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Evidence of sea water Boron in the lower layers of tropical woody peat

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ABSTRACT For the assessment and proper use of tropical peatlands, chemical problems such as nutrient deficiencies and toxicities should be solved. The concentration of the essential trace element boron, which is in tropical peat soil, is very low (about 1/10 of the cultivated mineral soil in Japan), however, in layers below 40 cm depth of inland peat B is abundantly fixed. The effect of sea water was estimated, because the water soluble Na content in these layers was high and the water soluble Mg/Ca ratio in them was as high as that of sea water. Therefore, in these layers the B appears to be fixing the high levels of B in the sea water. Various gaps have developed in the lower layer of the inland peat indicating that the sea water can infiltrate with the pressure of the flood-tide.

Key words: tropical woody peat, inland peat, lower peat layer, boron, sea water, Mg/Ca ratio

Tropical peat consists of plant residues of former forests in varying degrees of decomposition. Tropical peatland contains a greater diversity of woody plant species than that found in temperate regions. The latter developed from grass plants such as reeds, sedges and *Sphagnum*. In tropical peat, well-preserved woody materials are commonly found within the matrix of dark brown amorphous materials. The properties of tropical peat are based on several factors (Driessen, 1978; Bouman and Driessen, 1985), including the nature of the original plants, wood content, degree of decomposition, the supply of inorganic solutes, the environmental conditions, peat stratification, and compactions.

The total area of tropical peat swamps or tropical peatlands in the world amounts to about 30 Mha, two thirds of which are in Southeast Asia (Driessen, 1978). The peatlands are mostly in Sumatra, Kalimantan, and West Papua. Over 8 Mha of Indonesia's peatlands are deeper than 2 m. Inland peat deposits with greater than 15 m depth are found in the high altitude peatlands (Rieley *et al.*, 1992). Many of them appear to have been formed in the early and middle Holocene *era* (Neuzil, 1997).

Large areas of coastal lowland peatlands have been exploited for agricultural development, and the difficulties of their large-scale development are widely known. The low fertility (Chew *et al.*, 1978; Yonebayashi *et al.*, 1994) and polyphenolic toxicity (Driessen and Suhardjo, 1976) are among the factors causing agricultural production failure. The optimum utilization of peatlands depends on its characteristics.

Boron is one of the essential trace elements for vascular plants. It is important in the metabolism of saccharides and synthesis of the cell walls of plants. The range of B concentrations that are optimum for plant growth, is narrow. B deficiency and toxicity are common. B is essential for pollen tube growth (Marschner, 1986) and B deficiency reduces the root growth rate (Bohnsack and Albert, 1977).

In general, B in soil can be divided into three categories (Keren and Bingham, 1985): (1) B in primary minerals, such as tourmaline (borosilicate minerals), (2) B adsorbed by soil constituents, such as clay minerals, hydroxide of Al and Fe, organic matter, and (3) B in soil solutions such as boric acid and borate ions.

We previously reported that the available B content in tropical peat soils (Yonebayashi and Yamada, 2000) is markedly less than that in mineral soils. It is not clear whether this stems from the low solubility of soil B or from the low content of total B in peat soils.

In the peat soil ecosystems, many nutrient elements circulate between peat and plants, and the nutrients are repeatedly utilized. The regeneration of plants becomes possible in a closed ecosystem such as peatlands (Yonebayashi *et al.*, 1997). A new supply of nutrient elements is not provided in deep peat, because plant roots do not reach the mineral soil layer under the peat. In the peat ecosystem, most of the heavy metals are retained in the peat as chelates (Yonebayashi *et al.* 1994), and

there is little heavy metal run-off. Although B should combine with the cis-hydroxyl groups of the polysaccharide in the peat deposit by coordination bonding, thereby becoming stable, no study has reported this.

