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Impacts of acidic red soil on pH and aluminum under the soil-seawater interacting environment

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Abstract

The study was conducted to investigate the impacts of acidic red soil, on chemical composition of seawater. Two samples of red soil from Gushikawa recreation center (GRC) and Okinawa royal golf club (ORGC) were used for the experiments. Different weights (1, 3, 5, 10, 15, 20, 30, and 40 g) of bulk soil, ground bulk soil, coarse sand and silt+clay fractions were shook with 100mL of filtered seawater to obtain seawater extracts. The pH, EC and concentrations of Na⁺, K⁺, Ca²⁺, Mg²⁺, Al³⁺, dissolved SiO₂, SO₄²⁻, Cl⁻ and HCO₃⁻ were determined in the seawater extracts. Results showed a considerable decrease in pH, which was inversely related to released Al. The pH ranged from 8.13 (seawater) to 3.85 and 4.06, while Al ranged from $\sim 0.00 \text{ mgL}^{-1}$ (seawater) to 53.94 and 52.51 mgL⁻¹ in 40 g/100mL for GRC and ORGC silt+clay fractions, respectively. The decreases of the ions especially K⁺ and SO_4^{2-} was a common feature where K⁺ decreased by 22.60 and 32.90% while SO_4^{2-} decreased by 16.90 and 14.70 % in silt+clay fractions for GRC and ORGC samples, respectively. The dissolved SiO₂ increased from 0.42 mgL⁻¹ (seawater) to 34.23 and 32.43 mgL⁻¹ in 40 g of coarse sand for GRC and ORGC samples, respectively. The HCO3 decreased from 139 mgL^{-1} in the seawater to 1.58 mgL^{-1} in 10 g/100mL of silt+clay, and was not detected from 15 g/100 mL. The increase in Al concentrations that was concomitant with decrease in the major cations suggested the adsorption and/or ion exchange reactions while the lowering of pH was likely due to the dissociation of H⁺ from the soil mineral edges, exchange and hydrolysis of Al.

Introduction

Contamination of the acidic red soil along the coastal areas of Ryukyus Islands is a serious environmental problem that has aroused attention of many researchers. The red soil erosion which has accompanied our developmental projects has polluted water ways and beautiful coral waters, impacting on the ocean ecology and has negative reflection on ways of interaction with our natural environment (Ota, 1994). A survey made on accumulation of reddish clay in estuarine areas of Okinawa revealed very remarkable reddish clay

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pollution (Nishihira, 1987). The reddish soil pollution is often triggered by land development and other artificial factors in combination with the natural conditions of Okinawa, which tend toward soil inflow (Omija, 2000).

The acidic red soil is rich in clay minerals of kaolin or gibbsite of aluminum and iron hydroxide (Omura, 1999). Vuai et al. (2001) reported major clay minerals of the red soil as vermiculite-chlorite interlayer or mixed, kaolinite, quartz, muscovite, and illite where the dominant chemical species of the soil were SiO₂ (65.67, 79%), Al₂O₃ (9.58, 20.02%) and Fe₂O₃ (3.85, 5.36%) for GRC and ORGC, respectively. The soil minerals have major influence on physical and chemical behaviors of a soil (Kimpe, 1993).

Under very acidic soil condition (pH less than 5.0) much aluminum becomes soluble, presents in the form of aluminum or aluminum hydroxyl cations that are adsorbed in preference to other cations by negative charges of soil colloids (Brady, 1990). Chemically active or labile soil Al can have a variety of forms which are controlled primarily by the pH and mineralogical compositions of the system, and can bound to negatively charged clay surfaces by electrostatic forces, and thus can be freely exchanged by other cations such as Ca^{2+} , Mg^{2+} or K⁺ (Bertsch and Bloom, 1996). The release of Al is highly influenced by the technique, type and concentration of the extracting agent and pH (Jardine and Zelazny, 1996).

