1   **$\delta^{18}O$ as a tracer of PO_4^{3-} losses from agricultural landscapes**

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3   Naomi S. Wells[1,2*], Daren C. Gooddy[3], Mustefa Yasin Reshid[1], Peter J. Williams[3], Andrew C.

4   Smith[4], Bradley D. Eyre[1]

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6   [1]Centre for Coastal Biogeochemistry, School of Environment, Science & Engineering, Southern

7   Cross University, PO Box 157, East Lismore, 2480 NSW, Australia

8   [2]Department of Soil & Physical Sciences, Faculty of Agricultural & Life Sciences, Lincoln

9   University, Lincoln 7647, New Zealand

10   [3]British Geological Survey, Wallingford, Oxfordshire, OX10 8BB, UK

11   [4]British Geological Survey, Keyworth, Nottinghamshire, NG12 5GG, UK

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14   *Author for correspondence: naomi.wells@lincoln.ac.nz

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18   **Highlights**

19   • Isotope fingerprints of soil and fertiliser PO_4^{3-} ($\delta^{18}O_P$) vary within catchments

20   • Source mixing and biological turnover affect $\delta^{18}O_P$ signatures exported downstream

21   • Tracing agricultural pollution with $\delta^{18}O_P$ requires accounting for soil zone dynamics

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Abstract

Accurately tracing the sources and fate of excess PO_4^{3-} in waterways is necessary for sustainable catchment management. The natural abundance isotopic composition of O in PO_4^{3-} ($\delta^{18}O_P$) is a promising tracer of point source pollution, but its ability to track diffuse agricultural pollution is unclear. We tested the hypothesis that $\delta^{18}O_P$ could distinguish between agricultural PO_4^{3-} sources by measuring the integrated $\delta^{18}O_P$ composition and P speciation of contrasting inorganic fertilisers (compound v rock) and soil textures (sand, loam, clay). $\delta^{18}O_P$ composition differed between the three soil textures sampled across six working livestock farms: sandy soils had lower overall $\delta^{18}O_P$ values (21 ± 1 ‰) than the loams (23 ± 1 ‰), which corresponded with a smaller, but more readily leachable, PO_4^{3-} pool. Fertilisers had greater $\delta^{18}O_P$ variability (~8‰) driven by both fertiliser type and manufacturing year. Upscaling these values showed that 'agricultural soil leaching' $\delta^{18}O_P$ signatures could span from $18 - 25$ ‰, and are influenced by both fertiliser type and the time between application and leaching. These findings emphasise the potential of $\delta^{18}O_P$ to untangle soil-fertiliser P dynamics under controlled conditions, but that its use to trace catchment-scale agricultural PO_4^{3-} losses is limited by uncertainties in soil biological P cycling and its associated isotopic fractionation.
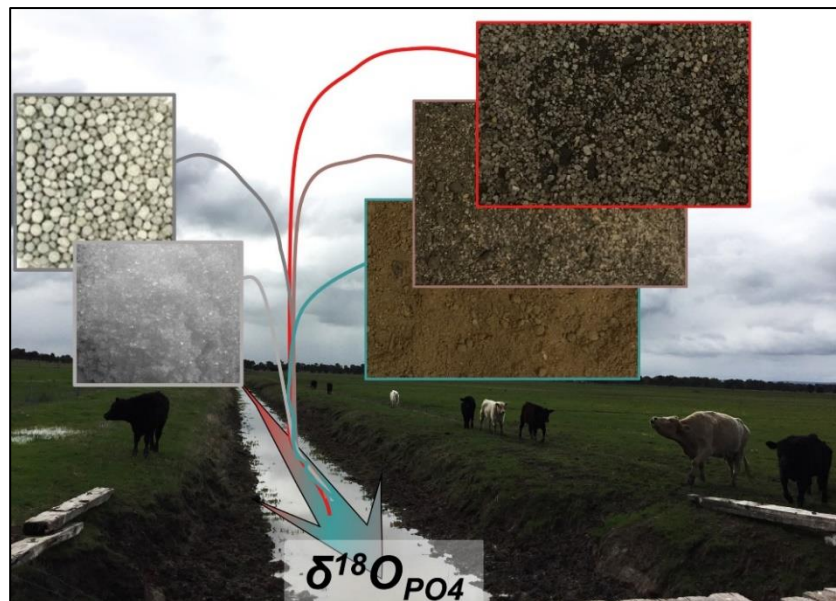
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1. Introduction

Population growth and agricultural intensification has doubled phosphorus (P) inputs to global rivers (Beusen et al., 2016). While point source (e.g., wastewater treatment plants) P pollution can be effectively managed, diffuse P export from agriculture remains a pernicious water quality threat (Haygarth et al., 2005). This is in part due to the difficulty tracing P from its origin (e.g., fertiliser application) through the soil zone (where multiple biological and abiotic reactions can occur) to the receiving waters (Melland et al., 2018). New tools to identify excess P transported from soils to waterways via leaching and overland flow (henceforth 'export') are required to mitigate aquatic ecosystem degradation from eutrophication (e.g., hypoxia, fish kills).

Calls to use the isotopic composition of oxygen within PO_4^{3-} ($\delta^{18}O_P$) as a P tracer date back >10 years (Davies et al., 2014; Gruau et al., 2005; Young et al., 2009). This stems from evidence that PO_4^{3-} sources (wastewater, tap water, fertilisers) can have distinct $\delta^{18}O_P$ signatures (Gooddy et al., 2018; Gooddy et al., 2015; Granger et al., 2017b). Additionally, knowledge that intracellular reactions with phosphatase enzymes impart a predictable temperature-dependent equilibrium signature as oxygen is exchanged between PO_4^{3-} and the surrounding water (Chang and Blake, 2015; Gross and Angert, 2015; Jaisi et al., 2011), means $\delta^{18}O_P$ can also indicate ecosystems P cycling efficiency (Paytan et al., 2017; Pistocchi et al., 2017). Numerous studies propose using $\delta^{18}O_P$ source and transformation data to constrain catchment-scale P pollution dynamics (Gooddy et al., 2016; Granger et al., 2017b; Ishida et al., 2019; Tonderski et al., 2017). However, models are limited by uncertainty around the $\delta^{18}O_P$ 'signatures' generated by different catchment P sources.

Controls on agricultural soil $\delta^{18}O_P$ values are poorly understood. This is a critical knowledge gap as agricultural soils can dominate catchment P exports (Metson et al., 2017). Previous reviews show soil $\delta^{18}O_P$ ranges from $11 - 25$ ‰ (Tian et al., 2020), and that agricultural soil $\delta^{18}O_P$ tends towards the higher end of the range predicted for biological equilibration with long-term soil water trends (Granger et al., 2017a; Ishida et al., 2019; Polain et al., 2018; Tamburini et al., 2010; Tian et al., 2020). Current models propose that systems reflect 'source' $\delta^{18}O_P$ values (e.g., fertilisers) when

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81 PO_4^{3-} is in excess of biological demand, and shift towards equilibrium when PO_4^{3-} is limiting due to

82 enhanced P recycling (Bauke, 2020). Yet $\delta^{18}O_P$ variability (~5‰ across a single paddock (Granger

83 et al., 2017a)) suggests additional factors are at play. And if P limitation were the main determinant

84 of $\delta^{18}O_P$ reaching equilibrium, soil $\delta^{18}O_P$ should correlate with PO_4^{3-} concentration, but this is not

85 typically observed (Granger et al., 2017a; Tamburini et al., 2010; Tian et al., 2020). Fertilisers

86 themselves cause further difficulty for defining the 'agricultural' $\delta^{18}O_P$ range: fertiliser $\delta^{18}O_P$

87 composition is variable (Gruau et al., 2005), but could account for up to 80 % of agricultural soil

88 PO_4^{3-} exports (McLaren et al., 2016; Nash et al., 2019).

89 The aim of this study was to parameterise the potential of $\delta^{18}O_P$ to trace agricultural PO_4^{3-}

90 export at the catchment scale. We hypothesised that fertiliser inputs and soil P fertility combine to

91 create unique $\delta^{18}O_P$ signatures. We tested this by measuring the $\delta^{18}O_P$ composition of contrasting

92 fertilisers and soils across an 1,800 km^2 catchment, then using mixing models to define the possible

93 range of exported $\delta^{18}O_P$ created by variable management (fertiliser application), biology (PO_4^{3-}

94 turnover), and hydrology (time before leaching, equilibrium $\delta^{18}O_P$ values).

95

96 **2. Materials & Methods**

97 2.1 Site description

98 Soil and fertiliser samples were collected from the 1,800 km^2 Peel-Harvey catchment in

99 southwestern Australia (Supporting Information (SI) S1 for maps). The catchment is flat (slope:

100 0.0015), with negligible elevation or aspect differences. Soils are P deficient, but their P retention

101 capacity varies with the underpinning geology: the alluvial soils have a clay texture and quickly

102 chemically immobilise fertiliser P inputs, while P is easily exported from the sand textured soils

103 formed on ancient dunes (Bolland and Allen, 1998; McArthur and Bettenay, 1974). The region has a

104 Mediterranean climate: hot, dry summers (27°C, 190 mm rain) v cool, wet winters (18°C, 1,000

105 mm rain). Fertilising to compensate for P immobilisation (clays) or leaching (sands) has contributed

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106 to the hyper-eutrophication of the Peel-Harvey Estuary (Valesini et al., 2019). Pasture soils still

107 contain twice the optimal P range and leach 140 T P y^{-1} (Rivers et al., 2013).

