Dissolved inorganic nitrogen in a tropical estuary at Malaysia: transport and transformation

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Abstract. Dissolved inorganic nitrogen (DIN), including nitrate, nitrite and ammonium, frequently acts as the limitation for primary productivity. Our study focused on the transport and transformation of DIN in a tropical estuary, i.e. the Rajang river estuary, in Borneo, Malaysia. Three cruises were conducted in August 2016, February-March and September 2017, covering both dry and wet seasons. Before entering the coastal delta, decomposition of the terrestrial organic matter and the subsequent soil leaching was assumed to be the main source of DIN in the river water. In the estuary, decomposition of dissolved organic nitrogen was an additional DIN source, which markedly increased DIN concentrations in August 2016 (dry season). In the wet season (February 2017), ammonium concentrations showed a relatively conservative distribution during the mixing and the nitrate addition was weak. La Niña events induced high precipitations and discharge rates, decreased reaction intensities of ammonification and nitrification. Hence similar distribution patterns of DIN species in the estuary were found in September 2017 (end of dry season). The magnitude of riverine DIN flux varied between 77.2 and 101.5 ton N d^{-1}, which might be an important support for the coastal primary productivity.

1 Introduction

Nitrogen (N) is an essential element for life. The concentration of N may significantly influence species composition and diversity in terrestrial, freshwater and ocean ecosystems (Vitousek et al., 1997). Apart from nitrogen gas (N_2), N is bioactive with highly variable chemical forms. Dissolved inorganic nitrogen (DIN), including nitrate (NO_3^-), ammonium (NH_4^+) and nitrite (NO_2^-), can be easily assimilated by terrestrial plants, algae and bacterial communities (Seitzinger et al., 2002). In addition, due to the high solubility, DIN can be easily transported among ecosystems as a part of the hydrologic cycle (Galloway et al., 2004). Consequently, DIN is assumed to be the most active component in the N cycle and the transport of DIN among ecosystems is a hotspot in biogeochemical research on a global scale (Gruber and Galloway, 2008).

Estuaries are the linkage between terrestrial surface water and coastal sea (Seitzinger et al., 2002) and received great attention from researchers and coastal managers with regard to the quantification of terrestrial DIN transport (e.g. Falco et al.,

2010; Holmes et al., 2012; Li et al., 2013; Kuo et al., 2017). The mixing between fresh and saline water develops physiochemical gradients in various parameters such as dissolved oxygen (DO), salinity and pH (Spiteri et al., 2008), which influence the growth of distinct bacterial communities (e.g. Goñi-Urriza et al., 2007; Spietz et al., 2015). These bacteria actively participate in DIN transformation processes, such as denitrification, DNRA (dissimilatory nitrate reduction to ammonium) and Anammox (anaerobic ammonium oxidation; Burgin and Hamilton, 2007). These processes strongly influence DIN concentrations (Canfield et al., 2010), adding uncertainties to the precise estimation of DIN fluxes. Moreover, environmental parameters related with these gradients vary significantly between seasons, leading to a highly dynamic DIN export. Additionally, riparian regions are the focus of anthropogenic processes, including agriculture, manufacture and wastewater treatment, etc. (Richardson et al., 2007). These activities strongly influence DIN cycling in rivers and estuaries.

Researchers increased the sampling frequency and introduced regional modeling work to improve the understanding of DIN transport and transformation processes. More importantly, stable isotope fractions, e.g. $\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$, $\delta^{15}N\text{-}PN$ (particle nitrogen), have been introduced to trace DIN transport and transformation processes (Middelburg and Nieuwenhuize, 2001). The stable isotope technique has been applied in a number of estuaries located in temperate and sub-tropical zones, such as the Changjiang estuary (China; Yu et al., 2015; Yan et al., 2017), the Seine River estuary (France; Sebilo et al., 2006), the Thames Estuary (U.K.; Middelburg and Nieuwenhuize, 2001) and Werribee River estuary (Australia; Wong et al., 2014). The delineated reaction pathways and DIN sources/sinks from these research outcomes largely improved our understanding of DIN cycle, which is crucial for projections as well as the regulation/law enactment.

Despite the significant advances made, knowledge gaps in DIN transport via estuaries still exist with geographic coverage as one of the major shortcomings. As aforementioned, previous research work was intensively conducted in temperate and sub-tropical zones. The tropical zone, characterized by the high annual temperature and intense precipitations, hosts substantial rivers and streams; while studies on DIN transport are scarce, especially in Southeast Asia. The lack of information potentially hampers the holistic understanding of DIN transport from rivers to oceans and increases uncertainties in the global DIN budget estimation (Voss et al., 2013). In addition, since the Second World War, a rapid development in tropical countries has been witnessed. For instance, from 1960 to 2008, the gross national income (GNI) per capita in Malaysia (3.3-5.3) is much higher than the global average level (0.7-1.8; Tran, 2013). Coupled with urbanization, land use change and population increasing, the tropical zone is becoming a hotspot for DIN production, utilization and transport (Seitzinger et al., 2002). The ecological and environmental response in tropical estuaries to the DIN related anthropogenic pressure is less documented and the magnitude of river borne DIN fluxes to coastal lines in the tropical zone is less evaluated. Moreover, the coastal ecosystem in the tropical zone is often complex in structure and harbors substantial seagrass meadow, fishes and coral reefs (Sale et al., 2014). The enhanced intrusion of allochthonous DIN from estuaries to coastal regions might be an ecological risk for local systems (Barbier et al., 2011). Adding these together, it is of urgency and importance to apply robust DIN studies in the tropical zone and cooperation between researchers from multiple disciplines is highly necessary.

In the present study, three cruises in a typically tropical estuary, i.e. the Rajang river estuary (hereafter Rajang estuary), in Malaysia were conducted, from August 2016 to September 2017, covering both dry and wet seasons. Each cruise started

from the upper stream and extended to the coastal ocean. Concentrations of PN, dissolved organic nitrogen (DON) and DIN were determined, and isotope fractions of $^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ as well as ^{15}N-PN were analyzed accordingly. The research aims for the current research included (1) identification of DIN sources in the river water; (2) exploration of transfers and reactions with regard to DIN at different tributaries in the Rajang estuary and influences on DIN concentrations; (3) estimation of the magnitude of DIN fluxes injected from the Rajang river to coastal oceans.

2 Materials and methods

2.1 Study site

The Rajang river (hereafter Rajang) is located in Sarawak state, Borneo (Fig. 1A and B). Sarawak is one of the largest states in Malaysia with an intensive tropical forest coverage. By 2000, the population in Sarawak was 2.5 million with the urbanization level of 47.9% (https://www.sarawak.gov.my/web/home/article_view/240/175). The climate in the Sarawak state is tropical ever-wet (Staub et al., 2000) and frequently influenced by the El Niño-Southern Oscillation (ENSO) and Madden-Julian Oscillation (Sa'adi et al., 2017). The annual precipitation in the Rajang watershed is approximately 4000 mm, especially in the period from November to next February due to Indian Ocean Monsoon (Müller et al., 2015). As a result, this period is usually identified as the wet season and the remaining months are attributed to the dry season. The temperature variation was limited between each month and the highest mean daily temperature reached 33 ℃ (Ling et al., 2017).

The Rajang is the largest river in Malaysia with a length of ca. 530 km. It originates from the Iran Mountains, flows through several cities, such as Kanowit, Song and Sibu, enters the Rajang Delta and discharges into the South China Sea (Staub et al., 2000). The watershed coverage is approximately 5.1×10^4 km^2. The river bed in the upper stream was mainly composed by Creaceous-Eocene age sediments. Igneous intrusive and extrusive rocks were observed along the river (Staub et al., 2000). Coupled with precipitation and erosion, suspended particles in the river water were frequently above a level of 200 mg L^{-1} (Ling et al., 2017; cf. Fig. S1). After 6000-year accumulation, sediment particles from the upper stream developed a large area of alluvial delta (from Sibu to estuary mouths). The delta plain is mainly composed of siliciclastic sediments (bottom) and organic matter enriched sediments (surface). A substantial fraction of surface sediments was identified as peat deposits with a maximum depth of 15 m (Staub et al., 2000). There are four major tributaries in the Rajang Delta, namely Rajang, Hulu Seredeng (further separates into two tributaries: Paloh and Lassa), Belawai and Igan (Fig. 1B). Apart from the Rajang tributary, the peat deposits were frequently observed in the remaining three tributaries (Fig. 1C). The tidal range in the Rajang estuary is from 2.8 to 5.6 m and decreases from the Rajang tributary (macro tidal range) to the Igan tributary (meso tidal range). The saltwater intrusion could reach the downstream of Sibu with a few kilometers to the city (Müller-Dum et al., 2019). The total discharge rate of the Rajang was estimated to be 3000 to 6000 m^3 s^{-1}, depending on seasons. The river water mainly injects through the Igan branch to the South China Sea (Jakhrani et al., 2013). The Rajang and its delta play an important role in the national economy. Fishery, logging and timber processing are traditional supports for local citizens (Salam and Gopinath, 2006; Miettinen et al., 2016). In addition, industry plantations for oil palm and acacia have boomed

recently (Lam et al., 2009), occupying more than 50% peatland (11% of the catchment size) in the Rajang watershed (Miettinen et al., 2016). These activities have led to patchy deforestation, from the upper steam to the coastal delta (Fig. 1C).

