Dissolved aluminum and silica release on the interaction of Okinawan subtropical red soil and seawater at different salinities: Experimental and field observations

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The experiment was conducted to investigate the dissolution of Al and silica when two red soils interact with seawater at different salinities. Different soil weights (3, 10 and 20 g) of bulk soil, coarse sand and silt + clay were mixed with 100 mL of natural seawater, 10, 100, and 1000 times diluted seawaters and shaken for 4 hours to obtain the extracts. Two field surveys were also carried out to observe the impact of red soil in four red soil-impacted estuaries in Okinawa Island during September (summer) and January (winter). Our results revealed that the red soils were acidic (pH ~5), dominated by SiO₂ and Al₂O₃ contents. During the interaction of red soils with the solutions, dissolved Al and silica increased with an increasing soil/solution ratio while the pH decreased to the lowest value of 3.96 in seawater extracts. The highest Al concentration ranged from 5.03 to 40.3 mgL⁻¹ in seawater extracts and differed with diluted extracts by 1 to 3 fold, 6 to 24 fold, and 12 to 45 fold for 10, 100 and 1000 times dilution, respectively. The highest silica concentrations of about 1 to ~11 mgL⁻¹ were observed in seawater extracts and in 10 times dilution, and they varied with 100 and 1000 times diluted extracts by about 1 to ~3 fold only. Salinity is more sensitive to Al release than silica but the pH significantly correlated to both logarithmic concentrations of Al ($P < 0.01$) and silica ($P < 0.001$) suggesting the exchange process and H⁺ promoted weathering of silicates, respectively. The field observation also revealed Al increase with salinity from <0.170 mgL⁻¹ in the river waters to the highest value of 0.474 mgL⁻¹ in seawater, suggesting an increasing Al solubility by exchange process. The trend of silica in the field differed from that of the laboratory with the highest concentration of 17.8 mgL⁻¹ in the river and the lowest value of 0.128 mgL⁻¹ in the seawater, which could be largely attributed to the diatom utilization in summer and dilution in seawater, particularly during winter.

Keywords: red soil, seawater, aluminum, dissolved silica, salinity

INTRODUCTION

Red soil pollution is a predominant feature in Okinawa Islands, which has contributed to the deterioration of corals, affecting both the reproduction of sea life and tourism (Onaga, 1992). The mineral composition in the Okinawan red soils are vermiculite, illite, kaolinite, vermiculite-illite mixed layer, halloysite, feldspar, goethite, quartz and muscovite (Nurcholis *et al.*, 1998; Vuai *et al.*, 2003a). The Okinawan red soil is acidic (pH 4.2 to 5.90) and exchangeable Al dominates the exchange sites on the clay mineral (Nurcholis *et al.*, 1998). The SiO₂ and Al₂O₃ are dominant compositions in the Okinawan red soil (Vuai *et al.*, 2003a) and the soil has low nutrients as well as a low percentage of base saturation (Tokashiki, 1993).

When acidic soil is mixing with solution, aluminum and H⁺ from the soil exchangeable pool can be displaced by base cations in the solution depending on ionic strength and pH. Chemically active or labile soil Al can have various forms, which are controlled primarily by the pH and mineral compositions of the system and Al may be exchanged with Ca²⁺, Mg²⁺, K⁺ or Na⁺ (Bertsch and Bloom, 1996; Hendershot *et al.*, 1996). Al in soil is released from both the inorganic Al pool and the strongly bound organic Al pool (Van der Salm *et al.*, 2000). Aluminum has drawn a great deal of research interest because soluble Al is a powerful toxicant to plants and aquatic organisms (Bertsch and Bloom, 1996; Van der Salm *et al.*, 2000; Driscoll *et al.*, 2003). In the range of 1–3 ppm, soluble aluminum is highly toxic to plants (Evangelou, 1998). Aluminum is a major problem in many acidic soils and its toxicity to organisms has been noted in several regions of the eastern United States, Canada and in the tropics, where acidic soils are found (Stevenson and Cole, 1999). The dissolution of Al needs to be understood in order to

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predict and correct environmental problems caused by aluminum (Lindsay and Walthall, 1996).

Silicate weathering depends on intrinsic factors (the physical and chemical properties of the silicates) and extrinsic features of the silicates (White and Brantley, 2003). For example, temperature, soil-solution ratio, pH, time and ionic strength are factors, which influence dissolution of silica (McKeague and Cline, 1963; Vogelsberger *et al.*, 1999). Specific solutes such as H^+ , Al^{3+} , Na^+ and organic materials have been shown to directly impact silicate weathering rates by aiding or retarding ligand exchange processes at silicate surfaces (Chen and Brantley, 1997). At acidic pH an increase of ionic strength enhances the dissolution rate due to an increase of the positive surface charge on mineral surfaces (Vogelsberger *et al.*, 1999 and Kasprzyk-Hordern, 2004). The interaction of dissolved silica with surface waters is an important issue to biological and chemical oceanographers (Marshall, 1980) partly because silica is an essential nutrient to certain marine phytoplankton such as diatoms.

