

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

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ABSTRACT

The concentrations of both the total dissolved ($<0.45 \mu\text{m}$) and colloidal (10 kDa – $0.45 \mu\text{m}$) 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.

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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 $12 \times 10^{13} \text{ m}^3 \text{ year}^{-1}$, 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 – $1 \mu\text{m}$) 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 $28 \pm 5\%$ for ^{210}Po

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and $40 \pm 5\%$ 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 $\sim 1830 \text{ km}^2$ (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 ($\sim 1900 \text{ mm year}^{-1}$), 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 ($0.03\text{--}40 \text{ m year}^{-1}$). The SGD-driven REE fluxes (e.g., $120 \pm 60 \text{ mol Nd d}^{-1}$) 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 ($1125 \text{ mm year}^{-1}$) 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 ($220 \pm 70 \text{ mol Nd d}^{-1}$) were found to be

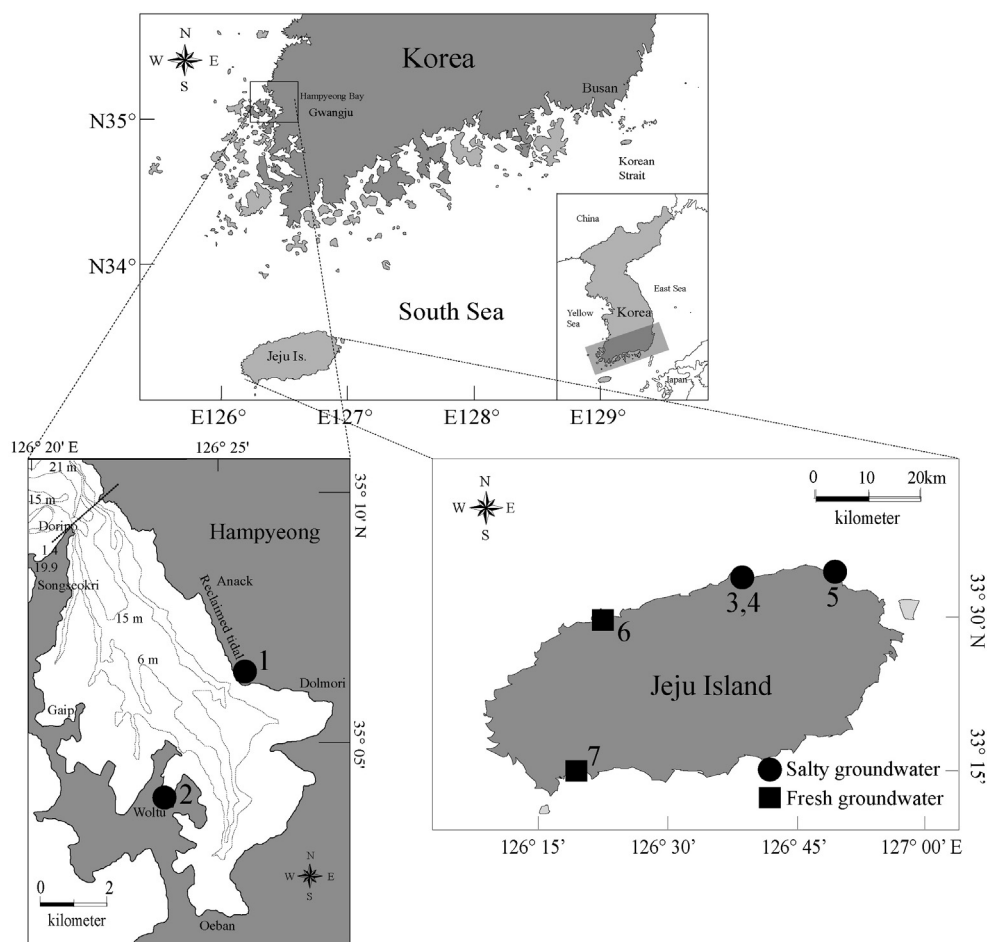


Fig. 1. Map of groundwater sampling sites at the southern coast of Korea. Black circles and black squares indicate the sites for brackish groundwater and fresh groundwater sampling, respectively.

comparable with the REE fluxes from some major rivers, such as Nile ($120 \text{ mol Nd d}^{-1}$) and Changjiang ($180 \text{ mol Nd d}^{-1}$).

