Distribution and Flux of Dissolved Iron in the 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 regarding the input of riverine dFe into coastal oceans, especially in tropical rivers in Southeast Asia. In the present study, the concentrations of dFe and distribution patterns of dFe were determined along the salinity gradient in the Rajang River and three blackwater rivers that drain from peatlands, including the Maludam River, the Sebuyau River, and the Simunjan River. In the Rajang River, the dFe concentration in freshwater samples (salinity<1) in the wet season (March 2017) was higher than that in the dry season (August 2016), which might be related to the resuspension of sediment particles and soil erosion from cropland. In the Rajang estuary, an intense removal of dFe in low salinity waters (salinity<15) was observed, which was likely due to salt-induced flocculation and absorption of dFe onto suspended particulate matter (SPM). However, increases in the dFe concentration in the wet season were also found, which may be related to dFe desorption from SPM and the influences of agricultural activities. In the blackwater rivers, the dFe concentration reached 44.2 µmol L^{-1}, indicating a strong contribution to the dFe budget 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 blackwater rivers, the dFe flux was approximately $1.1\pm0.5\times10^5$ kg yr^{-1} in the Maludam River. Anthropogenic activities may play an important role in the dFe yield, such as in 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 is deemed to be responsible for photosynthesis, respiration, and nitrogen fixation (Moore et al., 2009; Raven, 1988; Williams, 1981). Over the past four decades, Fe has been identified as a micronutrient that significantly supports 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 have verified the occurrence of Fe limitation on the growth of phytoplankton and its critical effect on CO_2 fixation (Boyd et al., 2007; Martin, 1990).

At the global scale, the amount of 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 quantity of dFe based on studies of 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 the dFe concentrations and transport patterns of tropical rivers in Southeast Asia, even though those rivers can account for approximately 30% of fluvial discharge to oceans (Milliman and Farnsworth, 2011).

Estuaries, which are the interaction zone between surface loading and coastal oceans, effectively modulate dFe concentrations during mixing and hence change the magnitude of the riverine dFe flux. A wide range of studies on the behaviors of dFe in estuaries have been conducted, and several distribution patterns have been documented (Boyle et al., 1977; Herzog et al., 2017; Oldham et al., 2017; Zhu et al., 2018). Generally, estuaries act as a sink for dFe due to flocculation occurring between cations and high-molecular-weight colloids (Bergquist and Boyle, 2006; Boyle et al., 1977; Stolpe and Hassellov, 2007). In some rivers with high concentrations of dissolved organic matter (DOM), dFe has been found to be conservative because of the chemical connection of Fe to DOM (Oldham et al., 2017; Sanders et al., 2015; Stolpe et al., 2010). The magnitude of dFe removal from estuaries can be quantified by removal factors (RF). Anthropogenic activities related to coal mining, the ore industry, and agriculture activities could significantly impact the concentrations and distributions of dFe in estuaries (Braungardt et al., 2003; Morillo et al., 2005; Xue et al., 2016).

Currently, only limited records of dFe concentrations have been provided for peatland-draining rivers (Batchelli et al., 2010; Krachler et al., 2010; Oldham et al., 2017). The dFe distribution in peatland-draining estuaries is also largely unknown. Coastal belts in Southeast Asia are covered by a large area of peatlands,

reaching approximately 9% of the global peatland coverage (Dommain et al., 2011; Joosten, 2012). To the best of the authors' knowledge, the dFe concentrations in Malaysia have only been determined (1) in Pelagus, where high concentrations of dFe were observed in freshwater due to the sediments there (Siong, 2015); (2) in Bebar, a blackwater river in Pahang, Malaysia, where the concentration of dFe was up to 30 $\mu mol\ L^{-1}$. However, information about the distribution and biogeochemistry of dFe is lacking (Shuhaimiothman et al., 2009). Such limitations in dFe data may markedly influence the regional estimations of the dFe budget.

To fill this gap in knowledge, two cruises were conducted in Sarawak State, Borneo, Malaysia, which included the largest river in Sarawak State (the Rajang River) and three blackwater rivers. This study aims to determine (1) the concentration and distribution of dFe in the studied rivers and their estuaries, (2) the seasonal variation in the concentration and distribution of dFe in the Rajang River and its estuary, and (3) the dFe yield and the magnitude of riverine dFe flux to the coastal areas.

2.   Materials and methods

2.1 Study area

Malaysia has the second largest peatland area (approximately $2.6\times10^4\ km^2$) in Southeast Asia (Mutalib et al., 1992). Sarawak State accounts for the largest peatland area of Malaysia and has widespread blackwater rivers (Joosten, 2012; Wetlands International, 2010). Approximately 23% of the peatland in Malaysia is defined as relatively undisturbed, of which 17% is in Sarawak (Wetlands International, 2010). Since the mid-1980s, the rubber, textiles, metals, food processing, petroleum, and electronics industries have been developed in the area, and they are the major economic supporters 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 palm and rubber tree plantations (Joosten, 2012).

The Rajang River, i.e., the largest river in Malaysia, which has a length of 530 km, flows from Iran Mountain to the South China Sea (Fig. 1a, 1b). The drainage basin is $51\times10^3\ km^2$ (Milliman and Farnsworth, 2011; Staub and Esterle, 1993). The drainage area of the Rajang estuary is 6,500 km^2, and 50% of it is covered with extensive peat at depths greater than 3 m (Staub and Gastaldo, 2003). The Rajang River is approximately 5-10 m and 8-20 m deep during the dry season and the wet season, respectively. The mainstream flow velocity ranges from 0.2-0.6 m s^{-1} and 0.8-1.2 m s^{-1} during the dry season and the wet

season, respectively (Tawan et al., 2019). The discharge rate for the Rajang River reaches 6000 m^3 s^{-1} in the wet season (December to March), with an average discharge of approximately 3600 m^3 s^{-1} (Jeeps, 1963; Staub et al., 2000; Staub and Gastaldo, 2003). The climate in the Rajang watershed is classified as the tropical ever-wet type (Morley and Flenley, 1987), while the precipitation rate varies between the dry and wet seasons. Sibu city is assumed to be the boundary line of the Rajang drainage basin and Rajang estuary according to physiographic conditions (Staub et al., 2000; Staub and Esterle, 1993), and saltwater intrusions can reach the downstream of the city (Jiang et al., 2019). Apart from mineral soils transported 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 are distributed in the brackish-water area in the southwestern estuary near the Rajang and Serendeng tributaries, and some freshwater trees, such as *Casuarina*, are observed in the northeastern and coastal areas (Scott, 1985). The thick coverage of vegetation, especially mangroves, in the Rajang estuary produces high-ash, high-sulfur, degraded sapric peats (Lampela et al., 2014). In the Rajang estuary, the tide is the diurnal to semidiurnal type and can extend to Sibu city (Staub et al., 2000; Staub and Gastaldo, 2003). The range of the tide increases from northeast (1.5 m) to southwest (2.5 m).

