Elemental dynamics in porewater of an acid sulfate paddy soil as affected by sodium bentonite and dolomite amendments: insights from field study

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Abstract. Rice productivity in acid sulfate soils are frequently limited due primarily to strong acidity, low phosphorus (P) availability and metal toxicity. A recent study has documented that the use of sodium bentonite (NaB), non-hazardous material uses in natural gas pipeline construction, could be a promising soil amendment for mitigating major concerns experiencing in acid sulfate soils. Here we examined the effects of NaB and dolomite (DL) on dynamics in dissolved contents of both nutrient and associated elements in an acid sulfate soil and rice yield from paddy field in natural gas pipeline Rights-of-Way. The results demonstrated that the NaB and DL utilization significantly alleviated soil acidity and metal (Al, Fe, and Mn) toxicity ($\alpha = 0.05$). Both soil amendments also significantly improved readily available P. Nonetheless, the soil NaB incorporation did elevate soluble sodium and did plummet soluble K, Ca, and Mg. Therefore, appropriate ratios and amounts of the K, Ca, and Mg along with N fertilizers are indisputable needed to maintain the nutrient balance when applying NaB as a soil amendment. Our finding implies that combined use of NaB and DL are suggested to soil amendment and could alleviate nutrient imbalance as compared to the sole NaB utilization.

1 Introduction

PTT Public Company Limited (PTT) is a national oil and gas company that has played an essential role in strengthening the national energy security of the Kingdom of Thailand by transporting natural gas via a pipeline system to customers, industrial and commercial sectors since 1981. PTT has been constructing and operating natural gas pipeline system network for more than 4,500 kilometers, including both onshore and offshore areas. Recently, PTT has been starting construction of the 5th Transmission Natural Gas Pipeline Project (5TP) with approximately 415 kilometers in length from eastern to central part of Thailand, laid through various kinds of soils which is mostly acid sulfate soil that occurred in area around pipeline Rights-of-Way (ROW).

Acid sulfate soils are vital resources for crop production in the world. However, these soils have primary concerns from their acidity, metal toxicity, and basic cation deficiency. Globally, they occur of about 12–13 million ha, most of which extensively occupy in the tropics, especially in Southeast Asia [1]. In Thailand, these soils are widely distributed in the central plain area, which is being used for paddy rice cultivation. Therefore, rice productivity in these soils is rather scanty due mainly to their chemical limitation.

Several measures have been adopted to alleviate soil acidity and metal toxicity in the soils, for example, neutralizing soil pH with liming materials such as limestone and dolomites (DL). In addition, sodium-bentonite (NaB), an alkaline muddy material used in the Horizontal Directional Drilling (HDD) technique for 5TP project construction, has been recently documented to increase pH of acid sulfate soils at laboratory scale [2]. Nonetheless, the incubation experiment in oxic conditions is different from paddy rice fields, which are frequently subjected to flooded and non-flooded cycles during rice growth and harvest stages. The anoxic and oxic environments strongly affect changes in dissolved elements in soil porewater, representing the most available form of elements for plant uptake.

To elucidate the roles of NaB and DL amendments on paddy rice production, the primary goals of the present study are thus to 1) examine the changes in element concentration in pore-water of an acid sulfate soil amended with NaB and DL during paddy rice cultivation under field condition and 2) investigate the combined effect of Na-bentonite and dolomite utilization on the productivity of

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rice (*Oryza sativa* L., cv. RD43). Our results provide a possible measure of NaB, a remnant from the natural gas pipeline construction activities, for enhancing paddy rice production in acid sulfate soils.

