https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

Biogeosciences Discussions
Open Access
EGU

Distribution and Flux of Dissolved Iron of the Rajang and Blackwater Rivers at Sarawak, Borneo

Xiaohui Zhang[1], Moritz Müller[2], Shan Jiang[1], Ying Wu[1], Xunchi Zhu[3], Aazani Mujahid[4], Zhuoyi Zhu[1], Mohd Fakharuddin Muhamad[4], Edwin Sien Aun Sia[2], Faddrine Holt Ajon Jang[2], Jing Zhang[1]

[1]State Key Laboratory of Estuarine and Coastal Research, East China Normal University, 200241 Shanghai, China

[2]Swinburne University of Technology, Faculty of Engineering, Computing and Science, 93350 Kuching, Sarawak, Malaysia

[3]School of Ecological and Environmental Sciences, East China Normal University, 200241 Shanghai, China

[4]Faculty of Resource Science & Technology, University Malaysia Sarawak, 94300, Sarawak, Malaysia

Correspondence to: Xiaohui Zhang (52163904020@stu.ecnu.edu.cn)

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

Biogeosciences Discussions Open Access EGU

Abstract Dissolved iron (dFe) is essential for biogeochemical reactions in oceans, such as photosynthesis, respiration and nitrogen fixation. Currently, large uncertainties remain on riverine dFe inputs, especially for tropical rivers in Southeast Asia. In the present study, dFe concentrations and distribution along the salinity gradient in the Rajang River in Malaysia, and three blackwater rivers draining from peatlands, including the Maludam River, the Sebuyau River, and the Simunjan River, were determined. In the Rajang River, the concentration of dFe in fresh water (salinity<1) in the wet season (March 2017) was higher than that in the dry season (Auguest 2016), which might be related to the resuspension of sediment particles and soil erosions from cropland in the watershed. In the Rajang Estuary, an intensive removal of dFe in low salinity waters (salinity<15) was observed, likely due to the salt-induced flocculation and the absorption onto suspended particulate matters (SPM). However, dFe concentration enhancements in the wet season occured in some sampling sites, which may be related to the desorption from SPM and agriculture activities. On the other hand, dFe was conservatively distributed in high salinity waters (salinity>15), which may result from the association between dFe and pelagic organic matters. In the blackwater rivers, concentrations of dFe reached 44.2 μmol L^{-1}, indicating a great contribution from peatland. The dFe flux derived from the Rajang Estuary to the South China Sea was $(6.4\pm2.3)\times10^5$ kg yr^{-1}. For the blackwater river, the dFe flux was approximately $(1.1\pm0.5)\times10^5$ kg yr^{-1} in the Maludam River. The anthropogenic activities may play an important role in the dFe yield, such as the Serendeng tributary of the Rajang River, and Simunjan River, where intensive oil palm plantations were observed.

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

1. Introduction

Iron (Fe) is an essential element for enzymes and deemed to be responsible for photosynthesis, respiration, and nitrogen fixation (Moore et al., 2009; Raven, 2010; Williams, 1981). In the past four decades, Fe has been identified as micronutrient, significantly supporing primary productivity in oceans (Brand and Sunda, 1983; Moore et al., 2009; Tagliabue et al., 2017). In particular, after a series of *in-situ* fertilization experiments, researchers verified the Fe limitation on the growth of phytoplankton and the critical role in the CO_2 fixation (Boyd et al., 2007; de Baar et al., 2005; Martin, 1990).

On a global scale, the riverine dissolved iron (dFe) transported to coastal oceans is estimated to be 1.5×10^9 mol yr^{-1} (Boyd and Ellwood, 2010; de Baar and de Jong, 2001; Jickells et al., 2005; Milliman and Farnsworth, 2011; Saitoh et al., 2008). Tropical rivers might contribute a significant amount of dFe based on studies from the Amazon River (Bergquist and Boyle, 2006; Gaillardet et al., 1997), and the Congo River (Coynel et al., 2005; Dupré et al., 1996). However, few studies have assessed dFe concentrations and transport in tropical rivers in Southeast Asia, even though those rivers can account for about 30% of fluvial discharge to oceans (Milliman and Farnsworth, 2011).

Estuaries, as the interaction zone between surface water and coastal oceans, could fundamentaly modulate dFe concentrations during the mixing, and hence change the magnitude of riverine dFe flux. There is a large volume of published studies on the behaviors of dFe in a wide range of estuaries (Boyle et al., 1977; Herzog et al., 2017; Oldham et al., 2017; Zhu et al., 2018). In particular, some estuarine environments are enriched with organic matters because of high primary productivity and terrestrial loading, as well as the great contributions from salt marshes and peatlands. These organic matters may deeply affect the distribution of riverine solutes (Hedges et al., 1997; Müller et al., 2015). Generally, estuaries act as a sink for dFe due to the flocculation between the cations and the high molecular colloids (Bergquist and Boyle, 2006; Boyle et al., 1977; Stolpe and Hassellov, 2007). The magnitude of dFe removal in the estuary can be quantified by removal factors (RF). However, in some rivers with high concentrations of dissolved organic matters (DOM), conservative distribution of dFe was found, because of the chemical connection of Fe to DOM (Oldham et al., 2017; Sanders et al., 2015; Stolpe et al., 2010). More importantly, large populations in estuaries are frequently observed. Anthropogenic activities, such as coal mining, ore industry, and agriculture activities, could

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

significantly impact concentrations and distributions of dFe in estuaries (Braungardt et al., 2003; Morillo et al.,2005; Xue et al., 2016).

Currently, only limited records on the dFe concentrations were provided in peatland draining rivers (Batchelli et al., 2010; Krachler et al., 2010; Oldham et al., 2017). The dFe distribution in the peatland draining estuaries is also largely unknown. Southeast Asia hosts a large area of peatlands along the coastal belts, with a coverage of approximately 9% on a global scale (Dommain et al., 2011; Joosten, 2012). For dFe research in Malaysia, to the authors' best knowledge, the dFe concentration was only determined (1) in the fresh water at Pelagus, where the high concentration of dFe was observed, resulting from sediment diffusion (Siong, 2015); (2) in Bebar, a blackwater river in Pahang, Malaysia, the concentration of dFe was up to 30 μmol L^{-1}, but the information about the distribution and biogeochemistry of dFe was missing (Shuhaimiothman et al., 2009). Such knowledge limitation may markedly influence the regional dFe budget estimation.

To fill this gap, two cruises were conducted in Sarawak state, Borneo, Malaysia, including the largest river in Sarawak State (the Rajang River) and three peat-draining rivers. This study aims to determine (1) the concentration and distribution of dFe, (2) the seasonal variation of dFe in the Rajang River, (3) the dFe yields and the magnitude of riverine fluxes to the coastal areas.

2. Materials and methods

2.1 Study area

Malaysia has the second largest peatland areas (about 2.6×10^4 km^2) in Southeast Asia (Mutalib et al., 1992). Sarawak State accounts for the largest peatland area in Malaysia, and has a wide spread of blackwater rivers (Joosten, 2012; Wetlands International, 2010). Approximately 23% of the peatland is defined as relatively undisturbed in Malaysia, in which 17% are in Sarawak (Wetlands International, 2010). Since the mid-1980s, rubber, textiles, metals, food processing, petroleum, and electronics have been developed, and have become the major economic support in Malaysia (Trade Chakra, 2009). As a response, deforestation rate in Sarawak increased to 2% yr^{-1} from 1990 to 2010 (Miettinen et al., 2012), and this rate is attributed to oil and rubber plantations (Joosten, 2012).

The Rajang River, i.e. the largest river in Malaysia, flows from the Iran Mountain to the South China Sea (Fig. 1a and b), with a length of 530 km. The drainage basin is 5.1×10^4 km^2 (Milliman and

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

Farnsworth, 2011; Staub and Esterle, 1993). The drainage area of the Rajang Estuary is 6,500 km^2, and 50% is covered with extensive peat in a depth of greater than 3 m (Staub and Gastaldo, 2003). The climate in the Rajang watershed is classified as tropical ever-wet type (Morley and Flenley, 1987), while the precipitation varies between dry and wet seasons. Water discharge rate for the Rajang River reaches 6000 m^3 s^{-1} in the wet season (December to March), with an average discharge of about 3600 m^3 s^{-1} (Jeeps, 1963; Staub et al., 2000; Staub and Gastaldo, 2003). Sibu city is assumed to be the boundary between the Rajang drainage basin and the Rajang Estuary (Staub et al., 2000; Staub and Esterle, 1993). Apart from mineral soils from the upper stream, the Rajang Estuary also receives a materials from the adjacent hill regions and the Retus River (Staub and Gastaldo, 2003). There are several tributaries for the Rajang River in the estuary, including Igan, Serendeng, and Rajang. The Igan tributary is the major outlet for freshwater (Jiang et al., 2019). Mangroves distributed in the brackish-water area in the southwestern of the estuary. *Casuarina* was observed in the northeastern and coastal area (Scott, 1985). The thick coverage of vegetation, especially mangroves, in the Rajang Estuary produces the high-ash, high-sulfur, degraded sapric peats (Lampela et al., 2014). Tide is diurnal to semidiurnal type in the Rajang Estuary and could extend to Sibu city (Staub et al., 2000; Staub and Gastaldo, 2003). The range increases from the northeast (1.5 m) to the southwest (2.5 m). Sediments in the Rajang Estuary are composed of gley soils, podzols soils, and alluvia soils (Staub and Gastaldo 2003). Gley consists of mixed-layered illite-smectite, illite, and chlorite. Gley is frequently observed in the central and southwestern part of the estuary (Staub and Gastaldo, 2003). Podzols is gray-white to white clay, which is composed of kaolinite and illite. Podzols is found in some low-lying areas and the landward part of the Rajang Estuary (Staub and Gastaldo, 2003). Alluvial soils, which is made up of illite, smectite, and kaolinite, is found in the landward part of the estuary (Staub and Gastaldo, 2003). The input of total suspended solids from the Rajang River is up to 30 Mt yr^{-1} (Milliman and Farnsworth, 2011).

