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 aquatic 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 (near or below the detection limits, i.e. 0.0063 nmol L^{-1}), 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. The 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 coastal waters. The TDSe flux delivered by the peat-draining rivers exceeded other small rivers reported so far, and it is quantitatively more significant than previously thought.

1. Introduction

Se is an essential trace element for aquatic organisms (Bodnar et al, 2014). Low levels of Se in the food chain lead to disease or death whereas high levels are toxic (Lobanov et al., 2009; Winkel et al., 2015). Selenium depletion in the Phanerozoic oceans may have contributed to three major mass extinction scenarios (Long et al., 2016). Thus, there has been great 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 (Fernández and Charlet, 2009). The behaviour of Se in natural waters is complicated, as it exists in several oxidation states (−II, IV, VI) (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 marine phytoplankton with Se(IV) being the preferred species (Wrench and Measures, 1982; Apte et al., 1986; Vandermeulen and Foda, 1988; Baines and Fisher, 2001). Direct uptake of seleno-methionine and seleno-cystine has been demonstrated in diatom (Doblin et al., 1999). Laboratory study showed that organic selenide released by algal cell lysis of the diatom or viral of the chrysophyte were also bioavailable to the marine phytoplankton (Gobler et al., 1997; Baines et al., 2001). 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 speciation was controlled by biological, physical, and redox processes in the estuaries; non-conservative processes resulting from phytoplankton uptake; absorption by suspended particles; and generation 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). The behaviour of Se in tropical estuaries, however, is still poorly understood.

In the high-latitude peatland-draining rivers, dissolved Se concentrations are spatial variable, with concentrations of up to 13 nmol L^{-1} being observed in northern Minnesota, US (Clausen and Brooks, 1983), from 0.38 to 5 nmol L^{-1} in the Krycklan catchment, Sweden (Lidman et al., 2011) and from 0.25 to 1.25 nmol L^{-1} in the Siberian (Pokrovsky et al., 2018). Although these various studies did not report different species of Se (Clausen and Brooks, 1983; Lidman et al., 2011; Pokrovsky et al., 2018), the DOSe probably the dominated species in peatland-draining river. In the open ocean, DOSe was assumed mainly associate with soluble peptides with low molecule weight in surface waters and were relatively refractory (Cutter and Cutter, 1995; 2004). Substantial amounts of dissolved Se also are known to be associated humic substances, Gustafsson and Johnsson (1994) assumed that Se was preferentially incorporated into low molecular weight humic substances fractions by means of microbial reductive incorporation, while Kamei-Ishikawa et al. (2008) found that Se associated with high molecular weights humic acid fractions. The current paucity of information on DOSe characteristics and its export by rivers from tropical peat-draining rivers remains a major gap in our understanding of Se biogeochemical cycling. Highest concentrations of dissolved organic carbon (DOC) globally were reported in tropical peat-draining rivers in Borneo (Moore et al., 2013; Wit et al., 2015). More works of Se in the fluvial systems of this region are therefore needed to provide an improved understanding of the biogeochemical processing of Se and the associations 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). We hypothesize that the DOSe is the major species in those peatland-draining rivers which mainly from peat soils and sizable Se from peatland is delivered to the coastal areas. The main objectives of the study were to 1) evaluate the fate of dissolved Se species in peatland-draining estuaries; 2) characterize the DOSe fractions; and 3) estimate the magnitude of Se fluxes delivered from to coastal ocean. 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). Sarawak has a tropical climate, with a mean annual air temperature at the capital Kuching 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) (Fig. 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). The physio-geographical parameters of sampled river basins are summarized in Table 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 (Table 1).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 (Staub et al., 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 Analytical methods

The Se(IV), DISe, and TDSe 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^{-1} = 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 $NaBH_4$ 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.

2.3 The calculation of TDSe flux and yield

TDSe fluxes (Q) transported to the ocean were estimated according the following equation:

$$Q = C \times V \quad (1)$$

Where C is the mean concentration of TDSe at the fresh endmember of the river (salinity < 1), and V is the river water discharge. Riverine TDSe yield is the ratio of TDSe flux to the drainage area.