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109 2.2 Sample collection

110   Fertiliser isotopic variability ($\delta^{18}O_{P(fert)}$) was constrained by analysing synthetic P fertilisers

111 from CSBP (Perth, Western Australia). These covered dominant fertiliser types: monoammonium

112 phosphate (MAP), superphosphate (SP), and a proprietary compound fertiliser with 16% N, 9% P,

113 14% S (AG). All three are water soluble (Nash et al., 2019). AG and SP were obtained for five

114 manufacturing years (2013-2017) and MAP from one year (2017). These fertilisers are the products

115 available to farmers in the catchment, but the exact mix applied to the sampled plots is unknown.

116   Soil samples (0 – 10 cm) were collected from 21 paddocks with contrasting soil textures

117 (clay, sand, loam) on six ~2 km^2 farms across the catchment (SI S1). Sampling was timed to winter

118 (July 2017) when soil PO_4^{3-} export occurs (Summers et al., 1999). Management effects, including

119 fertiliser contamination of the measured soil $\delta^{18}O_P$ composition ($\delta^{18}O_{P(soil)}$), were minimised by

120 selecting farms with the same land use (beef grazing) and vegetation (ryegrass/clover pasture)

121 participating in a multi-year P fertiliser minimisation trial. Triplicate samples (0-10 cm) spaced 10

122 m apart were collected over three transects from each paddock, and triplicates bulked to produce

123 three samples per paddock, which were homogenised, sieved, and air dried. Around this period ten

124 precipitation events were sampled for oxygen isotopes in water ($\delta^{18}O_{H2O}$).

125

126 2.3 Sample analyses

127   All 63 soils (21 paddocks x 3 replicates) were analysed for pH, organic matter, and P

128 concentration. A subset of 25 soils, selected to cover the different farms and textures and using P

129 concentration to identify representative samples, were analysed for $\delta^{18}O_{P(soil)}$.

130   Soil pH was measured in 2.5:1 deionised water:dry soil extracts. Soil organic matter was

131 determined via ignition (550 C for 4 h), and total (P_{total}) and organic (P_{org}) P concentration measured

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132 by extracting ignited v un-ignited soils with 1M H_2SO_4 (50:1) and measuring filtered extractant P

133 concentration via ICP (Saunders and Williams, 1955). Because chemical bonding between PO_4^{3-}

134 and the soil matrix means that the amount of PO_4^{3-} in P_{total} may not correspond to the amount of

135 biologically available or leachable P, PO_4^{3-} concentrations were additionally measured in sequential

136 extractions as per (Hedley et al., 1982) in order to parameterise potential export and turnover rates.

137 This defines PO_4^{3-} by decreasing extractability as a proxy for availability (Gu and Margenot, 2020).

138 Briefly, 2 g dry soil were extracted with 40 ml deionised water, 0.5M $NaHCO_3$ (pH 8.5), 0.1M

139 NaOH, and 1M HCl. Tubes were agitated for 18 h (rotary shaker), centrifuged (15 minutes), filtered

140 (Whatman 0.45 μm) into duplicate 12 ml vials, stored at 4°C, and PO_4^{3-} concentrations analysed via

141 flow injection analysis after neutralising NaOH and $NaHCO_3$ extracts.

142     $\delta^{18}O_{P(soil)}$ was measured on the total PO_4^{3-} extractable with 1M HCl (P_{TIP}). This enabled us

143 to directly compare values across strongly contrasting soil textures, as preliminary tests showed

144 clays had insufficient H_2O extractable PO_4^{3-} for $\delta^{18}O_P$ analyses, while sands had insufficient PO_4^{3-}

145 in the more tightly bound fractions. Using P_{TIP} is also advantageous because, by capturing the

146 majority of soil PO_4^{3-}, it integrates the daily/seasonal P fluctuations observed in the more easily

147 extracted fractions (Angert et al., 2011). So while sequential chemical extractions are useful

148 indicators of the amount of soil PO_4^{3-} likely to be exported (Rupp et al., 2018) the P_{TIP} $\delta^{18}O_{P(soil)}$

149 provides a more robust and scalable soil 'fingerprint': extracted PO_4^{3-} 'fractions' not actually exist

150 in soils as discrete pools (Gu and Margenot, 2020) and do not reflect the potential biological

151 recycling over export-relevant timeframes (Helfenstein et al., 2020; Wang et al., 2021).

152   The $\delta^{18}O_P$ compositions of soils ($n = 25$) and fertilisers ($n = 11$) were measured following

153 Tamburini et al. (2010) Extractions were carried out at BGS (Wallingford) and isotope analyses at

154 BGS (Keyworth). Briefly, 25 g dry soil (or 2 g fertiliser) were extracted overnight with 100 ml 1M

155 HCl, centrifuged, and filtered. Dissolved organic matter was removed with DAX resin (20 ml), then

156 ammonium phospho-molybdate precipitated with 4.2M ammonium nitrate and ammonium

157 molybdate (dissolved in ammonium citrate) and re-precipitated as magnesium ammonium

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158   phosphate. After removing cations (AG50 X8 resin), silver phosphate (Ag_3PO_4) was precipitated

159   using 5 ml of silver ammine solution. Triplicate subsamples (300 µg) of the produced Ag_3PO_4 were

160   weighed into silver capsules and the $\delta^{18}O_P$ composition determined via thermal conversion

161   elemental analyser (TC-EA, ThermoFinnigan, Germany) at 1400°C with graphite and glassy carbon

162   chips, coupled to a Delta+XL mass spectrometer (ThermoFinnigan, Germany). Triplicates'

163   precision was ≤0.3‰. Sample CO yield relative to Ag_3PO_4 standards was checked to ensure

164   deviations <10%. $\delta^{18}O_P$ values were calculated with an internal Ag_3PO_4 standard, ALFA-1 ($\delta^{18}O$:

165   14.2‰). There are no international reference materials, so ALFA-1 was calibrated to the Ag_3PO_4

166   standard 'B2207' (Elemental Microanalysis Ltd.) from an inter-laboratory comparison. Oxygen

167   isotope ($^{18/16}O$) values are reported in δ ‰ v VSMOW.

168

169   2.4 Calculations

170   Soil organic carbon (C_{org}) was estimated as 0.516×loss-on-ignition (Jensen et al., 2018).

171   Mineralisation of P_{org} to PO_4^{3-}, which can affect $\delta^{18}O_{P(soil)}$ values (Gross and Angert, 2015), was

172   parameterised as $P_{min(14)}$ (net mineralisation over 14 days) (Achat et al., 2010) based on measured

173   soil organic v inorganic P composition (see SI S2). Data analyses were performed using R.v4.0 /

174   RStudio.v1.3.959. Differences between farms and soil textures were determined via one-way

175   ANOVA with an estimated marginal means post-hoc (Bonferroni adjusted), and correlations

176   between soil parameters via Pearsons test (Kassambara, 2020). Figures were produced using

177   ggplot2, patchwork, and munsell (Pedersen, 2019; Wickham, 2018; Wickham, 2016). Significance

178   is defined as $p<0.05$ and values are reported as mean ± standard deviation.

179

180   2.4.1 Equilibrium $\delta^{18}O_P$

181        $\delta^{18}O_P$ values produced due to equilibrium fractionation during extracellular P cycling

182   ($\delta^{18}O_{P(eq)}$) were calculated using Eq. 1, as per (Chang and Blake, 2015; Hacker et al., 2019):

183   (Eq. 1) $\delta^{18}O_{P(eq)} = (\delta^{18}O_{H2O} + 1000)e^{\left(\frac{14.43*1000}{T}-26.54\right)/1000} - 1000$

7

184   where $\delta^{18}O_{P(eq)}$ is defined by temperature (T, in kelvin) and $\delta^{18}O_{H2O}$. Eq. 1 was solved two ways.

