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Isotopic Fingerprint for Phosphorus in Drinking Water Supplies

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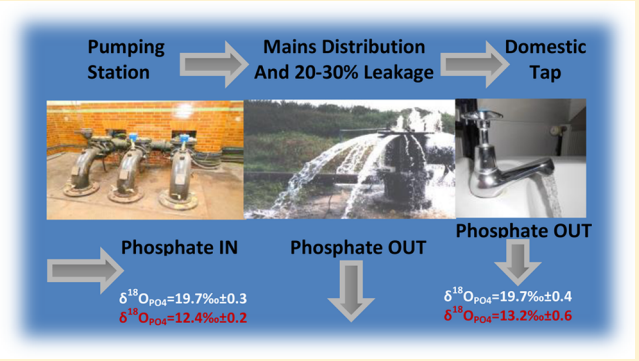
ABSTRACT: Phosphate dosing of drinking water supplies, coupled with leakage from distribution networks, represents a significant input of phosphorus to the environment. The oxygen isotope composition of phosphate ($\delta^{18}O_{PO_4}$), a novel stable isotope tracer for phosphorus, offers new opportunities to understand the importance of phosphorus derived from sources such as drinking water. We report the first assessment of $\delta^{18}O_{PO_4}$ within drinking water supplies. A total of 40 samples from phosphate-dosed distribution networks were analyzed from across England and Wales. In addition, samples of the source orthophosphoric acid used for dosing were also analyzed. Two distinct isotopic signatures for drinking water were identified (average = +13.2 or +19.7‰), primarily determined by $\delta^{18}O_{PO_4}$ of the source acid (average = +12.4 or +19.7‰). Dependent upon the source acid used, drinking water $\delta^{18}O_{PO_4}$ appears isotopically distinct from a number of other phosphorus sources. Isotopic offsets from the source acid ranging from −0.9 to +2.8‰ were observed. There was little evidence that equilibrium isotope fractionation dominated within the networks, with offsets from temperature-dependent equilibrium ranging from −4.8 to +4.2‰. While partial equilibrium fractionation may have occurred, kinetic effects associated with microbial uptake of phosphorus or abiotic sorption and dissolution reactions may also contribute to $\delta^{18}O_{PO_4}$ within drinking water supplies.



INTRODUCTION

In many developed countries, legacy lead piping is a major source of lead contamination in drinking water,[1,2] which has been associated with reduced cognitive development in young children[3,4] and an increased risk of coronary heart disease or stroke because of increased blood pressure.[5,6] Public water utilities in the U.K. and parts of Europe and North America routinely dose drinking water supplies with phosphate to prevent pipe corrosion and the dissolution of lead. For example, in the U.K., phosphate dosing is currently the only viable approach to achieve the drinking water standard of <10 $\mu g\ L^{-1}$ lead in the taps of customers.[7] Inorganic phosphate (commonly phosphoric acid or monosodium phosphate) is dosed to drinking water supplies, leading to the formation of lead phosphate or calcium phosphate precipitates on the inside of service lines and household plumbing. These precipitates have lower solubility than lead corrosion products (primarily lead carbonates) that otherwise line the inside of drinking water supply pipes, thereby reducing the concentration of lead in solution alongside the concentration of other solutes derived from pipe corrosion products, including copper.[7]

Phosphate dosing of drinking water supplies represents a pervasive and potentially significant source of phosphorus (P) within the environment. For example, on the basis of a U.S. survey conducted in 1992, more than half of water utilities used phosphate-based corrosion inhibitors,[8] and this figure has continued to rise.[9] In the U.K., approximately 95% of drinking water supplies are currently dosed to concentrations ranging from 500 to 1500 μg of P L^{-1}, depending upon alkalinity within the supply.[10] It is estimated that phosphate dosing of drinking water accounts for approximately 6% of the annual P load entering wastewater treatment works in the U.K.[11] Further, a significant proportion of the drinking water being distributed is lost because of leakage into the soil or shallow groundwater surrounding distribution networks. The latest statistics show that the biggest U.K. water utilities lose 25−27% of drinking water to leakage,[12] which equates to ∼50 L per customer per day. On the basis of these figures, a conservative estimate of drinking water leakage for the U.K. corresponds to around 1000 tonnes of phosphorus entering the environment annually. Given that phosphate dosing typically achieves concentrations of P in drinking water supplies that are some 30 times higher than current U.K. standards for P in rivers,[13] the leaking of drinking

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water could represent a significant source of P within the environment.[14] Similar issues surround dosing and leakage of drinking water supplies in many other parts of Europe and North America.[15−19]

However, identifying the relative contribution of drinking water to P within the environment, alongside the ecological significance of P from this source, remains a significant challenge, as it does for nearly all sources of P. The potential to use the stable oxygen isotope composition of phosphate ($\delta^{18}O_{PO_4}$) as both an inherent tracer of the P source and a dynamic tracer for reaction processes affecting P cycling in the environment has recently emerged.[20−24] Davies et al.[25] synthesized the existing data for $\delta^{18}O_{PO_4}$ within aquatic ecosystems (adapted in Figure 1).

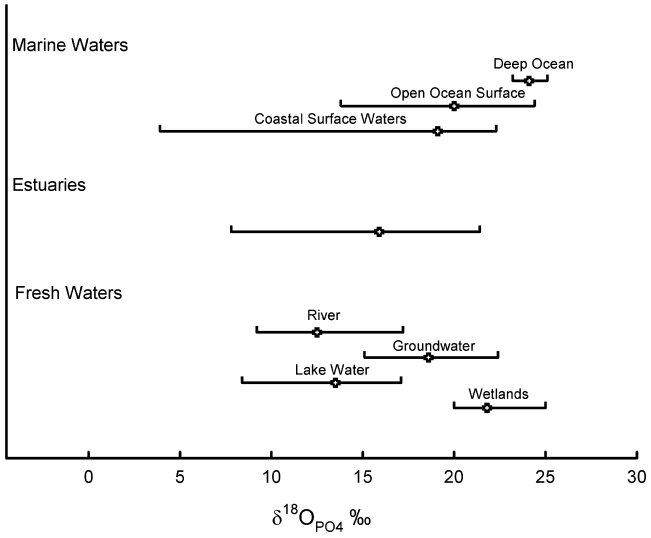

Figure 1. Global $\delta^{18}O_{PO_4}$ data from a range of aquatic ecosystems. Adapted from ref 25 and the references therein.

