

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

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November 22, 2022

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-} ($\delta^{18}\text{OP}$) is a promising tracer of point source pollution, but its ability to track diffuse agricultural pollution is unclear. We tested the hypothesis that $\delta^{18}\text{OP}$ could distinguish between agricultural PO_4^{3-} sources by measuring the integrated $\delta^{18}\text{OP}$ composition and P speciation of contrasting inorganic fertilisers (compound v rock) and soil textures (sand, loam, clay). $\delta^{18}\text{OP}$ composition differed between the three soil textures sampled across six working livestock farms: sandy soils had lower overall $\delta^{18}\text{OP}$ values (21 ± 1 smaller, but more readily leachable, PO_4^{3-} pool. Fertilisers had greater $\delta^{18}\text{OP}$ variability (~ 8 and manufacturing year. Upscaling these values showed that ‘agricultural soil leaching’ $\delta^{18}\text{OP}$ signatures could span from 18 – 25 influenced by both fertiliser type and the time between application and leaching. These findings emphasise the potential of $\delta^{18}\text{OP}$ 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 **$\delta^{18}\text{O}$ as a tracer of PO_4^{3-} losses from agricultural landscapes**

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16 Submitted to *Journal of Environmental Management*

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18 **Highlights**

- 19 • Isotope fingerprints of soil and fertiliser PO_4^{3-} ($\delta^{18}\text{O}_\text{P}$) vary within catchments
- 20 • Source mixing and biological turnover affect $\delta^{18}\text{O}_\text{P}$ signatures exported downstream
- 21 • Tracing agricultural pollution with $\delta^{18}\text{O}_\text{P}$ requires accounting for soil zone dynamics

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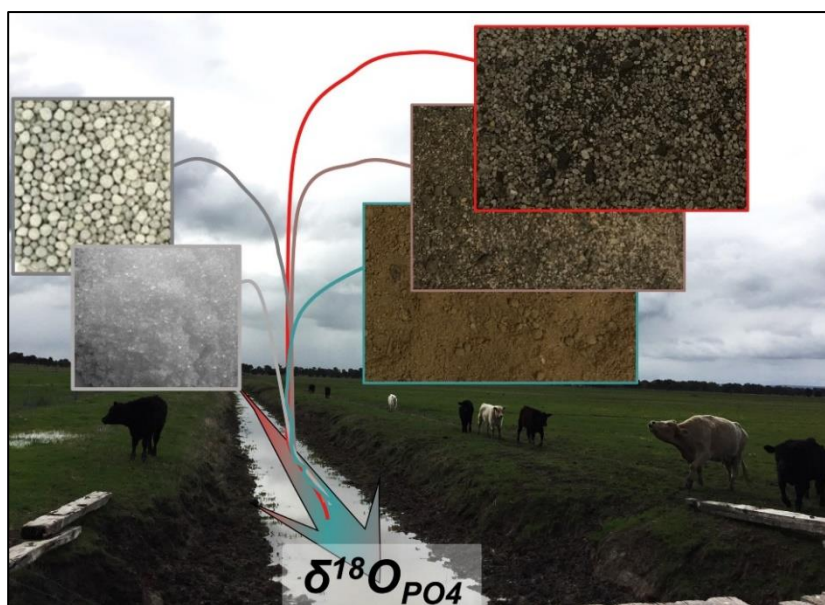
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29 catchment management. The natural abundance isotopic composition of O in PO_4^{3-} ($\delta^{18}\text{O}_\text{P}$) is a
30 promising tracer of point source pollution, but its ability to track diffuse agricultural pollution is
31 unclear. We tested the hypothesis that $\delta^{18}\text{O}_\text{P}$ could distinguish between agricultural PO_4^{3-} sources by
32 measuring the integrated $\delta^{18}\text{O}_\text{P}$ composition and P speciation of contrasting inorganic fertilisers
33 (compound v rock) and soil textures (sand, loam, clay). $\delta^{18}\text{O}_\text{P}$ composition differed between the
34 three soil textures sampled across six working livestock farms: sandy soils had lower overall $\delta^{18}\text{O}_\text{P}$
35 values ($21 \pm 1 \text{ ‰}$) than the loams ($23 \pm 1 \text{ ‰}$), which corresponded with a smaller, but more readily
36 leachable, PO_4^{3-} pool. Fertilisers had greater $\delta^{18}\text{O}_\text{P}$ variability ($\sim 8 \text{ ‰}$) driven by both fertiliser type
37 and manufacturing year. Upscaling these values showed that ‘agricultural soil leaching’ $\delta^{18}\text{O}_\text{P}$
38 signatures could span from 18 – 25 ‰, and are influenced by both fertiliser type and the time
39 between application and
40 leaching. These findings
41 emphasise the potential of
42 $\delta^{18}\text{O}_\text{P}$ to untangle soil-
43 fertiliser P dynamics under
44 controlled conditions, but that
45 its use to trace catchment-
46 scale agricultural PO_4^{3-} losses
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48 soil biological P cycling and its associated isotopic fractionation.



50
51 **Keywords:** Phosphate leaching, stable isotope tracers, eutrophication, diffuse agricultural pollution,
52 Peel-Harvey catchment, $\delta^{18}\text{O}-\text{PO}_4^{3-}$
53

55 1. Introduction

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

64 Calls to use the isotopic composition of oxygen within PO_4^{3-} ($\delta^{18}\text{O}_\text{P}$) as a P tracer date
65 back >10 years (Davies et al., 2014; Gruau et al., 2005; Young et al., 2009). This stems from
66 evidence that PO_4^{3-} sources (wastewater, tap water, fertilisers) can have distinct $\delta^{18}\text{O}_\text{P}$ signatures
67 (Gooddy et al., 2018; Gooddy et al., 2015; Granger et al., 2017b). Additionally, knowledge that
68 intracellular reactions with phosphatase enzymes impart a predictable temperature-dependent
69 equilibrium signature as oxygen is exchanged between PO_4^{3-} and the surrounding water (Chang and
70 Blake, 2015; Gross and Angert, 2015; Jaisi et al., 2011), means $\delta^{18}\text{O}_\text{P}$ can also indicate ecosystems
71 P cycling efficiency (Paytan et al., 2017; Pistocchi et al., 2017). Numerous studies propose using
72 $\delta^{18}\text{O}_\text{P}$ source and transformation data to constrain catchment-scale P pollution dynamics (Gooddy et
73 al., 2016; Granger et al., 2017b; Ishida et al., 2019; Tonderski et al., 2017). However, models are
74 limited by uncertainty around the $\delta^{18}\text{O}_\text{P}$ ‘signatures’ generated by different catchment P sources.

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

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 $\delta^{18}\text{O}_\text{P}$ variability ($\sim 5\%$ 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 $\delta^{18}\text{O}_\text{P}$ reaching equilibrium, soil $\delta^{18}\text{O}_\text{P}$ 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’ $\delta^{18}\text{O}_\text{P}$ range: fertiliser $\delta^{18}\text{O}_\text{P}$
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 $\delta^{18}\text{O}_\text{P}$ 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 $\delta^{18}\text{O}_\text{P}$ signatures. We tested this by measuring the $\delta^{18}\text{O}_\text{P}$ composition of contrasting
92 fertilisers and soils across an 1,800 km² catchment, then using mixing models to define the possible
93 range of exported $\delta^{18}\text{O}_\text{P}$ created by variable management (fertiliser application), biology (PO_4^{3-}
94 turnover), and hydrology (time before leaching, equilibrium $\delta^{18}\text{O}_\text{P}$ values).

95

96 **2. Materials & Methods**

97 **2.1 Site description**

98 Soil and fertiliser samples were collected from the 1,800 km² 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

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).

108

109 2.2 Sample collection

110 Fertiliser isotopic variability ($\delta^{18}\text{O}_{\text{P(fert)}}$) 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 km² farms across the catchment (SI S1). Sampling was timed to winter
118 (July 2017) when soil PO₄³⁻ export occurs (Summers et al., 1999). Management effects, including
119 fertiliser contamination of the measured soil $\delta^{18}\text{O}_{\text{P(soil)}}$ composition ($\delta^{18}\text{O}_{\text{P(soil)}}$), 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 ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$).

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 $\delta^{18}\text{O}_{\text{P(soil)}}$.

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

132 by extracting ignited v un-ignited soils with 1M H₂SO₄ (50:1) and measuring filtered extractant P
133 concentration via ICP (Saunders and Williams, 1955). Because chemical bonding between PO₄³⁻
134 and the soil matrix means that the amount of PO₄³⁻ in P_{total} may not correspond to the amount of
135 biologically available or leachable P, PO₄³⁻ 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 PO₄³⁻ 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 NaHCO₃ (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 PO₄³⁻ concentrations analysed via
141 flow injection analysis after neutralising NaOH and NaHCO₃ extracts.

142 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ was measured on the total PO₄³⁻ 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 H₂O extractable PO₄³⁻ for $\delta^{18}\text{O}_{\text{P}}$ analyses, while sands had insufficient PO₄³⁻
145 in the more tightly bound fractions. Using P_{TIP} is also advantageous because, by capturing the
146 majority of soil PO₄³⁻, 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 PO₄³⁻ likely to be exported (Rupp et al., 2018) the P_{TIP} $\delta^{18}\text{O}_{\text{P}(\text{soil})}$
149 provides a more robust and scalable soil ‘fingerprint’: extracted PO₄³⁻ ‘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 $\delta^{18}\text{O}_{\text{P}}$ 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

phosphate. After removing cations (AG50 X8 resin), silver phosphate (Ag_3PO_4) was precipitated using 5 ml of silver ammine solution. Triplicate subsamples (300 μg) of the produced Ag_3PO_4 were weighed into silver capsules and the $\delta^{18}\text{O}_\text{P}$ composition determined via thermal conversion elemental analyser (TC-EA, ThermoFinnigan, Germany) at 1400°C with graphite and glassy carbon chips, coupled to a Delta+XL mass spectrometer (ThermoFinnigan, Germany). Triplicates' precision was $\leq 0.3\%$. Sample CO yield relative to Ag_3PO_4 standards was checked to ensure deviations $< 10\%$. $\delta^{18}\text{O}_\text{P}$ values were calculated with an internal Ag_3PO_4 standard, ALFA-1 ($\delta^{18}\text{O}$: 14.2‰). There are no international reference materials, so ALFA-1 was calibrated to the Ag_3PO_4 standard 'B2207' (Elemental Microanalysis Ltd.) from an inter-laboratory comparison. Oxygen isotope ($^{18/16}\text{O}$) values are reported in δ ‰ v VSMOW.

2.4 Calculations

Soil organic carbon (C_org) was estimated as $0.516 \times \text{loss-on-ignition}$ (Jensen et al., 2018). Mineralisation of P_org to PO_4^{3-} , which can affect $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values (Gross and Angert, 2015), was parameterised as $\text{P}_{\text{min}(14)}$ (net mineralisation over 14 days) (Achat et al., 2010) based on measured soil organic v inorganic P composition (see SI S2). Data analyses were performed using R.v4.0 / RStudio.v1.3.959. Differences between farms and soil textures were determined via one-way ANOVA with an estimated marginal means post-hoc (Bonferroni adjusted), and correlations between soil parameters via Pearsons test (Kassambara, 2020). Figures were produced using ggplot2, patchwork, and munsell (Pedersen, 2019; Wickham, 2018; Wickham, 2016). Significance is defined as $p < 0.05$ and values are reported as mean \pm standard deviation.

2.4.1 Equilibrium $\delta^{18}\text{O}_\text{P}$

$\delta^{18}\text{O}_\text{P}$ values produced due to equilibrium fractionation during extracellular P cycling ($\delta^{18}\text{O}_{\text{P}(\text{eq})}$) were calculated using Eq. 1, as per (Chang and Blake, 2015; Hacker et al., 2019):

$$\text{(Eq. 1)} \quad \delta^{18}\text{O}_{\text{P}(\text{eq})} = (\delta^{18}\text{O}_{\text{H}_2\text{O}} + 1000)e^{\left(\frac{14.43 \times 1000}{T} - 26.54\right)/1000} - 1000$$

184 where $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ is defined by temperature (T, in kelvin) and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. Eq. 1 was solved two ways.
185 First, because the P_{TIP} used for $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ likely integrates long-term site conditions (Helfenstein et
186 al., 2018), $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ was calculated using long-term records of soil temperature at 10 cm (mean:
187 21°C, high: 26°C, low: 18°C) and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (mean: -3.96 ‰, low: -2.74 ‰, high: -5.18 ‰, based on
188 monthly precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ 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, $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ was also calculated using modelled daily winter soil
191 temperatures (mean: 13°C, high: 21°C, low: 8.2°C) (Kearney, 2019) and precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$
192 values measured during sampling ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$: -3.07 ± 2 ‰, $n = 10$). Precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ was
193 converted to soil water $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ based on evidence that soil $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is a mass balance of seasonal
194 precipitation (Benettin et al., 2018), $\pm +3\%$ 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 $\delta^{18}\text{O}_{\text{P}}$ range exported from farms to waterways ($\delta^{18}\text{O}_{\text{P}(\text{export})}$) 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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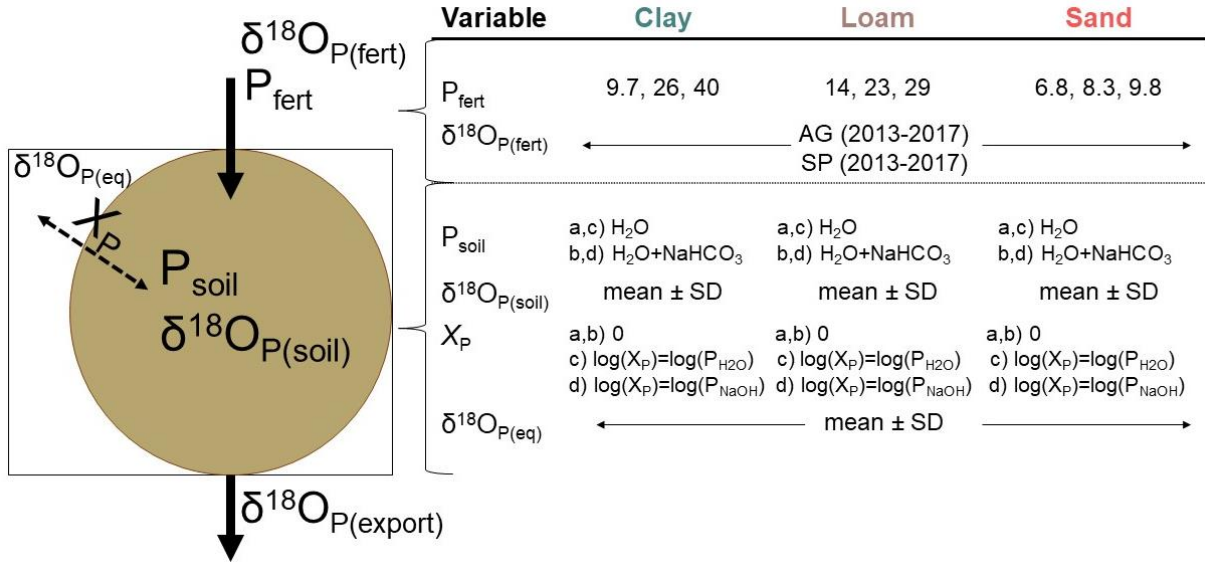


Fig. 1 Two-pool isotope mixing models (Eq. 2, Eq. 3) constrained the possible $\delta^{18}O_P$ range of PO_4^{3-} exported (leaching, run-off) from fertilised soils ($\delta^{18}O_{P(export)}$). The model was solved using recommended low, moderate, and high fertiliser applications rate (P_{fert} , in $\mu g P g^{-1}$ 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 \times fertiliser were ‘mixed’ with each 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 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 $\delta^{18}O_{P(eq)}$ (Eq. 1). Fast export X_P (c) was approximated by $[P_{H_2O} \cdot e^{\log(100+P_{H_2O})/100 \cdot 1}]/P_{TIP}$ and slow export X_P (d) by $[P_{NaOH} \cdot e^{\log(100+P_{NaOH})/100 \cdot 1}]/P_{TIP}$. Arrows indicate the same values were applied across all soil textures, otherwise soil-specific values (mean \pm 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):

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

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

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

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):

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

where an exchange factor (X_P) defines $\delta^{18}O_{P(\text{export.1})}$ mixing with $\delta^{18}O_{P(\text{eq})}$ (Gross and Angert, 2015). Eq. 3 constrains the effects of short-term (daily to monthly) biological P cycling, so $\delta^{18}O_{P(\text{eq})}$ was defined based on diurnal variations in winter soil temperatures (Eq. 1). As X_P is challenging to measure directly, values were approximated for each soil texture based on soil P mean residence time, calculated as the log-log linear relationship between H₂O extractable PO₄³⁻ and PO₄³⁻ turnover in <1 hr, or, 2) NaOH extractable PO₄³⁻ and PO₄³⁻ turnover in >1 hr – 3 months (Helfenstein et al., 2020). For biologically active ‘fast’ export (scenario c), X_P was defined as PO₄³⁻ exchange in < 1 hr and applied to scenario a $\delta^{18}O_{P(\text{export.1})}$ values. For biologically active ‘slow’ export (scenario d), X_P was defined as the proportion of PO₄³⁻ exchange in 1 hr – 3 months and applied to scenario b $\delta^{18}O_{P(\text{export.1})}$ values.

$\delta^{18}O_{P(\text{fert})}$ variability was parameterised two ways. First, models were run using the annual differences in $\delta^{18}O_{P(\text{fert})}$ measured 2013-2017 for different fertiliser types (AG and SP, but not MAP because only one year was sampled). Second, P_{fert} was varied to reflect the low, high, and median fertiliser application rates recommended for each soil texture: 14, 58, 37 kg P ha⁻¹ (clay), 18, 37, 28 kg P ha⁻¹ (loam), and 9, 13, 11 kg P ha⁻¹ (sand) (Summers and Weaver, 2011). Application rates (kg P ha⁻¹) were converted to concentrations (μg P g⁻¹) in the top 10 cm of soil (P_{fert}) using regional pasture soil bulk density (Viscarra Rossel et al., 2014): 1.44 ± 0.2 kg ha⁻¹ (clay), 1.25 ± 0.2 kg ha⁻¹ (loam), and 1.33 ± 0.1 kg ha⁻¹ (sand). This model does not consider the complex soil chemical processes affecting long-term fertiliser mobility, meaning fertiliser contributions to ‘slow’ export scenarios (b, d) may be overestimated.