Upon the red soil encountering seawater, the cation exchange reactions are favored by high ionic strength of seawater (~0.69) in which cations held by negatively charged sites on clay minerals are displaced by the dominant cations in the seawater. For example, Libes (1992) reported that most cations exchange occurs in estuaries and the coastal ocean after the clay minerals have been delivered to the ocean. Berner (1971) also argued that one of the first halmyrotic reactions to occur when clays enter seawater is cation exchange. Through the surface electrochemical properties, the soil minerals control adsorption and release behavior of chemical constituents to water or soil solution (Evengelou, 1998). Nurcholis et al. (1998) demonstrated that the clay mineral that has been prominently associated with the occurrence of exchangeable Al in Okinawa red and yellow soils contributed to the exchangeable Al.

The purpose of this study was to investigate the mechanism and to quantify the magnitude of decrease in pH accompanied with release of Al when the red soil interacts with seawater.

Materials and Methods

Two soil samples were collected from the central part of Okinawa, the surface soil from Gushikawa recreation center (GRC) and the mineral soil (1m deep) from Okinawa royal golf club (ORGC). They were then crashed and fractionated into bulk soil (≤ 2 mm), coarse sand (2 - 0.2 mm), silt+clay ($\leq 63 \ \mu$ m), and ground bulk soil fractions. The pH of the soils was measured in a suspension of the soil in distilled water at a ratio of 1: 2 by using the glass electrode pH meter. The salinity of seawater was determined by using

the salinometer. The different weights of the soils (1, 3, 5, 10, 15, 20, 30 and 40 g) were shook with 100 mL of filtered seawater from the Zampa cape for four hours and then centrifuged. The pH and EC were determined before filtration by using the pH meter and TOA electrical conductivity meter, respectively. After filtration through 0.45 μ m pore size membrane filter, the extracts were stored at 4°C for latter analysis. The concentrations of Na⁺ and K⁺ were determined using Flame emission spectrophotometer while those of Ca²⁺ and Mg²⁺ were determined using Atomic absorption spectrophotometer. The total dissolved monomeric Al³⁺ was determined by Tiron method (Yotsuyanagi et al., 1967) using a spectrophotometer. The dissolved SiO₂ was measured calorimetrically by Molybdate method (Mullin and Riley, 1955). The SO₄²⁻ was measured by using ion chromatography while the Cl⁻ was determined by titration with silver nitrate by using Na-Fluorescence as indicator (Fajans, 1956), and HCO₃⁻ was measured by titration with HCl by using BCP as indicator.

Results and Discussion

Soil pH and salinity of the seawater

Soil pH is the most informative parameter that can be used to predict other chemical properties of a given soil. Many chemical and biological reactions in a soil are controlled by the pH of the soil solution in equilibrium with soil particles surfaces, and soil pH measured in water is the closest to the pH of soil solution in the field (Hendershot et al., 1993). The decreasing trend of the soil pH in both samples was silt+clay < bulk soil < coarse sand < ground bulk soil (Table 1). The pH values of the bulk soils 4.65 and 5.04 for GRC and ORGC, respectively, indicate that both soil samples were acidic and hence the exchangeable Al ions (e.g. Al $(H_2O)^{3+}$) were dominant in preference to base forming cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺). At pH values of four to five, the presence of exchangeable trivalent Al is encountered in mineral soils and, even in certain organic soils (Thomas, 1996). The lowest pH values of 4.61 and 4.98 in 40 g/100mL of silt+clay fractions for GRC and ORGC, respectively reflect much clay minerals that were associated with Al. The relatively high pH obtained in the ground samples 4.78 and 5.39 for GRC and ORGC, respectively was also observed by Hannu et al. (2000), where the $CaCl_2$ -pH was < 3 for the normal soil and it was 5 for the ground sample. The soil pH was probably due to active acidity of H^+ and the dissolved aluminum.

Soil samples	pH _w (GRC)	pH _w (ORGC)
Bulk soil	4.65	5.04
Coarse sand	4.74	5.20
Silt+clay	4.61	4.98
Ground bulk soil	4.78	5.39

Table 1. Soil pH values measured in distilled water at ratio of 1:2

The salinity of the seawater (S) was 34.30 ‰ while the standard seawater has salinity of 35 ‰ (Grasshoff, 1983), and over 97 % of the seawater in the world has salinity between 33 to 37 ‰ (Stumm and Morgan, 1981).

