Distribution and Flux of Dissolved Iron in Peatland-draining Rivers and Estuaries of Sarawak, Malaysian Borneo

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Abstract Dissolved iron (dFe) is essential for multiple biogeochemical reactions in oceans, such as photosynthesis, respiration and nitrogen fixation. Currently, large uncertainties remain on the riverine input of dFe to coastal oceans, especially in tropical rivers in Southeast Asia. In the present study, dFe concentrations and the distribution along the salinity gradient in the Rajang River and Estuary 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 were found in several sampling sites, which may be related to the desorption from SPM and agriculture activities. limited records on the dFe concentrations w In the blackwater rivers, concentrations of dFe reached 44.2 $\mu mol\ L^{-1}$, indicating a great contribution to dFe budgets from peatland leaching. The dFe flux derived from the Rajang Estuary to the South China Sea was estimated to be $(6.4\pm2.3)\times10^5\ kg\ yr^{-1}$. 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.

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 a micronutrient, significantly supporting 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) flux 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 in 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 land source water and coastal oceans, can 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 matter resulting from high primary productivity and abundant 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 matter (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 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 with the coastal belts, with a coverage of approximately 9% of the global peatlands area (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 the sediments (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 Estuary) and three blackwater rivers. This study aims to determine (1) the concentration and distribution of dFe in the peatland-draining rivers and their estuaries, (2) the seasonal variation in the concentration and distribution of dFe in the Rajang River and Estuary, (3) dFe yield and the magnitude of riverine flux 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 of Malaysia and has a widespread 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, the deforestation rate in Sarawak increased to 2% yr^{-1} from 1990 to 2010 (Miettinen et al., 2012), and this rate is attributed to oil palms and rubber tree 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, 1b), with a length of 530 km. The drainage basin is 51×10^3 km^2 (Milliman and 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 Rajang River were around 5-10 m and 8-20 m deep in the dry season and the wet season respectively, whereas the tributaries <5 m deep in the Rajang Estuary. The flow velocity ranged from 0.2-0.6 m s^{-1} and 0.8-1.2 m s^{-1} at mainstream in the dry season and the wet season respectively (Tawan et al., 2019). The climate in the Rajang watershed is classified as the tropical ever-wet type (Morley and Flenley, 1987), while the precipitation varies between the dry and the wet seasons. The discharge rate for the Rajang River reached 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 line of the Rajang drainage basin and the Rajang Estuary according to the physiographic condition (Staub et al., 2000; Staub and Esterle, 1993), and the saltwater intrusion could reach the downstream of the city (Jiang et al., 2019). Apart from mineral soils from the upper stream, the Rajang Estuary also receives 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, Hulu Serendeng (further separated into two tributaries: Paloh and Lassa), Belawai and Rajang. The Igan tributary is the major outlet for freshwater (Jiang et al., 2019). Mangroves distribute in the brackish-water area in southwestern of the estuary near the Rajang and Serendeng tributary, and some freshwater trees like *Casuarina* are 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).

The substantial fraction of the surface sediment was peat deposits with a maximum depth of 15 m in the Rajang Estuary (Staub and Gastaldo, 2003). The Rajang riverine freshwater drains the mineral soil, so the mean grain sizes of the sediment were much coarser than the Rajang Estuary, where peatland is dominant in the delta region (Wu et al., 2019). 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 kaolinite miner amount of chlorite. Gley is frequently observed in the central and southwestern parts of the estuary (Staub and Gastaldo, 2003). Podzols is dominant of 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, alluvial soils as found in the landward part in the coastal area of the
estuary (Staub and Gastaldo, 2003). The input of total suspended solids from the Rajang River was up
to 30 Mt yr^{-1} (Staub and Gastaldo, 2003).

Three small rivers, Maludam, Simunjan, and Sebuyau are black water rivers, characterized by tea-
color, acidic, and oxygen deficit as described by Kselik and Liong (2004). The Maludam River, the
majority of which located in the Maludam National Park (the second-largest park in Sarawak), is a
pristine river with minor human influences. 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 is 4.4±0.6
m^3 s^{-1} (Müller et al., 2015). However, the other two blackwater rivers have been 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). The grain size of sediments in blackwater rivers
was much lower and received more woody material than that of the Rajang River (Wu et al., 2019).

2.2 Sample collection and process

The sampling stations are outlined in Fig. 1. The surveys in the Rajang River and its Estuary were
conducted in August 2016 (the dry season) and March 2017 (the wet season). Each survey lasted 4 to
5 days, covering both flooding tides and ebbing tides. The samples included river, brackish water in
different river tributaries and coastal saline water. In the Rajang watershed, the selection of sampling
stations depended on salinity gradient, anthropogenic activities, and water depth. In March 2017, we
failed to collect samples in the upstream of the Rajang River and the saline samples in Igan tributary
mainly due to the shallow water depth and strong current. However, three blackwater rivers, as
aforementioned, were included in the cruise. During two 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 was 3-4 m to avoid the contamination from the ship. The bottom
samples were collected using a pre-cleaned 5 L Teflon-coated Niskin-X bottle hung on a nylon rope.
Due to the limited sampling time and condition, only 3 bottom samples in August 2016 and 1 bottom
sample in March 2017 were collected. 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 to transform and preserve metal Fe in soluble inorganic form (Lee et al., 2011). All bottles used in the sample collection and storage were prepared in the clean laboratory, following the procedure of 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. The acidified samples were preprocessed by the single batch nitrilotriacetate (NTA)-type chelating resin (Qiagen Inc., Valencia, CA). The dissolved Fe can be recovered quantitatively after the oxidization of Fe^{2+} to Fe^{3+} by the addition of H_2O_2 (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 of the 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 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 via an Aurora 1030W total organic carbon analyzer at the Centre for Coastal Biogeochemistry at Southern

