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Simultaneous determination of picomolar level of dissolved silver with other key trace metals in seawater samples using solid phase extraction and isotope dilution methods

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ABSTRACT

Simultaneous determination of dissolved silver (dAg) with other key GEOTRACES trace metals is difficult because dAg in seawater tends to form negatively charged chloride species that result in only 75% recovery efficiency with commonly used NOBIAS PA-1 chelating resins. In this study, we developed a method using solid phase extraction coupled with isotope dilution that enables full quantification (97.9 ± 2.1%) of dAg along with other major trace metals including cadmium (Cd), copper (Cu), manganese (Mn), nickel (Ni), and lead (Pb) (recovery efficiency = 100% to 102%) in seawater samples. Seawater samples were first spiked with Ag-109 and allowed to reach isotopic equilibrium before extraction using NOBIAS PA-1 chelating resin. Then, dAg isotope ratios (Ag-109/Ag-107) before and after solid phase extraction were determined and used to quantify dAg. Determination of dAg with dissolved Cd, Cu. Mn, Ni, and Pb in reference seawater material CASS-6 resulted in deviations of between 1.0% and 8.8% from the consensus values, which are well within the standard error of measurement. We then successfully determined the concentrations of dissolved Cd (0.05–0.2 nM), Cu (0.5–13 nM), Mn (10–140 nM), Ni (2–12 nM), Pb (5–110 nM), and Ag (10–40 pM) in Otsuchi Bay, Japan and its surrounding rivers. Evaluation of the behavior of dAg under a salinity gradient using estuarine samples collected from Samunsam River, Malaysia shows increasing dAg concentration with salinity ($R^2 = 0.68$), which suggests release of sedimental Ag under high ambient chloride concentrations. Our new method enables rapid and simultaneous measurements of dAg with other key GEOTRACES trace metals in a single analysis, which is expected to expedite analysis and increase availability of oceanic dAg data globally.

1. Introduction

Trace metals play important roles in the world's ocean. For example, manganese (Mn) co-limits phytoplankton growth in some parts of the ocean (Wu et al., 2019; Browning et al., 2021). Meanwhile, trace metals such as copper (Cu) and cadmium (Cd) are important nutrient at natural open ocean concentrations but toxic to marine phytoplankton at high concentrations (Brand et al., 1986; Payne and Price, 2002; Paytan et al., 2009). Therefore, understanding the distributions and biogeochemical cycling of trace metals in the ocean is crucial to elucidate the roles of these metals in the marine ecosystem.

Recently, efforts of marine chemists participating in the International GEOTRACES Program produced a plethora of trace metal data in all the major oceans (Anderson, 2020). Thousands of newly updated dataset consisting of the distribution profiles of dissolved Cd, Cu, Mn, nickel (Ni), and lead (Pb) are currently freely available online (GEOTRACES Intermediate Data Product 2021). These data enabled numerical modelling that significantly improved our understanding of the biogeochemical cycling of trace metals in the global ocean. Trace metals that are associated with biogenic processes such as Cd, Cu, and Ni exhibit nutrient-type vertical profiles where uptake by phytoplankton in the surface waters and regeneration processes in the deep waters lead to

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