2 Materials and methods

2.1 Field experiment

The field trial was undertaken in an acid sulfate soil in 5TP project Right-of-Way, namely Rangsit series classified as Sulfic Endoaquepts according to USDA Soil Taxonomy. The value of soil pH before the experiment was 3.21, which is ultra-acidic. The trial was arranged into Randomized Complete Block Design (RCBD) with 4 treatments: control (T1) with no soil amendment, NaB utilization (T2) at a soil: NaB ratio of 1: 0.45, combined NaB and DL utilization (T3) at a soil: NaB: DL ratio of 1: 0.23: 0.0047, and DL utilization (T4) at a soil: DL ratio of 1: 0.0095. For field applications, the ratio of T2 corresponded to the rate of NaB at 585 T ha^{-1} and the ratio of T4 matched with the rate of DL at 12.35 T ha^{-1}, calculated from 10 cm depth and 1.3 g cm^{-3} bulk density of the studied soil. The applied NaB and DL rates were expected to raise soil pH to 6.0 based on the previous study [2]. The full details of chemical properties for these materials are given in Table 1.

Table 1. Some chemical properties of bentonite (NaB) and dolomite (DL) used in this experiment.

Parameter	Bentonite (NaB)	Dolomite (DL)
CCE (%)	32.7	126.1
pH (1:10)	9.74	9.59
EC_e (dS m^{-1})	1.43	0.18
SAR	28.8	0.4
ESP	67.6	38.4
Exchangeable Na (mg kg^{-1})	70.5	0.3
Exchangeable Ca (mg kg^{-1})	25.0	40.6
Exchangeable Mg (mg kg^{-1})	14.6	5.6
Soluble Na (mg kg^{-1})	204.3	6.38
Soluble Ca (mg kg^{-1})	2.01	4.30
Soluble Mg (mg kg^{-1})	0.56	5.93
Total N (g kg^{-1})	0.39	0.37
Available K (mg kg^{-1})	279.7	8.7
Available P (mg kg^{-1})	4.6	nd

The experiment was performed in four replicates. Each plot was divided by soil bunds with a plot size of 5x4 m. Before rice transplanting of 42 days, the NaB and DT materials had been thoroughly incorporated into each plot to ascertain soil acidity neutralization. Both amendments significantly increased soil pH and extractable bases (Ca, Mg, Na, and K), exchangeable sodium percentage (ESP) and sodium adsorption ratio (SAR) of the studied soil (Table 2). Subsequently, 20-day-old rice seeding of RD43 cultivar was transplanted to the plots with a spacing of 20x20 cm. Basal fertilizers in the forms of urea ($CO(NH_2)_2$) and diammonium phosphate ($(NH_4)_2HPO_4$) were applied 14 days after transplanting, corresponding to the respective N and P rates of 19 kg N ha^{-1} and 16 kg P ha^{-1}. Topdressing N fertilizer (19 kg N ha^{-1}) was then applied 42 days after the transplanting.

2.2 Porewater sampling and analysis

To examine changes in nutrient and relevant elements in the porewater of the acid sulfate soil amended with NaB and DL materials during the rice cultivation period, a rhizon sampler was deployed into surface soil of about 10 cm in each plot at the 45 degrees from the perpendicular expected to pass through rice roots. The aliquots were taken at 42, 56, 70, 84, 98, and 112 days after the soil amendment incorporation. The pH and Eh values had been concurrently measured after withdrawing aliquots from soils to minimize changes in Eh value from air oxidation.

The porewater samples were spiked with concentrated HNO_3 (1% v/v) and then kept in the fridge at 4 ºC before the quantification of plant nutrient (K, Ca, Mg, Si, P, S, Fe, Mn, Zn, Cu, and Ni) and other relevant elements (Na and Al) using Inductively Coupled Plasma Optical Emission Spectroscopy (Optima 8300 ICP-OES Spectrometer, PerkinElmer). The pH and Eh of the soil pastes were determined at the same days of the porewater sampling.

2.3 Plant data collection

At the harvest period of 12 weeks after the transplanted rice (126 days after the soil amendment incorporation), rice grain in each plot was taken and weighted. The rice weight was converted to 14% moisture content and reported as grain yield.

Table 2. Selected soil properties after 42 days of soil amendment incorporation.