MATERIALS AND METHODS

The chemical status of B in tropical peat was examined in samples collected from three peat deposits in Indonesia comprising 3 sites at Air Sugihan basin (AS-2, AS-3, AS-4) in South Sumatra, 3 sites in Rupert Island, and 4 sites at Sg. Sebangau (SAJ) and Sg. Kapuas basin (GR-1, GR-2, LA-3) in Central Kalimantan, as shown in Fig. 1.

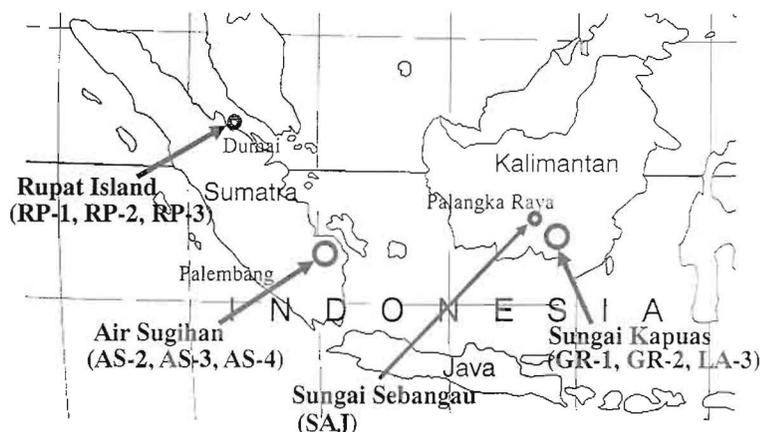


Fig. 1. Location of sampling sites of peat deposits.

To determine the total B in organic samples quantitatively, the explosive reaction generated in fusion with sodium peroxide must be prevented. A method for total B analysis without the explosive reaction was developed by decomposing the major organic substances with dry combustion and fusing the residue with sodium peroxide. B was measured by colorimetry. Mannitol soluble B was determined from an extract with 2% mannitol containing 0.05 M acetate buffer (pH 4.5) solution heated at 100°C for 15 min. B was measured using ICP-AES equipment.

The total organic carbon content of peat sample was determined by the dry combustion method using an NC analyzer (Sumigraph NC-800) after pretreatment with a dilute HCl solution to remove carbonates. Ash (mineral) content was determined by dry combustion overnight at 440°C. Kaila's pyrophosphate index (PPI) was determined by the method described in a previous paper (Anwar *et al.*, 2004). A 500 mg peat sample was extracted with 50 mL of 0.025M Na-pyrophosphate for 18 hr. Ten mL of the extract was diluted to 50 mL. The absorbance at 550 nm was determined, multiplied by 100, and the value that is equivalent to Kaila's PPI was obtained. Cation exchange capacity (CEC) and concentrations of exchangeable bases (Ca, Mg, K, and Na) were measured after successive extraction with 1M ammonium acetate at pH 7.0 and subsequently 10% NaCl solutions (Thomas, 1982). The amount of NH_4^+ replaced by Na was determined by titration with 0.01M HCl solution after steam distillation, whereas the contents of exchangeable bases were determined by atomic absorption spectrometry (Shimadzu, AA-640-01). Water-soluble bases (Ca, Mg, K, and Na) were extracted with water at a soil to water ratio of 1:5 (Rhoades, 1982) and determined by atomic absorption spectrometry.

RESULTS AND DISCUSSION

The samples collected near the margin or the edge of the peat deposits were termed marginal peat, while the samples collected from more inland areas were regarded as inland peat (Table 1). In general, inland peat is deeper than marginal peat. Soil pH of peat ranged from 2.9 to 4.8, and there was no significant difference in pH between inland peats and marginal peats. However the pH of the lower layer of Air Sugihan peat was significantly high (more than 4) shown in Fig. 2a. CEC of peat soil ranged from 87 to 156 $\text{cmol}(+) \text{kg}^{-1}$, and there was no significant difference in soil CEC between inland peats and marginal peats (Fig.2b).

