Distribution and behaviour of dissolved selenium in tropical peatland-draining rivers and estuaries of Malaysia

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Abstract

Selenium (Se) is an essential micronutrient for many organisms. Despite its importance, our current knowledge of the biogeochemical cycling of dissolved Se in tropical estuaries is limited, especially in Southeast Asia. To gain insights into Se cycling in tropical peat-draining rivers and estuaries, samples were collected from the Rajang, Maludam, Sebuyau, Simunjan, Sematan, Samunsam, and Lunda rivers and estuaries in western Sarawak, Malaysia, in March and September 2017 and analysed for various forms of Se (dissolved inorganic and organic). Mean total dissolved Se (TDSe), dissolved inorganic Se (DISe), and dissolved organic Se concentrations (DOSe) were 2.2 nmol L$^{-1}$ (range: 0.7 to 5.7 nmol L$^{-1}$), 0.18 nmol L$^{-1}$ (range: less than the detection limit to 0.47 nmol L$^{-1}$), and 2.0 nmol L$^{-1}$ (range: 0.42 to 5.7 nmol L$^{-1}$), respectively. In acidic, low-oxygen, organic-rich blackwater (peatland-draining) rivers, the concentrations of DISe were extremely low, whereas those of DOSe were high. In rivers and estuaries that drained peatland, DOSe/TDSe ratios ranged from 0.67 to 0.99, showing that DOSe dominated. The positive relationship between DISe and salinity and the negative relationship between DOSe and salinity indicate marine and terrestrial origins of DISe and DOSe, respectively. The positive correlations of DOSe with the humification index and humic-like chromophoric dissolved organic matter components in freshwater river reaches suggest that peat soils are probably the main source of DOSe. Discharges of water enriched with DOSe fractions associated with peatland-derived high-molecular-weight, high-aromaticity dissolved organic matter discharged from estuaries may promote productivity in the adjoining oligotrophic coastal waters. The results of this study suggest that the impacts of Se discharges on coastal ecosystems should be evaluated in the future.
1. Introduction

Selenium (Se) is an essential trace element for animals and most plants. Low levels of Se in the food chain lead to disease or death (Lobanov et al., 2009; Winkel et al., 2015), whereas high levels are toxic. The range of beneficial effects of Se is among the narrowest of all the elements and varies between dietary deficiency (<40 µg d\(^{-1}\)) and toxicity (>400 µg d\(^{-1}\)) (Fernández-Martínez and Charlet 2009; Schiavon et al., 2017). Selenium depletion in the Phanerozoic oceans may have contributed to three major mass extinction scenarios (Long et al., 2016). Thus, there has been interest in Se biogeochemical cycling in aquatic systems for many decades (e.g., Cutter and Bruland, 1984; Cutter and Cutter, 1995, 2001; Mason et al., 2018).

The bioavailability of Se is determined by its concentrations and species (Fernandez and Charlet, 2009). The behaviour of selenium in natural waters is complicated, as it exists in several oxidation states (−II, IV, VI) and as organic selenide (Conde and Sanz Alaejos 1997). A number of field and laboratory studies have found that selenite [Se(IV)] and selenate [Se(VI)] can be assimilated by phytoplankton and that Se(IV) is the preferred species for marine phytoplankton (Wrench and Measures, 1982; Apte et al., 1986; Vandermeulen and Foda, 1988; Baines and Fisher, 2001). Substantial amounts of dissolved Se in natural waters are known to be associated with organic matter, including water-soluble proteins, polysaccharides, and humic substances (Ferri and Sangiorgio, 1999; Cutter and Cutter, 1995, 2001; Kamei-Ishikawa et al., 2008), with the bioavailability of Se generally decreasing as the amount of organic matter increases (De Temmerman et al., 2014; Winkel et al., 2015). Se(IV), when added to raw humus layers in a forest, was found in a field study to be fixed very rapidly (Gustafsson and Johnsson, 1992, 1994). Laboratory studies have shown that Se(IV) is adsorbed by peat (Kharkar et al., 1968) and that Se
is accumulated and stored in dome-shaped peat swamps (Gonzalez et al., 2006, Vesper et al., 2008; Clark and Johnson, 2008). In a global study, Fernández-Martínez and Charlet (2009) summarized that the concentrations of Se in soils generally ranged from about 0.01 to 2 mg kg\(^{-1}\) and averaged about 0.44 mg kg\(^{-1}\). Gonzalez et al. (2006) reported Se concentrations of up to 28 mg kg\(^{-1}\) in peatland in Switzerland and from 0.9 to 2.2 mg kg\(^{-1}\) in peat cores in Spain. High spatial variability has been found in dissolved Se concentrations in runoff from peatlands at regional scales, with concentrations of up to 13 nmol L\(^{-1}\) being observed in northern Minnesota, US (Clausen and Brooks, 1983), and from 0.38 to 5 nmol L\(^{-1}\) in the Krycklan catchment, Sweden (Lidman et al., 2011).

Although these various studies did not report different species of Se, the organic form of Se is probably more important than inorganic forms in runoff from peatland. An understanding of Se speciation may therefore be important for determining the bioavailability of Se that is transported from land to oceans.

The chemical behaviour of Se in estuarine mixing plays an important role in overall geochemical cycling. From their investigation into dissolved Se species in various estuaries, Chang et al. (2016) found that Se was controlled by biological, physical, and redox processes in the estuaries; non-conservative processes resulting from phytoplankton uptake; absorption by suspended particles; and regeneration of particulate organic selenide in the water. Thus far, the behaviour of Se in estuaries has been studied mainly in the temperate zone of the northern hemisphere (between 20°N and 60°N) (Measures and Burton, 1978; Takayanagi and Wong, 1984; Van der Sloot et al., 1985; Cutter, 1989a; Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati, 1998; Yao et al., 2006; Chang et al., 2016). Wide spatial and temporal variations have been reported in total dissolved Se concentrations in runoff from high-latitude peatlands (Clausen and Brooks, 1983; Lidman et al., 2011). The behaviour of Se in tropical organic-rich estuaries, however, is still poorly understood. It is
also known that organic matter plays an important role in the bioavailability and fate of Se in the environment; for example, Moore et al. (2013) and Wit et al. (2015) reported very high concentrations (up to 5667 μmol L⁻¹) of dissolved organic carbon (DOC) in peat-draining rivers in Borneo. More studies of the behaviour of Se in fluvial systems in Southeast Asia are therefore needed to provide an improved understanding of the biogeochemical processing of Se fractions and their relationships with organic matter.