2.2. Sampling and handling

The groundwater samples were collected from two stations (Sts. 1–2) in Hampyeong Bay in July 2010 (summer) and five stations (Sts. 3–7) in Jeju Island in January 2011 (midwinter). The REE samples were collected only from Jeju Island (Sts. 3–7). Groundwater samples from shallow wells in near-shore sediments were collected during low tide, which is likely to be seeping groundwater. The recharge rate of groundwater to these shallow wells is fast enough to allow the collection of freshly recharging groundwater within a few minutes. Thus, it is easy to collect trace-element clean seeping groundwater from shallow pit wells (Jeong et al., 2012; Kim and Kim, 2011, 2014b). The sampling wells were located 5–10 m seaward from the mean tide line, and the samples were obtained during low tide after discarding a few fills. Since general borehole samples may not reflect geochemical alteration in the SGD interface, we used this method to collect seeping groundwater in this study.

Water samples were filtered immediately after sampling using a cellulose membrane filter (Millipore) to separate the total dissolved fraction ($<0.45 \mu\text{m}$). The samples for the total dissolved trace elements analyses were collected in polyethylene bottles (1 l) that had been pre-cleaned using 1 M ultra-pure HNO_3 and then rinsed with DIW. All the samples were acidified with 6 M ultra-pure HNO_3 and double-bagged with clean plastic zip-lock bags. The remaining samples were left for colloidal separations and radioactive ^{210}Po and ^{210}Pb analyses (Kim and Kim, 2014a).

The colloidal (10 kDa – $0.45 \mu\text{m}$) fraction of water was separated from the total dissolved fractions using a tangential flow filtration (TFF) system (PLCGC, Pellicon) within a few hours of sampling. The TFF cartridge was cleaned rigorously using 1 M HCl (20 min), 10 l of deionized water, 0.5 M NaOH, and 10 l of deionized water before and after use (Guéguen et al., 2002; Baskaran et al., 2003). The flow rate of the tangentially circulating fluid in the membrane was about 1 l min^{-1} . Filtration was completed immediately after sampling to minimize particle sinking, decomposition, and adsorption onto the walls of the sampling bottle. The filtered samples were stored in acid-cleaned polyethylene bottles. The recovery efficiencies of the colloidal separation for ^{210}Po and ^{210}Pb ranged from 85 to 105% (avg. $101 \pm 6\%$) and 92 to 107% (avg. $98 \pm 8\%$), respectively ($n = 5$) (Kim and Kim, 2014a). This shows that there was no loss (during filtration of colloids) of trace elements during the colloidal separation procedure. Buesseler et al. (2003) pointed out the methodological concerns in colloidal trace element separations and analyses: (1) colloids can be formed artificially by changing the redox conditions in the course of sampling, and (2) colloidal metals

can be lost by rinse water during ultrafiltration. In this study, we verified the mass balance using radioisotopes, ^{210}Po and ^{210}Pb , and the change of redox condition was not expected since we took surface groundwater samples from oxic sandy aquifer.

2.3. Analyses of trace elements and REEs

The concentrations of dissolved trace elements and REEs in the water samples were measured using the Chelex 100 resin column method, recently studied and improved by Kim et al. (2010, 2015) and Jeong et al. (2012). Briefly, the aqueous samples (100–500 ml) were adjusted to a pH of 5.7–5.9 using pure CH_3COOH (99.7%, Junsei, Japan) and NH_3 (28%, Junsei, Japan). They were passed through a Chelex 100 resin (1.2 g, wet weight) column at a flow rate of less than 1.2 ml min^{-1} . The Chelex 100 resin was pre-cleaned with 2 M HNO_3 followed by de-ionized water, and then soaked in 1 M-ammonium acetate (Sigma Aldrich, USA) overnight before being packed into a column to buffer the resin at pH 6 (Kim et al., 2010). Then, 8 ml of 1 M ammonium acetate solution and 5 ml of de-ionized water were used to wash out the interfering elements. The trace elements absorbed on the resin were then eluted with 1.5–2.0 ml of 2 M HNO_3 . All procedures for the extraction of trace elements from seawater were conducted on a clean bench (class-100) installed in the laboratory.