Treatment	Soil pH (1:1)	EC_e (dS $^{-1}$)	Extractable bases Ca (------- mg kg^{-1} -------)	Mg	Na	K	ESP	SAR
T1 (Control)	3.13^b	4.2	441^c	249^d	103^c	202^b	3.0^c	0.5^c
T2 (NaB)	5.95^a	3.7	3,245^a	1,412^c	5,188^a	301^a	44.6^a	31.5^a
T3 (NaB + DL)	6.00^a	3.7	3,498^a	1,808^b	3,483^b	349^a	31.4^b	8.1^b
T4 (DL)	5.24^a	4	2,149^b	2,137^a	305^c	335^a	3.2c	0.4^c
F-test	*	ns	*	*	*	*	*	*
CV (%)	9	22	21	11	18	21	13	25

Different letters in the same columns are significantly different at α = 0.05.

3 Results and discussion

3.1 pH and Eh dynamics

Soil pH in all treatments tended to decrease during the entire periods of rice cultivation (Fig. 1). Time average value of pH in the control treatment was lowest (pH = 3.20), whereas the other treatments were significantly higher. The pH value for the NaB treatment (T2) was higher than that of the DL treatment (T4).

Both soil NaB and DL amendments significantly affected the changes in soil Eh values (Fig. 1). The Eh values in both treatments decreased with the rice growth period, indicating the soil reduction. However, the Eh value in the control treatment remained stable, reflecting the soil was under suboxic conditions. The unexpected Eh fluctuations across the treatments could be attributable to the ultra-acidity in the control treatment that could inhibit microbial activity and limit soil reduction. The pH and Eh values in porewater showed somewhat similar patterns to soils that had a decrease in the pH and Eh with time.