Variability in soil inputs was parameterised by solving each export scenario (a: fast, b: slow, c: fast + turnover, d: slow + turnover) using the mean, mean+SD, and mean-SD of $\delta^{18}O_{P(\text{soil})}$ and P_{soil} for each soil texture, as well as for $\delta^{18}O_{P(\text{eq})}$ (Henry and Wickham, 2020): f_{fert} was calculated for each P_{soil} and P_{fert} combination, the minimum, mean-SD, mean, mean+SD, and maximum f_{fert} for scenarios (a, b) × soil texture used to solve Eq. 2 for each fertiliser × manufacturing year, and then

254 $\delta^{18}\text{O}_{\text{P}(\text{export.1})}$ values used to solve Eq. 3 for scenario (c, d) \times soil texture for each fertiliser \times
 255 manufacturing year (Fig. 1). Output $\delta^{18}\text{O}_{\text{P}(\text{export})}$ 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 $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ values ($p < 0.05$, $F = 52$). Values ranged from $17 \pm$
 264 1 ‰ (SP) to $22 \pm 0.05 \text{ ‰}$ (MAP) (Table 2). The $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ composition of SP and AG varied between
 265 manufacturing years: SP from $16 \pm 0.2 \text{ ‰}$ in 2015 to $19 \pm 0.2 \text{ ‰}$ in 2013, and AG from $20 \pm 0.4 \text{ ‰}$
 266 in 2014 to $22 \pm 0.01 \text{ ‰}$ in 2015.

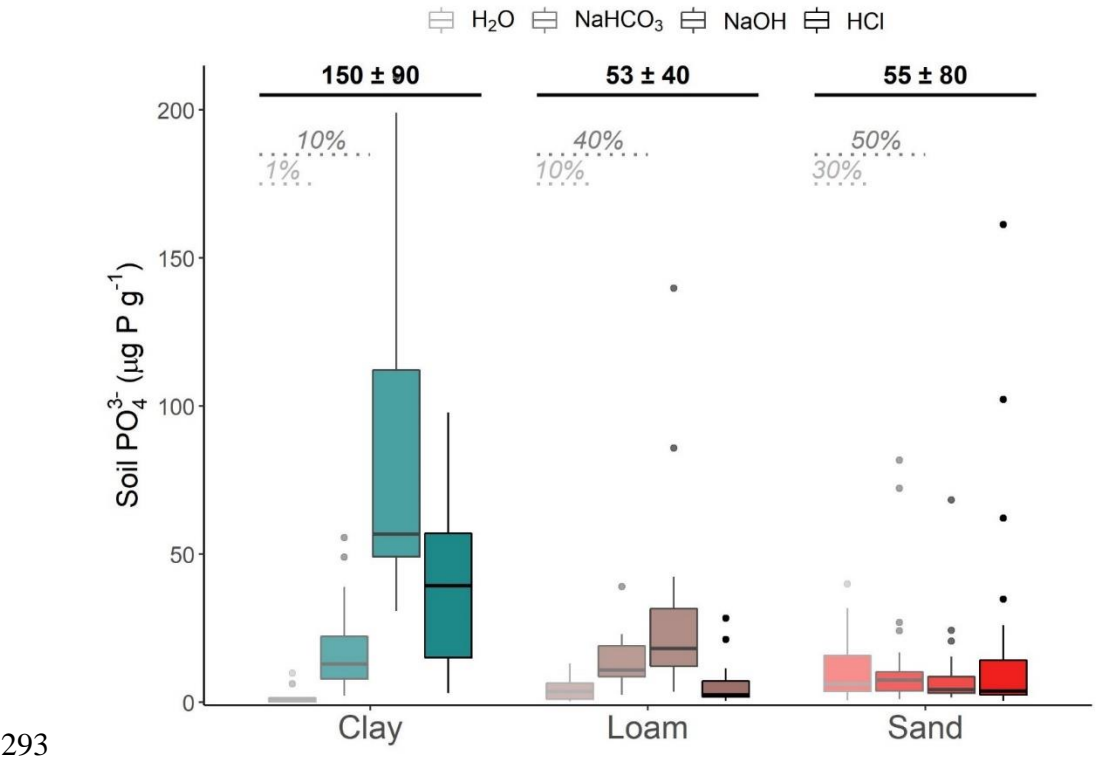
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268 **3.2 Soils**

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 ($66 \pm 20 \text{ mg C g}^{-1}$) than loams ($40 \pm 10 \text{ mg C g}^{-1}$) and sands ($38 \pm 30 \text{ mg C g}^{-1}$) ($F = 2.7$,
 271 $p < 0.05$) (Table 1), as was P_{total} (clay: $360 \pm 20 \text{ } \mu\text{g g}^{-1}$, loam: $190 \pm 90 \text{ } \mu\text{g g}^{-1}$, sand: $120 \pm 100 \text{ } \mu\text{g g}^{-1}$) ($F = 20$, $p < 0.05$). P_{org} did not differ between soil textures or farms (SI Table S1), so P_{org}
 272 accounted for a higher proportion of P_{total} in sands ($57 \pm 10 \text{ ‰}$) than loams ($45 \pm 10 \text{ ‰}$) and clays
 273 ($41 \pm 0.09 \text{ ‰}$) ($F = 12$, $p < 0.01$). The $\text{C}_{\text{org}}:\text{P}_{\text{org}}$ ratio was higher in sands ($630 \pm 500 \text{ g/g}$) than in clays
 274 ($540 \pm 300 \text{ g/g}$) or loams ($530 \pm 200 \text{ g/g}$) ($F = 3.3$, $p < 0.01$; Table 1). $\text{P}_{\text{min}(14)}$ was highest in absolute
 275 ($F = 10$, $p < 0.05$) terms in sands (SI Table S3), and decreased as a proportion of P_{TIP} from sands (14
 276 $\pm 10 \text{ mg g}^{-1}$) to loams ($4.4 \pm 3 \text{ mg g}^{-1}$) to clays ($0.74 \pm 0.4 \text{ mg g}^{-1}$) ($F = 23$, $p < 0.001$; Table 1).

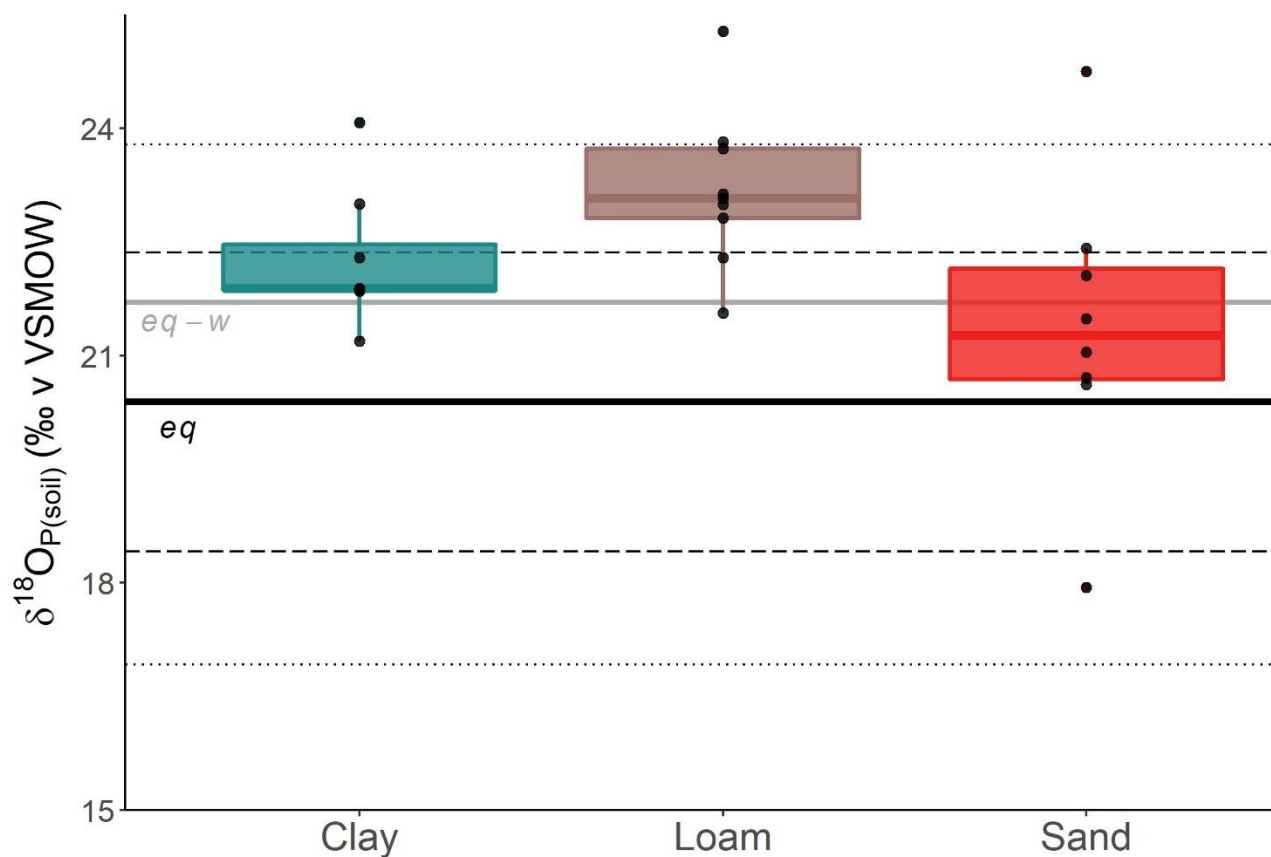
278 P_{TIP} (based on $\text{H}_2\text{O}+\text{NaHCO}_3+\text{NaOH}+\text{HCl}$ fractions) was higher in clays ($150 \pm 90 \text{ } \mu\text{g P g}^{-1}$)
 279 than loams ($53 \pm 50 \text{ } \mu\text{g P g}^{-1}$) or sands ($55 \pm 80 \text{ } \mu\text{g P g}^{-1}$) ($F = 11$, $p < 0.05$; Fig. 2). Water extractable

280 PO_4^{3-} differed between soil textures ($F = 9.6, p < 0.05$), with concentrations in sands ($11 \pm 10 \mu\text{g P g}^{-1}$)
 281 1) higher than in loams ($4.2 \pm 3 \mu\text{g P g}^{-1}$) and clays ($1.7 \pm 2 \mu\text{g P g}^{-1}$) (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 ($7.6 \pm 4 \mu\text{g P g}^{-1}$) and the predominantly sand soils in
 284 F1 had the highest ($27 \pm 20 \mu\text{g P g}^{-1}$) (see SI S2 for farm-level data). Clays had higher NaOH
 285 extractable PO_4^{3-} ($89 \pm 50 \mu\text{g P g}^{-1}$) than loams ($29 \pm 30 \mu\text{g P g}^{-1}$) or sands ($9.5 \pm 10 \mu\text{g P g}^{-1}$) ($F =$
 286 $26, p < 0.001$). Likewise, HCl extractable PO_4^{3-} was the highest in clays ($39 \pm 20 \mu\text{g P g}^{-1}$) and the
 287 lowest in loams ($6.0 \pm 8 \mu\text{g P g}^{-1}$) ($F = 3.9, p < 0.05$). 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 $\text{H}_2\text{O} + \text{NaHCO}_3$ fraction also decreased from sands ($54 \pm 20 \%$) to loams ($41 \pm 20 \%$) to clays ($13 \pm$
 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 $\text{H}_2\text{O} + \text{NaHCO}_3$ (seasonally leachable) fractions indicated with dashed lines.
 298 Boxes represent median ± 1 SD.

299 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values ranged from 25.3‰ (F4 loam) to 17.9‰ (F2 sand). Values negatively
 300 correlated with $\text{P}_{\text{min}(14)}$ ($p = 0.03$, $r = -0.45$) and positively correlated with C_{org} ($p = 0.03$, $r = 0.5$).
 301 Soil P concentrations did not correlate with $\delta^{18}\text{O}_{\text{P}(\text{soil})}$. $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values differed between soil
 302 textures but not farms, and were higher in loams (23.2 ± 1 ‰) than clays (22.3 ± 0.9 ‰) or sands
 303 (21.4 ± 2 ‰) ($p < 0.05$; $F = 3.8$; Fig. 3). $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ values calculated using long-term temperature and
 304 $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ records ranged from 16.9 to 23.8 ‰ (20.4 ± 1.97 ‰), versus from 19.3 – 24.1 ‰ based on
 305 winter soil temperatures and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (Fig. 3). This places loam $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values at or above the
 306 maximum $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ range, versus sand $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values around mean $\delta^{18}\text{O}_{\text{P}(\text{eq})}$.
 307



308
 309 **Fig. 3** The $\delta^{18}\text{O}_{\text{P}}$ of P_{TIP} in pasture soils (0-10 cm) classed as either clay, loam, or sand from six farms across the Peel-
 310 Harvey catchment (Western Australia). Boxes represent median ± 1 SD for each soil textures. Black lines represent the
 311 mean (solid line), ± 1 SD (dashed lines), and minimum/maximum (dotted lines) of the long-term local $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ range
 312 (Eq. 2); the grey line indicates the mean $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ calculated for conditions during the winter sampling ($eq-w$).
 313
 314

315 3.3 Export model

316 For scenario (a), f_{fert} (Eq. 2) decreased from 0.93 ± 0.1 (clays) via 0.84 ± 0.1 (loams) to 0.54
317 ± 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
318 ± 0.2 for sands (Fig. 4b). In scenario (a) $\delta^{18}\text{O}_{\text{P}(\text{export})}$ values track $\delta^{18}\text{O}_{\text{P}(\text{fert})}$, with clear differences
319 between AG v SP applied to all soil textures (Fig. 4c). Rapid P turnover (scenario c) shifted sand,
320 but not clays or loams, $\delta^{18}\text{O}_{\text{P}(\text{export})}$ away from low-end $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ values (Fig. 4e). Yearly $\delta^{18}\text{O}_{\text{P}(\text{fert})}$
321 differences in SP (2013 v 2014-2017) and AG (2014 v 2015) fertilisers affected modelled
322 $\delta^{18}\text{O}_{\text{P}(\text{export})}$ from clays and loams, but not sands, under ‘fast’ scenarios (a, c) (Fig. 4c,e). For ‘slow’
323 scenarios (b, d), differences in SP v AG $\delta^{18}\text{O}_{\text{P}(\text{export})}$ values were only expressed when $X_{\text{P}} = 0\%$ (Fig.
324 4d), and $\delta^{18}\text{O}_{\text{P}(\text{export})}$ from all soil textures and fertilisers normalised to $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ with \sim monthly P
325 turnover (Fig. 4f). Upscaling to sub-catchments, the possible $\delta^{18}\text{O}_{\text{P}(\text{export})}$ range is narrowest ($\sim 2\%$)
326 if export is slow and fertilisation type uniform (Table 3). In both sub-catchments fertiliser mixing
327 was more important than the export speed in defining the $\delta^{18}\text{O}_{\text{P}(\text{export})}$ values, and mixed fertilisers +
328 slow export produced the widest possible $\delta^{18}\text{O}_{\text{P}(\text{export})}$ range.

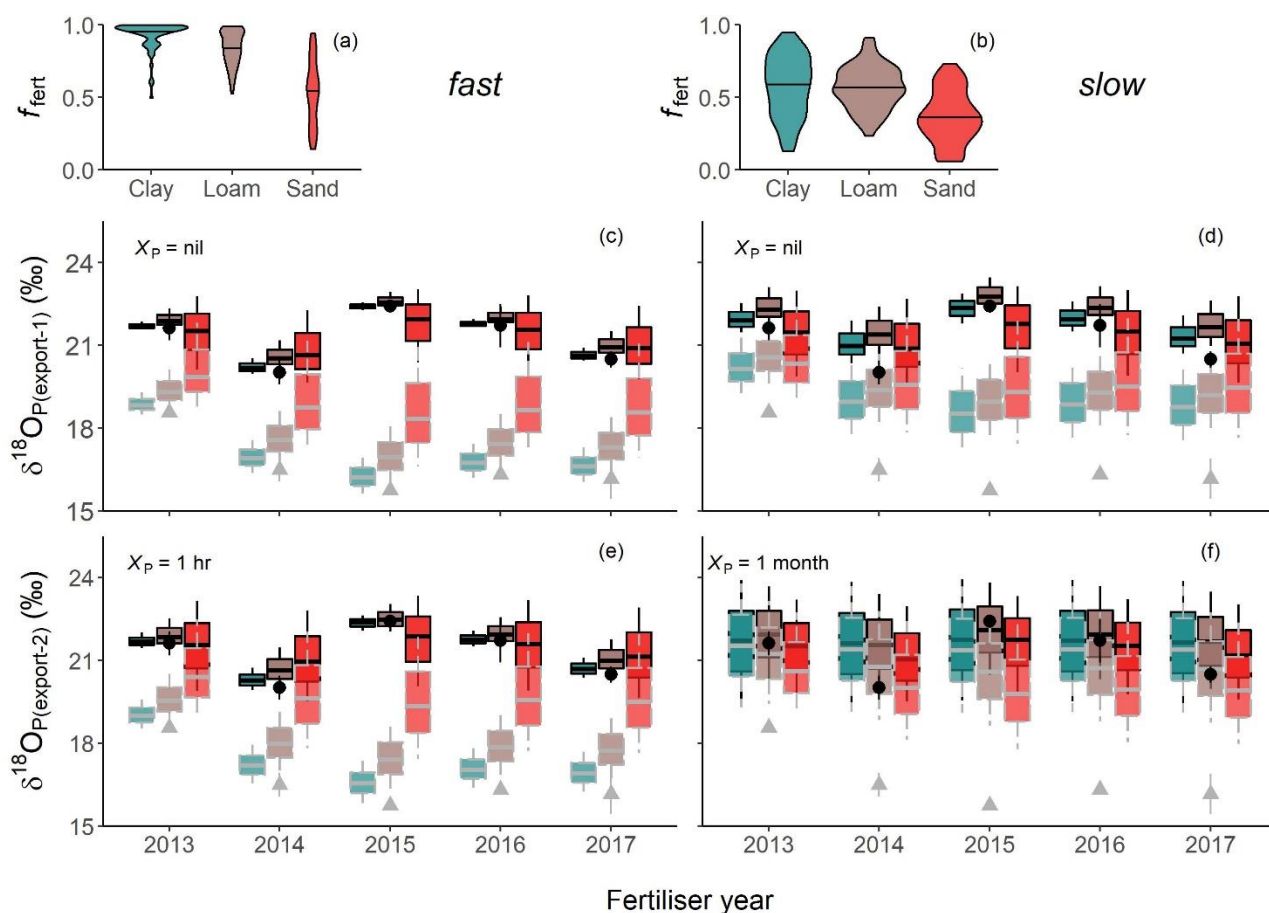


Fig. 4 The possible range of the isotopic composition of PO_4^{3-} export from clay, loam, and sand pasture soils ($\delta^{18}\text{O}_{\text{P}(\text{export})}$, ‰ v. VSMOW) within a catchment depends on fertiliser contribution to the leachable soil PO_4^{3-} pool (f_{fert}) and fertiliser $\delta^{18}\text{O}_{\text{P}}$ composition (AG: black circles, SP: grey triangles, manufactured 2013–2017). $\delta^{18}\text{O}_{\text{P}(\text{export})}$ 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: $X_{\text{P}} = 1 \text{ h}$ or 1 month) or without (c, d: $X_{\text{P}} = \text{nil}$) 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 $\pm 1 \text{ SD}$ for $\delta^{18}\text{O}_{\text{P}(\text{export})}$, 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 $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ range here (17 – 21 ‰) fits previous reports for inorganic commercial fertilisers (Table 2). Variations in $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ 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 $\delta^{18}\text{O}_{\text{P}}$ composition of the sedimentary rocks sourced to produce PO_4^{3-} fertilisers depend on age and/or equilibration with $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ during formation (Sun et al., 2020). Here the ~8 ‰ difference between N-bearing (AG, MAP) and rock (SP) fertilisers corresponded with different geologic

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 $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ during formation is
 354 unlikely given similarities in the $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ 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 $\delta^{18}\text{O}_{\text{P}}$ differences’ that is contributing to the consistent offset between
 357 fertiliser types. We note that geology-driven variations in $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ 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 $\delta^{18}\text{O}_{\text{P}}$ (Gooddy et al., 2015), and requires further consideration.