Cross University (Lismore, Australia). Reproducibility for concentrations was ±0.2 mg L^{-1}. For the samples collected in March 2017, DOC concentrations were determined by the high-temperature catalytic oxidation method with Total Organic Carbon Analyzer (Shimadzu) at the State Key Laboratory of Estuarine and Coastal Research in East China Normal University (Shanghai, China), 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 was 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). The salinity also increased along the water flow pathway in the Rajang Estuary with an exception in the Rajang tributary. 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 varied between two seasons. The high value was found in the west estuary in March 2017 (Fig. 2c, 2h). Water pH in the Rajang 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, the seasonal variation of pH was not significant.

In blackwater rivers, salinity ranged from 0 to 23.5 in the Maludam River and 0 to 13.6 in the Sebuyau River. The samples in the Simunjan River were only fresh water. All three blackwater rivers were anoxic in freshwater endmember, with DO<2 mg/L. 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). The distributions of these properties in blackwater rivers are shown in Supplement 1.

3.2 dFe in the Rajang River and Estuary

The contour of dFe in the Rajang surface water is shown in Fig. 2. We adopted Sibu as the separation of the Rajang River and the Rajang Estuary. The dFe concentrations in the Rajang River ranged from 3.3 to 7.3 μmol L^{-1} (mean: 5.5±1.7 μmol L^{-1}) in August 2016, and ranged from 4.2 to 8.3 μmol L^{-1} (mean: 6.4±2.9 μmol L^{-1}) in March 2017. In the Rajang Estuary, the dFe concentration 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 season and the wet season, respectively. The concentration of dFe in the wet season was higher than that in the dry season both in the Rajang River 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. The sites in tributary Paloh and Lassa were combined as Serendeng tributary, and the tributary Belawai and Rajang were combined as the Rajang tributary. 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 the 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 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 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 waters (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 not significant in the wet season.

3.3 dFe in blackwater rivers

The average dFe concentrations 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 Rajang Estuary. Moreover, there were significantly positive correlations between dFe and DOC in the Sebuyau River and the Simunjan River (Fig. 4c), while the correlation between dFe and DOC in the Maludam River was weak due to an outlier in the high salinity region (S=20.0).

4. Discussion

4.1 Seasonal and spatial variation of dFe in the Rajang River

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). As the precipitation enhanced in the wet season, the strong water flow from the upper stream scoured the watershed, carrying the Fe-enriched terrestrial particles to the drainage basin in the wet season (Meade et al., 1985; Taillefert et al., 2000). A great amount of dFe may result from the dissolution of these particle iron originating from mechanical and chemical weathering, which leads to a significant addition of dFe in the wet season (Bhatia et al., 2013). Moreover, the agriculture activities in the watershed, such as tillage, can result in rapid leaching in the wet season (Lehmann and Schroth, 2003; Tabachow et al., 2001). The changes in the soil structure were considered to enhance soil erosion in the cropping land, especially in 2017 (the occurrence of La Niñá events) (Jiang et al. 2019). Additionally, metal elements were transported from the catchment to the Rajang River (Johnes and Hodgkinson, 1998; Withers et al., 2001). In addition, the changes in 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 rainfall 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 stream-borne

dFe injected into the Rajang River via hydrological connections in the riparian ditches, and hence contributed a quantity of dFe to rivers from terrestrial runoff and flood discharges (Yan et al., 2016).

4.2 Seasonal and spatial variation of dFe in the Rajang Estuary

270　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). In addition, dFe was negatively correlated with SPM in low salinity waters (Fig. 3b), indicating that the dFe removal may also be

275　linked to the absorption of SPM as described in other researches (Beusekom and Jonge, 1994; Homoky et al., 2012; Zhang et al., 1995). However, there was an exceptionally high dFe concentration in the samples of 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 peatland soils host abundant dFe and organic ligand, and these organic compounds could enhance the solubility of Fe during the transport (Krachler et al.,

280　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

285　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 log of 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 main reason for dFe enhancement in the river mouth area of the Changjiang Estuary. In the wet season,

290　the samples in the Serendeng tributary were collected during a spring tide. Besides, the intensive plantation and agricultural activities in Serendeng tributary modified the soil structure and leached a considerable amount of SPM at flood tide. In Fig. 3a, there was a great dFe and SPM increase at salinity 5-15. Given a similar level in SPM content among the Rajang, Texas River (Jiann et al., 2013) and the Changjiang Estuary (Zhu et al., 2018), we assumed that the dFe enrichment in this special

295　condition may be related to the desorption from the riverine SPM, though we lacked solid supports

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like the mixing experiment. In addition, the limited bottom samples in the Rajang Estuary also revealed that the dFe addition within salinity 5-15 in the wet season might also result from the resuspension of bottom sediments, for the bottom dFe concentration was much higher than the surface dFe concentration.