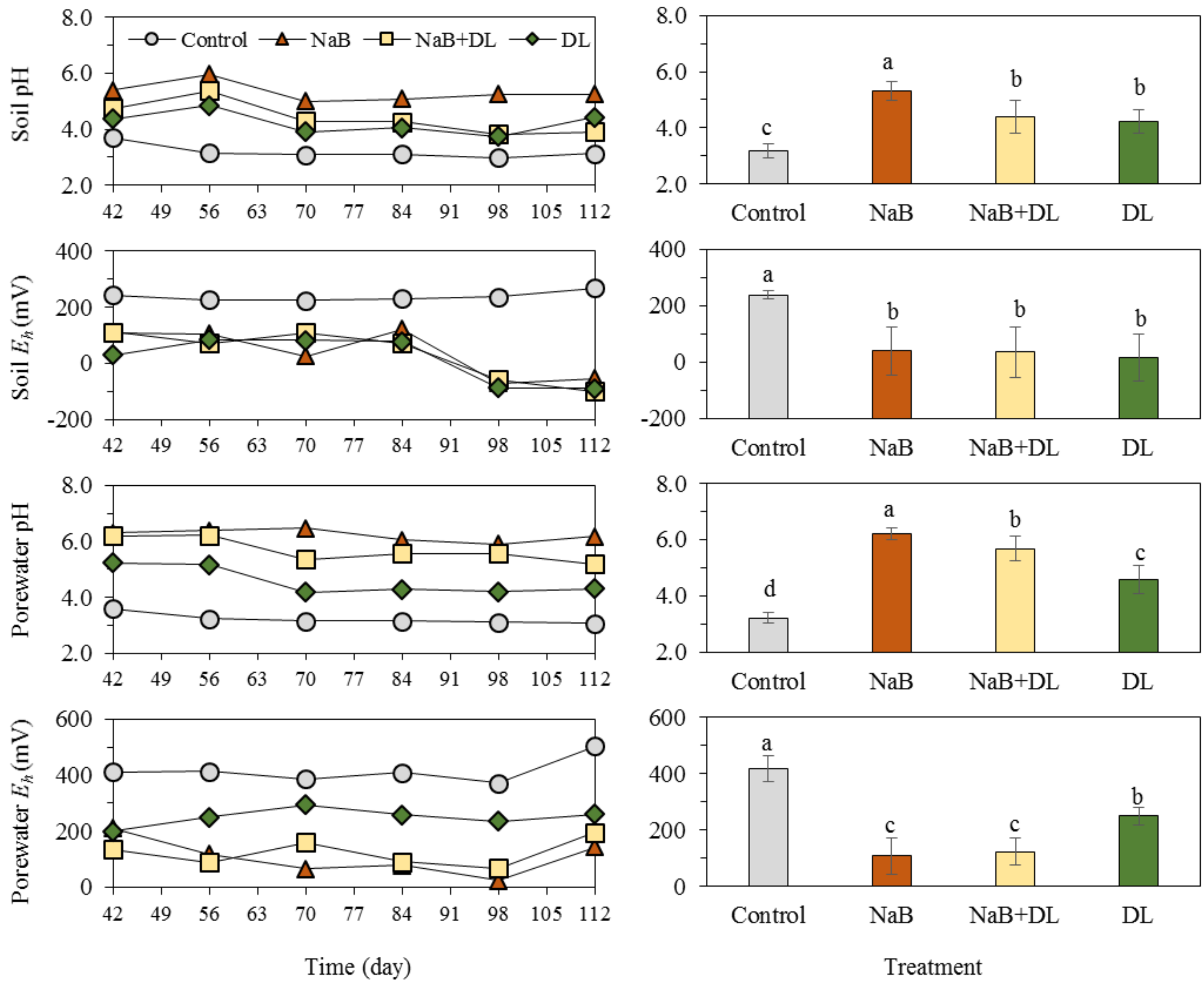

Fig. 1. Time-function (left panel) and time-average values (right panel) of pH and Eh of soil and porewater during the entire period of rice (*Oryza sativa* L., cv. RD43) grown in an acid sulfate soils amended with sodium bentonite (NaB) and dolomite (DL). Different letters above columns are significantly different at α = 0.05.

3.2 Porewater dynamics

Dynamics of essential nutrient elements (K, Ca, Mg, Si, P, S, Fe, Mn, Zn, Cu, and Ni) and associated relevant elements (Na and Al) in porewater of the studied acid sulfated soils incorporated with NaB and DL compared to the control treatment are given in Figs 2 and 3. The results showed somewhat intricate patterns (i.e., increased, decreased or stable) of dissolved elements among treatments against the rice growing period. In the control treatment with no soil amendment (T1), some elements including K, Ca, Mg, P, S, Al, Fe, Mn, Zn, Ni were likely to elevate with the flooding period, whereas the dissolved Cu demonstrated a clear reverse trend. The dissolved Na was stable upon the flooding. These deviations could be attributed to chemical processes including i) the releasing of adsorbed elements located inside mineral interlayers, ii) reductive dissolution of redox-sensitive elements (e.g., Fe,

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and Mn), and iii) releasing of elements adsorbed to Fe/Mn oxide induced by the reductive dissolution [3]. A previous study showed that the dominant clay mineral of acid soil in this area was smectite [4, 5], a highly expanding phyllosilicate, which had high capability to adsorb substantial amount of water in its interlayer and eventually released the adsorbed ions into the soil solution.

3.3 Time-average porewater

The time-average contents of the elements were calculated in order to gain inclusive interpretation of the effect of NaB and DL on the contents of relevant elements in porewater. The results demonstrated that NaB utilization decreased concentrations of metals, including Al, Fe, and Mn that are highly toxic and limit crop productivity in acid sulfate soils. The NaB treatment also increased dissolved P, which is likely to be a consequence of soil pH increment. However, this material deteriorates several essential macronutrients, including K, Ca, and Mg as well as a beneficial element for rice that is Si. Furthermore, dissolved Na concentration in the NaB treatment was higher than the control treatment of 5.9-fold. The increase of Na and the decrease of K, Ca, and Mg in the porewater after the NaB incorporation should be taken into a thoughtful consideration that nutrient imbalances could be experienced. Therefore, the use of NaB for soil amendment must be combined with proper management of nutrients.

For the DL treatment, the decreased concentrations of Si, Al, Fe, Mn, Zn, and Ni were observed, along with the increase of dissolved P. This again could be attributed to soil acidity alleviation from its liming effect. There were no significant differences in dissolved Ca and Mg in the DL treatment compared to the control treatment.