This global data set remains relatively small, and potentially important sources of P within the environment, including drinking water supplies, have yet to be analyzed for $\delta^{18}O_{PO_4}$ anywhere in the world. Distinctive $\delta^{18}O_{PO_4}$ within individual sources of P is a fundamental prerequisite for using $\delta^{18}O_{PO_4}$ to constrain the relative importance of different sources of P within a water sample. Therefore, proper evaluation of the potential of $\delta^{18}O_{PO_4}$ as a source apportionment tool requires expansion of the global library of source characterizations. Further, isotope fractionation of the oxygen atoms in phosphate ions only occurs at a typical Earth surface water temperature and pressure by enzyme-mediated biochemical reactions.[26] In particular, intracellular metabolic reactions catalyzed by the inorganic pyrophosphatase enzyme lead to rapid, temperature-dependent equilibrium between oxygen in phosphate and oxygen within the intracellular fluid. The latter is expected to be identical in oxygen isotope composition to water oxygen ($\delta^{18}O_{H_2O}$) in the extracellular environment. Given sufficient intracellular−extracellular exchange of P to maintain non-lethal intracellular P concentrations, a temperature-dependent equilibrium fractionation will be established between $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{H_2O}$ in the extracellular environment. The oxygen isotope fractionation between dissolved inorganic phosphate and water ($\alpha_{PO_4-H_2O}$) at surface temperatures has recently been determined, using laboratory solutions catalyzed by the inorganic pyrophosphatase enzyme.[27] These authors derived the equation:

$$10^3 \ln \alpha_{PO_4-H_2O} = 14.43 \times (10^3/T) - 26.54 \quad (1)$$

where T is in degrees kelvin. Because

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

by combining eqs 1 and 2, theoretical equilibrium $\delta^{18}O_{PO_4}$ may be calculated from

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

Proper interpretation of isotope fractionations affecting $\delta^{18}O_{PO_4}$ in the environment also requires the isotopic composition of sources of P to be characterized, to differentiate between biologically mediated isotope fractionation within an environmental sample and bulk mixing with an isotopically distinct but currently uncharacterized P source.

Beyond the use of $\delta^{18}O_{PO_4}$ to understand the sources and metabolism of P in the environment, $\delta^{18}O_{PO_4}$ may also have utility as a marker of leakage from drinking water distribution networks. Although water companies already have well-established protocols for tracing leaks based on a range of parameters, including residual chlorine and trihalomethane (THM) concentrations, these methods are far from perfect.[28] For example, the concentrations of both residual chlorine and THMs decrease dramatically with time to below detection limits, because of their volatile nature. Therefore, $\delta^{18}O_{PO_4}$ may provide a useful additional marker of leakage from drinking water supplies, distinguishing drinking water from other potential sources of P, such as leaking sewers, agricultural runoff, or geological P within groundwater.

In the research reported here, we hypothesized that (i) $\delta^{18}O_{PO_4}$ of phosphate used to dose supplies means that drinking water is isotopically distinct from other sources of P within the environment and (ii) $\delta^{18}O_{PO_4}$ of drinking water is conservative within the distribution network, because of suppression of metabolic activity through, for example, the chlorination of drinking water supplies.

This paper reports data from a wide range of drinking water supplies in England and Wales to evaluate these hypotheses and contribute to the global library of $\delta^{18}O_{PO_4}$ for a range of P sources within the environment.

MATERIALS AND METHODS

Sites and Sampling. Samples of drinking water were collected between July and October 2014 from the distribution network of 12 public water utilities across England and Wales where phosphate dosing occurs. A minimum of two but more generally three locations were sampled from the network of each water utility (Figure 2). Samples from each water utility were selected to come from different supply areas and, therefore, different raw water sources, including a range of groundwaters, river waters, and surface-impoundment reservoirs. Sample taps, which were either customer taps or main hydrants, were allowed to run until the water temperature stabilized, which generally took approximately 5 min. Temperature stability was used to indicate when water in the local system had been flushed by water representative of that within the drinking water distribution network. In addition, a sampling transect running for 7 km from the point of water entry into the drinking water distribution network was established at one site in the southeast of England. The transect included five sampling locations spaced at 1−2 km

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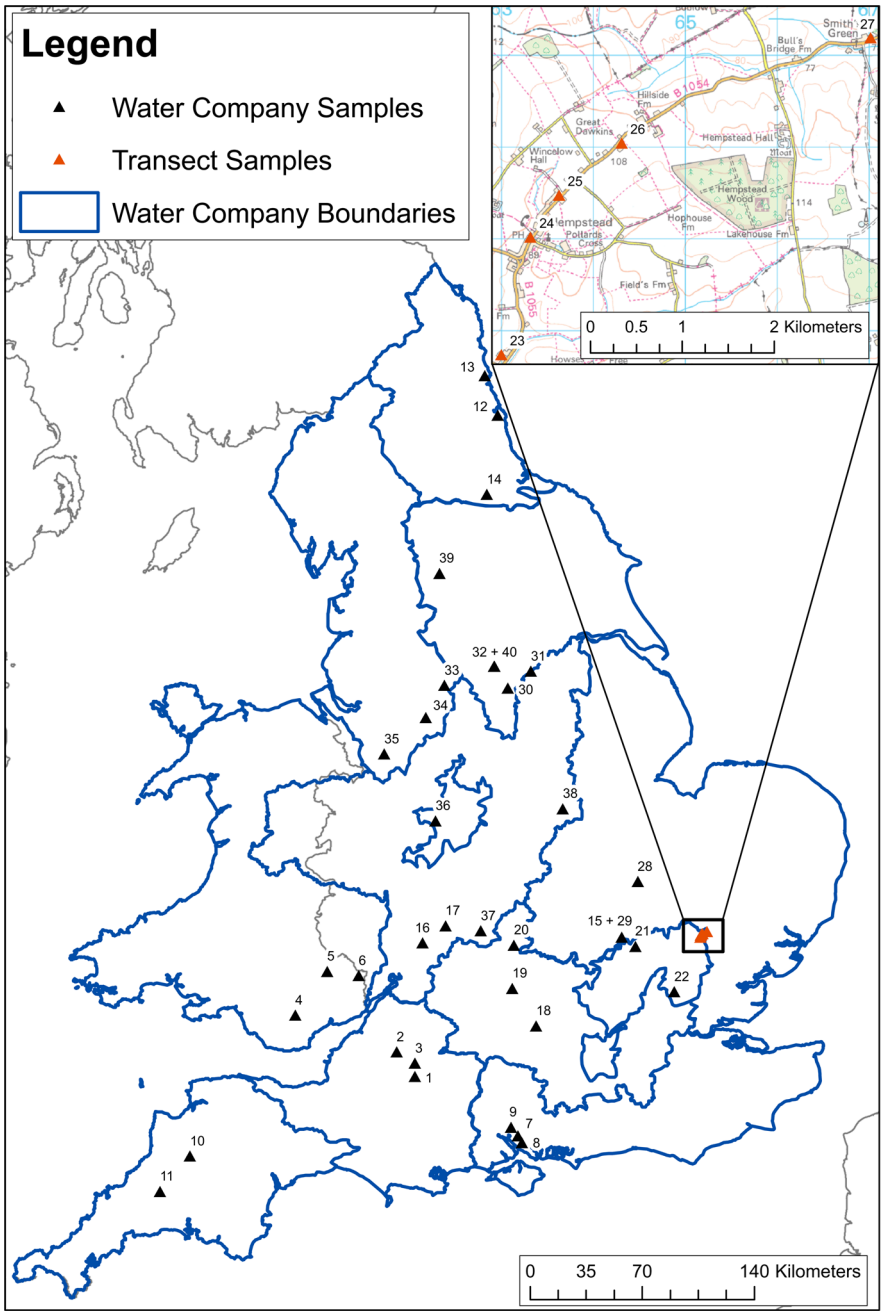

Figure 2. Geographical distribution of sites sampled for $\delta^{18}O_{PO_4}$ in public water supplies across England and Wales, containing Ordnance Survey data. Copyright 2015 Ordnance Survey.

intervals along the network, designed to allow for an initial evaluation of isotope changes within the distribution network that might be due to metabolic activity,[29] sorption, or precipitation/dissolution reactions that had not reached equilibrium during the residence time of water in the distribution network.[30] The residence time of water at the end of the distribution network is determined by water demand but can be of the order of hours to several days. All water samples for $\delta^{18}O_{PO_4}$ analysis were collected in 5 L Nalgene bottles and returned under ice to the laboratory for extraction. Additional samples for determination of $\delta^{18}O_{H_2O}$ and the phosphate concentration were also collected in 50 mL glass vials. All water utilities in this research used orthophosphoric acid to dose drinking water supplies. Samples of acid were acquired from the suppliers for these water companies and analyzed for $\delta^{18}O_{PO_4}$. For these samples, 4 mL of concentrated acid solution was added to 10 L of ultrapure water and the pH was raised to 6.8 ± 0.1 using 0.1 M NaOH, before being extracted and analyzed as described below.