Trace elements and REEs were measured by inductively coupled plasma mass spectrometry (ICP-MS) (Model: X-II, Thermo Scientific Inc., UK). The validity of this method is well documented in Kim et al. (2010, 2015) and Jeong et al. (2012). The procedural blank values ($n = 9$) were 240 ± 150 , 3 ± 1 , 12 ± 2 , 26 ± 4 , 5 ± 1 , 12 ± 8 , and $16 \pm 3 \text{ pM}$ for Al, Cr, Mn, Ni, Cu, Zn, and Pb, respectively. The blank concentrations were those of the pre-concentrated (about 250 fold) solutions. All blank values were lower than 5% of the average seawater concentrations, with the highest value occurring for Fe (about 5%). The chemical recoveries of Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were 103 ± 11 , 92 ± 6 , 97 ± 15 , 87 ± 17 , 93 ± 10 , 88 ± 16 , 75 ± 17 , 108 ± 31 , 118 ± 34 , and $110 \pm 9\%$ ($n = 3$), respectively.

The validity of this method for REEs was also demonstrated by Kim et al. (2010). The procedural blank values for La, Ce, Nd, Tb, Tm, and Lu were 4.5, 1.4, 1.3, 0.4, 0.7, and 0.5 pM, respectively, and the other REEs were not detectable. The detection limits of La and Gd were 4.0 and 2.7 pM, respectively, while those of the other elements were $<2 \text{ pM}$. The extraction efficiencies for REEs were $>95\%$. The relative standard deviations (RSD) of each REE measurement were lower than 2%, 3%, and 5% for the light, middle, and heavy REEs (LREE, MREE, and HREE), respectively. The BaO/Eu and CeO/Ce ratios were found to be lower than 2% and 1%, respectively. These findings indicate that polyatomic interferences of BaO or BaOH^+ for Eu were negligible (Kim et al., 2010).

Table 1

The concentrations of DOC (μM), total dissolved and colloidal phases of trace elements (nM) in groundwater.

Sample	Salinity	DOC		Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Y	Pb
1	30	71	Total	74	3.0	2.2	6.5	0.19	7.7	0.96	28	0.03	0.04	1.4
			Colloid	7.6	0.6	0.43	1.1	0.03	1.4	0.27	4.6	0.01	0.02	0.20
2	27.6	82	Total	93	0.6	3.4	3.6	0.01	14	1.1	29	0.38	0.06	2.9
			Colloid	7.1	0.04	0.52	0.4	0.02	1.0	0.17	4.4	0.05	0.02	0.14
3	20.4	38	Total	82	1.2	0.41	110	2.0	22	1.9	72	0.06	0.29	0.19
			Colloid	76	0.9	0.20	4.6	0.07	7.4	1.1	24	0.06	0.05	0.08
4	29.5	55	Total	162	1.7	0.80	170	4.8	17	5.4	103	0.28	1.10	3.7
			Colloid	118	0.3	0.28	30	0.46	13	1.9	69	0.03	0.26	1.9
5	30	64	Total	266	15	0.71	850	5.3	20	4.0	55	0.12	0.60	2.8
			Colloid	50	3.2	0.48	34	2.4	9.2	2.0	54	0.02	0.12	2.0
6	3	43	Total	8.7	0.3	4.4	140	0.14	5.1	1.5	7.0	n.d.	–	0.27
			Colloid	3.8	0.1	0.01	5.5	0.10	0.4	0.06	1.2	n.d.	–	0.06
7	1	35	Total	5.9	0.0	0.28	1.5	0.02	0.6	0.09	3.5	n.d.	–	1.9
			Colloid	4.8	n.d. ^a	0.15	8.1	0.00	1.0	0.13	1.4	n.d.	–	0.11

^a n.d. denotes the non-detectable.

Table 2

The concentrations of total dissolved and colloidal phases of REEs (pM) in groundwater.