364 Regardless of the exact driver (source, manufacturing), a single precise $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ value is
 365 unlikely to exist at the spatial and temporal scale of catchment studies. Establishing methods for
 366 predicting, and thus better constraining, $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ will be critical to any future attempts to use $\delta^{18}\text{O}_{\text{P}}$
 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 $\text{C}_{\text{org}}:\text{P}_{\text{org}}$ 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).

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 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ and $\delta^{18}\text{O}_{\text{P}(\text{export})}$.
 378 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ 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 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ towards $\delta^{18}\text{O}_{\text{P}(\text{eq})}$,
 382 more labile PO_4^{3-} fractions tends to have (higher) $\delta^{18}\text{O}_{\text{P}}$ values closer to $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ and more tightly
 383 bound PO_4^{3-} fractions tend to have (lower) $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values closer to the geologic parent material
 384 $\delta^{18}\text{O}_{\text{P}}$ (Roberts et al., 2015; Tian et al., 2020). This predicts that the sands' predominantly labile
 385 PO_4^{3-} pool would shift $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values higher than the clays, where most PO_4^{3-} is tightly bound
 386 (Rodionov et al., 2020). Instead, the sands had the lowest $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values, and almost all $\delta^{18}\text{O}_{\text{P}(\text{soil})}$
 387 values fell within the $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ range (Fig. 3). It is reasonable that all soil PO_4^{3-} was within the
 388 $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ 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 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ values fall into distinct 'soil texture' zones within this range?
 391 Variations within the $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ range could be driven by three factors: divergent equilibrium
 392 conditions (soil temperature, $\delta^{18}\text{O}_{\text{H}_2\text{O}}$), different PO_4^{3-} sources, and/or fractionation by competing
 393 biological processes. First, daily – seasonal parameter fluctuations are not seen to affect $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ of
 394 P_{TIP} (Angert et al., 2011; Lei et al., 2019). This suggests that long-term evaporation ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) or
 395 temperature differences between the soil textures would be needed to create a 'soil specific'
 396 $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ 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 $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ in coarse
 399 grained sands above $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ in the fine grained clays (Gazis and Feng, 2004), the opposite of the

400 observed pattern. Second, pastures receive P_{org} and PO_4^{3-} inputs. Inorganic fertilisers can be ruled
 401 out as $\delta^{18}\text{O}_{\text{P(fert)}}$ values were lower than loam $\delta^{18}\text{O}_{\text{P(soil)}}$ (Fig. 4), and likewise processed P_{org}
 402 (manure) likely has $\delta^{18}\text{O}_{\text{P}}$ below the $\delta^{18}\text{O}_{\text{P(soil)}}$ range here (Granger et al., 2017b). While raw P_{org}
 403 inputs (plants) can have $\delta^{18}\text{O}_{\text{P}}$ up to $\sim 30\text{‰}$ (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 ($9.2 \pm 2 \text{ mg C g}^{-1}$ v $7.7 \pm 2 \text{ mg C g}^{-1}$ and $4.9 \pm 2 \text{ mg C g}^{-1}$, respectively) (Viscarra
 408 Rossel et al., 2014). If char contains $20 \mu\text{g PO}_4^{3-}\text{-P g}^{-1}$ (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 $\delta^{18}\text{O}_{\text{P}}$ values may be too low ($\sim 15\text{‰}$)
 411 (Bigio and Angert, 2019) to explain the observed loam $\delta^{18}\text{O}_{\text{P(soil)}}$ values.

412 Alternatively, both the mineralisation of P_{org} to PO_4^{3-} and microbial PO_4^{3-} assimilation affect
 413 $\delta^{18}\text{O}_{\text{P}}$. Scavenging P_{org} in low fertility soils can decrease $\delta^{18}\text{O}_{\text{P(soil)}}$ below $\delta^{18}\text{O}_{\text{P(eq)}}$ (Liang and Blake,
 414 2006; Pistocchi et al., 2020), and estimates suggest that mineralisation is highest ($P_{\text{min}} = \sim 1\%$ of
 415 P_{TIP} per fortnight) in the P-poor, relatively low $\delta^{18}\text{O}_{\text{P(soil)}}$ sands (Table 1). Additionally, microbial
 416 PO_4^{3-} assimilation increases $\delta^{18}\text{O}_{\text{P(soil)}}$ (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 $\delta^{18}\text{O}_{\text{P(soil)}}$
 418 values. Low P in both sands and loams could promote microbial PO_4^{3-} uptake and increase $\delta^{18}\text{O}_{\text{P(soil)}}$
 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 $\delta^{18}\text{O}_{\text{P(soil)}}$ reset to the mean $\delta^{18}\text{O}_{\text{P(eq)}}$ 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 $\delta^{18}\text{O}_{\text{P(soil)}}$ patterns is not
 423 certain, the non-random distribution of $\delta^{18}\text{O}_{\text{P(soil)}}$ within the $\delta^{18}\text{O}_{\text{P(eq)}}$ range emphasises the need to
 424 move beyond simply defining $\delta^{18}\text{O}_{\text{P(soil)}}$ as ‘in’ or ‘out’ of equilibrium and start unpicking the
 425 competing biological and hydrologic processes at play.

426

427 4.3 $\delta^{18}\text{O}_\text{P}$ as a tracer of PO_4^{3-} export from agricultural systems

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

429 1) how much fertiliser is exported directly to water?, 2) which landscape units contribute
430 disproportionately to PO_4^{3-} export?, and, 3) how much does agriculture contribute to catchment
431 PO_4^{3-} loads? The mixing models used here generated clear constraints on how $\delta^{18}\text{O}_\text{P}$ data could be
432 used at each of these scales.

433 Directly exported P fertilisers are a significant financial and environmental risk. Although
434 difficult to measure, estimates suggest fertilisers account for 30-80% of PO_4^{3-} leached from
435 agricultural systems (Nash et al., 2019), and radiotracer studies show 20-30 % of fertiliser PO_4^{3-} is
436 leached from pastures within two months of application (McLaren et al., 2017; McLaren et al.,
437 2016). There is further uncertainty about the timing of these direct export events: how long
438 fertilisers stay in granular form depends on rainfall, temperature, and fertiliser type (McLaren et al.,
439 2017). The wide $\delta^{18}\text{O}_{\text{P(fert)}}$ range reported here indicates that $\delta^{18}\text{O}_\text{P}$ values could prove a uniquely
440 powerful tool for untangling these PO_4^{3-} leaching dynamics at the plot - paddock scale if
441 isotopically distinct fertiliser v soils were first identified. Yet the same $\delta^{18}\text{O}_{\text{P(fert)}}$ range complicates
442 efforts to identify soil and land-use specific $\delta^{18}\text{O}_{\text{P(export)}}$ signatures (Fig. 4, Table 3).

443 The twin possibilities of mixed fertiliser use and variable biological P turnover drive the
444 uncertainty in $\delta^{18}\text{O}_{\text{P(export)}}$. Across the modelled two sub-catchments the ‘agricultural’ $\delta^{18}\text{O}_{\text{P(export)}}$
445 could reasonably range between 18‰ and 25‰, a much wider range than would be predicted by
446 simply using the sub-catchment soil maps to upscale $\delta^{18}\text{O}_{\text{P(soil)}}$. This level of uncertainty means
447 large datasets of receiving water $\delta^{18}\text{O}_\text{P}$ values are needed to generate statistically robust
448 identification of the fertiliser and soil PO_4^{3-} sources. For instance, measuring an ‘out of equilibrium’
449 downstream $\delta^{18}\text{O}_\text{P}$ value of 19‰ could reasonably be evidence of SP export, but would not rule out
450 export of other fertilisers contributing up to 40% of PO_4^{3-} . Conversely, measuring a $\delta^{18}\text{O}_\text{P}$ value of
451 21‰, well above the SP $\delta^{18}\text{O}_{\text{P(fert)}}$ range, could not conclusively rule SP out as a PO_4^{3-} source (Fig.

452 4, Table 3). So while biological P turnover could ameliorate some of the variability created by
453 fertiliser-soil mixing by shifting $\delta^{18}\text{O}_{\text{P}(\text{export})}$ values towards $\delta^{18}\text{O}_{\text{P}(\text{eq})}$, it also highlights more
454 intransigent sources of uncertainty. First, the soil $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ range is itself uncertain due to questions
455 around the extent to which variations are caused by hydrology (temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (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 $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ dynamics is complicated by the fact that the PO_4^{3-} pools that can be extracted for $\delta^{18}\text{O}_{\text{P}}$
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 $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ must be resolved in order to
464 usefully incorporate $\delta^{18}\text{O}_{\text{P}}$ into P reactive transport models (Dorioz et al., 1998). One potential is
465 that improved $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ understanding could be used to construct $\delta^{18}\text{O}_{\text{P}}$ catchment models based on
466 temperature and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ regimens.

467

468 5. Conclusions

469 The ability of phosphate isotopes ($\delta^{18}\text{O}_{\text{P}}$) 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 $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ values to identify
472 diffuse agricultural pollution. Uncertainty from $\delta^{18}\text{O}_{\text{P}}$ 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 $\delta^{18}\text{O}_{\text{P}}$ signatures should be attributed to diffuse catchment sources
475 with caution.

476

477 **Associated content:** The Supporting Information pdf contains additional: S1) site maps (Figure S1:
478 Site map with farm locations, Figure S2: Sub-catchment maps with soil textures), S2) additional
479 soil data (Table S1: Background data on soil P status and N content, Table S2: Sequential extraction
480 soil PO_4^{3-} concentration information by farm \times soil texture, Table S3: $\text{P}_{\min(14)}$ data), S3) input
481 variables for $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ and mixing model calculations (Table S4: precipitation $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ for winter
482 2017, Table S5: Long-term soil temperature data, Table S6: Modelled daily winter soil
483 temperatures, Table S7: Estimated P turnover (X_{P}) by soil texture), and, S4) R scripts (S4.1: $\delta^{18}\text{O}_{\text{P}(\text{eq})}$
484 calculations, S4.2: mixing models, S4.3: up-scaling calculations). Soil data are available on
485 <https://figshare.com/s/e1416e6217fe0e7f3b10> (*link for review only, will be published with DOI*
486 *upon acceptance*).

488 **Acknowledgements:** Iain Alexander and Natasha Carlson-Perret (Southern Cross University)
489 assisted with soil P extractions. Robert Summers (Department of Primary Industries and Regional
490 Development, Western Australia) supplied background site data, soil sampling equipment, and
491 fertiliser samples. Fiona Valesini (Murdoch University) helped organise field work and secure
492 research funding. Thanks to Justin Mercy (CSBP) for information on fertiliser sources and
493 production, and to the six land owners for granting access to their properties. Research was funded
494 by Australian Research Council grant LP150100451 and by the UK's Natural Environment
495 Research Council Environmental Isotope Facility grant IP-1664-1116.

497 **Author contributions:** NSW, MYR, and BDE designed the study. NSW and MYR carried out the
498 study. PJW and ACS carried out isotopic extractions and analysed the samples. NSW and DCG
499 analysed the data. NSW and DCG wrote the manuscript, with input from all co-authors.

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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 $\delta^{18}\text{O}_{\text{P(soil)}}$. The contribution of P_{org} to P_{total} is calculated on a g/g basis. Potential P mineralisation over 14 days
736 ($\text{P}_{\text{min(14)}}$) 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} <i>mg C g⁻¹</i>	P_{total} <i>μg P g⁻¹</i>	% P_{org} $(\text{P}_{\text{org}}/\text{P}_{\text{total}}) \cdot 100$	$\text{C}_{\text{org}}:\text{P}_{\text{org}}$ g/g	$\text{P}_{\text{min(14)}}:\text{P}_{\text{TIP}}$ mg/g
		<i>all</i>	$\delta^{18}\text{O}_{\text{P}}$						
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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739 **Table 2** Inorganic fertiliser $\delta^{18}\text{O}_\text{P}$ values reported for this study and others ($\delta^{18}\text{O}_{\text{P(fert)}}$, values in ‰ v VSMOW), with respect to fertiliser type, where
740 the fertiliser was manufactured, and where the PO_4^{3-} raw material was sourced from ('unspecified' denotes data unavailable).
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Fertiliser type	Manufactured	Sourced	$\delta^{18}\text{O}_{\text{P(fert)}}$	Reference
Superphosphate	Australia	Christmas Island	16.7 ± 1 <i>15.6 – 18.7</i>	This study
	Europe	<i>Unspecified</i>	17.7 ± 0.2	Tamburini et al. (2010)
	Japan	Japan	12.7	Ishida et al. (2019)
	Australia	<i>Unspecified</i>	21.4 ± 0.5	Polain et al. (2018)
	Israel	<i>Unspecified</i>	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	<i>Unspecified</i>	20.2 ± 0.1	Polain et al. (2018)
N-P-S-K	Australia	USA	21.3 ± 1 <i>19.7 – 22.4</i>	This study
	Europe	Morocco & USA	21.8 ± 0.5	Gruau et al. (2005)
	Europe	<i>Unspecified</i>	20.9 ± 6	Granger et al. (2017b)
<i>Unspecified</i>	USA	USA	23.8 ± 1	Li et al. (2011)
	USA	<i>Unspecified</i>	19 ± 1	McLaughlin et al. (2006)
	USA	Israel	19.6	Young et al. (2009)
	China	China	11.5 ± 0.1	Tian et al. (2020)

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745 **Table 3** Possible $\delta^{18}\text{O}_{\text{P}(\text{export})}$ range from two sub-catchments with differing soil distributions (maps:
 746 SI S1). The $\delta^{18}\text{O}_{\text{P}(\text{export})}$ range was calculated by varying the relative proportion of SP v AG
 747 fertilisers and speed of PO_4^{3-} transport from soil to water (fast, scenario a: mixing with H_2O
 748 extractable PO_4^{3-} pool, $X_P = 0\%$; or scenario d: mixing with $\text{H}_2\text{O} + \text{NaHCO}_3$ extractable PO_4^{3-} , $X_P =$
 749 20 – 90%, depending on soil texture), see SI S4 for calculations.

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

750 ¹ 50% ‘d’ + 50% ‘a’

751 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 $\delta^{18}\text{O}_\text{P}$ range of PO_4^{3-}
770 exported (leaching, run-off) from fertilised soils ($\delta^{18}\text{O}_{\text{P}(\text{export})}$). The model was solved using
771 recommended low, moderate, and high fertiliser applications rate (P_{fert} , in $\mu\text{g P g}^{-1}$ soil) for each soil
772 texture (clay, loam, sand) and $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ values for two fertilisers (AG: N-P-K, SP: superphosphate)
773 manufactured between 2013 and 2017. $\delta^{18}\text{O}_{\text{P}(\text{fert})}$ for each year \times fertiliser were ‘mixed’ with each
774 soil texture using the measured $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ range for P_{TIP} and P_{soil} ($\mu\text{g P g}^{-1}$ soil), defined by H_2O
775 extractable PO_4^{3-} for fast export scenarios (a, c) and $\text{H}_2\text{O} + \text{NaHCO}_3$ extractable PO_4^{3-} for
776 slow/seasonal export scenarios (b, c). $\delta^{18}\text{O}_{\text{P}(\text{export})}$ for both fast and slow export was calculated with
777 (c, d) and without (a, b) soil biological P turnover (X_P), which shifts $\delta^{18}\text{O}_{\text{P}(\text{export})}$ towards $\delta^{18}\text{O}_{\text{P}(\text{eq})}$
778 (Eq. 1). Fast export X_P (c) was approximated by $[\text{P}_{\text{H}_2\text{O}} \cdot e^{(\log(100+\text{P}_{\text{H}_2\text{O}})/100 \cdot 1)}] / \text{P}_{\text{TIP}}$ and slow
779 export X_P (d) by $[\text{P}_{\text{NaOH}} \cdot e^{(\log(100+\text{P}_{\text{NaOH}})/100 \cdot 1)}] / \text{P}_{\text{TIP}}$. 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 $\text{H}_2\text{O}+\text{NaHCO}_3$ (seasonally leachable) fractions indicated with dashed lines. Boxes represent median
788 ± 1 SD.