2.4 Data statistics and analysis

The Statistical Package for Social Sciences (SPSS) version 23.0 was used to perform Student's t-tests, Mann Whitney U test and linear regression analyses. The significance level for all the analyses was $p < 0.05$.

3. Results

3.1 Water chemistry

The water chemistry in the freshwater reach of the Maludam, Simunjan, Sebuyau and Samunsam rivers are typical of blackwater rivers draining from peatland with acidic pH and low DO concentrations, and the mixing with coastal water increased the pH and DO (Table S1, Fig. S1). 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). In the Rajang estuary, values of pH and DO were lower in the riverine side, especially in the distributaries where covered by the peat (Fig. S2).

3.2 Se species distributions

TDSe concentrations in the studied rivers and estuaries ranged from 1.0 to 5.7 nmol L^{-1} in March and from 0.70 to 3.9 nmol L^{-1} in September (Fig. 2, Table S1). DOSe/TDSe ratios ranged from 0.56 to 0.99, indicating that DOSe was the major species of Se in the peat-draining rivers and estuaries in both the dry and wet seasons (Fig.2, Table S1). Considerable variation was observed in Se speciation between the studied rivers. The TDSe and DOSe concentrations and DOSe/TDSe ratios were higher in the Maludam, Simunjan, Sebuyau and Samunsam that drain catchment with higher peatland coverage than those in the Rajang, Sematan and Lundu estuaries, whereas the opposite trend for DISe

(Table 1, Fig. 2). Student's t-test results showed that the concentrations of TDSe, DISe and DOSe did not differ between the wet and dry seasons in the sampled rivers and estuaries (p > 0.05), which may reflect the La Niña conditions that caused high precipitation and high discharge rates in Malaysia in 2017 (Jiang et al., 2019).

In the Rajang estuary, Se(IV), Se(VI) and DISe concentrations were high in the coastal areas, whereas DOSe concentrations were higher in the distributaries than in the upper reach in both seasons (Fig. S3). DOSe/TDSe ratios were high in the distributaries and decreased in a seaward direction to around 0.7 (Fig. S3). In the Maludam estuary, DISe concentrations were extremely low (near or below the detection limits) in the freshwater reach and increased towards the sea, whereas the DOSe concentrations decreased in a seaward direction in both seasons (Fig. S4). DISe and DOSe concentrations followed similar patterns in the Sebuyau, Simunjan, Samunsam, Sematan and Lundu estuaries (Fig. S4). 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. 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 S4). The DOSe/TDSe ratios were between 0.8 and almost 1 in the Maludam, Sebuyau, Simunjan, and Samunsam estuaries as salinity < 1, indicating that DOSe was the only (or dominant) species in the freshwater of the blackwater rivers. The 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 high proportions of mineral soils (Fig. S4).

3.3 Se species relationship with salinity

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. DISe concentrations increased with salinity and, compared with the TML, DISe removals were observed in the Rajang branches in March, and DISe additions were observed in the upper reaches of the Rajang and Paloh branches (Fig. 3a, 3b). 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. 3e, 3f). TDSe concentrations in the mixing zone of the Rajang and Igan branches were also higher than the TML (Fig. 3i, 3j).

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. 3, Fig. S5). 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. 3j and 3h, 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. 3 and Fig. S5). 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.3 and Fig. S5).

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 (Fig. 3). In the Rajang estuary, 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. 3).

3.4 Correlation between Se species with DO, pH and DOM

For the freshwaters ($S < 1$) of the studied rivers, DISe concentrations were positively correlated with the DO concentrations and pH values, and the DISe/DOSe ratio was negatively related to DOC concentration (data from Martin et al., 2018; Fig. 4a, 4b). DOSe concentrations correlated positively with the humification index (HIX) and the sum of the humic-like chromophoric dissolved organic matter (CDOM components, C1, C2, C3, and C4) ($p < 0.05$) (data from Zhou et al., 2019) (Fig. 4c, 4d).