Sample	pM	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
3	Total	59.2	29.9	3.8	15.1	2.7	1.5	2.8	0.4	2.1	0.5	1.2	1.3	0.3
	Colloid	19.4	13.6	1.7	7.0	1.4	1.1	1.6	0.2	1.2	0.2	0.6	0.5	0.2
4	Total	192	92.2	19.4	79.5	11.8	3.7	14.8	1.9	11.8	2.5	7.8	5.8	0.9
	Colloid	85.5	45.2	5.5	21.3	3.6	1.4	3.6	0.5	2.7	0.7	1.8	1.4	0.5
5	Total	191	92.1	19.2	78.6	12.3	4.0	14.3	2.0	11.5	2.5	7.7	5.5	0.9
	Colloid	44.2	46.2	4.8	18.5	3.0	6.7	4.0	0.7	2.8	0.7	2.0	3.6	0.7
6	Total	386	333	54.5	221	41.5	12.6	57.0	8.7	56.1	12.6	38.3	33.3	5.5
	Colloid	116	80.3	10.2	42.4	8.6	3.0	11.1	2.0	12.1	3.0	9.4	8.7	1.8
7	Total	348	579	75.9	325	67.8	19.7	69.0	9.8	52.6	10.6	29.3	25.4	4.3
	Colloid	84.6	130	19.6	75.7	15.7	7.7	15.6	4.5	11.7	4.8	8.0	8.4	4.1

2.4. Analysis of DOC

The detailed procedure for dissolved organic carbon (DOC) analysis followed in this study was the method in Kim and Kim (2012). Briefly, 30 ml water samples were filtered through pre-combusted Whatman GF/F filters and then acidified with 0.02 ml of 6 M HCl. The samples were stored in fire sealed pre-combusted amber glass bottles (550 °C for 5 h). A Shimadzu TOC analyzer (VCPH model) was used for the high-temperature combustion oxidation (HTCO) analysis of DOC (Dittmar et al., 2006; Kim and Kim, 2012).

3. Results and discussion

3.1. Concentrations of dissolved trace elements, REEs, and DOC

The concentrations of total dissolved trace elements ranged from 6 to 270, 0.1 to 15, 0.3 to 4.4, 4 to 850, 0.02 to 4.5, 5.1 to 22, 1.0 to 5.4, 4 to 100, 0.1 to 0.4, and 0.3 to 3.7 nM for Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb, respectively (Table 1). These trace element concentrations are comparable to the previously reported values of Jeong et al. (2012) for the same sampling site and season but different year (2009). The concentrations of Nd (one representative element of the REEs) in groundwater ranged from 15 to 325 pM (Table 2), which is an order of magnitude lower than that of a previous study of Jeju groundwater in summer (100–3000 pM) (Kim and Kim, 2011). The change in the concentrations of each REE for different samples was similar to that of Nd. Jeong et al. (2012) showed that the concentrations of trace elements (Al, Mn, Fe, Co, Ni, and Cu) in Jeju groundwater in summer were approximately 20-fold higher than in winter due to the seasonal variations in DOM levels. Therefore, the lower REE concentrations recorded in this study can be explained by the different sampling period (midwinter).

The concentrations of DOC ranged from 31 to 78 for brackish groundwater (Sts. 1–5) and from 35 to 43 for fresh groundwater (Sts. 6 and 7). The behavior of DOC was different between Jeju Island and Hampyeong Bay in the fresh and saline groundwater mixing zone (Kim et al., 2012, 2013). DOC in fresh and saline groundwater is mixed linearly in Jeju Island (Kim et al., 2013), while DOC is enhanced significantly in the mixing zone in Hampyeong Bay (Kim et al., 2012). Although we did not measure pH and dissolved oxygen (DO) for our samples, pH values in fresh and saline groundwater in the same sites were in the range of 7–10 and 8.0–8.2, respectively, in Jeju Island (Lee

and Kim, 2015) and those in saline groundwater were in the range of 7.0–7.8 in Hampyeong Bay (unpublished data). The concentrations of DO varied from 2 to 3 mg l⁻¹ for all samples in the same sampling sites (unpublished data).