To the best of our knowledge, the present study is the first analysis of the distribution and behaviour of dissolved species of Se in seven rivers and estuaries in western Borneo (Sarawak, Malaysia, Southeast Asia). The main objectives of the study were to 1) investigate and compare the distribution of dissolved Se species, including dissolved inorganic Se [DISE, the sum of Se(IV) and Se(VI)] and dissolved organic Se (DOSe) along salinity gradients in rivers with high (Maludam, Simunjan, Sebuyau, and Samunsam) and limited (Rajang, Semetan, and Lundu) proportions of peatland in the wet and dry seasons; 2) evaluate the fate of Se species in multiple estuaries during the mixing of freshwater and salt water in different seasons; and 3) characterize the DOSe fractions in the peat-draining rivers and estuaries. The results of this study should contribute to an improved understanding of how Se behaves in tropical peat-draining rivers and estuaries.

2. Materials and methods

2.1 Study areas and sample collection

Sarawak, Malaysia’s largest state, is in the northwest of the island of Borneo, Malaysia (Müller et al., 2016). The coastline of Sarawak is about 1035 km long, and the offshore comprises a wide continental shelf area with high...
biological productivity (Long et al., 2014). Sarawak has a tropical climate, with a mean annual air temperature at the capital Kuching (1.56°N, 110.35°E) of 26.1 °C (Müller et al., 2016). Rainfall is abundant throughout the year but is pronounced during the northeastern monsoon, which occurs between November and February (wet season). The period from May to September, before the southwestern monsoon, constitutes the dry season (Sa’adi et al., 2017). About 12% of the coastal area of western Sarawak is covered by peatlands, of which approximately 41% has been converted to palm plantations (Müller et al., 2016).

Two sampling campaigns were conducted in peat-draining rivers and estuaries in Sarawak in 2017. The first was at the end of the northeastern monsoon (from 4 to 12 March 2017, just after the wet season), and the second was shortly before the beginning of the southwestern monsoon (from 4 to 17 September 2017, in the dry season) (Figure 1). Six rivers, namely, the Rajang, Maludam, Simunjan, Sebuyau, Sematan, and Samunsam, were sampled in March and September, and the Lundu River was sampled only in September (Fig. 1). Four of the rivers (the Maludam, Simunjan, Sebuyau, and Samunsam) drain catchments with high peatland coverages and are known as blackwater rivers, whereas the Sematan and Lundu drain catchments with high proportions of mineral soils and limited proportions of peatlands (Martin et al., 2018). The Rajang River drains mineral soils in its upper reaches (Staub et al., 2000) but, at Sibu, branches into multiple distributary channels (the Igan, Paloh, and Rajang) that flow from north to south through land covered with thick peat and form a delta (Staub et al., 1994, 2000) (Fig. 1).

Water samples were collected from a boat. As the boat moved forward, surface water was collected upstream and to the side of the boat into an acid-cleaned polyethylene bottle attached to the end of a plastic pole sampler (3–4 m long). Water temperature, salinity, pH, and dissolved oxygen (DO)
concentrations were measured in situ using a portable multifunction water-quality meter (AP–2000, Aquaread Company, Britain) at the time of sample collection. Water samples were filtered within 12 h of collection through pre-cleaned 0.4 µm filters (Nuclepore) at a laminar air flow cleanbench (Class 100). The filtrates were placed in acid-cleaned polyethylene bottles and were frozen and stored until analysis.

2.2 Mixing experiment

To supplement the field observations, a laboratory experiment that simulated estuarine mixing processes was carried out using freshwater collected from the Maludam (organic rich and yellow coloured, with humic substances) and Rajang rivers during September 2017. Samples of freshwater (salinity of 0) were collected from the Maludam River at Maludam National Park and from the Rajang River at Sibu (10 km downstream from the city dock). The dissolved organic carbon (DOC) concentrations of these samples were 121 and 3631 µmol L^{-1} (Martin et al., 2018), respectively. Coastal seawater with a salinity of 32 and a DOC concentration of about 80 µmol L^{-1} (Martin et al., 2018) was also collected. The river water and the coastal seawater samples were filtered (pre-cleaned 0.4 µm particle-free, polycarbonate membrane filters) and then mixed at various proportions to achieve salinity gradients of 0, 8, 16, 24, and 32 (Bergquist and Boyle, 2006). Following mixing, the samples were shaken and placed in the dark at 25–26 °C for 24 h and were then filtered through pre-cleaned 0.4 µm polycarbonate membrane filters. The filtrates were kept frozen until analysis.

2.3 Analytical methods

The Se(IV), DISe, and TDSε concentrations were determined in carbon-
containing plasma using a hydride generation (HG) system (Hydride FAST, ESI) combined with a sector field inductively coupled plasma–mass spectrometry (ICP–MS) instrument, as outlined in the operationally defined hydride generation-based speciation analysis methods described by Chang et al. (2014, 2017). Selenium was measured at m/z = 82 with low resolution. By adding methane (2 ml min⁻¹) to the carbon-containing plasma, Se sensitivity was increased and spectral interference was suppressed, which improved the detection limits. Briefly, Se(IV) at an acidity of 2 mol l⁻¹ HCl was reacted with NaBH₄ to produce hydrogen selenide and then quantified using HG–ICP–MS. Se(VI) was quantitatively reduced to Se(IV) by heating a sample acidified with 3 mol l⁻¹ HCl to 97 °C for 75 min and then quickly cooling to room temperature using an ice-water bath. The steps used to determine Se(IV) were then followed to obtain the concentration of DISe. The reduction recoveries ranged from 95% to 103%. The Se(VI) concentration was calculated as the difference between DISe and Se(IV). The total dissolved selenium (TDSe) concentrations were determined using the same method as for DISe, following ultraviolet digestion (Li et al., 2014). The concentration of DOSe was calculated as the difference between the TDSe and DISe concentrations (DOSe = TDSe − DISe). Detection limits for Se(IV), DISe, and TDSe were 0.0025, 0.0063, and 0.0097 nmol l⁻¹, respectively. The accuracy of the methods was tested with standard solutions, and Se(IV) GSBZ 50031-94, Se(VI) GBW10032, selenocysteine GBW10087, and selenomethionine GBW10034 showed differences within 3.0%, 0.7%, 1.6%, and 1.4%, respectively.