Isotope Analysis. The method used to isolate phosphate from drinking water samples for isotope analysis is described elsewhere[31] and shown in Figure 3. All samples were processed within 24 h of collection and were stored in the dark at 4 °C prior to processing. In brief, the majority of dissolved organic matter within a sample was first removed using a DAX-8 organic exchange resin and phosphate was then isolated from the remaining matrix by adsorption onto an anion-exchange resin. Phosphate was eluted and chromatographically separated from other anions (NO_3^- and SO_4^{2-}) using a 0.3 M KCl eluent. Eluted fractions containing only phosphate were combined and then processed

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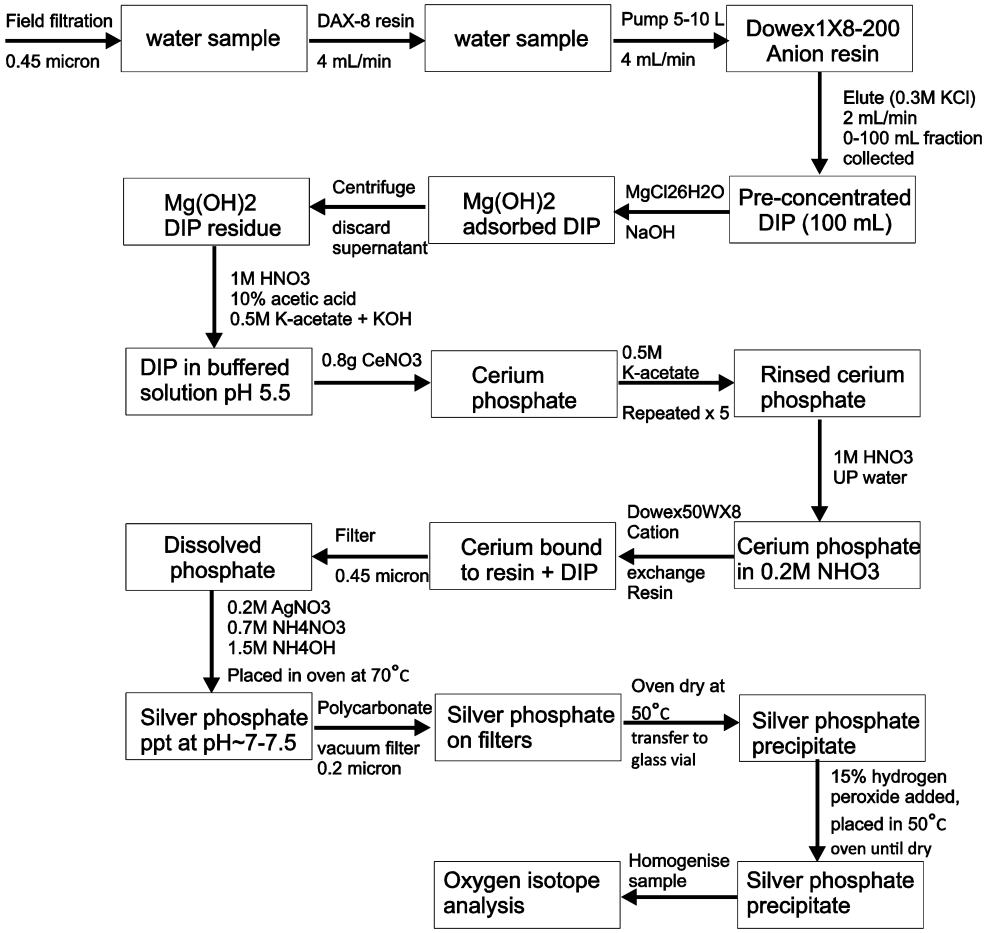

Figure 3. Schematic of the modified McLaughlin et al.[32] method used to process phosphate-dosed tap water samples.

using a modified version of the method of McLaughlin et al.[32] to yield a silver phosphate precipitate (Ag_3PO_4) for $\delta^{18}O_{PO_4}$ analysis.

$^{18}O/^{16}O$ ratios of Ag_3PO_4 were analyzed by thermal conversion to CO gas at 1400 °C in a high-temperature conversion−elemental analyzer (TC−EA) online to a Delta Plus XL mass spectrometer (ThermoFinnigan, Bremen, Germany). $\delta^{18}O$ values versus Vienna Standard Mean Ocean Water (VSMOW) were calculated by comparison to an internally calibrated laboratory standard (Alfa Aesar silver phosphate, 99%). In the absence of an international Ag_3PO_4 reference material, the $\delta^{18}O$ value of the laboratory standard was derived by comparison to the Ag_3PO_4 standard "B2207" (supplied by Elemental Microanalysis, Ltd., Okehampton, U.K.), measured in an interlaboratory comparison study to have a certified $\delta^{18}O$ value of +21.7‰ versus VSMOW. Carbon monoxide yields of Ag_3PO_4 samples were always within ±10% of those of the laboratory standard, and any organic contamination was deemed negligible on the basis that samples contained <0.2% carbon by weight (on the basis of separate elemental analysis). Precipitates were analyzed by mass spectrometry in duplicate.

RESULTS AND DISCUSSION

Orthophosphoric Acid Dosing Solutions. Water utilities in England and Wales buy their stock orthophosphoric acid solution from one of three distributors. Information obtained from the utilities indicated that they do not change distributors and have always used the same product. Therefore, the source of P used to dose drinking water supplies is assumed to remain constant, as is the isotopic composition of this source, on the basis that orthophosphoric acid is derived from a consistent source of rock P and manufacturing process by the original suppliers. Table 1 reports $\delta^{18}O_{PO_4}$ for the orthophosphoric acid used by water utilities in England and Wales. Each sample was extracted in duplicate using the scheme reported in Figure 3 and then analyzed in duplicate by mass spectrometry. The data indicate two distinct isotope compositions for the orthophosphoric acid used to dose drinking water supplies. For distributor 1, $\delta^{18}O_{PO_4}$ values ranged between +12.3 and +12.5‰, whereas for distributors 2 and 3, values varied between +19.3 and +20.0‰. Although the distributors differ, the original orthophosphoric acid for distributors 2 and 3 comes from a single supplier, explaining the similar $\delta^{18}O_{PO_4}$ composition and suggesting that these distributors can effectively been seen as supplying an isotopically consistent stock of orthophosphic acid. Therefore, average $\delta^{18}O_{PO_4}$ for the different stocks is +12.4 and +19.7‰, hereafter referred to as source A (+12.4‰) and source B (+19.7‰).