300   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 between dFe and organic matter. Specifically, the combination between 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).

305   The multiple linear regression analysis of dFe and environmental factors, including salinity, SPM, DOC, DO, and pH (the dry season: R^2=0.52, p<0.05; the wet season: R^2=0.73, p<0.05), revealed the observed pattern and explanations for more parameters. It shows that salinity and SPM were the main factors for the distribution of dFe in the Rajang Estuary (p<0.05). The correlation between dFe and pH was limited in the wet season, suggesting a little impact of pH on dFe. But in the dry season, the

310   concentration of dFe was negatively correlated with pH (Fig. 3e), because 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 and Estuary that we discussed above is summarized and conceptualized in Fig. 5a.

315   **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 watercolor, these peatland-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

320   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 oil 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 oil palm mill effluent were returned to the cropland after oil extraction (Carron et al., 2015; Nelson et al., 2015). The intensive agriculture activities, such as tillage, further enhanced their decomposition, and these activities might improve the mechanical and chemical weathering in the plantation areas, and increased dFe concentration in 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 River and the Sebuyau River. For the samples with the salinity range from 0 to 20.0, the dFe removal was not significant, which is markedly different from the trend obtained in the Rajang Estuary (Fig. 4b). The significant positive correlation between dFe and DOC concentration revealed 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. 5b. Compared with the Rajang Estuary, less dFe was flocculated from the blackwater rivers estuary due to the complexing with organic matter, and the desorption of SPM was negligible during the mixing process. Remineralization of peatland soil is a great source of dFe in blackwater river, while the resuspension of sediment plays a critical role in the Rajang River system.

4.4 dFe flux and yield in tropical rivers

For the Rajang River, the mean concentration of the river endmember of two seasons was 5.5±2.0 $\mu mol\ L^{-1}$, and the mean removal factor was 98.0±0.6%. The removal factor of dFe varied on a global scale. The Rajang RF is 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 $(6.4\pm2.3)\times10^5\ kg\ yr^{-1}$. For the Maludam River, the concentration of the river endmember was 14.6±6.8 $\mu mol\ L^{-1}$ and RF=0 due to the conservative distribution. The dFe flux in the Maludam River was approximately $(1.1\pm0.5)\times10^5\ kg\ yr^{-1}$, produced from 432 km^2 peatland in the Maludam National Park. It is the same magnitude with the Rajang River dFe flux, suggesting that the dFe input was considerable in

blackwater rivers. Malaysia hosts peatland area about 25,889 km^2, the dFe flux can be approximately (6.6±3.0)×10^6 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 productivity 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. 6. 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 greater amount of dFe to the coastal area with higher dFe yields, 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 that hold a similar discharge rate and drainage area with the Rajang River, like the Fraser River, a temperate river in Canada, dFe yield were significantly lower than that derived from the Rajang River (Cameron et al., 1995). The high concentration and yield in tropical rivers likely results from intensive weathering and leaching of rocks and sediments, as well as the decomposition of abundant plantations under high temperatures 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 yield was lower in the Rajang River. This may be related to the difference in 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 drain a savannah-rainforest area, and contain a considerable amounts 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 (Olivié-Lauquet et al., 1999), the Periyar River (Maya et al., 2007) and the Chalakudy River (Maya et al., 2007), dFe yields and DOC concentrations are higher than the Rajang River. In these small tropical rivers, the drainage basins were covered with organic matter enriched sediments, which may be a great source for dFe flux. In blackwater rivers, the dFe yields were much higher than the records from the Rajang River. The thick peatland soils were likely to be the main reason of the high dFe concentration in blackwater rivers, as discussed 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. 6b). The human impacts, such as agricultural activities and the plantations of oil palm, may also contribute to a bulk of dFe flux to blackwater rivers.

5. Conclusions

In this study, dFe was investigated in peatland-draining rivers and estuaries in Sarawak, Malaysia. The conclusions are as follow:

1. There was a significant seasonal variation of dFe concentration in the Rajang River with a higher dFe concentration in the wet season, likely due to the dissolution from the particle iron from upstream weathering. 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 from the desorption of SPM and anthropogenic inputs.

2. The concentration of dFe in the blackwater rivers was 3-10 times 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 Estuary, there wasn't remarkable dFe removal in the blackwater river estuary.

3. The dFe yield in blackwater rivers was much higher than that of the Rajang River. This result indicated that the dFe flux in blackwater rivers can be crucial for coastal zones in Malaysia.

This study improved the understanding of dFe distribution in the Rajang and confirmed its regional influence. In addition, we provided 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.