185   First, because the P_{TIP} used for $\delta^{18}O_{P(soil)}$ likely integrates long-term site conditions (Helfenstein et

186   al., 2018), $\delta^{18}O_{P(eq)}$ was calculated using long-term records of soil temperature at 10 cm (mean:

187   21°C, high: 26°C, low: 18°C) and $\delta^{18}O_{H2O}$ (mean: -3.96 ‰, low: -2.74 ‰, high: -5.18 ‰, based on

188   monthly precipitation $\delta^{18}O_{H2O}$ and amounts 1986-2012 for Perth, WA (Hollins et al., 2018;

189   IAEA/WMO, 2020)). Second, because loosely bound PO_4^{3-} in the sandy soils could be turning over

190   daily→seasonal intervals, $\delta^{18}O_{P(eq)}$ was also calculated using modelled daily winter soil

191   temperatures (mean: 13ºC, high: 21ºC, low: 8.2ºC) (Kearney, 2019) and precipitation $\delta^{18}O_{H2O}$

192   values measured during sampling ($\delta^{18}O_{H2O}$: -3.07 ± 2 ‰, n = 10). Precipitation $\delta^{18}O_{H2O}$ was

193   converted to soil water $\delta^{18}O_{H2O}$ based on evidence that soil $\delta^{18}O_{H2O}$ is a mass balance of seasonal

194   precipitation (Benettin et al., 2018), ± +3‰ evaporative enrichment (Sprenger et al., 2017; Wan and

195   Liu, 2016). See SI S3 for input data.

196

197   2.4.2 Export models

198   The possible $\delta^{18}O_P$ range exported from farms to waterways ($\delta^{18}O_{P(export)}$) was determined

199   using a two end-member mixing model that considered a range of fertilisers (type and application

200   rate), times between fertiliser application and PO_4^{3-} export, and soil biological P turnover (Fig. 1).
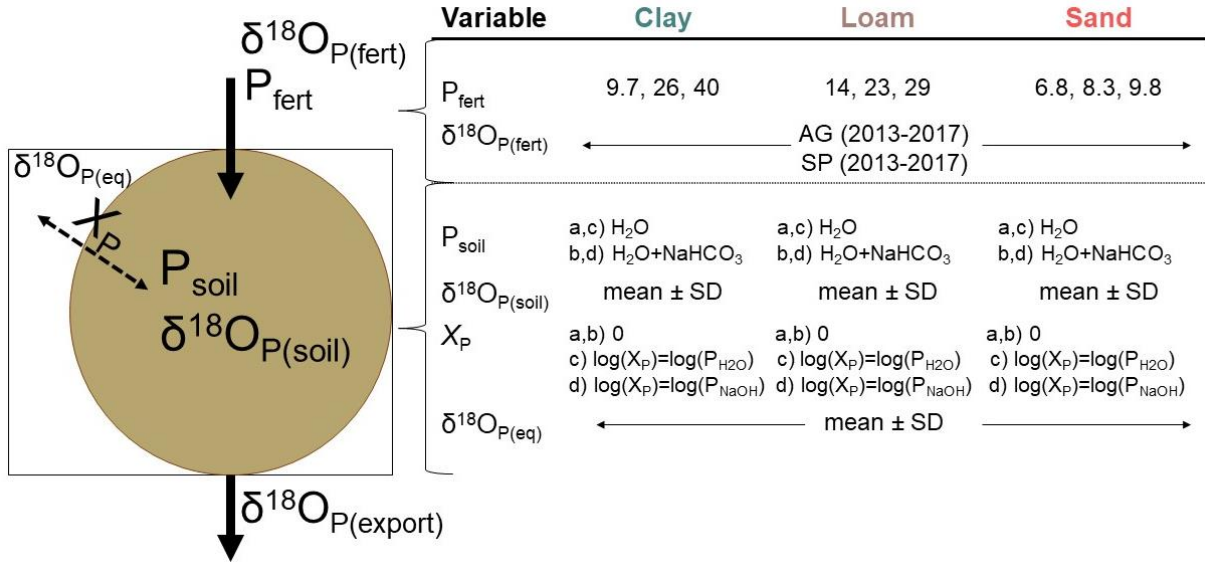
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Variable	Clay	Loam	Sand
P_{fert}	9.7, 26, 40	14, 23, 29	6.8, 8.3, 9.8
$\delta^{18}O_{P(fert)}$		← AG (2013-2017) → SP (2013-2017)	
P_{soil}	a,c) H_2O b,d) H_2O+$NaHCO_3$	a,c) H_2O b,d) H_2O+$NaHCO_3$	a,c) H_2O b,d) H_2O+$NaHCO_3$
$\delta^{18}O_{P(soil)}$	mean ± SD	mean ± SD	mean ± SD
X_P	a,b) 0 c) $\log(X_P)=\log(P_{H2O})$ d) $\log(X_P)=\log(P_{NaOH})$	a,b) 0 c) $\log(X_P)=\log(P_{H2O})$ d) $\log(X_P)=\log(P_{NaOH})$	a,b) 0 c) $\log(X_P)=\log(P_{H2O})$ d) $\log(X_P)=\log(P_{NaOH})$
$\delta^{18}O_{P(eq)}$		← mean ± SD →	

Fig. 1 Two-pool isotope mixing models (Eq. 2, Eq. 3) constrained the possible $\delta^{18}O_P$ range of PO_4^{3-} exported (leaching, run-off) from fertilised soils ($\delta^{18}O_{P(export)}$). The model was solved using recommended low, moderate, and high fertiliser applications rate (P_{fert}, in µg P g^{-1} soil) for each soil texture (clay, loam, sand) and $\delta^{18}O_{P(fert)}$ values for two fertilisers (AG: N-P-K, SP: superphosphate) manufactured between 2013 and 2017. $\delta^{18}O_{P(fert)}$ for each year × fertiliser were 'mixed' with each soil texture using the measured $\delta^{18}O_{P(soil)}$ range for P_{TIP} and P_{soil} (µg P g^{-1} soil), defined by H_2O extractable PO_4^{3-} for fast export scenarios (a, c) and H_2O + $NaHCO_3$ extractable PO_4^{3-} for slow/seasonal export scenarios (b, c). $\delta^{18}O_{P(export)}$ for both fast and slow export was calculated with (c, d) and without (a, b) soil biological P turnover (X_P), which shifts $\delta^{18}O_{P(export)}$ towards $d^{18}O_{P(eq)}$ (Eq. 1). Fast export X_P (c) was approximated by $[P_{H2O}\cdot e^{\wedge}(\log(100+P_{H2O})/100\cdot1)]/P_{TIP}$ and slow export X_P (d) by $[P_{NaOH}\cdot e^{\wedge}(\log(100+P_{NaOH})/100\cdot1)]/P_{TIP}$. Arrows indicate the same values were applied across all soil textures, otherwise soil-specific values (mean±SD) were used. See SI S4 for model scripts.

The $\delta^{18}O_{P(export)}$ range was first defined assuming no biological turnover prior to export (Eq. 2):

(Eq. 2) $\qquad \delta^{18}O_{P(export.1)} = f_{fert}\delta^{18}O_{P(fert)} + f_{soil}\delta^{18}O_{P(soil)}$

$\qquad\qquad 1 = f_{fert} + f_{soil}$

$\qquad\qquad f_{fert} = P_{fert}/P_{soil}$

where f_{fert} and f_{soil} are the contribution of PO_4^{3-} from fertiliser and soil, respectively, and $\delta^{18}O_{P(fert)}$

and $\delta^{18}O_{P(soil)}$ their isotopic composition; f_{fert} was estimated for each soil texture based on its

leachable soil P content (P_{soil}) and the recommended fertiliser application amount (P_{fert}). Two P_{soil}

scenarios were considered: scenario a (fast), where export occurs within ~1 day of application (P_{soil}

= H_2O extractable PO_4^{3-}), and scenario b (slow), where export occurs gradually over a whole season

(P_{soil} = H_2O + $NaHCO_3$ extractable PO_4^{3-} (Rupp et al., 2018)).

Next, scenarios a and b were rerun to consider biological P turnover pushing $\delta^{18}O_P$ values

towards $\delta^{18}O_{P(eq)}$, as per (Helfenstein et al., 2018):

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228   (Eq. 3) $\delta^{18}O_{P(export.2)} = X_P \cdot \left(\delta^{18}O_{P(eq)} - \delta^{18}O_{P(export.1)} \right) + \delta^{18}O_{P(export.1)}$

229   where an exchange factor (X_P) defines $\delta^{18}O_{P(export.1)}$ mixing with $\delta^{18}O_{P(eq)}$ (Gross and Angert, 2015).

230   Eq. 3 constrains the effects of short-term (daily to monthly) biological P cycling, so $\delta^{18}O_{P(eq)}$ was

231   defined based on diurnal variations in winter soil temperatures (Eq. 1). As X_P is challenging to

232   measure directly, values were approximated for each soil texture based on soil P mean residence

233   time, calculated as the log-log linear relationship between H$_2$O extractable PO$_4^{3-}$ and PO$_4^{3-}$ turnover

234   in <1 hr, or, 2) NaOH extractable PO$_4^{3-}$ and PO$_4^{3-}$ turnover in >1 hr – 3 months (Helfenstein et al.,

235   2020). For biologically active 'fast' export (scenario c), X_P was defined as PO$_4^{3-}$ exchange in < 1 hr

236   and applied to scenario a $\delta^{18}O_{P(export.1)}$ values. For biologically active 'slow' export (scenario d), X_P

237   was defined as the proportion of PO$_4^{3-}$ exchange in 1 hr – 3 months and applied to scenario b

238   $\delta^{18}O_{P(export.1)}$ values.