### 2.4 Data statistics and analysis

The Statistical Package for Social Sciences (SPSS) version 23.0 was used to perform Student’s t-tests and linear regression analyses. The significance level for all the analyses was p < 0.05.
3. Results

3.1 Water chemistry

Water temperature ranged from 26 to 32 °C throughout the study area during the two sampling periods (Table S1). In the Rajang estuary, salinity was almost 0 in the upper Igan distributary in both sampling periods, indicating strong freshwater inputs (Fig. 2). Salinity at the mouth of the Igan distributary was lower than that in the mouth of the Paloh and Rajang distributaries (Fig. 2a and 2b), reflecting the increase in tidal range from the Igan to the Rajang distributaries (Staub et al., 2000). Values of pH were lower in the riverine side, especially in the delta-plain distributaries, and increased towards the sea (Fig. S2). DO concentrations were higher in the freshwater reach than in the delta-plain distributaries in both sampling periods (Fig. S2).

In the freshwater reach of the Maludam River, pH was low (<4), and DO concentrations ranged from 1.08 to 2.4 mg L⁻¹; salinity, pH, and DO all increased with increasing proximity to the coast, similar to that observed for the Sebuyau, Simunjan, and Samunsam rivers in both March and September (Fig. S2). Values of pH and DO concentrations in freshwater were higher in the Samunsam than in the Maludam, Simunjan, and Sebuyau rivers, and values of pH and DO concentrations in the Sematan and Lundu, which drain mostly mineral soils, were higher than those in the blackwater rivers (Fig. S1). DO concentrations in the Simunjan River were significantly higher in September than in March ($p < 0.05$), but DO concentrations did not differ between seasons in the other rivers ($p > 0.05$). Similarly, there was no significant seasonal variation in pH in the studied rivers ($p > 0.05$).
3.2 Se species distribution and relationship with salinity

TDSe concentrations in the studied rivers and estuaries ranged from 1.0 to 5.7 nmol L\(^{-1}\) (mean of 2.4 nmol L\(^{-1}\)) in March and from 0.70 to 3.9 nmol L\(^{-1}\) (mean of 1.8 nmol L\(^{-1}\)) in September (Table S1). DISe concentrations ranged from below the detection limit (0.0063 nmol L\(^{-1}\)) to 0.41 nmol L\(^{-1}\) (mean of 0.19 nmol L\(^{-1}\)) in March and from below the detection limit (0.0063 nmol L\(^{-1}\)) to 0.47 nmol L\(^{-1}\) (mean of 0.18 nmol L\(^{-1}\)) in September (Table S1). DOSe concentrations ranged from 0.67 to 3.9 nmol L\(^{-1}\) (mean of 1.7 nmol L\(^{-1}\)) in March and from 0.42 to 0.47 nmol L\(^{-1}\) (mean of 0.18 nmol L\(^{-1}\)) in September (Table S1). DOSe/TDSe ratios ranged from 0.67 to 0.99 (mean of 0.91) and from 0.56 to 0.99 (mean of 0.88) in March and September, respectively, indicating that DOSe was the major species of Se in the peat-draining rivers and coastal estuaries in both the dry and wet seasons (Table S1).

3.2.1 Rajang estuary

In the Rajang estuary, TDSe concentrations in March and September ranged from 1.1 to 3.7 nmol L\(^{-1}\) (mean of 1.9 nmol L\(^{-1}\)) and from 1.7 to 3.0 nmol L\(^{-1}\) (mean of 2.2 nmol L\(^{-1}\)), respectively (Table S1). Student’s t-test results showed that the concentrations of TDSe, DISe, and DOSe did not differ between the wet and dry seasons (\(p > 0.05\)). TDSe, DISe, DOSe, Se(IV), and Se(VI) concentrations and DOSe/TDSe ratios in the Rajang estuary are shown in Fig. 2 and S1. Se(IV) concentrations varied from 0.05 to 0.15 nmol L\(^{-1}\) and were high in the coastal areas in both seasons (Fig. S1e and f). Se(IV) concentrations did not differ between the two seasons (\(p > 0.05\)). Se(VI) concentrations ranged from 0.068 to 0.39 nmol L\(^{-1}\) and were also high in the coastal areas (Fig. S1g and h). As with Se(IV), there was limited seasonal variation in the concentrations of Se(VI). DISe concentrations reached a
maximum in the coastal areas, whereas DOSe concentrations were higher in the delta-plains distributaries than in the upper reach in both seasons (Fig. 2c–f). TDSe concentrations did not show a clear pattern in March but in September were slightly higher in the delta-plains distributaries than in the upper reach (Fig. 2g and h). DOSe/TDSe ratios were high in the delta-plains distributaries and decreased in a seaward direction to around 0.7, indicating that DOSe dominated in the Rajang estuary (Fig. 2).

Variation in Se species concentrations along a salinity gradient in the three tributaries (the Igan, Lassa, and Rajang) of the Rajang Estuary in March and September are shown in Fig. 3. Theoretical mixing lines (TMLs) were developed using two endmembers, namely, a freshwater endmember in the freshwater reach of the Rajang River and a marine endmember with a salinity of >30. In March, Se(IV) and Se(VI) concentrations increased with salinity and, compared with the TML, Se(IV) and Se(VI) removals were commonly observed in the Rajang and Paloh branches (Fig. 3a and b). In September, Se(IV) and Se(VI) concentrations also increased with salinity, with additions of Se(IV) in the upper reaches of the Rajang and Paloh branches and relatively little variation in Se(VI) (Fig. 3d and e). DISe concentrations, the sum of Se(IV) and Se(VI), increased with salinity and during mixing, and in the low-salinity water were lower in March than in September (Fig. 3c and f). DOSe concentrations decreased with salinity and were much higher than the TML in the Rajang and upper Paloh branches in both March and September and in the Igan Branch in September (Fig. 3g and j). TDSe concentrations in the mixing zone of the Rajang and Igan branches were also higher than the TML (Fig. 3h and k). DOSe/TDSe ratios were around 0.9 in the freshwater reach, increased to almost 0.95 in the low-salinity water of the Igan, Paloh, and Rajang branches, then decreased towards the sea (Fig. 3i and l).
3.2.2 Peat-draining rivers and estuaries