The pH of the seawater extracts

Water pH is an important variable in nearly all of the reactions related to water quality (Boyd, 2000). In spite of relatively low pH of the seawater extracts, the decreasing trend was similar to the soil pH before the interaction (i.e. silt+clay < bulk soil < coursesand < ground bulk soil). The pH values ranged from 8.13 in the seawater to 3.85 and 4.06 in 40 g/100mL of silt+clay for GRC and ORGC, respectively (Fig. 1a, b).

The relatively low pH of the seawater extracts reflects the influence of the salt content. Thomas (1996) reported that the usual tendency of the salts is to lower the pH values due to both displacement of Al^{3+} from the exchange complex and increased hydrolysis of various kinds of Al species. Aluminum in the soil contributes to acidity as follows:

 $|Soil|Al^{3+} \leftrightarrow Al^{3+}$ (solution),

and then Al³⁺ in the solution is hydrolyzed as:

 $Al^{3+} + H_2O \longrightarrow Al(OH)^{2+} + H^+$,

where the released H^+ lower the pH of the solution (Brady, 1990). The lowest pH in silt+clay fractions was likely due to influence of more clay minerals in comparison to the other fractions.



Fig. 1. pH of the seawater Vs soil weights, GRC (a) and ORGC (b).

The exchangeable/dissolved Aluminum (Al)

The trend of Al in all samples exhibited significantly negative pH-Al correlations (Fig. 2a, b). The Al content was under detection level in seawater at the pH value of 8.13 but Boyd (2000) reported 0.01 mgL⁻¹ as an average concentration of Al in seawater. The

maxima Al concentrations were 53.94 and 52.51 mgL⁻¹ at the pH values of 3.85 and 4.06 in 40 g/100mL for GRC and ORGC silt+clay fractions, respectively. This is likely due to more clay minerals containing Al. The relatively low Al content in ground bulk soil was likely due to relatively high pH of the solution.

The concentrations of Al were relatively low at the pH values above $5 (< 1 \text{ mgL}^{-1})$ and increased rapidly from the pH values below 4. Driscoll and Postek (1996) reported an exponential increase in Al concentrations with decreasing solution pH. Drever (1982) claimed that in the solubility of gibbsite, at low pH, Al³⁺ is predominant species while at pH values around 5 and 6, Al(OH)₂⁺ is the predominant species and at pH values above 7, Al(OH),⁻ is the predominant species. Boyd (2000) also reported that the concentration of total aluminum in natural water with pH values above 5 is usually very low and water with pH values below 4 may have extremely high aluminum concentration. The increased trend of Al concentrations seemed to be favored by the low pH values and high salt contents of the seawater where the exchange of Al from the soil minerals and the cations from the seawater took place.

Comparing the seawater extracts and the distilled water extracts, the maxima concentrations of Al in the distilled water were 1.58 mgL⁻¹ (pH 4.88) and 0.14 mgL⁻¹ (pH 5.16) in 40 g/100mL of silt+clay soil samples of GRC and ORGC, respectively (Vuai, 2001). The distilled water extracts reflect Al dissolution while relatively high concentrations in seawater extracts were mainly as a result of ions exchange. One of the most important reactions that takes place when clay minerals are introduced in seawater involves cation exchange in which cations adsorbed by negatively charged sites on clay minerals are displaced by the cations that are much more abundant in seawater (Libes 1992). Upadhyay and Gupta (1995) also observed that the sorption/exchange processes dominated the



Fig. 2. Relation between Al and pH, GRC (a) and ORGC (b).

geochemical interactions of Al in waters of the Mandovi estuary, where Al was actively exchanged between solution and solid surfaces.

Brady (1990) reported that the exchangeable aluminum and hydrogen ions present in very acidic soils could be released into the solution by unbuffered salts such as KCl as follows:

 $\underbrace{\text{Micelle}}_{\text{Al}^{3+}}, \text{H}^{+}_{(\text{soil solid})} + 4\text{KCl}_{(\text{solution})} \longleftrightarrow \underbrace{\text{Micelle}}_{\text{Al}^{+}(\text{soil solid})} + \text{AlCl}_{3} + \text{HCl}_{(\text{solution})}.$

The quantity of Al displaced from soil by inorganic cations can be highly dependent on the used experimental conditions such as the time of extraction, pH and ionic strength of the extractant as well as the nature of displacing cations (Jarvis, 1986). Moreover, the result obtained in the red and yellow soil of Okinawa and Java revealed that the exchangeable Al increased with increasing amount of kaolin minerals, illite and vermiculite/ illite mixed layer minerals (Nurcholis et al., 1998).