Table 1. Study sites and their features

Sample No	Peat deposits/ Name of site	Province	Peat deposit type	Distance from sea (km)	Distance from river (km)	Land use
AS-2	Air Sugihan	South Sumatra	Inland	14.5	5	Cultivation
AS-3	Air Sugihan	South Sumatra	Inland	18.5	7	Tree/shrub ^{a)}
AS-4	Air Sugihan	South Sumatra	Inland	12	7	Tree/shrub ^{a)}
RP-1	Rupat Island	Riau	Inland	9	3.5	Rubber tree
RP-2	Rupat Island	Riau	Marginal	2.5	1	Forest
RP-3	Rupat Island	Riau	Inland	9.5	3.5	Forest
GR-1	Garung	Central Kalimantan	Marginal	83.5	2	Forest
GR-2	Garung	Central Kalimantan	Marginal	87	2.5	Forest
LA-3	Lamunti	Central Kalimantan	Marginal	93	3	Forest ^{b)}
SAJ	Setia Alam Jaya	Central Kalimantan	Inland	115	7	Forest

^{a)}Abandoned land after about 5 years of cultivation.

^{b)}Newly cut and felled forest (about 1 year)

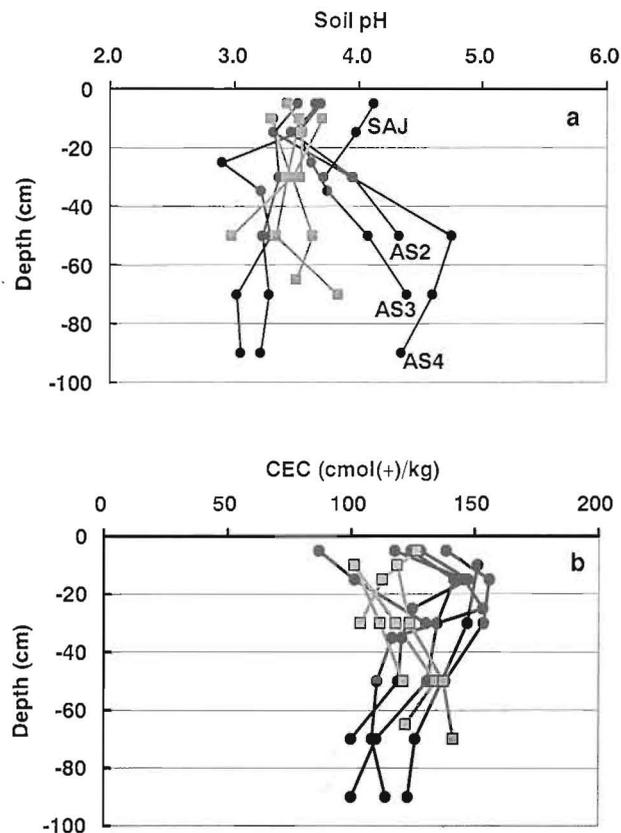


Fig. 2. Vertical profiles of pH (a) and CEC (b) of marginal peat deposits (squares) and inland peat deposits (circles).

The features of the inland peat show very low ash content of 9% or less, and 50% or greater carbon content, compared with the marginal peats in all layers, shown in Fig. 3a. The ash component, which is mainly in the marginal peat, consists of inorganic components such as clay minerals derived from mineral soils around the peatlands. However, inland peat has nearly no inorganic components. The inland peat has relatively low levels of nutrient elements, since these element ions are not supplied from the inorganic component (Driessen, 1978).

Kaila's pyrophosphate index (PPI) (Kaila, 1956) was determined and used as a key measure of the degree of decomposition of peat soils. As seen in Fig. 3b, the PPI of the inland peats tended to decrease with soil depth, however, the value of the PPI near the surface layer differs by peat soil. In contrast, the PPI of the marginal peat tended to increase with soil depth. It was recently shown that the pattern of lignin alteration (Anwar *et al.*, 2004) described by the acid/aldehyde ratio of lignin-derived phenols, displayed the same pattern as the PPI profile. The results suggested that in inland peat there is a more anaerobic history of alteration in the lower layers compared to marginal peat (Anwar *et al.*, 2004). Marginal peat areas were drier or occasionally aerated, were considerably influenced by environmental factors, such as the chemical quality of the surrounding formation and enrichment with fluvial materials, and were commonly exposed to more intensive microbial attacks (Driessen, 1978).