Peatland-draining rivers (Maludam, Simunjan, Sebuyau) are blackwater rivers, characterized by tea-color, acidic, and oxygen deficit as described by Kselik and Liong (2004). The Maludam River is a pristine river with minor human influences, since the majority of the river is located in the Maludam National Park (the second largest park in Sarawak). The peat thickness in the river bed reaches 10 m (Forest Department, 2014). The catchment of Maludam River is 91.4 km^2 and the average discharge

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

is 4.4±0.6 m^3 s^{-1} (Müller et al., 2015). However, other two blackwater rivers are undergoing severe human activities disturbance, mostly from the plantations of commercial crops like oil palm and sago, as shown in Fig. 1d (Wetlands International, 2010).

2.2 Sample collection and process

The sampling stations are outlined in Fig. 1. The surveys in the Rajang River were conducted in August 2016 (dry season) and March 2017 (wet season). Each survey lasts 4 to 5 days, covering both floolding tides and ebbing tides. The samples include fresh river samples, brackish water in different river tributaries and coastal saline water. In the Rajang watershed, the selection of sampling stations is dependent on the salinity, anthropogenic activities. In March 2017, the blackwater rivers, as aforementioned, were included in the filed. During the cruises, surface water samples were collected, using a pole sampler. The front of the sampler was attached to a 1 L high-density polyethylene bottle (Nalgene). The length of the pole is 3-4 m to avoid the contamination from the ship. Water samples were filtered through acid-cleaned 0.4 μm pore size polycarbonate membrane filters (Whatman) into a polyethylene bottle (Nalgene), then frozen at -20°C, and packed in triple bags. The samples then thawed at room temperature in the clean laboratory and acidified with ultrapure HCl to pH 1.7 in an ultra clean lab. All bottles used in the sample collection and storage were prepared in the clean laboratory, by rinsing with Milli-Q water, immersing in 2% Citranox detergent for 24 h, rewashing with Milli-Q water for 5-7 times, leaching for 7 days in 10% HCl, rinsing with Milli-Q water 5-7 times again, filling 0.06 mol L^{-1} ultrapure HCl for 2 days at 60°C, and sealing in plastic bags.

2.3 Sample analyses

The concentration of dFe was preprocessed using the single batch resin extraction and the isotope dilution method (Lee et al., 2011). It was quantified on a multi-collector inductively coupled plasma mass spectrometer in high-resolution mode (Neptune, Thermo). The inlet system contained an Apex IR desolvator (AEI) with a perfluoroalkoxy microconcentric nebulizer (ESI) at a solution uptake rate of 50 μL min^{-1}. All tubes used for the analyses were acid leached for two days with 10% HCl at 60°C, rinsed 5 times with Milli-Q water, later filled with 0.06 mol L^{-1} ultrapure HCl in a class 100 flow bench, and leached for another 2 days at 60°C. The analytical procedural blank and detection limit (three times the standard deviation of the procedural blank) were both 0.06 nmol L^{-1}. The accuracy

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

of the method was tested by analyzing intercalibration samples including one open ocean SAFe D1 and one estuary water SLEW-3. Measured dFe concentrations for SAFe D1 and SLEW-3 were 0.66±0.05 nmol L^{-1} and 10.0±0.4 nmol L^{-1} compared to consensus values of 0.70±0.03 nmol L^{-1} and 10.2±1.2 nmol L^{-1} (Zhang et al., 2015).

During the field investigation, salinity, temperature, pH, and dissolved oxygen (DO) concentrations were detected *in-situ* with a probe (AP2000, Aquared, U.K.). In the Rajang River, suspended particulate matters (SPM) samples were collected with pre-combusted 0.7 μm pore size Whatman GF/F filters, and SPM concentration was calculated by the weight difference of filters before and after filtration. Dissolved organic carbon (DOC) samples were collected by filtering through 0.2 μm pore size nylon filters. For the samples collected in August 2016, DOC concentrations were determined on an Aurora 1030W total organic carbon analyzer. Reproducibility for concentrations was ±0.2 mg L^{-1}. DOC concentrations were measured at the Centre for Coastal Biogeochemistry at Southern Cross University (Lismore, Australia). For the samples collected in March 2017, DOC concentrations were determined by the high-temperature catalytic oxidation method with Total Organic Carbon Analyzer (Shimadzu), and the coefficient of variation was 2% (Wu et al., 2013).

2.4 The calculation of dFe flux and yield

To estimate the magnitude of dFe flux from tropical rivers to coastal water, the following equation is adopted:

$$Q = C \times V \times (1 - RF) \qquad (1)$$

where Q is dFe flux, C is the mean dFe concentration at freshwater endmember (S<1), V is the river discharge, RF is the removal factor, based on the ratio of the integration area of dFe concentration versus salinity to that of the theoretical dilution line intercepts (Hopwood et al., 2014). Riverine dFe yield is the ratio of dFe flux to the drainage area.

3. Results

3.1 Hydrographic properties in the Rajang and blackwater rivers

In August 2016 (the dry season), the salinity in the Rajang water samples ranged from 0.0 to 32.0, which increased from Sibu city to the coastal zone (Table 1). In March 2017 (the wet season), the salinity varied from 0.0 to 30.1 (Table 1). In Serendeng tributary, some high salinity samples inside

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

the river mouth in the wet season were found. The concentration of SPM ranged from 24.2 mg L^{-1} to 327.2 mg L^{-1}, and decreased from freshwater to seawater, but the highest turbidity water varied among channels and seasons. In August 2016, the SPM peak was observed near the river mouth in Serendeng tributary but moved landward in other tributaries (Fig. 2b). In March 2017, the peak of SPM was located in freshwater in the Rajang tributary. DO in March 2017 (mean: 6.1±0.7 mg L^{-1}) was higher than August 2016 (mean: 3.8±0.6 mg L^{-1}), and decreased along the transportation in the Rajang drainage basin as shown in Fig. 2c. The DO distribution in the Rajang Estuary varied between two seasons. The high value was found in the west estuary in March 2017 (Fig. 2c, 2h). Water pH in the Rajang River increased along the salinity gradient with a mean value of 7.1±0.5 (August 2016) and 7.1±0.6 (March 2017), as outlined in Fig. 2d and 2i.

In blackwater rivers, salinity ranged from 0.0 to 23.5 in the Maludam River and 0.0 to 13.6 in the Sebuyau River. The samples in the Simunjan River are only fresh water. All three blackwater rivers were frequently anoxic (DO < 2 mg L^{-1}). The mixing between river water and ocean water markedly increased DO. Moreover, pH in these blackwater rivers was relatively low, especially in the Maludam River (minimum 3.7). DOC increased steadily in fresh water but decreased sharply in estuaries. The distributions of these properties in blackwater rivers are shown in the Supplement.

3.2 dFe in Rajang and its Estuary

The contour of dFe in the Rajang surface water is shown in Fig. 2. The dFe concentrations in the Rajang freshwater ranged from 2.8 to 7.3 μmol L^{-1} (mean: 5.2±1.8 μmol L^{-1}) in August 2016, and ranged from 4.2 to 8.3 μmol L^{-1} (mean: 6.4±2.0 μmol L^{-1}) in March 2017. In the Rajang Estuary, the concentration of dFe ranged from 1.7 nmol L^{-1} to 7.0 μmol L^{-1} (mean: 1.1±2.2 μmol L^{-1}) and 4.2 nmol L^{-1} to 11.3 μmol L^{-1} (mean: 4.2±4.0 μmol L^{-1}) in the dry and the wet season, respectively. The concentration of dFe in the wet season was higher than the dry season both in the Rajang freshwater and the Rajang Estuary.

The relationships between dFe concentrations and other factors, such as salinity, SPM, DOC, DO and pH in the Rajang Estuary can be found in Fig. 3. In the dry season, dFe concentration decreased exponentially in low salinity water (salinity<15) though we did not include the tidal influence. A linear relationship was found between dFe and SPM in low salinity area (R^2=0.29, p<0.05). In the high salinity area (S>15), dFe tended to be conservative (Fig. 3a), and displayed a linear relationship

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

with DOC (R^2=0.45, p<0.05), DO (R^2=0.50, p<0.05), and pH (R^2=0.39, p<0.05). In the wet season, dFe concentration was higher in the Igan tributary compared to other two branches. There was an intensive dFe addition between salinity 5-15, mainly in the Serendeng tributary (Fig. 3a). Specifically, the linear correlation between dFe and SPM was found in the water samples when salinity was <15 in the wet season (R^2=0.11, p<0.05) (Fig. 3b), especially in the Serendeng distributary. Moreover, a significant positive relationship between dFe and DOC was also identified in the wet season in low salinity water (R^2=0.61, p<0.001) (Fig. 3c). DO was negatively correlated with dFe in high salinity area (R^2=0.97, p<0.001), with a similar pattern in the dry season. The relationship between pH and dFe was insignificant in the wet season.

