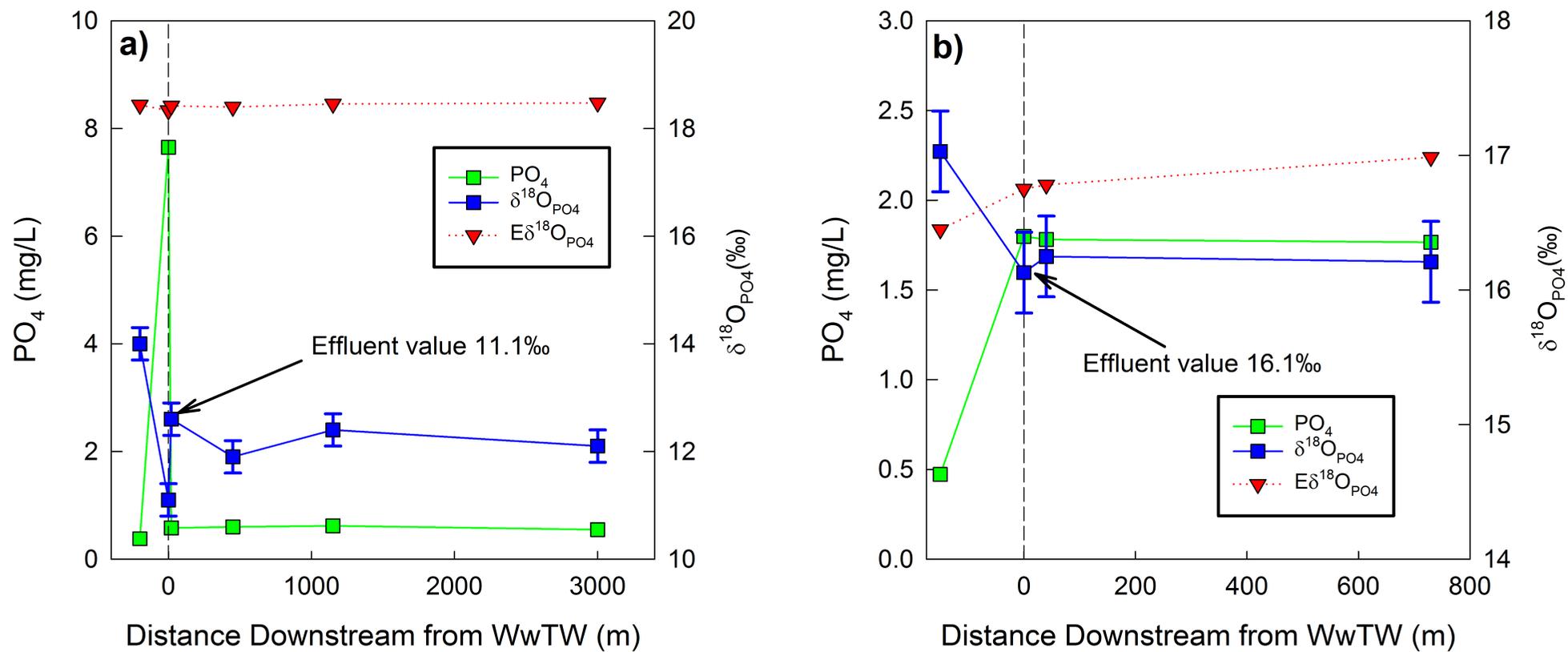


Figure 5. Measurements upstream and downstream of SRP, $\delta^{18}\text{O}_{\text{PO}_4}$ and calculated equilibrium ($E\delta^{18}\text{O}_{\text{PO}_4}$) from a) Site 1 and b) Site 18.

Highlights

- Extensive dataset of phosphate oxygen isotope ($\delta^{18}\text{O}_{\text{PO}_4}$) values from waste water effluents compiled
- Data shows differences in $\delta^{18}\text{O}_{\text{PO}_4}$ values between countries
- $\delta^{18}\text{O}_{\text{PO}_4}$ is found to be relatively constant over a 24 hour period despite changes in SRP
- Difference between $\delta^{18}\text{O}_{\text{PO}_4}$ and equilibrium values is controlled by water isotope composition
- $\delta^{18}\text{O}_{\text{PO}_4}$ effluent values can be preserved up to 3km downstream of the effluent source