The total B content in all layers of marginal peat was small, amounting to 10 mg kg⁻¹ or less, with an average of 4.5 mg kg⁻¹, which corresponds to about 1/10 of that of mineral soils that are heavily manured in Japan. The total B in the inland peat was also very small between 0 to 40 cm depth, at 5 mg kg⁻¹ or less. However, the quantity increased to greater than 10 mg kg⁻¹ in three layers which were deeper than 40 cm of the AS-3 and AS-4 samples (Fig. 4a). The mannitol soluble B content in most layers of inland peat was small at less than 0.7 mg kg⁻¹, with an average of 0.27 mg kg⁻¹, except for two layers which were deeper than 40 cm of inland peat AS-4 sample (Fig 4b). It was also less than 0.5 mg kg⁻¹ in all layers of the marginal peat and the average was 0.14 mg kg⁻¹.

The water-soluble Na content of all layers of marginal peat was very small, amounting to 0.1 cmol (+) kg⁻¹ or less. The water-soluble Na quantities of the inland peat were also small between 0 to 40 cm

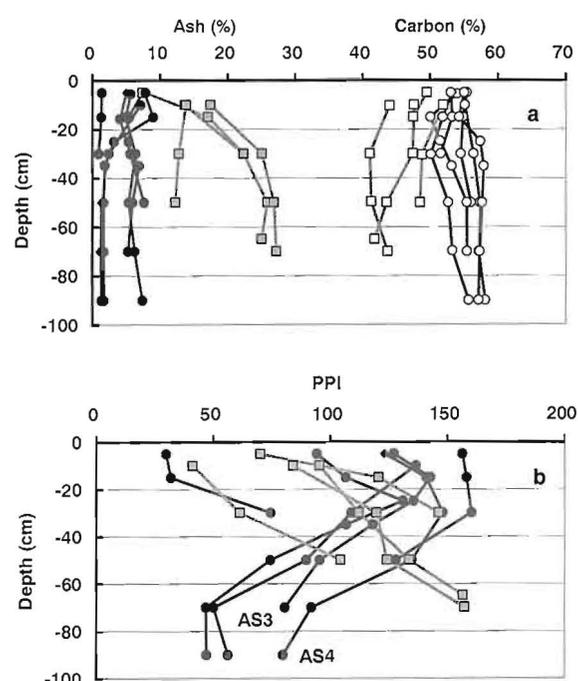


Fig. 3. Vertical profiles of ash and carbon contents as percentages of peat soils (a) and Kaila's pyrophosphate indices (PPI) of peat soils (b) of marginal peat deposits (squares) and inland peat deposits (circles).