In the Rajang estuary, a substantial fraction of the surface sediment is composed of peat deposits with a maximum depth of 15 m (Staub and Gastaldo, 2003). The Rajang riverine freshwater drains the mineral soil, so the mean grain sizes of the sediment are much coarser than those of 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, podzol soils, and alluvia soils (Staub and Gastaldo 2003). Gley consists of mixed-layered illite-smectite, illite, and kaolinite and minor amounts of chlorite. Gley is frequently observed in the central and southwestern parts of the estuary (Staub and Gastaldo, 2003). Podzols are dominant in gray-white to white clay, which are composed of kaolinite and illite. Podzols are found in some low-lying areas and in the landward part of the Rajang estuary (Staub and Gastaldo, 2003). Alluvial soils, which consist of illite, smectite, and kaolinite, are found in the landward part of the coastal area of the estuary (Staub and Gastaldo, 2003). The input of total suspended solids from the Rajang River is up to 30 Mt yr^{-1} (Staub and Gastaldo, 2003).

Three small blackwater rivers, namely, the Maludam, Simunjan, and Sebuyau Rivers, are characterized by their tea color, acidity, and oxygen deficits (Kselik and Liong, 2004). The Maludam River, mainly located in Maludam National Park (the second-largest park in Sarawak), is a pristine river with minor human influences. The peat thickness in the riverbed reaches 10 m (Forest Department, 2014). The catchment of the Maludam River is 91.4 km^2, and its 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 disturbances due to human activities, mostly from plantations of commercial crops, such as oil palm and sago, as shown in Fig. 1d (Wetlands International, 2010). The grain size of sediments in blackwater rivers is much lower and receives more woody material than that of the Rajang River (Wu et al., 2019).

2.2 Sample collection and process

The water sampling stations are outlined in Fig. 1. The data collection surveys of the Rajang River and Rajang estuary were conducted in August 2016 (the dry season) and March 2017 (the wet season). Each data collection survey lasted 4 to 5 days, covering both flooding tides and ebbing tides. The water samples included freshwater from rivers, brackish water from different river tributaries and coastal saline water. In the Rajang watershed, the selection of water sampling stations depended on the salinity gradient, anthropogenic activities, and water depth. In March 2017, we failed to collect samples upstream from the Rajang River in addition to saline samples from the Igan tributary, mainly due to the shallow water depth and strong current occurring at the time of collection. However, the three aforementioned blackwater rivers were included in the cruises. During the 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, USA). The length of the pole was 3-4 m to avoid contamination from the ship. The bottom water samples were collected using a precleaned 5 L Teflon-coated Niskin-X bottle that was hung on a nylon rope. Due to the limited sampling time and conditions, only 3 bottom water samples were collected in August 2016 and 1 bottom water sample was collected in March 2017. Water samples were filtered through acid-cleaned 0.4 μm pore size polycarbonate membrane filters (Whatman, U.K.) into a polyethylene bottle (Nalgene); then, the samples were frozen at -20°C and packed in triple bags. The samples were thawed at room temperature in the clean laboratory and were acidified with ultrapure HCl to pH 1.7 in an ultraclean lab to transform and preserve metallic Fe in a soluble inorganic form (Lee et al., 2011). All the bottles used in sample collection and storage were prepared in a clean laboratory: the bottles were rinsed with Milli-Q water,

immersed in 2% Citranox detergent for 24 h, rewashed 5-7 times with Milli-Q water, leached in 10% HCl for 7 days, rinsed 5-7 times with Milli-Q water again, filled with 0.06 mol L^{-1} ultrapure HCl, allowed to sit for 2 days at 60°C, and sealed in plastic bags.

2.3 Sample analyses

The dFe concentration was preprocessed using a single batch resin extraction and the isotope dilution method. The acidified samples were preprocessed by a single batch nitrilotriacetate (NTA)-type chelating resin (Qiagen, Valencia). Dissolved Fe can be quantitatively recovered after the oxidization of Fe^{2+} to Fe^{3+} by the addition of H_2O_2 (Lee et al., 2011). Here, dFe was quantified on a multicollector inductively coupled plasma mass spectrometer in the high-resolution mode (Neptune, Thermo, USA). The inlet system contained an Apex IR desolvator with a perfluoroalkoxy microconcentric nebulizer (ESI, USA) at a solution uptake rate of 50 μL min^{-1}. All the tubes used for the analyses were acid-leached with 10% HCl for two days at 60°C, rinsed 5 times with Milli-Q water, subsequently filled with 0.06 mol L^{-1} of ultrapure HCl under a class 100 clean 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 sample and one estuary water SLEW-3 sample (NRC, Canada). The measured dFe concentrations of the SAFe D1 and SLEW-3 samples were 0.66±0.05 nmol L^{-1} and 10.0±0.4 nmol L^{-1}, respectively, compared to the consensus values of 0.70±0.03 nmol L^{-1} and 10.2±1.2 nmol L^{-1}, respectively (Zhang et al., 2015).

