

**TRACE ELEMENTS IN RIVERS DRAINING TROPICAL PEAT SWAMP  
FORESTS**

Dissertation

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## Abstract

Tropical peat swamp forests are ecosystems characterized by the presence of peat, a type of soil formed from the accumulation of partially decomposed organic matter in coastal lowland areas. Tropical peat swamps cover an area of about  $248 \times 10^3 \text{ km}^2$  in southeast Asia, accounting for about 77% of the terrestrial organic carbon reservoir in tropical peatlands. Globally, they account for about 11-14% of the total carbon stored in all peatlands. These unique ecosystems are increasingly threatened by anthropogenic activities such as land-use change, excavation of drainage canals, deforestation, and bush burning. An example of such activity is converting tropical peat swamp forests to oil palm plantations for economic gains with the potential risk of converting them from sinks to carbon sources. However, not much is known about the influence of these anthropogenic activities on the export of trace elements, nutrients and dissolved organic carbon (DOC) from tropical peat swamp forests to the estuaries and coastal waters. Hence, there is a need to explore the interplay of anthropogenic activities and trace element biogeochemistry from the estuaries to coastal waters and the ocean.

This study investigated the following key issues: (1) trace element dynamics in rivers and estuaries draining tropical peat swamps on Borneo Island, (2) the influence of estuarine processes as well as DOC on the distribution and concentration of trace elements, (3) the influence of changes in seasonal climatic conditions on DOC, nutrient, and trace element fluxes from pristine peat swamp forests to blackwater rivers and estuaries, (4) the influence of anthropogenic activities on trace element export from tropical peat swamp forests in Kuala Langat District and (5) the effect of water properties (salinity, pH and DOC concentration) on the export efficiency of trace elements to coastal waters. The study focused on the following bio-essential elements, iron (Fe), manganese (Mn), cobalt (Co), silicon (Si), copper (Cu), nickel (Ni), molybdenum (Mo), and ammonium ( $\text{NH}_4^+$ ) and non-essential or elements that are toxic at elevated concentrations, arsenic (As), mercury (Hg), chromium (Cr), aluminum (Al), and uranium (U) and barium (Ba). The interaction of DOC with trace elements.

In Maludam, Sebuyau and Belait estuaries, our observations indicate acidic conditions ( $\text{pH} = 3.3$ ) and high DOC concentrations ( $3500 \mu\text{mol L}^{-1}$ ) at salinities  $<1$ . The influence of redox chemistry, where Mn and Fe oxyhydroxides undergo reductive dissolution under acidic conditions to form Mn(II) and Fe(II). The reductive dissolution of oxides may thus have accounted for enhanced trace

element concentrations at the head of the estuary. There was an initial release of trace elements at low salinity ( $0.05 < S < 0.5$ ) caused by the protonation of particle surface sites and competition with seawater cations. With increasing pH, and at intermediate salinities ( $0.5 < S < 10$ ), there was a gradual scavenging or removal of trace metals onto particles. The combined effect of pH, salinity and oxygen during the mixing of fresh and seawater would have initiated the oxidation of reduced Mn(II) and Fe(II), leading to flocculation of colloidal materials, co-precipitation and trace element scavenging onto particle surfaces. The concentration and flux of trace elements, DOC and nutrients in Maludam, Sebuyau and Belait estuaries were determined by catchment area, runoff volume, and seasonal variability in the transport of suspended materials. Peak concentrations of Al ( $24.9 \mu\text{mol kg}^{-1}$ ), Si ( $96.2 \mu\text{mol kg}^{-1}$ ), Mn ( $4.9 \mu\text{mol kg}^{-1}$ ), Cu ( $0.035 \mu\text{mol kg}^{-1}$ ) and Ni ( $0.047 \mu\text{mol kg}^{-1}$ ), Mo ( $68.5 \text{ nmol kg}^{-1}$ ), Co ( $26.7 \text{ nmol kg}^{-1}$ ), Cr ( $19.4 \text{ nmol kg}^{-1}$ ), U ( $7.6 \text{ nmol kg}^{-1}$ ), Ba ( $79.1 \text{ nmol kg}^{-1}$ ) were observed during the dry season (July), while the concentrations of Fe ( $43.2 \mu\text{mol kg}^{-1}$ ), As ( $44.4 \text{ nmol kg}^{-1}$ ), Hg ( $0.07 \text{ nmol kg}^{-1}$ ), and  $\text{NH}_4^+$  ( $45000 \mu\text{mol kg}^{-1}$ ) were highest during the wet season (December). The NICA-Donnan model was used to investigate the combined impact of DOC and pH on the formation of solid iron hydroxide ( $\text{Fe}(\text{OH})_3(\text{s})$ ). The Maludam River was predicted to be supersaturated for Fe hydroxides, and the field results affirmed our model prediction. The output showed Fe and Cu had a strong affinity for DOC and, to a lesser extent, Al and Ni in the conditions prevailing at the study sites. These findings indicated that fluxes of trace metals from the Borneo estuaries are high during the boreal winter, when flow through the Karimata Strait is a main component of the Indonesian Throughflow, indicating that peat swamp forests in western Borneo are potentially a major source of trace metals to the Indian Ocean.

In the peninsular Malaysia Kuala Langat district, enhanced DOC concentrations ( $12000 \mu\text{mol L}^{-1}$ ) were observed in a natural peat, while the disturbed sites (PC3) on Carey Island indicated low DOC concentration ( $530 \mu\text{mol L}^{-1}$ ). Compared to the natural peat, increased trace element concentrations were observed in the disturbed peat, especially at stations on Carey Island. The observed increase may be related to anthropogenic influence and catchment chemistry. Porewater data obtained from the natural, transition zone, and disturbed peat indicated enhanced trace element concentrations in the disturbed peat compared to the natural peat swamp forests. The mixing experiment results also indicated an increased trace element concentration in the disturbed peat, especially for Mn, Al, Cr, and Fe, compared to the natural peat. The NICA-Donnan model predicted the trace element association with dissolved organic matter (DOM). The experimental

data confirmed a strong association between DOM and trace elements, especially Fe, Al, Cu, Cr, and U. The triangle of master variables (pH-salinity-DOM), as well as Fe and Mn oxyhydroxides, play an essential role in regulating the geochemical cycling of trace elements. The findings of this study suggest that the destruction of peat swamps through peat drainage and canals releases organic matter and trace elements stored over time into the estuaries. However, further studies would be required to unravel the interplay between peat conversion, trace elements, and DOC fluxes.