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681   Table 1. Range and average of Salinity (S), pH, suspended particulate matter (SPM), dissolved oxygen (DO), dissolved iron (dFe), and dissolved

682   organic carbon (DOC).

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River-Time	Station	S	pH	SPM (mg L^{-1})	DO (mg L^{-1})	dFe (µmol L^{-1})	DOC (µmol L^{-1}) *in mmol L^{-1}
Rajang River-August, 2016	8	0	6.7-6.8 (6.7±0.05)	31.4-95.2 (51.5±22.1)	3.4-4.8 (4.4±0.4)	3.3-7.3 (5.5±1.7)	192-260 (219±24)
Rajang Estuary-August, 2016	20	0-32 (16.3±11.8)	6.5-8.1 (7.3±0.5)	24.2-130 (68.4±31.7)	2.7-4.6 (3.6±0.5)	0.002-7.0 (1.1±2.2)	150-357 (245±53)
Rajang River -March, 2017	2	0	6.0-6.5 (6.3±0.3)	116-188 (152±50.9)	6.3-6.7 (6.5±0.3)	4.2-8.3 (6.4±2.9)	126-128 (126 ± 1.5)
Rajang Estuary- March, 2017	13	0-30.1 (13.7±12.2)	6.5-8.2 (7.3±0.6)	47-327 (151±75)	4.6-7.6 (6.1±0.7)	0.004-11.3 (4.2±4.0)	98-238 (171±42)
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)	0.35*-4.6* (3.6*±1.3*)
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)	0.36*-2.1* (1.4*±0.67*)
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)	0.82*-3.1* (2.2*±0.95*)

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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

687   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.

688   Aucour et al., 2003; 10. Moreira-Turcq et al., 2003; 11. Dupré et al., 1996; 12. Coynel et al., 2005.

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

690   * dFe yield is a ratio of dFe flux and drainage area.
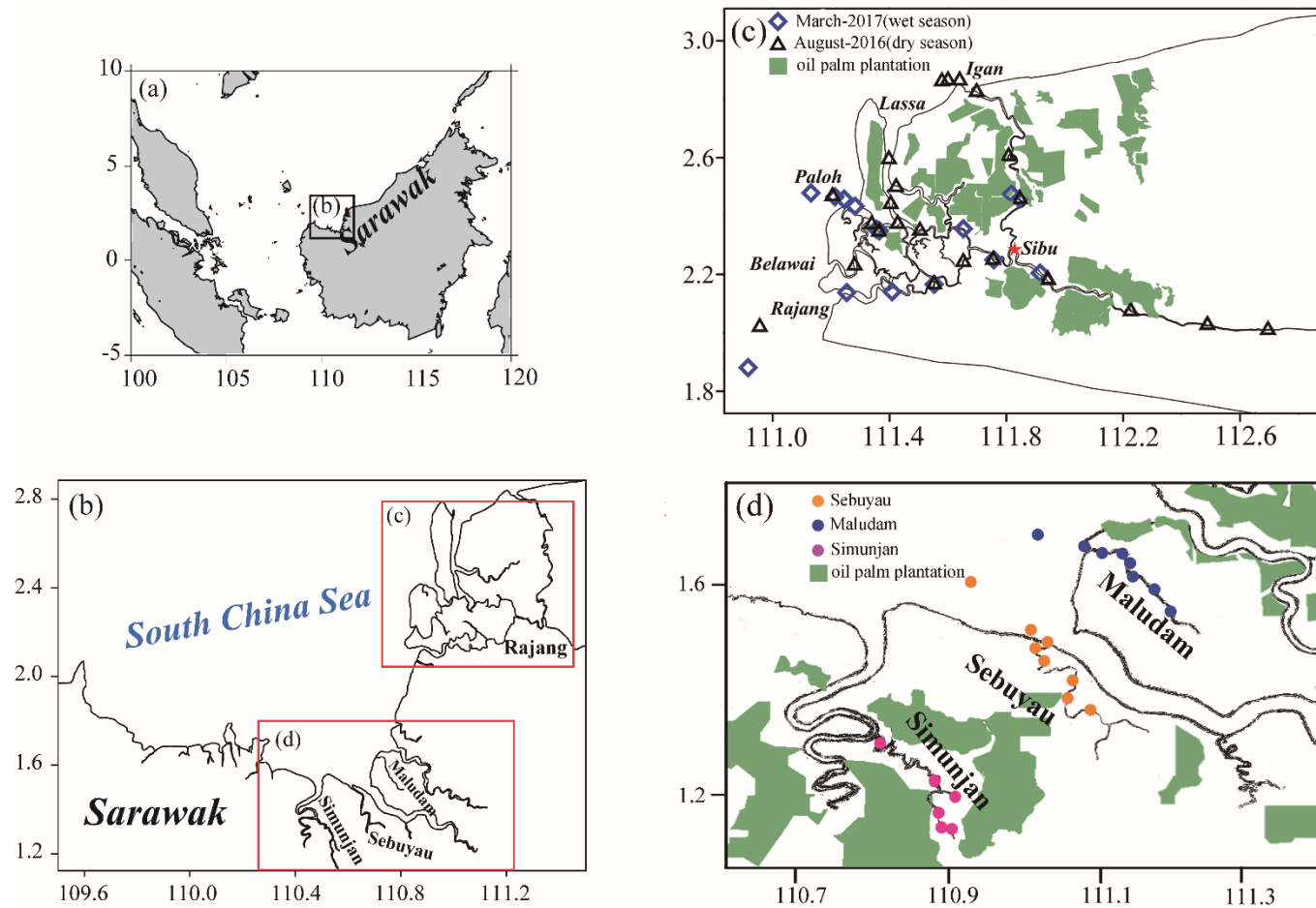
691