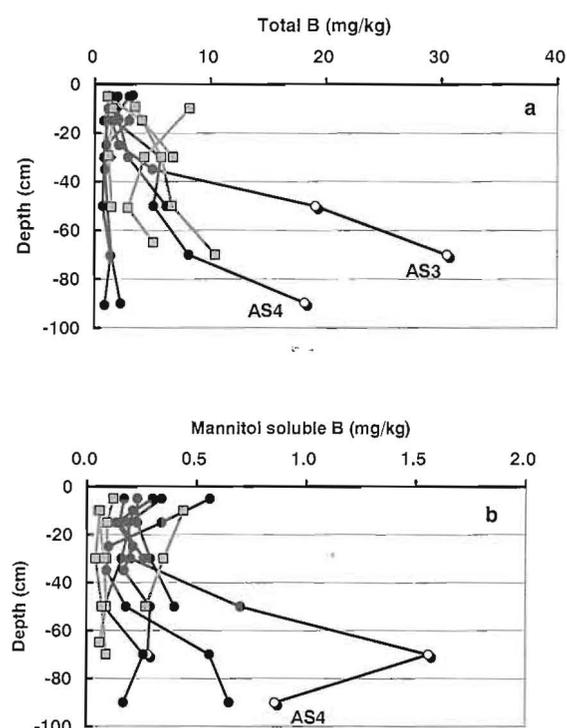


Fig. 4. Vertical profiles of total B content (a) and mannitol soluble B content (b) of peat soils of marginal peat deposits (squares) and inland peat deposits (circles). AS; Air Sugihan basin.

depth, at 1.2 cmol (+) kg⁻¹ or less. However, the quantity increased to greater than 1.2 cmol (+) kg⁻¹ in three layers which were deeper than 40 cm of AS-3 and AS-4 samples (Fig. 5a). The Mg/Ca ratios of their aqueous extracts were markedly higher than the other peat samples (Fig. 5b). The water soluble Mg/Ca ratio of the layer below 40 cm of inland peat was greater than 5.56, though for the marginal peat it was less than 3. The Mg/Ca ratio of sea water (Kitano, 1992) is constant at 5.56, and the mean value of the Mg/Ca ratio of river water (Kitano, 1992) worldwide is estimated at 0.38. Therefore, the peat which had a water-soluble Na content of the lower layer greater than 1.2 cmol (+) kg⁻¹ and a Mg/Ca ratio greater than 5.56, must have had contact with sea water.

As far as the cations which are adsorbed to peat are concerned, the exchangeable Ca/Mg ratio was less than 5.9, even in the samples that had a water-soluble Mg/Ca ratio between 5.56 to 12. The exchangeable Mg/Ca ratio which shows the composition of the adsorbed divalent cation was between that of the Mg/Ca ratio of seawater and that of river water. There was a highly positive correlation between the exchangeable Mg/Ca ratio (X) and the water-soluble Mg/Ca ratio (Y), in the inland peat, as follows: $Y = 1.73X + 0.13$, $r^2 = 0.88$. Because Ca²⁺ is more strongly adsorbed to the humic substances than Mg²⁺, and the stability constant of humic substances complexes with Ca²⁺ is higher than Mg²⁺ (Flaig *et al.*, 1975), Mg²⁺ dissociate in water more easily than Ca²⁺ and the water-soluble Mg/Ca ratio is larger than the exchange Mg/Ca ratio.

There was a highly positive correlation between the total B content and the water-soluble Na content and the Mg/Ca ratio, in the inland peat. It is known that the B concentration of sea water is markedly higher than that of river water. The B concentration in all sea water (Kitano, 1992) is constant at 4.7 mg L⁻¹, and the mean value of the B concentration of river water (Durum and Haffty, 1963) is 0.01 mg L⁻¹. This suggests that the B which has accumulated in some inland peat lower layers (AS-3 and AS-4 samples) is derived from sea water.

It is unclear how sea water infiltrated the lower layers of inland peat. Figure 6 shows the peat profile examined in the field of the Sg. Talau Peat Research Station in Sarawak, and shows typical features of tropical woody peat. Many morphological features of Southeast Asian tropical woody peat profiles have been examined in detail. In all inland peat, large amounts of various sized woody fragments are buried in deep layers below the stable water table, usually at 40 to 60 cm depth. The branches, twigs, trunks, and roots of trees have piled-up in a lattice-like structure in the lower layer of the inland peat. As a result, many gaps of various sizes exist in the lower layers. Water can go flow in and out of these lower layer gaps.

