Soil acidity and its impact on acidic-basic cations in recent sediments as influenced by micro-organisms and water contents

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Abstract

Laboratory column-leaching experiments were carried out by using soil sediments to evaluate the influence of soil microorganisms (SMO), duration of oxidation, rainfall and groundwater on the development of soil acidity and associated ion dynamics in the soils and percolating solutions. The soil contained 6.5 g kg^{-1} pyrite, 43 g kg^{-1} organic carbon and had pH 8.0 (sticky). The development of soil acidity at ≥ 150 % water (40± 2 % air v.) contents was mainly controlled by SMO but below 150 % water content and/or beyond the pH range of 3.5 to 5.8, it depends mainly on chemical oxidation and it's duration. Rainfall and groundwater treatments enhanced the development of acidity in the topsoils through the release of basic cations (Na, K, Ca and Mg) into the percolating solutions and simultaneous increment in the concentrations of acidic cations (Fe, Al, Mn and Zn) beyond the toxic limits for crop growth. The soluble Al was not traced in the soils at above pH 4.8, while it's concentrations increased about 5 folds for 1 unit pH decrease from 4 to 3 during 16-weeks and about 12 folds during 32-weeks. The correlation between the Ca, Mg, Fe, Mn, Zn, Al and the soil pH showed strong inverse relationship, suggesting that the availability of these elements are strongly pH depended.

Introduction

There is considerable interest in some natural factors and their interlinkage regarding to development of acid sulphate soils and associated ion dynamics. Basic research for determining the main factors responsible for the rate of pH-rise to levels beyond those at which Al, Fe toxicity occurs, should be conducted in order to increasing understanding about suitable reclamation and/or management practices (Ad hoc Commission[2]; Dent[4,5]). It is still difficult to predict the occurrence and potential severity of these soils accurately enough to warn against reclamation or to design appropriate management which

requires extensive studies (Dent & Pons[6]). Moreover, severity and reserve of soil acidity can not be quantitatively determined from morphology and field relationships, but rapid and simple methods are need to be developed to estimate the amount of acid present and the amount that will be generated after several practices (Ad hoc Commission[2]; Dent[4]).

Acid sulphate soils not only inhibited crop growth and aquatic life but also polluted and/or poisoning waterbodies or drinking water by the generation of sulphuric acid and toxic elements (Callinan et al.[3]; Lin & Melville[10]). Assessing soil sensitivity to acid-induced leaching of basic cations has also been emphasized (McFee[12]). Edwards et al.[8] revealed that relationship between rainfall intensity and movement of water and associated changes throughout the soil profiles is not known. Acidic atmosphere may detrimentally influence the fertility of soils by accelerating leaching losses of important nutrient cations such as Ca and Mg during periods of net water flow through topsoil (Liu et al.[11]). The processes which control soil pH and mobility of soluble ions are not yet clearly understood but have considerable importance regarding to the impacts of acidity (Dethier et al.[7]). Against this background, laboratory column-leaching experiments were conducted to evaluate the influence of soil microorganisms, rainfall intensity, groundwater levels and duration of oxidation in relation to development of acid sulphate soils from recent coastal sediments and simultaneous changes of acidic-basic cations in the topsoils and in percolating solutions.

Materials and Methods

Preparation of soil columns

The soil sediments of Kojima lake (Okayama, Japan) were collected from the bottom of the lake at a depth of about 4 m during September, 1992. The moist samples were stored in polyethylene bags in air-tight boxes until use for the laboratory experiments. The moist soil was puddled, uniformly packed and stacked into acrylic cylinders composed of sections (rings) 5.0 cm in length with an internal diameter of 5.0 cm. Total column lengths ranged from 60 to 70 cm depending on the groundwater levels and rainfall intensity. The bottom sections of some columns consisted of a hard plastic pipe with small holes distributed over its surface inside of the soil column. Each column was sequentially packed by slowly adding increments of moist soil and tapping until a desired bulk density was obtained. The resulting bulk density averaged over all columns was 0.53 Mg m^{-3}. Some physical and chemical properties of the studied soil sediments were determined following the methods of soil analysis by Klute[9]. The soil showed clay texture, contained 6.5 g kg^{-1} pyrite, 43.0 g kg^{-1} Organic carbon, and had pH value of 8.0 (sticky), exchangeable cations (1 M CH_3COONH_4 pH 7.0, AAS; in mM L^{-1}) viz. 14.2 K, 184.3 Na, 40.0 Ca, 92.2 Mg, 2.9 Mn, 0.10 Zn, and 1.0 Fe (1 M CH_3COONH_4, pH 4.8), water soluble cations (AAS of 1 : 5 extract; in mM L^{-1}): 6.8 K, 104.9 Na, 20.6 Ca, 18.0 Mg, 0.02 Fe and 0.40 Mn.