239         $\delta^{18}O_{P(fert)}$ variability was parameterised two ways. First, models were run using the annual

240   differences in $\delta^{18}O_{P(fert)}$ measured 2013-2017 for different fertiliser types (AG and SP, but not MAP

241   because only one year was sampled). Second, P$_{fert}$ was varied to reflect the low, high, and median

242   fertiliser application rates recommended for each soil texture: 14, 58, 37 kg P ha^{-1} (clay), 18, 37, 28

243   kg P ha^{-1} (loam), and 9, 13, 11 kg P ha^{-1} (sand) (Summers and Weaver, 2011). Application rates (kg

244   P ha^{-1}) were converted to concentrations (µg P g^{-1}) in the top 10 cm of soil (P$_{fert}$) using regional

245   pasture soil bulk density (Viscarra Rossel et al., 2014): 1.44 ± 0.2 kg ha^{-1} (clay), 1.25 ± 0.2 kg ha^{-1}

246   (loam), and 1.33 ± 0.1 kg ha^{-1} (sand). This model does not consider the complex soil chemical

247   processes affecting long-term fertiliser mobility, meaning fertiliser contributions to 'slow' export

248   scenarios (b, d) may be overestimated.

249   Variability in soil inputs was parameterised by solving each export scenario (a: fast, b: slow,

250   c: fast + turnover, d: slow + turnover) using the mean, mean+SD, and mean-SD of $\delta^{18}O_{P(soil)}$ and

251   P$_{soil}$ for each soil texture, as well as for $\delta^{18}O_{P(eq)}$ (Henry and Wickham, 2020): f_{fert} was calculated for

252   each P$_{soil}$ and P$_{fert}$ combination, the minimum, mean-SD, mean, mean+SD, and maximum f_{fert} for

253   scenarios (a, b) × soil texture used to solve Eq. 2 for each fertiliser × manufacturing year, and then

10

254     $\delta^{18}O_{P(export.1)}$ values used to solve Eq. 3 for scenario (c, d) × soil texture for each fertiliser ×

255   manufacturing year (Fig. 1). Output $\delta^{18}O_{P(export)}$ ranges were upscaled to possible 'agricultural soil'

256   signatures based on the measured PO_4^{3-} content and spatial coverage of soil textures for two sub-

257   catchments with contrasting soil distributions, see SI Fig. S2 (McArthur and Bettenay, 1974; Weller,

258   2019). Upscaling calculations varied the contribution of AG v SP fertilisers and timing between

259   fertilisation and export (a: fast v d: slow + turnover).

260

261   **3. Results**

262   3.1 Fertilisers

263   Fertiliser types had different $\delta^{18}O_{P(fert)}$ values ($p<0.05$, F = 52). Values ranged from 17 ±

264   1 ‰ (SP) to 22 ± 0.05 ‰ (MAP) (Table 2). The $\delta^{18}O_{P(fert)}$ composition of SP and AG varied between

265   manufacturing years: SP from 16 ± 0.2 ‰ in 2015 to 19 ± 0.2 ‰ in 2013, and AG from 20 ± 0.4 ‰

266   in 2014 to 22 ± 0.01 ‰ in 2015.

267

268   3.2 Soils

269   Soil pH was higher in clays than in loams or sands ($p<0.05$, F = 5.2) (Table 1). C_{org} was higher

270   in clays (66 ± 20 mg C g^{-1}) than loams (40 ± 10 mg C g^{-1}) and sands (38 ± 30 mg C g^{-1}) (F = 2.7,

271     $p<0.05$) (Table 1), as was P_{total} (clay: 360 ± 20 µg g^{-1}, loam: 190 ± 90 µg g^{-1}, sand: 120 ± 100 µg g^{-1}

272   ) (F = 20, $p<0.05$). P_{org} did not differ between soil textures or farms (SI Table S1), so P_{org}

273   accounted for a higher proportion of P_{total} in sands (57 ± 10 %) than loams (45 ± 10 %) and clays

274   (41 ± 0.09 %) (F = 12, $p<0.01$). The C_{org}:P_{org} ratio was higher in sands (630 ± 500 g/g) than in clays

275   (540 ± 300 g/g) or loams (530 ± 200 g/g) (F = 3.3, $p<0.01$; Table 1). $P_{min(14)}$ was highest in absolute

276   (F = 10, $p<0.05$) terms in sands (SI Table S3), and decreased as a proportion of P_{TIP} from sands (14

277   ± 10 mg g^{-1}) to loams (4.4 ± 3 mg g^{-1}) to clays (0.74 ± 0.4 mg g^{-1}) (F = 23, $p<0.001$; Table 1).

278   P_{TIP} (based on H_2O+$NaHCO_3$+$NaOH$+HCl fractions) was higher in clays (150 ± 90 µg P g^{-1})

279   than loams (53 ± 50 µg P g^{-1}) or sands (55 ± 80 µg P g^{-1}) (F = 11, $p<0.05$; Fig. 2). Water extractable

11

280 PO_4^{3-} differed between soil textures (F = 9.6, $p<0.05$), with concentrations in sands (11 ±10 µg P g⁻

281 ¹) higher than in loams (4.2 ± 3 µg P g⁻¹) and clays (1.7 ± 2 µg P g⁻¹) (Fig. 2). $NaHCO_3$ extractable

282 PO_4^{3-} did not differ between soil textures, but differed between farms (F = 3.0, $p = 0.019$): heavy

283 clay soils in F6 had the lowest concentrations (7.6 ± 4 µg P g⁻¹) and the predominantly sand soils in

284 F1 had the highest (27 ± 20 µg P g⁻¹) (see SI S2 for farm-level data). Clays had higher NaOH

285 extractable PO_4^{3-} (89 ± 50 µg P g⁻¹) than loams (29 ± 30 µg P g⁻¹) or sands (9.5 ± 10 µg P g⁻¹) (F =

286 26, $p<0.001$). Likewise, HCl extractable PO_4^{3-} was the highest in clays (39 ± 20 µg P g⁻¹) and the

287 lowest in loams (6.0 ± 8 µg P g⁻¹) (F = 3.9, $p<0.05$). 30% of P_{TIP} was H_2O extractable in sands,

288 versus 10% in loams and 1% in clays (F = 28, $p<0.001$; Fig. 2). The proportion of P_{TIP} in the

289 $H_2O+NaHCO_3$ fraction also decreased from sands (54 ± 20 %) to loams (41 ± 20 %) to clays (13 ±

290 5 %) (F = 40, $p<0.001$; Fig. 2). X_P (Eq. 3) estimated for <1 hr was 30% (sand), 10% (loam), and 1%

291 (clay), while X_P estimated for turnover >1 hr – 3 months was 20% (sand), 60% (loam), and 90%

292 (clay), see SI Table S7.
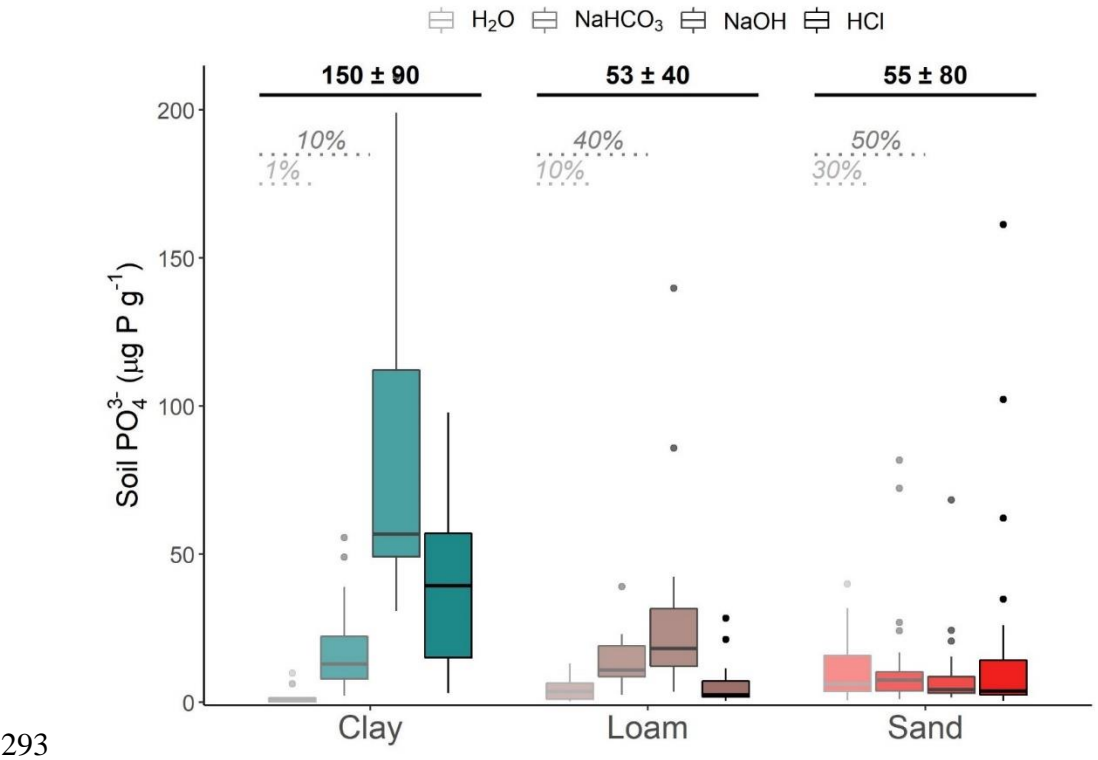
294 **Fig. 2** Phosphate in surface soils (0 – 10 cm) of 21 pastures with different soil textures in the Peel-Harvey catchment
295 (Western Australia) based on sequential extraction with H_2O (left, light outline), $NaHCO_3$, NaOH, and HCl (right, dark
296 outline). P_{TIP} concentrations (sum of four fractions) for each soil textures is indicated at the top, and the percentage
297 contribution of H_2O (easily leachable) and $H_2O+NaHCO_3$ (seasonally leachable) fractions indicated with dashed lines.
298 Boxes represent median ± 1 SD.