Electrical conductivity (EC), and the dissolved cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) The EC

Although the decreasing trend of EC was not continuous, it was similar to that of the soil pH (i.e. silt+clay < bulk soil < course sand < ground bulk soil). The EC decreased from 5.12 S/m (seawater) to minima values of 4.95 and 4.97 S/m in 40 g/100mL of GRC and ORGC samples, respectively. This reflects the consequences of the ion exchange because the EC of solution is a function of total dissolved ions, types of ions and their potential to form charged or non-charged pairs or complexes (Evangelou, 1998).

Na⁺, K⁺, Ca²⁺ and Mg²⁺

The decreases in concentrations of the Na⁺, Ca²⁺ and Mg²⁺ and particularly K⁺ were a common feature as soil to solution ratio increased especially in silt+clay. This was presumably due to adsorption and/or cation exchange between seawater and soil minerals. Dissociation of -Al-OH group in soil minerals produces -Al-O-, which attracts cations and forms surface-metal complexes such as -Al-O. nH₂OM, where M donates any metal cation (Evangelou, 1998). Thorjorn et al. (1999) observed much decrease in potassium from soil solution while magnesium and calcium did not follow the pattern. The great decreases in silt+clay reflected much clay mineral for adsorption and/or exchange reactions. Xu-Chen and Lee (1993) also observed that the smallest particles in the sediments showed the highest adsorption capacity. Francesco et al. (1999) attributed the high ion exchange capacity of the clays to their layer-lattice structure and large surface areas.

The sodium concentration in seawater was $10,565 \text{ mgL}^{-1}$ relatively similar to $10,500 \text{ mgL}^{-1}$ as reported by Boyd (2000). Except in silt+clay in both samples and bulk soil for GRC, the concentrations of sodium decreased with increasing soil weight. The minimum concentration was $10,162 \text{ mgL}^{-1}$ (-3.81%) in 40 g/100mL of ORGC bulk soil while the maximum was 10,688 (+1.16%) in 15 g/100mL for silt+clay fraction of GRC sample (Table

	GRC				ORGC			
	Na ⁺	K⁺	Ca ²⁺	Mg ²⁺	Na^+	K ⁺	Ca ²⁺	Mg ²⁺
Seawater	10565	368	391	1334	10565	368	391	1334
Bulk soil								
1'	10312	355	376	1303	10330	348	375	1307
3	10576	351	383	1293	10338	344	383	1303
5	10592	334	382	1289	10313	337	382	1295
10	10661	326	380	1285	10249	330	379	1293
15	10630	310	373	1284	10224	327	379	1 293
20	10600	301	373	1284	10245	314	379	1293
30	10589	288	373	1284	10255	302	378	1287
40	10421	276	373	1275	10162	291	375	1279
Coarse sand								
1	10437	360	377	1322	10419	348	377	1325
3	10334	353	383	1328	10335	349	376	1331
5	10420	336	380	1328	10505	344	377	1331
10	10386	331	378	1 328	10471	336	383	1331
15	10334	320	378	1328	10334	333	382	1331
20	10217	307	377	1328	10250	329	377	1331
30	10193	304	377	1328	10301	318	378	1331
40	10173	294	376	1322	10284	306	377	1331
Silt+clay								
1	10398	336	377	1317	10482	339	380	1309
3	10599	320	382	1327	10472	330	378	1310
5	10611	318	375	1325	10539	328	377	1312
10	10628	300	372	1325	10570	320	377	1297
15	10688	285	369	1325	10683	315	375	1307
20	10405	276	375	1317	10657	305	373	1310
30	10340	260	373	1267	10586	299	371	1282
40	10212	247	365	1263	10547	285	366	1273
Ground b	ulk soil							
1	10509	350	377	1312	10549	354	375	1325
3	10548	344	381	1318	10529	351	380	1331
5	10548	338	380	1315	10509	347	372	1303
10	10391	325	376	1321	10470	343	375	1303
15	10372	317	373	1318	10489	336	372	1315
20	10313	311	368	1303	10377	327	376	1303
30	10332	305	369	1303	10258	312	373	1309
40	10180	298	367	1291	10198	308	370	1300

Table 2. Concentrations of Na⁺, K^+ , Ca^{2+} and Mg^{2+} (mgL⁻¹) in seawater, GRC and ORGC.

