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Role of colloids in the discharge of trace elements and rare earth elements from coastal groundwater to the ocean

Intae Kim [a,b], Guebuem Kim [a,*]

[a] Seoul National University, School of Earth and Environmental Sciences/RIO, Seoul National University, Seoul 151-747, Republic of Korea
[b] Division of Polar Ocean Environment, Korea Polar Research Institute (KOPRI), Incheon 406-840, Republic of Korea

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ABSTRACT

The concentrations of both the total dissolved (<0.45 μm) and colloidal (10 kDa–0.45 μm) phases of trace elements and rare earth elements (REEs) in coastal groundwater were measured to evaluate the role of colloids in transporting trace elements and REEs to the ocean through submarine groundwater discharge (SGD). Samples were collected from two different hydrogeological conditions, Hampyeong Bay in the southwestern coast of Korea and Jeju Island, Korea. The average colloidal proportions of Al, Mn, Zn, Ni, Cu, Cd, Pb, ^{210}Po, and ^{210}Pb were 35–45% of the total dissolved phase, which were relatively higher than those of Cr, Fe, Co, and REEs (10–30%), although hydrogeological conditions were variable. Most of the colloidal trace elements (including ^{210}Pb and REEs), except Mn, correlate most significantly with Fe, indicating that their presence is dependent on Fe-containing oxide minerals in the subterranean estuary (STE). On the other hand, the colloidal Mn and ^{210}Po correlated more significantly with dissolved organic carbon (DOC), indicating that dissolved organic matter (DOM) cycling associated with bacterial activity plays an important role in their presence in the colloidal phase in the STE. Our results suggest that the fluxes of trace elements through SGD are greatly dependent on the presence of Fe (for Al, Zn, Ni, Cu, Cd, Pb, and REEs) and DOM (for ^{210}Po and Mn) in coastal groundwater.

1. Introduction

Submarine groundwater discharge (SGD) occurs as undersea springs and seeps across the seafloor from coastal aquifers. The global magnitude of SGD has been estimated to be approximately 12×10^{13} m^3 year^{-1}, which is 3 to 4 times the river water flux, on the basis of inverse modeling of ^{228}Ra distributions (Kwon et al., 2014). In general, the marine fraction of SGD accounts for more than 90% of the total SGD to the oceans worldwide (Burnett et al., 2003; Kim and Swarzenski, 2010; Moore et al., 2008). The fluxes of chemical constituents (i.e., nutrients, trace elements, and carbon) associated with SGD are also known to be very significant (Moore, 2010; Kim and Swarzenski, 2010; Kim and Kim, 2011). In this respect, biogeochemical transformation in subterranean estuaries (STE), a mixing zone where fresh groundwater is mixed with seawater intruding into the land, is very important since it determines the amount of chemical species in seeping groundwater. In general, the cycling of trace elements in STE (i.e., the co-precipitation with Fe and Mn oxides) is influenced greatly by redox conditions and dissolved organic matter (DOM) (Moore, 1999; Charette and Sholkovitz, 2006; Spiteri et al., 2006). In addition, the chemical forms of trace elements, such as colloids and organo-metallic complexes, affect the presence of trace elements in STE (Sañudo-Wilhelmy et al., 2002; Santos et al., 2009; Beck et al., 2010).

In fact, the filter passing "dissolved" fraction does not represent the truly dissolved metals, but is composed of free metals, complex ions, and metals bound to a various ligands, which may further be bound to larger particles of colloidal size (1 kDa–1 μm) for both organic and inorganic particles (Guo and Santschi, 1997; Santschi et al., 2003). In general, colloids account for a significant fraction of the DOM, and a significant fraction of dissolved trace elements in natural water has also been shown to be associated with colloids (Guéguen and Dominik, 2003; Guo et al., 2000; Wells, 1998). Metals associated with colloids have an intermediate form, which may eventually aggregate into particles (Guo et al., 2000; Sañudo-Wilhelmy et al., 1996).

The metals bound to particles are quickly incorporated into sediments whereas free-metals and metals bound to dissolved ligands have a longer residence time in water and may be transported over long distances (Dai et al., 1995; Moran and Buesseler, 1993; Wen et al., 1999). A series of laboratory experiments also showed that colloids in groundwater might enhance the transport of solute (Sañudo-Wilhelmy et al., 1996). Sañudo-Wilhelmy et al. (2002) also showed that the colloids (mostly humic substances) in the coastal groundwater around Long Island Bay contribute the substantial proportions (>50%) of the total dissolved trace elements concentrations. More recently, Kim and Kim (2014a) reported that the proportions of the colloidal phase to the total dissolved phase were 28 ± 5% for ^{210}Po

* Corresponding author.
E-mail address: gkim@snu.ac.kr (G. Kim).

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and 40 ± 5% for ^{210}Pb in coastal groundwater in Jeju Island and Hampyeong Bay, Korea. Nevertheless, the role of colloids in the geochemical distributions of the trace elements in STE has been poorly documented, yet. Thus, in this study, we extended the study of Kim and Kim (2014a) for the same samples and attempted to determine the role of colloids on the presence of dissolved trace elements and REEs, which are highly reactive to particles, in the STE.