3.3 dFe in blackwater rivers

The average dFe concentration in three blackwater rivers were 14.6±6.7 μmol L^{-1} (the Maludam River), 44.2±11.8 μmol L^{-1} (the Simunjan River), and 17.6±12.0 μmol L^{-1} (the Sebuyau River). The dFe concentration increased along the river flow (Fig. 4a), but decreased during the mixing. The distribution of dFe in blackwater rivers tended to be conservative in the estuary of Maludam and Sebuyau (Fig. 4b), which was different from the pattern in the Rajang Estuary. Moreover, there was a significant positive correlation between dFe and DOC in the blackwater rivers (Fig. 4c), except the Maludam River because of low DOC in high salinity region (S=20.0).

4. Discussion

4.1 Seasonal variation of dFe in the Rajang freshwater

In the dry season, dFe concentrations in the Rajang water (near the Sibu city) ranged from 2.8 to 7.3 μmol L^{-1}. In the wet season, dFe concentrations increased (Fig. 2). Considering the limited temperature variation in the tropical zone, the dFe elevation may be related to the stronger weathering derived from intensive precipitations. In particular, once precipitations elevated (in the wet season), water mass from the upper stream scoured the soils along the river banks, carring the Fe-enriched terrestrial particles to the down stream (Meade et al., 1985; Taillefert et al., 2000). Moreover, the agriculture activities in the watershed, such as tillage, can result in the rapid leaching in the wet season (Lehmann and Schroth, 2003; Tabachow et al., 2001), especially in 2017 (the occurance of La Niná events) (Jiang et al. 2019). Additionaly metal elements were transported from the catchement to the

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

Rajang River (Johnes and Hodgkinson, 1998; Withers et al., 2001). In addition, the changes of soil structure during agriculture activities can influence the exchange route of dissolved matters in vertical profiles; hence the large proportion of dFe is likely to be transported during the rainfull via water exchanges (Haygarth et al., 1998; Johnes and Hodgkinson, 1998). Such dFe addition from the cropland was also observed in many other study areas, like the Krishna river drainage area (Kannan, 1984), the Palar and Cheyyar river basin (Rajmohan and Elango, 2005), and the Guadalquivir River (Lorite-Herrera and Jiménez-Espinosa, 2008). Eventually, the terrestrial -borne dFe injected into the Rajang River via hydrological connections in the riparian ditches, and hence contributed quantities of dFe to rivers from terrestrial runoff and flood discharges (Yan et al., 2016).

4.2 dFe in the Rajang Estuary

In the Rajang Estuary, there was an intensive removal of dFe when the salinity < 15, especially in the dry season (Fig. 3a). This may be mainly related to the flocculation of the negatively charged colloids with cations in the fresh-saline water mixing. This has been observed in many rivers and simulation experiments (Boyle et al., 1977; Oldham et al., 2017; Zhu et al., 2018). Furthermore, dFe was negatively correlated with SPM in low salinity waters (Fig. 3b), indicating that the dFe removal may also be linked to the absorption of SPM as described by other researches (Beusekom and Jonge, 1994; Homoky et al., 2012; Zhang et al., 1995). However, there was exceptionally high dFe concentration at salinity 5-15 in the Serendeng tributary in the wet season. On the one hand, it may result from peatland soils in the adjacent area, because the peatland soils host abundant dFe and organic ligand, and these organic compounds could enhance the solubility of Fe during the transport (Krachler et al., 2010; Oldham et al., 2017; Shuhaimiothman, 2009). On the other hand, there could be other processes for dFe addition in the Rajang Estuary, such as the desorption of SPM-bounded Fe to the river water. The balance between adsorption and desorption of trace metal ions onto/from SPM is complicated. These two processes could occur simultaneously and be influenced by different environmental conditions, like SPM content, pH, salinity, and adsorption strength between ions and SPM (Hatje et al., 2003; Jiann et al., 2013; Zhang et al., 2008). It has been confirmed that the partition coefficient of dFe decreased with increasing SPM concentration, and became inversely proportional to the SPM concentration, termed as particle concentration effect (Benoit, 1995; Jiann et al., 2013; Turner and Millward, 2002). Furthermore, Zhu et al. (2018) suggested that desorption from particles was the

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

main reason for dFe enhancement in the river mouth of the Changjiang. Although we didn't conduct any adsorption/desorption experiments in these cruises, we could deduce that the great dFe increase at salinity 5-15 in the wet season may be also related to the desorption because of the high SPM content. Moreover, the samples in these area was collected during a spring tide, and the high concentration of SPM was within the range of the result in the Texas river (Jiann et al., 2013) and some observations in the Changjiang estuary (Zhu et al., 2018), where dFe enhancements resulted from the desorption of SPM. Furthermore, the intensive agricultural activities in the Serendeng distributary changed the soil structure and contributed a considerable amount of SPM at flood tide, which may stimulate the dFe desorption.

In the high salinity zone (S>15), the dFe tended to be conservative. The positive relationship between dFe and DOC in the dry season (Fig. 3c) may be a mirror of the chemical association of dFe and DOM. Specifically, the combination betwen dFe and organic matter, especially the pelagic organic matter, can resist to salt-induced aggregation and lead to an input of bioavailable dFe to the coastal zone (Breitbarth et al., 2009; Krachler et al., 2005; Stolpe and Hassellov, 2007).

The multiple linear regression analysis of dFe and environmental factors, including salinity, SPM, DOC, DO, and pH (dry season: R^2=0.52, p<0.05; wet season: R^2=0.73, p<0.05), was also used to explore the observed patterns. It showed that salinity and SPM were the main factors for the distribution of dFe in the Rajang Estuary (p<0.05). For pH, the correlation between dFe and pH was limited in the wet season, suggesting a little impact of pH on dFe. In the dry season, the concentration of dFe was negatively correlated with pH (Fig. 3e), becasue Fe-enriched sediments can be acidized and mineralized by inorganic acids (H_2CO_3, HNO_3, and H_2SO_3) and organic acids (oxalic acid, citric acid, and siderophore) generated from the chemical weathering and biological progress (Banfield et al., 1999; Lerman et al., 2007). The biogeochemical behavior of dFe in the Rajang River that we discussed above is summarized and conceptualized in Fig. 6a.

4.3 dFe in blackwater rivers

In blackwater rivers, the dFe was accumulated from the upper stream to the downstream before mixing. In the mixing zone, high concentrations of dFe were rapidly diluted (Fig. 4b). As evidenced by the water color, these peat-draining rivers are characterized by extremely high levels of terrigenous DOM (Martin et al., 2018; Zhou et al., 2018).Given such high concentrations of DOM and the positive

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

correlation between dFe and DOC (Fig. 4c), peatland should be a strong source for dFe. Consequently, the gradual enrichment of dFe along the rivers was observed. Compared with the Maludam River, i.e. the drainage from an undisturbed peatland, dFe concentrations in the Sebuyau River and the Simunjan River were significantly higher (Table 1). The difference in the dFe concentration among three blackwater rivers may come from the variation of environmental parameters around the drainage basin, especially the vegetation types and anthropogenic activities. The palm oil plantations covered a significant area in the watershed of the Sebuyau River and Simunjan River, as shown in Fig. 1d. In order to stimulate seedings in plantations, the empty fruit bunches and the palm oil mill effluent were returned to the cropland after oil extraction (Carron et al., 2015; Nelson et al., 2015), indicating an enhancement in terrestrial organic matter. The intensive agriculture activities, such as tillage, also facilitated the transport of terrestrial dFe into the Sebuyau River and the Simunjan River as discussed in chapter 4.1.

During the cruise, the high salinity samples were not obtained in the Maludam and Sebuyau rivers. For the samples with the salinity range from 0 to 20, the dFe removal is insignificant, which is markedly different from the trend obtained in the Rajang Estuary (Fig. 4b). The significant positive correlation between dFe and DOC concentration reinforced the tight connection between dFe and organic ligands in blackwater rivers (Fig. 4b). Recent studies have also pointed out that organic ligands originating from peatland enhanced the iron-carrying capacity of the river water (Krachler et al., 2005; Oldham et al., 2017). Approximately 20% of dFe didn't flocculate during a laboratory mixing experiment (Krachler et al., 2010). The biogeochemical behavior of dFe in blackwater rivers that we discussed above is summarized and conceptualized in Fig. 6b.

4.4 dFe fluxs and yields

For the Rajang River, the mean dFe concentration at the river endmember of two seasons was 5.5±2.0 μmol L^{-1}, and mean removal factor was 98.0±0.6%. Removal factor of dFe varied on a global scale. The Rajang RF was predominant among the recent results (Table 2). Coupled with the discharge rate (about 3600 m^3 s^{-1}), the dFe flux from the Rajang River was estimated to be (6.4±2.3)×10^5 kg yr^{-1} besed on the equation (1). For the Maludam River, the concentration of river endmember was 14.6±6.8 μmol L^{-1}, and RF=0 due to the conservative distribution. The dFe flux in the Maludam River was approximately (1.1±0.5)×10^5 kg yr^{-1}, produced from 432 km^2 peatland in the Maludam National

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

Park. It is the same magnitude with the Rajang dFe flux, suggesting that the dFe input were considerable in blackwater rivers. Malaysia hosts peatland area about 25,889 km^2, the dFe flux can be $(6.6\pm3.0)\times10^6$ kg yr^{-1} on the basis of the yield from the Maludam River. Consequently, the blackwater rivers contributed 10 times greater dFe than the Rajang River to the coastal zone in Malaysia, even though their discharges are small (Milliman and Farnsworth, 2011). This terrestrial dFe may play an important role in supporting primary producers in the adjacent ocean (Breitbarth et al., 2009; Laglera and Berg, 2009).