The environmental problem of the red soil has attracted the attention of many researchers in Okinawa Islands, but there is little published information on the chemical aspects of the interaction between red soil and seawater solutions. Therefore the aim of this study was to investigate the dissolution of Al and silica when two Okinawan red soils interact with natural seawater at different salinities. The wide ranges of salinities in the natural seawater solutions were used to reflect river waters and estuaries whereas most of the red soil is discharged from the terrestrial areas. We conducted field surveys at two red soil distribution areas (the central and the northern parts of Okinawa Island) to observe the impact of red soil in four estuaries during September (summer) and January (winter).

MATERIALS AND METHODS

Sampling sites

The study was conducted on Okinawa Island, which is located at $26^\circ N$ and $128^\circ E$, at the southern part of Japan. The red soils were sampled from two sites at the central part of the Island: the surface soil (0–15 cm) from Gushikawa Recreation Center (GRC) and the sub-surface soil (85–100 cm) from Okinawa Royal Golf Club (ORGC) (Fig. 1). The seawater sample was collected at Cape Zampa (Fig. 1). The field surveys were conducted in two estuaries at the central part (Okukubi and Katabaru) and two estuaries at the northern part (Gesashi and Oura) of Okinawa to represent red soil affected estuaries on the Island (Fig. 1). The red soil (*Kunigami Mahji*) covers about 55% of the total land area of Okinawa Islands (2254 km^2) and distributes from the central to the northern area Okinawa Island (Fig. 1), as well as in Ishigaki and in

Fig. 1. A map showing the location of Okinawa Island, soil distribution, sampling sites of red soil and waters at the central and the northern parts of the Island.

Iriomote Islands. The Island has a subtropical climatic condition with an average annual rainfall of 2155 mm and an average annual temperature of $22.3^\circ C$. The average temperatures are $28.3^\circ C$ in summer and $16.8^\circ C$ in winter.

Sample treatments

The red soil samples were air dried at room temperature to constant weight. The samples were then slightly crushed and sieved to pass through a 2 mm mesh. In order to assess the effect of particle size, the soils were fractionated into three: bulk soil ($<2 \text{ mm}$), coarse sand ($2-0.2 \text{ mm}$) and silt + clay ($<0.063 \text{ mm}$). The pH and chemical compositions of the soil fractions were initially determined. By using milli-Q water, the seawater was diluted into 10, 100, 1000 times to reflect salinity gradient ranging from fresh water to seawater and its chemical composition was determined.

Different soil weights (3, 10 and 20 g) were mixed with 100 mL of seawater, 10, 100 and 1000 times diluted seawaters. The mixtures were shaken at a constant speed of 165 RPM at temperature of $25^\circ C$ for 4 hours on a shaking machine (an end-over-end Miyamoto shaker) to obtain the extracts. The suspensions were centrifuged for 20 minutes and then pH and electric conductivity of the supernatants were immediately measured before filtration. A portion for each sample was filtered using $0.45 \mu m$ filter membrane for analysis of the dissolved Al and silica within three days after the shaking.

Table 1. pH and chemical composition (%) of GRC and ORGC red soil fractions

Sample	pH	Na ₂ O	K ₂ O	MgO	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	MnO	Ignition loss	Total (%)
GRC												
Bulk soil	4.65	0.044	0.770	0.356	0.073	5.55	10.7	75.9	0.802	0.003	5.55	99.7
Coarse sand	4.73	0.041	0.775	0.325	0.054	5.74	10.1	77.1	0.697	0.005	4.94	99.8
Silt + clay	4.61	0.047	1.21	0.518	0.057	8.17	15.3	64.9	1.07	0.006	7.37	98.6
ORGC												
Bulk soil	5.06	0.139	3.28	1.00	0.039	5.87	17.8	64.6	0.766	0.018	5.27	98.9
Coarse sand	5.19	0.083	2.17	0.848	0.040	6.32	14.3	69.8	0.055	0.018	4.94	98.6
Silt + clay	4.97	0.134	3.15	1.06	0.038	5.64	18.9	62.0	0.735	0.017	5.52	97.2

Note; Bulk soil: <2 mm; Coarse sand: 2–0.2 mm and Silt + clay: <0.063 mm.

During the field surveys, the surface waters were collected along the salinity gradient from rivers to the seawater at the coastal areas in September 2004 (summer) and January 2005 (winter) and were analyzed for pH, EC, salinity, dissolved Al and silica. The pH and EC were measured at the field while the other parameters were analyzed in the laboratory within three days after sampling. Dissolved Al and silica were determined after filtration of the water samples using 0.45 μ m filter membrane.