During the field investigation, the 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 matter (SPM) samples were collected with precombusted 0.7 μm pore size Whatman GF/F filters, and the SPM concentration was calculated according to the weight difference of the filters before and after filtration. Dissolved organic carbon (DOC) samples were collected by filtering samples through 0.2 μm pore size nylon filters. For the samples collected in August 2016, the DOC concentrations were determined via an Aurora 1030W total organic carbon analyzer at the Center for Coastal Biogeochemistry at Southern Cross University (Lismore, Australia). The reproducibility of the concentrations was ±0.2 mg L^{-1}. For the samples collected in March 2017, the DOC concentrations were determined by the high-temperature catalytic oxidation method with a total organic carbon analyzer (Shimadzu, Japan) 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 Calculation of dFe flux and yield

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

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

where Q is the dFe flux, C is the mean dFe concentration at the freshwater endmember (S<1), V is the river discharge, and RF is the removal factor, which has based on the ratio of the integrated area of the dFe concentration versus salinity to that of the line intercepts of the theoretical dilution (Hopwood et al., 2014). The 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 of the Rajang water samples ranged from 0.0 to 32.0 and increased in salinity 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 the exception of the Rajang tributary. The SPM concentration ranged from 24.2 mg L^{-1} to 327.2 mg L^{-1} and decreased in concentration from freshwater to seawater, but the highest water turbidity varied among channels and seasons. In August 2016, the peak SPM concentration was observed near the river mouth in the Serendeng tributary but moved landward in other tributaries (Fig. 2b). In March 2017, the peak of SPM concentration was located in freshwater of the Rajang tributary. The DO content recorded in March 2017 (mean: 6.1±0.7 mg L^{-1}) was higher than that recorded in August 2016 (mean: 3.8±0.6 mg L^{-1}) and decreased along the transport pathway of the Rajang drainage basin (Fig. 2c). The distribution of the DO concentration in Rajang varied between the two seasons, and a high value was found in the western estuary in March 2017 (Fig. 2c, 2h). The pH of water in the Rajang samples increased along the salinity gradient with mean values of 7.1±0.5 (August 2016) and 7.1±0.6 (March 2017). As outlined in Fig. 2d and 2i, the seasonal variation in pH was not significant.

In blackwater rivers, salinity ranged from 0 to 23.5 in the Maludam River and from 0 to 13.6 in the Sebuyau River. The samples from the Simunjan River only included freshwater. All three blackwater rivers were

anoxic at the freshwater endmembers, with DO concentrations <2 mg/L. The mixing that occurred between river water and ocean water markedly increased the DO concentration. Moreover, the pH measured in these blackwater rivers was relatively low, especially in the Maludam River (minimum 3.7). The distributions of these properties in blackwater rivers are outlined in Supplement 1.

3.2 dFe in the Rajang River and estuary

The contour of dFe in Rajang surface water is shown in Fig. 2. We adopted Sibu as the separation location 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 varied 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 varied from 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. In both the Rajang River and the Rajang estuary, the concentration of dFe measured in the wet season was higher than that measured in the dry season.

The relationships between the 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 Paloh and Lassa were combined with the Serendeng tributary, and the Belawai and Rajang tributaries were combined with the Rajang tributary. In the dry season, the dFe concentration exponentially decreased 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 the DOC concentration (R^2=0.45, p<0.05), DO concentration (R^2=0.50, p<0.05), and pH (R^2=0.39, p<0.05). In the wet season, the dFe concentration was higher in the Igan tributary than that in the other branches. There was an intense addition of dFe that occurred between salinity of 5-15, mainly in the Serendeng tributary (Fig. 3a). Specifically, a linear correlation was found between dFe and SPM 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 was identified between dFe and the DOC concentration in the wet season in low salinity waters (R^2=0.61, p<0.001) (Fig. 3c). The DO concentration was negatively correlated with dFe in the high salinity area (R^2=0.97, p<0.001), with a similar pattern observed 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 the 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 from the upper stream to the lower stream (Fig. 4a) but decreased during mixing. The distribution of dFe in blackwater rivers tended to be conservative in the Maludam and Sebuyau estuaries (Fig. 4b). Moreover, there were significantly positive correlations observed between dFe and the DOC concentration in the Sebuyau River and the Simunjan River (Fig. 4c), while the correlation between dFe and the DOC concentration in the Maludam River was weak due to an outlier in high salinity water (S=20.0).

4. Discussion

4.1 Seasonal and spatial variation of dFe in the Rajang River

In the dry season, the dFe concentration in the Rajang water (near Sibu city) ranged from 2.8 to 7.3 µmol L^{-1}. In the wet season, the dFe concentration increased (Fig. 2). As precipitation is enhanced in the wet season, the strong water flow from the upper stream scours the watershed, delivering Fe-enriched terrestrial particles to the lower stream in the wet season (Meade et al., 1985; Taillefert et al., 2000). A large quantity of dFe may result from the dissolution of these particles originating from mechanical and chemical weathering, which leads to a significant addition of dFe in the wet season (Bhatia et al., 2013). Moreover, agricultural activities in the watershed, such as tillage, can result in rapid leaching in the wet season (Lehmann and Schroth, 2003; Tabachow et al., 2004). The changes in the soil structure likely enhanced soil erosion in the cropping land, especially in 2017 (the occurrence of La Niná events) (Jiang et al. 2019). In addition, the changes in soil structure during agricultural activities can influence the exchange route of dissolved matter in vertical profiles; hence, a large proportion of dFe is likely to be transported during rainfall via water exchanges that occur (Haygarth et al., 2003; Johnes and Hodgkinson, 1998; Withers et al., 2001). The addition of dFe from cropland was also observed in many other study cases, such as the Krishna River drainage area (Kannan, 1984), the Palar and Cheyyar River basins (Rajmohan and Elango, 2005), and the Guadalquivir River (Lorite-Herrera and Jiménez-Espinosa, 2008). Eventually, stream-borne dFe was injected into the Rajang River via hydrological connections in the riparian ditches, causing dFe to be distributed to rivers from terrestrial runoff and flood discharges (Yan et al., 2016).

4.2 Seasonal and spatial variation of dFe in the Rajang Estuary

In the Rajang estuary, there was an intense removal of dFe when the water salinity was <15, especially in the dry season (Fig. 3a). This finding may be related to the flocculation of the negatively charged colloids with cations during the mixing of fresh-saline water. This phenomenon 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 dFe removal may also be linked to the absorption of SPM, as described in other studies (Van Beusekom and Jonge, 1994; Homoky et al., 2012; Zhang et al., 1995). However, there was an exceptionally high dFe concentration in samples with salinity from 5-15 in the Serendeng tributary in the wet season. On the one hand, this high dFe concentration may be the result of peatland soils in the adjacent area because peatland soils host abundant dFe and organic ligands, and these organic compounds can enhance the solubility of Fe during 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 river water.