789

790 **Fig. 3** The $\delta^{18}\text{O}_\text{P}$ 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 ± 1 SD for
792 each soil texture. Black lines represent the mean (solid line), ± 1 SD (dashed lines), and

793 minimum/maximum (dotted lines) of the long-term local $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ range (Eq. 2); the grey line
794 indicates the mean $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ 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 ($\delta^{18}\text{O}_{\text{P}(\text{export})}$, ‰ v. VSMOW) within a catchment depends on fertiliser contribution to
798 the leachable soil PO_4^{3-} pool (f_{fert}) and fertiliser $\delta^{18}\text{O}_{\text{P}}$ composition (AG: black circles, SP: grey
799 triangles, manufactured 2013-2017). $\delta^{18}\text{O}_{\text{P}(\text{export})}$ 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: $X_{\text{P}} = 1$ h or 1 month)
802 or without (c, d: $X_{\text{P}} = \text{nil}$) 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 $\delta^{18}\text{O}_{\text{P}(\text{export})}$, 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

Supporting Information

for

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

by

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submitted to

Journal of Environmental Management

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S1: Site maps

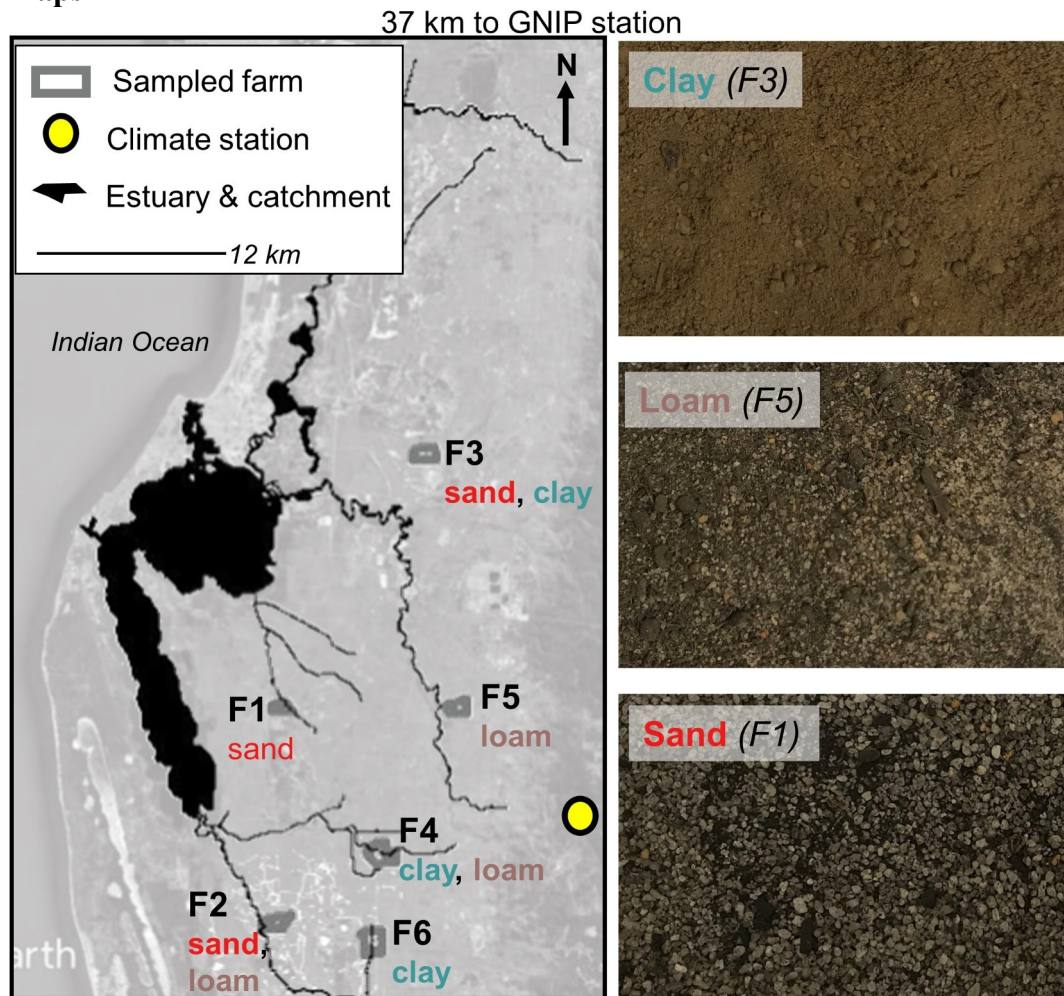


Fig. S1 Soil samples were collected from farms along the southern coast of Western Australia. Soils were collected from a total of 21 fields, which had either sand, loam or clay soil textures. Locations of the climate station used for long-term and daily soil temperature data is shown; the GNIP station used for long-term precipitation data is 37 km north of the mapped area. Base image on left panel from GoogleEarth. Soil photos from NS Wells.

S2: Additional soil data

Phosphorus mineralisation

The mineralisation of soil organic P forms to inorganic PO_4^{3-} is difficult to measure directly (Bünemann et al., 2015). However, it is important to parametrise in soil $\delta^{18}\text{O}_\text{P}$ studies as net mineralisation is a fractionating process. Here we estimated mineralisation rates using a modified version of the empirical equation developed by Achat et al. (2010):

$$(Eq. S1) \quad P_{\min(14)} = 0.6976 \left(P_{H_2O} \cdot \frac{P_{org}}{P_{TIP}} \right) \cdot (1 - e^{-0.0078}) + 0.00026 \cdot P_{org} \cdot 14$$

where $P_{\min(14)}$ ($\mu\text{g g}^{-1}$) is the net amount of PO_4^{3-} mineralised over 14 days, estimated from the measured P_{org} . The original equation bases rates on microbial biomass P, which here was approximated by applying the ratio of P_{org} to P_{TIP} to the measured H_2O extractable PO_4^{3-} (P_{H_2O}). Values generated from this equation should thus be treated as approximations rather than certainties.

Table S1: Additional soil P data. The phosphorus buffering index (PBI) and phosphorus environmental risk index (PERI) values are based on field sampling carried out prior to the presented work. Higher PBI values denote greater capacity to store P; higher PERI values denote greater likelihood of P export. Data from Rob Summers (Department of Primary Industries and Regional Development, Western Australia). See Burkitt et al. (2002) for details on index calculations. The P_{org} , TN, and N:P ratios were measured on samples collected during the presented July 2017 campaign, and are shown here to provide additional context on soil fertility differences.

Site	Soil texture	PBI	PERI	P_{org} $\mu\text{g g}^{-1}$	TN $\mu\text{g g}^{-1}$	N:P g/g
F1	Sand	1 – 4	2 – 10	220 (300)	320 (400)	0.95 (0.3)
F2	Loam	19 – 36	0.7	63 (20)	190 (31)	1.3 (0.3)
	Sand	3 – 5	2	72 (60)	290 (200)	2.7 (1)
F3	Clay	190	0.3	120 (40)	270 (70)	0.68 (0.1)
	Sand	1 – 2	2 – 4	41 (20)	170 (100)	2.6 (1)
F4	Clay	60 – 170	0.4	170 (70)	350 (100)	0.80 (0.1)
	Loam	50	0.7	120 (60)	310 (70)	1.0 (0.2)
F5	Loam	25 – 30	0.3 – 0.5	87 (30)	220 (70)	1.3 (0.2)
F6	Clay	90 – 100	0.1 – 0.2	120 (40)	330 (90)	1.3 (0.2)

Table S2: Sequential PO_4^{3-} extraction information for soils collected from pastures from six different farms (F1 – F6) across the Peel-Harvey catchment in Western Australia. ‘Total’ is the sum of the four sequential extractions, %leachable is the concentration of either H_2O extractable or $\text{H}_2\text{O}+\text{NaHCO}_3$ extractable PO_4^{3-} relative to the total, Soils are separated by dominant text (sand, loam, clay). Each sample (n) represents triplicate bulked soil cores (0-10 cm), which were each extracted in duplicate, and each extract analysed in duplicate.

Site	Soil texture	n	P- H_2O	P- NaHCO_3	P- NaOH	P- HCl	Total	% leachable (H_2O)	% leachable ($\text{H}_2\text{O}+\text{NaHCO}_3$)
F1	Sand	9	15 (10)	27 (30)	18 (20)	46 (50)	110 (100)	18 (10)	42 (20)
F2	Loam	6	7.4 (4)	16 (7)	16 (10)	6.3 (4)	45 (20)	20 (10)	55 (10)
	Sand	6	12 (9)	6.5 (4)	5.1 (4)	6.3 (6)	30 (20)	40 (20)	62 (20)
F3	Clay	3	0.24 (0.1)	34 (20)	130 (40)	48 (10)	210 (70)	0.11 (0.04)	16 (9)
	Sand	9	5.5 (4)	4.7 (3)	3.7 (1)	2.9 (3)	17 (5)	32 (20)	60 (20)
F4	Clay	9	3.4 (3)	25 (10)	120 (60)	59 (20)	210 (80)	1.5 (1)	13 (3)
	Loam	3	5.3 (4)	24 (10)	88 (50)	18 (10)	130 (80)	4.7 (5)	24 (10)
F5	Loam	9	2.3 (2)	9.7 (4)	18 (7)	1.9 (1)	32 (10)	7.4 (5)	37 (10)
F6	Clay	9	0.56 (0.6)	7.6 (4)	45 (9)	16 (9)	9.4 (70)	0.75 (0.7)	11 (5)

Table S3 $\text{P}_{\min(14)}$ rates (Eq. S1) estimated for different pasture soil textures (clay, loam, sand) collected from six different farms within the coastal Peel-Harvey catchment (Western Australia). Values are mean (\pm SD)

Soil Texture	Farm	$\text{P}_{\min(14)}$ $\mu\text{g g}^{-1}$
Clay	F3	0.049 (0.02)
	F4	0.15 (0.1)
	F6	0.061 (0.02)
Loam	F2	0.25 (0.2)
	F4	0.18 (0.1)
	F5	0.12 (0.07)
Sand	F1	0.40 (0.4)
	F2	0.55 (0.4)
	F3	0.27 (0.2)

S3: Input data for isotope mixing models

Table S4: The isotopic composition of rain collected across the farm sites within 1 month of collecting soils for $\delta^{18}\text{O}_{\text{P}(\text{soil})}$ analysis.

Date	Amount (mm)	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰ v. VSMOW)
30/06/2017	3	-2.8
01/07/2017	2.6	0.6
01/07/2017	18	-5.8
03/07/2017	12	-2.7
11/07/2017	4.4	-6.3
11/07/2017	4.4	-2.3
21/07/2017	1.6	-2.5
26/07/2017	3	-0.9
28/07/2017	4.6	-2.7
08/08/2017		-5.3

Table S5 Temperature data used to calculate $\delta^{18}\text{O}_{\text{P}(\text{eq})}$ values. $T_{\text{soil}(\text{avg})}$ is from 86 years Medina Research Station data (http://www.bom.gov.au/climate/averages/tables/cw_009194.shtml); T_{air} is daily highs and lows for the sampled months (downloaded from the Bureau of Meteorology <http://www.bom.gov.au/climate/dwo/IDCJDW6038.latest.shtml>), and the expected offset between T_{soil} and T_{air} is based on data published in van den Hoogen et al. (2021).

Month	$T_{\text{soil}(\text{avg})}$ °C	$T_{\text{air}(2017)}$ °C	Modelled offset ($T_{\text{soil}} - T_{\text{air}}$)
January	22	-	-2.34
February	22.2	-	-0.0114
March	20.0	-	-0.553
April	16.4	-	-0.256
May	13.1	-	-0.213
June	11.2	8.8 – 23	-0.372
July	10.3	7.2 – 21	-0.704
August	10.6	5.7 – 26	-1.90
September	11.9	-	-3.44
October	14.1	-	-5.20
November	17.2	-	-2.57
December	20	-	-3.62
Annual average	15.8	-	-1.8 ± 3

Table S6: To get a better picture of likely daily variations in soil temperatures, we also used the Global Soil Microclimate Forecaster (Kearney 2019) to estimate temperatures at the soil surface (0 cm) and at 5 and 10 cm depth for winter the study area (Pinjarra, WA). Data can be accessed at: http://bioforecasts.science.unimelb.edu.au/app_direct/soil/

Time	T _{0cm}	T _{5cm}	T _{10cm}
00:00	8.6	11	12
04:00	7.9	9.3	11
08:00	7.3	9.1	10
12:00	20	18	12
16:00	23	20	14
20:00	11	13	13
Daily Mean	13 ± 7	13 ± 4	13 ± 2

Table S7: The proportion of the total HCl extractable PO₄³⁻ pool of each soil texture that was likely to be recycled (X_P) was estimated over, 1) 1 hr, and, 2) >1 hr – 3 months, based on a 1:1 log-log relationships between exchangeable PO₄³⁻ and H₂O extractable PO₄³⁻ and NaOH extractable PO₄³⁻ (Helfenstein et al. 2020). Values are mean (±SD).

Soil texture	<i>n</i>	X_P (1 hr)	X_P (~ 1 month)
Clay	21	1.0 (1)	110 (40)
Loam	18	12 (10)	66 (40)
Sand	24	33 (20)	21 (9)

S4: R scripts for mixing models and up-scaling calculations

S4.1 Isotope equilibrium calculations

#formula for calculating d18Op(eq), just need to define a dataframe w temperature data and another w d18OH2O data

#this handles converting precip data into long-term d18OH2O average for the location

```
d18Op_equilibrium<-function(df_temp,df_isotope) {
```

```
  #define factors
```

```
  e_evap<-3 #from Mathieu 1996, this should range between 3.5 and 5, ~3 for Sprenger et al 2017
```

```
  e_evap0<-0 #from Baenettin et al 2018, say mixing masks any evaporation signature
```

```
  #define temperature dataset & calculate long-term averages in C
```

```
  T_min<-mean(df_temp$Min_avg_soil_temp)
```

```
  T_max<-mean(df_temp$Max_avg_soil_temp)
```

```
  T_mean<-mean(df_temp$Avg_soil_temp)
```

```
  #calculate relevant d18OH2O range, including evaporative enrichment factor to correct precip to soil
```

```
  (d18O_H2O_soil_mean<-sum(df_isotope$d18O_H2O_avg*df_isotope$Precipitation_mm_avg)/  
    sum(df_isotope$Precipitation_mm_avg)+e_evap)
```

```
  (d18O_H2O_soil_mean0<-  
sum(df_isotope$d18O_H2O_avg*df_isotope$Precipitation_mm_avg)/  
  sum(df_isotope$Precipitation_mm_avg)+e_evap0)
```

```
  (d18O_H2O_soil_min<-sum((df_isotope$d18O_H2O_avg-  
df_isotope$d18O_H2O_sd)*df_isotope$Precipitation_mm_avg)/  
    sum(df_isotope$Precipitation_mm_avg)+e_evap)
```

```
  (d18O_H2O_soil_min0<-sum((df_isotope$d18O_H2O_avg-  
df_isotope$d18O_H2O_sd)*df_isotope$Precipitation_mm_avg)/  
    sum(df_isotope$Precipitation_mm_avg)+e_evap0)
```

```
  (d18O_H2O_soil_max<-  
sum((df_isotope$d18O_H2O_avg+df_isotope$d18O_H2O_sd)*df_isotope$Precipitation_mm_avg)  
/
```

```
  sum(df_isotope$Precipitation_mm_avg)+e_evap)
```

```
  (d18O_H2O_soil_max0<-  
sum((df_isotope$d18O_H2O_avg+df_isotope$d18O_H2O_sd)*df_isotope$Precipitation_mm_avg)  
/
```

```
  sum(df_isotope$Precipitation_mm_avg)+e_evap0)
```

```
  #create a table that summarises mean +/- SD for soil T and water d18O for the site
```

```
  #create a table that summarises mean +/- SD for soil T and water d18O for the site
```

```
  d18O_soil<-
```

```
  rbind("d18O_H2O"=c(d18O_H2O_soil_mean,d18O_H2O_soil_min,d18O_H2O_soil_max,d18O_  
H2O_soil_mean0,
```

```
    d18O_H2O_soil_min0,d18O_H2O_soil_max0))
```

```
  T_soil<-rbind("T_soil"=c(T_mean,T_min,T_max))
```



```

Parameter_summary<-expand.grid("d18O_H2O"=d18O_soil,"T_soil"=T_soil)

#print(as.data.frame(Parameter_summary))

#solve equilibration offset calculations using max, min, and mean temperature & d18O-H2O
values, & two parameterisations
#equation 1 (Longinelli & Nuti 1973)

d18Oeq1_output=list(((111.4-Parameter_summary$T_soil)/4.3+Parameter_summary$d18O_H2O)

#equation 2 (Chang & Blake 2015 GCA)  $1000\ln\alpha=14.43*1000/T-26.54$ , where T is in K, so
d18Op = output+d18OH2O
#rearrange to  $(d18OH2O + 1000)*e^{((14.43*1000/T-26.54)/1000)}-1000$ , see Hacker et al 2019
GCA

d18Oeq2_output=list(
(Parameter_summary$d18O_H2O+1000)*exp((14.43*1000/(273.1+Parameter_summary$T_soil)-
26.3)/1000)-1000
)

d18Op_eq<-list("d18O_eq1"=unlist(d18Oeq1_output),"d18O_eq2"=unlist(d18Oeq2_output))

#list2env(d18Op_eq,.GlobalEnv)

#output data

return(as.data.frame(d18Op_eq)
)
}

```

S4.2 Mixing models

```
#load packages
library("grid")
library("plyr")
library("tidyverse")
library("munsell")
library("patchwork")

#import fertiliser data
Fertiliser_df<-read.csv("C:/All/Data/WA/PO4-isotopes/PO4iso-R/FertiliserDataPO4iso.csv")
View(Fertiliser_df)
#import soil data
Soils_df<-read.csv("C:/All/Data/WA/PO4-isotopes/PO4iso-R/WAsoils10.csv")
View(Soils_df)

#calculations box model based on different fertiliser mixing scenarios
#Model 1: immediate leaching (PO4=H2O extractable)
#Model 2: slower leaching (PO4=NaHCO3 extractable)
#Model 3: immediate leaching (PO4=H2O extractable) + fast equilibration (based on H2O pool)
#Model 4: slower leaching (PO4=NaHCO3 extractable) + slow equilibration (based on NaOH pool)

#input 1: fertiliser type (AG v SP d18O values)
#input 2: fertiliser application rate (high v low range based on PBI of soil texture)
#fertilisation rate are in kg ha-1, so need to convert to ug g-1 of top 10 cm based on soil bulk
density.

#input 3: soil texture (P content, bulk density, PBI)
#input 4: equilibrium d18O value (use for soil+fert) & P turnover rate (Xp)

#output: d18Oleach values for each soil texture for each fert type 2013-2017

#define soil texture specific fertiliser rates
#depend on BD, recommended rates based on PBI range
#SoilType PBI_mean PBI_sd
#<chr> <dbl> <dbl>
# 1 Clay 116. 42.5
#for 90% yield: 90 58 48 37 25 14 2, so high = 58, low = 14, mean = 37
#2 Loam 30.4 9.95
#for 90% yield: 44 37 32 28 23 18 11, so high = 37, low = 18, mean = 28
#3 Sand 2.41 1.52
#for 90% yield: 16 13 9 4, so high = 13, low = 9, mean = 11
#rates from Summer & Weaver 2011 report on P app rates to clover pastures in WA

#implementing the model
#first, transform data into a series of nested lists based on soil texture
```

```
Soils_nested<- Soils_df%>%
  group_by(SoilType)%>%
  nest()
```