In the Maludam estuary, DISe concentrations were extremely low (near or below the detection limits) in the freshwater reach and were around 0.3 nmol L\(^{-1}\) near the sea in both seasons (Fig. 4a). DISe concentrations followed similar patterns in the Sebuyau, Simunjan, and Samunsam rivers and were lower in the river than in the area closer to the sea. DISe concentrations ranged from 0.12 to 0.35 nmol L\(^{-1}\) in the Sematan and Lundu and showed little seasonal variation (Fig. 4b–e). Se(IV) and Se(VI) concentration are not presented but were even lower than those of DISe and commonly lay below the detection limit, especially in the freshwater reaches. In the Maludam estuary, DOSe concentrations ranged from 1.5 to 4 nmol L\(^{-1}\) and increased with distance downstream in the freshwater area to the river mouth and then decreased towards the sea (Fig. 4f). DOSe concentrations in the Sebuyau estuary ranged from around 1.3 to 3.8 nmol L\(^{-1}\) and followed a similar trend to those in the Maludam estuary (Fig. 4g). In the Simunjan and Samunsam estuaries, DOSe concentrations decreased in a seaward direction in both seasons (Fig. 4i and j). In the Sematan and Lundu estuaries, DOSe concentrations ranged from 0.42 to 2.5 nmol L\(^{-1}\), were slightly lower than those in the blackwater rivers, and decreased in a seaward direction. DOSe/TDSe ratios were between 0.8 and almost 1 in the freshwater reaches of the Maludam, Sebuyau, Simunjan, and Samunsam estuaries, indicating that DOSe was the only (or dominant) species in the freshwater of the blackwater rivers. DOSe/TDSe ratios were between 0.6 and 0.9 in the Sematan and Lundu, indicating that more than half of the Se was still present in the form of DOSe in those rivers and estuaries with limited peatland cover (Fig. 4l). As TDSe is the sum of the DISe and DOSe concentrations, and DOSe generally dominated in the sampled rivers and estuaries, the distributions of TDSe and DOSe were similar (Fig. 4m–q). TDSe,
DISe, and DOSe concentrations did not differ between seasons in the Maludam, Sebuyau, Samunsam, Sematan or in the Rajang ($p > 0.05$). In the Simunjan estuaries, DOSe concentrations ranged from around 1.8 to 5.7 nmol L$^{-1}$ in March and were significantly higher than those in September ($p < 0.05$); TDSe concentrations in this river also differed between the two seasons. The limited seasonal variations in the Se species in the rivers and estuaries sampled in this study may reflect the La Niña conditions that caused high precipitation and high discharge rates in Malaysia in 2017 (Jiang et al., 2019).

Plots of DISe concentration against salinity show a positive linear regression between DISe and salinity in the Maludam, Sebuyau, and Samunsam estuaries ($p < 0.05$) in both seasons, but not in the Sematan estuary ($p > 0.05$), where DISe concentrations in the freshwater and marine water endmembers were similar in both seasons (Fig. 5a–d). The salinities varied little, either between the two seasons in the Simunjan and Lundu estuaries or in the Sebuyau estuary in September, and therefore Se concentration–salinity relationships were not examined. As shown in Fig. 4f and g, DOSe concentrations in the freshwater parts of the Maludam and Sebuyau rivers varied widely and increased downstream, so the geographical location nearest to the river mouth with a salinity of $<1$ was selected as the freshwater endmember in the linear mixing models. A negative linear correlation was observed between DOSe concentration and salinity ($p < 0.05$) in the Maludam, Sebuyau, and Samunsam estuaries for both seasons, but DOSe concentrations did not vary significantly with salinity ($p > 0.05$) in the Sematan estuary (Fig. 5e–h). TDSe concentrations were also negatively correlated with salinity ($p < 0.05$) in the Maludam, Sebuyau, and Samunsam estuaries but not in the Sematan Estuary (Fig. 5i–l). DOSe/TDSe ratios in the Maludam and Samunsam estuaries were almost 1 when salinity was less than 10 and decreased to around 0.8 as salinity increased. In the Sebuyau estuary, the
The DOSe/TDSe ratio decreased from nearly 1 to 0.8 along the salinity gradient (Fig. 345). In the Sematan estuary, DOSe/TDSe ratios remained at around 0.9 along the salinity gradient and varied widely in the coastal area in March but did not follow any clear pattern in September (Fig. 35p).

Generally, relationships between the Se species and salinity fell into three groups. In the blackwater estuaries (the Maludam, Sebuyau, and Samunsam), DISe concentrations were positively correlated with salinity; DOSe and TDSe concentrations were negatively correlated with salinity. In the Rajang estuary, which has a large area of peatland in its delta area, DISe increased with salinity but behaved non-conservatively and was removed in the brackish water; whereas DOSe and TDSe decreased with salinity, behaved non-conservatively, and were added during estuarine mixing (Fig. 3). In the Sematan estuary, TDSe, DOSe, and DISe behaved non-conservatively and showed little change during estuarine mixing (Fig. 5).

### 3.3 Mixing experiments

To simulate the behaviour of selenium species in different organic matter conditions, simple mixing experiments without suspended particles were conducted in the laboratory using water from the Rajang and Maludam estuaries. The results of these laboratory mixing experiments are shown in Fig. 5. DISe concentrations were lower in the Maludam estuary than in the Rajang, whereas DOSe concentrations were higher. The TML obtained when the river and seawater components were mixed showed that when suspended particles were excluded, there was a near-linear increase in DISe concentration with salinity in the Rajang estuary, which indicates a marine source of DISe (Fig. 6a). In the Maludam estuary, DISe concentrations also increased with salinity, but the measured values were lower than the theoretical values, with removal rates of 52% to 74%, indicating intense removal during mixing with marine water (Fig. 6b).
In contrast to DISe, there was a near-linear decrease in DOSe concentration with salinity in both the Rajang and Maludam estuaries, indicating riverine sources of DOSe (Fig. 6b). In the Rajang estuary, TDSs showed a near-linear decrease along the salinity gradient. While in the Maludam estuary, TDSs concentrations decreased with salinity (Fig. 6c), with the measured values being lower than the theoretical values, indicating removal processes at high salinity (>16), mainly due to the removal of DISe (Fig. 6c). In the Maludam estuary, DOSe/TDSs ratios ranged from nearly 1 to 0.8 in the mixing experiments, indicating that DOSe was the major species of TDSs, with ratios close to 1 when the salinity was less than 15, confirming the in situ results (Fig. 6d).