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693 Figure 1: The distribution of sample stations in Sarawak (b), Malaysia (a). Including Rajang in August 2016, and Rajang, Maludam, Sebuyau, and Simunjan in March

694 2017. In figure (c) and (d), the green feature layer was redrawn by the dataset from Global Forest Watch (http://gfw2-

695 data.s3.amazonaws.com/country/mys/zip/mys_oil_palm.zip)

697
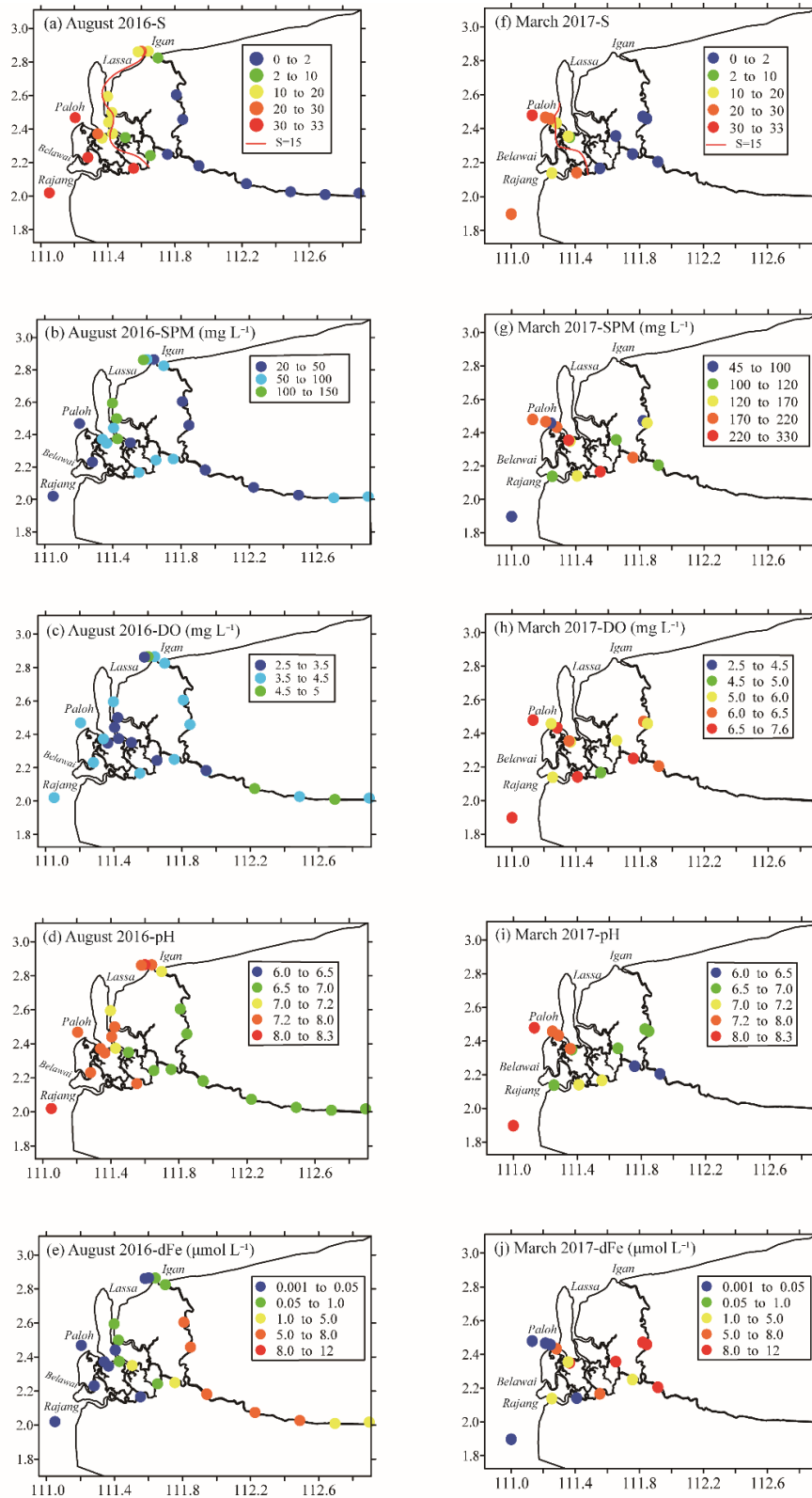
Figure 2. Spatial distributions of salinity (a) (f), suspended particulate matter (SPM) (b) (g), dissolved oxygen (DO) (c) (h), pH (d) (i), dissolved iron (dFe) (e) (j) in