*Numbers in the first column show the weights of red soil in 100mL of the seawater.

2). This suggests the ion exchange process between the soil and the solution. The adsorption and exchange behavior of the alkali metals in soils and other exchange media is strongly a function of their hydrated radii that results K, Rb and Cs being retained more than Li and Na (Helmke et al., 1996).

The decreasing trend of potassium was clear and higher than any other cations in the order of silt+clay > bulk soil > course sand > ground bulk soil. The concentration of K^+ ranged from 368 mgL⁻¹ in seawater to 247 mgL⁻¹ (-32.90%) and 285 mgL⁻¹ (-22.60%) in 40 g/100mL of silt+clay fractions for GRC and ORGC samples, respectively (Fig. 3 a, b). Thorjorn et al. (1999) claimed that the decrease trend in potassium from soil solution in Chinese acid forest soils was accounted for much of the aluminum release or possible K⁺ exchanged with H⁺, which in turn released aluminum to the solution. The large decreasing of K^+ than other cations was probably due to the smallest hydrated radius (i.e. $K^+ = 5.32$, Na = 7.90, Ca^{2+} = 9.6 and Mg^{2+} = 10.8 Å). According to selectivity rule for the same valence cations, the ion with the smallest hydrated radius is preferentially adsorbed (Evengelou, 1998). Jardine and Zelazny (1996) argued that the potassium selectivity by clays from among larger hydrated ions (e.g. Ca^{2+} , or Mg^{2+}), is because of the space limitations for diffusion of the latter in the wedge zone, and they showed that amount of exchangeable aluminum released was influenced by the cation in the order of $NH_4^+ > K^+ > Ca^{2+} > Na^+$. Libes (1992) also reported that due to the strong attractive force, relatively small cation, potassium, is adsorbed but not readily exchanged in illites.



Fig. 3. Percentage of decreasing K^+ Vs soil weights, GRC (a) and ORGC (b).

The calcium concentration in seawater was 391 mgL⁻¹, but Boyd (2000) reported 400 mgL⁻¹. The minima concentrations of Ca²⁺ were 365 mgL⁻¹ (-6.65%) and 366 mgL⁻¹ (-6.39%) in silt+clay fractions of GRC and ORGC samples, respectively (Table 2).

On the other hand, the magnesium concentration in seawater was $1,334 \text{ mgL}^{-1}$, but Boyd (2000) reported $1,350 \text{ mgL}^{-1}$. With the increase of soil to solution ratio, the percentage of decreasing Mg²⁺ was lower than Ca²⁺. The minima Mg²⁺ concentrations of $1,263 \text{ mgL}^{-1}$ (-5.32 %) and $1,273 \text{ mgL}^{-1}$ (-4.57 %) were found in silt+clay for GRC and ORGC samples, respectively (Table 2). Thorjorn et al. (1999) also observed decreases in calcium concentration from soil solution while magnesium content was relatively stable to changes as compared to amount of released aluminum into the solution in Chinese acid forest soils.

The anions, $(Cl^-, SO_4^{2-} and HCO_5^-)$

Like the major cations, the Cl⁻, SO²⁻ and HCO³⁻ contents were also decreased with increasing soil to solution ratio. Xu-Chen and Lee (1993) observed that the positively charged species were greatly adsorbed by clays than negatively charged ones. The concentrations of Cl⁻ in seawater was 18,985 mgL⁻¹, while Boyd (2000) reported 19,000 mgL⁻¹. With increasing the soil weights, there was relatively slight decrease of Cl⁻ concentrations reaching to the minima of 18,337 mgL⁻¹ (-3.41 %) and 18,469 mgL⁻¹ (-2.72 %) in silt+clay fractions for GRC and ORGC samples, respectively. This might be due to the high concentration of Cl⁻ in seawater.