Treatments

The experiments were set up in a randomized design with three levels (0, 9.6 and 19.3 mm per week) of rainfall (Rf), two levels (without = 0 and with = 50 cm beneath the soil surface) of groundwater (Gw), and two levels of soil microorganisms (SMO+: presence and SMO⁻: absence; soil used for these columns was initially autoclaved for SMO at about 150°C temperature and 2 kg cm² pressure by steam sterilizer SP-203, Oval ace) and they were arranged in three replications. The treatment combination for these experiments are presented in Table 1.

Sample collection and analysis

Artificial rainfall was applied by using distilled water for about 40 minutes once a week during the experimental period. Resultant leachates were collected (only from SMO set) in fractions and analyzed for concentrations of acidic and basic cations. Groundwater level was maintained by the addition of distilled water as required. At the conclusion of each sampling time, the tape was removed and forced between consecutive rings in order to slice the column into sections. Each section of soil was then analyzed following methods of soil analysis by Klute[9] for water content (weight basis), sticky point pH and water (1 : 5 extract) soluble cations.

Results and Discussion

Dynamics in soil pH

The pH of the topsoils (0-15 cm depth) ranged between 5.7 and 7.2 up to 2-weeks after incubation with SMO (T_1 to T_6), which turned towards acidic range from the 4th week leading to acute drops of pH (3 to 4) after 32-weeks of incubation in all the treatments (data are not shown). The striking decreases of soil pH at about 3 were detected in the soil column of T_1 (with SMO) treatment during 32-weeks after incubation. Whereas at the same period of incubation, the pH of the soils were around 5 in the topsoils of T_7 (without SMO) treatment, indicating that these decreases of the soil pH were due to chemical oxidation and activities of soil microorganisms. Below pH 3.5, acid sulphate soils are very poor in microorganisms. If the pH is low enough (<4) then the ferric iron is appreciably soluble and will remain in dissolved form after oxidation and react rapidly with pyrite. The higher amount (19.3 mm/week) of rainfall in absence of groundwater (T_3) gradually increased the soil pH towards the lower depths throughout the incubation and this trend was more pronounced in presence of the same rainfall and groundwater treatment (T_6), though the soil pH was lower in the topsoils at this treatment. This may be attributed to the replacement of exchange acidity and dissociated organic acids by the base exchange in the topsoils. In absence of SMO (T_7 to T_{10}), the alkaline pH (8.0) of the initial soil turned towards more alkaline range (pH >8.5), except for the pH values of the soils after 2-weeks. At that time, the soil pH decreased towards slightly acid pH range (6.5 to 6.8), which might be due to chemical oxidation. The results of this investigation are agreed well with the findings of Dent & Pons[6]. They

reported that raw acid sulphate soils produced by drainage become severely acid within weeks or months. Adachi et al.[1] reported that soil pH decreased from 7.6 to 3-4 with prolonged (2 years) oxidation in the coastal soil having considerable amounts (16 g kg^{-1}) of pyrite.