In the Maludam Estuary, DOSe concentrations were negatively correlated with the CDOM spectral slope from 275 to 295 nm ($S_{275\text{-}295}$) and were positively correlated with the humic-like C3 component and specific UV absorbance at 254 nm ($SUVA_{254}$) during estuarine mixing in both seasons (data from Martin et al., 2018; Zhou et al., 2019, Fig. 5a-c). In addition, DOSe/DOC and DOSe/DISe ratios were negatively correlated with C2/C1 components ratios (Fig. 5d, 5e).

4. Discussion

4.1 Fate of Se species during estuarine mixing

On a global perspective, TDSe concentrations in the sampled rivers were comparable with those in other reported rivers (between 0.2 and 30 nmol L^{-1}); however, in contrast to our findings, DISe generally dominates in other rivers (Table 2, Cutter, 1989b; Conde and Sanz Alaejos, 1997; Pilarczyk et al., 2019). DOSe concentrations in rivers worldwide range from <0.02 to 0.82 nmol L^{-1} (Takayanagi and Wong, 1984; Huang and Shy, 1995; Cutter and Cutter, 2001, 2004). In the blackwaters of the Orinoco in South America, TDSe concentrations were found to range from 0.07 to 0.25 nmol L^{-1} (Yee et al., 1987). Although they did not analyse DOSe fractions directly, Yee et al. (1987) assumed that DOSe was likely to constitute about 10%–15% of the total Se, a much lower value than the DOSe proportions observed in peat-draining rivers in Sarawak.

Species of Se are very sensitive to redox conditions and pH values (Sharma et al., 2015). Se(IV) and the Se(VI) are soluble in water which exists under mild and strong oxidizing conditions (Torres et al., 2010), thus DISe concentrations be expected to increase with DO values (Fig. 4a). Sorption to solid surfaces is 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). Adsorption of Se(IV) and Se(VI) by solid surfaces when pH is between 4 and 6 may help to explain the low DISe concentrations in the sampled freshwater, and DISe concentrations be expected to increase as pH increases (Fig. 4b). In addition 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). The DISe/DOSe ratios negatively related with DOC concentrations (Fig. 4c). 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.

During estuarine mixing, reversed DISe concentration–salinity relationships were observed in the Rajang, Maludam, Sebuyau, and Samunsam estuaries (Fig. 3, Fig S5), which were 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). 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 those peat-draining estuaries are controlled mainly by conservative mixing of ocean-derived DISe. In addition, DISe was removed in March but was added in September in the Rajang estuary. 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). DISe 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.

In contrast to DISe, DOSe concentrations were high in the rivers and decreased in a seaward direction as salinity increased (Fig. 3, Fig S5). DOSe has been shown to behave non-conservatively in other estuaries, with concentrations decreasing along salinity gradients or with mid-estuarine input (Cutter, 1989a; Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati, 1998). DOSe concentrations in the estuaries studied in Sarawak were higher than those reported in other estuaries (0.1 to 2.5 nmol L^{-1}) (Cutter, 1989a; Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati, 1998). 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. In the distributary channels of Rajang, there are large inputs of organic matter from peat, thus higher DOSe concentrations than the TML values be expected in most of the brackish waters (Fig. 3).

4.2 Character of the DOSe fractions

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. Moreover the peat-draining rivers demonstrated a liner relationship between DOSe concentrations and HIX and humic-like CDOM components (Fig. 4d, 4e) indicating that DOSe may be associated with dissolved humic substances. In addition, DOSe correlated with $S_{275-295}$ and $SUVA_{254}$ (Fig. 5a, 5c) suggesting that DOSe was associated closely with high-molecular-weight and highly aromatic DOM. Also, the positive correlations between DOSe and the humic-like C3 component (Fig. 5b) which derived corresponded to aromatic and black carbon compounds with high molecular weight, also indicates that DOSe fractions are associated with high-molecular-weight aromatic DOM (Fig. 6). Pokrovsky et al. (2018) also found that Se were transport in the form of high molecular weights organic aromatic-rich complexes from peat to the rivers and lakes in the Arctic. Bruggeman et al. (2007) and Kamei-Ishikawa et al. (2008) both found that 50% to 70% of Se(IV)–humic substances associates had high molecular weights (>10 kDa), that consistent with our findings.