12

$\delta^{18}O_{P(soil)}$ values ranged from 25.3‰ (F4 loam) to 17.9‰ (F2 sand). Values negatively

correlated with $P_{min(14)}$ ($p = 0.03$, $r = -0.45$) and positively correlated with C_{org} ($p = 0.03$, $r = 0.5$).

Soil P concentrations did not correlate with $\delta^{18}O_{P(soil)}$. $\delta^{18}O_{P(soil)}$ values differed between soil

textures but not farms, and were higher in loams (23.2 ± 1 ‰) than clays (22.3 ± 0.9 ‰) or sands

(21.4 ± 2 ‰) ($p<0.05$; F = 3.8; Fig. 3). $\delta^{18}O_{P(eq)}$ values calculated using long-term temperature and

$\delta^{18}O_{H2O}$ records ranged from 16.9 to 23.8 ‰ (20.4 ± 1.97 ‰), versus from 19.3 – 24.1 ‰ based on

winter soil temperatures and $\delta^{18}O_{H2O}$ (Fig. 3). This places loam $\delta^{18}O_{P(soil)}$ values at or above the

maximum $\delta^{18}O_{P(eq)}$ range, versus sand $\delta^{18}O_{P(soil)}$ values around mean $\delta^{18}O_{P(eq)}$.
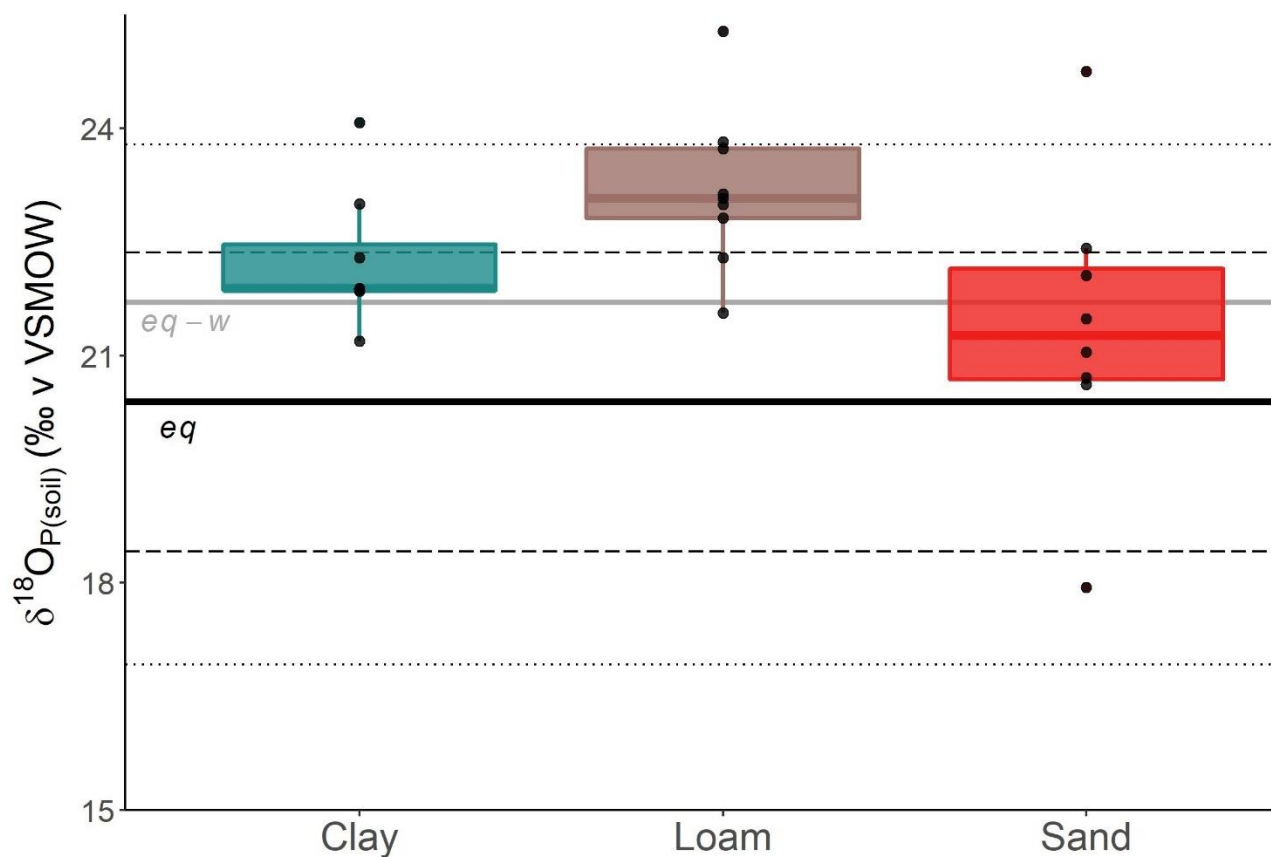
Fig. 3 The $\delta^{18}O_P$ of P_{TIP} in pasture soils (0-10 cm) classed as either clay, loam, or sand from six farms across the Peel-Harvey catchment (Western Australia). Boxes represent median ± 1 SD for each soil textures. Black lines represent the mean (solid line), ±1 SD (dashed lines), and minimum/maximum (dotted lines) of the long-term local $\delta^{18}O_{P(eq)}$ range (Eq. 2); the grey line indicates the mean $\delta^{18}O_{P(eq)}$ calculated for conditions during the winter sampling (*eq-w*).

3.3 Export model

For scenario (a), f_{fert} (Eq. 2) decreased from 0.93 ± 0.1 (clays) via 0.84 ± 0.1 (loams) to 0.54 ± 0.2 (sands) (Fig. 4a). For scenario (b), f_{fert} was 0.57 ± 0.1 for clays, 0.57 ± 0.1 for loams, and 0.37 ± 0.2 for sands (Fig. 4b). In scenario (a) $\delta^{18}O_{P(export)}$ values track $\delta^{18}O_{P(fert)}$, with clear differences between AG v SP applied to all soil textures (Fig. 4c). Rapid P turnover (scenario c) shifted sand, but not clays or loams, $\delta^{18}O_{P(export)}$ away from low-end $\delta^{18}O_{P(fert)}$ values (Fig. 4e). Yearly $\delta^{18}O_{P(fert)}$ differences in SP (2013 v 2014-2017) and AG (2014 v 2015) fertilisers affected modelled $\delta^{18}O_{P(export)}$ from clays and loams, but not sands, under 'fast' scenarios (a, c) (Fig. 4c,e). For 'slow' scenarios (b, d), differences in SP v AG $\delta^{18}O_{P(export)}$ values were only expressed when $X_P = 0\%$ (Fig. 4d), and $\delta^{18}O_{P(export)}$ from all soil textures and fertilisers normalised to $\delta^{18}O_{P(eq)}$ with ~monthly P turnover (Fig. 4f). Upscaling to sub-catchments, the possible $\delta^{18}O_{P(export)}$ range is narrowest (~2‰) if export is slow and fertilisation type uniform (Table 3). In both sub-catchments fertiliser mixing was more important than the export speed in defining the $\delta^{18}O_{P(export)}$ values, and mixed fertilisers + slow export produced the widest possible $\delta^{18}O_{P(export)}$ range.
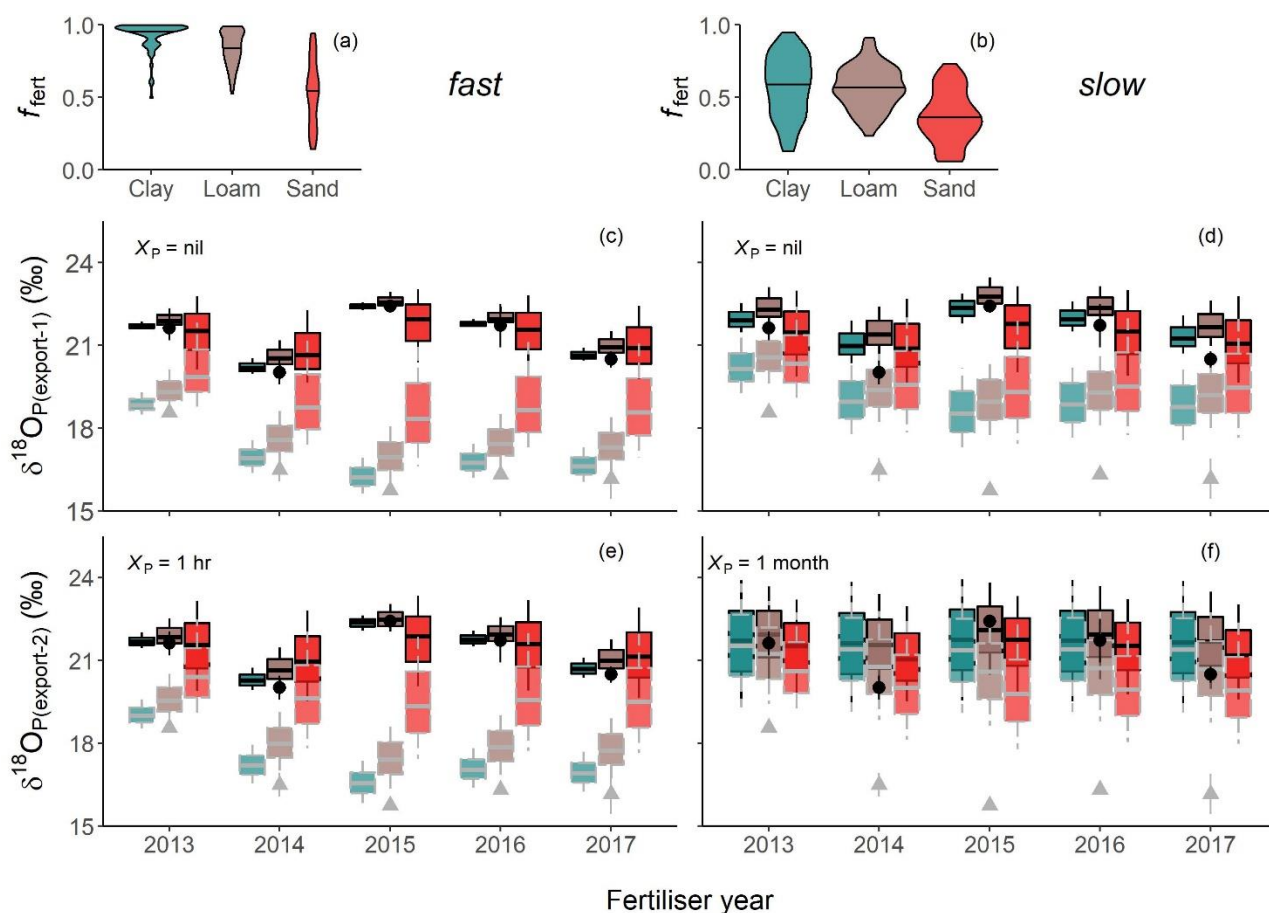
14