3.2. Colloidal proportions of trace elements in groundwater

The average colloidal proportions of dissolved Al, Mn, Zn, Ni, Cu, Cd, and Pb were 35–45% (up to 70–80% for some samples), which is relatively higher than those of Cr, Fe, Co, and REEs (<30%) (Fig. 2a and b). The colloidal proportions of dissolved REEs (except Lu) ranged 25–40% (Fig. 2b). Abnormally high proportions of Lu could be due to an analytical artifact since the Lu concentrations approached the detection limit. These values were similar to the proportions of the colloidal phase of ²¹⁰Po (28 ± 5%) and ²¹⁰Pb (40 ± 5%), for the same samples (Kim and Kim, 2014a) and those (~40%) for Mn, Cu, Zn, and Cd in coastal groundwater from Long Island (Sañudo-Wilhelmy et al., 2002). It is notable that the average colloidal proportions of various trace elements were consistent in our sample sites, although hydrogeological conditions (pH, DO, and salinity) were variable. These results also agree well with the previously reported values for not only terrestrial groundwater but also peat soil and pore water (Dabrin et al., 2013; Huerta-Diaz et al., 2007; Pokrovsky et al., 2005) (Table 3). This implies that the results found in this study occur commonly over different geographic/hydrological settings.

3.3. Factors controlling the behavior of dissolved and/or colloidal trace elements

Most of the total dissolved trace elements (Al, Fe, Ni, Cu, Zn, Cd, Y, and Pb) correlated significantly with each other ($R^2 > 0.60$) except for Mn and ²¹⁰Po (Table 4). Interestingly, Mn and ²¹⁰Po correlated significantly ($R^2 > 0.90$) with each other and also significantly correlated with DOC ($R^2 > 0.84$) (Table 4). These trends were shown more distinctly ($R^2 > 0.92$) in the colloidal phase of trace elements (Table 4) relative to those in the total dissolved phase.

To determine the potential factors controlling the behavior of dissolved and/or colloidal trace elements, factor analysis was conducted for 15 variables (DOC, ²¹⁰Pb, ²¹⁰Po, 11 trace elements, and Nd). The calculated Kaiser-Meyer-Olkin (KMO)–Bartlett values were 0.578 ($p = .000$) and 0.632 ($p = .000$) for our total dissolved and colloidal data, respectively, using the SPSS software ver. 11.0 (Table 5). Since factor

Table 3

Colloidal proportions (%) of some trace elements in coastal groundwater in comparison with those from previous studies.

Source	Al	Mn	Fe	Co	Cu	Zn	Cd	Pb	Reference
SGD	47 ± 36	34 ± 24	10 ± 7	26 ± 24	32 ± 21	41 ± 31	35 ± 37	31 ± 26	This study
Coastal groundwater	85 ± 14	37 ± 22	–	–	55	42	42	–	Sañudo-Wilhelmy et al., 2002
Peat soil	10 ± 15	–	35	–	–	–	–	–	Pokrovsky et al., 2005
Pore water	–	8 ± 10	90 ± 10	–	60 ± 30	15 ± 28	55 ± 40	60 ± 50	Huerta-Diaz et al., 2007
Pore water	–	5 ± 3	13 ± 10	10 ± 11	44 ± 32	31 ± 27	–	–	Dabrin et al., 2013

Table 4
Correlation coefficients (R^2) between each element. The bold values indicate the significant correlation ($r \geq 0.7$) with some specific representative elements, such as DOC, ^{210}Po Al, Mn, and Fe.