Information from the manufacturers indicates that source A acid is derived from rock P mined in China and produced via the thermal process by burning phosphorus in air. In contrast, source B acid is derived from rock P mined in Morocco and produced via the "wet" process, also commonly used in fertilizer manufacture, by adding concentrated sulfuric acid to phosphate rock. It remains unclear whether the difference in isotope composition between source A and source B acids is due to the geographical

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Table 1. $\delta^{18}O_{PO_4}$ Composition of Stock Orthophosphoric Acid Solution from Three Distributors Used by Water Utilities in England and Wales[a]

distributor	$\delta^{18}O_{PO_4}$ (‰)	± (‰)	average (‰)	source solution
1	12.3	0.22		A
	12.5	0.06	12.40	
2	19.6	0.22		B
	20.0	0.06	19.78	
3	19.3	0.47		B
	20.0	0.01	19.65	

[a]Data reported are duplicate extractions, and the standard deviation quoted is from duplicate mass spectrometry analyses.

location of the mined rock P reserves, the orthophosphoric acid production process, or indeed both. This is an area that should be subject to further investigation but was beyond the scope of the research reported here.

Drinking Water Supplies. Table 2 reports the full data set from all 40 samples collected from the drinking water distribution networks. Of these sites, 70% were dosed with orthophosphoric acid from source A and 30% were dosed with orthophosphoric acid from source B, to final concentrations that range from 375 to 1725 μg of P L^{-1}. While significantly elevated in comparison to natural surface water or groundwater, these P concentrations are typical for dosed drinking water supplies under low- and high-alkalinity conditions, respectively. Measured $\delta^{18}O_{PO_4}$ within samples of drinking water ranged from +12.5 to +20.3‰. However, if these data are subdivided on the basis of the stock orthophosphoric acid solution used for dosing, $\delta^{18}O_{PO_4}$ for samples of drinking water dosed with source A (hereafter type A) averaged +13.2‰ (range from +12.5 to +15.2‰), while

Table 2. Measured Phosphate Concentration, $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{H_2O}$ Values, and Temperature for Tap Waters Sampled[a]

sample	PO_4-P (μg L^{-1})	$\delta^{18}O_{PO_4}$ (‰)	± (‰)	acid source	$\delta^{18}O_{H_2O}$ (‰)	temperature (°C)	theoretical equilibrium $\delta^{18}O_{PO_4}$ (‰)
TAP-1	960	20.3	0.14	B	−6.72	20.1	16.1
TAP-2	750	20.2	0.08	B	−6.67	20.0	16.1
TAP-3	955	19.9	0.07	B	−6.83	20.3	15.9
TAP-4	375	13.0	0.01	A	−6.98	19.0	16.0
TAP-5	764	13.0	0.03	A	−7.02	19.1	15.9
TAP-6	745	12.8	0.10	A	−6.98	19.0	16.0
TAP-7	1320	14.4	0.21	A	−6.48	21.7	16.0
TAP-8	1290	15.2	0.07	A	−6.51	16.4	16.9
TAP-9	1245	13.9	0.00	A	−6.60	20.9	16.0
TAP-10	645	18.8	0.24	B	−5.15	17.7	18.1
TAP-11	865	19.3	0.07	B	−5.43	19.1	17.5
TAP-12	640	12.8	0.09	A	−7.90	15.9	15.6
TAP-13	590	13.3	0.21	A	−7.35	19.9	15.4
TAP-14	690	13.2	0.10	A	−7.32	19.7	15.5
TAP-15	515	12.7	0.11	A	−7.30	19.5	15.6
TAP-16	805	12.9	0.14	A	−7.13	17.3	16.1
TAP-17	860	13.9	0.01	A	−7.12	18.8	15.9
TAP-18	920	13.1	0.09	A	−7.05	12.0	17.1
TAP-19	730	12.7	0.19	A	−6.24	18.0	16.9
TAP-20	775	12.8	0.02	A	−6.28	20.0	16.5
TAP-21	765	19.6	0.05	B	−7.48	16.0	16.0
TAP-22	540	19.4	0.00	B	−7.18	15.0	16.5
TAP-23	730	19.9	0.03	B	−7.16	11.7	17.1
TAP-24	675	19.8	0.04	B	−7.18	14.2	16.6
TAP-25	675	19.9	0.03	B	−7.17	15.4	16.4
TAP-26	665	19.5	0.01	B	−7.21	15.8	16.3
TAP-27	645	19.6	0.04	B	−7.25	15.4	16.3
TAP-28	590	13.0	0.06	A	−5.52	16.9	17.8
TAP-29	775	13.4	0.01	A	−7.29	15.1	16.3
TAP-30	600	12.9	0.04	A	−7.52	13.6	16.4
TAP-31	870	13.2	0.00	A	−7.88	13.5	16.0
TAP-32	1195	13.3	0.00	A	−7.42	13.2	16.5
TAP-33	1725	13.2	0.24	A	−7.08	13.5	16.8
TAP-34	1650	12.5	0.39	A	−7.15	15.0	16.5
TAP-35	1675	12.9	0.31	A	−6.73	15.0	16.9
TAP-36	1480	13.3	0.11	A	−7.02	14.0	16.8
TAP-37	1360	13.2	0.09	A	−7.06	14.0	16.8
TAP-38		13.1	0.01	A	−7.70	6.0	17.6
TAP-39		13.4	0.01	A	−7.86	14.5	15.9
TAP-40		13.0	0.01	A	−7.27	15.3	16.3

[a]Data for $\delta^{18}O_{PO_4}$ values of the acid source are given in Table 1. Theoretical equilibrium values are calculated from ref 27.

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samples of drinking water dosed with source B (hereafter type B) averaged +19.7‰ (range from +18.8 to +20.3‰). The difference between measured $\delta^{18}O_{PO_4}$ in samples of drinking water and in the relevant acid dosing solutions is reported in Figure 4, where $\Delta_{T-S} = \delta^{18}O_{tap\ PO_4} - \delta^{18}O_{source\ PO_4}$. The average difference between measured $\delta^{18}O_{PO_4}$ in samples of drinking water and in source A was +0.82‰ (range from +0.1 to +2.8‰), while for samples dosed with source B, the average difference was +0.04‰ (range from −0.9 to +0.6‰).

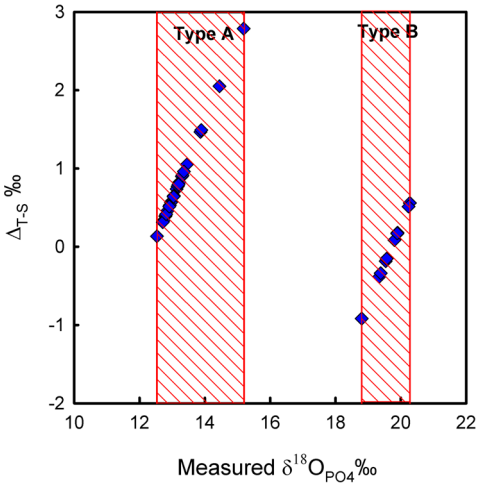

Figure 4. Cross-plot showing the difference between the measured $\delta^{18}O_{PO_4}$ value for water samples and the orthophosphoric acid dosing solution (where $\Delta_{T-S} = \delta^{18}O_{tap\ PO_4} - \delta^{18}O_{source\ PO_4}$) as a function of the two different source acids and the resulting water types.