The combined uses of NaB and DL amendments (T3) had both effects of these materials that are decreasing metal toxicity, increasing soil pH and P availability, and lowering K, Ca, and Mg availability. This treatment (NaB+DL) less deteriorated the macronutrient availability than the sole NaB utilization (T2).

3.4 Rice yield

The rice grain yield in the control treatment was unobtainable (Fig. 4.), which is due to a very strong acidity of the studied soil with the high toxicity of several metals including Al, Fe, Mn, and Ni. However, the use of both soil amendments (NaB and DL) had a significantly positive effect on rice yield. This obtained yield resulted from the alleviation of soil acidity and metal toxicity along with enhancing soil nutrient availability. There was no statistical difference in rice yield between the NaB and DL treatments, which is due to the soil inversion during the land preparation caused a heterogeneity of soil materials in each plot. The DL application tended to provide a higher yield than the NaB treatment.

4 Conclusions

Our results demonstrated that the studied acid sulfate soil was ultra-acidic (pH = 3.21), which soil pH remained constant throughout the entire period of rice production (vegetative and grain-filling stages). The strong acidity exaggerated a high solubility of several metals including Al, Fe, Mn, Zn, and Ni, and could induce the death of rice (*Oryza sativa* L., cv. RD43). The sole utilization of sodium bentonite (NaB) and dolomite (DL) or the combined uses of both materials can raise soil pH, demote metal toxicity, and promote phosphorus (P) availability. These beneficial effects rehabilitated rice growth and productivity. The soil NaB incorporation could suppress the availability of essential plant nutrients (K, Ca, Mg) and considerably enhance the soluble magnitude of sodium (Na). Therefore, the use of the NaB material must be stipulated that adequate K, Ca, and Mg, along with N fertilizers, are needed to be applied to prevent nutrient imbalance. The combined use of DL and NaB could in part alleviate Ca and Mg imbalance as compared to the sole NaB utilization. Nonetheless, the suitable ratio of NaB and DL materials along with N and P fertilizers for improving rice productivity in such acid sulfate soils are required for further investigation.