4. Discussion

4.1 Se speciation in freshwater

Considerable variation was observed in Se speciation between the studied rivers. DISe concentrations in the blackwater rivers (Maludam, Simunjan, Sebuyau, and Samunsam) were lower than, or close to, the detection limits (0.0063 nmol L\(^{-1}\)) in the freshwater, and DOSe (from 1.3 to 5.7 nmol L\(^{-1}\)) dominated TDSs in both seasons (Fig. 3). DISe concentrations were slightly higher (from 0.12 to 0.25 nmol L\(^{-1}\)) and DOSe concentrations (1.0 to 2.7 nmol L\(^{-1}\)) lower in the freshwater of the Rajang and Sematan rivers than in the blackwater rivers (Fig. 7). TDSs concentrations in the sampled rivers were comparable with those measured in other rivers worldwide (between 0.2 and 6.4 nmol L\(^{-1}\); however, in contrast to our findings, DISe generally dominates in other rivers (Cutter, 1989b; Conde and Sanz Alaejos, 1997; Pilarczyk et al., 2019). The limited data available show that DOSe concentrations in rivers...
worldwide range from <0.02 to 0.82 nmol L\(^{-1}\) (Takayanagi and Wong, 1984; Wang and Shy, 1995; Cutter and Cutter, 2001, 2004). In the blackwaters of the Orinoco in South America, TDS\(e\) concentrations were found to range from 0.07 to 0.25 nmol L\(^{-1}\) (Yee et al., 1987). Although they did not analyse D\(OSe\) fractions directly, Yee et al. (1987) assumed that D\(OSe\) was likely to constitute about 10%–15% of the total Se, a much lower value than the D\(OSe\) proportions observed in peat-draining rivers in Sarawak.

The behaviour of Se in the environment is complex, as it can exist in multiple oxidation states and as organic species (Conde and Sanz Alaejos, 1997). As shown in Fig. 7a–d, DI\(Se\) concentrations were positively correlated with the DO concentrations and pH values in the freshwaters of the studied rivers. Se(IV)/Se(VI) ratios represent the relative proportions of Se(IV) and Se(VI) in DI\(Se\). Se(IV)/Se(VI) ratios increased as DO concentrations and pH values increased in March, indicating that the proportion of Se(IV) in DI\(Se\) increased as DO and pH increased. Species of Se are very sensitive to redox conditions and pH values (Sharma et al., 2015). Sorption to solid surfaces (including metallic oxides, hydroxides, and clays) is also a pH-dependent process, with substantial sorption of Se(IV) and Se(VI) occurring at pH values of 4 to 6 and negligible sorption under more alkaline conditions (pH > 8) (BarYosef and Meek, 1987; Balistrieri and Chao, 1987; Papelis et al., 1995; Sharma et al., 2015). Se(VI) adsorption onto solid surfaces is weaker than that of Se(IV) (Balistrieri and Chao, 1987; Zhang and Sparks, 1990; Seby et al., 1998). Thus, adsorption of Se(IV) and Se(VI) by metal oxyhydroxides and clays when pH is between 4 and 6 may help to explain the low DI\(Se\) concentrations in the sampled freshwater, and DI\(Se\) concentrations and Se(IV)/Se(VI) ratios might be expected to increase as pH increases.

Peat has a high content of natural organic matter, which also plays an important role in Se speciation (Tam et al. 1999; Li et al., 2017). Martin et al.
(2018) reported that DOC concentrations in the sampled rivers ranged from 120 to 4400 µmol L\(^{-1}\). As shown in Fig. 7e, the DISe/DOSe ratio was negatively related to DOC concentration (data from Martin et al., 2018). Almost 15% of Se(IV) is removed by adsorption to peat (Kharkar et al., 1968). Se(IV) and Se(VI) associated with humic and fulvic substances appear to be responsible for the immobilization of inorganic Se (Kang et al., 1991; Zhang and Moore, 1996; Wang and Gao, 2001), and Se sorption kinetics on humic acids can be expressed by a pseudo-second-order equation (Kamei-Ishikawa et al., 2007).

The Maludam, Sebuyau, and Simunjan catchments are mainly peat, whereas the Samunsam River drains an extensive area of peatland in its upper reaches (Müller et al., 2016; Martin et al., 2018). The Rajang catchment is dominated by mineral soils, with peatland being found only in the delta surrounding the distributaries (Staub et al., 1994, 2000). The catchments of the Sematan and Lundu also have limited peat deposits (Martin et al., 2018). DO, pH, and DOC concentrations of the water probably contributed to the observed variations in Se species, and the acidic, low-oxygen, and organic-rich blackwater rivers were not a suitable environment for DISe.

Coal deposits in Kanawha County in the USA have been interpreted as a dome-shaped peat swamp, analogous to those in Malaysia. Coal Se contents reached 10.7 mg/kg, and sequential extraction results showed that the concentrations of the organically bound fraction were the highest (Vesper et al., 2008). It is therefore expected that organic matter that is solubilized and leached from peat would cause Se concentrations to increase, and therefore leaching from Se-rich peat soils is inferred to be the major source of DOSe in our sampled rivers. A study of chromophoric dissolved organic matter (CDOM) in these rivers and estuaries have found that humic-like CDOM components (C1, C2, C3, and C4) were derived from peatlands (Zhou et al., 2019). DOSe concentrations measured in the present study correlate positively with the
humification index (HIX, which represents the humification degree of dissolved organic matter) and the sum of the humic-like CDOM components (C1, C2, C3, and C4) (p < 0.05) (data from Zhou et al., 2019) in the freshwater of the studied rivers (Fig. 7f and g). These results indicate that DOSe in Sarawak may be associated with dissolved humic substances, which is consistent with the findings of Zhang and Moore (1996), who reported that substantial amounts of dissolved Se in natural waters were associated with organic matter. Gustafsson and Johnsson (1992, 1994) found that a high proportion of the Se(IV) added to humic lake water was adsorbed by humic substances in the form of Se(IV) to metal–humic complexes, which is similar to phosphate adsorption by iron–humic complexes. A study of Finnish lakes has also shown that about half of the TDSe was present in humic substances, whereas DISe represented between 12% and 24% of the TDSe (Wang et al., 1995). However, the mechanisms behind the interactions between Se and dissolved organic ligands are still poorly understood. Three hypotheses have been proposed to explain organic-matter-mediated retention of Se, as follows: 1) direct complexation of organic matter with Se, 2) indirect complexation via Se-cation–organic-matter complexes, or 3) microbial reduction and incorporation into amino acids, proteins, and natural organic matter (Winkel et al., 2015). Depending on the type of binding, Se may be easily mobilized (e.g., through adjusting pH) or immobilized (e.g., by covalent incorporation to organic matter) (Winkel et al., 2015). However, there is ambiguity about the molecular structure and species of Se that bind to organic matter, and further work is needed to identify the mechanisms by which Se is bound to, and released from, organic matter.

