## What is difference between orthophosphate and SRP in lake waters?

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## 1. Introduction

In view of phosphorus as an important macronutrient in aquatic ecosystem, accurate determination of P species, especially bioavailable P form (orthophosphate ions:  $PO_4^{3-}$ ), is a prerequisite for understanding biogeochemical cycling of the element. Current accepted method for analyzing dissolved inorganic phosphorus concentration is spectrophotometric analysis using phosphomolybdenum blue complex (soluble reactive phosphorus, SRP), and has been shown to be interfered with other chemicals, which will result in overestimation or further misunderstanding phosphorus species transformation in a lake. In this study, we selectively determined dissolved phosphate (orthophosphate) concentrations by ion chromatography in lake waters and compared with those by the most widely used method (SRP), to clarify environmental factors, which may influence the difference between orthophosphate and SRP concentrations.

## 2. Materials and Methods

Water samples were monthly collected at inlet, outlet, and the surface and just above the bottom of a pelagic site in Lakes Yanagihira and Hira, and at inlet, outlet and shore site in Lakes Hasuike and Kohoku-Nodanuma, all of these lakes are connected to Lake Biwa, the largest lake in Japan, from Jul. to Dec. 2016 and Feb. to Oct. 2017. Water temperature, pH, and DO were measured with a multi-parameter water quality meter (Horiba, U-50). The water samples were used for measuring chl.a, SS, TN, PN, NO<sub>2</sub>-N, NO<sub>3</sub>-N, NH<sub>4</sub>-N, TP, TDP, SRP and orthophosphate. SRP was measured with an auto-analyser (BRAN+LUEBBE: AACS II). Orthophosphate was measured by ion chromatography (Column: Thermo Scientific AS-23A) with electrochemical suppression in external mode. Some metal ions were also determined with an ICP-AES (SII: SPS3100). We calculated dissolved organic phosphorus (DOP) by subtracting SRP from TDP.

## 3. Results and Discussion

SRP and orthophosphate concentrations varied below detection limit (BDL)  $-4.69~\mu$ M and 0.004 -  $2.57~\mu$ M, respectively. Both SRP and orthophosphate (both called as DP) in Lakes Yanagihira and Hira decreased from inlet through the lakes and toward outlet sites at almost sampling dates excluding Feb. 2017. In Lake Hasuike, DP concentrations were always lower than those in other three lakes (<1.35 $~\mu$ M). In Lake Kohoku-Nodanuma, DP concentrations were steadily high during the study period (0.52 $~-2.92~\mu$ M), and mostly increased from inlet to outlet sites through the lake. SRP was always higher than orthophosphates in all the lakes studied. Orthophosphate/SRP ratios varied 0.11-1.04 (Ave. 0.56), suggesting that inorganic phosphate concentrations as SRP were always overestimated. In Lakes Yanagihira and Hira, these ratios spatially and temporally varied, with the greatest values in Oct. and Nov. 2016 (mean: 0.8) along water flow. In Lake Hasuike, the ratios ranged 0.2-0.93 with no significant trend along with the waterflow throughout all sampling period. In Kohoku-Nodanuma, the ratios ranged 0.29-0.86, being always higher within the lake than those at the inlet and outlet except for Jul. and Aug. 2017.

Large gaps in concentrations between orthophosphate and SRP were observed in this study. To some extent, differences between orthophosphate and SRP can be represented as dissolved acid hydrolysable phosphorus (DAHP) including both organic and inorganic origins, because of hydrolysis under the

colorimetric method. Correlation analysis showed that orthophosphate/SRP ratios were negatively correlated with the differences between them, e.g. DAHP, and chl.a concentrations, while no relationships with calculated DOP and mostly metal ions measured. These relationships were somewhat different among the lakes, e.g. no correlation with chl. a in Lakes Hasuike and Kohoku-Nodanuma. These results suggest that the DAHP may include mainly organic origins but not inorganic ones. DOP calculated in the usual manner might be conservative estimation, not indicating real values.

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