	^{210}Po	^{210}Pb	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Y	Pb
<i>Total dissolved</i>													
DOC	0.875	0.569	−0.006	0.070	0.876	−0.085	−0.412	−0.713	−0.346	−0.718	0.474	−0.405	0.489
^{210}Po		0.769	0.203	0.407	0.692	0.251	−0.305	−0.431	−0.402	−0.824	0.235	−0.523	0.277
^{210}Pb			0.581	0.813	0.173	0.649	0.165	−0.308	−0.007	−0.535	−0.209	−0.159	0.264
Al				0.883	−0.457	0.949	0.867	0.435	0.735	0.303	0.041	0.607	0.553
Cr					−0.367	0.965	0.624	0.277	0.383	−0.065	−0.303	0.224	0.221
Mn						−0.504	−0.761	−0.724	−0.645	−0.755	0.501	−0.640	0.195
Fe							0.770	0.491	0.548	0.152	−0.194	0.401	0.283
Co								0.608	0.944	0.727	−0.018	0.886	0.460
Ni									0.470	0.608	−0.036	0.445	−0.111
Cu										0.829	0.188	0.985	0.617
Zn											0.093	0.895	0.236
Cd												0.213	0.736
Y													0.583
<i>Colloidal phase</i>													
DOC	0.947	0.368	−0.741	−0.136	0.929	−0.212	0.008	−0.638	−0.526	−0.414	−0.295	−0.321	−0.100
^{210}Po		0.430	−0.865	0.026	0.963	−0.294	0.094	−0.732	−0.560	−0.540	−0.166	−0.537	−0.214
^{210}Pb			−0.260	0.839	0.635	0.556	0.876	0.080	0.367	0.262	−0.700	0.051	0.575
Al				0.045	−0.752	0.633	0.141	0.940	0.789	0.845	0.110	0.858	0.584
Cr					0.226	0.629	0.943	0.352	0.623	0.410	−0.385	0.092	0.572
Mn						−0.038	0.330	−0.546	−0.333	−0.318	−0.343	−0.355	0.044
Fe							0.801	0.850	0.939	0.946	−0.417	0.821	0.990
Co								0.466	0.719	0.585	−0.436	0.317	0.773
Ni									0.949	0.964	−0.091	0.894	0.802
Cu										0.953	−0.216	0.795	0.887
Zn											−0.253	0.939	0.927
Cd												−0.248	−0.483
Y													0.835

analysis results are meaningful if the value exceeds 0.60 (Garson, 2008), our result seems to be acceptable under given variables and sample data (Henson and Roberts, 2006; Garson, 2008). We used only Nd for this factor analysis since the results with Nd were the same as the other REEs due to their identical distribution patterns. The factor analysis

Table 5
The result of (2 variables) factor analysis for all the total dissolved and colloidal trace elements, ^{210}Po , ^{210}Pb , and DOC. The bold values indicate the factors larger than 0.6.

Elements	Factor	
	1	2
<i>Total dissolved</i>		
Al	0.993	−0.058
Nd	0.970	−0.223
Fe	0.911	−0.041
Co	0.851	−0.514
Cu	0.750	−0.530
Pb	0.644	0.238
DOC	0.078	0.953
^{210}Po	0.239	0.936
Zn	0.292	−0.884
Mn	−0.383	0.845
Ni	0.357	−0.715
^{210}Pb	0.593	0.669
KMO = 0.578, Bartlett (χ^2) = 60.968 (p = .000)		
<i>Colloidal phase</i>		
Nd	0.982	−0.032
Fe	0.978	−0.178
Pb	0.970	−0.103
Co	0.902	0.254
Cu	0.888	−0.450
Zn	0.860	−0.463
Ni	0.739	−0.667
^{210}Pb	0.700	0.605
Mn	0.130	0.982
^{210}Po	−0.131	0.974
DOC	−0.092	0.910
Al	0.472	−0.856
KMO = 0.632, Bartlett (χ^2) = 93.923 (p = .000)		

(using the SPSS software version 12.0) result suggests that both the total dissolved and colloidal phases of trace elements can be divided into two groups, (1) Al, Fe, Cr, Co, Ni, Cu, Zn, Y, Pb, REE, and ^{210}Pb and (2) Mn, ^{210}Po , and DOC (Table 5). This categorization is consistent with the correlation matrix tables (Table 4). The grouping is more significant for the colloidal phase than the total dissolved phase (Tables 4 and 5). Here, we note that ^{210}Pb showed a significant correlation ($R^2 > 0.50$) with both stable Pb (group 1) and ^{210}Po (group 2). This is because ^{210}Pb has the same chemical behavior as stable Pb although ^{210}Po is produced from its parent, ^{210}Pb .

The first group (Al, Fe, Zn, Ni, Cu, Y, REEs and Pb) appears to be associated more significantly with inorganic (nano-) particles such as Fe-oxide minerals. Recently, Guo et al. (2011) reported that around 50% of Fe, OC, and Al, and around 30% of Cr, Cu, U, and V in groundwater were bound to colloids with grain sizes between 5 kDa and 0.45 μm . They found two types of colloids in groundwater samples, large-size Fe colloids and small-size organic colloids. These results imply that Fe can also be an important carrier of colloidal phases of other trace elements.