Fig. 4 The possible range of the isotopic composition of PO_4^{3-} export from clay, loam, and sand pasture soils ($\delta^{18}O_{P(export)}$, ‰ v. VSMOW) within a catchment depends on fertiliser contribution to the leachable soil PO_4^{3-} pool (f_{fert}) and fertiliser $\delta^{18}O_P$ composition (AG: black circles, SP: grey triangles, manufactured 2013-2017). $\delta^{18}O_{P(export)}$ values were calculated for two export scenarios: fast (a, c, e), where PO_4^{3-} is exported <1 day after fertilisation, and slow (b, d, f), where PO_4^{3-} is leached over weeks-months. Both fast and slow export could occur with (e, f: X_P = 1 h or 1 month) or without (c, d: X_P = nil) soil biological P turnover (Eq. 3). Violins (a, b) show the distribution of f_{fert} values around the mean (solid line); boxes (c-f) show the mean ± 1 SD for $\delta^{18}O_{P(export)}$, with whiskers to the minimum and maximum. Box colours distinguish soil textures (as defined in a and b) and outlines the fertiliser (AG: black, SP: grey).

4. Discussion

4.1 Fertilisers

The $\delta^{18}O_{P(fert)}$ range here (17 – 21 ‰) fits previous reports for inorganic commercial fertilisers (Table 2). Variations in $\delta^{18}O_{P(fert)}$ are generally attributed to geologic differences in the rocks sourced to make the fertilisers (Davies et al., 2014; Gruau et al., 2005). This is because the $\delta^{18}O_P$ composition of the sedimentary rocks sourced to produce PO_4^{3-} fertilisers depend on age and/or equilibration with $\delta^{18}O_{H2O}$ during formation (Sun et al., 2020). Here the ~8 ‰ difference between N-bearing (AG, MAP) and rock (SP) fertilisers corresponded with different geologic

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348   source materials: AG and MAP were manufactured using materials from Florida, USA (Eocene –

349   Miocene, ~55 MBP (Trueman, 1965)), while SP was manufactured using Christmas Island rocks

350   (Oligocene – Pliocene, ~33 MBP (Van Kauwenbergh et al., 1990)). However, this explanation for

351   the 5 - 8 ‰ difference between the fertiliser types does not hold up to scrutiny. The ~20 MY gap is

352   negligible in geologic time (e.g., the 3 ‰ difference between PO_4^{3-} in China v the Middle East

353   corresponds to ~300 MY (Sun et al., 2020)). Likewise, different $\delta^{18}O_{P(eq)}$ during formation is

354   unlikely given similarities in the $\delta^{18}O_{H2O}$ and temperature regimens between the Indian Ocean and

355   tropical Atlantic (LeGrande and Schmidt, 2006). This suggests that there is an additional factor than

356   the commonly cited 'geologic $\delta^{18}O_P$ differences' that is contributing to the consistent offset between

357   fertiliser types. We note that geology-driven variations in $\delta^{18}O_{P(fert)}$ is not robustly supported by the

358   literature, with source material origins provided in only four of nine published studies (Table 2).

359   This suggests that future work should encompass isotopic fractionation during manufacturing,

360   which is theoretically possible given the filtration and solubilisation processes used (Chien et al.,

361   2011), especially given the consistent differences between fertilisers made from raw (SP) v pre-

362   processed (AG, MAP) materials. A similar mechanism was proposed to explain differences in tap

363   water $\delta^{18}O_P$ (Gooddy et al., 2015), and requires further consideration.

364   Regardless of the exact driver (source, manufacturing), a single precise $\delta^{18}O_{P(fert)}$ value is

365   unlikely to exist at the spatial and temporal scale of catchment studies. Establishing methods for

366   predicting, and thus better constraining, $\delta^{18}O_{P(fert)}$ will be critical to any future attempts to use $\delta^{18}O_P$

367   to trace aquatic PO_4^{3-}. As first steps, we recommend future isotope studies report both the chemical

368   form and geologic (rather than commercial) origin of P fertilisers.

369

370   4.2 Soils

371   Soil P variations fit expectations (Table 1, Fig. 2). P_{TIP} content was at the very low end for

372   agricultural soils and $C_{org}:P_{org}$ ratios at the high end for mineral soils, both typical for weathered

373   southwestern Australian soils (Helfenstein et al., 2020; Spohn, 2020; Turner and Laliberte, 2015).

16

374   Phosphate partitioning followed the anticipated shift from sands with low, highly leachable, PO_4^{3-}

375   pools, to clays with larger, less leachable, PO_4^{3-} pools (Nash et al., 2019; O'Halloran et al., 1987).

376   These soil texture differences provide a solid basis to test how P buffering capacity controls

377    $\delta^{18}O_{P(soil)}$ and $\delta^{18}O_{P(export)}$.

378        $\delta^{18}O_{P(soil)}$ is hypothesised to reflect differences in the size and availability of soil PO_4^{3-}

379   (Bauke, 2020). Loosely bound PO_4^{3-} (H_2O or $NaHCO_3$ fractions) can be completely recycled in

380   days, whereas more tightly bound PO_4^{3-} (NaOH or HCl fractions) turnover may take centuries

381   (Helfenstein et al., 2020). Because biological PO_4^{3-} turnover moves $\delta^{18}O_{P(soil)}$ towards $\delta^{18}O_{P(eq)}$,

382   more labile PO_4^{3-} fractions tends to have (higher) $\delta^{18}O_P$ values closer to $\delta^{18}O_{P(eq)}$ and more tightly

383   bound PO_4^{3-} fractions tend to have (lower) $\delta^{18}O_{P(soil)}$ values closer to the geologic parent material

384    $\delta^{18}O_P$ (Roberts et al., 2015; Tian et al., 2020). This predicts that the sands' predominantly labile

385   PO_4^{3-} pool would shift $\delta^{18}O_{P(soil)}$ values higher than the clays, where most PO_4^{3-} is tightly bound

386   (Rodionov et al., 2020). Instead, the sands had the lowest $\delta^{18}O_{P(soil)}$ values, and almost all $\delta^{18}O_{P(soil)}$

387   values fell within the $\delta^{18}O_{P(eq)}$ range (Fig. 3). It is reasonable that all soil PO_4^{3-} was within the

388    $\delta^{18}O_{P(eq)}$ range as geologic PO_4^{3-} is unlikely to persist in any of these ~300,000 year old soils (Shen

389   et al., 2020; Turner and Laliberte, 2015). But if PO_4^{3-} is in isotopic equilibrium with soil water, why

390   do $\delta^{18}O_{P(soil)}$ values fall into distinct 'soil texture' zones within this range?

