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Review

Phosphate oxygen isotopes within aquatic ecosystems: Global data synthesis and future research priorities

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HIGHLIGHTS

- Oxygen isotope ratio in dissolved inorganic phosphate a novel stable isotope tracer.
- Theoretical basis for application of this tracer in aquatic ecosystems reviewed.
- Protocols for determining phosphate oxygen isotope ratio summarised.
- Synthesis of global data from marine and freshwater ecosystems reported.
- Priorities for future research in this rapidly evolving field identified.

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ABSTRACT

The oxygen isotope ratio of dissolved inorganic phosphate ($\delta^{18}O_p$) represents a novel and potentially powerful stable isotope tracer for biogeochemical research. Analysis of $\delta^{18}O_p$ may offer new insights into the relative importance of different sources of phosphorus within natural ecosystems. Due to the isotope fractionations that occur alongside the metabolism of phosphorus, $\delta^{18}O_p$ could also be used to better understand the intracellular and extracellular reaction mechanisms that control phosphorus cycling. In this review focussed on aquatic ecosystems, we examine the theoretical basis to using stable oxygen isotopes within phosphorus research. We consider the methodological challenges involved in accurately determining $\delta^{18}O_p$, given aquatic matrices in which potential sources of contaminant oxygen are ubiquitous. Finally, we synthesise the existing global data regarding $\delta^{18}O_p$ in aquatic ecosystems, concluding by identifying four key areas for future development of $\delta^{18}O_p$ research. Through this synthesis, we seek to stimulate broader interest in the use of $\delta^{18}O_p$ to address the significant research and management challenges that continue to surround the stewardship of phosphorus.

Contents

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1. Introduction

Phosphorus (P) is an essential element for all life, being integral to the structure and function of key biomolecules including DNA, RNA, adenosine triphosphate (ATP) and phospholipids. Under ambient conditions in natural ecosystems, P is tightly cycled within the biosphere and can limit or co-limit primary producer and microbial communities (Ruttenberg, 2003). However, inputs of P to terrestrial and aquatic ecosystems from a range of sources, alongside fluxes of P between these ecosystems, have increased significantly as a result of global population growth and attempts to expand and intensify food production for human society (Filippelli, 2008; Liu et al., 2008). Recent increases in bioavailable P fluxes and concentrations have been linked to undesirable ecosystem changes, including increases in primary production, shifts in community composition, increased frequency of algal blooms and hypoxia, and reduced biodiversity within aquatic ecosystems (Sondergaard and Jeppesen, 2007; Smith and Schindler, 2009).

Inefficient P use and the lack of effective recycling of P within urban and agricultural systems define a 'broken' P biogeochemical cycle, leading to concern over whether human use of P resources is sustainable (Cordell et al., 2009; Childers et al., 2011; Elser and Bennett, 2011). Whilst estimates of mineral P reserves have increased dramatically in recent years (Jasinski, 2012), these estimates remain highly uncertain and future exhaustion of reserves is likely without major advances in P mining and recycling technologies (Vaccari and Strigul, 2011; Seyhan et al., 2012). Securing access to P remains a globally significant issue, given the reliance of agricultural production on inorganic P fertilisers and the current lack of alternative sources for P beyond mineral reserves (Beardsley, 2011).

Despite the importance of P to human society, and the implications for natural ecosystems of perturbations to the P cycle, understanding of the sources and reaction mechanisms controlling biogeochemical cycling of P within ecosystems remains limited (Blake et al., 2005; Slomp, 2011). A critical reason for this is the lack of inherent tracers for analysing the sources and the metabolism of P in natural ecosystems (Karl, 2000). For example, quantifying the importance of different sources of P in aquatic ecosystems has previously relied on mass flux budgets, spatial and temporal analysis of P concentration, export coefficient models and indirect tracers such as boron as a marker for waste water treatment plant (WWTP) effluent, or microbial source tracking to identify human versus agricultural sources of faecal contamination (Dillon and Kirchner, 1975; Smith et al., 1989; Neal et al., 2000; Jarvie et al., 2002; Scott et al., 2002; Simpson et al., 2002; Holt et al., 2003; Bowes et al., 2008). However, none of these approaches provides an inherent label for P. As a result, none offers a direct means of tracing specific sources or biogeochemical processes relevant to the P cycle.