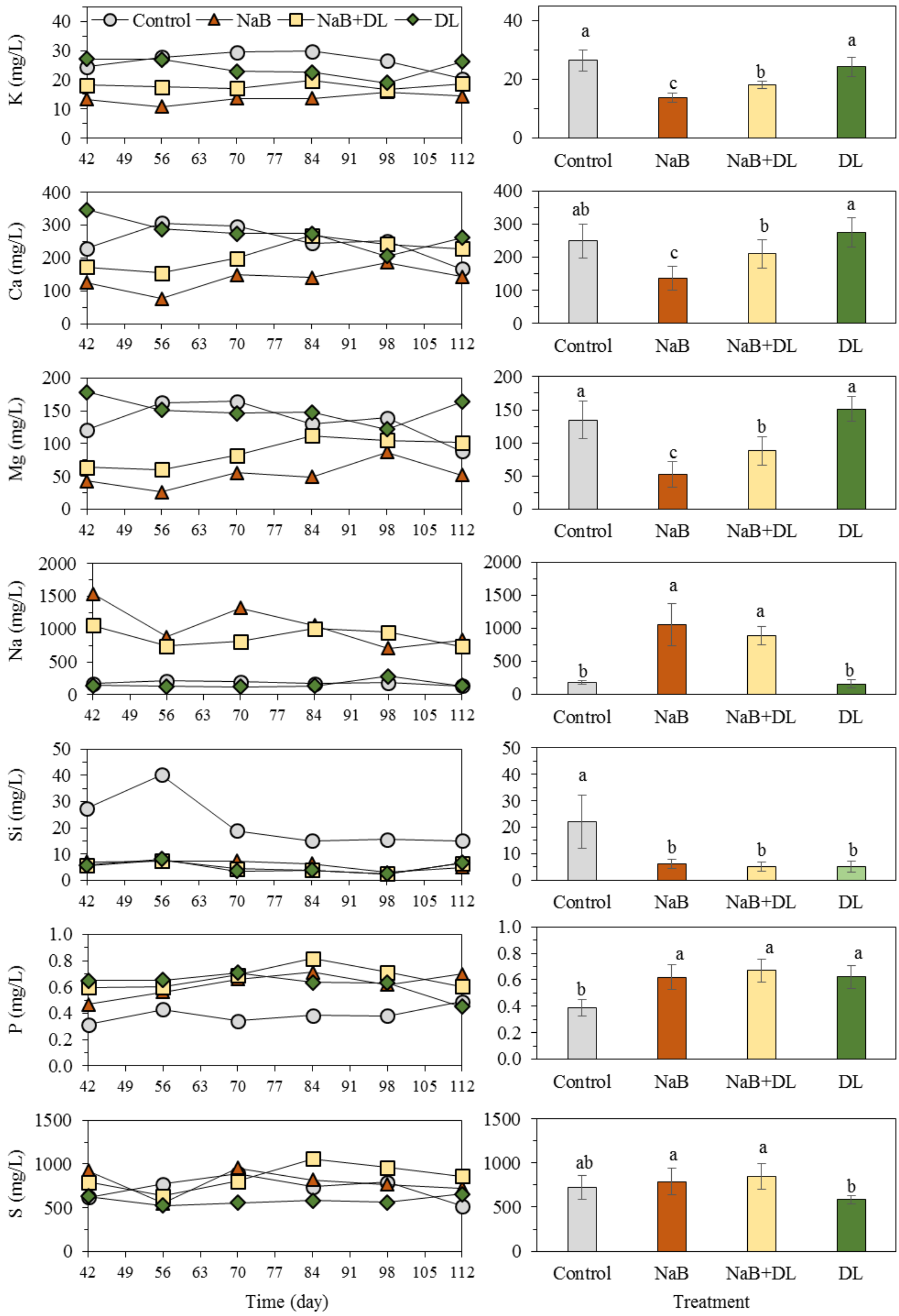

Fig. 2. Time-function (left panel) and time-average values (right panel) of dissolved K, Ca, Mg, Na, Si, P, and S in porewater during entire period of rice (*Oryza sativa* L., cv. RD43) grown in an acid sulfate soils amended with sodium bentonite (NaB) and dolomite (DL). Different letters above columns are significantly different at α = 0.05.