During the estuarine mixing, the negatively correlation between DOSe/DOC and DOSe/DISe ratios with C2/C1 ratios which is enhanced by photodegradation (Wang et al., 2019; Fig. 5d, 5e), indicating that compared to bulk DOM, the DOSe fractions were more susceptible to photodegradation, and that DOSe was probably photodegraded to DISe. As suggested by Martin et al (2018) that most photochemical transformations of DOM in Sarawak likely take place after DOM reaches the sea. Thus, photodegradation plays an important role in DOSe processing once transported to offshore, 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. 6). Considerable amounts of Se may be volatilized when methylselenide compounds form (Lidman et al., 2011). A field study found that volatile species of Se 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. Studies have shown that photodegradation of DOM results in a range of bioavailable products (Miller and Moran, 1997). Peatland-derived DOSe might be degraded to a lower molecular weight or DISe in the coastal areas, both of which are bioavailable for phytoplankton and may stimulate their growth, and thereby impact the marine animals via food chain. The photoreactive DOSe fractions are probably transported across the marginal sea and circulated globally. 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.

4.3 TDSe flux

Information on the biogeochemistry of peat-draining rivers is scare, and so their possible quantitative significance for the oceanic TDSe budget is unexplored as yet. The TDSe flux was estimated to be 16 × 10^3 and 0.044 × 10^3 kg yr^{-1} for Rajang and Maludam, respectively (Table 2). On a global scale, the TDSe delivered from Rajang were less than those large rivers including Changjiang, Amozon, Zhujiang, Orinoco and St.Lawrence River, but exceeded other small rivers reported so far (Table 2). The TDSe delivered by Rajang and Maludam contributed nearly 1% of the total riverine TDSe input to the ocean

with only 0.3% of freshwater discharge (Nriagu, 1989; Milliman and Farnsworth, 2013). The TDSe yields for Rajang and Maludam were just below the second largest river Changjiang and the polluted Scheldt River, but were exceed the other rivers (Table 2). As for the DOSe yields for Rajang and Maludam were one or even two orders of magnitude higher than other reported rivers so far (Table 2). This indicates that the numerous small blackwater rivers draining from peatland are very efficient TDSe and DOSe sources for the coastal waters. The roughly estimated TDSe flux from tropical peatland (439,238 km^2, Page et al., 2011) could be roughly around 120× 10^3 kg yr^{-1}, which were nearly 35% of the current total riverine TDSe flux, based on average TDSe yield from Rajang and the Maludam (0.27 kg km^{-2} yr^{-1}). On a global perspective, TDSe export from peat-draining rivers is quantitatively more significant than previously thought. It can be expected that increasing anthropogenic disturbing of peat can release a great amount of Se to rivers, and then transported to the coastal areas, the impact to the ecosystem should receive more attention in future studies.

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 the results from studies elsewhere, DOSe, not DISe, was the major species in the peat-draining rivers and estuaries of Sarawak, Malaysia. Contrary to our expectations, reversed DISe concentration–salinity relationships were observed in those estuaries, indicating a marine origin, while DOSe concentrations decreased with salinity, indicating terrestrial sources. The 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 stimulate the growth of phytoplankton. The DOSe yields in the peatland-

draining rivers were one or even two orders of magnitude higher than other reported rivers. The TDSe flux delivered by the exceeded other small rivers, and it is quantitatively more significant than previously thought. The impact of the sizable Se from increasing anthropogenic disturbing of peat to the ecosystem should be evaluated in the future.

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.