2.2 Cruises and sample collection

Three cruises were conducted during 2016-2017, covering two dry seasons (August 2016, September 2017) and a wet season (February to March 2017). The sampling in each cruise included the river water sites, and brackish water sites in the Igan, Lassa/Paloh and Rajang tributaries. High salinity water samples (>30‰) from the adjacent coastal ocean were also collected. The total sampling sites in each cruise ranged between 16 and 32 stations. In September 2017, pore water samples from the edge of a mangrove forest, peatland and coastal sandy beach were collected. Rainwater was gathered once during the September cruise.

The river water and coastal seawater were collected into 1 L acid-prewashed high density polyethylene (HDPE) sampling bottles via a pole-sampler that decreases the contamination from boat surface and engine cooling water (Zhang et al., 2015). Apart from four stations in September 2017, salinity, temperature, DO and pH were measured *in-situ* by an Aquaread® multiple parameters probe (AP-2000). For pore water samples, a sampling hole with a depth of approximately 20 cm was dug at low tide. The seeped pore water that accumulated in the bottom of the sampling hole was discarded three times before collection. Subsequently, pore water was sucked into a 50 mL syringe and then transferred to 250 mL acid-prewashed sampling bottles. The rainwater was collected under the roof at a local primary school in a strong precipitation event. The rainwater from the first 10 min was discarded. Salinity of the pore water and rainwater was determined by a refractometer.

The filtration was conducted immediately after sampling. The harvest water samples were shaken and then divided into two portions (excluding pore water and rainwater). The first portion was filtered via polycarbonate membrane filters (0.4 μm pore size, Whatman®) into 60 mL sampling bottles for the determination of dissolved nitrogen species in three cruises and NO_3^- isotope fractions ($^{15}N\text{-}NO_3^-$ and $^{18}O\text{-}NO_3^-$) in the last two cruises. The other portion was filtered via pre-combusted (450 °C, 4 hours) glass fiber filters (average pore size 0.7 μm, Whatman®) for the analyses of SPM and PN concentration, as well as $\delta^{15}N$-PN. Both liquid and membrane samples were kept at -20 °C environment until laboratory analyses.

2.3 Mixing experiments

In September 2017, a mixing experiment was conducted to explore the influence of river-borne suspended particles on DIN transformation along the salinity gradient. In particular, river water samples (salinity: 0) from Sibu (10 km downstream from the city dock) and coastal ocean (salinity: 32‰) were collected. All the seawater and half of the river water were filtered through polycarbonate membrane filters to remove particle matters. The first treatment group was assigned to be the mixture between the filtered seawater and the particle-free river water. In practice, they were mixed and placed in 1 L acid prewashed HDPE bottles with a volume of 500 mL. The percentage of river water in the system was 0% (purely filtered seawater), 25%, 50%, 75% and 100% (pure river water). The second treatment group contained filtered seawater and unfiltered river water, while the total volume and percentage of river water were identical with the first treatment. The HDPE bottles were placed in

the darkness at 25-26 ℃ for 24 hours. During the incubation, all the bottles were rotated to sustain the suspension of particles. Afterwards, all the mixture was filtered again and the liquid was stored in 60 mL bottles in a freezer for the determination of DIN, DON, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$.

2.4 Laboratory analyses

After thawing and thoroughly remixing, concentrations of NH_4^+, NO_2^- and NO_3^- were determined on a flow-through injection system (SKALAR Analytical B.V., The Netherlands) using standard colorimetric methods (Grasshoff et al., 2007) after modification by manufactures. The determination limit for these species was below 0.1 μM and analysis precision was 3.5%. The content of total dissolved nitrogen (TDN) was measured by the potassium persulfate digestion method (121 ℃, 30 min digestion) according to Ebina et al. (1983). The difference in the concentration between TDN and DIN was assumed to be the level of DON. Both $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were determined using the bacterial reduction method on the basis of Weigand et al. (2016). In practice, NO_3^- in the water samples were transformed into N_2O via the denitrifier (*P. aureofaciens*; Sigman et al., 2001) after removal of NO_2^- by sulfanilamide acid solution (Weigand et al., 2016). The produced N_2O was injected into a Thermo-Fisher Precon system (Thermo Fisher, USA) and then flowed through Finngan chromatographically loops, finally into a Thermo-Fisher Delta V isotope system. The calculation from N_2O isotope fraction to $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ followed Casciotti and Mcilvin (2007). The determination limit for the original NO_3^- concentration was approximately 0.9 μM. The method precision was 0.2‰ ($\delta^{15}N\text{-}NO_3^-$) and 0.5‰ ($\delta^{18}O\text{-}NO_3^-$), respectively.

2.5 Mathematical analyses

To understand the addition or removal of solutes during the mixing, a two-endmember mixing model (Liss, 1976) used for the conservative distribution of solute concentration and related isotope fractionations was invoked:

$$N_{mix} = f_r \times N_r + (1 - f_r) \times N_o, \quad (1)$$

where N_{mix} is the conservative concentration of a specific N solute at a particular salinity; N_r is the solute concentration at the fresh water endmember (obtained from the starting site in each tributary); N_o is the concentration at the ocean endmember (the high salinity site near each tributary outlet); f_r is the fraction of fresh river water, which is calculated as:

$$f_r = (S_o - S_{mix})/(S_o - S_r), \quad (2)$$

where S_{mix} is the sample salinity; S_r and S_o are salinity at the river and saline water, respectively. For the conservative isotope fraction in each sample, it can be calculated as:

$$\delta_{mix} = [f_r \times N_r \times \delta_r + (1 - f_r) \times N_o \times \delta_o]/N_{mix}, \quad (3)$$

where δ_{mix} is the conservative isotope fraction, such as $\delta^{15}N\text{-}NO_3^-$ or $\delta^{18}O\text{-}NO_3^-$; δ_r and δ_o are isotope values at the river and seawater, respectively. The difference in concentration between the conservative and the observed level was defined as the offset concentration, i.e. an indicator for benthic N reactions. Considering the limited distance and similar environmental

settings between the Polah and Lassa tributary, the measurement data from these two tributaries were merged together in the calculation and related plots.

Total DIN fluxes (Q) transported to the coastal ocean were estimated according to the following equation:

$$Q = C \times V \times (1 - {}^{(f_{Rajang} + f_{Lassa} + f_{Igan})}/_{3}), \quad (4)$$

where C is the mean concentration of DIN species at the fresh river water (salinity: 0), V is the river water discharge (3000 $m^3\ s^{-1}$ in the dry season, 6000 $m^3\ s^{-1}$ in the wet season), and f is the reaction factor for each DIN species. It was estimated on the basis of concentration differences between the observed pattern and the conservative distribution for each solute (calculation process described in the legend of Fig. S2) in each tributary (i.e. f_{Rajang}, f_{Lassa} and f_{Igan}). The positive value indicates the solute addition during the mixing and vice versa. The magnitude of f is closely linked to the magnitude of reaction intensity in addition/removal at estuary. In the flux calculation, the average (${}^{(f_{Rajang} + f_{Lassa} + f_{Igan})}/_{3}$) from three tributaries was used.

All the statistical analyses, such as student t-test and linear regression were conducted in Minitab 17.0 (Minitab Inc., Pennsylvania State University, USA). The significant threshold for all the analyses was α=0.05.

2.6 Data plot

The spatial distribution of each parameter, e.g. salinity, temperature and solute concentration, was plotted in Surfer 14.0 (Golden Software Inc., USA) and the dot plots were done in Sigmaplot 12.5 (Systat Software Inc., USA). Given the limited space, a portion of plots was displayed in supplementary materials (Fig. S3 to Fig. S11).

3 Results

3.1 Water chemistry

In August 2016, the salinity in the sampled water ranged from 0.02 to 31.2‰ (Fig. 2, left panel). Similar salinity range was observed in the remaining cruises. The water temperature ranged from 27.7 to 31.8 ℃ in August 2016 and the variation among cruises was also limited. The pH varied from 6.03 to 8.12 and displayed a steady increase from the river water to coastal oceans (Fig. S3 and S4). DO fell in the range between 8.2 and 2.7 mg L^{-1}. The DO content in the majority of sites was undersaturated, especially in the August cruise. Accordingly, the oxygen undersaturation degree (OUD), i.e. the difference between DO saturation level and observed DO concentration, was calculated. It varied from 0.6 and 132 μmol L^{-1} and decreased from fresh river water to coastal saline water (Fig. S5). In the light of the seasonality, the mean OUD at the fresh river water and the estuary in three tributaries in August 2016 was significantly higher than the values from the remaining two cruises.

3.2 Particle nitrogen and its isotope fraction

In August 2016, SPM concentrations ranged from 24 to 120 mg L^{-1} (Fig. 2). Compared with the coastal ocean (24 mg L^{-1}), the SPM content in the river water was markedly higher and presence of estuarine turbidity maximum was obtained in river branches. In the cruises at 2017, the SPM concentration in the river water markedly increased (exceeding 500 mg L^{-1}). By contrast, the SPM content in the ocean endmember was similar among cruises. Percentages of PN in SPM varied between 0.1% and 0.6% (Fig. S6). For the PN concentration, i.e. the multiplication product of SPM concentration and PN percentage, varied from 5.0 to 40.7 μM (Fig. S6). Due to the low concentration of SPM, the range of PN concentration in August 2016 was lower than that obtained from February 2017 and September 2017. The δ^{15}N-PN from three cruises was from 1.9‰ to 11.8‰ (Fig. 2). Apart from several sites in the mixing zone, δ^{15}N-PN in the fresh river water and seawater was similar. A seasonal variation in δ^{15}N-PN was found. The highest value was observed in September 2017, while the lowest fraction was obtained in February 2017 (Fig. 2).