Measured $\delta^{18}O_{H_2O}$ ranged from −7.90 to −5.15‰, typical for freshwaters in the U.K.,[33] while temperature variation (6.0−21.7 °C) largely reflected average daily air temperature on the day of sampling. The temperature and $\delta^{18}O_{H_2O}$ data resulted in a relatively narrow range of theoretical equilibrium $\delta^{18}O_{PO_4}$ values (from +15.4 to +18.1‰) based on eq 3. In comparison of measured and theoretical equilibrium $\delta^{18}O_{PO_4}$, only one sample of drinking water was within 1‰ of the theoretical equilibrium, with an average offset from equilibrium of ±2.9‰ (range from −4.2 to +4.8‰). There was no correlation between the magnitude of the departure from equilibrium and either water temperature or $\delta^{18}O_{H_2O}$ (panels a and b of Figure 5).

Samples "TAP-23−TAP-27" in Table 2 represent increasing distance along a 7 km sampling transect from the point of entry of water into a distribution network from a treatment works that dosed water with source B orthophosphoric acid. Over the full length of the 7 km transect, the PO_4 concentration decreased from 730 to 645 μg of P L^{-1}, $\delta^{18}O_{PO_4}$ decreased from +19.9 to +19.6‰, and calculated equilibrium $\delta^{18}O_{PO_4}$ decreased from +17.1 to +16.3‰ (Figure 6).

Controls on $\delta^{18}O_{PO_4}$ within Drinking Water Supplies.

Within the distribution networks sampled across England and Wales, $\delta^{18}O_{PO_4}$ is primarily determined by $\delta^{18}O_{PO_4}$ of the stock orthophosphoric acid solution dosed into supplies by water companies to reduce plumbosolvency. Our research reveals two distinct isotopic signatures for drinking water (Figure 4), reflecting the influence of two orthophosphoric acid solutions with average $\delta^{18}O_{PO_4}$ of either +12.4 or +19.7‰. There was little evidence for isotope fractionation causing $\delta^{18}O_{PO_4}$ within samples of drinking water to reach the expected theoretical equilibrium, with an average offset from equilibrium of approximately ±3‰ across the full data set. This is likely the result of light limitation within distribution networks minimizing photoautotrophic activity, alongside chlorination of drinking water supplies suppressing autotrophic or heterotrophic metabolic activity.

Our data indicate that $\delta^{18}O_{PO_4}$ has the potential to act as a source marker for P derived from drinking water supplies. In relation to the isotope composition of other sources of P within the environment (Figure 7), isotopic differentiation of P within drinking water appears to depend upon which orthophosphoric acid solution has been used to dose drinking water supplies. On the basis of our data set, isotopic differentiation following dosing with source A acid (the most commonly used in this study) could be expected, while drinking water samples dosed with source B acid would have an isotopic composition that overlaps with a number of alternative sources of P. However, currently, the U.K. is fairly unique in its exclusive use of orthophosphoric acid as a

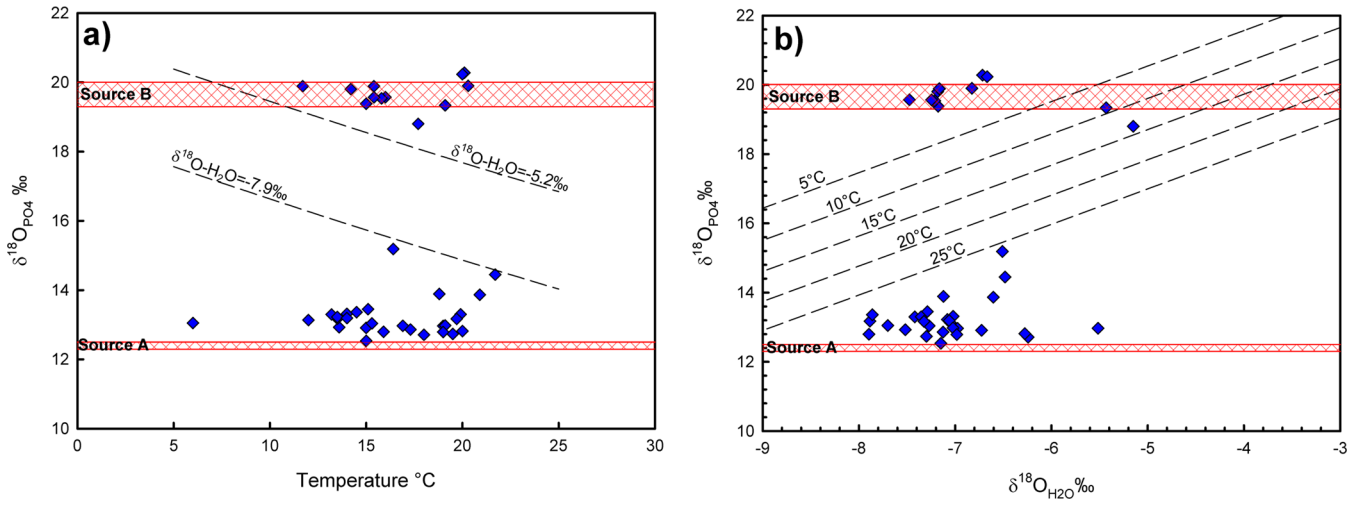

Figure 5. Comparison of (a) $\delta^{18}O_{PO_4}$ and temperature and (b) $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{H_2O}$ for collected tap waters that have been dosed with phosphate. Diagonal dashed lines represent the $\delta^{18}O_{PO_4}$ equilibrium values for ambient water (a) between the measured range of $\delta^{18}O_{H_2O}$ and (b) between 5 and 25 °C calculated using the equation given in ref 27. Horizontal hashed lines represent maximum/minimum $\delta^{18}O_{PO_4}$ values for source A and source B.

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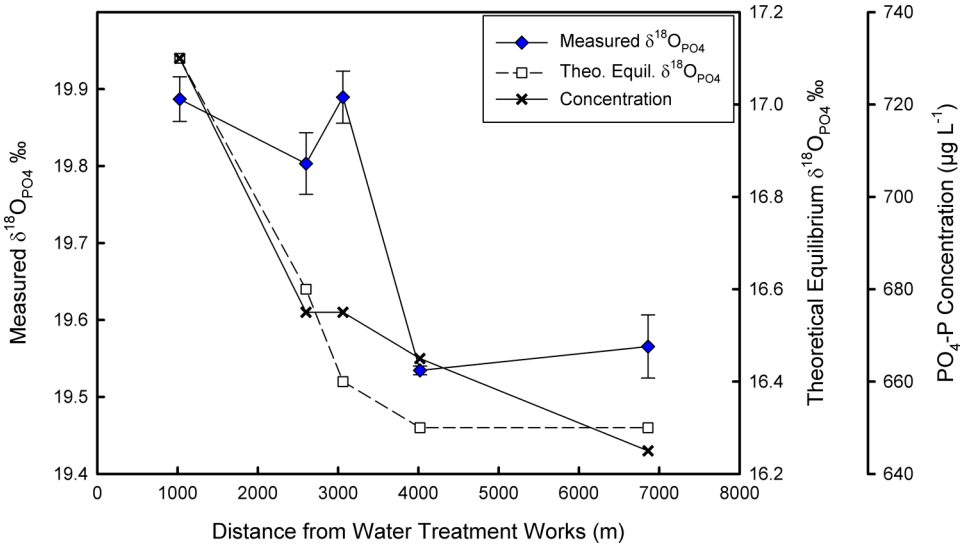

Figure 6. Comparison of measured $\delta^{18}O_{PO_4}$, theoretical equilibrium $\delta^{18}O_{PO_4}$, and PO_4-P concentration as a function of the distance along a mains tap water distribution network from a water treatment works. Note different scales for measured and theoretical $\delta^{18}O_{PO_4}$ values.