#second, define fertiliser functions specific for each soil texture

```
F_low_fun<-function(x) {
```

```
  BD_kgha = case_when(
    x=="Clay" ~ 1.44,
    x=="Loam"~1.24,
    x=="Sand"~1.33
  )
```

```
  F_low=case_when(
    x=="Clay" ~ 14*(10*10000*10000/1000)/(1000*1000*BD_kgha),
    x=="Loam" ~ 18*(10*10000*10000/1000)/(1000*1000*BD_kgha),
    x=="Sand" ~ 9*(10*10000*10000/1000)/(1000*1000*BD_kgha)
  )
```

```
  return(F_low)
}
```

```
F_high_fun<-function(x) {
```

```
  BD_kgha = case_when(
    x=="Clay" ~ 1.44,
    x=="Loam"~1.24,
    x=="Sand"~1.33
  )
```

```
  F_high=case_when(
    x=="Clay" ~ 58*(10*10000*10000/1000)/(1000*1000*BD_kgha),
    x=="Loam" ~ 37*(10*10000*10000/1000)/(1000*1000*BD_kgha),
    x=="Sand" ~ 13*(10*10000*10000/1000)/(1000*1000*BD_kgha)
  )
```

```
  return(F_high)
}
```

```
F_mean_fun<-function(x) {
```

```
  BD_kgha = case_when(
    x=="Clay" ~ 1.44,
    x=="Loam"~1.24,
    x=="Sand"~1.33
  )
```

```

F_mean=case_when(
  x=="Clay" ~ 37*(10*10000*10000/1000)/(1000*1000*BD_kgha),
  x=="Loam" ~ 28*(10*10000*10000/1000)/(1000*1000*BD_kgha),
  x=="Sand" ~ 11*(10*10000*10000/1000)/(1000*1000*BD_kgha)
)

return(F_mean)
}

Soils_nested<-Soils_nested%>%
  mutate(F_low=map(SoilType,~{(F_low_fun(.))}))%>%
  mutate(F_high=map(SoilType,~{(F_high_fun(.))}))%>%
  mutate(F_mean=map(SoilType,~{(F_mean_fun(.))}))

#F application formula for scenario (a)
F_formula_a<-function(P_leach1,F_low,F_high,F_mean) {

  f_1=F_low/(P_leach1+F_low)
  f_2=F_high/(P_leach1+F_high)
  f_3=F_mean/(P_leach1+F_mean)

  x<-tibble::tibble(f_1,f_2,f_3) #this exports 3 columns of data
}

#F application formula for scenario (b)
F_formula_b<-function(P_leach2,F_low,F_high,F_mean) {

  f_1=F_low/(P_leach2+F_low)
  f_2=F_high/(P_leach2+F_high)
  f_3=F_mean/(P_leach2+F_mean)

  x<-tibble::tibble(f_1,f_2,f_3) #this works to export 4 columns of data, yay, where list etc didn't
}

#simplifies outputs info mean, min, max
F_formula2<-function(f_Fert) {

  mean_f=mean(f_Fert,na.rm=TRUE)
  low_f=mean(f_Fert,na.rm=TRUE)-sd(f_Fert,na.rm=TRUE)
  high_f=mean(f_Fert,na.rm=TRUE)+sd(f_Fert,na.rm=TRUE)
  x<-list(mean_f,low_f,high_f)

}

#solve d18O_soil range

```

```

d18O_formula<-function(d18O.PO4) {
  mean_d18O_s=mean(d18O.PO4,na.rm=TRUE)
  low_d18O_s=mean(d18O.PO4,na.rm=TRUE)-sd(d18O.PO4,na.rm=TRUE)
  high_d18O_s=mean(d18O.PO4,na.rm=TRUE)+sd(d18O.PO4,na.rm=TRUE)

  x<-list(mean_d18O_s,low_d18O_s,high_d18O_s)
  #how to make column instead of rows?
}

#use previously established formulas to solve (a) and (b)
Soils_nested<-Soils_nested%>%
  mutate(P_leach1=map(data,~.x$PO4_ug_g_H2O))%>%
  mutate(P_leach2=map(data,~.x$PO4_ug_g_H2O+.x$PO4_ug_g_NaHCO3))%>%
  mutate(f_range_a=pmap(list(P_leach1,F_low,F_high,F_mean),F_formula_a))%>%
  mutate(f_range_b=pmap(list(P_leach2,F_low,F_high,F_mean),F_formula_b))%>%
  mutate(f_Fert_a=map(f_range_a,rowMeans))%>%
  mutate(f_Fert_b=map(f_range_b,rowMeans))%>%
  mutate(f_summary_a=map(f_Fert_a,F_formula2))%>%
  mutate(f_summary_b=map(f_Fert_b,F_formula2))%>%
  mutate(d18O.PO4 = map(data,~.x$d18O.PO4))%>% #this extracts soil data
  mutate(d18O_soil=map(d18O.PO4,d18O_formula))#so now all soil data is ready

```

#now solve isotope leaching formula

```

#first create nested df so each mean d18O_fert value is a 'list' to be iterated over
Fertiliser_df<-Fertiliser_df%>%
  mutate(Year=parse_number(as.character(ID))
  )%>%
  mutate(Year=as.numeric(Year))%>%
  mutate(Year=Year+2000)
Fertiliser_df<-Fertiliser_df%>%
  mutate(Brand=case_when(
    grepl("AG",ID)~"AG",
    grepl("M",ID)~"MAP",
    grepl("S",ID)~"SP"
  ))

Fert_means<-Fertiliser_df%>%
  group_by(as.factor(Brand),Year)%>%
  summarise(
    d18O_mean=mean(d18O_PO4),
    d18O_sd=sd(d18O_PO4),
    d18O_min=min(d18O_PO4),
    d18O_max=max(d18O_PO4)
  )%>%
  rename(Brand="as.factor(Brand)")

```

```

Fert_means_nest<-Fert_means%>%
  dplyr::select(Brand,Year,d18O_mean)%>%
  filter(Brand!="MAP")%>% #remove MAP as only one year of data
  dplyr::group_by(Brand,Year)%>%
  nest()

#now separate data by soil texture

#for clays
{Soils_clay<-Soils_nested%>%
  dplyr::filter(SoilType=="Clay")%>%
  dplyr::mutate(f_summary_a=map(f_summary_a,~tibble(f_summary_a=.x)))%>%
  dplyr::mutate(f_summary_b=map(f_summary_b,~tibble(f_summary_b=.x)))%>%
  dplyr::mutate(d18O_soil=map(d18O_soil,~tibble(d18O_soil=.x)))%>%
  unnest(cols=c(f_summary_a,f_summary_b,d18O_soil))%>%
  dplyr::select(f_summary_a,f_summary_b,d18O_soil)%>%
  ungroup()
Soils_clay$f_summary_a<-as.numeric(Soils_clay$f_summary_a)
Soils_clay$f_summary_b<-as.numeric(Soils_clay$f_summary_b)
Soils_clay$d18O_soil<-as.numeric(Soils_clay$d18O_soil)

#generate all possible combinations of f v d18O_soil
Soils_clay_a<-Soils_clay%>%tidyr::expand(f_summary_a,d18O_soil)
Soils_clay_b<-Soils_clay%>%tidyr::expand(f_summary_b,d18O_soil)

#now to expand so I can apply to the nested fertiliser df
d18O_leach_formula<-function(d18O_mean) {

  #define equations for mixing
  formula_leach_a<-function(f_summary_a,d18O_soil) {
    f_summary_a*d18O_mean+(1-f_summary_a)*d18O_soil
  }

  formula_leach_b<-function(f_summary_b,d18O_soil) {
    f_summary_b*d18O_mean+(1-f_summary_b)*d18O_soil
  }

  #add equilibration formulas,based on Gross & Angert 2015 GCA:
  #%phosphate turnover = 100* (d18OP-MEAS - d18OP-RELES)/(d18OP-EQ - d18OP-RELES)
  #which modifies to: d18O_leach = %phos_turnover*(d18OP_eq-d18OP_Fert)+d18OP_Fert
  #w/in 1 day: 0 - 2 % turnover, so say 1% for H2O extractable (based on 1:1 log:log relationship
w H2O, see Helfenstein 2020)
  #w/in days-months: 70 - 150% turnover, so say 90% for NaHCO3 extractable

  formula_Leq_a<-function(d18O_leach_a) {

    Leq_1=0.06*(d18O_eq_low-d18O_leach_a)+d18O_leach_a

```

```

Leq_2=0.06*(d18O_eq_high-d18O_leach_a)+d18O_leach_a
Leq_3=0.06*(d18O_eq_mean-d18O_leach_a)+d18O_leach_a

x=do.call(c,list(Leq_1,Leq_2,Leq_3)) #combines into one list

return(x)
}

formula_Leq_b<-function(d18O_leach_b) {

  Leq_1=0.9*(d18O_eq_low-d18O_leach_b)+d18O_leach_b
  Leq_2=0.9*(d18O_eq_high-d18O_leach_b)+d18O_leach_b
  Leq_3=0.9*(d18O_eq_mean-d18O_leach_b)+d18O_leach_b

  x=do.call(c,list(Leq_1,Leq_2,Leq_3))

  return(x)
}

#define d18Op(eq) range, assuming generated mean+/-SD w d18O_eq2
H2O_df<-winter_eq

d18O_eq_low=H2O_df[2,]
d18O_eq_high=H2O_df[3,]
d18O_eq_mean=H2O_df[1,]

#define mixing model terms
f_summary_a=Soils_clay_a$f_summary_a
f_summary_b=Soils_clay_b$f_summary_b
d18O_soil=Soils_clay_a$d18O_soil

#map equations to data
d18O_leach_a=map2(f_summary_a,
                  d18O_soil,
                  formula_leach_a)

d18O_leach_b=map2(f_summary_b,
                  d18O_soil,
                  formula_leach_b)

d18O_Leq_a=map(d18O_leach_a,
               formula_Leq_a)
d18O_Leq_b=map(d18O_leach_b,
               formula_Leq_b)

#then make outputs

d18O_leach_min_a=min(unlist(d18O_leach_a))

```

```
d18O_leach_max_a=max(unlist(d18O_leach_a))
d18O_leach_mean_a=mean(unlist(d18O_leach_a))
d18O_leach_sd_a=sd(unlist(d18O_leach_a))
```

```
d18O_leach_min_b=min(unlist(d18O_leach_b))
d18O_leach_max_b=max(unlist(d18O_leach_b))
d18O_leach_mean_b=mean(unlist(d18O_leach_b))
d18O_leach_sd_b=sd(unlist(d18O_leach_b))
```

```
d18O_leach_min_c=min(unlist(d18O_Leq_a))
d18O_leach_max_c=max(unlist(d18O_Leq_a))
d18O_leach_mean_c=mean(unlist(d18O_Leq_a))
d18O_leach_sd_c=sd(unlist(d18O_Leq_a))
```

```
d18O_leach_min_d=min(unlist(d18O_Leq_b))
d18O_leach_max_d=max(unlist(d18O_Leq_b))
d18O_leach_mean_d=mean(unlist(d18O_Leq_b))
d18O_leach_sd_d=sd(unlist(d18O_Leq_b))
```

```
x<-tibble(d18O_leach_mean_a,d18O_leach_sd_a,d18O_leach_min_a,d18O_leach_max_a,
          d18O_leach_mean_b,d18O_leach_sd_b,d18O_leach_min_b,d18O_leach_max_b,
          d18O_leach_mean_c,d18O_leach_sd_c,d18O_leach_min_c,d18O_leach_max_c,
          d18O_leach_mean_d,d18O_leach_sd_d,d18O_leach_min_d,d18O_leach_max_d
)
}
```

```
clay_leach<-Fert_means_nest%>%
  mutate(d18O_mean=map(data,~.x$d18O_mean))%>%
  mutate(map(d18O_mean,
             d18O_leach_formula))%>%
  unnest()
}
```

#this works! now to make it a bit more universal so this is all less annoying

#for loams

```
{Soils_loam<-Soils_nested%>%
  dplyr::filter(SoilType=="Loam")%>%
  dplyr::mutate(f_summary_a=map(f_summary_a,~tibble(f_summary_a=.x)))%>%
  dplyr::mutate(f_summary_b=map(f_summary_b,~tibble(f_summary_b=.x)))%>%
  dplyr::mutate(d18O_soil=map(d18O_soil,~tibble(d18O_soil=.x)))%>%
  unnest(cols=c(f_summary_a,f_summary_b,d18O_soil))%>%
  dplyr::select(f_summary_a,f_summary_b,d18O_soil)%>%
  ungroup()
Soils_loam$f_summary_a<-as.numeric(Soils_loam$f_summary_a)
Soils_loam$f_summary_b<-as.numeric(Soils_loam$f_summary_b)
Soils_loam$d18O_soil<-as.numeric(Soils_loam$d18O_soil)
```



```

#generate all possible combinations of f v d18O_soil
Soils_loam_a<-Soils_loam%>%tidyr::expand(f_summary_a,d18O_soil)
Soils_loam_b<-Soils_loam%>%tidyr::expand(f_summary_b,d18O_soil)

#now to expand so I can apply to the nested fertiliser df
d18O_leach_formula_loam<-function(d18O_mean) {

  #define equations for mixing
  formula_leach_a<-function(f_summary_a,d18O_soil) {
    f_summary_a*d18O_mean+(1-f_summary_a)*d18O_soil
  }

  formula_leach_b<-function(f_summary_b,d18O_soil) {
    f_summary_b*d18O_mean+(1-f_summary_b)*d18O_soil
  }

  #add equilibration formulas,based on Gross & Angert 2015 GCA:
  #%phosphate turnover = 100* (d18OP-MEAS - d18OP-RELES)/(d18OP-EQ - d18OP-RELES)
  #which modifies to: d18O_leach = %phos_turnover*(d18OP_eq-d18OP_Fert)+d18OP_Fert
  #w/in 1 day: 2 - 22 % turnover, so say 10% for H2O extractable (based on 1:1 log:log
relationship w H2O, see Helfenstein 2020)
  #w/in days-months: 26 - 100% turnover, so say 60% for NaHCO3 extractable (based on NaOH,
as per above)

  formula_Leq_a<-function(d18O_leach_a) {

    Leq_1=0.1*(d18O_eq_low-d18O_leach_a)+d18O_leach_a
    Leq_2=0.1*(d18O_eq_high-d18O_leach_a)+d18O_leach_a
    Leq_3=0.1*(d18O_eq_mean-d18O_leach_a)+d18O_leach_a

    x=do.call(c,list(Leq_1,Leq_2,Leq_3)) #combines into one list

    return(x)
  }

  formula_Leq_b<-function(d18O_leach_b) {

    Leq_1=0.6*(d18O_eq_low-d18O_leach_b)+d18O_leach_b
    Leq_2=0.6*(d18O_eq_high-d18O_leach_b)+d18O_leach_b
    Leq_3=0.6*(d18O_eq_mean-d18O_leach_b)+d18O_leach_b

    x=do.call(c,list(Leq_1,Leq_2,Leq_3))

    return(x)
  }

  #define d18Op(eq) range, assuming generated mean+/-SD w d18O_eq2
  H2O_df<-winter_eq

```

```

d18O_eq_low=H2O_df[1,]
d18O_eq_high=H2O_df[3,]
d18O_eq_mean=H2O_df[2,]

#define mixing model terms
f_summary_a=Soils_loam_a$f_summary_a
f_summary_b=Soils_loam_b$f_summary_b
d18O_soil=Soils_loam_a$d18O_soil

#map equations to data
d18O_leach_a=map2(f_summary_a,
                  d18O_soil,
                  formula_leach_a)
d18O_leach_b=map2(f_summary_b,
                  d18O_soil,
                  formula_leach_b)
d18O_Leq_a=map(d18O_leach_a,
                formula_Leq_a)
d18O_Leq_b=map(d18O_leach_b,
                formula_Leq_b)

#then make outputs

d18O_leach_min_a=min(unlist(d18O_leach_a))
d18O_leach_max_a=max(unlist(d18O_leach_a))
d18O_leach_mean_a=mean(unlist(d18O_leach_a))
d18O_leach_sd_a=sd(unlist(d18O_leach_a))

d18O_leach_min_b=min(unlist(d18O_leach_b))
d18O_leach_max_b=max(unlist(d18O_leach_b))
d18O_leach_mean_b=mean(unlist(d18O_leach_b))
d18O_leach_sd_b=sd(unlist(d18O_leach_b))

d18O_leach_min_c=min(unlist(d18O_Leq_a))
d18O_leach_max_c=max(unlist(d18O_Leq_a))
d18O_leach_mean_c=mean(unlist(d18O_Leq_a))
d18O_leach_sd_c=sd(unlist(d18O_Leq_a))

d18O_leach_min_d=min(unlist(d18O_Leq_b))
d18O_leach_max_d=max(unlist(d18O_Leq_b))
d18O_leach_mean_d=mean(unlist(d18O_Leq_b))
d18O_leach_sd_d=sd(unlist(d18O_Leq_b))

x<-tibble(d18O_leach_mean_a,d18O_leach_sd_a,d18O_leach_min_a,d18O_leach_max_a,
          d18O_leach_mean_b,d18O_leach_sd_b,d18O_leach_min_b,d18O_leach_max_b,
          d18O_leach_mean_c,d18O_leach_sd_c,d18O_leach_min_c,d18O_leach_max_c,
          d18O_leach_mean_d,d18O_leach_sd_d,d18O_leach_min_d,d18O_leach_max_d

```

```

)
}

loam_leach<-Fert_means_nest%>%
  mutate(d18O_mean=map(data,~.x$d18O_mean))%>%
  mutate(map(d18O_mean,
             d18O_leach_formula_loam))%>%
  unnest()
}

#for sand
{Soils_sand<-Soils_nested%>%
  dplyr::filter(SoilType=="Sand")%>%
  dplyr::mutate(f_summary_a=map(f_summary_a,~tibble(f_summary_a=.x)))%>%
  dplyr::mutate(f_summary_b=map(f_summary_b,~tibble(f_summary_b=.x)))%>%
  dplyr::mutate(d18O_soil=map(d18O_soil,~tibble(d18O_soil=.x)))%>%
  unnest(cols=c(f_summary_a,f_summary_b,d18O_soil))%>%
  dplyr::select(f_summary_a,f_summary_b,d18O_soil)%>%
  ungroup()
Soils_sand$f_summary_a<-as.numeric(Soils_sand$f_summary_a)
Soils_sand$f_summary_b<-as.numeric(Soils_sand$f_summary_b)
Soils_sand$d18O_soil<-as.numeric(Soils_sand$d18O_soil)

#generate all possible combinations of f v d18O_soil
Soils_sand_a<-Soils_sand%>%tidyr::expand(f_summary_a,d18O_soil)
Soils_sand_b<-Soils_sand%>%tidyr::expand(f_summary_b,d18O_soil)

#now to expand so I can apply to the nested fertiliser df
d18O_leach_formula_sand<-function(d18O_mean) {

  #define equations for mixing
  formula_leach_a<-function(f_summary_a,d18O_soil) {
    f_summary_a*d18O_mean+(1-f_summary_a)*d18O_soil
  }

  formula_leach_b<-function(f_summary_b,d18O_soil) {
    f_summary_b*d18O_mean+(1-f_summary_b)*d18O_soil
  }

  #add equilibration formulas,based on Gross & Angert 2015 GCA:
  #%phosphate turnover = 100* (d18OP-MEAS - d18OP-RELES)/(d18OP-EQ - d18OP-RELES)
  #which modifies to: d18O_leach = %phos_turnover*(d18OP_eq-d18OP_Fert)+d18OP_Fert
  #w/in 1 day: 13 - 53 % turnover, so say 30% for H2O extractable (based on 1:1 log:log
  relationship w H2O, see Helfenstein 2020)
  #w/in days-months: 11 - 30% turnover, so say 20% for NaHCO3 extractable (based on NaOH
  extractable w 1:1 log:log relationship, Helfenstein et al 2020)