3.3 Dissolved nitrogen and related isotope fractions

Compared with the PN concentration, the content of dissolved fractions was relatively minor. In August 2016, DON concentrations varied from 2.6 to 14.8 μM and high levels were found in estuary channels (Fig. S8). In the remaining two cruises, DON concentrations in many sites were comparable to the range obtained from the first cruise. NH_4^+ concentrations were 0.39 to 17.3 μM (Fig. 3). Similar with DON, the seasonal variation in NH_4^+ concentrations was minor. In the estuary, a slight increase in the NH_4^+ concentration during the August cruise was found (Fig. 4), especially in the Lassa tributary; while the remaining two cruises showed a limited variation. For NO_3^- concentrations, a range from 1.6 to 14.8 μM was found in August 2016 (Fig. 3). Concentrations in the remaining two cruises slightly decreased. The highest concentration was below 10 μM. The similar NO_3^- concentration distribution in 2017 cruises led to an insignificant variation in the range for δ^{15}N-NO_3^- and δ^{18}O-NO_3^- between seasons (Fig. 3). In terms of NO_2^-, i.e. the minimum component in the DIN inventory, the concentration varied between 0.09 and 3.3 μM in August 2016. Similar levels were found in the remaining samples.

Along the salinity gradient, positive offsets (a positive deviation from conservative mixing) for NO_3^- concentration were frequently observed, especially in the Lassa and Igan, which suggests net generations (NO_3^- release) during the mixing (Fig. 5). Coupled with the NO_3^- generation, negative offsets in δ^{15}N-NO_3^- and δ^{18}O-NO_3^- at most sites were observed (Fig. 5). The offsets of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- were linearly correlated (Fig. 5). The slope was 0.99 and R^2 was 0.63 (p<0.05).

3.4 Mixing experiments

In the particle-free (filtered) group, the mean DON concentration was 7.1 μM in the river water and 4.7 μM in the seawater (Fig. 6). In the experiment, DON concentrations slightly departed from the conservative mixing. A similar pattern was found in the unfiltered (particle-contained) group. Different from DON, NH_4^+ concentrations in both groups were nearly conservative and the concentration difference between groups was minor. For NO_3^-, apart from the seawater (identical

between groups), the concentration in the particle-contained group was markedly lower than that in the filtered group. As a mirror of concentration variation, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ elevated in the particle-contained group. Furthermore, compared to the conservative distribution, a deficit in NO_3^- content in the brackish water (salinity: 24‰) at the unfiltered group was obtained. Concurrently, increases in both $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ at the identical salinity were observed. For NO_2^-, the unfiltered group showed a strong removal while the filtered group maintained a conservative distribution (Fig. 6).

3.5 Pore water and rainwater

The salinity of the rainwater was 0 (Table 1). The concentration of NH_4^+ was 18.9 μM. The NO_3^- level was 16.4 μM with a markedly high value of $\delta^{18}O\text{-}NO_3^-$ (55.3‰) compared to the river water. Salinities of pore water samples varied from 1.0 to 21.5‰. These samples were enriched with NH_4^+ (22.8 to 121 μM) and DON (34.5 to 89.2 μM). In comparison, levels of NO_3^- and NO_2^- in pore water samples were low (<1.2 μM). Isotope fractions were similar with the river water.

4 Discussion

4.1 DIN sources in the Rajang river water

The Rajang is the largest river in Sarawak and receives substantial materials from its watershed. In the present study, we collected samples in the drainage basin (river water, salinity 0) and the estuarine. In the river water, the proportion of DIN in the N inventory was minor, accounting for 20% to 30% (Fig. 7A). In comparison to rivers located in dense population areas, such as the Pearl River in China, the Mississippi River in the USA, the Danshui River in Taiwan, China, and the Mekong River in Vietnam, concentrations of NO_3^- and NH_4^+ in the Rajang water were low (Table 2).

In Fig. 7B, $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ were plotted together to identify the potential sources of NO_3^-. Apart from errors introduced from biogeochemical reactions on the signal, according to the isotope composition in different sources, the decomposition of the terrestrial organic matter and its subsequent leaching from soils was an important source of NO_3^- in the river water. Despite the relatively low DIN concentration, the DIN yield of the Rajang was higher than values from other tropical rivers due to higher ENSO induced rain fall and the resulting high surface water discharges (Fig. 7C and D). Among the tropical rivers around the South China Sea, e.g. the Mae Klong River in Thailand and the Langat River in Malaysia (Malaysian Peninsular), the yield in NH_4^+ and NO_3^- in the Rajang at August 2016 was higher (Fig. 7C). The NH_4^+ production is even higher than that of the Wanquan River (China), which features intensive human activities and a large number of tourists. Such high yield may result from the abundant storage of organic matter and ammonification induced NH_4^+ accumulation in Sarawak peatland (Melling et al., 2007). Moreover, because of the overlap in isotope signals (Fig. 7B), fertilizers may also be deemed to be responsible for the DIN yield. In particular, DIN concentrations in the river water exceeded those detected in pristine tropical black water rivers (Baum and Rixen, 2014), suggesting a potential influence from anthropogenic activities. In Sarawak, the chemical fertilizer requirement in oil palm plantation (Tarmizi and Mohd

Tayeb, 2006) may be the most likely DIN source since the unconsumed fertilizer likely drained into the Rajang water coupled with precipitations.

Notably, levels of NO_2^- and NO_3^- in the river water were stable among cruises, while the NH_4^+ concentration significantly varied in two dry seasons. Apart from dilution, biogeochemical production for NH_4^+ also influences its concentration. Specifically, NH_4^+ can be the reaction output of DON and PN mineralization and subsequent ammonification in the upper stream water. The transformation can be occurred in terrestrial aquifers and/or the Rajang. Among cruises, the concentration of DON was stable. The level of PN increased in September 2017 (Fig. 7A). Consequently, the production of NH_4^+ may not be constrained in the water and the drop of NH_4^+ concentration resulted from the declined NH_4^+ production in terrestrial soils. Generally, ammonification in soils is strongly dependent on the moisture content (Hopmans et al., 1980). A strong El Niño event was observed from January to June 2016, the Niño 3.4 Index reached 2.5 (threshold 0.5). Subsequently, La Niña events occurred and introduced stronger precipitations in Malaysia (Fig. 7D). Consequently, the weather in September 2017 was comparably 'wetter' than the dry season in August 2016. Reichman et al. (1963) observed that NH_4^+ concentrations in the tested soils decreased after 10-day incubation at high moisture content. Hopmans et al. (1980) found that the NH_4^+ concentration in the culture soils at the 20% moisture content was markedly higher than the levels from 30% and 35% moisture content groups. Abera et al. (2012) also revealed a significant reduction in the extractable NH_4^+ content in tropical soils when precipitations enhanced. They addressed that the possible reason for the decrease of ammonification intensity was the enhanced moisture in soils, because high moisture could significantly restrain the aeration in peat and tropical soils and further lead to a depletion of oxygen (Daniels et al., 2012). A similar phenomenon might also occur in the Rajang watershed, the NH_4^+ production in the soils likely decreased in September 2017. Concurrently, strong precipitations enhanced river water volume that caused solute dilution. Adding these together, the decline of NH_4^+ concentration in the Rajang water was found. Such variation reflects the dynamic linkage between global climate events and local N storage.

4.2 N transformations in the estuary

In August 2016, concentrations of NO_3^-, NO_2^- and NH_4^+ in the estuary mixing zone were higher than levels in the river water and the coastal seawater. This concentration increase generally results from (1) a direct input from tributary streams or pore water exchange and (2) N transformations. In the Rajang Delta, there are several small streams (Fig. 1), continuously adding solutes into the estuary water (Staub et al., 2000; Gaslto, 2010). Compared with the Rajang, these streams were not the major surface flows in Sarawak (Sa'adi et al., 2017), due to small discharge rates. The solutes from these small loadings can be rapidly diluted in the estuary (Allen, 1982). In addition, the carbon content (pCO_2) and dissolved organic carbon during the same survey did not show significant peaks in the outlet of these streams (Martin et al., 2018; Müller-Dum et al., 2019). Consequently, the influence introduced from these streams might be minor. Precipitations, adding solutes on a regional scale, could enhance NH_4^+ concentrations in the river water but only within a small temporal scale (Fig. 8A). Alternatively, exchanges between pore water in both cohesive and sandy sediments and surface water can add DIN in river water on a regional scale due to large contact areas (Fig. 8A). In coastal zones, this exchange can be driven by tidal pumping, wave

actions and density difference (Santos et al., 2012a). In particular, during flooding tide, the tidal sediment marsh was flushed by the estuary water. The overlying water seeped into the sediment along the conduits created by crabs and worms, or plant roots. During ebbing tide, pore water slowly drains and adds solutes in the receiving water (Santos et al., 2012b; Tait et al., 2016). In the current research, NH_4^+ concentrations in all pore water samples were significantly higher than the level found in the estuary water. Coupled with the macro-meso tides in the Rajang estuary, the magnitude of NH_4^+ flux from pore water to the Rajang might be great, as outlined in Fig. 8A, likely to be the main reason for the concentration elevation. Moreover, the diffusion from the benthic sediment to the overlying water also increases NH_4^+ concentrations (Fig. 8A). Notably, low NO_3^- levels were found in pore water samples, suggesting that the direct effect on the river water NO_3^- concentration and its isotope fractions was limited.