Analytical methods

Soil pH in distilled water at 1:2.5 (w/v) was determined by using a pH electrode (TOA HM-21P model). Chemical compositions of soils were measured by X-ray fluorescence (XRF). Ignition loss was determined as the weight loss from 105°C to 1000°C prior to the XRF analysis. The XRF measurement was carried out using the RIGAKU X-Ray spectrometer, model RIX-3000. The pH and EC of the solution extracts were measured using the pH electrode and TOA electric conductivity cell type CGP-110P, respectively. The Jarrel-Ash AES was used to measure Na⁺ and K⁺, while the AAS was used to determine Mg²⁺ and Ca²⁺ concentrations in 0.45 μ m filtered seawater. The Cl⁻ and SO₄²⁻ concentrations in the filtered seawater were determined by using an ion chromatography, the Hitachi L-7470 model. The HCO₃⁻ was determined by titration with HCl using a BCP indicator. Total monomeric Al and silica concentrations were analyzed colorimetrically, using the Tiron method (Yotsuyanagi, 1967) and the Molybdate blue method, respectively by using a spectrophotometer, the Hitachi-U1500 model. The salinity (S) was calculated from the measured chloride concentrations ($S = 1.80655Cl$). In analyzing the dissolved Al and silica at high salinity, the standard solutions were added with known concentrations of synthetic seawater to maintain similar salt effect in the standards and the samples.

RESULTS AND DISCUSSION

Chemical characteristics of red soil samples

The soil pH and chemical composition for both soil samples are shown in Table 1. The soil samples were acidic with pH values of 4.65 and 5.06 for the bulk soils, GRC and ORGC, respectively. These pH values slightly increased in both coarse sand fractions but slightly decreased in silt + clay fractions. At soil pH values of four to five, the presence of exchangeable H⁺ and Al³⁺ is encountered (Reuss *et al.*, 1987; Thomas, 1996). The relatively low pH in surface GRC soil compared to ORGC sub-surface soils suggests much exchangeable H⁺ and Al³⁺ and may reflect the low content of base cations in GRC soil. Acidification in GRC surface soil could also be enhanced by microbial oxidation on the accumulated organic matter. The surface soil tends to be more acidic due to more intense weathering, leaching effect and decomposition of organic matter (Hendershot *et al.*, 1996).

Chemical composition indicated that SiO₂ content accounted for 75.9 and 64.6%; Al₂O₃ content accounted for 10.7 and 17.8% and oxides of base cations accounted for 1.24 and 4.51% for GRC and ORGC soils, respectively. The domination of SiO₂ and Al₂O₃ contents in the chemical composition of soils reflects the underlying silicate rocks and the inherent acidic nature of the red soils. Coarse sands showed relatively high SiO₂ content probably due to a relatively large amount of primary minerals such as quartz, muscovite and feldspars, while silt + clay revealed a relatively high Al₂O₃ content due to much clay mineral such as vermiculite, illite and kaolinite. Aluminum is largely associated with aluminosilicate minerals such as clay in well-weathered soil (Driscoll and Postek, 1996), but sands are mostly silica.

In fact, oxides of alkali and alkaline earth metals were generally low, dominated by K₂O (1–3%), followed by MgO (Table 1). Enrichment of K₂O and MgO in the mineral soil could be attributed to retention of K-feldspar and

Table 2. pH, EC (mSm^{-1}), salinity (S) and concentrations (mgL^{-1}) of the chemical species in the Zampa cape seawater sample

Specie	pH	EC	S (g Kg^{-1})	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Al	D-SiO ₂
Seawater	8.23	5140	34.3	10565	388	1300	391	18990	2706	140	0.262	0.388

Note; D: dissolved.

micaceous (White and Brantley, 2003). The low content of base cations in GRC soil compared to ORGC soil could be partly contributed by leaching of base cations due to high annual rainfall (2155 mm), which is usually acidic with pH of 4.66 to 4.73 (Vuai *et al.*, 2003b). When the atmospheric acidic deposition contacts with surface soil, it depletes labile pools of nutrient cations (i.e., Ca^{2+} , Mg^{2+}), accumulates sulfur and nitrogen, and mobilizes inorganic monomeric aluminum (Driscoll *et al.*, 2003).

Characteristics of the seawater samples from the Zampa Cape

The pH of seawater was 8.23 with its electric conductivity of 5140 mSm^{-1} (Table 2). In diluted solutions without soil, the pH values of seawater decreased to 7.29 in 10 times dilution, 6.42 in 100 times dilution and 6.30 in 1000 times dilution. Seawater sample showed salinity of 34.3 gkg^{-1} and its major composition (Table 2) was similar to the average composition of seawater reported by Boyd (1990). The aluminum concentration of 0.262 mgL^{-1} in the Zampa seawater sample was higher than the average value of 0.010 mgL^{-1} in seawater (Boyd, 1990) and that of $1.89 \times 10^{-3} \text{ mgL}^{-1}$ in the Mandovi seawater (India) Upadhyay and Gupta (1995). In case of silica concentration, seawater sample from the Zampa cape revealed 0.388 mgL^{-1} while Kamatani and Takano (1984) observed 0.280 mgL^{-1} in seawater from Tokyo Bay. The relatively higher aluminum and silica concentrations in the Zampa seawater could be largely attributed to inflow of red soil from the terrestrial environment. Aluminum is mobilized largely to surface waters from acidic soil in terrestrial areas (Driscoll and Postek, 1996) while dissolved silica is due to the dissolution of silicates, which are abundant in the Okinawan red soil.