The balance between the adsorption and desorption of trace metal ions onto and from SPM, respectively, is complicated. These two processes could occur simultaneously and be influenced by different environmental conditions, such as the 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 decreases with increasing SPM concentration and is inversely proportional to the log of the SPM concentration, termed the 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 the dFe enhancement occurring in the river mouth area of the Changjiang estuary. In the wet season, Serendeng tributary samples were collected during a spring tide. In addition, the intensive plantation and agricultural activities in the Serendeng tributary modified the soil structure and leached a considerable amount of SPM at the flood tide. In Fig. 3a, a strong increase in the dFe and SPM contents at salinities of 5-15 are shown. Given a similar level of SPM content among the Rajang, Texas River (Jiann et al., 2013) and Changjiang estuary (Zhu et al., 2018), we assumed that the dFe enrichment under this special condition may be related to desorption from the riverine SPM, though we lacked experimental confirmation, e.g., a mixing experiment to validate our assumptions. In addition, the limited number of bottom water samples

studied in the Rajang estuary also revealed that the addition of dFe from salinities of 5-15 in the wet season might also be the result of the resuspension of bottom water sediments because the bottom water dFe concentration was much higher than the surface dFe concentration.

In the high salinity zone (S>15), dFe tended to be conservative. The positive relationship observed 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 of dFe and organic matter, especially pelagic organic matter, can resist 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 results 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. These results show 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 minor impact of pH on dFe. However, in the dry season, the dFe concentration was negatively correlated with pH (Fig. 3e) because Fe-enriched sediments can be acidified and mineralized by inorganic acids (H_2CO_3, HNO_3, and H_2SO_3) and organic acids (oxalic acid, citric acid, and siderophore) derived from chemical weathering and biological processes (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.

4.3 dFe in blackwater rivers

In blackwater rivers, dFe 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 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 correlation between dFe and DOC (Fig. 4c), peatland should be a strong source of dFe. Consequently, the gradual enrichment of dFe along the river pathways was observed. Compared with the Maludam River, i.e., the drainage from an undisturbed peatland, the dFe concentrations in the Sebuyau River and the Simunjan River were significantly higher (Table 1). The difference in the dFe concentrations among the three blackwater rivers may result from the variation in environmental parameters around the drainage basin, especially the vegetation types and anthropogenic activities. Oil palm plantations covered a significant area in the

watershed of the Sebuyau River and Simunjan River, as shown in Fig. 1d. To stimulate seedings in plantations, empty fruit bunches and oil palm mill effluent were returned to the cropland after oil extraction (Carron et al., 2015; Nelson et al., 2015). Intensive agricultural activities, such as tillage, further enhanced the decomposition of environmental parameters around the drainage basin, and these activities might improve the mechanical and chemical weathering that occurs in the plantation areas and increase the dFe concentration in the Sebuyau River and the Simunjan River, as discussed in chapter 4.1.

During the cruise, high salinity samples were not obtained from the Maludam River or the Sebuyau River. For the samples with salinities ranging from 0 to 20.0, dFe removal was not significant, which is markedly different from the trend obtained in the Rajang estuary (Fig. 4b). The significant positive correlation observed between the dFe and DOC concentration revealed the tight connection between dFe and organic ligands in blackwater rivers (Fig. 4b). Recent studies have also noted that organic ligands originating from peatland enhance the iron-carrying capacity of river water (Krachler et al., 2005; Oldham et al., 2017). Approximately 20% of dFe did not flocculate during a laboratory mixing experiment (Krachler et al., 2010). The biogeochemical behavior of dFe in blackwater rivers discussed above is summarized and conceptualized in Fig. 5b. Compared with the Rajang estuary, less dFe flocculated from the blackwater river estuaries due to complexing that occurred 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 rivers, 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 the two seasons was 5.5 ± 2.0 μmol L^{-1} and the mean removal factor was $98.0 \pm 0.6\%$. The removal factor of dFe varied at the global scale. The Rajang RF is dominant among the recent results (Table 2). Coupled with the discharge rate (approximately 3600 m^3 s^{-1}), the dFe flux from the Rajang River was estimated to be $6.4 \pm 2.3 \times 10^5$ kg yr^{-1}. 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 (Fig. 5). For the Maludam River, the dFe concentration of the river endmember was 14.6 ± 6.8 μmol L^{-1} and RF=0 due to the conservative dFe. The dFe flux in the Maludam River was approximately $1.1 \pm 0.5 \times 10^5$ kg yr^{-1}, produced from 432 km^2 of peatland in Maludam National Park. This value was the same magnitude as the Rajang River dFe flux, suggesting that the dFe input was considerable in blackwater rivers. Malaysia hosts a peatland area of approximately 25,889 km^2, and the dFe

flux can reach approximately $6.6 \pm 3.0 \times 10^6$ kg yr^{-1} on the basis of the yield from the Maludam River. Consequently, blackwater rivers contribute 10 times greater amounts of dFe than that contributed by 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, such as the Changjiang River (Zhu et al., 2018) and the Mississippi River (Shiller, 1997; Stolpe et al., 2010), tropical rivers contribute a greater amount of dFe to coastal areas 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 have a similar discharge rate and drainage area as the Rajang River, such as the Fraser River in Canada, the dFe yield is significantly lower than that derived from the Rajang River (Cameron et al., 1995). The high dFe concentration and yield in tropical rivers likely results from the intensive weathering and leaching of rocks and sediments, as well as the decomposition of abundant plantations under high temperatures and heavy precipitation (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 is lower in the Rajang River and 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 passes through a dry savanna (Picouet et al., 2002). In contrast to the Niger River, the Sanaga River drains a savanna rainforest area and contains considerable amounts of SPM compared to that of the Rajang River. The dFe yield is comparable with that of the Rajang River. For some small tropical rivers, such as 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), the dFe yields and DOC concentrations are higher compared to those of the Rajang River. In these small tropical rivers, the drainage basins were covered with sediment-enriched organic matter, which may be a great source of dFe flux.