N transformations, including ammonification, nitrification, DNRA (Burgin and Hamilton, 2007), may also markedly contribute to the enhancement of NH_4^+/NO_3^- concentration. Besides N fixation, ammonification is the only reaction that increases the total DIN concentration, which is coupled with the decomposition of PN and/or DON. In August 2016, the undersaturated DO and high values of OUD were obtained in the mixing zone, suggesting the occurrence of active aerobic respiration on the basis of organic matter decomposition. Concurrently, the abundant SPM in the estuary water was observed, providing a significant amount of PN (Fig. 2 and Fig. 7A). However, the PN concentration was relatively conservative in the mixing zone and the δ^{15}N-PN variation was limited (Fig. S6). Consequently, PN may not be involved in the biogeochemical reaction and hence it was not the major reactant for the ammonification. Instead, DON, especially the reactive portions, can serve as an active reactant (Brandes et al., 2007). In the mixing experiment, a reduction in the DON concentration was observed, compared to the conservative mixing, which confirms the biogeochemical activity. In the Rajang estuary, despite the injection from sediment pore water (Fig. 8A), net DON consumptions were obtained. DON may be continuously transformed to NH_4^+ via mineralization and subsequent ammonification (Fig. 8B). Photo-degradation in tropical rivers also accelerates the DON decomposition and benefits accumulation of NH_4^+ in the river water (Martin et al., 2018). In the Lassa branch, a clear DON consumption and the possibility for the occurrence of ammonification was obtained (Fig. 7E and F).

The elevation in the concentrations of NO_2^- and NO_3^- was attributed to nitrification, relying on the mineralized NH_4^+ and pore water derived NH_4^+ (Fig. 8B). In February 2017, coupled with NO_3^- concentration increases, declines in δ^{15}N-NO_3^- and δ^{18}O-NO_3^- were found, which reinforced the statement for the occurrence of nitrification (Fig. 8B). Notably, the enhancement in DIN species varied between tributaries. Compared with the Lassa/Paloh and Rajang tributary, the distribution of NO_2^- and NO_3^- in the Igan tributary during the mixing tended to be conservative and *f* values were comparatively small (Table S1), while the NH_4^+ concentration remained to be high during the mixing. In addition, the OUD in the Igan channel was relatively low in comparison to other tributaries. It could be deduced that the pore water exchange process during the mixing still occurred, while the nitrification intensity in the Igan tributary was relatively weak, which likely results from the significant difference in hydrologic environments. In particular, the Igan channel was the main freshwater outlet because of the comparatively small tidal amplitude but a high discharge rate (Jakhrani et al., 2013). The large freshwater plume pushed the mixing zone towards the coastal ocean (Fig. 2). Consequently, the brackish water could

be rapidly diluted by the seawater, leading to a short residence time for the mixing. By contrast, the mixing in other river tributaries occurred in the river channels, leading to a slow dilution and a long residence time for the brackish water. The difference in the water residence time likely created the varied reaction intensity (Zarnetske et al., 2011). In the light of the reactions between the Lassa and Rajang tributary, the difference in the reaction pattern (addition) and intensity (*f* value) was small, although the proportion of peatland coverage varied due to deforestation (Fig. 1). In the same estuary, Müller-Dum et al. (2019) also reported a limited difference in CO_2 emissions between the peat and non-peat areas. Such pattern may relate with the temporal scale. In particular, the peatland was the product of 6000-year deposition as aforementioned. The regional deforestation in the estuary occurred in recent 15 years (Miettinen et al., 2016), indicating that the disturbance has not been developed into deep sediments. The influence may not reach a significant level. However, disturbances from the shrinkage of peatland may be enhanced in the future.

The distribution of DIN species and related isotopes in the mixing zone between cruises was also observed, indicating the seasonal variability. In February 2017, the wet season in the Sarawak (Müller et al., 2015), productions of NO_3^- and NO_2^- during the mixing were mild compared to August 2016. Accordingly, declines in the magnitude of *f* were observed, suggesting a weak nitrification intensity. Decreases in the residence time for the brackish water column due to the high river discharge can be the first reason. The second factor that influences the generation of NO_3^- and NO_2^- in the estuary water might be SPM related biogeochemical reactions because suspended particles can be versatile. On the one hand, the N content on the particle could release into the water via decomposition (Brandes et al., 2007), subsequently increasing DIN concentration. On the other hand, the suspended particles could provide a large number of anoxic micro-niches for denitrifiers coupled with the oxic degradation (Jia et al., 2016). Together with sediment denitrification, the NO_3^- removal in the estuary could occur. Consequently, the addition or removal (two possibilities) for NO_3^- content in estuary water likely depends on the reaction capability of these two controversial pathways.

In the Rajang estuary, the PN content in SPM frequently ranged from 0.1% to 0.3%, mainly terrestrial-derived solids because of the low concentration of chlorophyll (Martin et al., 2018), smaller than other tropical rivers located in adjacent regions, e.g. the Wonokromo River (0.5%) and the Rorong River (0.85%) at Indonesia (Jennerjahn et al., 2004), the Godavari River at India (0.36%; Gupta et al., 1997). In the mixing experiment, small differences in DON concentration between groups were found, indicating that the decomposition of PN was weak. The oxic consumption of these particles in the upper stream might be the reason for the low reactivity for particles in the degradation potential. Therefore, the presence of high concentrations of PN cannot enhance NO_3^- addition. Alternatively, the denitrification capability evoked by the SPM can be significant. In the Rajang estuary, suspended particles were enriched in trace metals, such as Fe and Mn (Staub et al., 2000), which potentially accelerate the NO_3^- removal process by serving as an electron donor or catalyzer (Burgin and Hamilton, 2007). Furthermore, in estuaries, the presence of flocculation and adsorption attract metal ions on the surface of suspended particles, enhancing the denitrification potential. In the mixing experiment, the presence of suspended particles markedly decreased levels of NO_3^- and NO_2^- regardless of salinity when compared to the particle-removed group. Additionally, both $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ markedly increased, confirming the presence of denitrification. Moreover, the NH_4^+ concentration during the

mixing was conservatively distributed, indicating Anammox, that utilizes both NH_4^+ and NO_3^-, may not be the dominant pathway for NO_{2+3}^- removal.

In September 2017, the end of the dry season according to historical records, the DIN distribution trend was markedly different from the pattern from August 2016. Specifically, the generation of NO_3^- and NO_2^- was weaker than the pattern in August. For example, the *f* value was significantly smaller (Table S1) and the NO_3^- concentration offset in three tributaries were markedly lower than these values obtained in August 2016. The variation of both $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ during the mixing process was similar to the trend observed in February 2017. Such pattern likely results from the increase in the river discharge in September 2017 due to the continuous occurrence of La Niña events, as aforementioned. This observation reinforced that the biogeochemical reactions in the tropical zone are mainly constrained by precipitations (Daniels et al., 2012; Xu et al., 2013) and hence the global climate events markedly influence the N transformations on a local scale. Moreover, it is worth noticing the co-existence of NO_3^- concentration increase and positive $\delta^{15}N\text{-}NO_3^-$ offset in the Rajang branch in September 2017 (Fig. 5). Apart from the bias introduced from the endmember selection, such distribution indicates an introduction of NO_3^- from human activities. Compared with the Lassa and Igan tributary, the Rajang tributary is adjacent to Sirikei city (Fig. 1C). Anthropogenic activities likely introduced $^{15}N\text{-}NO_3^-$ enriched water, i.e. wastewater or sewage, into the Rajang (Fig. 7B), along several streams. In the future, coupled with population increases in the Rajang watershed, NO_3^- with anthropogenic signature may increase in the Rajang Delta, which should receive more attention.

4.3 DIN fluxes and implications

After the consumption/addition in estuaries, DIN injects into coastal oceans. As outlined in Table S1, the magnitude of NH_4^+ fluxes ranged from 4.57 to 24.7 t N day^{-1} and the magnitude of NO_3^- fluxes peaked at 82.4 t N day^{-1}. The DIN loading was 77.2 t N day^{-1} in the dry season and 101.5 t N day^{-1} in the wet season. On a global scale, the DIN delivered from the Rajang to coastal ocean is relatively minor (Table 2). For the rivers around the South China Sea, the magnitude of Rajang-borne DIN fluxes was less than 1/10 of the DIN loading from the Mekong River and similar with 1/6 of the DIN from the Pearl River. The terrestrial NO_3^- and NO_2^- was rapidly removed in the coastal ocean. Coupled with concentration decreases, $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ rapidly increased. In addition, the offset between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ was closely correlated (Fig. 5). Therefore, the decline in NO_3^- concentration resulted from the consumption of primary producers (Granger et al., 2010). Along Sarawak coasts, there are abundant tropical coral reefs and fish resources (Hamli et al., 2012; Praveena et al., 2012; Arai, 2015), relying on phytoplankton and seagrass. The input of DIN likely sustained the growth of primary producers and maintained ecosystem functions. Currently, the riverine DIN input was mild, which did not markedly change the stoichiometry in coastal water. The dominant phytoplankton group was diatom (Saifullah et al., 2014) and harmful algae blooms were not recorded in Sarawak coasts. In addition, the fishery industry flourishes and plays an important role in the local economy (Ikhwanuddin et al., 2011; Hamli et al., 2012). However, the Rajang estuary is subject to increasing human pressures, especially from agricultural fields, fallow shrubland and industrial plantations (Ting and Rose, 2014; Miettinen et al., 2016). Logging and oil palm plantations have resulted in peatland deforestation and the scale is enlarging (Miettinen et

al., 2016). It has increased suspended particle concentration and accelerates erosion of terrestrial organic matter (Ling et al., 2017), indicating that a long-term influence derived from the human transformations should be noticed in future studies.