the Rajang River in August 2016 and March 2017. The red solid line is the isosalinity line (S=15) linear interpolated from S in this region.
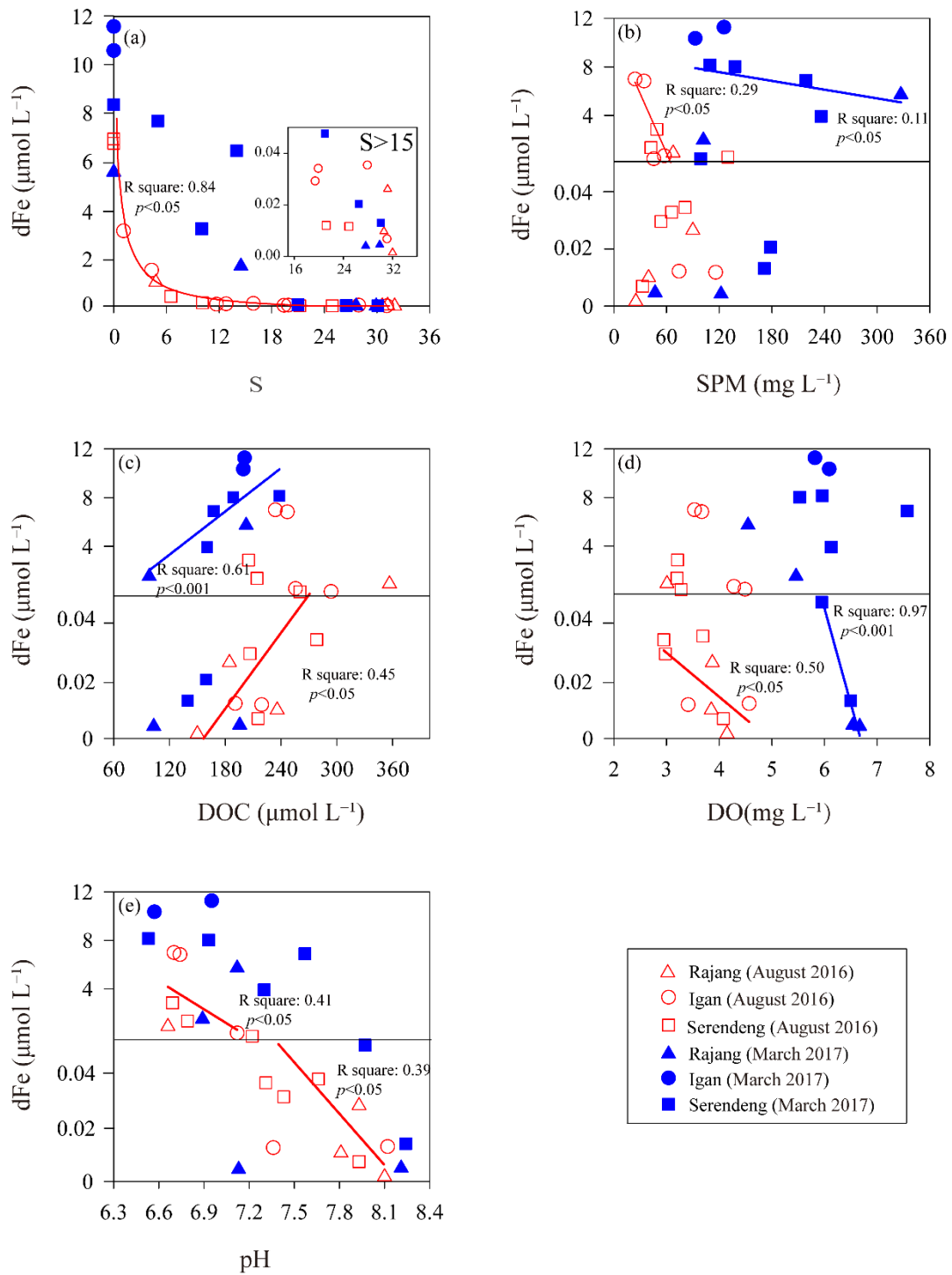
Figure 3: Dissolved iron (dFe) correlation with salinity (S) (a), suspended particulate matter (SPM) (b), dissolved organic carbon (DOC) (c), dissolved oxygen (DO) (d), and pH (e) in Rajang estuary. The solid lines were the linear regressions between dFe and other factors, and the colors of the lines were coincident with the data points in different salinity range. Serendeng is the stations in tributary Paloh and Lassa, and Rajang is the stations in tributary Belawai and Rajang.