In blackwater rivers, the dFe yields were much higher than the amounts obtained in the Rajang River. The thick peatland soils were likely to be the main reason for the high dFe concentration in the blackwater rivers, as previously reported for the Kiiminkijoki 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). Human impacts, such as agricultural activities and plantations of oil palm trees, may also contribute to the bulk 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 follows:

1. There was a significant seasonal variation in the dFe concentration in the Rajang River with a higher dFe concentration observed in the wet season, which is likely due to the dissolution of particular iron from upstream weathering. dFe removal was intense in the low salinity area (salinity<15) of the Rajang estuary due to salt-induced flocculation and adsorption onto the SPM. In contrast, dFe tended to be conservative in the high salinity area (salinity>15), which may be due to binding between dFe and organic matter. In addition, there were significant additions of dFe in some tributaries from the desorption of SPM and anthropogenic inputs.

2. The dFe concentration in the blackwater rivers was 3-10 times greater than the dFe concentration in the Rajang River, which was related to the contribution of peatland soil. Anthropogenic activities in the watershed also influenced the dFe concentrations in the blackwater rivers. In contrast to the patterns observed in the Rajang estuary, there was no remarkable dFe removal occurring in the blackwater river estuary.

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

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

Data availability. The datasets will be provided upon reasonable request by the corresponding author.

Supplement. The supplement related to this article is available online at https://www.biogeosciences-discuss.net/bg-2019-204/bg-2019-204-supplement.pdf.

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695 Table 1. Range and average of salinity (S), pH, suspended particulate matter (SPM), dissolved oxygen (DO), dissolved iron (dFe), and dissolved
696 organic carbon (DOC).

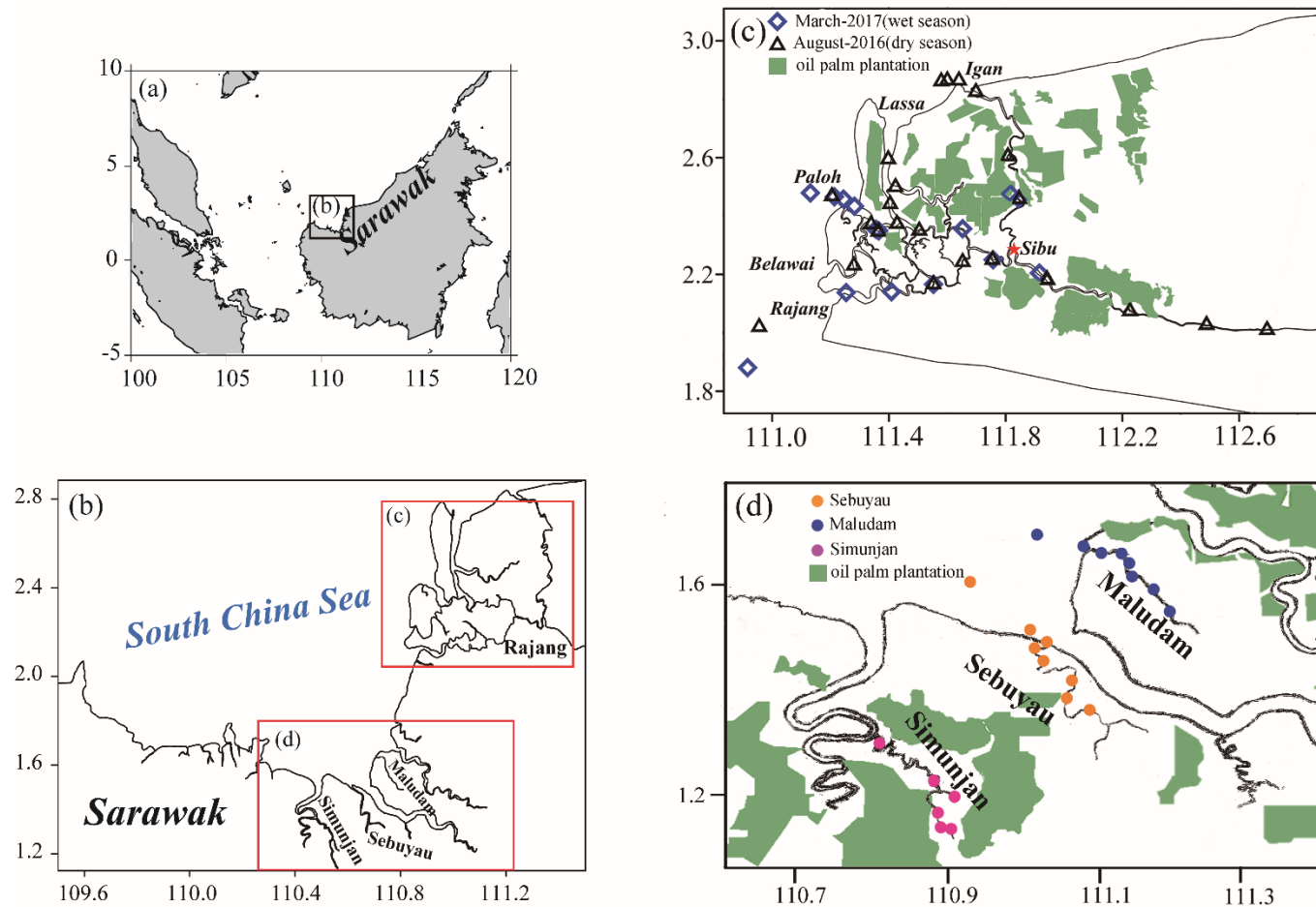| River-Time	Station	S	pH	SPM (mg L^{-1})	DO (mg L^{-1})	dFe (µmol L^{-1})	DOC (µmol L^{-1}) *in mmol L^{-1}
Rajang River-August, 2016	8	0	6.7-6.8 (6.7±0.05)	31.4-95.2 (51.5±22.1)	3.4-4.8 (4.4±0.4)	3.3-7.3 (5.5±1.7)	192-260 (219±24)
Rajang Estuary-August, 2016	20	0-32 (16.3±11.8)	6.5-8.1 (7.3±0.5)	24.2-130 (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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698 Table 2. Concentration of dFe and the 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

699 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.