5 Conclusions

The DIN concentration in the river water varied between seasons in the Rajang, mainly resulting from the decomposition of terrestrial organic matter. Strong precipitations, induced by La Niña events, might inhibit soil ammonification in the watershed and hence decreased NH_4 concentrations in the river water in September 2017. This indicates a causal chain between climate events and N cycling in tropical soils and rivers. In the estuary, pore water exchanges and decomposition of terrestrial DON increased NH_4^+ concentration and nitrification increased NO_2^- and NO_3^- levels, while denitrification likely occurred on particle surfaces. Since nitrification exceeded denitrification, NO_3^- addition was observed in the mixing zone. The riverine DIN loading to the coastal ocean ranged from 77.2 t N day^{-1} in the dry season and 101.5 t N day^{-1} in the wet season. Due to the mild concentration in the river water, Rajang-borne DIN likely adds positive effects to the coastal system, sustaining the primary productivity in the coastal zone. Currently, the Rajang estuary is subject to intensive human developments, which may add significant impacts on DIN transport and transformations in the future. In addition, the reaction trends and N solute distributions obtained from the present study may benefit global N budget estimations.

Author contribution

JZ, MM, YW and SJ designed the study. JZ, EA, FJ and MM performed the sample collection and *in-situ* measurements for the first cruise. SJ, KZ, AM, EA, FJ and MM performed samplings and *in-situ* measurements for the second and third cruise. SJ, JJ, GZ, YW, KZ, TR completed laboratory analyses. All co-authors equally participated in the interpretation and discussion of the results. SJ prepared the manuscript with suggestions from all co-authors.

Competing interesting

The authors declare that there is no conflict of interesting.

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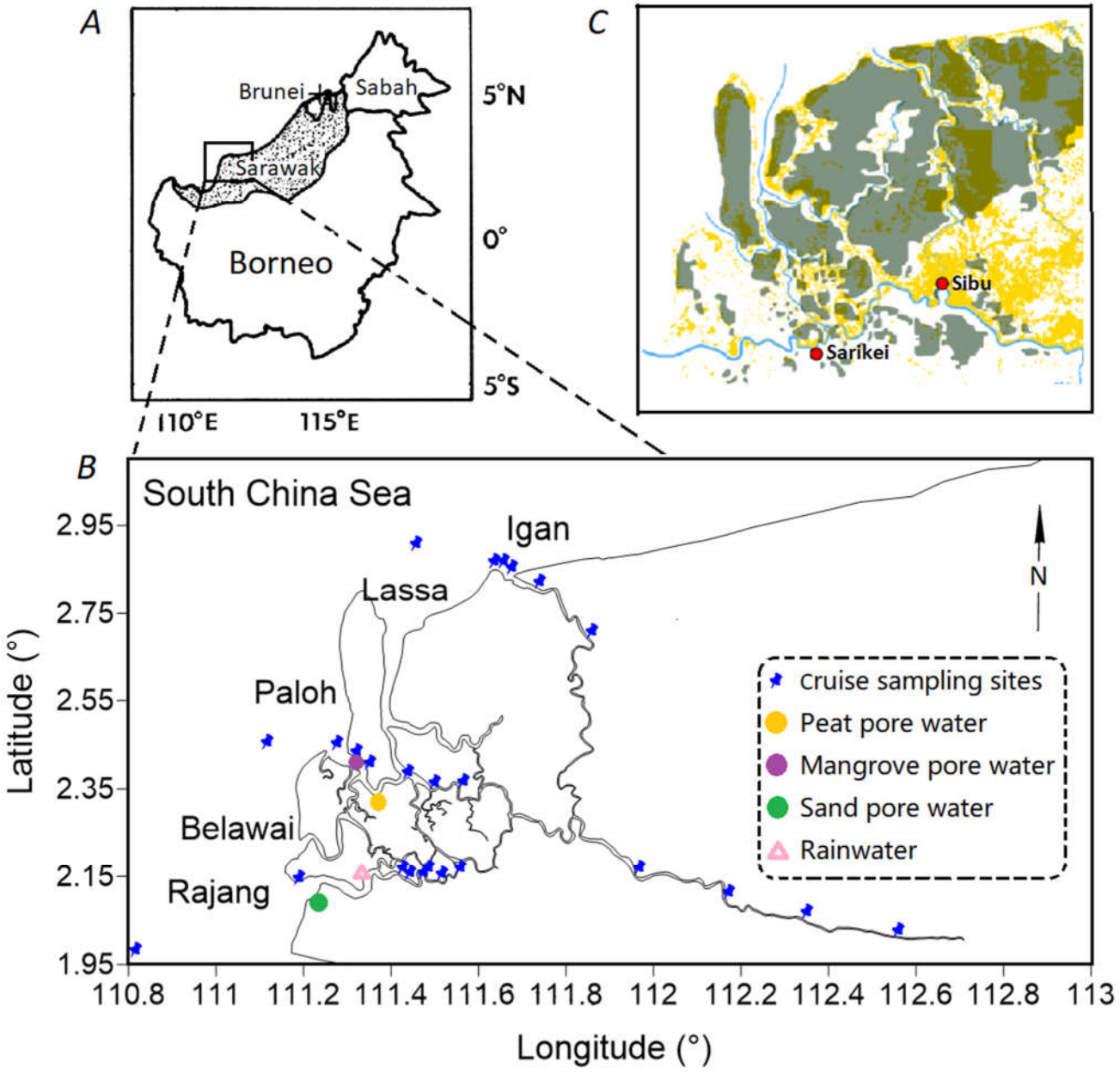

Figure 1: Maps of the sampling area: (A) shows the location of the Rajang lower stream in Borneo, which is invoked from Staub et al. (2000); (B) highlights the sampling sites in the September 2017 cruise; (C) outlines the distribution of peatland in the Rajang lower steam and coastal region (dark green) and deforestation (yellow) in 2010 (Sarawak Geoportal: www.bmfmaps.ch). The cyan line indicates the Rajang river. The red dots represent Sarikei and Sibu. Both are important cities in the Rajang watershed.

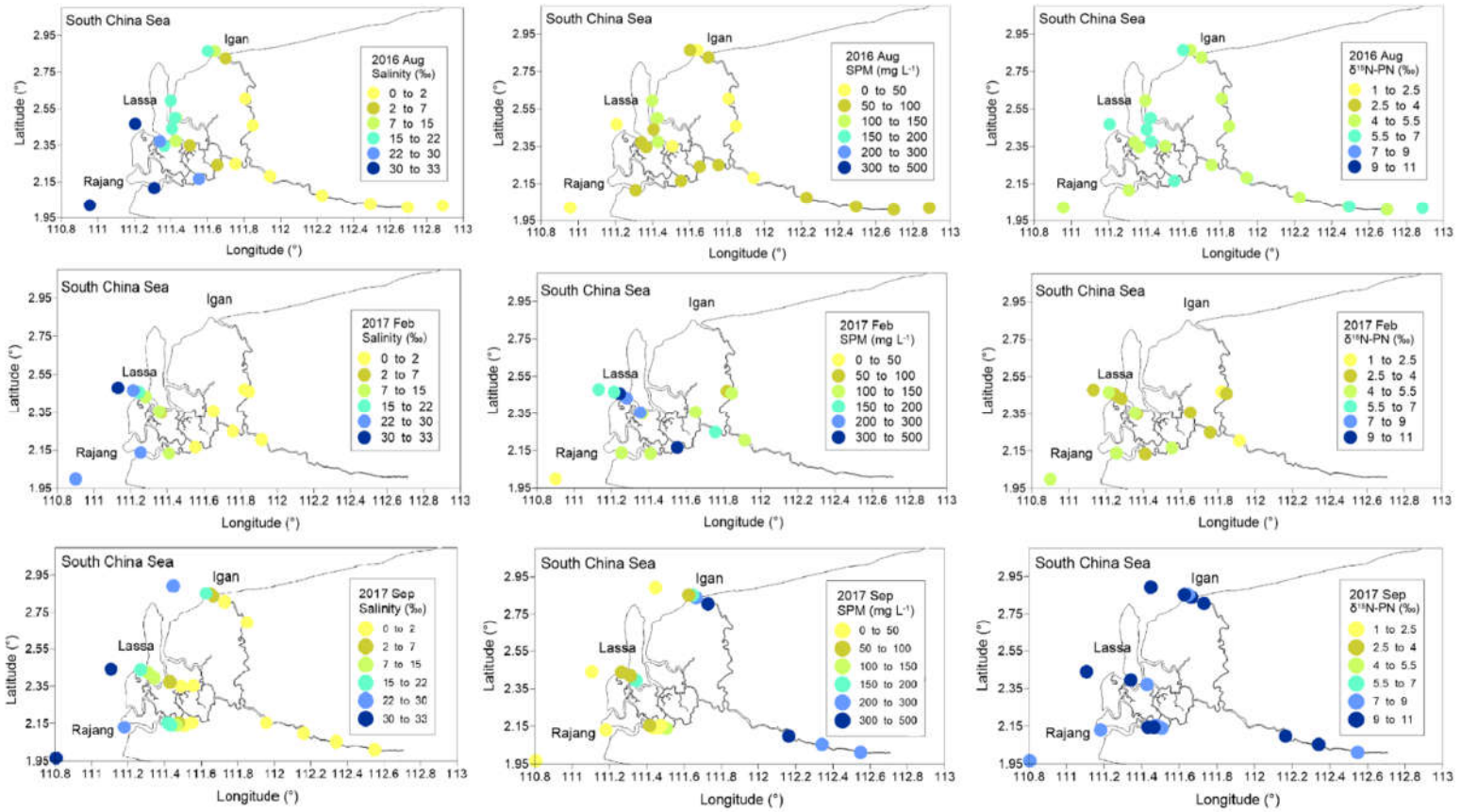

Figure 2: Distribution of salinity, suspended particle matter (SPM) and δ^{15}N-PN in the Rajang estuary and adjacent coastal ocean.