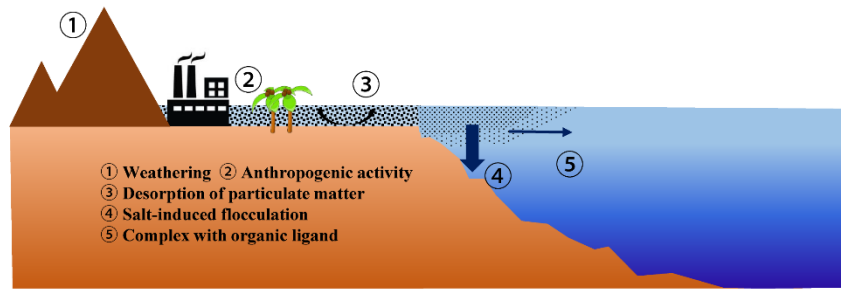
30
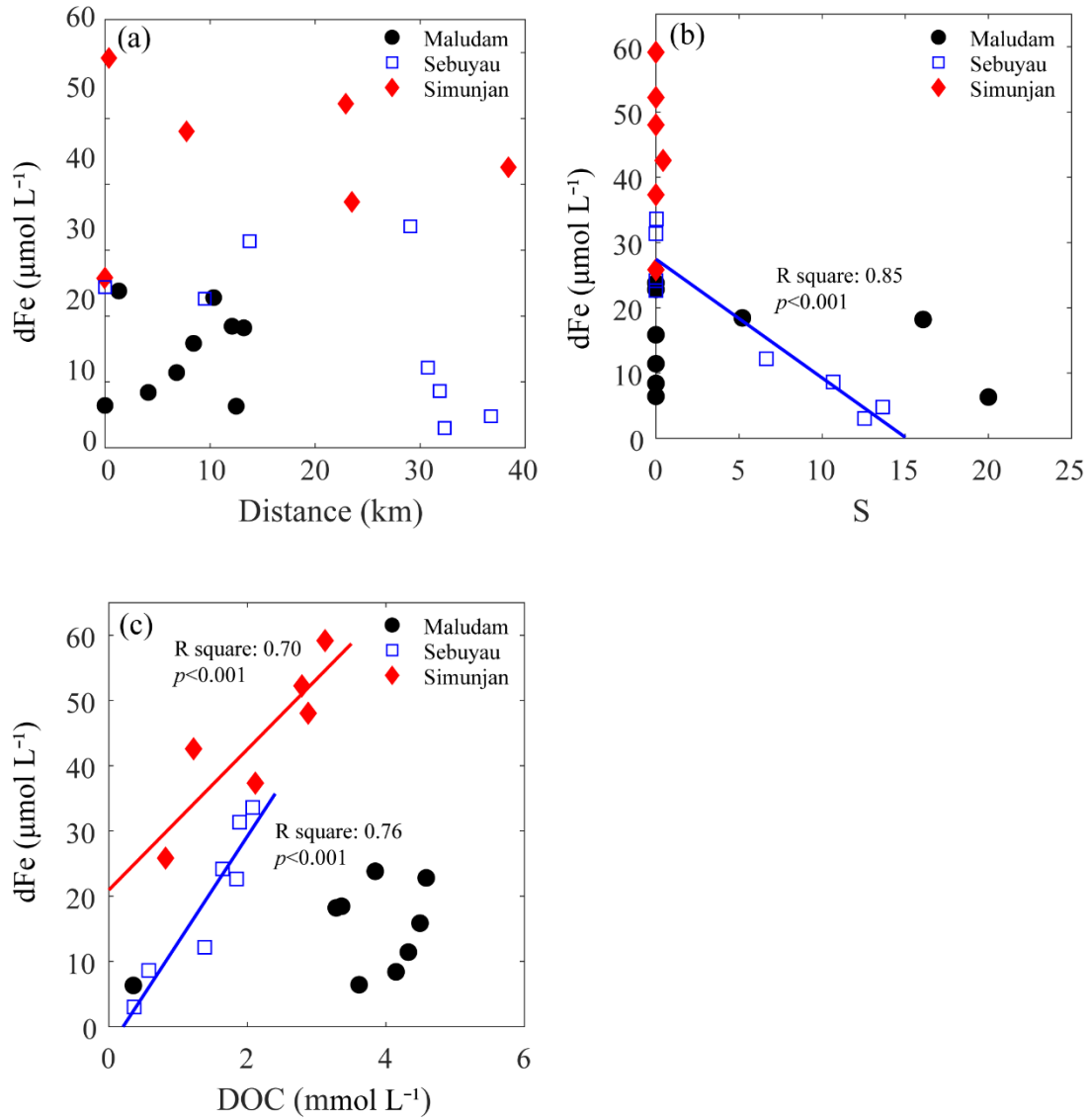
Figure 4. the correlations between distance (a), salinity (S) (b), dissolved organic carbon (DOC) (c), and dissolved iron (dFe) in blackwater rivers: Maludam, Sebuyau and Simunjan. The solid lines were the linear regressions between dFe and other factors, and the colors of the regression lines were coincident with the data points.
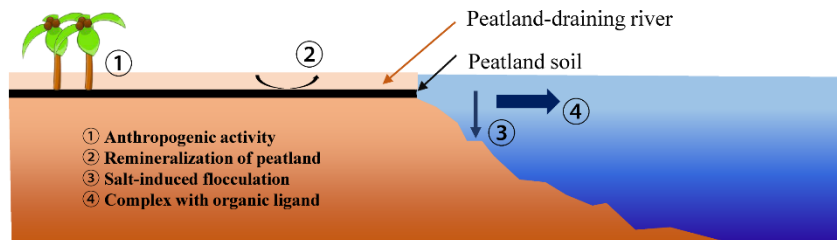
*We adopted the station at the upper stream as distance=0, and the downstream direction as positive.