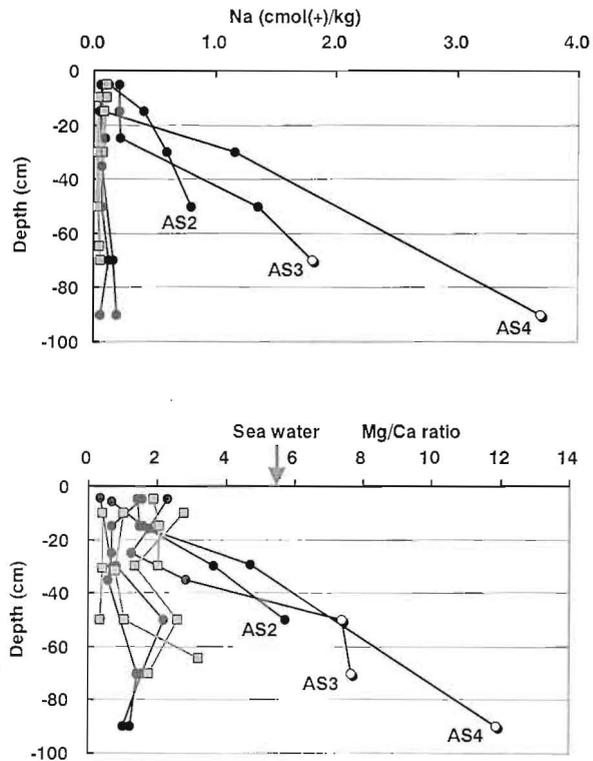


Fig. 5. Vertical profiles of water soluble Na contents (a) and water soluble Mg/Ca ratios of peat soils (b) of marginal peat deposits (squares) and inland peat deposits (circles).

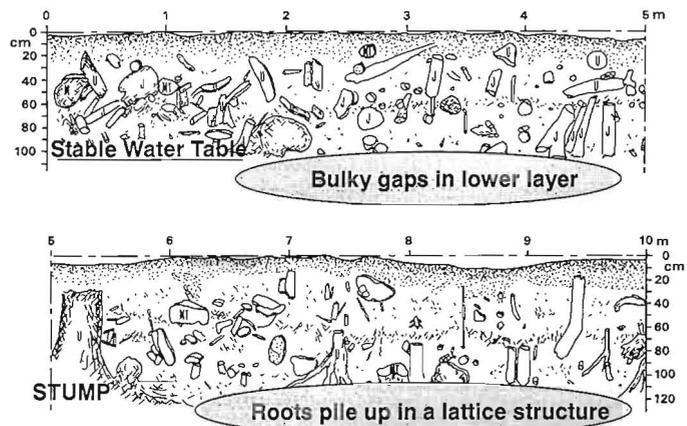


Fig. 6. Typical profile of tropical woody peat (Sg. Talau Peat Research Station, Mukah, Sarawak)

Sea water appears to have infiltrated through the bulky gaps of lower peat from the pressure of the flood-tide. This invasion and retreat of sea water in the lower peat layers appears to follow the ebb and flow of the tides. Various base ions in the sea water are adsorbed with the cation exchange units in the peat materials, and are extracted in the water dissolving part of the cation by dissociation.

In general, B is adsorbed by the clay minerals and hydroxide of Al or Fe, and organic substances in the soil (Keren and Bingham, 1985). The inland peat contains hardly any clay minerals or Al hydroxide. Sea water derived B appears to have adsorbed to the iron hydroxide and/or the organic substances, especially carbohydrates, by forming borate-diol complexes. B complexed with cis-diol of carbohydrates can be easily extracted in mannitol solution. The mannitol soluble B content in the marginal peat was small, averaging 7.4% of the total B content. The mannitol soluble B content of inland peats of all layers except for two layers deeper than 40 cm of AS-4 sample, averaged 14% of the total B content. It averaged 12% of the total B content in the lower layers of AS-4 sample. Therefore, it is unlikely that borate-diol complexes selectively adsorbed the B in the lower layers of inland peat. Because $B(OH)_3$ is the dominant species in low pH (Keren and Bingham, 1985) tropical peat, it can be assumed that most of the B adsorbed on the surface of the peat as the molecule of $B(OH)_3$.

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