The concentration and yield of dFe varied among tropical rivers as shown in Fig. 5. Compared with subtropical rivers, like the Changjiang (Zhu et al., 2018) and the Mississippi River (Shiller, 1997; Stolpe et al., 2010), the tropical rivers contributed a great amount of dFe, such as the Amazon River (Aucour et al., 2003; Bergquist and Boyle, 2006) and the Congo River (Coynel et al., 2005; Dupré et al., 1996). For rivers hold a similar discharge rate and drainage area with the Rajang River, like the Fraser River, a temperate river in Canada, dFe concentrations and yield was significantly lower than that derived from the Rajang River (Cameron et al., 1995). One reason for the high concentration and yield in tropical rivers likely results from intensive weathering, leaching of the rocks and sediments, and abundant plantations under high temperature and heavy precipitations (Bergquist and Boyle, 2006; Fantle and Depaolo, 2004). Compared with other tropical rivers, such as the Amazon River and the Congo River, the dFe concentration in the Rajang River was similar, however dFe yield was lower in the Rajang River. This may be related to the difference of plantation types (Aucour et al., 2003; Coynel et al., 2005; Dupré et al., 1996). The peatland soils in the Rajang Estuary may contribute to the higher dFe yield, as the Niger River passing through a dry savanna (Picouet et al., 2002). Different from the Niger River, the Senaga River drains from a savannah-rainforest area, and contains a considerable amount of SPM, similar to the Rajang River. The dFe yield was comparable with the Rajang River. As for some small tropical rivers, like the Swarna River (Tripti et al., 2013), the Nyong River (Oliviéé-Lauquet et al., 1999), the Periyar River (Maya et al., 2007) and the Chalakudy River (Maya et al., 2007), the dFe concentration was similar to the Rajang River, but with higher dFe yields and DOC concentrations. In these small tropical rivers, the drainage basins were covered with organic matter enriched sediments, which may be a great source of dFe.

In blackwater rivers, the dFe concentration and yield were much higher than the records from Rajang

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

River. The high concentration of DOM is likely to be the main reason of high dFe contents in the blackwater rivers, such as the situations in the Kiiminkijo River (Heikkinen, 1990), the Tannermoor River (Krachler et al., 2005), the Halladale River (Krachler et al., 2010), the Bebar River (Gastaldo, 2010), and the Taieri River (Hunter, 1983) (Fig. 5b). The human impacts, such as agricultural activities and the plantations of oil palm, may also contribute to a bulk of dFe to the blackwater rivers.

5. Conclusions

In this study, dFe was investigated in the Rajang River and three blackwater rivers in Sarawak, Malaysia. The conclusions are as follow:

1. There was a significant seasonal variation of dFe concentration in the Rajang freshwater with a higher dFe concentration in the wet season, likely due to the increased leaching and terrestrial erosion. The dFe removal was intensive in low salinity area (salinity<15) of the Rajang Estuary due to the salt-induced flocculation and absorption onto the SPM. On the contrary, dFe tended to be conservative in the high salinity area (salinity>15), which may be due to the binding between dFe and the organic matter. In addition, there were significant additions of dFe in some tributaries due to the desorption of SPM and anthropogenic inputs.
2. The concentration of dFe in the blackwater rivers was 3-10 times higher than that of the Rajang River, which was related to the contribution of peatland soil. Anthropogenic activities in the watershed also influenced the dFe concentration in blackwater rivers. Different from the pattern observed in the Rajang River, there wasn't remarkable dFe removal in blackwater river estuaries.
3. The dFe yield in blackwater rivers was much higher than that of the Rajang River. This result indicated that the dFe flux from blackwater rivers can be crucial for coastal zones in Malaysia.

This study improved the understanding of dFe distribution in the Rajang River and confirmed its regional influence. In addition, we provided the direct evidence that blackwater rivers had an extremely high yield of dFe. Furthermore, anthropogenic activities may have a critical impact on the concentration and distribution of dFe in these tropical rivers in Malaysia.

Acknowledgment

The present study was kindly funded by the National Natural Science Foundation of China (41476065). Further funding was provided under the MOHE FRGS 15 Grant

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

(FRGS/1/2015/WAB08/SWIN/02/1), SKLEC Open Research Fund (SKLEC-KF201610) and Overseas Expertise Introduction Project for Discipline Innovation (111 Project, B08022). We would like to thank the Sarawak Forestry Department and Sarawak Biodiversity Centre for permission to conduct collaborative research in Sarawak waters under permit numbers NPW.907.4.4 (Jld.14)-161, Park Permit No WL83/2017, and SBC-RA-0097-MM. Thanks to Lukas Chin and the "SeaWonder" crew for their support during the cruises. Technical support by Dr. Patrick Martin and Dr. Gonzalo Carrasco at Nanyang Technological University during the cruises and Ms. Yun Xue, Ms. Shuo Jiang and Ms. Wanwan Cao at East China Normal University in the laboratory analysis are also gratefully acknowledged.

References

Aucour, A.M., Tao, F.X., Moreiraturcq, P., Seyler, P., and Sheppard, S.: The Amazon River: behaviour of metals (Fe, Al, Mn) and dissolved organic matter in the initial mixing at the Rio Negro/Solimões confluence, Chemical Geology, 197, 271-285, 2003.

Banfield, J. F., Barker, W. W., Welch, S. A., and Taunton, A.: Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere, Proceedings of the National Academy of Sciences of the United Station of America, 96, 3404-3411, 1999.

Batchelli, S., Muller, F. L. L., Chang, K. C., and Lee, C. L.: Evidence for strong but dynamic iron−humic colloidal associations in humic-rich coastal waters, Environmental Science & Technology, 44, 8485-8490, 2010.

Bergquist, B. A. and Boyle, E. A.: Iron isotopes in the Amazon River system: weathering and transport signatures, Earth & Planetary Science Letters, 248, 54-68, 2006.

Benoit, G.: Evidence of the particle concentration effect for lead and other metals in fresh waters based on ultraclean technique analyses, Geochimica et Cosmochimica Acta, 59, 2677-2687, 1995.

Beusekom, J. E. E. V. and Jonge, V. N. D.: The role of suspended matter in the distribution of dissolved inorganic phosphate, iron and aluminium in the Ems estuary, Netherland Journal of Aquatic Ecology, 28, 383-395, 1994.

Boyd, P. W. and Ellwood, M. J.: The biogeochemical cycle of iron in the ocean, Nature Geoscience,

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

3, 675, 2010.

Boyd, P. W., Jickells, T., Law, C. S., Blain, S., Boyle, E. A., Buesseler, K. O., Coale, K. H., Cullen, J. J., Baar, H. J. W. D., and Follows, M.: Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions, Science, 315, 612-617, 2007.

Boyle, E., Collier, R., Dengler, A. T., Edmond, J. M., Ng, A. C., and Stallard, R. F.: On the chemical mass-balance in estuaries, Geochimica Et Cosmochimica Acta, 38, 1719-1728, 1974.

Boyle, E. A., Edmond, J. M., and Sholkovitz, E. R.: The mechanism of iron removal in estuaries, Geochimica Et Cosmochimica Acta, 41, 1313-1324, 1977.

Brand, L. E. and Sunda, W. G.: Limitation of marine phytoplankton reproductive rates by zinc, manganese, and iron, Limnology & Oceanography, 28, 1182-1198, 1983.

Braungardt, C. B., Achterberg, E. P., Elbaz-Poulichet, F., and Morley, N. H.: Metal geochemistry in a mine-polluted estuarine system in Spain, Applied Geochemistry, 18, 1757-1771, 2003.

Breitbarth, E., Gelting, J., Walve, J., Hoffmann, L. J., Turner, D. R., Hassellöv, M., and Ingri, J.: Dissolved iron (II) in the Baltic Sea surface water and implications for cyanobacterial bloom development, Biogeosciences, 6, 2397-2420, 2009.

Bruland, K. W., Lohan, M. C., Aguilar-Islas, A. M., Smith, G. J., Sohst, B., and Baptista, A.: Factors influencing the chemistry of the near-field Columbia River plume: Nitrate, silicic acid, dissolved Fe, and dissolved Mn, Journal of Geophysical Research Oceans, 113, 2008.

Cameron, E. M., Hall, G. E. M., Veizer, J., and Krouse, H. R.: Isotopic and elemental hydrogeochemistry of a major river system: Fraser River, British Columbia, Canada, Chemical Geology, 122, 149-169, 1995.

Carron, M. P., Auriac, Q., Snoeck, D., Villenave, C., Blanchart, E., Ribeyre, F., Marichal, R., Darminto, M., and Caliman, J. P.: Spatial heterogeneity of soil quality around mature oil palms receiving mineral fertilization, European Journal of Soil Biology, 66, 24-31, 2015.