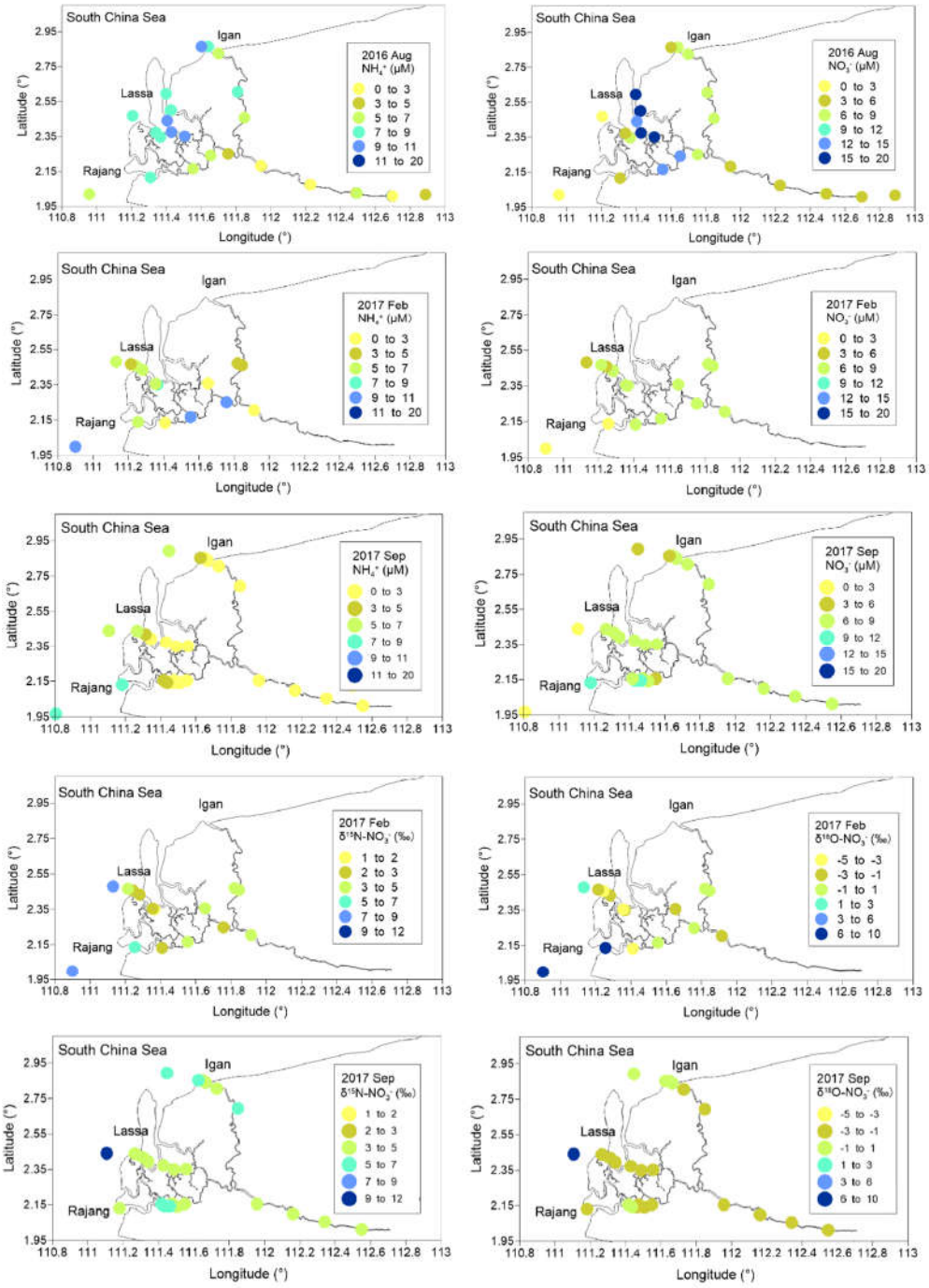

Figure 3: Concentrations of NH_4^+ and NO_3^-, as well as its stable isotope fractions ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$) in the Rajang estuary and adjacent coastal ocean.

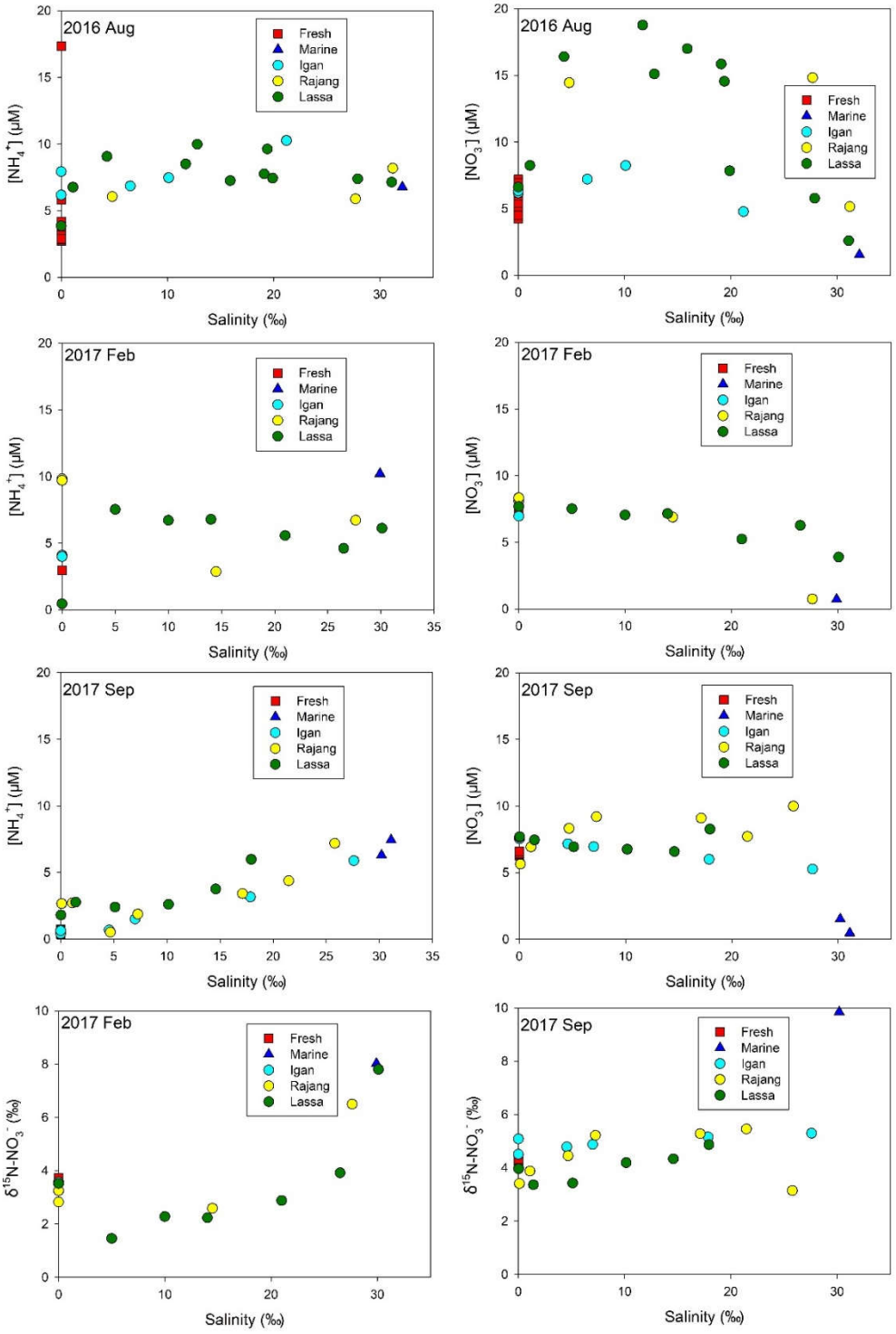

Figure 4: Distribution of NH_4^+ and NO_3^- concentrations, as well as $\delta^{15}N\text{-}NO_3^-$, along the salinity gradient in the Rajang estuary.