```

```

formula_Leq_a<-function(d18O_leach_a) {

  Leq_1=0.3*(d18O_eq_low-d18O_leach_a)+d18O_leach_a
  Leq_2=0.3*(d18O_eq_high-d18O_leach_a)+d18O_leach_a
  Leq_3=0.3*(d18O_eq_mean-d18O_leach_a)+d18O_leach_a

  x=do.call(c,list(Leq_1,Leq_2,Leq_3)) #combines into one list

  return(x)
}

formula_Leq_b<-function(d18O_leach_b) {

  Leq_1=0.2*(d18O_eq_low-d18O_leach_b)+d18O_leach_b
  Leq_2=0.2*(d18O_eq_high-d18O_leach_b)+d18O_leach_b
  Leq_3=0.2*(d18O_eq_mean-d18O_leach_b)+d18O_leach_b

  x=do.call(c,list(Leq_1,Leq_2,Leq_3))

  return(x)
}

#define d18Op(eq) range, assuming generated mean+/-SD w d18O_eq2
H2O_df<-winter_eq

d18O_eq_low=H2O_df[1,]
d18O_eq_high=H2O_df[3,]
d18O_eq_mean=H2O_df[2,]

#define mixing model terms
f_summary_a=Soils_sand_a$f_summary_a
f_summary_b=Soils_sand_b$f_summary_b
d18O_soil=Soils_sand_a$d18O_soil

#map equations to data
d18O_leach_a=map2(f_summary_a,
                  d18O_soil,
                  formula_leach_a)
d18O_leach_b=map2(f_summary_b,
                  d18O_soil,
                  formula_leach_b)
d18O_Leq_a=map(d18O_leach_a,
               formula_Leq_a)
d18O_Leq_b=map(d18O_leach_b,
               formula_Leq_b)

#then make outputs

```

```

d18O_leach_min_a=min(unlist(d18O_leach_a))
d18O_leach_max_a=max(unlist(d18O_leach_a))
d18O_leach_mean_a=mean(unlist(d18O_leach_a))
d18O_leach_sd_a=sd(unlist(d18O_leach_a))

d18O_leach_min_b=min(unlist(d18O_leach_b))
d18O_leach_max_b=max(unlist(d18O_leach_b))
d18O_leach_mean_b=mean(unlist(d18O_leach_b))
d18O_leach_sd_b=sd(unlist(d18O_leach_b))

d18O_leach_min_c=min(unlist(d18O_Leq_a))
d18O_leach_max_c=max(unlist(d18O_Leq_a))
d18O_leach_mean_c=mean(unlist(d18O_Leq_a))
d18O_leach_sd_c=sd(unlist(d18O_Leq_a))

d18O_leach_min_d=min(unlist(d18O_Leq_b))
d18O_leach_max_d=max(unlist(d18O_Leq_b))
d18O_leach_mean_d=mean(unlist(d18O_Leq_b))
d18O_leach_sd_d=sd(unlist(d18O_Leq_b))

x<-tibble(d18O_leach_mean_a,d18O_leach_sd_a,d18O_leach_min_a,d18O_leach_max_a,
          d18O_leach_mean_b,d18O_leach_sd_b,d18O_leach_min_b,d18O_leach_max_b,
          d18O_leach_mean_c,d18O_leach_sd_c,d18O_leach_min_c,d18O_leach_max_c,
          d18O_leach_mean_d,d18O_leach_sd_d,d18O_leach_min_d,d18O_leach_max_d
)

}

sand_leach<-Fert_means_nest%>%
  mutate(d18O_mean=map(data,~.x$d18O_mean))%>%
  mutate(map(d18O_mean,
             d18O_leach_formula_sand))%>%
  unnest()
}

#collate and organise outputs
#try making boxplots instead as more accurate for changes over years, need to
#pivot longer to collate mean, min, max
{
  #first add columns for +- SD
  sand_leach<-sand_leach%>%
    mutate(mean_a_1=d18O_leach_mean_a-d18O_leach_sd_a,
           mean_a_2=d18O_leach_mean_a+d18O_leach_sd_a,
           mean_b_1=d18O_leach_mean_b-d18O_leach_sd_b,
           mean_b_2=d18O_leach_mean_b+d18O_leach_sd_b,
           mean_c_1=d18O_leach_mean_c-d18O_leach_sd_c,
           mean_c_2=d18O_leach_mean_c+d18O_leach_sd_c,

```

```

      mean_d_1=d18O_leach_mean_d-d18O_leach_sd_d,
      mean_d_2=d18O_leach_mean_d+d18O_leach_sd_d)
clay_leach<-clay_leach%>%
  mutate(mean_a_1=d18O_leach_mean_a-d18O_leach_sd_a,
         mean_a_2=d18O_leach_mean_a+d18O_leach_sd_a,
         mean_b_1=d18O_leach_mean_b-d18O_leach_sd_b,
         mean_b_2=d18O_leach_mean_b+d18O_leach_sd_b,
         mean_c_1=d18O_leach_mean_c-d18O_leach_sd_c,
         mean_c_2=d18O_leach_mean_c+d18O_leach_sd_c,
         mean_d_1=d18O_leach_mean_d-d18O_leach_sd_d,
         mean_d_2=d18O_leach_mean_d+d18O_leach_sd_d)
loam_leach<-loam_leach%>%
  mutate(mean_a_1=d18O_leach_mean_a-d18O_leach_sd_a,
         mean_a_2=d18O_leach_mean_a+d18O_leach_sd_a,
         mean_b_1=d18O_leach_mean_b-d18O_leach_sd_b,
         mean_b_2=d18O_leach_mean_b+d18O_leach_sd_b,
         mean_c_1=d18O_leach_mean_c-d18O_leach_sd_c,
         mean_c_2=d18O_leach_mean_c+d18O_leach_sd_c,
         mean_d_1=d18O_leach_mean_d-d18O_leach_sd_d,
         mean_d_2=d18O_leach_mean_d+d18O_leach_sd_d)

sand_leach_long<-sand_leach%>%
  dplyr::select(-contains("sd"))%>% #removes the sd columns
  dplyr::select(-c(d18O_mean,d18O_mean1))%>%
  pivot_longer(cols=!c("Brand","Year"),
               names_to="stat",values_to="d18Oleach")
sand_leach_long<-sand_leach_long%>%
  mutate(scenario=case_when(
    endsWith(stat,"a") ~ "a",
    endsWith(stat,"b")~"b",
    endsWith(stat,"c")~"c",
    endsWith(stat,"d")~"d"
  ))%>%
  mutate(Soil_Type="sand")
clay_leach_long<-clay_leach%>%
  dplyr::select(-contains("sd"))%>% #removes the sd columns
  dplyr::select(-c(d18O_mean,d18O_mean1))%>%
  pivot_longer(cols=!c("Brand","Year"),
               names_to="stat",values_to="d18Oleach")
clay_leach_long<-clay_leach_long%>%
  mutate(scenario=case_when(
    endsWith(stat,"a") ~ "a",
    endsWith(stat,"b")~"b",
    endsWith(stat,"c")~"c",
    endsWith(stat,"d")~"d"
  ))%>%
  mutate(Soil_Type="clay")
loam_leach_long<-loam_leach%>%
  dplyr::select(-contains("sd"))%>% #removes the sd columns
  dplyr::select(-c(d18O_mean,d18O_mean1))%>%

```

```

    pivot_longer(cols=!c("Brand","Year"),
      names_to="stat",values_to="d18Oleach")
loam_leach_long<-loam_leach_long%>%
  mutate(scenario=case_when(
    endsWith(stat,"a") ~ "a",
    endsWith(stat,"b")~"b",
    endsWith(stat,"c")~"c",
    endsWith(stat,"d")~"d"
  ))%>%
  mutate(Soil_Type="loam")
}

#upscale to see what can be picked out v not at catchment scale
#use model estimates of %P from each soil texture, and then just vary over time

leach_all_long<-rbind(sand_leach_long,loam_leach_long,clay_leach_long)
write.csv(leach_all_long,"leach_all_long.csv")
leach_SP_long<-leach_all_long%>%
  dplyr::filter(Brand=="SP")
leach_AG_long<-leach_all_long%>%
  dplyr::filter(Brand=="AG")
#or nonpivoted
sand_leach<-sand_leach%>%
  mutate(Soil_Type="sand")
loam_leach<-loam_leach%>%
  mutate(Soil_Type="loam")
clay_leach<-clay_leach%>%
  mutate(Soil_type="clay")
leach_all<-rbind(sand_leach, loam_leach,clay_leach)
leach_SP<-leach_all%>%
  dplyr::filter(Brand=="SP")
leach_AG<-leach_all%>%
  dplyr::filter(Brand=="AG")
write.csv(leach_all,"leach_all_wide.csv")

#summary stats

Soils_clay_a%>%
  summarise(
    avg_f=mean(f_summary_a),
    sd_f=sd(f_summary_a)
  )

Soils_clay_b%>%
  summarise(
    avg_f=mean(f_summary_b),
    sd_f=sd(f_summary_b)
  )

Soils_loam_b%>%

```

```

summarise(
  avg_f=mean(f_summary_b),
  sd_f=sd(f_summary_b)
)

Soils_sand_b%>%
  summarise(
    avg_f=mean(f_summary_b),
    sd_f=sd(f_summary_b)
  )

#Plot data

#sort out aesthetics
{
  PERI_colours<-c(mnsl("7.5BG 5/6"),mnsl("7.5R 5/4"),mnsl("7.5R 5/18")) #clay #loam #sand
  clay_colour<-mnsl("7.5BG 5/6")
  clay_colour2<-mnsl("7.5BG 8/6")
  loam_colour<-mnsl("7.5R 5/4")
  loam_colour2<-mnsl("7.5R 4/4")
  sand_colour<-mnsl("7.5R 5/18")

  #colours for fert brands
  Fert_colours2<-c(mnsl("N 0/0"),mnsl("N 7/0"))
}

#plots w separated soil texture
{ #plot f_summary values for each soil texture for reference
  f_a<-ggplot()+
    geom_violin(data=
      Soils_nested%>% #extract relevant data
      unnest(f_range_a)%>%
      dplyr::select(SoilType,f_1,f_2,f_3)%>%
      pivot_longer(cols = c(f_1,f_2,f_3)),
      aes(x=SoilType,y=value,fill=SoilType),alpha=0.8,
      draw_quantiles = 0.5,scale = "area",
      adjust=0.8, colour="black")+
    scale_colour_manual(values=PERI_colours)+
    scale_fill_manual(values=PERI_colours)+
    annotate("text",x=3.4,y=0.9,label="(a)",size=4)+
    scale_y_continuous(limits=c(0,1),expand=c(0,0),
      breaks=c(0,0.5,1.0))+
    labs(y=expression(italic("f")["fert"]))+
    theme_classic()+
    theme(legend.position="none",axis.title.x = element_blank(),
      text=element_text(size=16))+
    annotation_custom(grob=grid::textGrob(label="fast",

```



```

      gp=grid::gpar(fontsize=18,fontface="italic")),
      xmin=5,xmax=5,ymin=0.5,ymax=0.7)+
coord_cartesian(clip="off")

#plot f_summary values for each soil texture for reference
f_b<-ggplot()+
  geom_violin(data=
    Soils_nested%>% #extract relevant data
    unnest(f_range_b)%>%
    dplyr::select(SoilType,f_1,f_2,f_3)%>%
    pivot_longer(cols = c(f_1,f_2,f_3)),
    aes(x=SoilType,y=value,fill=SoilType),alpha=0.8,
    draw_quantiles = 0.5,scale = "area",
    adjust=0.8, colour="black")+
  scale_colour_manual(values=PERI_colours)+
  scale_fill_manual(values=PERI_colours)+
  annotate("text",x=3.4,y=0.9,label="(b)",size=4)+
  scale_y_continuous(limits=c(0,1),expand=c(0,0),
    breaks=c(0,0.5,1.0))+
  labs(y=expression(italic("f")["fert"]))+
  theme_classic()+
  theme(legend.position="none",axis.title.x = element_blank(),
    text=element_text(size=16))+
  annotation_custom(grob=grid::textGrob(label="slow",
    gp=grid::gpar(fontsize=18,fontface="italic")),
    xmin=5,xmax=5,ymin=0.5,ymax=0.7)+
coord_cartesian(clip="off")

#for scenario (a), immediate leaching but with no turnover
iso_a_2<-ggplot()+
  geom_boxplot(data=leach_AG_long%>%filter(scenario=="a"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 0/0"),alpha=.9,size=.6,linetype="solid")+
  geom_boxplot(data=leach_SP_long%>%filter(scenario=="a"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 7/0"),linetype="longdash",alpha=0.7,
    size=.6)+
  geom_point(data=Fert_means%>%dplyr::filter(Brand!="MAP"),aes(
    x=as.factor(Year),y=d18O_mean,shape=Brand,colour=Brand),size=3)+
  geom_linerange(data=Fert_means%>%dplyr::filter(Brand!="MAP"),
    aes(x=as.factor(Year),ymin=d18O_mean-d18O_sd,ymax=d18O_mean+d18O_sd,
    colour=Brand))+
  annotate("text",x="2013",y=24.5,label=expression(italic("X")["P"]*~"=" nil"))+
  annotate("text",x="2017",y=25,label="(c)",size=4)+
  scale_y_continuous(limits=c(15,25.5),expand=c(0,0),breaks=c(15,18,21,24))+
  scale_colour_manual(values=Fert_colours2)+
  scale_fill_manual(values=PERI_colours)+
  labs(y=expression(delta^18*"O"["P(export-1)"]*~"(%o)"))+
  theme_classic()+
  theme(legend.title=element_blank(),text=element_text(size=18),

```

```

legend.position = "none",axis.title.y = element_text(size=16),
axis.text.x = element_blank(),axis.title.x=element_blank())

```

#for scenario (b), seasonal leaching but with no turnover

```

iso_b_2<-ggplot()+
  geom_boxplot(data=leach_AG_long%>%filter(scenario=="b"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 0/0"),alpha=.9,size=.6,linetype="solid")+
  geom_boxplot(data=leach_SP_long%>%filter(scenario=="b"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 7/0"),linetype="longdash",alpha=0.7,
    size=.6)+
  geom_point(data=Fert_means%>%dplyr::filter(Brand!="MAP"),aes(
    x=as.factor(Year),y=d18O_mean,shape=Brand,colour=Brand),size=3)+
  geom_linerange(data=Fert_means%>%dplyr::filter(Brand!="MAP"),
    aes(x=as.factor(Year),ymin=d18O_mean-d18O_sd,ymax=d18O_mean+d18O_sd,
    colour=Brand))+
  annotate("text",x="2013",y=24.5,label=expression(italic("X")["P"]*~"= nil"))+
  annotate("text",x="2017",y=25,label="(d)",size=4)+
  scale_y_continuous(limits=c(15,25.5),expand=c(0,0),breaks=c(15,18,21,24))+
  scale_colour_manual(values=Fert_colours2)+
  scale_fill_manual(values=PERI_colours)+
  labs(y=expression(delta^18*"O"["P(export)"]*~"(% v. VSMOW)"))+
  theme_classic()+
  theme(legend.title=element_blank(),text=element_text(size=16),
    legend.position = "none",axis.title=element_blank(),
    axis.text=element_blank())

```

#for scenario (c), immediate leaching but with ~1 hr of turnover

```

iso_c_2<-ggplot()+
  geom_boxplot(data=leach_AG_long%>%filter(scenario=="c"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 0/0"),alpha=.9,size=.6,linetype="solid")+
  geom_boxplot(data=leach_SP_long%>%filter(scenario=="c"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 7/0"),linetype="longdash",alpha=0.7,
    size=.6)+
  geom_point(data=Fert_means%>%dplyr::filter(Brand!="MAP"),aes(
    x=as.factor(Year),y=d18O_mean,shape=Brand,colour=Brand),size=3)+
  geom_linerange(data=Fert_means%>%dplyr::filter(Brand!="MAP"),
    aes(x=as.factor(Year),ymin=d18O_mean-d18O_sd,ymax=d18O_mean+d18O_sd,
    colour=Brand))+
  annotate("text",x="2013",y=24.5,label=expression(italic("X")["P"]*~"= 1 hr"))+
  annotate("text",x="2017",y=25,label="(e)",size=4)+
  scale_y_continuous(limits=c(15,25.5),expand=c(0,0),breaks=c(15,18,21,24))+
  scale_colour_manual(values=Fert_colours2)+
  scale_fill_manual(values=PERI_colours)+
  labs(y=expression(delta^18*"O"["P(export-2)"]*~"(% v. VSMOW)"))+