Coynel, A., Seyler, P., Etcheber, H., Meybeck, M., and Orange, D.: Spatial and seasonal dynamics of total suspended sediment and organic carbon species in the Congo River, Global Biogeochemical Cycles, 19, GB4019, 2005.

de Baar, H. J. W., Boyd, P. W., Coale, K. H., Landry, M. R., Tsuda, A., Assmy, P., Bakker, D. C. E., Bozec, Y., Barber, R. T., and Brzezinski, M. A.: Synthesis of iron fertilization experiments: from

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

the iron age in the age of enlightenment, Journal of Geophysical Research Oceans, 110, C09S16, 2005.

de Baar, H.J.W., de Jong, J.T.M.: Distributions, sources and sinks of iron in seawater. In: Turner D.R., Hunter K.A., editors. The Biogeochemistry of Iron in Seawater, vol 7. IUPAC Series on analytical and physical chemistry of environmental systems; 2001. p. 123–234.

Dommain, R., Couwenberg, J., and Joosten, H.: Development and carbon sequestration of tropical peat domes in South-east Asia: links to post-glacial sea-level changes and Holocene climate variability, Quaternary Science Reviews, 30, 999-1010, 2011.

Dupré, B., Gaillardet, J., Rousseau, D., and Allègre, C. J.: Major and trace elements of river-borne material: the Congo Basin, Geochimica Et Cosmochimica Acta, 60, 1301-1321, 1996.

Fantle, M. S. and Depaolo, D. J.: Iron isotopic fractionation during continental weathering, Earth & Planetary Science Letters, 228, 547-562, 2004.

Forest Department Sarawak: National Parks: available at: www.forestry.sarawak.gov.my/modules/web/pages.php?mod=webpage&sub=page&id=1012&menu_id=0&sub_id=257 (last access: 20 June 2018), 2014.

Gaillardet, J., Dupre, B., Allegre, C. J., and Négrel, P.: Chemical and physical denudation in the Amazon River Basin, Chemical Geology, 142, 141-173, 1997.

Gastaldo, R. A.: Peat or no peat: Why do the Rajang and Mahakam Deltas differ? International Journal of Coal Geology, 83, 162-172, 2010.

Guieu, C., Huang, W. W., Martin, J.-M., and Yong, Y. Y.: Outflow of trace metals into the Laptev Sea by the Lena River, Marine Chemistry, 53, 255-267, 1996.

Hatje, V., Payne, T. E., Hill, D. M., McOrist, G., Birch, G. F., and Szymczak, R.: Kinetics of trace element uptake and release by particles in estuarine waters: effects of pH, salinity, and particle loading, Environment International, 29, 619-629, 2003

Haygarth, P. M., Hepworth, L., and Jarvis, S. C.: Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland, European Journal of Soil Science, 49, 65-72, 1998.

Hedges, J. I., Keil, R. G., and Benner, R.: What happens to terrestrial organic matter in the ocean? Organic Geochemistry, 27, 195-212, 1997.

Heikkinen, K.: Seasonal changes in iron transport and nature of dissolved organic matter in a humic

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

river in northern Finland, 1990.

Herzog, S. D., Persson, P., and Kritzberg, E. S.: Salinity effects on iron speciation in boreal river waters, Environmental Science & Technology, 51, 9747-9755, 2017.

Homoky, W. B., Severmann, S., Mcmanus, J., Berelson, W. M., Riedel, T. E., Statham, P. J., and Mills, R. A.: Dissolved oxygen and suspended particles regulate the benthic flux of iron from continental margins, Marine Chemistry, 134-135, 59-70, 2012.

Hopwood, M. J., Statham, P. J., and Milani, A.: Dissolved Fe (II) in a river-estuary system rich in dissolved organic matter, Estuarine Coastal & Shelf Science, 151, 1-9, 2014.

Hunter, K. A.: On the estuarine mixing of dissolved substances in relation to colloid stability and surface properties, Geochimica Et Cosmochimica Acta, 47, 467-473, 1983.

Jeeps, M. D.: Physical aspects of the January-February 1963 floods in Sarawak, Hydrological year book for the water year 1962-3, 1963.

Jiang, S., Müller, M., Jin, J., Wu, Y., Zhu, K., Zhang, G., Mujahid, A., Rixen, T., Muhamad, M. F., Sia, E. S. A., Jang, F. H. A., and Zhang, J.: Dissolved inorganic nitrogen in a tropical estuary at Malaysia: transport and transformation, Biogeosciences Discuss., 2019, 1-27, 2019.

Jiann, K.T., Santschi, P. H., and Presley, B. J.: Relationships between geochemical parameters (pH, DOC, SPM, EDTA Concentrations) and trace metal (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) concentrations in river waters of texas (USA), Aquatic Geochemistry, 19, 173-193, 2013.

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N., Cao, J. J., Boyd, P. W., Duce, R. A., and Hunter, K. A.: Global iron connections between desert dust, ocean biogeochemistry, and climate, Science, 308, 67-71, 2005.

Johnes, P. J. and Hodgkinson, R. A.: Phosphorus loss from agricultural catchments: pathways and implications for management, Soil Use and Management, 14, 175-185, 1998.

Joosten, H.: Peatlands: guidance for climate change mitigation through conservation, rehabilitation and sustainable use, Food and Agriculture Organization of the United Nations and Wetlands International, 2012.

Kannan, S.: Problems of iron deficiency in different crop plants in India: causative factors and control measures, Journal of Plant Nutrition, 7, 187-200, 1984.

Krachler, R., Jirsa, F., and Ayromlou, S.: Factors influencing the dissolved iron input by river water

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

to the open ocean, Biogeosciences, 2, 311-315, 2005.

Krachler, R., Krachler, R. F., Kammer, F. V. D., Süphandag, A., Jirsa, F., Ayromlou, S., Hofmann, T., and Keppler, B. K.: Relevance of peat-draining rivers for the riverine input of dissolved iron into the ocean, Science of the Total Environment, 408, 2402-2408, 2010.

Kselik, R. A. L. and Liong, T. Y.: Hydrology of the peat swamp in the Maludam National Park, Betong Division, Sarawak, Alterra, the Netherlands/Forest Department Sarawak and Sarawak Forestry Corporation, Malaysia, 2004.

Laglera, L. M. and Berg, C. M. G. V. D.: Evidence for geochemical control of iron by humic substances in seawater, Limnology & Oceanography, 54, 610-619, 2009.

Lampela, M., Jauhiainen, J., and Vasander, H.: Surface peat structure and chemistry in a tropical peat swamp forest, Plant and Soil, 382, 329-347, 2014.

Lee, J. M., Boyle, E. A., Echegoyen-Sanz, Y., Fitzsimmons, J. N., Zhang, R., and Kayser, R. A.: Analysis of trace metals (Cu, Cd, Pb, and Fe) in seawater using single batch nitrilotriacetate resin extraction and isotope dilution inductively coupled plasma mass spectrometry, Analytica Chimica Acta, 686, 93-101, 2011.

Lehmann, J. and Schroth, G.: Nutrient leaching, CABI Publishing, Wallingford, 2003.

Lemaire, E., Blanc, G., Schäfer, J., Coynel, A., and Etcheber, H.: Dissolved Trace Metal–Organic Complexes in the Lot–Garonne River System Determined Using the C18 Sep-Pak System, Aquatic Geochemistry, 12, 21-38, 2006.

Lerman, A., Wu, L., and Mackenzie, F. T.: CO_2 and H_2SO_4 consumption in weathering and material transport to the ocean, and their role in the global carbon balance, Marine Chemistry, 106, 326-350, 2007.

Lorite-Herrera, M. and Jiménez-Espinosa, R.: Impact of agricultural activity and geologic controls on groundwater quality of the alluvial aquifer of the Guadalquivir River (province of Jaén, Spain): a case study, Environmental Geology, 54, 1391-1402, 2008.

Martin, J. H.: Glacial-interglacial CO_2 change: The Iron Hypothesis, Paleoceanography, 5, 1-13, 1990.

Martin, J. M., Guan, D. M., Elbaz-Poulichet, F., Thomas, A. J., and Gordeev, V. V.: Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: The Lena River estuary (Russia), Marine Chemistry, 43, 185-199,

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

1993.

Martin, P., Cherukuru, N., Tan, A. S. Y., Sanwlani, N., Mujahid, A., and Müller, M.: Distribution and cycling of terrigenous dissolved organic carbon in peatland-draining rivers and coastal waters of Sarawak, Borneo, Biogeosciences, 15, 6847-6865, 2018.

Maya, K., Babu, K. N., Padmalal, D., and Seralathan, P.: Hydrochemistry and dissolved nutrient flux of two small catchment rivers, south-western India, Chemistry & Ecology, 23, 13-27, 2007.

Meade, R. H., Dunne, T., Richey, J. E., Santos, U. D. M., and Salati, E.: Storage and remobilization of suspended sediment in the lower amazon river of brazil, Science, 228, 488-490, 1985.

Miettinen, J., Shi, C., and Liew, S. C.: Two decades of destruction in Southeast Asia's peat swamp forests, Frontiers in Ecology & the Environment, 10, 124-128, 2012.

Milliman, J. D. and Farnsworth, K. L.: River discharge to the coastal ocean: runoff, erosion, and delivery to the coastal ocean, 2011.

Morillo, J., Usero, J, and Gracia, I.: Biomonitoring of trace metals in a mine-polluted estuarine system (Spain), Chemosphere, 58, 1421-1430, 2005.