4.2 Behaviour of DISe during estuarine mixing

As shown in Figures 3 and 5, DISe concentrations increased as salinity
increased in the Rajang, Maludam, Sebuyau, and Samunsam estuaries. These reversed concentration–salinity relationships contrast with those reported for other estuaries (Measures and Burton, 1978; Takayanagi and Wong, 1984; Van der Sloot et al., 1985; Cutter, 1989a; Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati, 1998; Yao et al., 2006; Chang et al., 2016). Laboratory mixing experiments conducted using water from the Rajang and Maludam rivers also revealed that DISe concentration increased as salinity increased (Fig. 6a). During estuarine mixing, DISe has been shown in some other studies to behave conservatively \((R^2 > 0.9)\), with concentrations decreasing along a salinity gradient in the estuaries of the Scheldt (Van der Sloot et al., 1985), Test (Measures and Burton, 1978), Rhone (Guan and Martin, 1991), and James (Takayanagi and Wong, 1984) rivers. DISe has also been shown to behave non-conservatively, with concentrations decreasing along the salinity gradient in the Changjiang estuary (Chang et al., 2016), Zhuijiang estuary (Yao et al., 2006), Mex Bay (Abdel-Moati, 1998), San Francisco Bay (Cutter, 1989a), and Kaoping and Erhjen estuaries (Hung and Shy, 1995). The marine endmember of the DISe concentrations in the sampled estuaries (salinity > 31) was \(0.30\) nmol L\(^{-1}\) (range: \(0.12\) to \(0.47\) nmol L\(^{-1}\)), encompassing or close to the values reported for surface water in the South China Sea (around \(0.38\) nmol L\(^{-1}\), Nakaguchi et al., 2004) and the Pacific (mean of \(0.24\) nmol L\(^{-1}\), range: \(0.02\) to \(0.69\) nmol L\(^{-1}\)) (Cutter and Bruland, 1984; Sherrard et al., 2004; Mason et al., 2018). The salinity-related increases in DISe in a seaward direction indicate that the patterns of distribution of DISe in the Rajang, Maludam, Sebuyau, and Samunsam estuaries are controlled mainly by conservative mixing of ocean-derived DISe. Nitrate behaves in a similar way in the Dumai River estuary (Sumatra, Indonesia), another tropical blackwater river (Alkhaitb and Jennerjahn, 2007). The Maludam, Sebuyau, Samunsam, and Simunjan rivers are peat-draining rivers, and most of the coastal areas in the Rajang delta are
also covered by peat; thus, DISE in the black-water estuaries and in the Rajang may have been mainly ocean derived.

In the Rajang estuary, DISE was removed in March and was added in September during estuarine mixing (Fig. 3g and j). DISE removal rates of between 52% and 74% were calculated for Maludam River water in the laboratory mixing experiments (Fig. 6a). At low salinity, DISE concentrations were slightly scattered around the linear mixing model for the Maludam and Samunsam rivers (Fig. 5c and 4c). The Rajang River drains mineral soils in its upper reaches, and peatland is found only in the delta surrounding the distributaries (Staub et al., 1994, 2000). In the distributary channels, DOC concentrations reached around 240 \( \mu \text{mol L}^{-1} \), almost double the concentrations further upstream, indicating large inputs of organic matter from peat. High DOC concentrations (between 3100 and 4400 \( \mu \text{mol L}^{-1} \)) have also been reported for the Maludam River (Martin et al., 2018). As discussed above, organic matter can immobilize Se(IV) and Se(VI). Laboratory studies have shown that Se(IV) can be adsorbed by peat and that 60% of the adsorbed Se(IV) can be desorbed upon exposure of the solid phase to seawater (Kharkar et al., 1968). Selenium may have been added to the Rajang estuary in September via release of Se(IV) from peat in brackish waters. Other studies have reported removal of the humic fractions of DOM, colloidal iron, and phosphorus by flocculation in the river–sea mixing zones (Eckert and Sholkovitz, 1976; Forsgren et al., 1996; Asmala et al., 2014). Some of the DISE may exist in colloidal form in natural water (Takayanagi and Wong, 1984), and DISE may be removed by flocculation. In peat-draining estuaries, ocean-derived DISE may be adsorbed to peat and may be associated with DOM, which is then converted to DOSe and/or flocculated to particulate Se.
4.3 Behaviour of DOSe during estuarine mixing

In contrast to DISe, DOSe concentrations were highest in the rivers and decreased in a seaward direction as salinity increased, indicating a terrestrial origin of DOSe. During estuarine mixing in other estuaries, DOSe has been shown to behave non-conservatively, with concentrations decreasing along salinity gradients in the Rhone estuary (Guan and Martin, 1991), Mex Bay (Abdel-Moati, 1998), and Kaoping and Erhjen estuaries (Hung and Shy, 1995), and with mid-estuarine input in the San Francisco Bay (Cutter, 1989a). DOSe concentrations in the estuaries studied in Sarawak were higher than those reported in other estuaries, such as the Rhone, Kaoping, and Erhjen estuaries (0.1 to 0.7 nmol L\(^{-1}\)) (Guan and Martin, 1991; Hung and Shy, 1995), and in San Francisco and Mex bays (0.1 to 2.5 nmol L\(^{-1}\)) (Cutter, 1989a; Abdel-Moati, 1998).