The pH of the studied soils in almost all the treatments showed significant (p≤0.01) positive relationship with the corresponding water contents of the soils at different sampling times (Fig. 1). These relationships indicating that the development of acidity (pH <6) was started after 16-weeks of incubation at about 200 % water contents of soils in the T_1 (with SMO) treatment, while at the same water contents during 32nd week, the soil pH was found at about 1 (pH 5) unit lower than those of the 16th week which might be due to elapse period of chemical oxidation. But in the T_7 (without SMO) treatment, the development of acidity (pH <6) was noticed after 32-weeks of incubation at about 150 % water contents, whereas at these (about 150 %) water contents, the pH of the soils had dropped to about 3.0 in all the treatments with SMO (T_1-T_6), indicating that the oxygenation condition makes no pronounced difference in pH levels. This might be due to reduced activity of microorganisms and more solubility as well as chemical oxidation of ferric iron at low pH (<4). In this acid environment, Al and other toxic elements kill aquatic life or in sub-lethal doses, render many species stunted and sickly (Dent & Pons[6]; Phung & Liew[13]).

Concentrations of basic cations in topsoils

The largest increase in the concentration of soluble Na in the topsoils was determined during 32-weeks after incubation, except for the higher rainfall and groundwater treatments (Fig. 2), indicating that drying was mainly responsible for the increment of Na concentrations in the soils. The solubility of K was strikingly increased during 8th week and then quite decreased up to 32-weeks of incubation (Fig. 2). This might be attributed to the fixation of K during the elapse period of alternate