Moore, C. M., Mills, M. M., Achterberg, E. P., Geider, R. J., Laroche, J., Lucas, M. I., Mcdonagh, E. L., Pan, X., Poulton, A. J., and Rijkenberg, M. J. A.: Large-scale distribution of Atlantic nitrogen fixation controlled by iron availability, Nature Geoscience, 2, 867-871, 2009.

Moore, S., Evans, C. D., Page, S. E., Garnett, M. H., Jones, T. G., Freeman, C., Hooijer, A., Wiltshire, A. J., Limin, S. H., and Gauci, V.: Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes, Nature, 493, 660–663, 2013.

Moreira-Turcq, P., Seyler, P., Guyot, J. L., and Etcheber, H.: Exportation of organic carbon from the Amazon River and its main tributaries, Hydrological Processes, 17, 1329-1344, 2003.

Morley, R. J. and Flenley, J. R.: Tectonic and climatic controls on the distribution and quality of Cretaceous coals, Oxford University Press, Oxford, U.K., 1987.

Müller, D., Warneke, T., Rixen, T., Müller, M., Jamahari, S., Denis, N., Mujahid, A., and Notholt, J.: Lateral carbon fluxes and CO_2 outgassing from a tropical peat-draining river, Biogeosciences, 12, 5967-5979, 2015.

Mutalib, A. A., Lim, J. S., Wong, M. H., and Koonvai, L.: Characterization, distribution and utilization of peat in Malaysia., Malaysian Agricultural Research and Development Institute., Kuala

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

559 Lumpur, 7-16 pp., 1992.
560 Nelson, P. N., Banabas, M., Goodrick, I., Webb, M. J., Huth, N. I., and O'Grady, D.: Soil sampling in
561 oil palm plantations: a practical design that accounts for lateral variability at the tree scale, Plant
562 and Soil, 394, 421-429, 2015.
563 Oldham, V. E., Miller, M. T., Jensen, L. T., and Luther, G. W.: Revisiting Mn and Fe removal in humic
564 rich estuaries, Geochimica Et Cosmochimica Acta, 209, 2017.
565 Olivié-Lauquet, G., Allard, T., Benedetti, M., and Muller, J. P.: Chemical distribution of trivalent iron
566 in riverine material from a tropical ecosystem: a quantitative EPR study, Water Research, 33,
567 2726-2734, 1999.
568 Picouet, C., Dupré, B., Orange, D., and Valladon, M.: Major and trace element geochemistry in the
569 upper Niger River (Mali): physical and chemical weathering rates and CO 2 consumption,
570 Chemical Geology, 185, 93-124, 2002.
571 Rajmohan, N. and Elango, L.: Distribution of Iron, Manganese, Zinc and Atrazine in Groundwater in
572 Parts of Palar and Cheyyar River Basins, South India, Environmental Monitoring and
573 Assessment, 107, 115-131, 2005.
574 Raven, J. A.: The iron and molybdenum use efficiencies of plant growth with different energy, carbon
575 and nitrogen sources, New Phytologist, 109, 279-287, 2010.
576 Saitoh, Y., Kuma, K., Isoda, Y., Kuroda, H., Matsuura, H., Wagawa, T., Takata, H., Kobayashi, N.,
577 Nagao, S., and Nakatsuka, T.: Processes influencing iron distribution in the coastal waters of the
578 Tsugaru Strait, Japan, Journal of Oceanography, 64, 815-830, 2008.
579 Sanders, C. J., Santos, I. R., Maher, D. T., Sadat-Noori, M., Schnetger, B., and Brumsack, H. J.:
580 Dissolved iron exports from an estuary surrounded by coastal wetlands: Can small estuaries be
581 a significant source of Fe to the ocean, Marine Chemistry, 176, 75-82, 2015.
582 Scott, I. M.: Soils of the Central Sarawak Lowlands, East Malaysia: Kuching, Sarawak, East Malaysia,
583 Department of Agriculture, 2302, 1985.
584 Shiller, A. M.: Dissolved trace elements in the Mississippi River: Seasonal, interannual, and decadal
585 variability, Geochim Cosmochim Acta, 61, 4321–4330, 1997.
586 Shuhaimiothman, M., Ahmad, A. K., and Lim, E. C.: Metals concentration in water and sediment of
587 Bebar peat swampy forest river, Malaysia, Journal of Biological Sciences, 9, 2009.

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

588 Siong, V. L. E.: Determination of heavy metals in water and sediment of Rajang River at Pelagus
589 Area, 2015. Faculty of Resource Science and Technology, Universiti Malaysia Sarawak,
590 Malaysia, 2015.
591 Staub, J. R., Among, H. L., and Gastaldo, R. A.: Seasonal sediment transport and deposition in the
592 Rajang River delta, Sarawak, East Malaysia, Sedimentary Geology, 133, 249-264, 2000.
593 Staub, J. R. and Esterle, J. S.: Provenance and sediment dispersal in the Rajang River delta/coastal
594 plain system, Sarawak, East Malaysia, Sedimentary Geology, 85, 191-201, 1993.
595 Staub, J. R. and Gastaldo, R.: Late quaternary sedimentation and peat development in the Rajang
596 river delta, Sarawak, east Malaysia. In: Tropical deltas of Southeast Asia, Sidi, F. H., Nummedal,
597 D., Imbert, P., Darman, H., and Posamentier, H. W., editors, Society for Sedimentary Geology
598 Special Publication, Tulsa, Oklahoma, U.S.A., 2003.
599 Stolpe, B., Guo, L., Alan, M. S., Hassellöv, M.: Size and composition of colloidal organic matter and
600 trace elements in the Mississippi River, Pearl River and the northern Gulf of Mexico, as
601 characterized by flow field-flow fractionation, Marine Chemistry, 118, 119-128, 2010.
602 Stolpe, B. and Hassellöv, M.: Changes in size distribution of fresh water nanoscale colloidal matter
603 and associated elements on mixing with seawater, Geochimica Et Cosmochimica Acta, 71, 3292-
604 3301, 2007.
605 Tabachow, R. M., Peirce, J. J., and Richter, D. D.: Biogeochemical Models Relating Soil Nitrogen
606 Losses to Plant-Available N, Environmental Engineering Science, 18, 81-89, 2001.
607 Tagliabue, A., Bowie, A. R., Boyd, P. W., Buck, K. N., Johnson, K. S., and Saito, M. A.: The integral
608 role of iron in ocean biogeochemistry, Nature, 543, 51-59, 2017.
609 Taillefert, M., And, A. B. B., and Iii, G. W. L.: Reactivity of freshly formed Fe (III) in synthetic
610 solutions and pore waters: voltammetric evidence of an aging process, Environmental Science
611 & Technology, 34, 2169-2177, 2000.
612 Trade Chakra: available at: www.tradechakra.com/economy/malaysia/industry-in-malaysia-179.php
613 (last access: 20 June 2018), 2009.
614 Tripti, M., Gurumurthy, G. P., Balakrishna, K., and Chadaga, M. D.: Dissolved trace element
615 biogeochemistry of a tropical river, Southwestern India, Environmental Science & Pollution
616 Research, 20, 4067-4077, 2013.

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

617 Turner, A. and Millward, G. E.: Suspended particles: their role in estuarine biogeochemical cycles,
618 Estuarine Coastal and Shelf Science, 55, 857-883, 2002.
619 Wetlands International: A quick scan of peatlands in Malaysia, wetlands international, Petaling Jaya,
620 Malaysia, 50 pp., 2010.
621 Williams, R. J. P.: The Bakerian Lecture, 1981: Natural Selection of the Chemical Elements,
622 Proceedings of the Royal Society of London, 213, 361-397, 1981.
623 Withers, P. J. A., Edwards, A. C., and Foy, R. H.: Phosphorus cycling in UK agriculture and
624 implications for phosphorus loss from soil, Soil Use and Management, 17, 139-149, 2001.
625 Wu, Y., Bao, H. Y., Unger, D., Herbeck, L. S., Zhu, Z. Y., Zhang, J., and Jennerjahn, T. C.:
626 Biogeochemical behavior of organic carbon in a small tropical river and estuary, Hainan, China,
627 Continental Shelf Research, 57, 32-43, 2013.
628 Xue, Y., Xia, H., Christie, P., Zhang, Z., Li, L., and Tang, C.: Crop acquisition of phosphorus, iron
629 and zinc from soil in cereal/legume intercropping systems: a critical review, Annals of Botany,
630 117, 363-377, 2016.
631 Yan, B., Guan, J., Shesterkin, V., and Zhu, H.: Variations of dissolved iron in the Amur River during
632 an extreme flood event in 2013, Chinese Geographical Science, 26, 679-686, 2016.
633 Zhang, J.: Geochemistry of trace metals from Chinese river/estuary systems: an overview, Estuarine,
634 Coastal and Shelf Science, 41, 631-658, 1995.
635 Zhang, R., John, S. G., Zhang, J., Ren, J., Wu, Y., Zhu, Z., Liu, S., Zhu, X., Marsay, C. M., and Wenger,
636 F.: Transport and reaction of iron and iron stable isotopes in glacial meltwaters on Svalbard near
637 Kongsfjorden: From rivers to estuary to ocean, Earth & Planetary Science Letters, 424, 201-211,
638 2015.
639 Zhang, Y. Y., Zhang, E. R., and Zhang, J.: Modeling on adsorption–desorption of trace metals to
640 suspended particle matter in the Changjiang Estuary, Environmental Geology, 53, 1751-1766,
641 2008.
642 Zhou, Y., Martin, P., and Müller, M.: Composition and cycling of dissolved organic matter from
643 tropical peatlands of coastal Sarawak, Borneo, revealed by fluorescence spectroscopy and
644 PARAFAC analysis, Biogeosciences Discuss., 2018, 1-25, 2018.
645 Zhu, X., Zhang, R., Wu, Y., Zhu, J., Bao, D., and Zhang, J.: The remobilization and removal of Fe in

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

estuary—a case study in the changjiang estuary, China, Journal of Geophysical Research Oceans, 2018.