Aluminum release on the interaction of red soil and seawater solutions

In the solution extracts, Al concentrations relatively increased with soil weight showing a consistent trend of silt + clay > bulk soil > coarse sand in both soil samples (Table 3). The increased aluminum concentration with soil weight (Fig. 2) could be due to increased exchange sites and hence much release of Al as observed by Nurcholis *et al.* (1998). The slightly high Al concentrations in the extracts of silt + clay coincided with the highest Al_2O_3 content and the lowest pH values in the fractions, the fea-

tures that could promote much release of Al concentration in the soil fractions. The small soil particles such as silt + clay also have a large surface area and much exchange reaction might occur compared to bulk soil and coarse sand fractions. Generally, Al concentrations were slightly higher in surface GRC soil than in sub-surface ORGC soil, perhaps due to its high amount of exchangeable Al in GRC soil. The exchangeable Al increased in the topsoil compared to the sub-surface soil (Liao *et al.*, 1997) because the surface horizons are more acidic, potentially richer in dissolved Al and contain more organic matter that can decompose to produce organic ligands capable of complexing Al (Hendershot *et al.*, 1996). However both GRC and ORGC soils showed similar trends of released Al concentrations and hence we plotted Figs. 2 and 4 using only GRC soil.

Table 3 shows the extracted Al concentrations with marked variations among the four seawater solutions. The overall ranges of Al concentrations were 5.03 to 40.3 mgL^{-1} in seawater extracts, 3.03 to 17.2 mgL^{-1} in 10 times dilution, 0.720 to 1.85 mgL^{-1} in 100 times dilution and 0.330 to 0.980 mgL^{-1} in 1000 times diluted seawater extracts. The average Al concentrations in the seawater extracts for both soils were higher than in diluted solutions by 1 to 3 fold, 6 to 24 fold and 12 to 45 fold for 10, 100 and 1000 times diluted extracts, respectively. The observed differences in Al concentrations among the examined seawater extracts could be largely explained by variation in total cations in their solutions, which enhanced exchange process with salinity. The salt effect results in the replacement of Al^{3+} on the soil exchange sites by cations such as Ca^{2+} , Mg^{2+} , K^+ , or Na^+ (Hendershot *et al.*, 1996). The decrease in electric conductivity and pH with increasing soil/solution ratio in the seawater and 10 times diluted seawater extracts (Table 3) suggests adsorption and/or exchange of base cations (Na^+ , K^+ , Ca^{2+} and Mg^{2+}) with the acidic cations (Al^{3+} and H^+). Kombo *et al.* (2003) also demonstrated that when red soil interacted with seawater solutions, the salt effect enhanced H^+ and aluminum release to the solutions through the exchange with Na^+ , K^+ , Ca^{2+} and Mg^{2+} and consequently decreased pH in the extracts. A very significant linear relationship between pH and logarithmic Al concentration ($P < 0.001$) observed in the seawater and 10 times diluted seawater extracts (Fig. 4) also indicated that exchange process controlled soluble aluminum (Gérard *et al.*, 2003).

Table 3. pH, EC (mS cm^{-1}), dissolved SiO_2 and Al (mg L^{-1}) with their averages (AV.) and standard deviations (SD. ($\pm$)) in seawater extract solutions ($\text{g}/100 \text{ mL}$) for two red soils at four shaking hours

