

# Oxygen isotopes in phosphate as a tracer for sources and pathways of dissolved P in stream water

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## Introduction and aim

Efforts to reduce eutrophication rely on methods to quantify the most important sources of nutrient loads to water bodies. A great uncertainty is associated with the partitioning of riverine P load between various sources. This is often assessed from mean leachate coefficients for agricultural land and standard estimates of rural wastewater discharges, but more precise methods are needed. Stable P isotope ratios cannot be used to quantify P sources as there is only one stable isotope. However, phosphate ( $\text{PO}_4^{3-}$ ) can be analyzed for the O isotope composition ( $\delta^{18}\text{O}_\text{P}$ ), and this could hypothetically be used for source apportionment of the dissolved  $\text{PO}_4^{3-}$ -P fraction. The P-O bond in phosphate is resistant to inorganic hydrolysis and does not exchange O with water without biological mediation. A recent study [1] proved that  $\delta^{18}\text{O}_\text{P}$  values can be used to study sources and pathways of dissolved phosphate (DIP), though data on the isotopic composition of  $\text{PO}_4^{3-}$  from various sources is still relatively scarce.

With the aim of investigating the usefulness of this principle, we present oxygen isotope measurements on DIP in rural wastewater, drainage water from agricultural fields in S. Sweden (Fig. 1), and  $\text{PO}_4^{3-}$  in soil extracts. The data are related to the surface water composition in one small (7.6 km<sup>2</sup>) agricultural catchment (H in Fig. 1).

## Methods

Sampling, sample handling, and isotope measurements were done similar to the procedures described by [2]. At Linköping University, all samples were shaken with activated carbon powder before filtering due to the high concentrations of DOC [3]. Phosphate was subsequently co-precipitated with  $\text{Mg}(\text{OH})_2$ , the supernatant was discarded, and  $\text{Mg}(\text{OH})_2$  finally dissolved with acetic and nitric acid. In the buffered solution (pH 5.5), phosphate was again precipitated as ceriumphosphate by adding ceriumnitrate, and finally rinsed with DI water.

At Tübingen University, the Ce was removed from the ceriumphosphate after dissolution with  $\text{HNO}_3$  using a Biorad exchange resin (AG50), the sample neutralized and finally phosphate was precipitated as  $\text{Ag}_3\text{PO}_4$  by adding  $\text{AgNO}_3$ . O-isotope measurements were carried out on approximately 0.4 to 0.5 mg of  $\text{Ag}_3\text{PO}_4$ , using a continuous flow TCEA-IRMS Finnigan Delta Plus XL. The given  $\delta^{18}\text{O}_\text{P}$  value is an average of three measurements of each sample and are reported relative to V-SMOW. Water samples were also analysed for the O isotope composition of water ( $\delta^{18}\text{O}_\text{W}$ ) using  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibration in a Gasbench II device coupled with a Finnigan MAT 252.

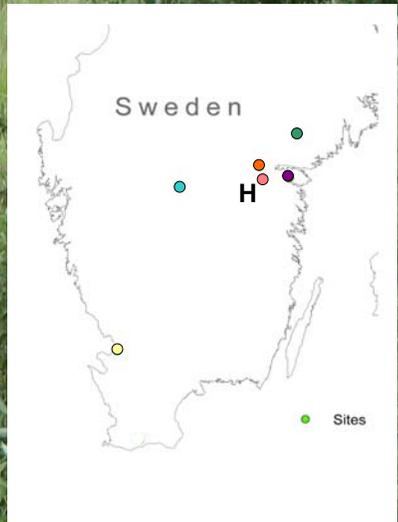


Fig. 1. Location of study catchment (H) with all sample types, and of agricultural fields where additional drain water samples were taken for analysis of  $\delta^{18}\text{O}_\text{P}$ .

## Results and interpretation

The first results showed that the wastewater from rural septic tanks could be clearly distinguished from water from agricultural field drains by the  $\delta^{18}\text{O}_\text{P}$  values of DIP (Fig. 2). Wastewater had  $\delta^{18}\text{O}_\text{P}$  values of +13.2 to +16.3 ‰, whereas both the drain water samples and the water extractable  $\text{PO}_4^{3-}$  in erosion soils had  $\delta^{18}\text{O}_\text{P}$  values at +11 ‰ or below, with one exception (13.9 ‰). Preliminary, the data also indicated that drain water composition varies with flow conditions, as the value during snow melt was +2 ‰ higher than during lower flow (red arrow in Fig. 2).

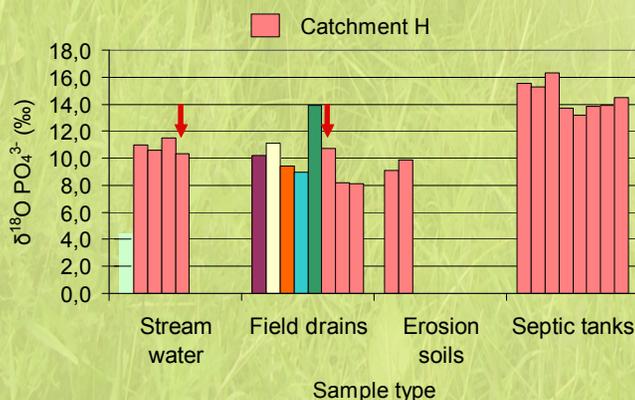


Fig. 2.  $\delta^{18}\text{O}_\text{P}$  values in different types of water from an agricultural catchment (H) and in drain water from five agricultural fields in S. Sweden (see Fig. 1 for locations). Red arrows denote a snowmelt occasion with high flow.

Hypothetically, phosphate in streams with low DIP concentrations is in equilibrium with ambient water, at least during the warmer months. Based on the temperature of the water, one can model the expected  $\delta^{18}\text{O}_\text{P}$  values if equilibrium was achieved. Preliminary calculations suggested that some of the samples in our study may have been in equilibrium, whereas others were not. The high P concentration sewage was not in equilibrium, and thus reflected the isotope signature of the source. Those  $\delta^{18}\text{O}_\text{W}$  values were stable (Table 1).

Table 1. DIP concentrations and O-isotope measurements on water and phosphate samples from the studied catchment (H in Fig. 1).

	$\delta^{18}\text{O}_\text{P}$	$\delta^{18}\text{O}_\text{W}$	$\text{PO}_4^{3-}$ -P
	‰ relative to V-SMOW		( $\mu\text{g l}^{-1}$ )
<b>Drain waters</b>			
H A	8,10	-11,7	120
H B	8,20	-11,0	130
H B snowmelt	10,70	-13,5	350
<b>Septic tank wastewater</b>			
H I, 24 h	13,17	-11	4900
H II, 24 h	13,85	-10,7	3400
H III, 24h	13,93	-10,4	7500
H IV, 24 h	14,47	-10,5	7700
<b>Surface water</b>			
H	10,99	-9,7	387
H	10,59	-9,8	270
H	11,50	-10,2	490
H Snowmelt	10,30	-12,4	

## Conclusion

In our study area, oxygen isotope measurement of phosphate seems an efficient tool for source apportionment of DIP. More measurements of  $\delta^{18}\text{O}_\text{P}$ ,  $\delta^{18}\text{O}_\text{W}$ , DIP and water temperature variations in time will hopefully allow us to model the total DIP contribution from different sources in the catchment.