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711 Table 1 The physio-geographical parameters of sampled rivers. (n.a. stands

712 for not available.)

River Names	Total Basin [a]	Runoff ($km^3 yr^{-1}$)	Coverage rate by peat (%) [a]	Degree of affection by palm plantations (%) [a]
Rajang	50000	114 [b]	7.7	9.1
Maludam	197	0.14 [c]	87	8.1
Sebuyau	538	n.a.	54	4.5
Simunjan	788	n.a.	44	30
Samusam	163	n.a.	10	0
Sematan	287	n.a.	0	0

713 [a] Modified from Bange et al., 2019

714 [b] Cited from Staub et al., 2000

715 [c] Cited Müller et al., 2016

Table 2 Overview of the TDSe concentrations and DOSe/TDSe ratios in the river and the magnitude of riverine TDSe flux and TDSe and DOSe yield to the ocean.

River Name	TDSe ($nmol\ L^{-1}$)	DOSe/TDSe Ratio	TDSe flux [a] ($10^3\ kg\ yr^{-1}$)	TDSe yield [a] ($kg\ km^{-2}\ yr^{-1}$)	DOSe yield [a] ($kg\ km^{-2}\ yr^{-1}$)	Reference
Rajang (Malysia)	1.76	0.90	16	0.32	0.28	This study
Maludam (Malysia)	4.04	0.99	0.044	0.22	0.22	This study
Amazon (Brazil)	0.48	0.85	250	0.041	0.035	Cutter and Cutter, 2001
Changjiang (China)	4.59 [b]	n.a. [c]	652	0.72	n.a. [c]	Chang et al., 2016
Zhujiang (China)	4.87 [b]	n.a. [c]	100	0.20	n.a. [c]	Yao et al., 2006
Orinoco (Venezuela)	0.45	n.a. [c]	39	0.036	n.a. [c]	Yee et al., 1987
St.Lawrence (Canada)	2.12	0.11	57	0.047	0.0051	Takayanagi and Wong, 1985
Rhone (France)	2.18	0.14	9.3	0.10	0.013	Guan and Martin, 1991
James river (America)	2.08	0.40	1.4	0.020	0.008	Takayanagi and Wong, 1983; 1984
Sacramento (America)	0.91	0.38	1.2	0.023	0.009	Cutter and Cutter, 2004
San Joaquin (America)	15.8	0.23	5.0	0.060	0.014	Cutter and Cutter, 2004
Jiulongjiang (China)	2.44	0.21	1.6	0.11	0.022	Hu et al., 1995
Kaoping (China)	1.19	0.47	0.26	0.081	0.038	Hung and Shy, 1995;
Erhjen (China)	1.11	0.47	0.044	0.13	0.059	Hung and Shy, 1995;
Shinano (Japan)	0.50	<0.1	0.55	0.046	0.006	Suzuki et al., 1981
Scheldt (Belgium)	29.2 [b]	n.a. [c]	13.83	0.63	n.a. [c]	Van der Sloot et al., 1985

[a] The calculation used river basin areas and discharge rate were cited from Milliman and Farnsworth, 2013

[b] The data were DISe species.

[c] The DOSe were not measured.