4.3.1 Rajang estuary

In the Rajang estuary, DOSe exhibited non-conservative mixing, and DOSe concentrations in most of the brackish waters were higher than the TML values (Fig. 3g, 3j). Compared with the TML, removals of DISe were greater than additions of DOSe in the distributary channels, indicating that not all of the DOSe was from the conversion of DISe. High DOSe concentrations observed in coastal areas such as San Francisco Bay have been attributed to \textit{in situ} production of DOSe by phytoplankton (Cutter, 1989a). However, chlorophyll-a concentrations in our study area very rarely exceed 2.5 µg L\(^{-1}\) and are ubiquitously 1 µg L\(^{-1}\) in the Rajang (Martin et al., 2018), which means that phytoplankton production is not a major source of DOSe in Sarawak.

In the Rajang delta, DOC also exhibited non-conservative mixing, with additions from peatlands in the delta areas (Martin et al., 2018). Leaching from
peat soils in the delta areas may be an important source of DOSe in estuarine mixing zones of the distributary channels in the Rajang estuary. However, there was no significant correlation between DOSe concentration and the CDOM spectral slope from 275 to 295 nm ($S_{275-295}$, data from Martin et al., 2018), specific UV absorbance at 254 nm (SUVA$_{254}$, data from Martin et al., 2018), or the humic-like C3 component (data from Zhou et al., 2019) in the Rajang estuary for March ($p > 0.05$) (Fig. 8a-c). The maxima excitation wavelength of the humic-like component C1 was 330 nm, which is higher than the maxima excitation wavelength of the humic-like component C2 (275 nm) (data from Zhou et al., 2019), showing that the C2/C1 ratio is enhanced by photodegradation (Wang et al., 2019). DOSe/DOC and DOSe/DISe ratios were not correlated with C2/C1 ratios ($p > 0.05$) (Fig. 8d and e). As suggested by Martin et al. (2018), sediment loads are high and attenuate very strongly within the Rajang delta, so the selective removal of a high-molecular-weight CDOM fraction may be due to sediment adsorption rather than photodegradation.

DOSe was added to, rather than removed from, the brackish waters in the Rajang estuary (Fig. 3c and f).

4.3.2 Peat-draining rivers and estuaries

The blackwaters in Sarawak are characterized by high levels of terrigenous DOM with high average molecular weight and high aromaticity (Martin et al., 2018). In the peat-draining Maludam River, DOSe concentrations were negatively correlated with $S_{275-295}$ (data from Martin et al., 2018) and SUVA$_{254}$ (data from Martin et al., 2018) during estuarine mixing in both seasons (Fig. 8f and 8g), which differed from the pattern observed for the Rajang. DOC concentrations ranged from 96 to 200 µmol L$^{-1}$ in the Rajang estuary and were nearly 20 times lower than those in the peat-draining river estuary (the Maludam, range: 256 to 4386 µmol L$^{-1}$) in March, and the CDOM concentration and C1–
C5 components in the Rajang estuary were also almost 10 times lower than those in the Maludam estuary (Martin et al., 2018; Zhou et al., 2019), indicating that, depending on the geochemical setting, the concentration and molecular weight distribution of DOM in the Rajang estuary were unlike those in the Maludam. $S_{275-295}$ is inversely related to the mean molecular weight of DOM (Helms et al., 2008), and $SUVA_{254}$ is positively related to the aromaticity of DOM (Weishaar et al., 2003). These correlations suggest that DOSe was associated closely with high-molecular-weight and highly aromatic DOM in the Maludam estuary. Also, DOSe concentrations were strongly and positively correlated with the humic-like C3 component (data from Zhou et al., 2019) during estuarine mixing in the two seasons (Fig. 8h). As reported by Zhou et al. (2019), the C3 components derived corresponded to aromatic and black carbon compounds with high molecular weight. The positive correlation between DOSe and the C3 component (Fig. 8g) also indicates that DOSe fractions are associated with high-molecular-weight aromatic DOM in the Maludam estuary (Fig. 9). Kamei-Ishikawa et al. (2008) investigated the binding between Se(IV) and humic acid in a laboratory study and found that the Se remaining in solution was associated with the dissolved humic acid fractions, and those authors' ultrafiltration experiments suggested that 50% to 60% of these Se–humic acid associates had high molecular weights (>10 kDa). Bruggeman et al. (2007) studied the interactions between Se(IV) and humic substances in aqueous sediment extracts and found that consistent with our findings, over 70% of the original Se(IV) was associated with high molecular weights (>30 kDa). Gustafsson and Johnsson (1994) reported that forest soil fixed 10% of added Se(IV) into low-molecular-weight fractions of the humic substances by means of microbial reductive preferential incorporation.

In the Maludam estuary, DOSe/DOC ratios were negatively correlated with C2/C1 ratios (Fig. 8j), indicating that compared to bulk DOM, the DOSe
fractions were more susceptible to photodegradation during estuarine mixing; similarly, other researchers have found that aromatic DOM structures are particularly photoreactive (Ospal and Benner, 1998; Stubbins et al., 2012). As shown in Fig. 8k, DOSe/DISe ratios are also correlated negatively with C2/C1 ratios, indicating that DOSe was probably photodegraded to DISe. Thus, photodegradation plays an important role in DOSe processing in the study area, and DOSe might contain a significant photoreactive fraction that facilitates photodegradation of DOSe into lower mean molecular weights or gaseous Se or photomineralization to DISe (Fig. 9). Considerable amounts of Se may be volatilized when methylselenide compounds form (Lin et al., 2003; Lidman et al., 2011). A field study conducted in Switzerland found that volatile species of Se, including dimethyl selenide, dimethyl diselenide, methane seleninic acid, and dimethyl selenoxide, were naturally emitted from peatland at concentrations of around 33 nmol L\(^{-1}\) (Vriens et al., 2015). As a result of the method used in the present study, volatile methylselenide compounds in the DOSe fractions may not have been detected, so DOSe may have been underestimated. In future work, particular attention should be given to methylselenide. Martin et al. (2018) suggested that because of the short residence time in rivers, most photodegradation of terrestrial DOM in the rivers of Sarawak likely took place after it reached the sea rather than within the rivers and estuaries. Studies have shown that photodegradation of DOM results in a range of bioavailable products (Miller and Moran, 1997). In the coastal areas of the Sarawak, the high temperature promotes rapid microbial metabolism, the residence time is longer, and solar irradiation is high (Martin et al., 2018). Once transported to offshore, peatland-derived DOSe might be degraded to a lower molecular weight or DISe, both of which are bioavailable for phytoplankton and may enhance the productivity of oligotrophic waters.

