

Chromatographic determination of trace orthophosphate in water of North basin of Lake Biwa

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Introduction: Phosphorus is essential nutrient for primary production in waters and often acts as limiting factor in many lakes in Japan. Orthophosphate is thought to be the main chemical form of phosphorous directly available to organisms in water. For the determination of soluble reactive phosphorous (SRP) in water, spectrophotometry of reduced form of phosphomolybdate is widely used. However, there are some problems concerning interference of other oxoanions (arsenate (As(V)), and silicate) forming similar molybdenum blue complexes. Moreover, other phosphorus compounds such as polyphosphates and organic phosphates in natural water are hydrolyzed during the analytical process and release orthophosphate, which causes overestimation of orthophosphate in water. Although detection limit of this method can be improved at some tens of nmol/L to 1 nmol/L levels by using liquid waveguide capillary cell (LWCC) [1], the problems on interference of various compounds and CDOMs (especially in humic waters) were not solved [2].

Ion chromatographic determination has advantage to separate orthophosphate from other interfering compounds in natural waters. As detection limit of the method was not so enough in conventional analytical condition, we investigated both decrease in background conductivity and increase in injection volume to enhance detection limit below 1 nmol/L [3]. This method was applied to measure orthophosphate in waters of phosphorous limiting freshwater lake (Lake Biwa, Japan: mesotrophic). Obtained results of orthophosphate concentration was compared with those obtained by conventional molybdenum blue method (SRP).

Materials and Methods: Lake waters were sampled from April to October in 2015 at the north basin of Lake Biwa (35° 22' N, 135° 06' E, max. depth 90m). Waters were collected by X-Niskin sampler (Teflon coated, 5L) on the research ship Hassaka (The Univ. of Shiga Pref.). Samples were filtered with Acropak-200 capsule filter (0.8/0.2 micro meter pore size) onboard and stored in a cool dark container below 10 degree in Celsius. Orthophosphate concentration was measured by suppressed ion chromatography. Dionex AS-23A analytical column (250mm in length) was applied with electrochemical suppressor in electric suppression mode (external mode: supplying pure water as regenerant of suppressor membrane). Injection of high volume sample (5 mL) enhanced detection limit of orthophosphate to 1 nmol/L or less (blank peak height < 0.2 nmol/L). SRP was measured according to the method JIS K0102 using ascorbic acid as reducing reagent. Micro glass cells of 50 mm path length (approximate volume: 3 mL), or LWCC (light path length 1000 mm) was used.

Results and discussion: Determined value of orthophosphate dynamically varied from 0.8 to 466 nmol/L. Eplimnetic water usually showed very low orthophosphate concentration in the range 0.8 to 8.8 nmol/l (0 to 40 m in sampling depth). From 50 m or 60 m to the bottom, orthophosphate concentration steeply increased regardless of the sampling dates.

SRP values were only obtained in the samples having concentrations higher than 68 nmol/L because of low sensitivity by 50mm cell. LWCC was also applied for SRP determination but enough performance was not obtained because of high blank absorption probably caused by contamination of reagents by phosphate impurity. By comparing the concentrations of SRP in hypolimnetic waters with those of orthophosphate by this ion chromatographic method, we found that orthophosphate content increased with the depth and almost matched with SRP values in the depth close to the lake bottom. This trend became more prominent according to the succession of the season from spring to autumn.

References: [1] Anagnostou & Sherrell (2008) *Limnol. Oceanogr Methods* 6, 64-74. [2] Zimmer & Cutter

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Keywords: Trace orthophosphate, Chromatography, Lake Biwa