650 Table 1. Range and average of Salinity (S), pH, suspended particulate matter (SPM), dissolved oxygen (DO), dissolved iron (dFe), and dissolved
651 organic carbon (DOC).
652

River-Time	Station	S	pH	SPM (mg L^{-1})	DO (mg L^{-1})	dFe (µmol L^{-1})	DOC (µmol L^{-1})
Rajang-August 2016 (dry season)	28	0-32.0 (11.7±12.1)	6.5-8.1 (7.2±0.5)	24.2-129 (62.3±30.4)	2.7-4.8 (3.8±0.6)	0.002-7.3 (2.3±2.9)	181-357 (218±78.2)
Rajang-March 2017 (wet season)	15	0-30.1 (11.9±12.3)	6.0-7.1 (7.1±0.7)	47.1-327 (151±70.4)	4.6-7.6 (6.1±0.7)	0.004-11.3 (4.6±4.1)	98.1-238 (165 ± 41.8)
Maludam-March 2017	9	0-20.0 (5.4±6.1)	3.7-7.6 (4.6±1.4)	0.4-388 (53.1±121)	1.1-6.8 (2.7±1.9)	6.3-23.8 (14.6±6.8)	353-4581 (3609±1229)
Sebuyau-March 2017	8	0-13.6 (5.4±6.1)	4.3-7.0 (5.2±1.1)	0.4-388 (53.1±121)	1.4-5.9 (3.2±1.9)	3.0-33.6 (17.6±12.0)	364-2078 (1396±671)
Simunjan-March 2017	6	0-0.4	4.7-6.3 (5.2±0.6)	14-481 (135±197)	1.0-2.6 (1.9±0.7)	25.8-59.2 (44.2±11.8)	818-3121 (2157±950)

653
654
655

Table 2: Concentration of dFe and removal factor (RF) in some rivers.

Rivers	Estury location	Climate	dFe (μmol/L, '*' in nmol/L)	RF (%)	Reference
Lena	Russia	arctic	0.54	67.5	1, 2, 3
Changjiang	China	subtropical	44.6*	79.1	1, 4
Jiulongjiang	China	subtropical	17.9*	37.7	5
Columbia	United States	subtropical	71.4*	72.5	6
Garonne	France	temperate	0.1	59.7	7
Merrimack	United States	temperate	3.7	44.6	1.8
Amazon	Brazil	tropical	1.9	77.8	1.9.10
Congo	Congo	tropical	3.2	57.3	1,11,12
Rajang	Malaysia	tropical	5.5	98	1, this study

1. Milliman and Farnsworth, 2011; 2. Martin et al., 1993; 3. Guieu et al., 1996; 4. Zhu et al., 2018; 5. Zhang 1995; 6. Bruland et al., 2008; 7. Lemaire et al., 2006; 8. Boyle et al., 1974; 9. Aucour et al., 2003; 10. .Moreira-Turcq et al., 2003; 11. Dupré et al., 1996; 12. Coynel et al., 2005.

* RF is the ratio of the integration of dFe concentration versus salinity and the product of theoretical dilution line intercepts (Hopwood et al., 2014).

* dFe yield is a ratio of dFe flux and drainage area.

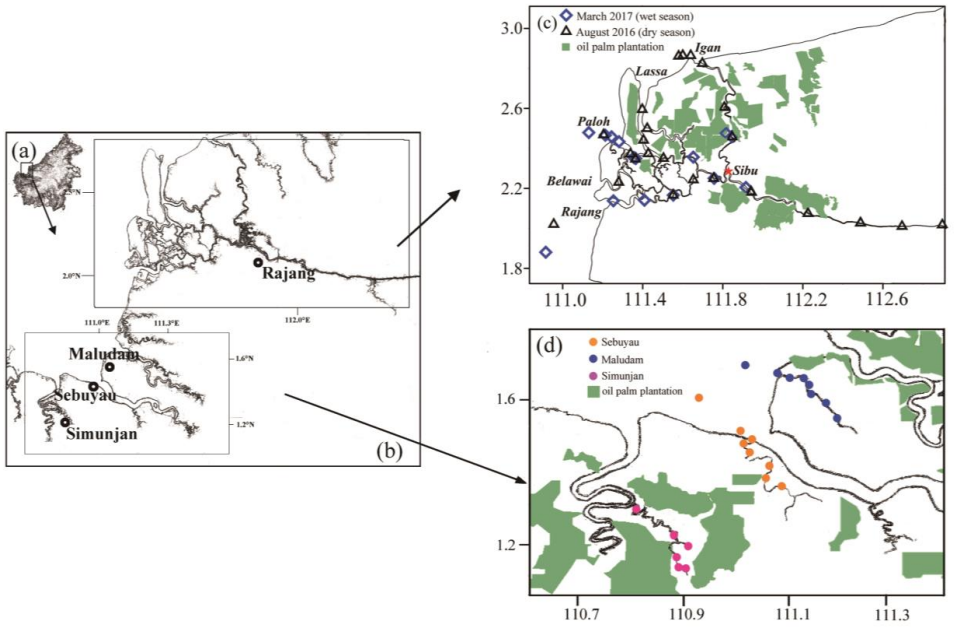

Figure 1. Locations of sample stations in Malaysia (a), including the Rajang River, the Maludam River, the Sebuyau River, and the Simunjan River (b). In figure (c) and (d), the green layer indicates oil palm plantations, based on the dataset from Global Forest Watch (http://gfw2-data.s3.amazonaws.com/country/mys/zip/mys_oil_palm.zip).

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

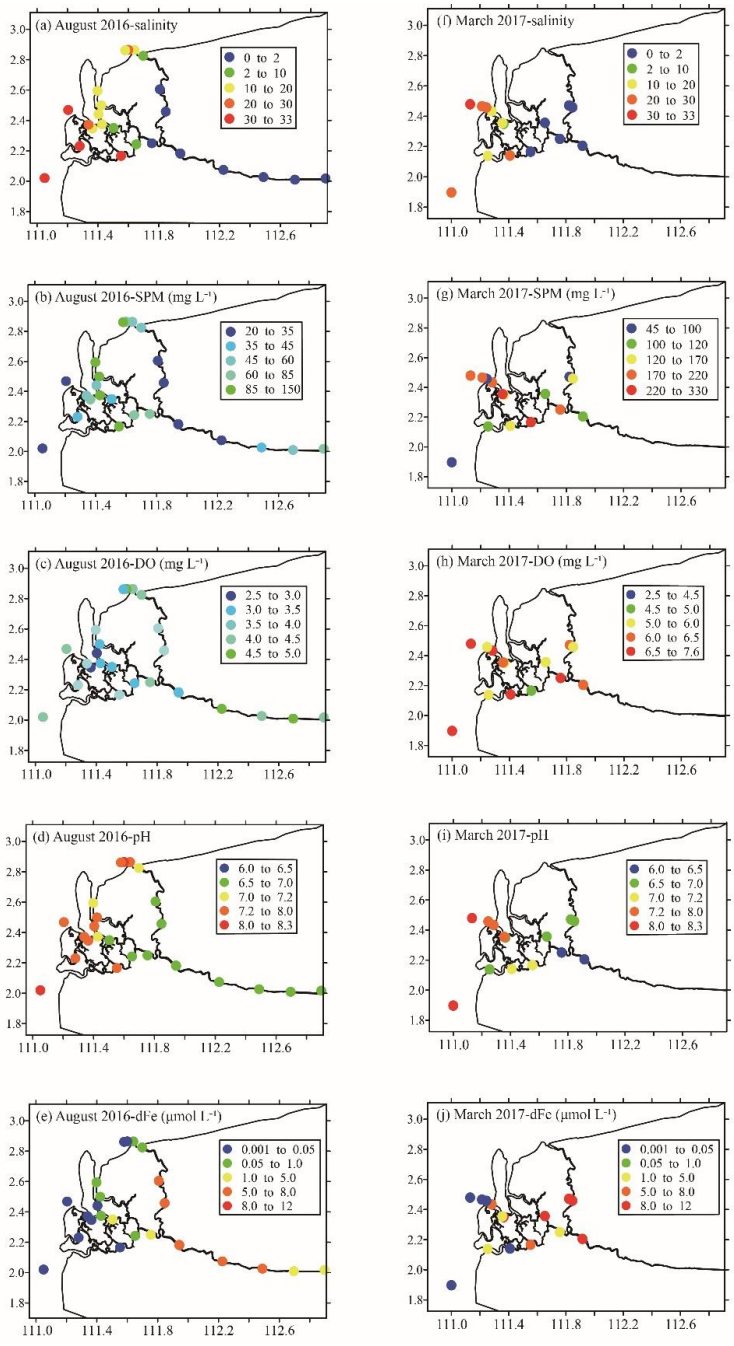

Figure 2. Spatial distributions of salinity (a) (f), suspended particulate matter (SPM) (b) (g), dissolved oxygen (DO) (c) (h), pH (d) (i), dissolved iron (dFe) (e) (j) in the Rajang River in August 2016 and March 2017.