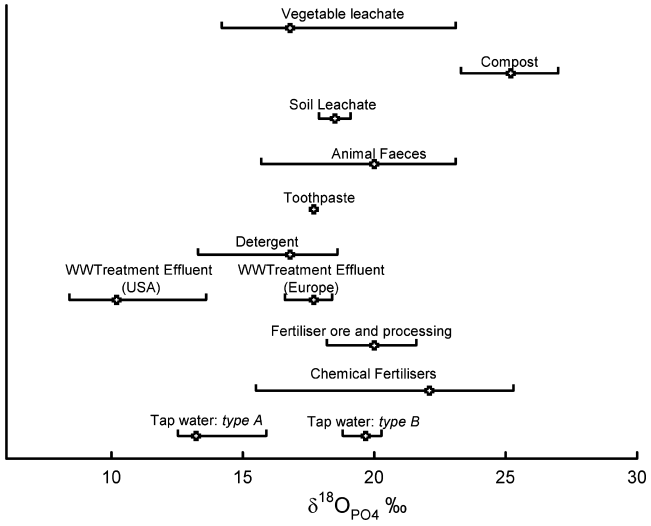

Figure 7. Range of $\delta^{18}O_{PO_4}$ in sources of P to the environment (from ref 25), including the range of measured $\delta^{18}O_{PO_4}$ values in U.K. mains tap water networks split according to type A and type B.

phosphate inhibitor. In the U.S.A., a wide range of inhibitors are used,[34] including zinc orthophosphate, zinc polyphosphate, and polyorthophosphate blends, of which the $\delta^{18}O_{PO_4}$ composition is not known. Therefore, extrapolating our results to other geographical locations would require additional source characterization work.

Initial leakage of drinking water that has been dosed with phosphate would deliver P-rich water into soils and shallow groundwater aquifers that immediately surround a distribution network. While characterization of $\delta^{18}O_{PO_4}$ in soil water and groundwater remains extremely limited, initial data indicate a range from +15.1 to +22.4‰ in groundwater samples from the U.S.A.[22,29,35] and from +10.7 to +24.5‰ in soil leachate or soil extracts that represent water-soluble or loosely adsorbed P,[36] although these soil water analyses were based on samples incubated with additional fertilizer or wastewater sources of P. These initial soil water and groundwater $\delta^{18}O_{PO_4}$ data again indicate potential for isotopic differentiation compared to drinking water, depending upon the isotopic composition of the stock orthophosphoric acid used to dose drinking water supplies. However, the global data set used to derive Figure 7 and the $\delta^{18}O_{PO_4}$ ranges for soil water and groundwater remains small. Expansion of this data set is required, both geographically and through time, to properly assess the isotopic composition and differentiation of P sources within the environment.[23] In addition, while the isotopic composition of individual sources of P may overlap on a global scale, isotopic differentiation may exist at more local scales. Therefore, the isotope composition of significant sources of P should be constrained at a scale appropriate to individual research or management questions rather than relying solely on globally averaged values for $\delta^{18}O_{PO_4}$ of individual sources of P.

For approximately 45% of the samples of drinking water, measured $\delta^{18}O_{PO_4}$ was within ±0.5‰ of $\delta^{18}O_{PO_4}$ of the relevant orthophosphoric acid solution. However, substantial differences were observed for the remaining samples, particularly type A with a maximum difference compared to the source orthophosphoric acid of +2.8‰. For 6 of the 40 drinking water samples (all dosed with source B), isotopic changes appeared to move samples further away from rather than toward theoretical equilibrium. However, for the remaining type B samples and for all type A samples, the direction of apparent isotopic change was consistent with movement toward theoretical equilibrium. Along the sampling transect within the drinking water supply network (Figure 6), $\delta^{18}O_{PO_4}$ moved toward the theoretical equilibrium by 0.3−0.4‰ and there was a positive correlation between $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{H_2O}$ (r = 0.92). Taken together, these data suggest that uptake, intracellular metabolic reactions catalyzed by the inorganic pyrophosphatase enzyme, and subsequent release of P to the extracellular environment may have occurred within the distribution network, partially imposing an equilibrium fractionation on P within drinking water.[27] Indeed, despite chlorination and other disinfection processes, the presence of bacteria in public distribution networks is well-documented.[37−39] However, on average, samples remained approximately ±3‰ offset from the actual theoretical equilibrium value, indicating that the rate and extent of extracellular−intracellular cycling of P were not sufficient to establish full equilibrium. Further, across the entire data set, there was no positive correlation between $\delta^{18}O_{PO_4}$ and $\delta^{18}O_{H_2O}$, suggesting limited intracellular metabolism of P within the distribution networks.[29] This is likely to reflect the limited

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residence time of water within the distribution networks, the suppression (although not exclusion) of metabolic activity because of chlorination of water supplies, and the high P concentration in drinking water supplies that is significantly in excess of metabolic requirements.

For all drinking water samples dosed with source A acid, measured $\delta^{18}O_{PO_4}$ was higher than that of the source orthophosphoric acid. While equilibrium fractionations associated with intracellular metabolic reactions catalyzed by the inorganic pyrophosphatase enzyme may have been responsible for this observed difference, the data are also consistent with isotope effects because of other potential mechanisms operating within the distribution network. The uptake of P by microbial cells is accompanied by a kinetic effect that affects the partitioning of phosphate ions rather than fractionation of the oxygen atoms in phosphate, favoring uptake of isotopically lighter phosphate ions and resulting in an increase in $\delta^{18}O_{PO_4}$ within the extracellular environment.[20] Further, the initial stages of the sorption of P to iron oxides have also been shown to preferentially remove isotopically lighter phosphate ions from solution and to be independent of temperature.[30] If the formation of lead phosphate or calcium phosphate precipitates within a distribution network was at disequilibrium and was associated with a similar kinetic effect, this may also have contributed to the increase in $\delta^{18}O_{PO_4}$ observed in our data when comparing the isotopic composition of samples of drinking water to the source orthophosphoric acid solution.