```

```

    x=expression("Manufacturing year"))+
theme_classic()+
theme(legend.title=element_blank(),text=element_text(size=16),
      legend.position = "none",axis.title.y = element_text(size=16),
      axis.title.x=element_blank())

#for scenario (d), seasonal leaching but with hourly - seasonal turnover
iso_d_2<-ggplot()+
  geom_boxplot(data=leach_AG_long%>%filter(scenario=="d"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 0/0"),alpha=.9,size=.6,linetype="solid")+
  geom_boxplot(data=leach_SP_long%>%filter(scenario=="d"),
    aes(x=as.factor(Year),y=d18Oleach,fill=Soil_Type),
    colour=mnsi("N 7/0"),linetype="longdash",alpha=0.7,
    size=.6)+
  geom_point(data=Fert_means%>%dplyr::filter(Brand!="MAP"),aes(
    x=as.factor(Year),y=d18O_mean,shape=Brand,colour=Brand),size=3)+
  geom_linerange(data=Fert_means%>%dplyr::filter(Brand!="MAP"),
    aes(x=as.factor(Year),ymin=d18O_mean-d18O_sd,ymax=d18O_mean+d18O_sd,
    colour=Brand))+
  annotate("text",x="2013",y=24.5,label=expression(italic("X"))["P"]*~"= 1 month"))+
  annotate("text",x="2017",y=25,label="(f)",size=4)+
  scale_y_continuous(limits=c(15,25.5),expand=c(0,0),breaks=c(15,18,21,24))+
  scale_colour_manual(values=Fert_colours2)+
  scale_fill_manual(values=PERI_colours)+
  labs(y=expression(delta^"18"*"O"["P(export)"]*~"(% v. VSMOW)"))+
  theme_classic()+
  theme(legend.title=element_blank(),text=element_text(size=16),
    legend.position = "none",axis.title.y = element_blank(),
    axis.text.y = element_blank(),axis.title.x=element_blank())

#combine into one model figure
(f_a+plot_spacer())|f_b+plot_spacer()/
(iso_a_2|iso_b_2)/
(iso_c_2|iso_d_2)+
plot_annotation(theme=theme(plot.margin=margin(0,0,0,0,unit="pt")))+
wrap_elements(grid::textGrob(label="Fertiliser year",
  gp=grid::gpar(fontsize=15)),
  clip=FALSE)+
plot_layout(heights=(c(1,2,2,0.3)))
}

```

S4.3 Up-scaling calculations

```
#to calculate the 'catchment scale' variations that would be caused by
#different %fertiliser use, & proportion of fast v slow leaching (both w/ turnover as this is most
#likely)
#P load is 145 t y-1, catchment area is 11930 km2 (if including all the way up into the Wheatbelt),
#50% of P from beef grazing
#in coastal plain catchment is ~1,800 km2 and ~1,100 km2 is beef grazing
#but here we're ignoring land-use and just focusing on soil texture to calculate need %P from sandy
v #loam v clay
```

```
#install packages
library("countcolors")
```

```
#figure out soil coverage: key for maps from McArthur 1974 CSIRO maps of soils
#W = Wellesley = Clay
#R = Ridge Hill Shelf = Basically rock, exclude
#C = Coolup = Sand
#B = Boyanup = Loam
#Bh = Belhus = Sand
#D = Dardanup = Loam
#Ba = Bassendean = Sand
#Bw = Blythewood = Sand
#Ca = Cannington = Sand
#S = Spearwood = Sand
#V = Vasse = Clay
```

```
#bring in pinjarra (Murray River catchment) map
pinjarra<-jpeg::readJPEG("pinjarra.jpg")
#identify colour ranges
colordistance::plotPixels("pinjarra.jpg",lower=NULL,upper=NULL,n=5000)
clusters.pinjarra<-colordistance::getKMeanColors("pinjarra.jpg",n=13)
colordistance::extractClusters(clusters.pinjarra)
```

```
#then define values / percents
colour_1<-c(0.8834396,0.7051185,0.6842976)
pinjarra_1<-countcolors::sphericalRange(pinjarra,center=colour_1,radius=0.07,
target.color="red"); names(pinjarra_1)
Bw<-pinjarra_1$img.fraction
colour_2<-c(0.97,0.51,0.5)
pinjarra_2<-countcolors::sphericalRange(pinjarra,center=colour_2,radius=0.06,
target.color="red"); names(pinjarra_2)
Bh<-pinjarra_2$img.fraction
colour_3<-c(0.9919349,0.9900777,0.76423475)
pinjarra_3<-countcolors::sphericalRange(pinjarra,center=colour_3,radius=0.07,
target.color="red"); names(pinjarra_3)
Ba<-pinjarra_3$img.fraction
colour_4<-c(0.8808570,0.9222708,0.5781587)
pinjarra_4<-countcolors::sphericalRange(pinjarra,center=colour_4,radius=0.07,
```

```

        target.color="red"); names(pinjarra_4)
C<-pinjarra_4$img.fraction
colour_5<-c(0.4587057,0.4162613,0.2991963) #line colour, ignore
pinjarra_5<-countcolors::sphericalRange(pinjarra,center=colour_5,radius=0.07,
        target.color="red"); names(pinjarra_5)
colour_6<-c(0.9429240,0.7212089,0.5159612)
pinjarra_6<-countcolors::sphericalRange(pinjarra,center=colour_6,radius=0.07,
        target.color="red"); names(pinjarra_6)
Ca<-pinjarra_6$img.fraction
colour_7<-c(0.2248027,0.2046666,0.1042162)
pinjarra_7<-countcolors::sphericalRange(pinjarra,center=colour_7,radius=0.07,
        target.color="red"); names(pinjarra_7)
#line colour, ignore
colour_8<-c(0.6892578,0.6781974,0.65941717)
pinjarra_8<-countcolors::sphericalRange(pinjarra,center=colour_8,radius=0.08,
        target.color="red"); names(pinjarra_8)
W<-pinjarra_8$img.fraction
colour_9<-c(0.9974429,0.9975196,0.99377882)
pinjarra_9<-countcolors::sphericalRange(pinjarra,center=colour_9,radius=0.07,
        target.color="red"); names(pinjarra_9)
#white space, but struggling with V
colour_10<-c(0.8918985,0.9560049,0.92361884)
pinjarra_10<-countcolors::sphericalRange(pinjarra,center=colour_10,radius=0.05,
        target.color="red"); names(pinjarra_10)
V<-pinjarra_10$img.fraction
colour_11<-c(0.7156843,0.8310881,0.71357728)
pinjarra_11<-countcolors::sphericalRange(pinjarra,center=colour_11,radius=0.05,
        target.color="red"); names(pinjarra_11)
B_p<-pinjarra_11$img.fraction

#make recoloured figure for SI
loam_centre<-colour_11
clay_centre.1<-colour_10
clay_centre.2<-colour_8
sand_centre.1<-colour_6
sand_centre.5<-colour_4
sand_centre.2<-colour_3
sand_centre.3<-colour_2
sand_centre.4<-colour_1
bkg_centre<-c(0.7066147,0.8467714,0.70303157)

pinjarra_map_coloured<-countcolors::countColors("pinjarra.jpg",color.range = "spherical",
        center=c(loam_centre,clay_centre.1,
        clay_centre.2,sand_centre.4,
        sand_centre.1,sand_centre.3,
        sand_centre.2,sand_centre.5),
        radius=c(0.07,0.05,0.08,0.07,0.07,0.07,0.07,0.07),
        plotting=TRUE,bg.lower = bkg_centre,
        target.color=c("salmon2","cyan2",
        "cyan2","firebrick1",

```

```
"firebrick1","firebrick1",  
"firebrick1","firebrick1"))
```

```
#normalise area to soil area  
pinjarra_soils<-sum(B_p,V,W,Ca,C,Ba,Bh,Bw)  
pinjarra_clay<-(W+V)/pinjarra_soils  
pinjarra_loam<-B_p/pinjarra_soils  
pinjarra_sand<-(Ca+C+Ba+Bh+Bw)/pinjarra_soils  
pinjarra_sand  
  
#bring in harvey (Harvey River catchment) map  
harvey<-jpeg::readJPEG("harvey3.jpg")  
#identify colour ranges  
colordistance::plotPixels("harvey3.jpg",lower=NULL,upper=NULL,n=6000)  
clusters.harvey<-colordistance::getKMeanColors("harvey3.jpg",n=10)  
colordistance::extractClusters(clusters.harvey)  
  
#then define values / percents  
H_1<-c(0.9799629,0.5392124,0.4162087)  
harvey_1<-countcolors::sphericalRange(harvey,center=H_1,radius=0.04,  
target.color="red"); names(harvey_1)  
D_H<-harvey_1$img.fraction  
H_2<-c(0.6634102,0.6426091,0.6494207)  
harvey_2<-countcolors::sphericalRange(harvey,center=H_2,radius=0.07,  
target.color="red"); names(harvey_2)  
W_H<-harvey_2$img.fraction  
H_4<-c(0.9952840,0.9960592,0.7311766)  
harvey_4<-countcolors::sphericalRange(harvey,center=H_4,radius=0.07,  
target.color="red"); names(harvey_4)  
Ba_H<-harvey_4$img.fraction  
H_5<-c(0.8437691,0.5067290,0.3829869)  
harvey_5<-countcolors::sphericalRange(harvey,center=H_5,radius=0.06,  
target.color="red"); names(harvey_5)  
R_H<-harvey_5$img.fraction  
H_6<-c(0.8828925,0.8986511,0.5540137)  
harvey_6<-countcolors::sphericalRange(harvey,center=H_6,radius=0.07,  
target.color="red"); names(harvey_6)  
C_H<-harvey_6$img.fraction  
H_7<-c(0.6770744,0.8317865,0.6913081)  
harvey_7<-countcolors::sphericalRange(harvey,center=H_7,radius=0.07,  
target.color="red"); names(harvey_7)  
B_H<-harvey_7$img.fraction  
H_8<-c(0.4427807,0.4320241,0.3742824)  
harvey_8<-countcolors::sphericalRange(harvey,center=H_8,radius=0.07,  
target.color="red"); names(harvey_8)  
#lines, ignore  
H_9<-c(0.5658113,0.2799842,0.1750493)  
harvey_9<-countcolors::sphericalRange(harvey,center=H_9,radius=0.07,
```

```

        target.color="red"); names(harvey_9)

#lines, ignore
H_10<-c(0.2151338,0.1874336,0.1253385)
harvey_10<-countcolors::sphericalRange(harvey,center=H_10,radius=0.07,
        target.color="red"); names(harvey_10)

#normalise area to soil area
harvey_soils<-sum(D_H,W_H,Ba_H,C_H,B_H)
harvey_clay<-(W_H)/harvey_soils
harvey_loam<-(B_H+D_H)/harvey_soils
harvey_sand<-(Ba_H+C_H)/harvey_soils

#make recoloured figure for SI
loam_H1<-H_7
loam_H2<-H_1
clay_H1<-H_2
sand_H1<-H_4
sand_H2<-H_6

harvey_map_coloured<-countcolors::countColors("harvey3.jpg",color.range = "spherical",
        center=c(loam_H1,loam_H2,
        clay_H1,sand_H1,
        sand_H2),
        radius=c(0.07,0.07,0.07,0.07,0.07),
        plotting=TRUE,bg.lower = bkg_centre,
        target.color=c("salmon2","salmon2",
        "cyan2","firebrick1",
        "firebrick1"))

#so then to apply this to P data, need:
#1) Pfert+Psoil for fast v slow for each soil texture
#2) d18Op for scenarios a v d for each fertiliser & soil texture

#then calculate 'leachable P content' (as P_leach+Fert) for each soil texture
P_a_formula<-function(P_leach1,F_low,F_high,F_mean) {

  P_1=(P_leach1+F_low)
  P_2=(P_leach1+F_high)
  P_3=(P_leach1+F_mean)

  P_all<-tibble::tibble(P_1,P_2,P_3) #table w three columns

  P_summary=rowMeans(P_all) #makes one column

  mean_P=mean(P_summary,na.rm=TRUE)
  low_P=mean(P_summary,na.rm=TRUE)-sd(P_summary,na.rm=TRUE)
  high_P=mean(P_summary,na.rm=TRUE)+sd(P_summary,na.rm=TRUE)

```

```

x<-c(mean_P,low_P,high_P)

return(x)

}

P_b_formula<-function(P_leach2,F_low,F_high,F_mean) {

  P_1=(P_leach2+F_low)
  P_2=(P_leach2+F_high)
  P_3=(P_leach2+F_mean)

  P_all<-tibble::tibble(P_1,P_2,P_3) #table w three columns

  P_summary=rowMeans(P_all) #makes one column

  mean_P=mean(P_summary,na.rm=TRUE)
  low_P=mean(P_summary,na.rm=TRUE)-sd(P_summary,na.rm=TRUE)
  high_P=mean(P_summary,na.rm=TRUE)+sd(P_summary,na.rm=TRUE)

  x<-c(mean_P,low_P,high_P)

  return(x)

}

#set up dfs
Soils_nested<-Soils_nested #start w df set up after running MM
sand_leach<-sand_leach%>%
  mutate(Soil_Type="sand")
loam_leach<-loam_leach%>%
  mutate(Soil_Type="loam")
clay_leach<-clay_leach%>%
  mutate(Soil_type="clay")

sand_leach_long<-sand_leach%>%
  dplyr::select(-c(contains("sd"),Soil_Type))%>% #removes the sd columns
  dplyr::select(-c(d18O_mean,d18O_mean1))%>%
  pivot_longer(cols=!c("Brand","Year"),
               names_to="stat",values_to="d18Oleach")
sand_leach_long<-sand_leach_long%>%
  mutate(scenario=case_when(
    endsWith(stat,"a")~"a",
    endsWith(stat,"b")~"b",
    endsWith(stat,"c")~"c",
    endsWith(stat,"d")~"d"
  ))%>%
  mutate(Soil_Type="sand")
clay_leach_long<-clay_leach%>%

```



```

dplyr::select(-c(contains("sd"),Soil_type))%>% #removes the sd columns
dplyr::select(-c(d18O_mean,d18O_mean1))%>%
pivot_longer(cols=!c("Brand","Year"),
              names_to="stat",values_to="d18Oleach")
clay_leach_long<-clay_leach_long%>%
mutate(scenario=case_when(
  endsWith(stat,"a") ~ "a",
  endsWith(stat,"b")~"b",
  endsWith(stat,"c")~"c",
  endsWith(stat,"d")~"d"
))%>%
mutate(Soil_Type="clay")
loam_leach_long<-loam_leach%>%
dplyr::select(-c(contains("sd"),Soil_Type))%>% #removes the sd columns
dplyr::select(-c(d18O_mean,d18O_mean1))%>%
pivot_longer(cols=!c("Brand","Year"),
              names_to="stat",values_to="d18Oleach")
loam_leach_long<-loam_leach_long%>%
mutate(scenario=case_when(
  endsWith(stat,"a") ~ "a",
  endsWith(stat,"b")~"b",
  endsWith(stat,"c")~"c",
  endsWith(stat,"d")~"d"
))%>%
mutate(Soil_Type="loam")

#separate df into a,c v b,d
Soils_nested<-Soils_nested%>%
mutate(P_a=pmap(list(P_leach1,F_low,F_high,F_mean),P_a_formula))%>%
mutate(P_b=pmap(list(P_leach2,F_low,F_high,F_mean),P_b_formula))

#create nested dfs based on fertiliser and scenario
sand_nested<-sand_leach_long%>%
dplyr::group_by(Soil_Type,Brand,scenario)%>%
nest()
clay_nested<-clay_leach_long%>%
dplyr::group_by(Soil_Type,Brand,scenario)%>%
nest()
loam_nested<-loam_leach_long%>%
dplyr::group_by(Soil_Type,Brand,scenario)%>%
nest()

#add in P content info
sand_nested<-sand_nested%>%
dplyr::mutate(P_conc=case_when(
  scenario%in%c("a","c")~(Soils_nested[[1,17]]),
  scenario%in%c("b","d")~Soils_nested[[1,16]]
))

```

```

loam_nested<-loam_nested%>%
  dplyr::mutate(P_conc=case_when(
    scenario%in%c("a","c")~(Soils_nested[[2,17]]),
    scenario%in%c("b","d")~Soils_nested[[2,16]]
  ))

clay_nested<-clay_nested%>%
  dplyr::mutate(P_conc=case_when(
    scenario%in%c("a","c")~(Soils_nested[[3,17]]),
    scenario%in%c("b","d")~Soils_nested[[3,16]]
  ))

#combine dfs
nested_all<-rbind(sand_nested,loam_nested,clay_nested)

#add in spatial info
nested_all<-nested_all%>%
  mutate(area_pinjarra=case_when(
    Soil_Type=="sand"~pinjarra_sand,
    Soil_Type=="clay"~pinjarra_clay,
    Soil_Type=="loam"~pinjarra_loam
  ))%>%
  mutate(area_harvey=case_when(
    Soil_Type=="sand"~harvey_sand,
    Soil_Type=="clay"~harvey_clay,
    Soil_Type=="loam"~harvey_loam
  ))

#make up-scaling formula
#d18O_catchment=(d18O_sand*f_sand*P_sand+d18O_clay*f_clay*P_clay+d18O_loam*f_loam*P_lo
am)/(P_sand+P_clay+P_loam)
nested_all<-nested_all%>%
  mutate(d18O_leach=map(data,~.x$d18O_leach))

#separate out by scenarios
nested_ac<-nested_all%>%
  filter(scenario%in%c("a","c"))
nested_bd<-nested_all%>%
  filter(scenario%in%c("b","d"))

#make formula to calculate f based on area and P conc
totals_fun<-function(df,scen) {

  #calculate total amount of P leached for Pinjarra & Harvey

```

```

totals_H<-df%>%
  dplyr::select(Soil_Type,P_conc,area_harvey,area_pinjarra)%>%
  unnest(cols=c(P_conc,area_harvey,area_pinjarra))%>%
  mutate(Phos_H=P_conc*area_harvey,
         Phos_P=P_conc*area_pinjarra)%>%
  filter(Brand=="AG"&scenario==scen)%>% #keep it simple
  ungroup()%>%
  dplyr::select(Soil_Type,Phos_H)%>%
  mutate(x=c(1,2,3,1,2,3,1,2,3))%>%
  pivot_wider(names_from=Soil_Type,values_from=Phos_H)%>%
  rowwise()%>%
  mutate(P_total=sum(across(c(sand,loam,clay))))

Hf_sand_high<-totals_H[[3,2]]/totals_H[[3,5]]
Hf_sand_low<-totals_H[[2,2]]/totals_H[[2,5]]
Hf_sand_avg<-totals_H[[1,2]]/totals_H[[1,5]]

Hf_loam_high<-totals_H[[3,3]]/totals_H[[3,5]]
Hf_loam_low<-totals_H[[2,3]]/totals_H[[2,5]]
Hf_loam_avg<-totals_H[[1,3]]/totals_H[[1,5]]

Hf_clay_high<-totals_H[[3,4]]/totals_H[[3,5]]
Hf_clay_low<-totals_H[[2,4]]/totals_H[[2,5]]
Hf_clay_avg<-totals_H[[1,4]]/totals_H[[1,5]]

H_f<-tibble::tibble(H_high=c(Hf_sand_high,Hf_loam_high,Hf_clay_high),
                    H_low=c(Hf_sand_low,Hf_loam_low,Hf_clay_low),
                    H_avg=c(Hf_sand_avg,Hf_loam_avg,Hf_clay_avg))

totals_P<-df%>%
  dplyr::select(Soil_Type,P_conc,area_harvey,area_pinjarra)%>%
  unnest(cols=c(P_conc,area_harvey,area_pinjarra))%>%
  mutate(Phos_H=P_conc*area_harvey,
         Phos_P=P_conc*area_pinjarra)%>%
  filter(Brand=="AG"&scenario==scen)%>% #keep it simple
  ungroup()%>%
  dplyr::select(Soil_Type,Phos_P)%>%
  mutate(x=c(1,2,3,1,2,3,1,2,3))%>%
  pivot_wider(names_from=Soil_Type,values_from=Phos_P)%>%
  rowwise()%>%
  mutate(P_total=sum(across(c(sand,loam,clay))))

Pf_sand_high<-totals_P[[3,2]]/totals_P[[3,5]]
Pf_sand_low<-totals_P[[2,2]]/totals_P[[2,5]]
Pf_sand_avg<-totals_P[[1,2]]/totals_P[[1,5]]

Pf_loam_high<-totals_P[[3,3]]/totals_P[[3,5]]
Pf_loam_low<-totals_P[[2,3]]/totals_P[[2,5]]
Pf_loam_avg<-totals_P[[1,3]]/totals_P[[1,5]]