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

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

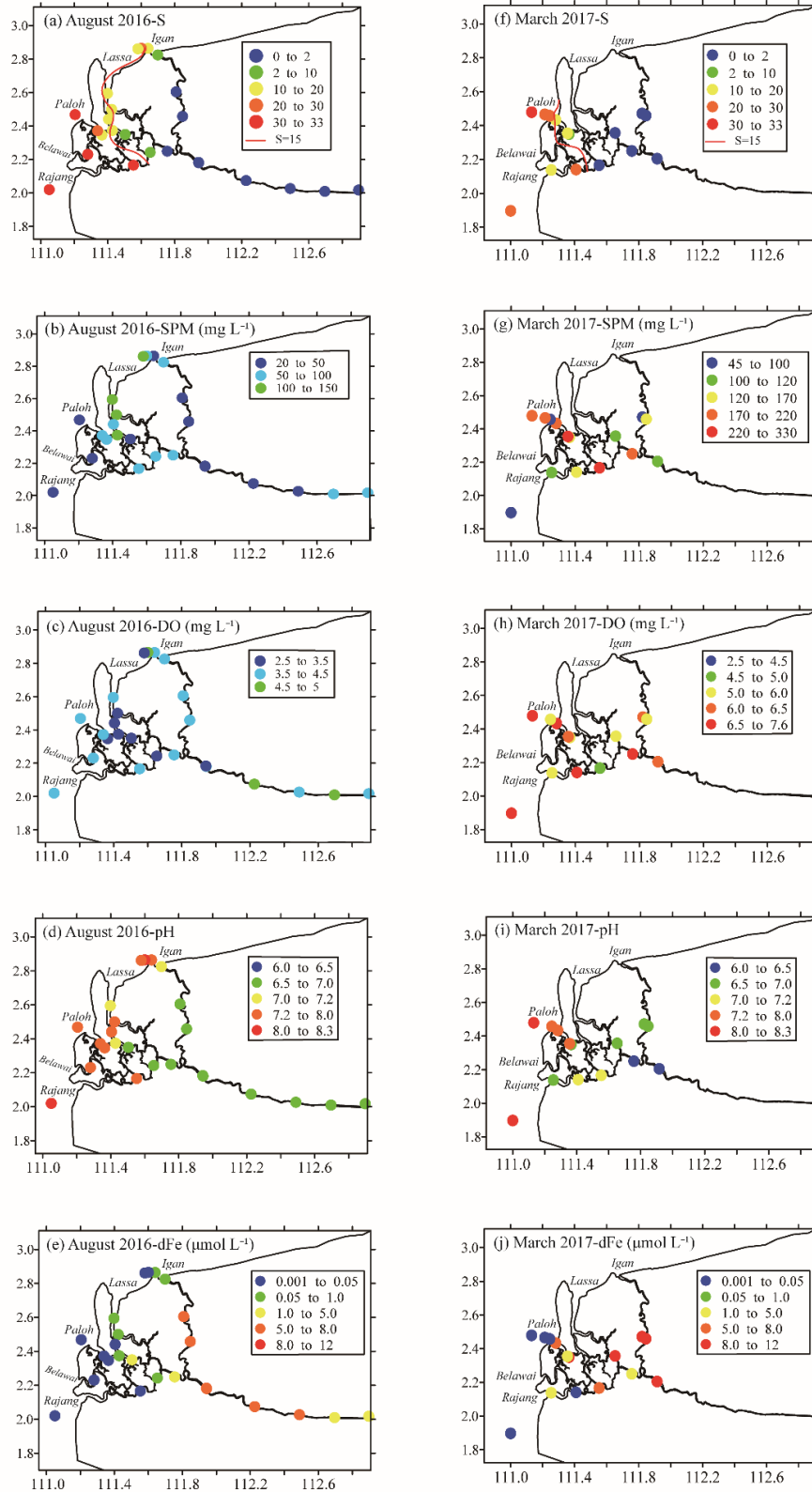702 * dFe yield is a ratio of dFe flux and drainage area.