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

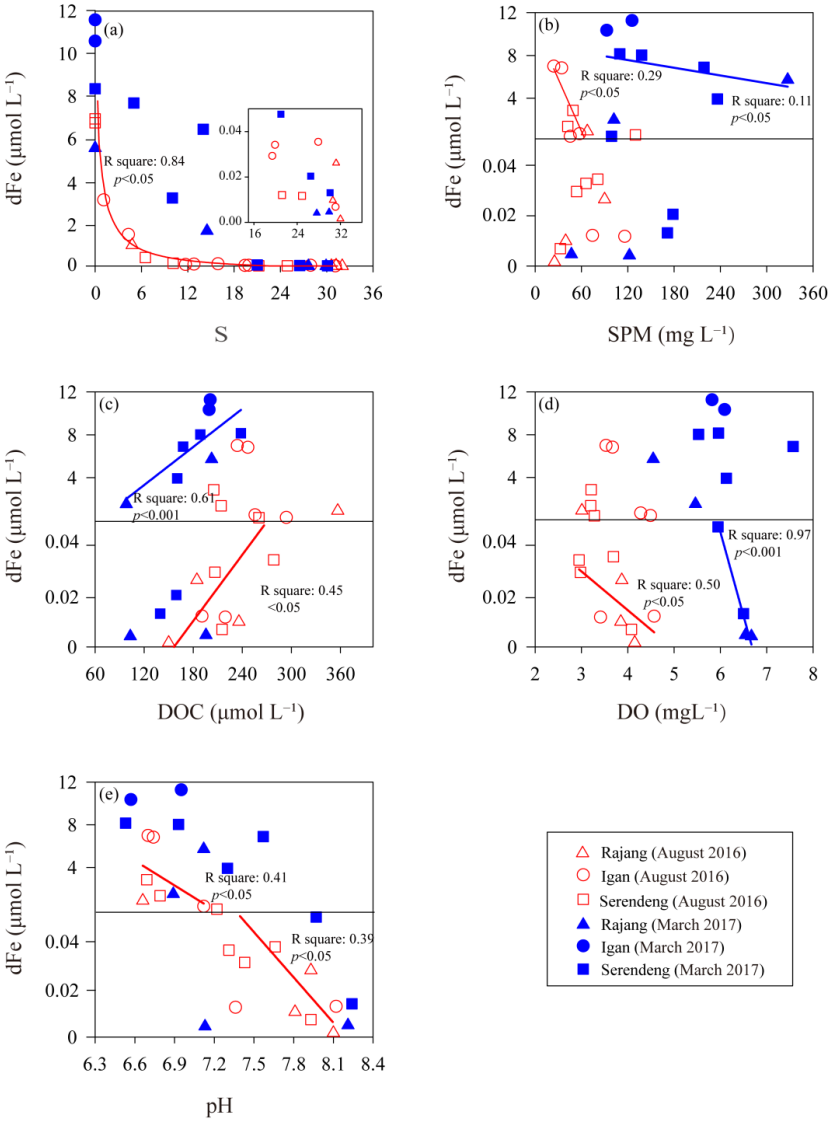

Figure 3. Dissolved iron (dFe) correlation with salinity (S) (a), suspended particulate matter (SPM) (b), dissolved organic carbon (DOC) (c), dissolved oxygen (DO) (d), and pH (e) in Rajang estuary. The solid lines were the linear regressions between dFe and other factors, and the colors of the lines were coincident with the data points in different salinity range.

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

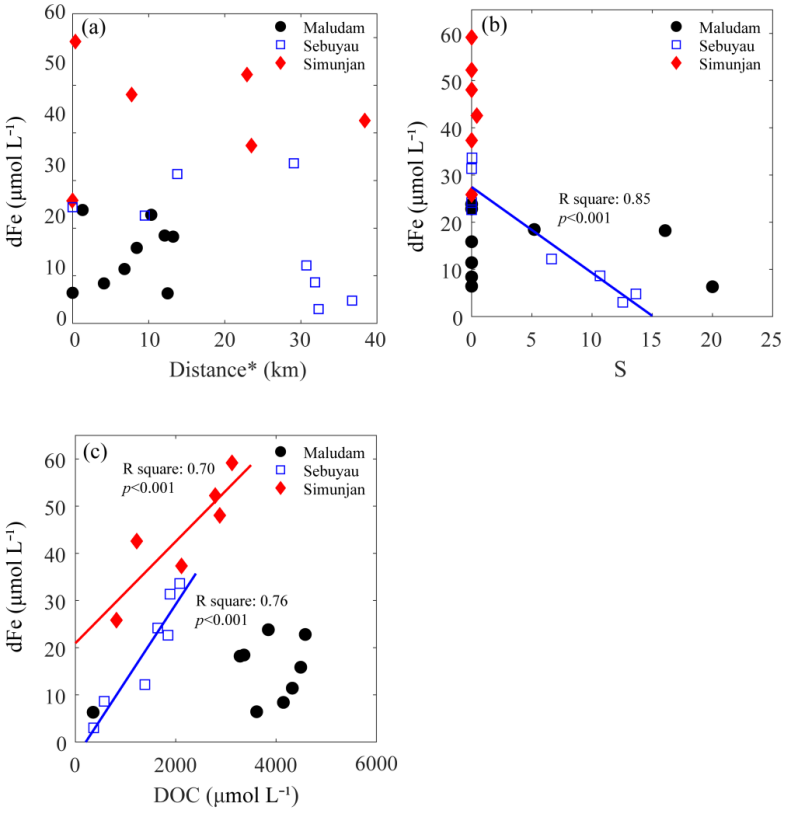

Figure 4. the correlations between distance (a), salinity (S) (b), dissolved organic carbon (DOC) (c), and dissolved iron (dFe) in blackwater rivers: Maludam, Sebuyau and Simunjan. The solid lines were the linear regressions between dFe and other factors, and the colors of the regression lines were coincident with the data points.

*We adopted the station at the upper stream as distance=0, and the downstream direction as positive.

https://doi.org/10.5194/bg-2019-204
Preprint. Discussion started: 18 June 2019

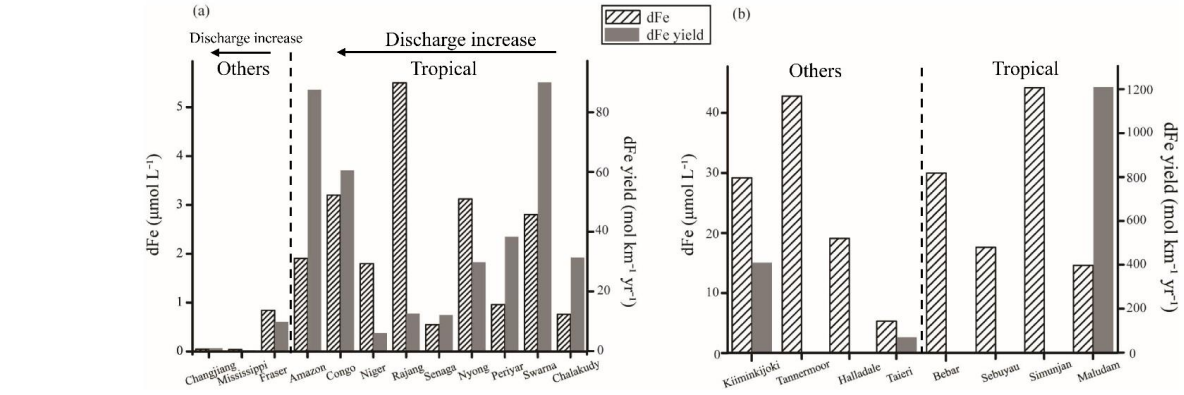

Figure 5. The concentration and yield of dFe in large rivers (a) and blackwater rivers (b).

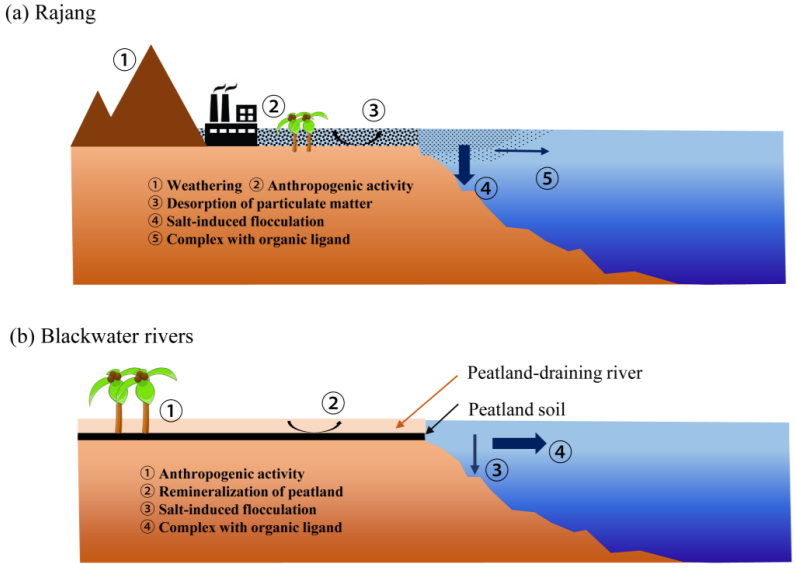

Figure 6. A schematic representation of dFe biogeochemical behaviors in the Rajang River (a) and blackwater rivers (b)