Solution	Soil weight (g)	Bulk soil				Coarse sand				Silt + Clay				Al		D- SiO_2	
		pH	EC	Al	D- SiO_2	pH	EC	Al	D- SiO_2	pH	EC	Al	D- SiO_2	AV.	SD.	AV.	SD.
GRC SW	3	5.51	5150	5.66	0.940	5.54	5160	5.03	0.820	5.39	5160	7.09	0.959	5.93	1.1	0.907	0.08
	10	4.35	5130	18.2	4.05	4.38	5130	17.2	4.35	4.31	5140	20.7	4.71	18.7	1.8	4.37	0.33
	20	4.02	5110	36.6	10.3	4.09	5090	32.8	10.9	3.96	5120	40.3	10.5	36.6	3.7	10.6	0.26
$10 \times$ Dil. SW	3	4.41	620	4.61	1.48	4.50	619	4.13	1.87	4.40	619	6.44	1.97	5.06	1.2	1.77	0.26
	10	4.29	618	7.64	4.10	4.22	614	7.03	5.17	4.19	616	10.9	4.71	8.51	2.1	4.66	0.54
	20	4.12	610	12.4	9.81	4.15	612	10.8	10.4	4.05	610	17.2	10.3	13.5	3.3	10.2	0.31
$100 \times$ Dil. SW	3	4.57	78.6	0.960	1.45	4.59	71.8	0.89	1.18	4.53	80.9	1.01	1.61	0.95	0.06	1.41	0.22
	10	4.46	77.6	1.03	3.59	4.48	72.7	0.95	4.04	4.45	79.2	1.41	4.43	1.13	0.25	3.65	0.34
	20	4.42	76.3	1.39	5.63	4.44	73.1	1.21	6.00	4.41	77.1	1.85	6.45	1.48	0.33	6.03	0.41
$1000 \times$ Dil. SW	3	5.08	9.66	0.450	1.17	5.09	8.49	0.380	1.46	4.96	8.85	0.660	1.41	0.50	0.15	1.35	0.16
	10	4.80	9.75	0.550	2.79	4.80	8.86	0.580	3.10	4.76	9.41	0.870	3.07	0.67	0.18	2.99	0.17
	20	4.77	9.58	0.760	3.65	4.77	9.36	0.690	4.40	4.71	10.2	0.980	4.31	0.81	0.15	4.12	0.41
ORGC SW	3	6.74	5150	5.68	0.830	6.97	5190	5.22	0.972	6.81	5110	6.91	0.939	5.94	0.87	0.914	0.07
	10	5.22	5130	14.4	3.683	5.38	5080	12.7	4.65	5.04	5080	15.4	3.98	14.1	1.3	4.11	0.50
	20	4.29	5060	30.8	9.543	4.35	5060	27.8	11.4	4.28	5070	34.8	10.9	31.2	3.5	10.6	0.97
$10 \times$ Dil. SW	3	4.50	622	3.08	1.251	4.51	619	3.03	1.60	4.49	618	4.01	1.83	3.37	0.6	1.56	0.29
	10	4.32	616	7.57	4.032	4.35	617	5.90	5.35	4.31	613	10.4	5.27	7.94	2.2	4.88	0.74
	20	4.24	609	12.0	9.456	4.26	612	10.3	11.3	4.16	615	16.4	11.1	12.9	3.1	10.6	1.0
$100 \times$ Dil. SW	3	4.62	77.2	0.860	1.111	4.64	74.8	0.720	1.26	4.60	74.3	1.01	1.72	0.9	0.1	1.36	0.32
	10	4.54	76.2	0.980	3.159	4.57	74.0	0.880	4.11	4.52	72.1	1.37	4.37	1.1	0.3	3.88	0.64
	20	4.52	74.9	1.21	6.059	4.53	72.4	0.990	7.82	4.51	69.1	1.64	8.12	1.3	0.3	7.33	1.1
$1000 \times$ Dil. SW	3	5.15	9.02	0.570	1.28	5.16	7.98	0.330	1.31	5.10	8.91	0.640	1.41	0.5	0.2	1.33	0.07
	10	5.11	9.06	0.590	2.96	5.11	7.93	0.460	3.25	5.05	9.13	0.770	3.15	0.6	0.2	3.12	0.15
	20	5.06	8.94	0.620	3.88	5.07	8.37	0.560	5.04	4.99	9.41	0.890	4.91	0.7	0.2	4.61	0.64

Note; SW; Seawater; Dil.; Dilution; D; Dissolved

Fig. 2. Change of average (bulk, coarse and silt + clay) concentration of Al with soil weight in the seawater, 10, 100 and 1000 times diluted seawater extracts in GRC soil.

Fig. 3. Change of average (bulk, coarse and silt + clay) concentration of dissolved SiO₂ with soil weight in the seawater, 10, 100 and 1000 times diluted seawater extracts in GRC soil.

The difference in Al concentrations between 100 and 1000 times dilution (Fig. 2) seems to be small, but the effect of salinity is clearly shown as Al values in 100 times diluted extracts exceeded that of 1000 times dilution by almost 2 fold. The relatively low Al concentrations in the 100 and 1000 times dilution suggest a poor exchange process and perhaps the lowest Al concentration in 1000 times dilution could be largely due to typical aluminosilicate dissolution. The general increase of electric conductivity and slight decrease in pH in 1000 times diluted seawater extracts suggest dissolution of both the base and the acidic cations to the solution extracts. Generally, our results agreed with the finding of Liao *et al.* (1997) that the Al concentrations in extract solutions from the soil exposed to different amounts of electrolytes depended mainly on their ionic strengths.