wetting and drying through the rainfall practices. The concentrations of soluble Ca and Mg in the topsoils gradually increased with time and the striking increments were observed at the latter periods of incubation (Fig. 2), suggesting that these increases in concentrations of Ca and Mg were the results of dissolution products in the soils due to strong acidic conditions. The maximum concentrations of Ca and Mg were detected in the presence of groundwater but decreased with the higher amount of rainfall. The amount of Mg in the soil was very high in relation to Ca, which is an indicative of old marine deposits in which the Ca is largely leached and Mg is maintained at a relatively high level, probably as a result of progressive clay disintegration and release of Mg. Moreover, the higher amount of Mg content is presumably due to the connection with sea water of a high Mg content. The present results are partially fit with the findings of Prenzel and Schute-Bisping[14]. They noticed that there was a remarkable change in cation compositions with decreasing pH and the main process was explained by the displacement of Ca by Al.
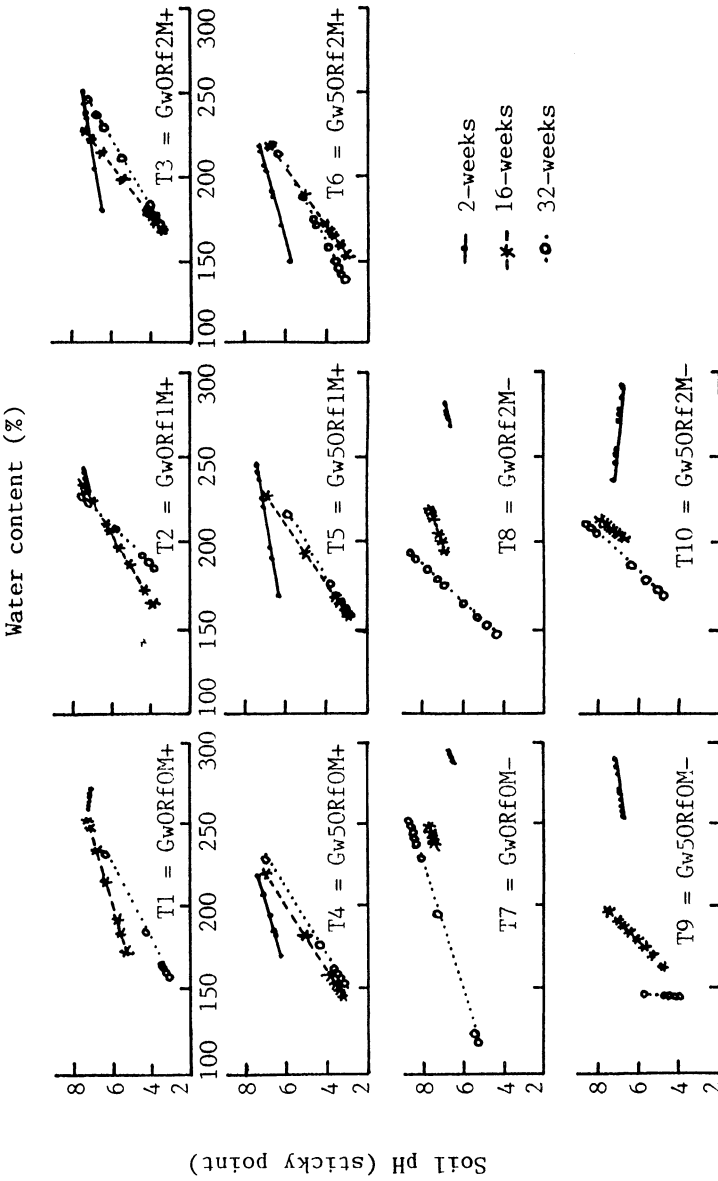
Figure 1: Relationship between soil water content and pH as influenced by soil microorganisms (M+ : with, M− : without), rainfall (Rf0 : without, Rf1 : 9.6 and Rf2 : 19.3 mm per week) and groundwater (Gw0 : without, Gw50 : 50 cm beneath the soil surface) levels during 32 weeks of incubation.
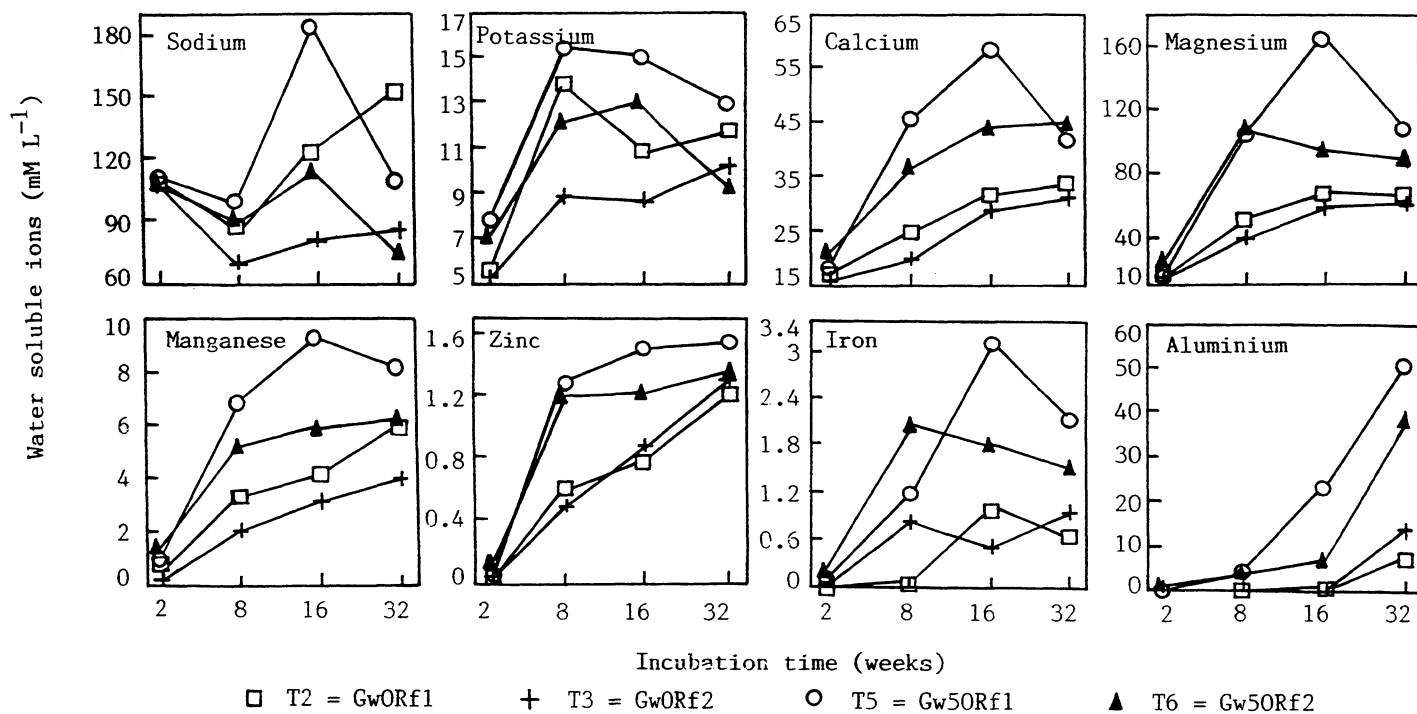
Figure 2: Typical responses in concentrations of acidic-basic cations in topsoils (0–15 cm) as influenced by rainfall (Rf1 : 9.6 and Rf2 : 19.3 mm per week) and groundwater (Gw0 : without, Gw50 : 50 cm beneath the soil surface) levels during 32 weeks of incubation.