Phosphate release from iron/steel distribution pipes themselves also represents a potential source of P in distribution networks.[40] Corrosion of pipes can lead to dissolution of phosphate that was previously sorbed to poorly crystalline iron oxides or was added during the manufacture of the iron/steel pipes. This release of phosphate into solution could result in a kinetic isotope effect, in which isotopically lighter phosphate ions are preferentially released back into solution.[41] This may partly explain the observed decline in $\delta^{18}O_{PO_4}$ reported in Figure 6 and observations of $\delta^{18}O_{PO_4}$ in drinking water samples below that in the corresponding source acid used to dose a supply. Experimental data using 100 μg/L P showed that PO_4 released from iron pipes is of the order of 10 times less than the rate at which it is supplied.[40] Taking into account the concentrations of $PO_4 \gg 100$ μg/L P that have been used in the systems studied here, we believe that release from iron pipes is unlikely to be a significant source of phosphate and that any associated isotope effects would likely be insignificant compared to the isotope composition of the source acid. However, distribution networks are clearly complex biogeochemical reactors that accumulate a large reservoir of phosphate with the potential to subsequently exchange with phosphate in drinking water. The precise isotope effects associated with this exchange should be subject to further research.

Finally, it is possible that the shift in $\delta^{18}O_{PO_4}$ observed in samples of drinking water compared to the relevant stock orthophosphoric acid was not caused by isotope fractionation or kinetic effects but instead by mixing of at least two different sources of P that were isotopically distinct, for example, stock orthophosphoric acid and P already present in raw water sources before dosing. While this may account for small shifts in the isotopic composition of some drinking water samples compared to the source acid, we believe this is unlikely to account for large shifts, particularly up to the maximum of +2.8‰ that was observed in our data. For example, assuming a P concentration in raw water of 50 μg of P L^{-1}, a raw water dosed with source A acid and the average P concentration and average $\delta^{18}O_{PO_4}$ reported in Table 2 for type A samples, isotope mass balance suggests that $\delta^{18}O_{PO_4}$ for raw water of +28.3‰ would be required to explain the observed shift in $\delta^{18}O_{PO_4}$ because of mixing alone. Given that a raw water concentration of 50 μg of P L^{-1} is high for many raw water sources in the U.K., alongside the fact that +28.3‰ is above $\delta^{18}O_{PO_4}$ reported to date for any natural water sample across the world,[25] we believe that mixing alone is unlikely to explain our observations.

Future Development of $\delta^{18}O_{PO_4}$ in the Context of Drinking Water Supplies. The data set reported here represents, to the best of our knowledge, the first attempt to characterize $\delta^{18}O_{PO_4}$ within drinking water supplies. Given the widespread use of phosphate dosing in drinking water, coupled with evidence of isotopic differentiation between drinking water supplies and other sources of P within the environment, we believe that the application of $\delta^{18}O_{PO_4}$ analyses in this area deserves further attention. First, the global library for $\delta^{18}O_{PO_4}$ within drinking water distribution networks should be expanded to include other countries in which dosing with phosphate occurs. This research should cover different forms of phosphate inhibitor as well as phosphate stocks that potentially differ significantly in $\delta^{18}O_{PO_4}$ compared to those analyzed in our research. In addition, particularly for distribution networks that do not receive phosphate dosing, $\delta^{18}O_{PO_4}$ of raw water should also be characterized. Second, isotope fractionation or abiotic isotope effects that influence $\delta^{18}O_{PO_4}$ within the drinking water distribution network require further analysis, spanning a range of residence times with different network configurations and pipe construction materials, as well as different approaches to suppress metabolic activity within a network that are likely to have variable impacts on isotope fractionations associated with metabolism. Third, $\delta^{18}O_{PO_4}$ could be used to explore biogeochemical cycling of P derived from drinking water supplies in the wider environment. Research could focus on locations of drinking water leakage, the cycling of drinking-water-derived P within soil or groundwater, and subsequent delivery to surface waters. Alternatively, drinking water $\delta^{18}O_{PO_4}$ could be examined as one constraint on the isotopic composition of influent water to wastewater treatment works, as part of understanding the isotope effects associated with subsequent treatment processes.

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Notes

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REFERENCES

(1) Edwards, M.; Triantafyllidou, S.; Best, D. Elevated blood lead in young children due to lead-containing drinking water. *Environ. Sci. Technol.* **2009**, *43*, 1618−1623.

(2) Edwards, M. Fetal death and reduced birth rates associated with exposure to lead-contaminated drinking water. *Environ. Sci. Technol.* **2014**, *48*, 739−746.