```

```

Pf_clay_high<-totals_P[[3,4]]/totals_P[[3,5]]
Pf_clay_low<-totals_P[[2,4]]/totals_P[[2,5]]
Pf_clay_avg<-totals_P[[1,4]]/totals_P[[1,5]]

```

```

P_f<-tibble::tibble(P_high=c(Pf_sand_high,Pf_loam_high,Pf_clay_high),
  P_low=c(Pf_sand_low,Pf_loam_low,Pf_clay_low),
  P_avg=c(Pf_sand_avg,Pf_loam_avg,Pf_clay_avg))

```

```

output<-cbind(Soil_Type=c("sand","loam","clay"),H_f,P_f)

```

```

return(as.data.frame(output))

```

```

}

```

```

#merge left so soil textures match up

```

```

nested_ac<-left_join(nested_ac,totals_fun(nested_ac,"a"),by="Soil_Type")

```

```

nested_bd<-left_join(nested_bd,totals_fun(nested_bd,"b"),by="Soil_Type")

```

```

#then a d18O_catchment calculation

```

```

d18O_weight_fun<-function(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg) {

```

```

  d18O<-tibble(x=d18Oleach)

```

```

  P_low<-expand.grid(d18O$x,P_low)%>%

```

```

    mutate(d18O_f=Var1*Var2)%>%

```

```

    summarise(

```

```

      mean=mean(d18O_f,na.rm=TRUE)

```

```

      #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE),

```

```

      #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)

```

```

    )

```

```

  P_high<-expand.grid(d18O$x,P_high)%>%

```

```

    mutate(d18O_f=Var1*Var2)%>%

```

```

    summarise(

```

```

      mean=mean(d18O_f,na.rm=TRUE)

```

```

      #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE),

```

```

      #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)

```

```

)

P_avg<-expand.grid(d18O$x,P_avg)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  mean=mean(d18O_f,na.rm=TRUE)
  #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE),
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

H_low<-expand.grid(d18O$x,H_low)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  mean=mean(d18O_f,na.rm=TRUE)
  #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE),
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

H_high<-expand.grid(d18O$x,H_high)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  mean=mean(d18O_f,na.rm=TRUE)
  #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE),
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

H_avg<-expand.grid(d18O$x,H_avg)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  mean=mean(d18O_f,na.rm=TRUE)
  #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE),
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

x<-tibble::tibble(P_frac=c("low","high","avg"),
  P=c(P_low,P_high,P_avg),
  H=c(H_low,H_high,H_avg))
return(x)

}

#calc for low range
d18O_weight_fun2<-function(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg) {

d18O<-tibble(x=d18Oleach)

P_low<-expand.grid(d18O$x,P_low)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)

```

```

    #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )

P_high<-expand.grid(d18O$x,P_high)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  #mean=mean(d18O_f,na.rm=TRUE)
  low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

P_avg<-expand.grid(d18O$x,P_avg)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  #mean=mean(d18O_f,na.rm=TRUE)
  low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

H_low<-expand.grid(d18O$x,H_low)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  #mean=mean(d18O_f,na.rm=TRUE)
  low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

H_high<-expand.grid(d18O$x,H_high)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  #mean=mean(d18O_f,na.rm=TRUE)
  low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

H_avg<-expand.grid(d18O$x,H_avg)%>%
mutate(d18O_f=Var1*Var2)%>%
summarise(
  #mean=mean(d18O_f,na.rm=TRUE)
  low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
  #high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
)

x<-tibble::tibble(P_frac=c("low","high","avg"),
  P=c(P_low,P_high,P_avg),
  H=c(H_low,H_high,H_avg))
return(x)
}

```

```

#calc for high range
d18O_weight_fun3<-function(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg) {

  d18O<-tibble(x=d18Oleach)

  P_low<-expand.grid(d18O$x,P_low)%>%
  mutate(d18O_f=Var1*Var2)%>%
  summarise(
    #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
    high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )

  P_high<-expand.grid(d18O$x,P_high)%>%
  mutate(d18O_f=Var1*Var2)%>%
  summarise(
    #mean=mean(d18O_f,na.rm=TRUE)
    #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
    high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )

  P_avg<-expand.grid(d18O$x,P_avg)%>%
  mutate(d18O_f=Var1*Var2)%>%
  summarise(
    #mean=mean(d18O_f,na.rm=TRUE)
    #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
    high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )

  H_low<-expand.grid(d18O$x,H_low)%>%
  mutate(d18O_f=Var1*Var2)%>%
  summarise(
    #mean=mean(d18O_f,na.rm=TRUE)
    #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
    high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )

  H_high<-expand.grid(d18O$x,H_high)%>%
  mutate(d18O_f=Var1*Var2)%>%
  summarise(
    #mean=mean(d18O_f,na.rm=TRUE)
    #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
    high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )

  H_avg<-expand.grid(d18O$x,H_avg)%>%
  mutate(d18O_f=Var1*Var2)%>%
  summarise(
    #mean=mean(d18O_f,na.rm=TRUE)
    #low=mean(d18O_f,na.rm=TRUE)-sd(d18O_f,na.rm=TRUE)
    high=mean(d18O_f,na.rm=TRUE)+sd(d18O_f,na.rm=TRUE)
  )
}

```

```

)

x<-tibble::tibble(P_frac=c("low","high","avg"),
                  P=c(P_low,P_high,P_avg),
                  H=c(H_low,H_high,H_avg))
return(x)
}

nested_ac<-nested_ac%>%
  mutate(d18Op=pmmap(list(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg),
                        d18O_weight_fun))
nested_bd<-nested_bd%>%
  mutate(d18Op=pmmap(list(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg),
                        d18O_weight_fun))

nested_ac2<-nested_ac%>%
  mutate(d18Op=pmmap(list(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg),
                        d18O_weight_fun2))
nested_bd2<-nested_bd%>%
  mutate(d18Op=pmmap(list(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg),
                        d18O_weight_fun2))
nested_ac3<-nested_ac%>%
  mutate(d18Op=pmmap(list(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg),
                        d18O_weight_fun3))
nested_bd3<-nested_bd%>%
  mutate(d18Op=pmmap(list(d18Oleach,P_low,P_high,P_avg,H_low,H_high,H_avg),
                        d18O_weight_fun3))

#so now add together some mixes, so:

#mix 1: 90% SP, 20%c + 80%d
#mix 2: 90% SP, 50%c + 50%d
#mix 3: 90% SP, 5%c + 95%d

#need outputs for both Harvey v Pinjarra
#make df that just has d18O and f_area info in it
upscaled_d18O_df<-rbind(nested_ac%>%
  dplyr::select(area_pinjarra,area_harvey,d18Op)%>%
  unnest(cols=c(d18Op),names_sep="_"),
  nested_bd%>%
  dplyr::select(area_pinjarra,area_harvey,d18Op)%>%
  unnest(cols=c(d18Op),names_sep="_")
)%>%
  rename(frac=d18Op_P_frac)

#convert columns from lists to numeric
upscaled_d18O_df$d18Op_H<-as.numeric(upscaled_d18O_df$d18Op_H)
upscaled_d18O_df$d18Op_P<-as.numeric(upscaled_d18O_df$d18Op_P)

```



```

#for low range
upscaled_d18O_df2<-rbind(nested_ac2%>%
  dplyr::select(area_pinjarra,area_harvey,d18Op)%>%
  unnest(cols=c(d18Op),names_sep="_"),
nested_bd2%>%
  dplyr::select(area_pinjarra,area_harvey,d18Op)%>%
  unnest(cols=c(d18Op),names_sep="_")
)%>%
  rename(frac=d18Op_P_frac)

#convert columns from lists to numeric
upscaled_d18O_df2$d18Op_H<-as.numeric(upscaled_d18O_df2$d18Op_H)
upscaled_d18O_df2$d18Op_P<-as.numeric(upscaled_d18O_df2$d18Op_P)

#for high range
upscaled_d18O_df3<-rbind(nested_ac3%>%
  dplyr::select(area_pinjarra,area_harvey,d18Op)%>%
  unnest(cols=c(d18Op),names_sep="_"),
nested_bd3%>%
  dplyr::select(area_pinjarra,area_harvey,d18Op)%>%
  unnest(cols=c(d18Op),names_sep="_")
)%>%
  rename(frac=d18Op_P_frac)

#convert columns from lists to numeric
upscaled_d18O_df3$d18Op_H<-as.numeric(upscaled_d18O_df3$d18Op_H)
upscaled_d18O_df3$d18Op_P<-as.numeric(upscaled_d18O_df3$d18Op_P)

#function to play around with mixing
mixing_fun<-function(df,f_SP,f_a) {

  #define terms
  f_AG=1-f_SP #so either SP or AG fertilisers
  f_d=1-f_a #either scenario a or d

  {P_avg<-(f_SP*(f_a*(as.double(df%>%ungroup())%>%
    filter(Brand=="SP",scenario=="a",
      Soil_Type=="sand",frac=="avg"))%>%
    dplyr::select(d18Op_P))+
    as.double(df%>%ungroup())%>%
    filter(Brand=="SP",scenario=="a",
      Soil_Type=="clay",frac=="avg"))%>%
    dplyr::select(d18Op_P))+
    as.double(df%>%ungroup())%>%
    filter(Brand=="SP",scenario=="a",
      Soil_Type=="loam",frac=="avg"))%>%
    dplyr::select(d18Op_P))
  }+f_d*(as.double(df%>%ungroup())%>%
    filter(Brand=="SP",scenario=="d",

```

```

        Soil_Type=="sand",frac=="avg"))%>%
      dplyr::select(d18Op_P))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
        Soil_Type=="clay",frac=="avg"))%>%
      dplyr::select(d18Op_P))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
        Soil_Type=="loam",frac=="avg"))%>%
      dplyr::select(d18Op_P))
  )
)+f_AG*(f_a*(as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="a",
    Soil_Type=="sand",frac=="avg"))%>%
  dplyr::select(d18Op_P))+
  as.double(df%>%ungroup())%>%
    filter(Brand=="AG",scenario=="a",
      frac=="avg",Soil_Type=="clay"))%>%
    dplyr::select(d18Op_P))+
  as.double(df%>%ungroup())%>%
    filter(Brand=="AG",scenario=="a",
      Soil_Type=="loam",frac=="avg"))%>%
    dplyr::select(d18Op_P))
)+f_d*(as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="d",
    Soil_Type=="sand",frac=="avg"))%>%
  dplyr::select(d18Op_P))+
  as.double(df%>%ungroup())%>%
    filter(Brand=="AG",scenario=="d",
      Soil_Type=="clay",frac=="avg"))%>%
    dplyr::select(d18Op_P))+
  as.double(df%>%ungroup())%>%
    filter(Brand=="AG",scenario=="d",
      Soil_Type=="loam",frac=="avg"))%>%
    dplyr::select(d18Op_P))
  )
))

P_low<-(f_SP*(f_a*(as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="a",
    Soil_Type=="sand",frac=="low"))%>%
  dplyr::select(d18Op_P))+
  as.double(df%>%ungroup())%>%
    filter(Brand=="SP",scenario=="a",
      frac=="low",Soil_Type=="clay"))%>%
    dplyr::select(d18Op_P))+
  as.double(df%>%ungroup())%>%
    filter(Brand=="SP",scenario=="a",
      frac=="low",Soil_Type=="loam"))%>%
    dplyr::select(d18Op_P))

```

```

)+f_d*(as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="d",
    frac=="low",Soil_Type=="sand")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="d",
    frac=="low",Soil_Type=="clay")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="d",
    frac=="low",Soil_Type=="loam")%>%
  dplyr::select(d18Op_P))
)
)+f_AG*(f_a*(as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="a",
    frac=="low",Soil_Type=="sand")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="a",
    frac=="low",Soil_Type=="clay")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="a",
    frac=="low",Soil_Type=="loam")%>%
  dplyr::select(d18Op_P))
)+f_d*(as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="d",
    frac=="low",Soil_Type=="sand")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="d",
    frac=="low",Soil_Type=="clay")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="AG",scenario=="d",
    frac=="low",Soil_Type=="loam")%>%
  dplyr::select(d18Op_P))
)
))

P_high<-(f_SP*(f_a*(as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="a",
    frac=="high",Soil_Type=="sand")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="a",
    frac=="high",Soil_Type=="clay")%>%
  dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
  filter(Brand=="SP",scenario=="a",

```

```

        frac=="high",Soil_Type=="loam")%>%
        dplyr::select(d18Op_P))
)+f_d*(as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="d",
        frac=="high",Soil_Type=="sand")%>%
        dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="d",
        frac=="high",Soil_Type=="clay")%>%
        dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="d",
        frac=="high",Soil_Type=="loam")%>%
        dplyr::select(d18Op_P))
)
)+f_AG*(f_a*(as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="a",
        frac=="high",Soil_Type=="sand")%>%
        dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="a",
        frac=="high",Soil_Type=="clay")%>%
        dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="a",
        frac=="high",Soil_Type=="loam")%>%
        dplyr::select(d18Op_P))
)+f_d*(as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="d",
        frac=="high",Soil_Type=="sand")%>%
        dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="d",
        frac=="high",Soil_Type=="clay")%>%
        dplyr::select(d18Op_P))+
as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="d",
        frac=="high",Soil_Type=="loam")%>%
        dplyr::select(d18Op_P))
)
))
}
#harvey calcs
H_avg<-(f_SP*(f_a*(as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="a",
        frac=="avg",Soil_Type=="sand")%>%
        dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="a",
        frac=="avg",Soil_Type=="clay")%>%

```

```

      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="a",
             frac=="avg",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)+f_d*(as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
             frac=="avg",Soil_Type=="sand")%>%
      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
             frac=="avg",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
             frac=="avg",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)
)+f_AG*(f_a*(as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="a",
             frac=="avg",Soil_Type=="sand")%>%
      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="a",
             frac=="avg",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="a",
             frac=="avg",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)+f_d*(as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="d",
             frac=="avg",Soil_Type=="sand")%>%
      dplyr::select(d18Op_P))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="d",
             frac=="avg",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="d",
             frac=="avg",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)
))

H_low<-(f_SP*(f_a*(as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="a",
             frac=="low",Soil_Type=="sand")%>%
      dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%

```

```

        filter(Brand=="SP",scenario=="a",
              frac=="low",Soil_Type=="clay")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="a",
              frac=="low",Soil_Type=="loam")%>%
        dplyr::select(d18Op_H))
)+f_d*(as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="d",
              frac=="low",Soil_Type=="sand")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="d",
              frac=="low",Soil_Type=="clay")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="d",
              frac=="low",Soil_Type=="loam")%>%
        dplyr::select(d18Op_H))
)
)+f_AG*(f_a*(as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="a",
              frac=="low",Soil_Type=="sand")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="a",
              frac=="low",Soil_Type=="clay")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="a",
              frac=="low",Soil_Type=="loam")%>%
        dplyr::select(d18Op_H))
)+f_d*(as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="d",
              frac=="low",Soil_Type=="sand")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="d",
              frac=="low",Soil_Type=="clay")%>%
        dplyr::select(d18Op_H))+
    as.double(df%>%ungroup())%>%
        filter(Brand=="AG",scenario=="d",
              frac=="low",Soil_Type=="loam")%>%
        dplyr::select(d18Op_H))
)
))

H_high<-(f_SP*(f_a*(as.double(df%>%ungroup())%>%
        filter(Brand=="SP",scenario=="a",
              frac=="high",Soil_Type=="sand")%>%

```

```

      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="a",
            frac=="high",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="a",
            frac=="high",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)+f_d*(as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
            frac=="high",Soil_Type=="sand")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
            frac=="high",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="SP",scenario=="d",
            frac=="high",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)
)+f_AG*(f_a*(as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="a",
            frac=="high",Soil_Type=="sand")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="a",
            frac=="high",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="a",
            frac=="high",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)+f_d*(as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="d",
            frac=="high",Soil_Type=="sand")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="d",
            frac=="high",Soil_Type=="clay")%>%
      dplyr::select(d18Op_H))+
as.double(df%>%ungroup())%>%
      filter(Brand=="AG",scenario=="d",
            frac=="high",Soil_Type=="loam")%>%
      dplyr::select(d18Op_H))
)
))

```

```
output<-list(Pinjarra_avg=P_avg,Pinjarra_high=P_high,Pinjarra_low=P_low,
```

```

    Harvey_avg=H_avg,Harvey_low=H_low,Harvey_high=H_high)

return(output)

}

#outputs using mean d18OP(export)
upscale_table<-data.frame(rbind(S1=mixing_fun(upscaled_d18O_df,1,0.1), #range for scenario w
100% SP fertiliser, 10% scenario a
    S2=mixing_fun(upscaled_d18O_df,1,0.5),
    S3=mixing_fun(upscaled_d18O_df,0.6,0.1),
    S4=mixing_fun(upscaled_d18O_df,0.6,0.5))) #range for scenario w 60% SP
fertiliser, 50% scenario a
#outputs using low range d18OP(export)
upscale_table2<-data.frame(rbind(S1=mixing_fun(upscaled_d18O_df2,1,0.1),
    S2=mixing_fun(upscaled_d18O_df2,1,0.5),
    S3=mixing_fun(upscaled_d18O_df2,0.6,0.1),
    S4=mixing_fun(upscaled_d18O_df2,0.6,0.5)))
#outputs using high range d18OP(export)
upscale_table3<-data.frame(rbind(S1=mixing_fun(upscaled_d18O_df2,1,0.1),
    S2=mixing_fun(upscaled_d18O_df3,1,0.5),
    S3=mixing_fun(upscaled_d18O_df3,0.6,0.1),
    S4=mixing_fun(upscaled_d18O_df3,0.6,0.5)))
#Table 3 - select max-min for each scenario x sub-catchment

```


S5: References

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