The stable oxygen isotope ratio within phosphate (hereafter, $\delta^{18}O_p$) has recently emerged as a novel and potentially powerful inherent tracer for the sources and metabolism of P in natural ecosystems (McLaughlin et al., 2004; Elsbury et al., 2009; Young et al., 2009; Goldhammer et al., 2011a; Li et al., 2011). This review focusses on the use of $\delta^{18}O_p$ in aquatic ecosystems and particularly within freshwater ecosystems, complimenting a recent review dealing with $\delta^{18}O_p$ in soil–plant systems (Tamburini et al., 2014). Our objectives are to: i) examine the theoretical basis to the use of $\delta^{18}O_p$ in P research; ii) consider the methodological challenges involved in the analysis of $\delta^{18}O_p$ in aquatic ecosystems; and iii) synthesise global data from initial application of $\delta^{18}O_p$ within aquatic ecosystems. We conclude by identifying future priorities for $\delta^{18}O_p$ research within freshwater ecosystems, aiming to stimulate further development and application of this technique.

2. Stable isotopes and P biogeochemistry: theoretical background

Phosphorus has three major isotopes, ^{31}P (stable), ^{32}P ($t_{1/2}$ = 14.36 days) and ^{33}P ($t_{1/2}$ = 25.34 days) (Smith et al., 2011). Biogeochemical cycling of P in aquatic ecosystems has previously been explored using the radioactive isotopes ^{32}P and ^{33}P (Benitez-Nelson and Buesseler, 1999; Benitez-Nelson, 2000). However, the use of radioisotopes is constrained by short isotope half-lives, perturbation of experimental systems associated with labelling, or the use of incubations which omits irregular events that occur in natural ecosystems, such as seasonal algal blooms (Levine et al., 1986; Thingstad et al., 1993; Benitez-Nelson, 2000).

Stable isotope ratios have been widely used to understand long-term trends and processes in both local and global biogeochemical cycles (Beveridge and Shackleton, 1994; Newton and Bottrell, 2007 and references therein). Stable isotope analysis requires an element to have a minimum of two naturally-occurring stable isotopes, with changes in the ratio of individual isotopes of an element in a sample, against a known ratio in a reference, providing insight into biogeochemical processes controlling the element cycle. Carbon (C), nitrogen (N) and oxygen (O) are commonly used in stable isotope research on the basis of ratios of $^{13}C/^{12}C$, $^{15}N/^{14}N$ and $^{18}O/^{16}O$ respectively. However, stable isotope analyses cannot be conducted on the P atom in P-containing compounds, because ^{31}P is the only stable P isotope.

In natural aquatic ecosystems, P is often bound strongly to O in the form of the dissolved inorganic phosphate ion, defined hereafter as P_i. Therefore, attention has recently focussed on whether the stable isotope composition of O in P_i can be used to gain insight into the biogeochemical cycling of P. Isotope fractionation involves the preferential incorporation of one isotope from a starting material over another into a reaction product. Kinetic fractionation describes a process that preferentially selects one isotope (generally the lighter isotope) due to a faster reaction rate in a unidirectional reaction. In contrast, equilibrium fractionation is a thermodynamic effect in which a system has time to exchange isotopes continuously in order to achieve the lowest energy system, wherein the heavier isotope forms the strongest bond possible (Hoefs, 2008). The P – O bonds in P_i are resistant to inorganic hydrolysis under typical temperature and pressure conditions in the Earth's surface water and groundwater ecosystems (O'Neil et al., 2003). Therefore, without biological mediation, negligible isotope exchange occurs between P_i and water within these ecosystems (Tudge, 1960; Blake et al., 2001). Whilst the initial stages of some abiotic reactions, including the sorption of P_i to solid-phase iron-oxide or the formation of apatite, may be associated with kinetic fractionation, this does not persist and through time the stable isotope composition of the solid-phase P_i approaches that of the aqueous-phase P_i (Liang and Blake, 2007; Jaisi et al., 2010, 2011). In contrast, enzyme-catalysed processes cleave P – O bonds leading to kinetic or equilibrium fractionation between the isotopes of O in P_i and O in a surrounding fluid, either within a cell or within the extracellular environment (Blake et al., 2005). The fractionation between the stable isotopes of O (^{16}O and ^{18}O) within a