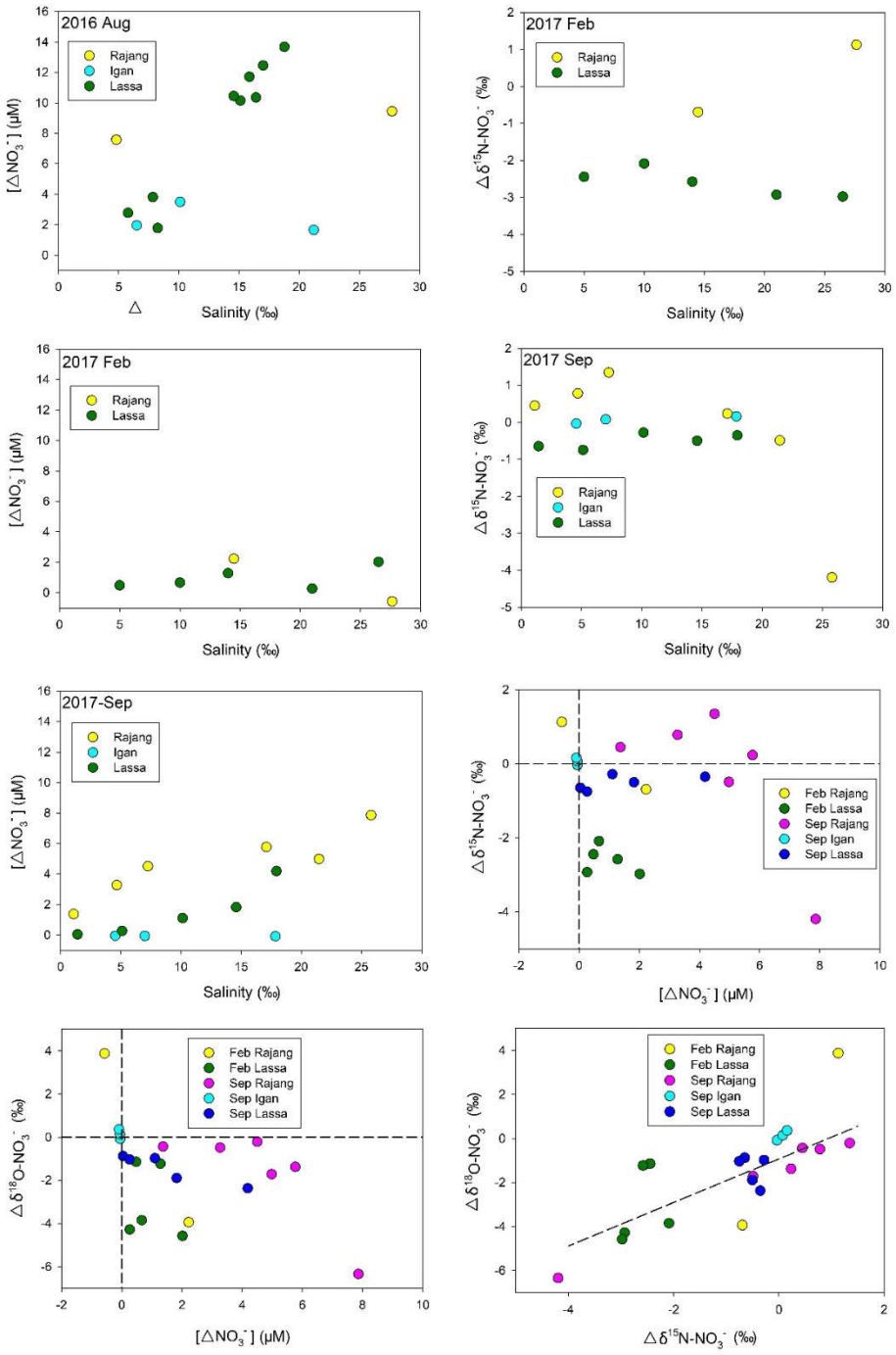

Figure 5: Distribution of NO_3^- concentration offset ([ΔNO_3^-] in the figure) in three Rajang tributaries (Igan, Lassa and Rajang) along the salinity gradient from three cruises; Distribution of $\delta^{15}N\text{-}NO_3^-$ offset ($\Delta\delta^{15}N\text{-}NO_3^-$in the figure) in three Rajang tributaries along the salinity gradient in 2017; Comparison between $\delta^{15}N/^{18}O\text{-}NO_3^-$ offset and NO_3^- concentration offset for the cruises in 2017; Correlation between $\delta^{15}N\text{-}NO_3^-$ and $^{18}O\text{-}NO_3^-$ offset, the slope of the correlation curve between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ was 0.99 (R^2: 0.64).

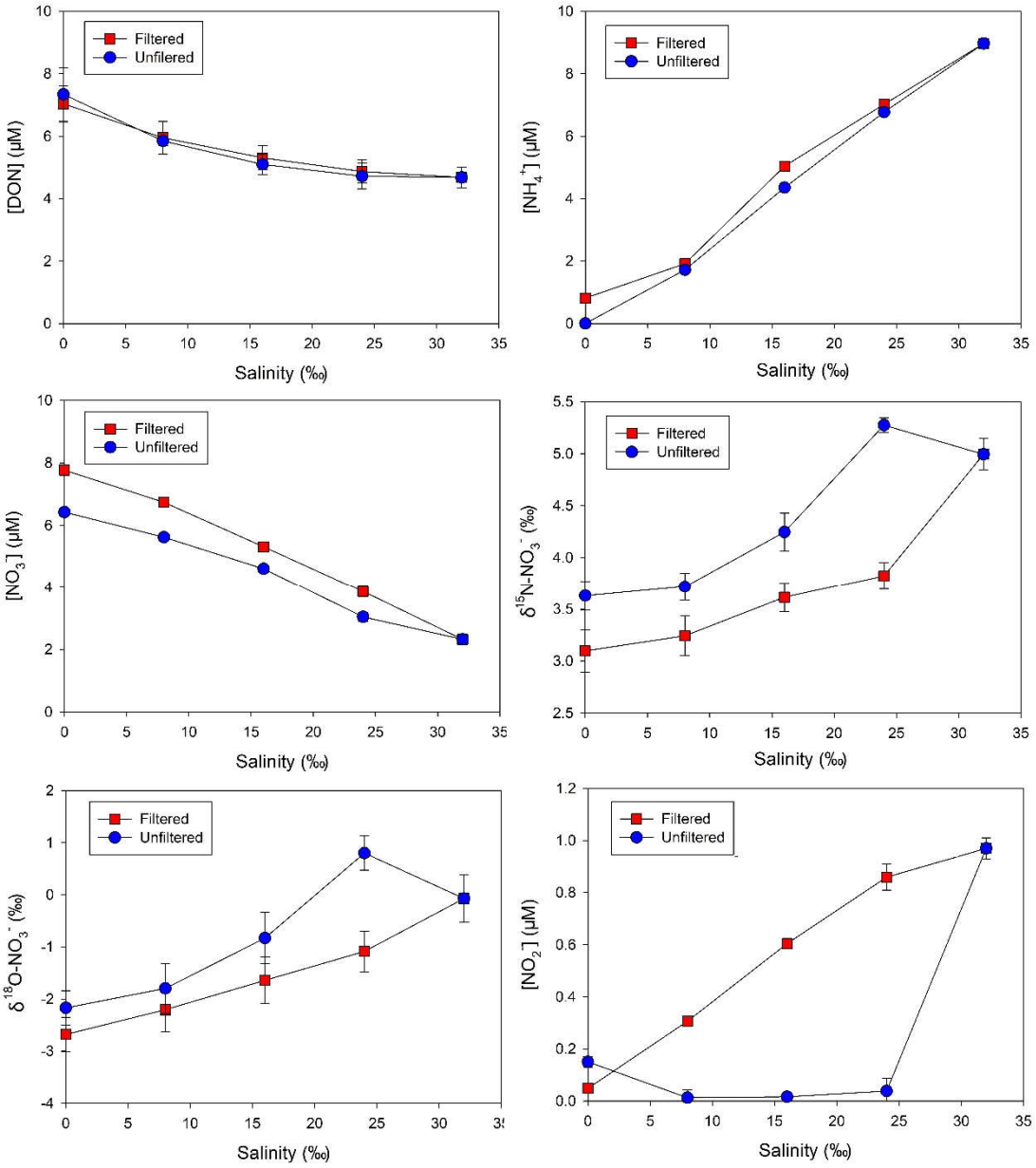

Figure 6: Concentrations of DON, NO_3^-, NH_4^+ and NO_2^-, as well as $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the mixing experiment (mean ± standard deviation).