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705 Figure 1: Distribution of sample stations in Sarawak (b), Malaysia (a). Including Rajang in August 2016, and Rajang, Maludam, Sebuyau, and
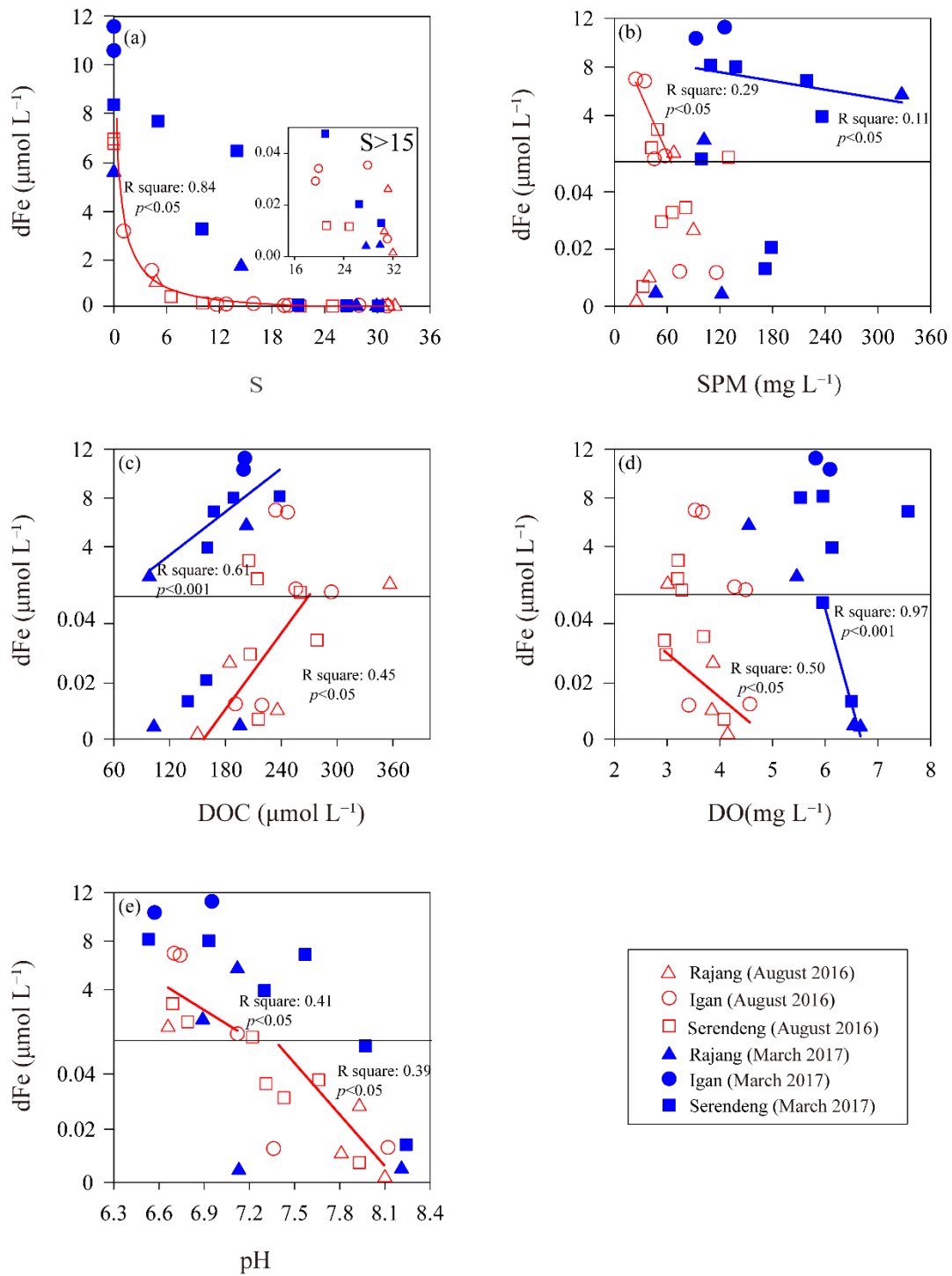706 Simunjan in March 2017. In figure (c) and (d), the green feature layer was redrawn by the dataset from Global Forest Watch (http://gfw2-
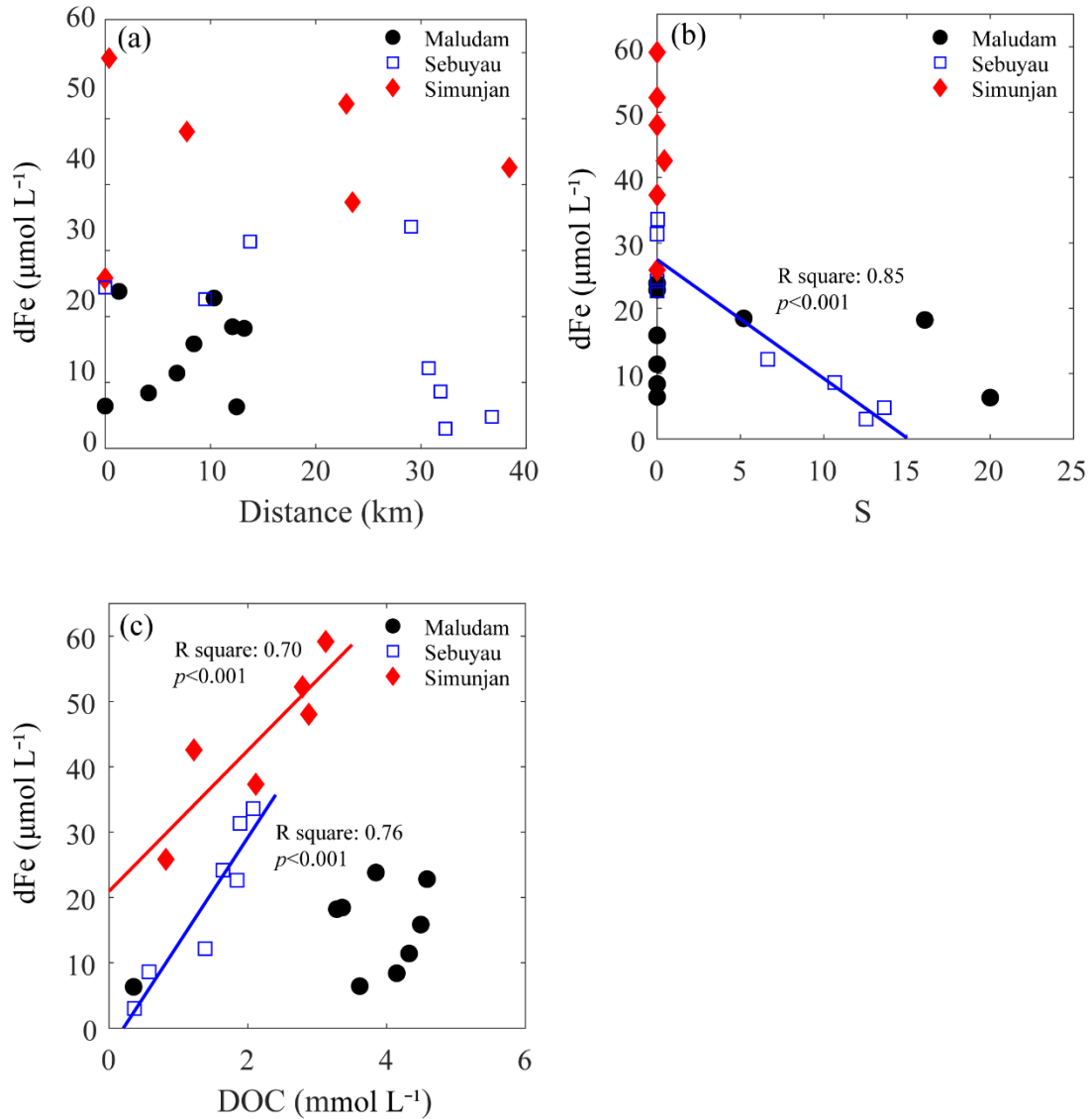707 data.s3.amazonaws.com/country/mys/zip/mys_oil_palm.zip).

Figure 2. Spatial distributions of the salinity (a) and (f), suspended particulate matter (SPM) (b) and (g), dissolved oxygen (DO) (c) and (h), pH (d) and (i), and dissolved iron (dFe) (e) and (j) in the Rajang River in August 2016 and March 2017, respectively. The red solid line is the isosalinity line (S=15) linear interpolated from S in this region.