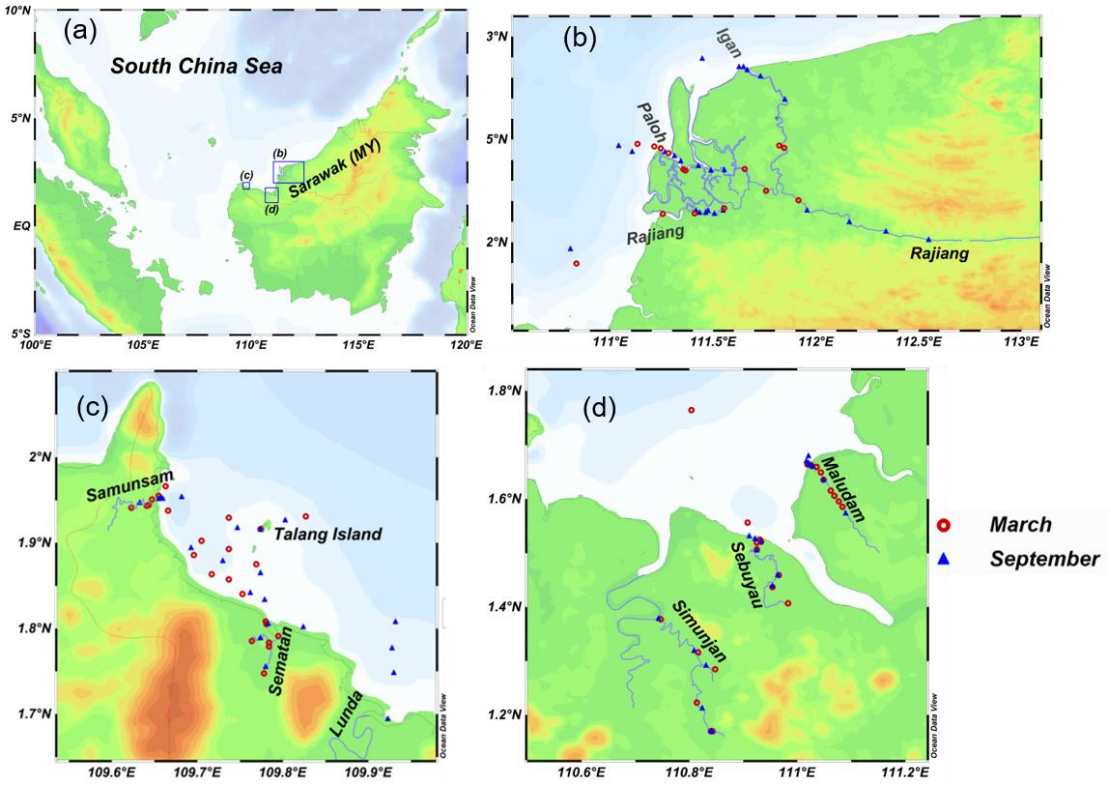


Figure 1. (a) Map of the study area showing the location of Sarawak on the island of Borneo. Blue boxes with letters indicate the areas shown in panels b–d. (b–d) Station locations for the Rajang River (b), the Samunsam, Sematan, and Lunda rivers (c), and the Maludam, Sebuyau, and Simunjan rivers (d) in March and September 2017. The maps were made with Ocean Data View (2019).