(a) Rajang

① Weathering ② Anthropogenic activity
③ Desorption of particulate matter
④ Salt-induced flocculation
⑤ Complex with organic ligand

(b) Blackwater rivers

Peatland-draining river
Peatland soil

① Anthropogenic activity
② Remineralization of peatland
③ Salt-induced flocculation
④ Complex with organic ligand

Figure 5. A schematic representation of dFe biogeochemical behaviors in the Rajang River (a) and blackwater rivers (b). It highlights the anthropogenic influences on the dFe concentrations in the tropical rivers. Compared to the Rajang River, salt-induced flocculation in blackwater rivers was weak, leading to a more effective transport of riverine dFe to the coastal ocean.
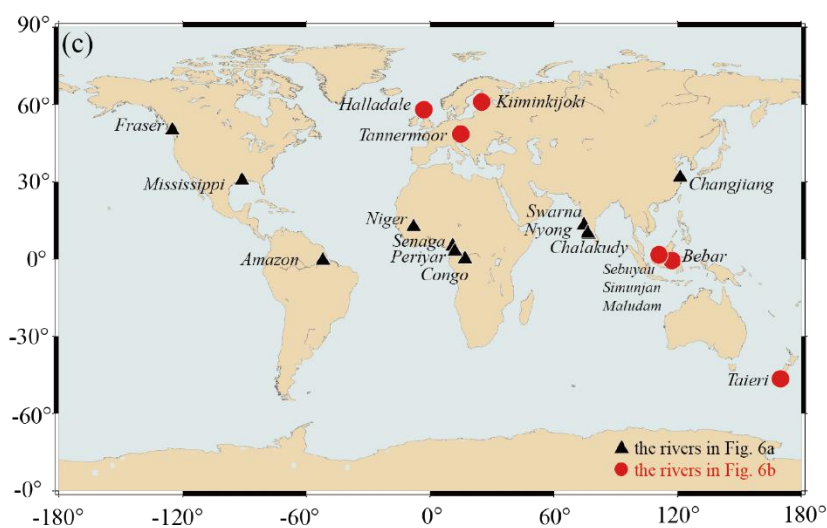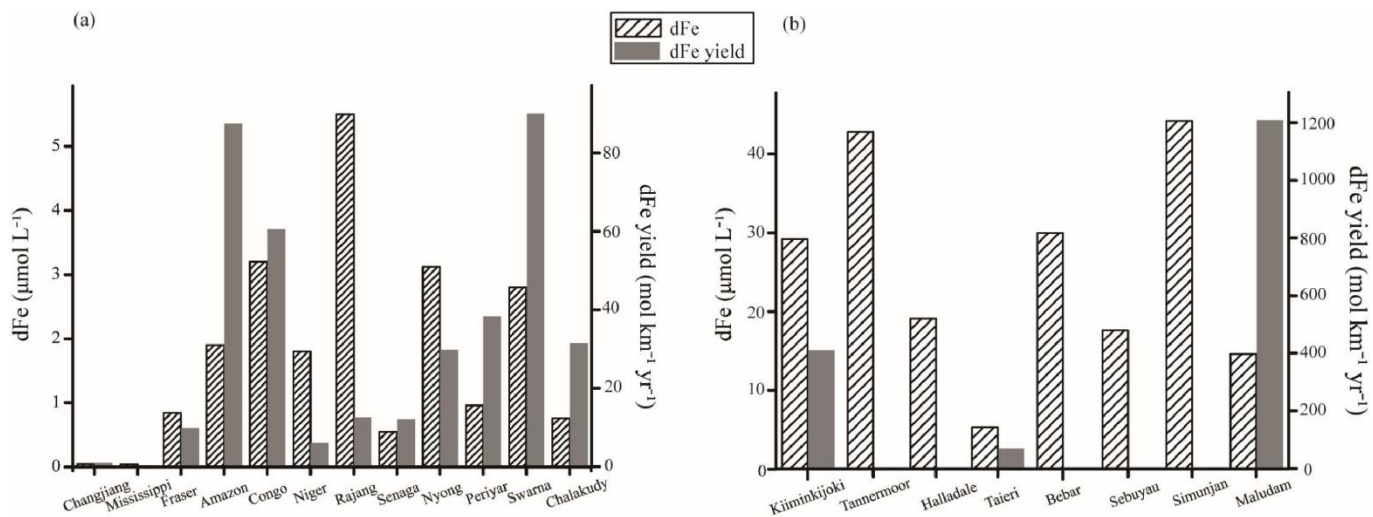
Figure 6. The concentration and yield of dFe in large rivers (a) and blackwater rivers (b). The distribution of the rivers are figured in (c).

*The concentration of dFe in the Rajang is the average of dFe in fresh water river section.