DOI: 10.1021/acs.est.5b01137
Environ. Sci. Technol. 2015, 49, 9020−9028

(3) Langphear, B. P.; Hornung, R.; Khoury, J.; Yolton, K.; Baghurst, P.; Bellinger, D. C.; Canfield, R. L.; Dietrich, K. N.; Bornschein, R.; Greene, T.; Rothenberg, S. J.; Needleman, H. L.; Schnaas, L.; Wasserman, G.; Graziano, J.; Roberts, R. Low-level environmental lead exposure and children's intellectual function: An international pooled analysis. *Environ. Health Perspect.* **2005**, *113*, 894−899.
(4) World Health Organization (WHO). *Booklet on Childhood Lead Poisoning*; WHO: Geneva, Switzerland, 2010; ISBN: 978-924-150033-3.
(5) Gordon, C.; Hutchinson, T. *Global Perspectives on Lead, Mercury and Cadmium Cycling in the Environment*; Franklin Book Company: Elkins Park, PA, 1994.
(6) Pocock, S. J.; Shaper, A. G.; Ashby, H. T.; Dewes, H. T.; Clayton, B. E. The relationship between blood lead, blood pressure, stroke and heart attacks in middle-aged British men. *Environ. Health Perspect.* **1988**, *78*, 23−30.
(7) Comber, S.; Cassé, F.; Brown, B.; Martin, J.; Hillis, P.; Gardner, M. Phosphate treatment to reduce plumbosolvency of drinking water also reduces discharges of copper into environmental surface waters. *Water Environ. J.* **2011**, *25*, 266−270.
(8) Dodrill, D.; Edwards, M. Corrosion control on the basis of utility experience. *J.—Am. Water Works Assoc.* **1995**, *87*, 74.
(9) Edwards, M.; Jacobs, S.; Dodrill, D. Desktop guidance for mitigating Pb and Cu corrosion by-products. *J.—Am. Water Works Assoc.* **1999**, *95*, 66−77.
(10) Chartered Institution of Water and Environmental Management (CIWEM). *Policies: Lead in Drinking Water*; CIWEM: London, U.K., 2007; http://www.ciwem.org/policy/policies/lead.asp.
(11) Comber, S.; Gardner, M'; Georges, K.; Blackwood, D.; Gilmour, D. Domestic source of phosphorus to sewage treatment works. *Environ. Technol.* **2013**, *34* (10), 1349−1358.
(12) Water Services Regulation Authority (OFWAT). 2012; http://www.ofwat.gov.uk/sustainability/waterresources/leakage/rpt_com121012smcsell.pdf.
(13) Willby, N.; Phillips, G.; Kelly, M.; Mainstone, C. *A Revised Approach to Setting Nutrient Standards in UK Rivers*; Freshwater Task Team (FTT) of UK Technical Advisory Group (UKTAG): U.K., 2012; FTT017.
(14) Holman, I. P.; Whelan, M. J.; Howden, N. J. K.; Bellamy, P. H.; Wilby, N. J.; Rivas-Casado, M.; McConvey, P. Phosphorus in groundwater—An overlooked contributor to eutrophication. *Hydrol. Processes* **2008**, *22*, 5121−5127.
(15) United States Environmental Protection Agency (U.S. EPA). *Innovation and Research for Water Infrastructure for the 21st Century*; U.S. EPA: Washington, D.C., 2007; Publication 600/X-09/003.
(16) Flem, B.; Reimann, C.; Birke, M.; Banks, D.; Filzmoser, P.; Frengstag, B. Inorganic chemical quality of European tap-water: 2. Geographical distribution. *Appl. Geochem.* **2015**, DOI: 10.1016/j.apgeochem.2015.01.016.
(17) Gallet, D.; Chen, A.; Choi, J.; Nichols, K. *Water Loss Control in the Great Lakes States: A Utility Survey Report*; Center for Neighborhood Technology (CNT): Chicago, IL, 2012; http://www.cnt.org/resources/water-loss-control-in-the-great-lakes-states-a-utility-survey-report-2/.
(18) Lerner, D. N. Identifying and quantifying urban recharge: A review. *Hydrogeol. J.* **2002**, *10*, 143−152.
(19) McFeters, G. A.; Kippin, J. S.; LeChevallier, M. W. Injured coliforms in drinking water. *Appl. Environ. Microbiol.* **1986**, *51* (1), 1−5.
(20) Blake, R. E.; O'Neil, J. R.; Surkov, A. V. Biogeochemical cycling of phosphorus: Insights from oxygen isotope effects of phosphoenzymes. *Am. J. Sci.* **2005**, *305* (6−8), 596−620.
(21) Gruau, G.; Legeas, M.; Riouu, C.; Gallacier, E.; Martineau, H.; Hénin, O. The oxygen isotope composition of dissolved anthropogenic phosphates: A new tool for eutrophication research? *Water Res.* **2005**, *39*, 232−238.
(22) McLaughlin, K.; Cade-Menun, B. J.; Paytan, A. The oxygen isotope composition of phosphate in Elkhorn Slough, California: A tracer of phosphate sources. *Estuarine, Coastal Shelf Sci.* **2006**, *70*, 499−506.
(23) Elsbury, K. E.; Paytan, A.; Ostrom, N. E.; Kendall, C.; Young, M. B.; McLaughlin, K.; Rollog, M. E.; Watson, S. Using oxygen isotopes of phosphate to trace phosphorus sources and cycling in Lake Erie. *Environ. Sci. Technol.* **2009**, *43*, 3108−3114.
(24) Li, X.; Wang, Y.; Stern, J.; Gu, B. Isotopic evidence for the source and fate of phosphorus in Everglades wetland ecosystems. *Appl. Geochem.* **2011**, *26*, 688−695.
(25) Davies, C. L.; Surridge, B. W. J.; Gooddy, D. C. Phosphate oxygen isotopes within aquatic ecosystems: Global data synthesis and future research priorities. *Sci. Total Environ.* **2014**, *496*, 563−575.
(26) Blake, R. E.; O'Neil, J. R.; Garcia, G. A. Oxygen isotope systematics of biologically mediated reactions of phosphate: 1. Microbial degradation of organophosphorus compounds. *Geochem. Cosmochim. Acta.* **1997**, *61*, 4411−4422.
(27) Chang, S. J.; Blake, R. E. Precise calibration of equilibrium oxygen isotope fractionations between dissolved phosphate and water from 3 to 37 °C. *Geochem. Cosmochim. Acta.* **2015**, *150*, 314−329.
(28) Barrett, M. H.; Hiscock, K. M.; Pedley, S.; Lerner, D. N.; Tellam, J. H.; French, M. J. Marker species for identifying urban groundwater recharge sources: A review and case study in Nottingham, UK. *Water Res.* **1999**, *33* (14), 3083−3097.
(29) Blake, R. E.; Alt, J. C.; Martini, A. M. Oxygen isotope ratios of PO_4: An inorganic indicator of enzymatic activity and P metabolism and a new biomarker in the search for life. *Proc. Natl. Acad. Sci. U. S. A.* **2001**, *98*, 2148−2153.
(30) Jaisi, D. P.; Blake, R. E.; Kukkadapu, R. K. Fractionation of oxygen isotopes in phosphate during its interaction with iron oxides. *Geochim. Cosmochim. Acta* **2010**, *74*, 1309−1319.
(31) Lapworth, D. J.; Surridge, B. W. J.; Williams, P. J.; Heaton, T. H. E.; Gooddy, D. C. *Method for Analysis of Phosphate $^{18}O/^{16}O$ Ratios for Waters with High C:P Ratios*; British Geological Survey: Keyworth, Nottingham, U.K., 2014; Report OR/14/67.
(32) McLaughlin, K.; Silva, S.; Kendall, C.; Stuart-Williams, H.; Paytan, A. A precise method for the analysis of $\delta^{18}O$ of dissolved inorganic phosphate in seawater. *Limnol. Oceanogr.: Methods* **2004**, *2*, 202.
(33) Darling, W. G.; Bath, A. H.; Talbot, J. C. The O & H stable isotopic composition of fresh waters in the British Isles. 2. Surface waters and groundwater. *Hydrol. Earth Syst. Sci.* **2003**, *7* (2), 183−195.
(34) McNeill, L. S.; Edwards, M. Phosphate inhibitor use at US utilities. *J.—Am. Water Works Assoc.* **2002**, *94* (7), 57−63.
(35) Young, M. B.; McLaughlin, K.; Kendall, C.; Stringfellow, W.; Rollog, M.; Elsbury, K.; Donald, E.; Paytan, A. Characterising the oxygen isotope composition of phosphate sources to aquatic ecosystems. *Environ. Sci. Technol.* **2009**, *43*, 5190−5196.
(36) Zohar, I.; Shaviv, A.; Young, M.; Kendall, C.; Silva, S.; Paytan, A. Phosphorus dynamics in soils irrigated with reclaimed waste water or freshwater: A study using oxygen isotopic composition of phosphate. *Geoderma* **2010**, *159*, 109−121.
(37) LeChevallier, M. W.; Welch, N. J.; Smith, D. B. Full-scale studies of factors related to coliform regrowth in drinking water. *Appl. Environ. Microbiol.* **1996**, *62* (7), 2201−2211.
(38) Chowhury, S. Heterotrophic bacteria in drinking water distribution system: A review. *Environ. Monit. Assess.* **2012**, *184*, 6086−6137.
(39) El-Chakhtoura, J.; Prest, E.; Saikaly, P.; van Loosdrecht, M.; Hammes, F.; Vrouwenvelder, H. Dynamics of bacterial communities before and after distribution of full-scale drinking water network. *Water Res.* **2015**, *74*, 180−190.
(40) Morton, S. C.; Zhang, Y.; Edwards, M. A. Implications of nutrient relaease from iron metal for microbial regrowth in water distribution systems. *Water Res.* **2005**, *39*, 2883−2892.
(41) Jaisi, D. P.; Blake, R. E. Advances in using oxygen isotope ratios of phosphate to understand phosphorus cycling in the environment. *Adv. Agron.* **2014**, *125*, 1−51.

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This article was published ASAP on June 22, 2015. In the second paragraph of the Introduction, a value related to the loss of drinking water to leakage has been changed from 200 L to 50 L. The correct version of the manuscript was published on July 15, 2015.

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