The marine endmember of the DOSe concentrations in the sampled
estuaries (salinity >31) ranged from 0.42 to 2.91 nmol L\(^{-1}\) (mean: 1.32 nmol L\(^{-1}\)) and exceeded those in surface water of the South China Sea (mean: 0.20 nmol L\(^{-1}\), range: 0.33 to 0.14 nmol L\(^{-1}\), Nakaguchi et al., 2004) and the Pacific (mean: 0.36 nmol L\(^{-1}\), range: 0.01 to 0.67 nmol L\(^{-1}\) (Cutter and Bruland, 1984; Sherrard et al., 2004; Mason et al., 2018). The high DOSe concentrations in coastal waters in Sarawak (S > 30) suggest a significant contribution from terrigenous DOSe. Several studies have observed that phytoplankton can excrete organic selenides after assimilating Se(IV) (Vandermeulen and Foda, 1988; Besser et al. 1994; Hu et al. 1997). As described by Cutter and Cutter (1995, 2001), DOSe in ocean surface waters, which is associated mainly with soluble peptides, appears to have a low molecular weight and, as shown in a laboratory study (Baines et al., 2001), can be taken up again by phytoplankton at rates of between 4% and 53%. Photoreactive DOSe fractions, in which Se may be associated with aromatic and black carbon compounds with high molecular weight, are discharged offshore by peat-draining rivers (Fig. 8g), from where they are probably transported across the marginal sea and circulated globally (Fig. 9). Given that the bioavailability and biogeochemical cycling of the peatland-derived DOSe fractions may differ from those of peptides produced in situ by phytoplankton in the ocean, the impact on coastal and open ocean ecosystems should be evaluated in the future.

5. Conclusion

To the best of our knowledge, this is the first study of seasonal variations in Se speciation in peat-draining rivers and estuaries in Southeast Asia. Contrary to our expectations and the results from studies elsewhere, DOSe, not DISe, was the major species in the peat-draining rivers and estuaries of Sarawak, Malaysia. In blackwater estuaries, DISe was positively related to salinity, indicating a marine origin, and DOSe was negatively related to salinity,
indicating terrestrial sources. In the delta area of the Rajang River, where peatland dominates, DISe concentrations increased with salinity, and DOSe concentrations generally decreased with salinity but increased in the middle parts of the estuary. In the Maludam, DOSe fractions may be associated with high-molecular-weight peatland-derived aromatic and black carbon compounds and may photodegrade to more bioavailable forms once transported to oligotrophic coastal waters, where they may promote productivity.

6. Author contribution

JZ, MM, YW, SJ and YC conceptualized the research project and planned the field expeditions. SJ, AM, EA, FJ and MM performed sample collection and in-situ measurement for the cruises. YC, WWC, JGQ, JLR, EMR and XLW completed laboratory analyses. YC, XNW, YW, JS, JZ and MM processed and analysed the data. All co-authors participated in the interpretation and discussion of the results. YC prepared the manuscript with suggestions from all co-authors.

7. Competing interests

The authors declare that there is no conflict of interesting.

8. Acknowledgements

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Figure 1. (a) Map of the study area showing the location of Sarawak on the island of Borneo. Blue boxes with letters indicate the areas shown in panels b–d. (b–d) Station locations for the Rajang River (b), the Samunsam, Sematan, and Lunda rivers (c), and the Maludam, Sebuyau, and Simunjan rivers (d) in March and September 2017. The maps were made with Ocean Data View (2019).
Figure 2. Distributions of salinity, of DISe, DOSe, and TDSe concentrations, and of DOSe/TDSe ratio in surface waters of the Rajang estuary in March and September 2017. All distribution plots were made with Ocean Data View (2019).
Figure 3. Relationships between Se(IV) (a, d), Se(VI) (b, e), DISe (c, f), DOSe (g, j), and TDSe (h, k) concentrations, and DOSe/TDSe ratio (i, l) with salinity in the Rajang and three Rajang tributaries (Igan, Lassa, and Rajang) in March and September 2017. TML refers to the theoretical mixing line, which was defined using two endmembers: freshwater in the riverine system and seawater.
Figure 4. DlSe, DOSe, and TDSSe concentrations and DOSe/TDSSe ratio along the Maludam, Sebuyau, Simunjan, Samunsam, Sematan, and Lunda estuaries in March and September 2017.
Figure 5. Relationships between DISe, DOSe, and TDSe concentrations and DOSe/TDSe ratio with salinity in the Maludam, Sebuyau, Samunsam, and Sematan estuaries. Red circles and blue triangles represent data for March and September 2017, respectively.
Figure 6. Results of laboratory mixing experiments showing variation in DISe, DOSe, and TDSe concentrations and DOSe/TDSe ratio as a function of salinity using filtered riverine water from the Rajang and Maludam rivers and filtered coastal seawater. TML refers to theoretical mixing line.
Figure 7. Relationships between (a, b) DISe concentrations and DO and pH values, (c, d) Se(IV)/Se(VI) ratios and DO and pH values, and (e–g) DOSe concentrations with the humification index (HIX) and the sum of humic-like CDOM components (C1, C2, C3, and C4) in freshwater (Salinity < 1) for the Rajang, Sematan, Maludam, Sebuyau, Samunsam, and Simunjan rivers in March and September. The HIX and C1, C2, C3, and C4 components are from Zhou et al. (2019) from the same cruises. DO concentrations and pH values were not available for the Sematan River for September, and the HIX and CDOM components were not available for the Rajang River for September. Se(IV)/Se(VI) ratios were calculated only if Se(IV) and Se(VI) concentrations were both above the detection limits, meaning that the data are limited.
Figure 8. Relationships between DOSe concentrations and $S_{275-295}$, C3 components and SUVA$_{254}$, DOSe/DOC ratio and C2/C1 component ratios, and DOSe/DISe ratios and C2/C1 component ratios in the Rajang and Maludam estuaries. The $S_{275-295}$, SUVA$_{254}$, C1, C2, and C3 components are from Martin et al. (2018) and Zhou et al. (2019) from the same cruises.
Figure 9. Conceptual diagram of the behaviour of Se species in the Maludam estuary. HMW, LMW, and DMSe represent high molecular weight, low molecular weight, and dimethyl selenide, respectively.