391   Variations within the $\delta^{18}O_{P(eq)}$ range could be driven by three factors: divergent equilibrium

392   conditions (soil temperature, $\delta^{18}O_{H2O}$), different PO_4^{3-} sources, and/or fractionation by competing

393   biological processes. First, daily – seasonal parameter fluctuations are not seen to affect $\delta^{18}O_{P(soil)}$ of

394   P_{TIP} (Angert et al., 2011; Lei et al., 2019). This suggests that long-term evaporation ($\delta^{18}O_{H2O}$) or

395   temperature differences between the soil textures would be needed to create a 'soil specific'

396    $\delta^{18}O_{P(eq)}$ range. Factors like slope, aspect, and vegetation (Hacker et al., 2019; Sprenger et al., 2016)

397   are excluded here due to the flat terrain and relatively homogenous land-use, but soil texture can

398   affect evaporation. However, a textural impact on evaporation would elevate $\delta^{18}O_{P(soil)}$ in coarse

399   grained sands above $\delta^{18}O_{P(soil)}$ in the fine grained clays (Gazis and Feng, 2004), the opposite of the

17

400 observed pattern. Second, pastures receive P_{org} and PO_4^{3-} inputs. Inorganic fertilisers can be ruled

401 out as $\delta^{18}O_{P(fert)}$ values were lower than loam $\delta^{18}O_{P(soil)}$ (Fig. 4), and likewise processed P_{org}

402 (manure) likely has $\delta^{18}O_P$ below the $\delta^{18}O_{P(soil)}$ range here (Granger et al., 2017b). While raw P_{org}

403 inputs (plants) can have $\delta^{18}O_P$ up to ~30 ‰ (Pfahler et al., 2013; von Sperber et al., 2015), the

404 mechanism through which they could differently affect soil textures under similar management

405 (including pasture plants) is unclear. Charred organic matter is also a potentially significant P input

406 (Baldock et al., 2013). A survey of nearby pastures suggests that loams contain more char than

407 sands or clays (9.2 ± 2 mg C g^{-1} v 7.7 ± 2 mg C g^{-1} and 4.9 ± 2 mg C g^{-1}, respectively) (Viscarra

408 Rossel et al., 2014). If char contains 20 µg PO_4^{3-}-P g^{-1} (Pluchon et al., 2015), this could be the

409 source of 30% of loam PO_4^{3-}, v 5% of clay PO_4^{3-}. This is an intriguing possibility, but

410 measurements of combusted organic material suggest char $\delta^{18}O_P$ values may be too low (~15 ‰)

411 (Bigio and Angert, 2019) to explain the observed loam $\delta^{18}O_{P(soil)}$ values.

412 Alternatively, both the mineralisation of P_{org} to PO_4^{3-} and microbial PO_4^{3-} assimilation affect

413 $\delta^{18}O_P$. Scavenging P_{org} in low fertility soils can decrease $\delta^{18}O_{P(soil)}$ below $\delta^{18}O_{P(eq)}$ (Liang and Blake,

414 2006; Pistocchi et al., 2020), and estimates suggest that mineralisation is highest ($P_{min} = $ ~1% of

415 P_{TIP} per fortnight) in the P-poor, relatively low $\delta^{18}O_{P(soil)}$ sands (Table 1). Additionally, microbial

416 PO_4^{3-} assimilation increases $\delta^{18}O_{P(soil)}$ (Blake et al., 2005), with stronger fractionation when P is

417 limiting (Lis et al., 2019). This gives a plausible explanation for the relatively high loam $\delta^{18}O_{P(soil)}$

418 values. Low P in both sands and loams could promote microbial PO_4^{3-} uptake and increase $\delta^{18}O_{P(soil)}$

419 of both soil textures (Bünemann et al., 2012), but the low sand C_{org} and P content causes its

420 microbial P to be more efficiently recycled and $\delta^{18}O_{P(soil)}$ reset to the mean $\delta^{18}O_{P(eq)}$ range. This

421 supports the assumption in catchment models that sand PO_4^{3-} is completely exhausted every winter

422 (Summers et al., 1999). Although the exact driver of the soil textures $\delta^{18}O_{P(soil)}$ patterns is not

423 certain, the non-random distribution of $\delta^{18}O_{P(soil)}$ within the $\delta^{18}O_{P(eq)}$ range emphasises the need to

424 move beyond simply defining $\delta^{18}O_{P(soil)}$ as 'in' or 'out' of equilibrium and start unpicking the

425 competing biological and hydrologic processes at play.

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4.3 $\delta^{18}O_P$ as a tracer of PO_4^{3-} export from agricultural systems

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There are three main questions about agricultural P export that $\delta^{18}O_P$ models look to answer:

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1) how much fertiliser is exported directly to water?, 2) which landscape units contribute

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disproportionately to PO_4^{3-} export?, and, 3) how much does agriculture contribute to catchment

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PO_4^{3-} loads? The mixing models used here generated clear constraints on how $\delta^{18}O_P$ data could be

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used at each of these scales.

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Directly exported P fertilisers are a significant financial and environmental risk. Although

433

difficult to measure, estimates suggest fertilisers account for 30-80% of PO_4^{3-} leached from

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agricultural systems (Nash et al., 2019), and radiotracer studies show 20-30 % of fertiliser PO_4^{3-} is

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leached from pastures within two months of application (McLaren et al., 2017; McLaren et al.,

436

2016). There is further uncertainty about the timing of these direct export events: how long

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fertilisers stay in granular form depends on rainfall, temperature, and fertiliser type (McLaren et al.,

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2017). The wide $\delta^{18}O_{P(fert)}$ range reported here indicates that $\delta^{18}O_P$ values could prove a uniquely

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powerful tool for untangling these PO_4^{3-} leaching dynamics at the plot - paddock scale if

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isotopically distinct fertiliser v soils were first identified. Yet the same $\delta^{18}O_{P(fert)}$ range complicates

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efforts to identify soil and land-use specific $\delta^{18}O_{P(export)}$ signatures (Fig. 4, Table 3).

442

The twin possibilities of mixed fertiliser use and variable biological P turnover drive the

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uncertainty in $\delta^{18}O_{P(export)}$. Across the modelled two sub-catchments the 'agricultural' $\delta^{18}O_{P(export)}$

444

could reasonably range between 18‰ and 25‰, a much wider range than would be predicted by

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simply using the sub-catchment soil maps to upscale $\delta^{18}O_{P(soil)}$. This level of uncertainty means

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large datasets of receiving water $\delta^{18}O_P$ values are needed to generate statistically robust

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identification of the fertiliser and soil PO_4^{3-} sources. For instance, measuring an 'out of equilibrium'

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downstream $\delta^{18}O_P$ value of 19‰ could reasonably be evidence of SP export, but would not rule out

449

export of other fertilisers contributing up to 40% of PO_4^{3-}. Conversely, measuring a $\delta^{18}O_P$ value of

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21‰, well above the SP $\delta^{18}O_{P(fert)}$ range, could not conclusively rule SP out as a PO_4^{3-} source (Fig.

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452   4, Table 3). So while biological P turnover could ameliorate some of the variability created by

453   fertiliser-soil mixing by shifting $\delta^{18}O_{P(export)}$ values towards $\delta^{18}O_{P(eq)}$, it also highlights more

454   intransigent sources of uncertainty. First, the soil $\delta^{18}O_{P(eq)}$ range is itself uncertain due to questions

455   around the extent to which variations are caused by hydrology (temperature and $\delta^{18}O_{H2O}$ (Benettin

456   et al., 2018; Skrzypek et al., 2019)) v biology (balance between biological P cycling pathways

457   (Helfenstein et al., 2018; Siegenthaler et al., 2020)). Second, evaluating these questions about soil

458    $\delta^{18}O_{P(eq)}$ dynamics is complicated by the fact that the PO_4^{3-} pools that can be extracted for $\delta^{18}O_P$

459   analysis do not necessarily align with those that are environmentally relevant (Gu and Margenot,

460   2020; McConnell et al., 2020). Both situations contrast with the established approaches to tracing

461   PO_4^{3-} pollution point sources like wastewater effluent (Gooddy et al., 2018), where biological

462   modification of the defined source signature will occur post export to the waterway (Davies et al.,

463   2014). The interconnected uncertainties about P turnover and $\delta^{18}O_{P(eq)}$ must be resolved in order to

464   usefully incorporate $\delta^{18}O_P$ into P reactive transport models (Dorioz et al., 1998). One potential is

465   that improved $\delta^{18}O_{P(eq)}$ understanding could be used to construct $\delta^{18}O_P$ catchment models based on

466   temperature and $\delta^{18}O_{H2O}$ regimens.

467

468   **5. Conclusions**

469   The ability of phosphate isotopes ($\delta^{18}O_P$) to trace diffuse agricultural pollutants through

470   catchments is limited by variations in soil zone inputs and reactions. The analytical template here

471   highlights the importance, but also the limitations, of using site-specific $\delta^{18}O_{P(fert)}$ values to identify

472   diffuse agricultural pollution. Uncertainty from $\delta^{18}O_P$ can reasonably be constrained via site-

473   specific measurements in smaller catchments, but until biological turnover (fractionation and rates)

474   is better defined surface water $\delta^{18}O_P$ signatures should be attributed to diffuse catchment sources

475   with caution.