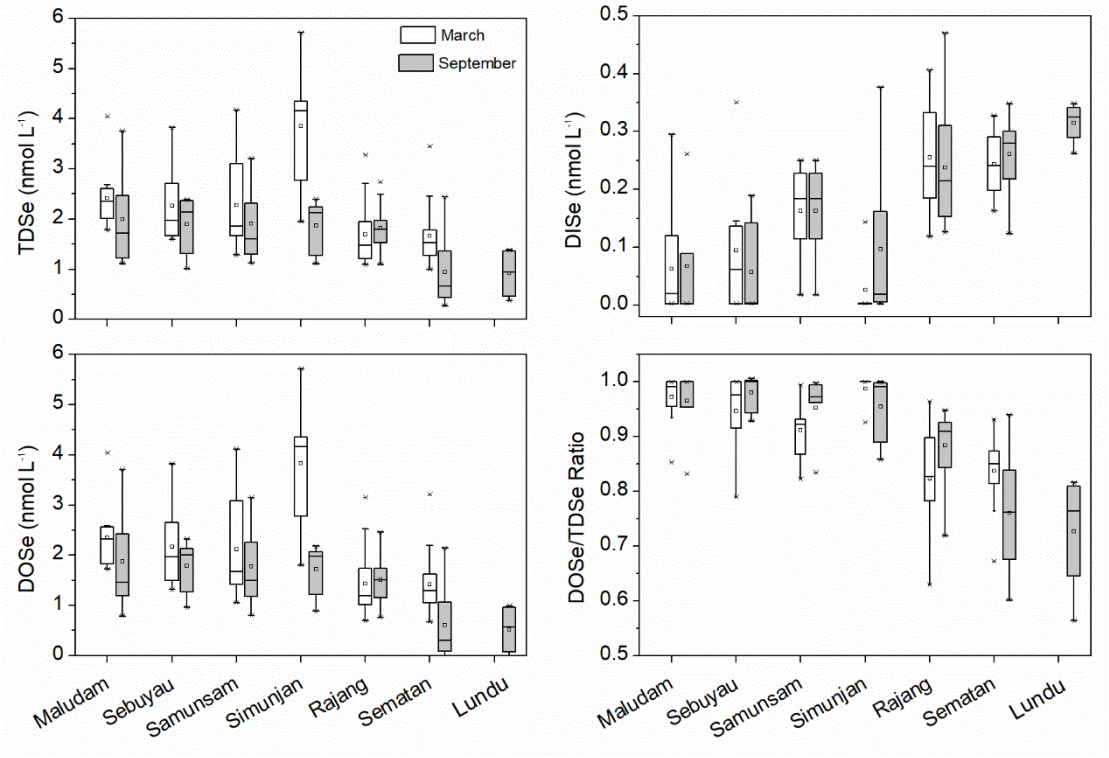
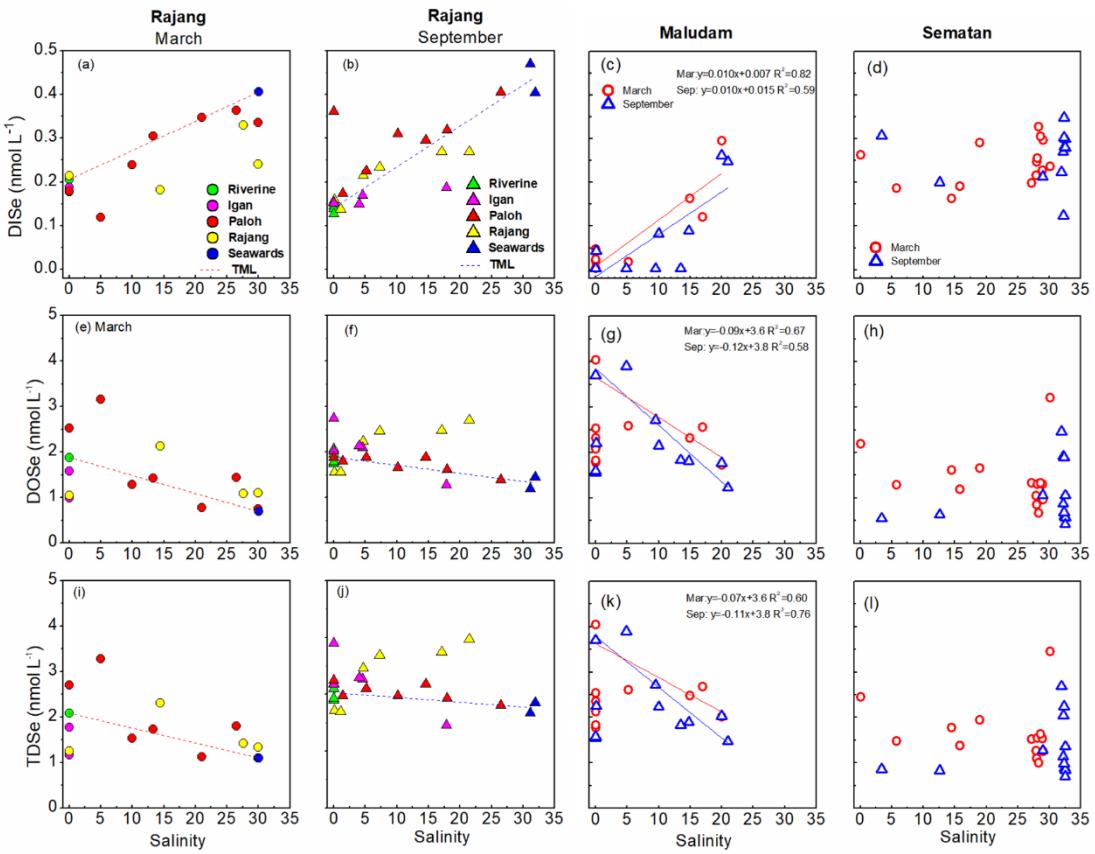