Concentrations of acidic cations in topsoils

The concentrations of soluble Mn and Zn increased strikingly with time and the maximum concentrations were determined in the presence of groundwater having no rainfall treatments (Fig. 2). The concentrations of soluble Fe and Al (Fig. 2) in the topsoils of the columns increased strikingly during the 16-32 weeks after incubation and ranged from 0.7 to 23.7 for 16-weeks and 3.9 to 63.4 mM L^{-1} of Al for 32-weeks with the SMO set. These values were beyond the toxic limits for crops (e.g. rice: 0.9 to 1.5 mM L^{-1}). The soluble Al was not traced in the soils at above pH 4.8, while it's concentrations increased about 5 folds for 1 unit pH decrease from 4 to 3 during 16-weeks after incubation and about 12 folds during 32-weeks, suggests that the prolonged oxidation has strong influence on the release of Al in acid sulphate soils. Studies on the correlation between the amounts of available Ca, Mg, Fe, Mn, Zn, Al and their corresponding pH values of the soils showed strong inverse relationship at different sampling times, suggesting that the availability of these elements are strongly pH depended.

Concentrations of some cations in percolating solutions

Weekly distribution of Na, K, Ca, Mg and Mn concentrations in the studied leachates are shown in Figure 3. The minimum concentrations of Na in the leachates were detected in all the treatments during the earlier (2-4 weeks) periods of incubation and increased markedly after 5th week, and then decreased gradually with the lapse of time. The striking increment of K in the leachates indicates that the K was released by the disintegration of clay minerals through strong acidity in the soils. The minimum concentrations of Ca and Mg were detected in all the treatments during the earlier periods and increased strikingly during the later periods of incubation, except for the treatment having the lowest rainfall without groundwater (T_2), which showed a gradually decrease trend from the 12-32 weeks. The lowest concentration of Mn was detected in the first half (2-17 weeks) of the incubation period and increased steadily with time, except for the T_2 treatment. The concentrations of Fe, Al and Zn were not traced in the percolating solutions during the entire periods of incubation, which might be due to the pH levels (pH >6.5) beyond their availability at the lower depths (35-50 cm) of the soil columns.

   The above results demonstrated that the leaching losses of these elements are directly related to the acidic conditions of the soils. The strong acidic conditions in the soils induced the availability of the basic cations but the soils did not hold these available cations, because of the striking increment in the concentrations of the acidic cations in the topsoils at very low pH. As a result, the available basic cations were leached into the percolating solutions through exchange reactions by the acidic cations. The present results have similarities with the findings of Liu et al.[11].

   The maximum concentrations of the basic cations were detected in the leachates from the soils of the T_5 (9.6 mm rain + Gw) followed by the T_3 (19.3 mm rain only) and T_6 (19.3 mm rain + Gw) treatments, indicated that the rainfall and groundwater enhanced the release of these elements into the percolating solutions, whereas the maximum concentrations of the acidic cations were also

