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Phosphate oxygen isotopes as a tool to trace phosphorus sources and cycling in a watershed

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Introduction

Phosphorus (P), which is an essential element for all of life on the earth, often limits the productivity of aquatic ecosystems, especially of freshwater ecosystems, because of its scarcity relative to other macronutrients. In contrast, modern anthropogenic P loadings have caused serious eutrophication and deteriorated ecosystem services all over the world, stimulating social needs for studies on P cycling. Although identification of the primary P sources can provide useful information for designing the best ecosystem management practices to control eutrophication, standard methods have not yet been established because P-involved chemical processes are complicated and P has no stable isotopes as natural tracers. With traditional P transport models, for instance, we have difficulty in estimating the relative contribution of P loadings from a variety of sources. Recently, however, a new isotopic technique has been developed to measure oxygen isotope ratio of dissolved inorganic phosphate (d$^{18}O_p$), which distinguishes different phosphate sources and also reflects the degree of phosphate turnover by organisms.

Here we apply the phosphate oxygen isotope analysis to a synoptic survey to identify natural and anthropogenic P sources and evaluate its relative importance to biological P recycling in the Yasu River, the largest tributary river of the Lake Biwa Watershed.

Materials & Methods

We collected river waters in October 2012 from 36 sites across the mainstream of the Yasu River and its branches, whose catchment areas greatly vary in land use pattern. We also collected water samples from 8 sewage treatment plants, 2 agricultural waste water plants and 1 livestock farm as potential point sources of anthropogenic P. A concentrated liquid phosphate fertilizer which is commonly propagated for agricultural purposes in this region was provided by a fertilizer manufacturer and evaluated as an indicator of agricultural non-point P source. Furthermore, we collected sands from the riverbed of 5 headwaters as natural P sources. The sand samples saturated with pure water were shaken at the ambient water temperature to naturally desorb dissolved inorganic phosphates. These samples were treated with magnesium-induced coprecipitation (MagIC) method for phosphate extraction and then converted to silver phosphate after purification through the sequence of resin separation and precipitation. We determined $^{18}O_p$for each of these silver phosphate samples using a thermal conversion elemental analyzer coupled to a continuous flow isotope ratio mass spectrometer via a helium stream. The delta value was calculated as follows,

d$^{18}O_p$ = (R_{sample} /R_{VSMOW} - 1)*1000

where R_{sample} is the ratio of $^{18}O/^{16}O$ in our sample and R_{VSMOW} is the ratio of $^{18}O/^{16}O$ in the isotopic standard for oxygen, Vienna standard mean ocean water (VSMOW). The raw values were corrected by normalizing to internal working standards of silver phosphate, which have been calibrated to the VSMOW.

Results & Discussion

We detected significant differences in the d$^{18}O_p$ among a variety of potential P sources, showing this technique is applicable to trace P sources in the river ecosystems. River waters also showed a marked variation in their d$^{18}O_p$ among sites within the river. Based on an isotopic equilibrium model which assumes theoretical equilibrium of temperature-specific oxygen isotope exchange between dissolved phosphate and ambient water under rapid biological P turnover, we evaluated the relative importance of biological P recycling to external P loadings. Our data revealed that P is completely recycled by organisms in some sites while there is a surplus of P in other sites. We discuss how human density and land use pattern can affect P pollution and also what conditions increase the potential for biological P recycling in the watershed ecosystems.

キーワード: Biological recycling, Lake Biwa Watershed, Land use, Non-point source, Phosphate oxygen isotope analysis
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