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732 **Tables**

733 **Table 1:** Characteristics of pasture soils (0 – 10 cm) with contrasting textures (sand, clay, loam) collected from six farms (F1 – F6) across the coastal

734 Peel-Harvey catchment in southwestern Western Australia (see SI S1 maps). Sample numbers indicate the total bulked ($n = 3$) cores collected for P

735 content and the subset analysed for $\delta^{18}O_{P(soil)}$. The contribution of P_{org} to P_{total} is calculated on a g/g basis. Potential P mineralisation over 14 days

736 ($P_{min(14)}$) is reported relative to the total HCl extractable PO_4^{3-} concentration (P_{TIP}). See SI S2 for additional soil chemistry data.

Texture	Farm	sample #s		pH	C_{org}	P_{total}	% P_{org}	$C_{org}:P_{org}$	$P_{min(14)}:P_{TIP}$
		all	$\delta^{18}O_P$		*mg C g^{-1}*	*µg P g^{-1}*	*(P_{org}/P_{total}) · 100*	*g/g*	*mg/g*
Clay	F3	3	1	5.8 (0.1)	33	390 (70)	33 (9)	290 (100)	0.27 (0.07)
	F4	9	4	6.5 (0.3)	68 (20)	450 (200)	37 (7)	440 (100)	0.68 (0.3)
	F6	9	3	6.3 (0.1)	76 (20)	250 (60)	46 (7)	700 (300)	0.90 (0.4)
Loam	F2	6	4	6.1 (0.09)	34 (9)	150 (50)	41 (7)	590 (200)	6.6 (4)
	F4	3	2	6.4 (0.06)	58 (20)	320 (100)	37 (10)	540 (200)	1.9 (2)
	F5	9	3	6.3 (0.2)	38 (10)	170 (50)	51 (8)	490 (200)	3.9 (2)
Sand	F1	9	4	5.8 (0.3)	46 (40)	470 (600)	53 (10)	340 (200)	7.7 (7)
	F2	6	2	6.3 (0.09)	54 (30)	120 (80)	55 (10)	1000 (600)	18 (10)
	F3	9	2	6.2 (0.1)	16 (7)	63 (20)	61 (20)	510 (200)	16 (10)

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Table 2 Inorganic fertiliser $\delta^{18}O_P$ values reported for this study and others ($\delta^{18}O_{P(fert)}$, values in ‰ v VSMOW), with respect to fertiliser type, where the fertiliser was manufactured, and where the PO_4^{3-} raw material was sourced from ('unspecified' denotes data unavailable).

Fertiliser type	Manufactured	Sourced	$\delta^{18}O_{P(fert)}$	Reference
Superphosphate	Australia	Christmas Island	16.7 ± 1 *15.6 – 18.7*	This study
	Europe	*Unspecified*	17.7 ± 0.2	Tamburini et al. (2010)
	Japan	Japan	12.7	Ishida et al. (2019)
	Australia	*Unspecified*	21.4 ± 0.5	Polain et al. (2018)
	Israel	*Unspecified*	21.8 ± 0.3	(Gross and Angert, 2015)
	Europe	Morocco & USA	23 ± 0.3	Gruau et al. (2005)
Monoammonium phosphate	Australia	USA	21.6 ± 0.05	This study
	Australia	*Unspecified*	20.2 ± 0.1	Polain et al. (2018)
N-P-S-K	Australia	USA	21.3 ± 1 *19.7 – 22.4*	This study
	Europe	Morocco & USA	21.8 ± 0.5	Gruau et al. (2005)
	Europe	*Unspecified*	20.9 ± 6	Granger et al. (2017b)
Unspecified	USA	USA	23.8 ± 1	Li et al. (2011)
	USA	*Unspecified*	19 ± 1	McLaughlin et al. (2006)
	USA	Israel	19.6	Young et al. (2009)
	China	China	11.5 ± 0.1	Tian et al. (2020)

Table 3 Possible $\delta^{18}O_{P(export)}$ range from two sub-catchments with differing soil distributions (maps: SI S1). The $\delta^{18}O_{P(export)}$ range was calculated by varying the relative proportion of SP v AG fertilisers and speed of PO_4^{3-} transport from soil to water (fast, scenario a: mixing with H_2O extractable PO_4^{3-} pool, $X_P = 0\%$; or scenario d: mixing with $H_2O+NaHCO_3$ extractable PO_4^{3-}, $X_P = 20 - 90\%$, depending on soil texture), see SI S4 for calculations.

Sub-catchment	Fertiliser	$\delta^{18}O_{P(export)}$ range	
		Transport	
		Fast+Slow[1] $\rightarrow$	Mostly slow[2]
Pinjarra	1 SP + 0 AG	17.7 – 21.3	18.5 – 20.5
19% clay, 4.4% loam, 76% sand	0.6 SP + 0.4 AG	18.7 – 21.9	19.1 – 22.6
Harvey	1 SP + 0 AG	17.7 – 21.1	18.7 – 20.5
21% clay, 29% loam, 50% sand	0.6 SP + 0.4 AG	18.8 – 23.0	19.2 – 24.9

[1] 50% 'd' + 50% 'a'

[2] 90% 'd' + 10% 'a'

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768 **Figure captions**

769 **Fig. 1** Two-pool isotope mixing models (Eq. 2, Eq. 3) constrained the possible $\delta^{18}O_P$ range of PO_4^{3-}

770 exported (leaching, run-off) from fertilised soils ($\delta^{18}O_{P(export)}$). The model was solved using

771 recommended low, moderate, and high fertiliser applications rate (P_{fert}, in $\mu g\ P\ g^{-1}$ soil) for each soil

772 texture (clay, loam, sand) and $\delta^{18}O_{P(fert)}$ values for two fertilisers (AG: N-P-K, SP: superphosphate)

773 manufactured between 2013 and 2017. $\delta^{18}O_{P(fert)}$ for each year $\times$ fertiliser were 'mixed' with each

774 soil texture using the measured $\delta^{18}O_{P(soil)}$ range for P_{TIP} and P_{soil} ($\mu g\ P\ g^{-1}$ soil), defined by H_2O

775 extractable PO_4^{3-} for fast export scenarios (a, c) and H_2O + $NaHCO_3$ extractable PO_4^{3-} for

776 slow/seasonal export scenarios (b, c). $\delta^{18}O_{P(export)}$ for both fast and slow export was calculated with

777 (c, d) and without (a, b) soil biological P turnover (X_P), which shifts $\delta^{18}O_{P(export)}$ towards $d^{18}O_{P(eq)}$

778 (Eq. 1). Fast export X_P (c) was approximated by $[P_{H2O}\cdot e\hat{\ }(log(100+P_{H2O})/100\cdot 1)]/P_{TIP}$ and slow

779 export X_P (d) by $[P_{NaOH}\cdot e\hat{\ }(log(100+P_{NaOH})/100\cdot 1)]/P_{TIP}$. Arrows indicate the same values were

780 applied across all soil textures, otherwise soil-specific values (mean$\pm$SD) were used. See SI S4 for

781 model scripts.

782

783 **Fig. 2** Phosphate in surface soils (0 – 10 cm) of 21 pastures with different textures in the Peel-

784 Harvey catchment (Western Australia) based on sequential extraction with H_2O (left, light outline),

785 $NaHCO_3$, $NaOH$, and HCl (right, dark outline). P_{TIP} concentrations (sum of four fractions) for each

786 soil texture is indicated at the top, and the percentage contribution of H_2O (easily leachable) and

787 $H_2O+NaHCO_3$ (seasonally leachable) fractions indicated with dashed lines. Boxes represent median

788 $\pm$ 1 SD.

789

790 **Fig. 3** The $\delta^{18}O_P$ of P_{TIP} in pasture soils (0-10 cm) classed as either clay, loam, or sand from six

791 farms across the Peel-Harvey catchment (Western Australia). Boxes represent median $\pm$ 1 SD for

792 each soil texture. Black lines represent the mean (solid line), $\pm$1 SD (dashed lines), and

793   minimum/maximum (dotted lines) of the long-term local $\delta^{18}O_{P(eq)}$ range (Eq. 2); the grey line

794   indicates the mean $\delta^{18}O_{P(eq)}$ calculated for conditions during the winter sampling (*eq-w*).

795

796   **Fig. 4** The possible range of the isotopic composition of PO_4^{3-} export from clay, loam, and sand

797   pasture soils ($\delta^{18}O_{P(export)}$, ‰ v. VSMOW) within a catchment depends on fertiliser contribution to

798   the leachable soil PO_4^{3-} pool (f_{fert}) and fertiliser $\delta^{18}O_P$ composition (AG: black circles, SP: grey

799   triangles, manufactured 2013-2017). $\delta^{18}O_{P(export)}$ values were calculated for two export scenarios:

800   fast (a, c, e), where PO_4^{3-} is exported <1 day after fertilisation, and slow (b, d, f), where PO_4^{3-} is

801   leached over weeks-months. Both fast and slow export could occur with (e, f: X_P = 1 h or 1 month)

802   or without (c, d: X_P = nil) soil biological P turnover (Eq. 3). Violins (a, b) show the distribution of

803   f_{fert} values around the mean (solid line); boxes (c-f) show the mean ± 1 SD for $\delta^{18}O_{P(export)}$, with

804   whiskers to the minimum and maximum. Box colours distinguish soil textures (as defined in a and

805   b) and outlines the fertiliser (AG: black, SP: grey).

806