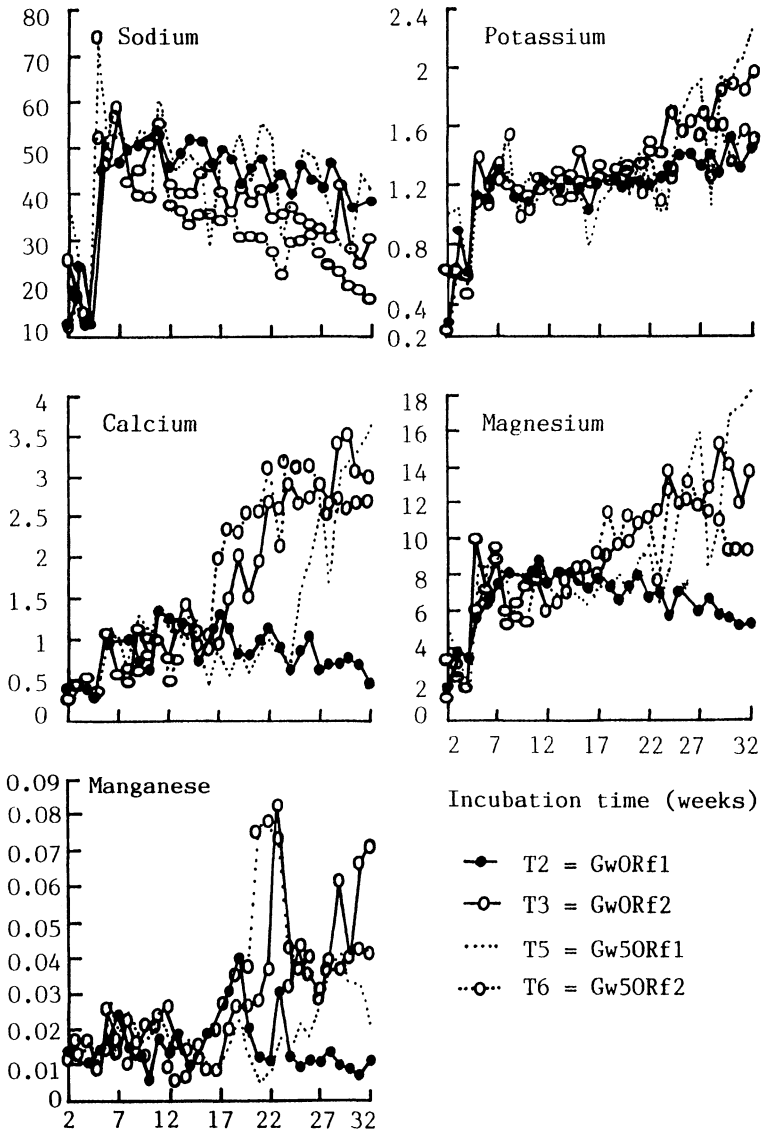204   Environmental Engineering Education

Figure 3: Typical responses in concentrations of some cations in percolating solutions as influenced by rainfall (Rf1 : 9.6 and Rf2 : 19.3 mm per week) and groungwater (Gw0 : without, Gw50 : 50 cm below soil surface) levels during 32 weeks of incubation.

determined in the topsoils of the same treatments, indicating that soil acidity may be enhanced through leaching practices.

Conclusions

Development of acidity mainly controlled by soil microorganisms at $\geq$ 150 % water (40 $\pm$ 2 % air v.) contents of soils, while less than 150 %, it depends mainly on the chemical oxidation and it's duration. The application of rainfall and groundwater enhanced the development of acidity in the topsoils through the release of basic cations into the percolating solutions and simultaneous many fold increments of acidic cations by exchange reactions, suggesting that soil acidity can be enhanced through leaching losses of basic cations.

Acknowledgments

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Table 1: Treatment combination for the experiments.

Treatment No.	Groundwater (Gw)	Rainfall (Rf: mm/week)	Soil micro-organisms (SMO)
T1	Gw0(without)	Rf0 (without)	SMO+ (with)
T2	Gw0	Rf1(with 9.6)	SMO+
T3	Gw0	Rf2(with 19.3)	SMO+
T4	Gw50 (with)	Rf0	SMO+
T5	Gw50	Rf1	SMO+
T6	Gw50	Rf2	SMO+
T7	Gw0	Rf0	SMO- (without)
T8	Gw0	Rf2	SMO-
T9	Gw50	Rf0	SMO-
T10	Gw50	Rf2	SMO-