It was revealed in all solution extracts that the pH values significantly correlated to logarithmic Al concentrations at $P < 0.01$, suggesting their interdependence (Fig. 4). The metal most commonly associated with soil acidification is Al³⁺, which hydrolyzes to produce H⁺ (Evangelou, 1998) and the H⁺ ions could participate in further release of Al from the soil surfaces (Reuss *et al.*, 1987). The Al³⁺ is the dominant species in the solution at pH value below 5 (Lindsay and Walthall, 1996), and this pH dominated in almost all our solution extracts and thus Al³⁺ could be hydrolyzed as:

It is recognized that the major Al-controlling processes in acidic soils are reversible formation of hydroxyl-Al compounds and adsorbed soluble Al on soil organic matter (Breggren and Mulder, 1995). Van der Salm *et al.* (2000) also revealed a strong decline in the amount of inorganic and organic Al pools which corresponded to an increase in the Al concentration in solution at different soil horizons. These aluminum-controlling processes depend on surface characteristics of adsorbent, the pH value of the solution, ionic strength, composition of the solution and the physicochemical properties of organic and inorganic compounds (Kasprzyk-Hordern, 2004).

Dissolved silica release on the interaction of red soil and seawater solutions

The extracted silica concentrations in all solutions are shown in Table 3. The dissolved silica significantly increases with soil weight (Fig. 3) but did not differ significantly among the bulk soil, coarse sand and silt + clay fractions in both soil samples. The increasing trend of dissolved silica with soil/solution ratio suggests that the amount of soil is an important factor in the transformation of silicates to dissolved silica as observed in other studies (White and Brantley, 2003). There was no significant difference in released silica concentrations between GRC and ORGC soil extracts and both soils showed similar patterns; thus, we plotted Figs. 3 and 5 using only GRC soil.

Table 3 shows the released silica concentration in the four examined seawater solutions, whereas salinities did

Fig. 4. Relationship between logarithmic concentrations of Al and pH in the seawater, 10, 100, and 1000 times diluted the seawater extracts of GRC soil fractions.

Fig. 5. Relationship between logarithmic concentrations of dissolved SiO_2 and pH in the seawater, 10, 100 and 1000 times diluted seawater extracts of GRC soil fractions.

not show much difference as in the case of aluminum. For example, at the lowest soil weight (3 g/100 mL) the seawater extracts showed a relatively low concentration of silica ranging from 0.820 to 0.972 mgL^{-1} in comparison to 1.25–1.97 mgL^{-1} in other diluted solutions (Table 3). Moreover, from 10 g/100 mL to the highest soil weight, both seawater extracts and 10 times diluted extracts showed similar silica concentrations ranging from 3.68 to ~11 mgL^{-1} (Fig. 3). At the two low salinities the range of dissolved silica were 3.16 to 8.12 mgL^{-1} and 2.79 to 5.04 mgL^{-1} for 100 and 1000 times diluted seawater extracts, respectively. Generally this study revealed that ionic strength or salinity tends to influence dissolved silica as reported by many authors (e.g., Cresser and Edwards 1987; Sposito, 1987; Vogelsberger *et al.*, 1999; Icenhower and Dove, 2000; Kasprzyk-Hordern, 2004), but in small magnitude (i.e., 1–3 fold in comparison to Al which revealed the difference of 1 to 45 fold). Kato and Kitano (1968) also observed that the dissolution rate of amorphous silica was relatively higher in natural and artificial seawaters than in distilled water, and ascribed it to the amount of salt. The influence of ionic strength on silicate dissolution has been attributed to the increasing dissociation of species on the surface of silicate minerals (Vogelsberger *et al.*, 1999).

Significant correlations between logarithmic concentration of dissolved silica and pH at $P < 0.001$ were obtained (Fig. 5) that suggest the influence of pH on dissolution of silica. By this analogy, the slightly higher pH values at 3 g/100 mL in seawater extracts could explain the lowest silica concentration in comparison to other diluted seawater extracts at the same solution ratio (Table 3). Generally, solubility of aluminosilicate decreases as pH increases (Lindsay and Walthall, 1996). The similar concentrations of dissolved silica in both seawater and in 10 times diluted seawater extracts at soil weight >3 g (Fig. 3) could also be explained by their similar pH values (Fig. 5). Significant relationship between logarithmic concentration of silica and pH in acidic condition also indicated surface-controlled and proton-promoted weathering of silicates (Gérard *et al.*, 2002). At below pH ~5, silicate dissolution mostly involves a proton (H^+) as the reacting specie and is known as proton promoted weathering (Gérard *et al.*, 2003). In almost all the extract solutions (except at 3 g/100 mL in seawater), the pH value was ≤ 5 suggesting involvement of H^+ in the weathering and was further reinforced by significant relation between the pH and dissolved silica. The low pH to enhance silicate dissolution is a typical characteristic of chemical weathering in acidic soil (Chesworth, 1992). Metal ox-

Table 4. pH, EC (mSm^{-1}), salinity (gkg^{-1}), Al concentrations and dissolved silica (D-SiO_2) (mgL^{-1}) in the river and estuarine waters at the central and the northern parts of Okinawa Island