2. Study area and methods

2.1. Study area

Jeju Island is a volcanic island located in the southern sea of Korea, with an area of ~1830 km^2 (Fig. 1). The island was formed by an episode of basaltic and trachytic volcanism in the period encompassing Pliocene to Quaternary. The average soil layer thickness is 0.6 m, and it is less than 1 m over 85% of the total area of the island (Koh et al., 2007). Basaltic rocks cover more than 90% of the island's surface. Owing to the high permeability of the rocks on Jeju, there is little sustained stream flow on the island even though the rainfall is heavy (~1900 mm year^{-1}), particularly in summer (Hahn et al., 1997; Won et al., 2005). The western and eastern parts of the island show a remarkable difference in hydrogeology. The western Jeju is composed of consolidated sedimentary rocks with a number of fresh artesian springs and wells, while there is active re-circulation of seawater in the eastern Jeju due to the high-permeability basaltic layer (Kim et al., 2003; Won et al., 2005). Kim et al. (2003) showed that the seepage rate in Jeju Island ranges from 50 to 300 m year^{-1}, which is much higher than that in typical continental margins (0.03–40 m year^{-1}). The SGD-driven REE fluxes (e.g., 120 ± 60 mol Nd d^{-1}) were found to be particularly large from Jeju Island (Kim and Kim, 2011). These fluxes were comparable with the REE fluxes from major rivers, such as Mississippi River (130 mol d^{-1}). Jeong et al. (2012) also showed that SGD-driven trace element fluxes contribute considerably to the budget of trace elements in the coastal ocean. For example, SGD-driven inventories for Al, Fe and Co were about 4.6-, 29-, and 4.8-fold higher, respectively, than the background seawater (with no effect of SGD) inventories, in a semi-enclosed bay (Bangdu Bay), especially in summer (Jeong et al., 2012).

Hampyeong Bay is a mesotidal (mean tidal range: 3.5 m), semi-enclosed bay located in the southeastern Yellow Sea, and is one of the largest tidal flat ecosystems globally (Fig. 1). The tidal flat is composed of fine-grained sediments and covers 50% of the total bay area (85 km^2) (Ryu, 2003). Since most of the rainfall comes from the summer monsoon (1125 mm year^{-1}) and no major rivers flow into the bay, SGD is the major and continuous source of terrestrial material to the bay water (Waska and Kim, 2010). Because there is no major city along the coast, the inputs of anthropogenic sources are relatively small in Hampyeong Bay. SGD contributed 50–70% of the nutrient fluxes into this bay, and thus, fueled substantial primary production in both the water column and the intertidal benthic environments of the bay (Waska and Kim, 2011). Kim and Kim (2014b) reported that SGD was the major source of REEs in this bay seawater. The SGD-driven REE fluxes from this bay (220 ± 70 mol Nd d^{-1}) were found to be

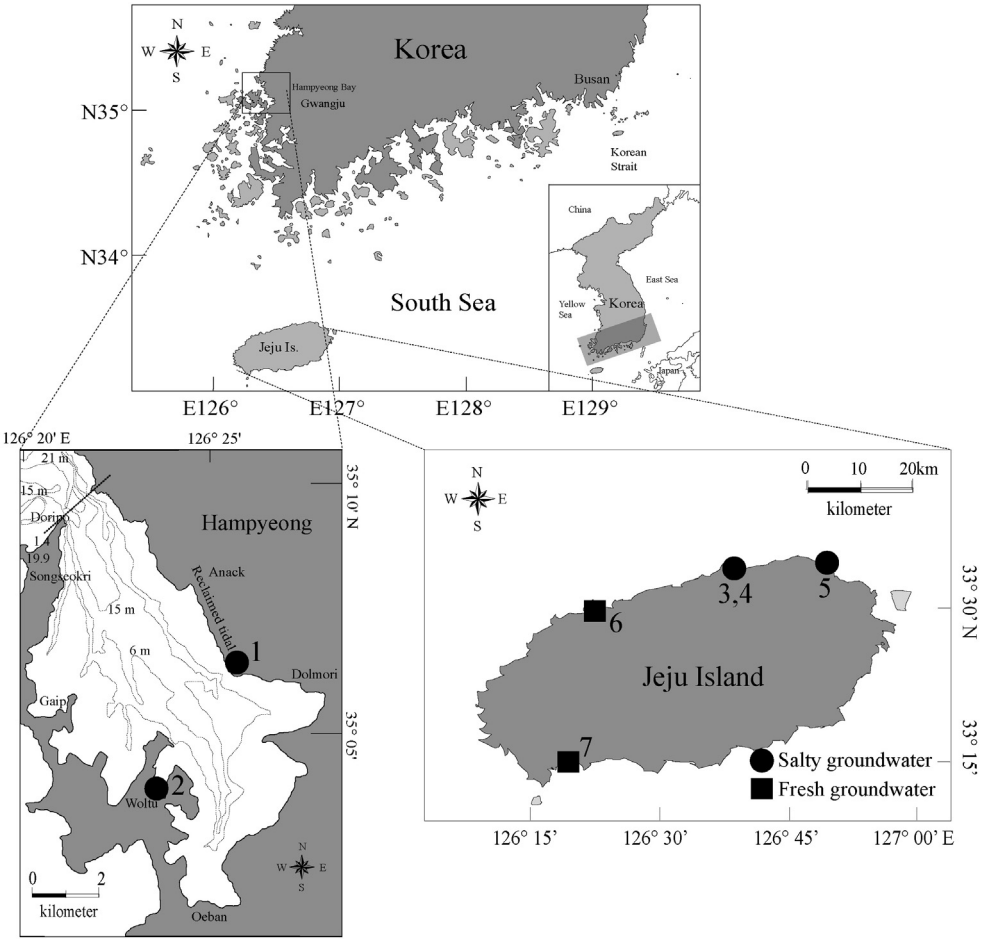

Fig. 1. Map of groundwater sampling sites at the southern coast of Korea. Black circles and black squares indicate the sites for brackish groundwater and fresh groundwater sampling, respectively.