Figure 3: Correlation of the dissolved iron (dFe) with the salinity (S) (a), suspended particulate matter (SPM) (b), dissolved organic carbon (DOC) (c), dissolved oxygen (DO) (d), and pH (e) in the 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.
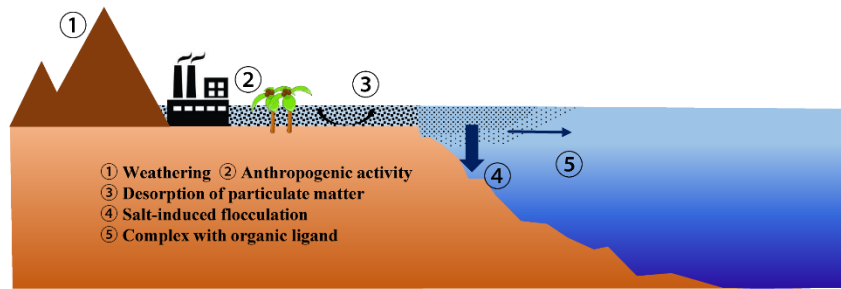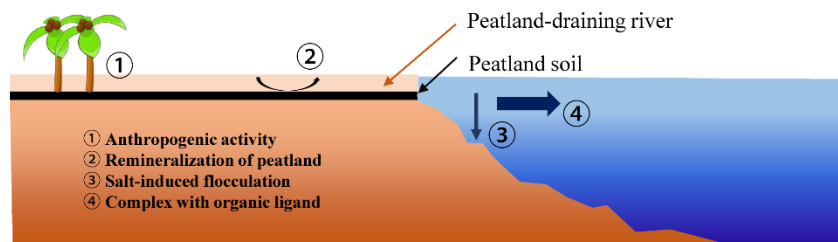
Figure 4. Correlations among the distance (a), salinity (S) (b), dissolved organic carbon (DOC) (c), and dissolved iron (dFe) in blackwater rivers: Maludam, Sebuyau and Simunjan. The solid lines were the linear regressions between dFe and other factors, and the colors of the regression lines were coincident 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. Schematic representation of the 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.
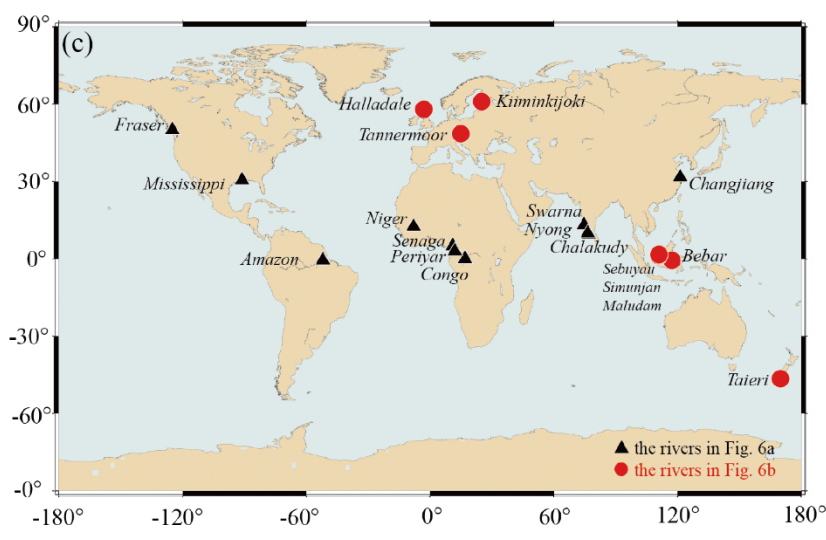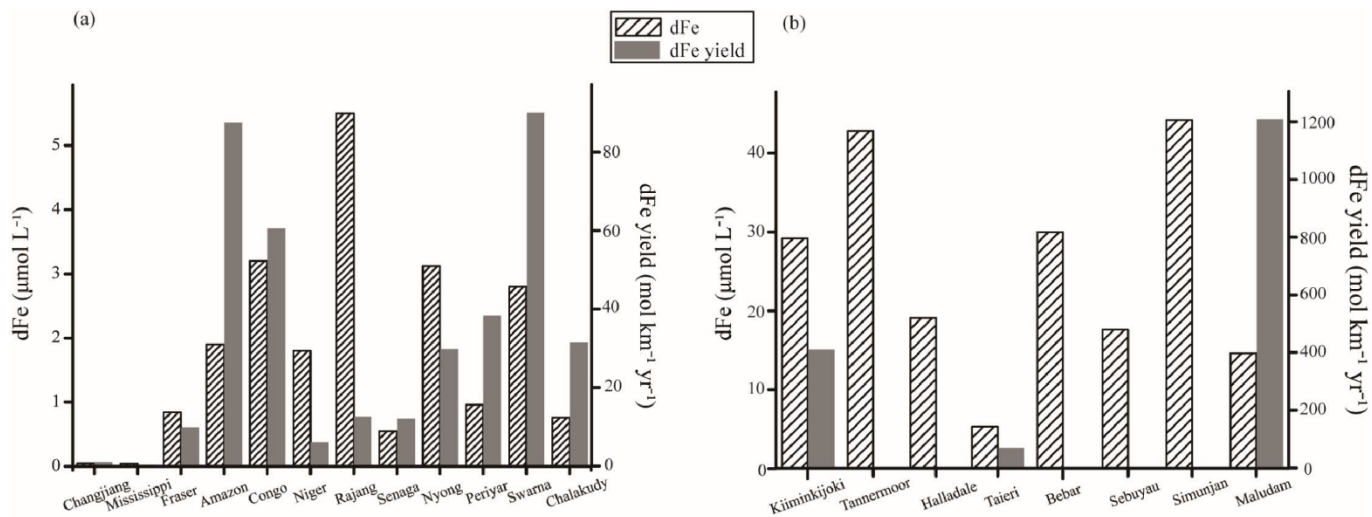
Figure 6. Concentration and yield of dFe in large rivers (a) and blackwater rivers (b). The locations of the rivers are shown in (c).

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