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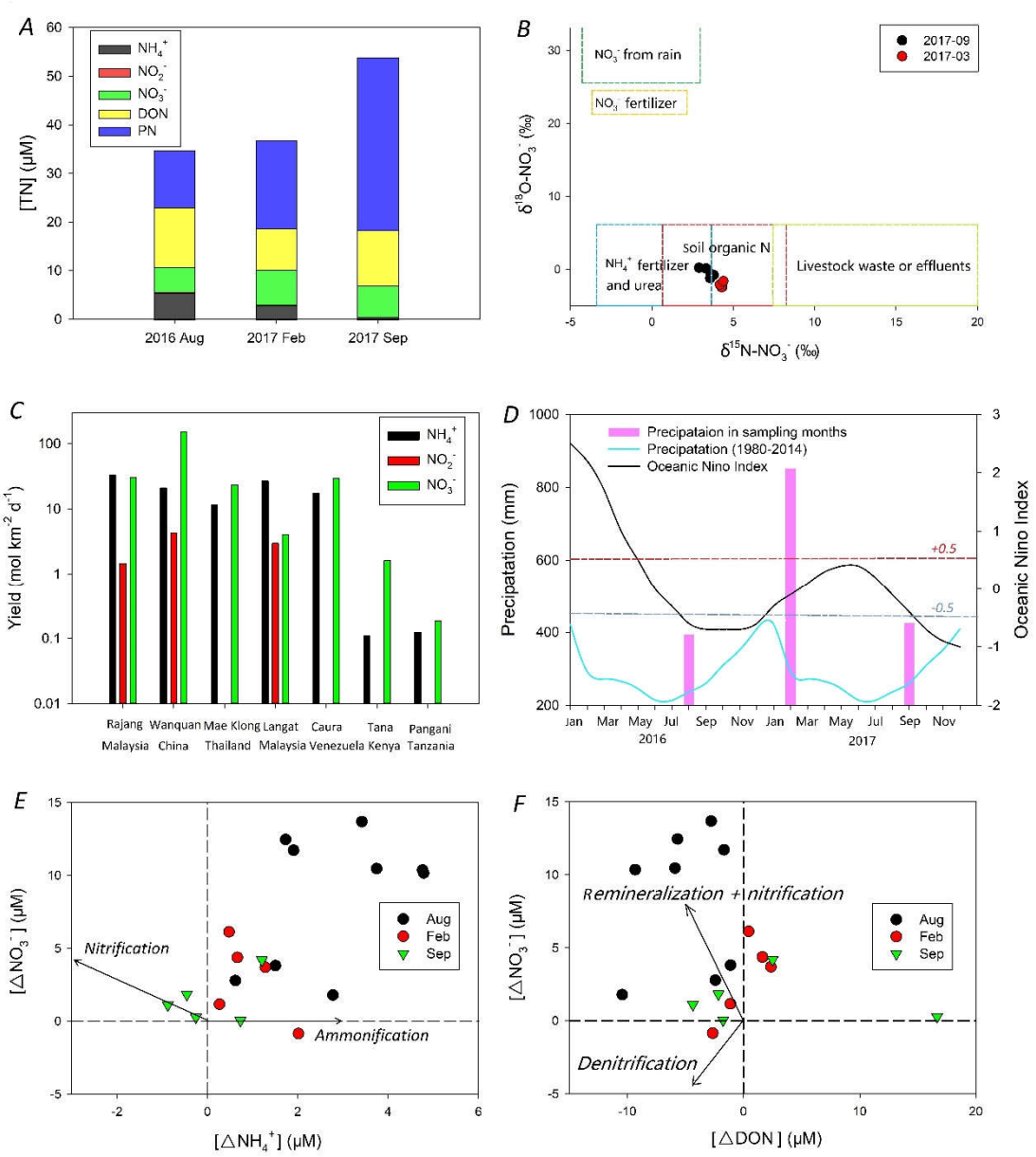

Figure 7: (A) Mean concentration of different N species in the fresh Rajang water (salinity: 0, sampling sites ranged from upper stream to Sibu city); (B) $\delta^{15}N\text{-}NO_3^-$ to $\delta^{18}O\text{-}NO_3^-$ in the fresh Rajang water. The figure also highlights the range of both isotope fractions in rainwater, fertilizer, terrestrial organic matter and sewage (Li et al., 2010); (C) Comparison of DIN yield among different tropical rivers on a global scale; (D) Annual precipitation curve derived from (Müller et al., 2016) in Sarawak and precipitation in the sampling months during 2016 and 2017, measured at Sibu station. The figure also shows the Ocean Niño Index in 2016 and 2017. Clearly, in the beginning of 2016, an El Niño event occurred because the index was much higher than the threshold (red dash line: 0.5). Afterwards, two La Niña events were observed (lower than the threshold, highlighted by the blue dash line); (E) and (F) are comparisons among offsets (Δ in the figure) for NO_3^-, NH_4^+ and DON concentrations in the Lassa branch. The arrows outlined in the figure highlights the possible reaction pathways according to the variations in the offsets.

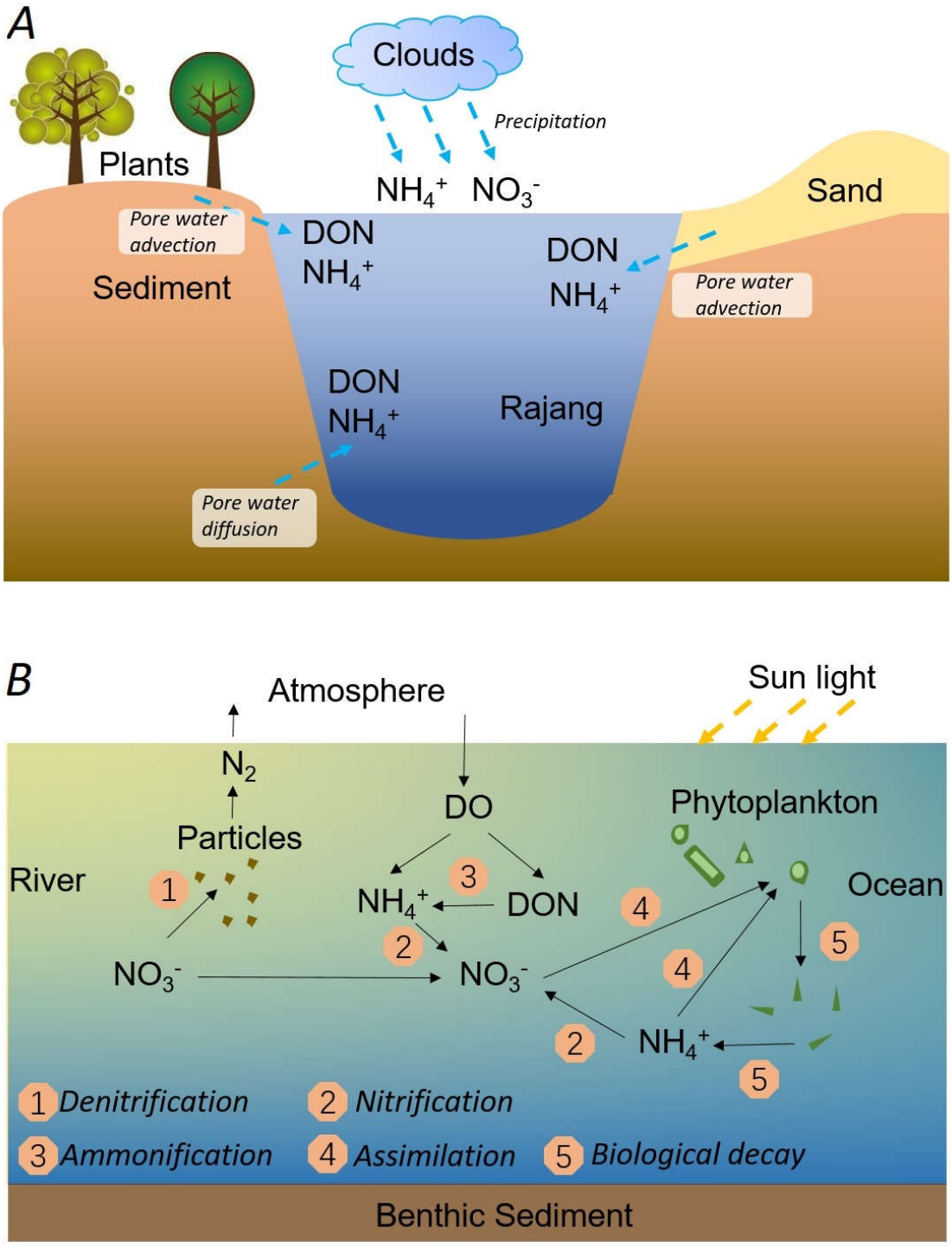

Figure 8: Sketch of the N input pathways in the Rajang estuary (A) and N reactions during the mixing between the river water and the coastal ocean water obtained in the current research (B).

Table 1: Chemical properties in the rainwater and pore water from mangrove swamp, sandy beach and peatland.

Sample	Salinity (‰)	NH_4^+ (μM)	NO_2^- (μM)	NO_3^- (μM)	$\delta^{15}N\text{-}NO_3^-$ (‰)	$\delta^{18}O\text{-}NO_3^-$ (‰)	DON (μM)
Rainwater	0	18.9	0.05	16.4	5.2	55.3	22.3
Mangrove	21.5	33.4	0.36	1.0	3.7	2.6	46.2
Sandy beach	17.5	22.8	0.05	0.3	---	---	34.5
Peatland	1.0	121	0.63	1.2	3.8	2.1	89.2

Table 2: A global view on the NH_4^+ and NO_3^- concentration in the fresh river water and the magnitude of riverine DIN flux. # Dry season record * Monsoon Season record

Site	NH_4^+ (μM)	NO_{2+3}^- (μM)	DIN flux (t N d^{-1})	Reference
Rajang River (Malaysia)#	5.5	5.4	77.2	This study
Mekong River (Vietnam)	11	15	789	Iida et al., 2007 Liljeström et al., 2012
Danshui River (Taiwan, China)	137	57.1	49.1	Kuo et al., 2017
Pearl River (China)	207	211	468	Cai et al., 2015
Amazon River (Brazil)	0.2	11.8	2322	Santos et al., 2008
Mississippi River (U.S.A)	0.9	113	3720	Battaglin et al., 2010
Meghna River (Bangladesh)*	0.1	15.8	85.0	Uddin et al., 2014
Pangani River (Tanzania)	4.5	42.8	0.87	Selemani et al., 2018
Tana River (Kenya)	0.62	9.6	1.57	Bouillon et al., 2009
Wanquan River (China)	21	157	10.2	Li et al., 2013