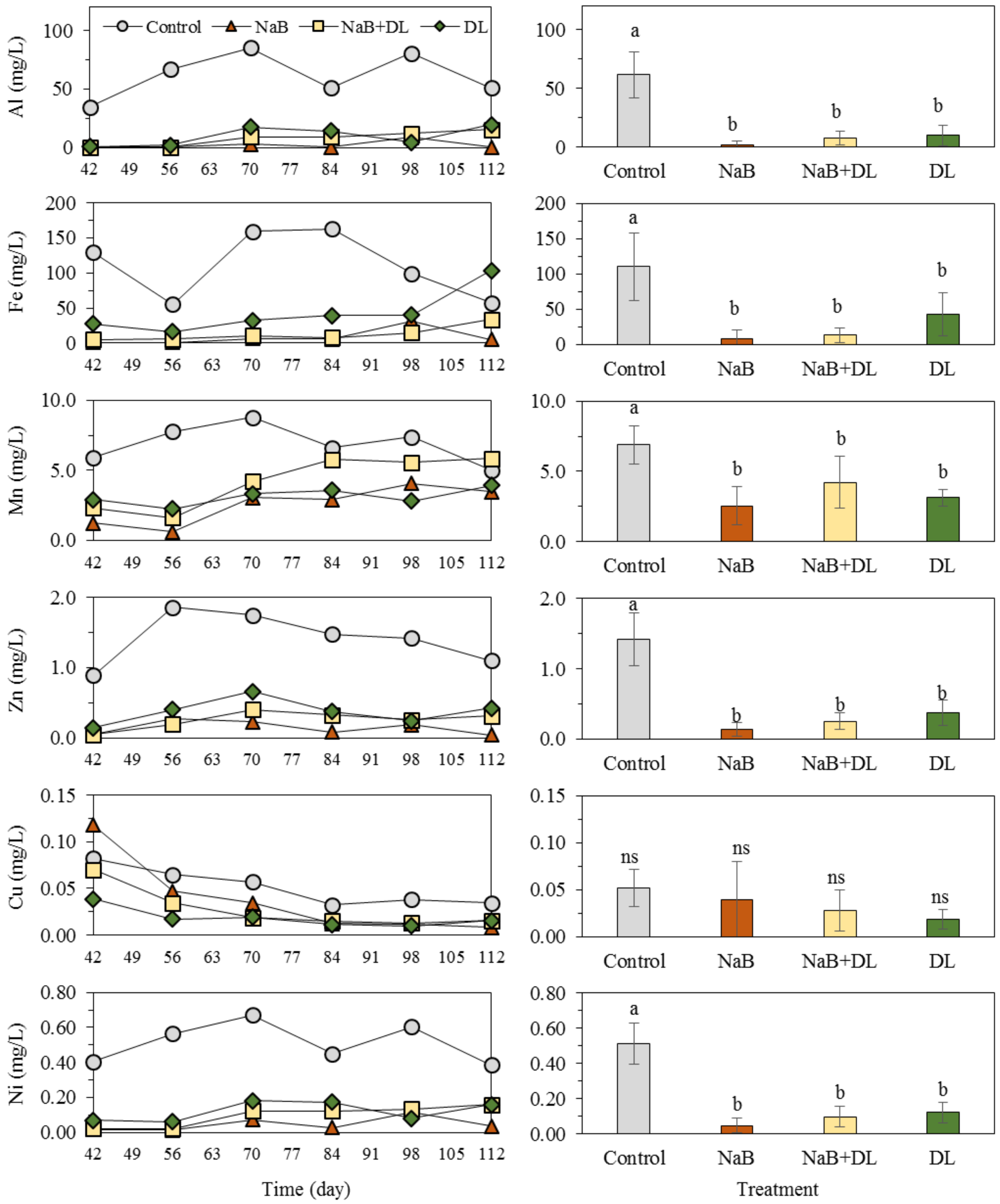

Fig. 3. Time-function (left panel) and time-average values (right panel) of dissolved Al, Fe, Mn, Zn, Cu, and Ni in porewater during the entire period of rice (*Oryza sativa* L., cv. RD43) grown in an acid sulfate soils amended with sodium bentonite (NaB) and dolomite (DL). Different letters above columns are significantly different at $\alpha = 0.05$.

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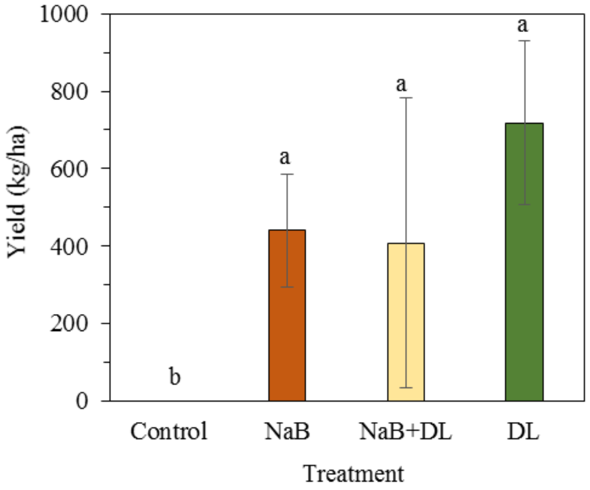

Fig. 4. The yield of rice (*Oryza sativa* L., cv. RD43) grown in an acid sulfate soils amended with sodium bentonite (NaB), combined NaB and dolomite (DL), and DL compared to the control treatment. Different letters above columns are significantly different at α = 0.05.

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