The SO.²⁻ concentration in the seawater was 2,706 mgL⁻¹, but Boyd (2000) reported 2,700 mgL⁻¹. The minima contents were 2,250 mgL⁻¹ (-16.90 %) and 2,307 mgL⁻¹ (-14.70 %) in silt+clay for GRC and ORGC samples, respectively (Fig. 4a, b).



Fig. 4. Percentage of decreasing SO²⁻ Vs soil weights, GRC (a) and ORGC (b).

This might be due to the effect of exchange reactions in the medium where larger anions show greater polarization potential than smaller ions and hence larger anions would be preferred by positively charged surfaces (Evangelou 1998). Jardine and Zelazny (1996) observed that the effectiveness of anions to stabilize montmorilonite interlayering was in the order of citrate $>> SO^{3^-} > Cl^-$.

The concentration of bicarbonate in seawater was 139 mgL⁻¹, but Drever (1982) and Boyd (2000) reported 142 mgL⁻¹. In contrast to Al^{3+} , HCO_{3-} decreased from 139 mgL⁻¹ to 1.58 mgL⁻¹ in 10 g/100mL (ORGC sample) and was not detectable from 15 g/100mL due to low pH (< 5).

Dissolution of silicate (SiO₂)

The dissolved silicate in the seawater was 0.42 mgL^{-1} , but Boyd (2000) reported 6.4 mgL⁻¹. The observed low concentration reflects the non-conservative behavior of dissolved SiO₂ that is usually affected by biological and chemical processes in seawater. The trend of dissolved silicate continuously increased as soil to solution ratio increased, in the order of coarse sand > ground bulk soil > bulk soil > silt+clay. The maxima concentrations were 34.43 and 32.23 mgL⁻¹ in 40 g/100mL of coarse sand for GRC and ORGC samples, respectively (Fig. 5a, b).



Fig. 5. Dissolved SiO₂ in different soil weights, GRC (a) and ORGC (b).

The total percentage compositions of SiO_2 in the red soils reported by Yonaha (2002) were 75.92, 77.07 and 64.86% for GRC bulk soil, course sand and silt+clay fractions, respectively, while for ORGC samples were 64.63, 62.03 and 69.80% for bulk, coarse sand and silt+clay particles, respectively. McKeague and Cline (1962) revealed the concentration of silica in the soil-water mixture increased with increasing soil-water ratio and with temperature and decreased with increasing pH.

In contrast to Al³⁺, the maximum dissolution of silicate was found in coarse sand that containing more silicate. The coarse particles of mineral soils are to large extent quartz

and feldspar, which have locked most of the silicon in the mineral soil (Clemens et al., 1998), such quartz and feldspar are responsible for low contents of Al (Yeong-gill 1999).

Conclusions

When the acidic red soil interacted with seawater, it influenced the chemical compositions of the seawater. Processes such as ions exchange, adsorption, hydrolysis, dissolution and dissociation took place. As the soil to solution ratio increased, the ions exchange and/or adsorption from the seawater also increased and hence the concentrations of the Na⁺, Ca^{2+} , Mg^{2+} and particularly K⁺, as well as the anions generally decreased from the solution.

Like Al^{3+} , the dissolved SiO_2 was also continuously increased as the soil to solution ratio increased. The increasing trend of the Al was accompanied by decreasing of the major cations and the anions that suggested the ion exchange reactions, but the dissolved SiO_2 trend was likely due to dissolution of the soil mineral containing silicate.

The pH values of seawater extracts were inversely related to aluminum concentrations in the solution, and also influenced the bicarbonate content and that was a possible reason for below detection of HCO_3^- from 15 g/100mL. The H⁺ dissociation from the clay mineral edges, the hydrolysis of Al, and high salt contents of seawater likely favored the lowering of the pH in the seawater extracts.

Although the magnitude of the impacts observed in this study might differ from the field environment, but the study qualitatively succeeded to show types of processes that take place when the red soil is discharged to the coastal area. The deviation might be due to amounts of reddish soil discharged, organic matter content and pH of seawater that may cause exchanged Al to precipitate as aluminum hydroxide.

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