Estuary	8th Sept. 2004 (summer)					1st Jan. 2005 (winter)				
	pH	EC	S	Al	D-SiO ₂	pH	EC	S	Al	D-SiO ₂
Central Part										
Okukubi										
1*	7.00	40.8	0.0994	0.168	9.97	7.43	35.0	0.0632	0.0966	9.72
2	7.38	1724	10.3	0.221	4.99	7.62	3980	23.6	0.127	2.87
3	7.77	2410	15.2	0.282	4.28	8.03	5010	29.3	0.294	0.415
4	8.05	4960	33.6	0.474	0.785	8.22	5120	33.8	0.377	0.128
Katabaru										
1*	7.06	57.4	0.0794	0.075	13.5	7.25	36.7	0.0596	0.0612	13.4
2	7.21	168	1.06	0.069	8.05	7.63	2500	15.2	0.118	7.34
3	7.95	320	2.11	0.072	6.80	8.16	3750	24.8	0.174	3.17
Northern Part										
Oura										
1*	6.96	23.5	0.0632	0.067	16.9	7.57	26.8	0.0650	0.060	15.2
2	7.95	1950	12.3	0.208	7.00	7.90	3600	23.9	0.244	3.22
3	8.08	2370	15.2	0.257	6.21	8.38	4920	33.0	0.262	0.280
Gesashi										
1*	7.05	22.0	0.0614	0.060	17.8	7.64	30.4	0.0632	0.162	15.0
2	7.63	760	4.23	0.130	8.33	8.09	1780	10.6	0.130	8.91
3	7.94	2350	14.4	0.247	5.10	8.16	3540	22.1	0.194	4.06
4	8.05	4720	33.8	0.422	2.21	8.29	5030	34.7	0.330	0.192

*The river waters.

ides and silicate minerals possess a pH dependent charge, which arises from the protonation and deprotonation of functional groups at surface of the mineral particles (Evangelou, 1998).

Field observation in red soil-impacted estuaries

The pH of river waters ranged from 6.96 to 7.64 with their corresponded EC of 22 to 57 mSm^{-1} (Table 4). Both the pH and EC increased with salinity to 8.38 and 5120 mSm^{-1} , respectively in seawater. Upadhyay and Gupta (1995) also made a similar observation that the pH of the estuarine waters increased continuously with salinity from ~7 in the fresh water to ~8 at the high salinity. Our field observation during the low tide at the central and the northern parts of Okinawa Island revealed a very remarkable reddish soil color on the inter-tidal flats. Moreover the reddish coloration was clearly observed on the filter papers after filtration of all the estuarine waters. The reddish color reflects the contamination of the red soil from terrestrial areas.

Aluminum concentration revealed the lowest values of $<0.170 \text{ mgL}^{-1}$ in all surveyed rivers, and increased with salinity to 0.474 mgL^{-1} in the seawater at Okukubi (Table 4). Lin and Coller (1998) reported up to 0.260 mgL^{-1} of Al at pH of 6.5 in Yarra river water (Australia) while Zhang *et al.* (1999) found 0.0594 mgL^{-1} in Shuangtaizihe

estuary (China). Al inputs to surface waters appear to be associated largely with particulate matter derived from soil/sediment (Driscoll and Postek, 1996). However, occurrence of acidic precipitation in Okinawa Island (Vuai *et al.*, 2003b) may also contributed Al content on surface waters because strong acid anions such as SO_4^{2-} and NO_3^- are readily transporting H^+ and Al out of the soil during acidic rainfall (Reuss *et al.*, 1987; Driscoll *et al.*, 2003).

Salinity of the river waters is ranging between 100 and 1000 times diluted seawater extracts which revealed low Al solubility (0.330 to 1.85 mgL^{-1}) in our laboratory experiment, as observed in the field river waters. The low Al concentration at low salinity in river water has been largely attributed to flocculation with organic matter or adsorption on clay colloids (Mackin and Aller, 1984; Zhang *et al.*, 1999). The rising of Al concentration with salinity in the estuarine water could be ascribed to increased exchange process as observed in the laboratory study. The riverine particulates with adsorbed Al are transported from river to estuary and act as a source of dissolved Al into the overlaying waters through the exchange process (Upadhyay and Gupta, 1995). The variation in magnitudes of Al concentration between seawater extracts in the laboratory investigation and the field observation could be due to their different soil solution ratios.