The second group (Mn and ^{210}Po) appears to be associated with DOC. The Mn concentration in natural water can be elevated by bacterial activity (Böttcher and Thamdrup, 2001; Kim et al., 2005). Previous studies also suggested that Mn is closely coupled to the diagenetic cycling of sulfur (−group elements) (Canfield, 1993; Kostka and Nealson, 1995). The good correlation of DOC with both total dissolved and colloidal Mn in our samples (Tables 4 and 5) supports the fact that the elevation of Mn might be related to (i.e., bacterial-involved) organic particles in the STE. Since we did not measure colloidal organic carbon (COC), we assume that DOC is proportional to COC in our interpretation as found in other previous studies (Guo and Santschi, 1997; Guo et al., 2000; Pan and Wang, 2004). In general, significant proportion of the total DOC (avg. >62%) is presented as the COC form in seawater (Guo and Santschi, 1997).

Kim and Kim (2012) also reported that ^{210}Po co-varied with DOC in open-ocean seawater. Po is also known to be taken up rapidly by bacteria and dispersed between the cell walls, cytoplasm, and HMW-proteins

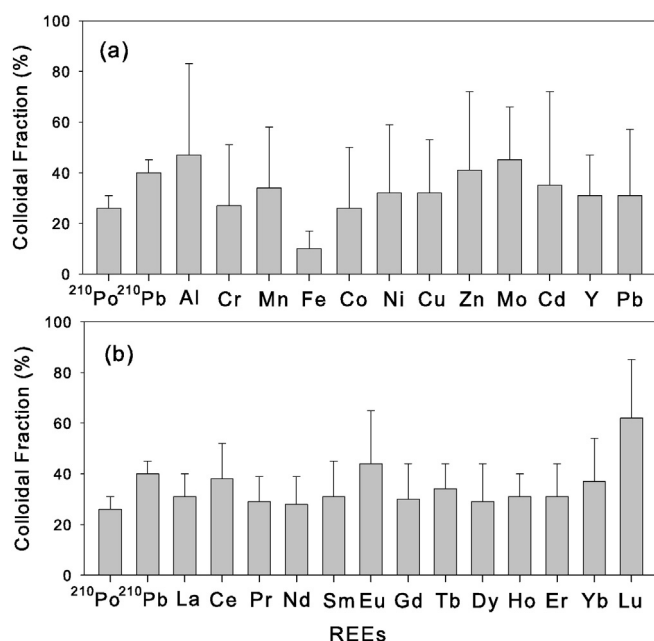


Fig. 2. The colloidal proportions of (a) trace elements, and (b) REEs in coastal groundwater compared to the ^{210}Po and ^{210}Pb in the same samples (Kim and Kim, 2014a).

in a similar manner as sulfur (Carvalho and Fowler, 1994; Cherry et al., 1994). The organic forms of Po can be related to the reactions involving organic-species with Mn. In general, Mn or Fe oxides/oxyhydroxides that settle under oxic conditions are also known to serve as important carriers of Po (Kim et al., 2005). The difference between Fe and Mn in this study seems to be associated with the fact that Mn is more diagenetically redox sensitive than Fe. Mn (IV) is generally reduced more quickly than Fe (III) under the same redox condition (Engstrom and Wright, 1984).

4. Conclusions

The average colloidal proportions of dissolved Al, Zn, Ni, Cu, Pb, and REEs were 35–45%. The average colloidal proportions of Cr, Fe, and Co were less than 30%. We found that the colloidal Al, Fe, Cr, Co, Ni, Cu, Zn, Y, Pb, and REE concentrations were controlled mainly by inorganic nanoparticles, such as Fe-oxides, while the colloidal Mn and Po were controlled more significantly by DOM, which is associated with bacterial activity. Thus, our results suggest that the fluxes of trace elements through SGD are greatly dependent on the presence of Fe (for Al, Zn, Ni, Cu, Pb, and REEs) and DOM (for ^{210}Po and Mn) in coastal groundwater. Further studies are necessary to better understand the behavior and cycling of trace elements and REEs in STEs.

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