The solubility of Al in surface waters is enhanced by

Fig. 6. Change of Al concentration with salinity in the estuarine waters impacted by red soil in Okinawa Island.

ionic strength, pH and the presence of complexing ligands (Driscoll and Postek, 1996; Kasprzyk-Hordern, 2004). Dissolved Al is at a minimum near pH 6.5 and increases at higher pH values due to the formation of $\text{Al}(\text{OH})_4^-$ and Al may increase with increasing DOC, due to high amount of available complex ligands (Driscoll and Postek, 1996). The influence of salinity on soluble Al can be explained by their very significant correlation at $P < 0.001$ (Fig. 6) similar to the influence of pH on Al, which also revealed significant correlation coefficient at $P < 0.001$. Beside the salinity and pH, the complex organic ligands from the decomposed mangrove litters in the three-surveyed mangrove estuaries (Gesashi, Okukubi and Oura) could also enhance release of soluble Al.

The analysis of waters from the surveyed areas revealed the highest concentration of dissolved silica up to 17.8 mgL^{-1} in Gesashi river water and lowered to 0.128 mgL^{-1} in seawater (Table 4). The similar behavior in dissolved silica was also observed in other studies (Mackin and Aller, 1984; Kamatani and Takano, 1984). The supply of dissolved silica into the waters is attributed to silicate dissolution or desorption processes involving suspended particles (Upadhyay and Gupta, 1995). The silica concentration may also be slightly enriched to the surface seawater from deposited diatom skeletons on the marine sediments (Kamatani and Takano, 1984).

Dissolved silica in a marine system decreases with salinity due to diatom utilization (formation of siliceous skeleton), dilution by seawater and slightly by precipitation with Mg^{2+} as Mg-hydroxysilicate (i.e., sepiolite) (Kamatani and Takano, 1984; Kent and Kastner, 1985).

Fig. 7. Change of dissolved SiO_2 concentration with salinity in estuarine waters impacted by red soil in Okinawa Island.

Figure 7 shows that river waters are major sources of dissolved silica in estuaries with the highest values in Gesashi. During September (summer) not only two plotted estuarine data in Fig. 7 but in almost all estuaries, dissolved silica shows significant decrease with salinity with correlation coefficients at $P < 0.01$, that largely suggest active diatom utilization. The estuarine water in Gesashi showed maximum removal effect (Fig. 7), which suggests much biological activity in comparison to other surveyed estuaries. These results give speculation that during summer, environmental conditions such as temperature and sunlight favor biological activities in the estuaries in Okinawa as also observed by Kamatani and Takano (1984) in Tokyo bay. In contrary, during January (winter) almost all estuaries show minimum removal effect of silica concentration with salinity probably due to passive biological activity owing to low solar radiation and temperature. This is indicated by the plotted data that located about the simple mixing line with very significant correlations at $P < 0.001$ (Fig. 7), suggesting the dominance of a simple dilution process. Behaviors of dissolved silica in estuaries are results of physical, chemical and biological processes and the significance of each process varies from one estuary to another and may differ with seasons (Kamatani and Takano, 1984). The dissolved silica in the field environment differed from that of laboratory observation largely due to biological utilization in the estuaries.

CONCLUSION

The experiment was conducted to examine the chemical composition of red soils and the dissolution of Al and silica when the two Okinawan red soils interact with seawater solutions at different salinities. The field surveys were also carried out at the central and the northern parts of Okinawa Island (red soil distributed areas) to observe the actual effect of red soil in four red soil-impacted estuaries during September (summer) and January (winter).

Chemical constituents of both soils revealed that the red soils are acidic (pH ~5), with appreciable amounts of SiO₂ and Al₂O₃ that may be transformed into soluble forms when the soils are mixed with seawater solutions depending on soil content, salinity and pH. The important processes that control the release of dissolved Al and silica are the cation exchange processes and the H⁺ promoted weathering of silicates, which could be indicated by significant correlations between pH and logarithmic concentrations of both Al and silica, respectively.

Both dissolved Al and silica increased with soil to solution ratio due to an increasing amount of the aluminosilicates. In case of soil particle sizes, silt + clay fractions consistently showed a slightly high concentration of Al in all the extracts but there was no significant difference for dissolved silica among the bulk soil, coarse sand and silt + clay fractions. These could be largely explained by chemical and mineral distribution in different soil particles.

The laboratory experiment and the field study revealed increasing Al concentrations with salinity only varied in their magnitudes probably due to different soil solution ratios. The salinity enhances the cation exchange process, but the observed low concentration of Al at the low salinity in both the laboratory and the field observation could be largely due to typical aluminosilicate dissolution and a poor exchange process. The revealed Al concentrations in the estuarine waters and reddish soil color on tidal flats during the field observation indicated contamination of red soil on the surveyed estuaries at the central and the northern parts of Okinawa Island.

The laboratory experiment showed that salinity slightly influenced silica concentration that varied by about 1 to ~3 fold between seawater and other diluted seawater extracts. The field observations showed that river waters are major sources of dissolved silica but decreased with salinity, largely due to diatom utilization in summer, dilution by poor-silica seawater in winter and slightly by inorganic removal such as Mg-hydroxysilicate formation. Inconsistent results on dissolved silica between the field and the laboratory studies could be largely due to biological consumption of silica in a marine environment.

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