Figure 2 The box plot of TDSe, DISe and DOSe concentration and DOSe/TDSe ratio in the sampled rivers and estuaries in Malaysia in March and September 2017, respectively. In the plot of the upper panel, the ends of the box and the ends of the whiskers, and the line across each box represent the 25th and 75th percentiles, the fifth and 99th percentiles, and the median, respectively; the open square indicates the mean value.



738

739 Figure 3. Relationships between DISe (a - d), DOSe (e - h), and TDSe (i - l)

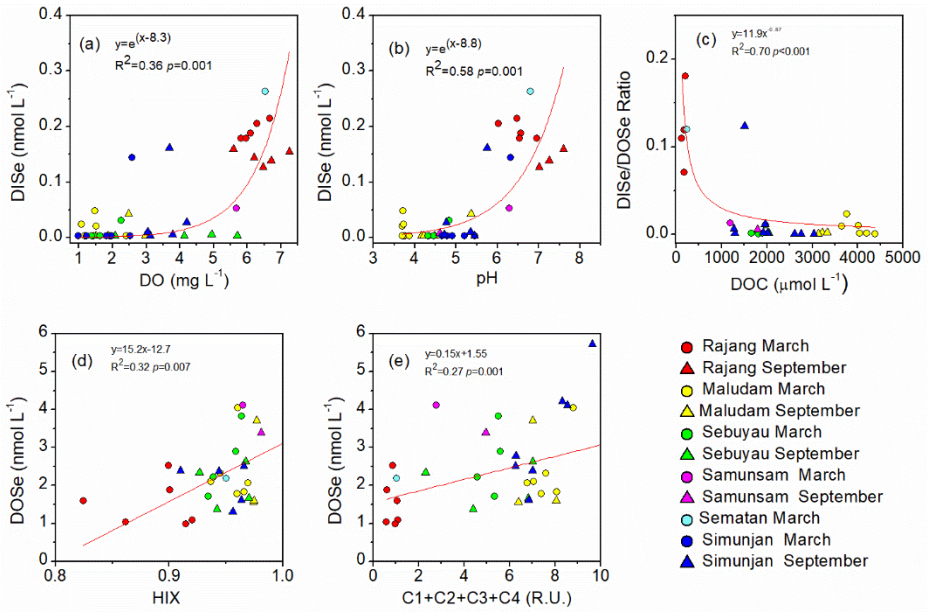
740 concentrations with salinity in the Rajang and three Rajang tributaries (Igan,

741 Lassa, and Rajang), and in the Maludam and Sematan estuaries in March and

742 September 2017. TML refers to the theoretical mixing line, which was defined

743 using two endmembers: freshwater in the riverine system and seawater.

744



745

746 Figure 4. Relationships between (a, b) DISe concentrations and DO and pH

747 values, (c) DISe/DOSe ratios and DOC concentration values, and (d–e) DOSe

748 concentrations with the humification index (HIX) and the sum of humic-like

749 CDOM components (C1, C2, C3, and C4) in freshwater (Salinity < 1) for the

750 Rajang, Sematan, Maludam, Sebuyau, Samunsam, and Simunjan rivers in

751 March and September. The HIX and C1, C2, C3, and C4 components are

752 from Zhou et al. (2019) from the same cruises. DO concentrations and pH

753 values were not available for the Sematan River for September, and the HIX

754 and CDOM components were not available for the Rajang River for

755 September.

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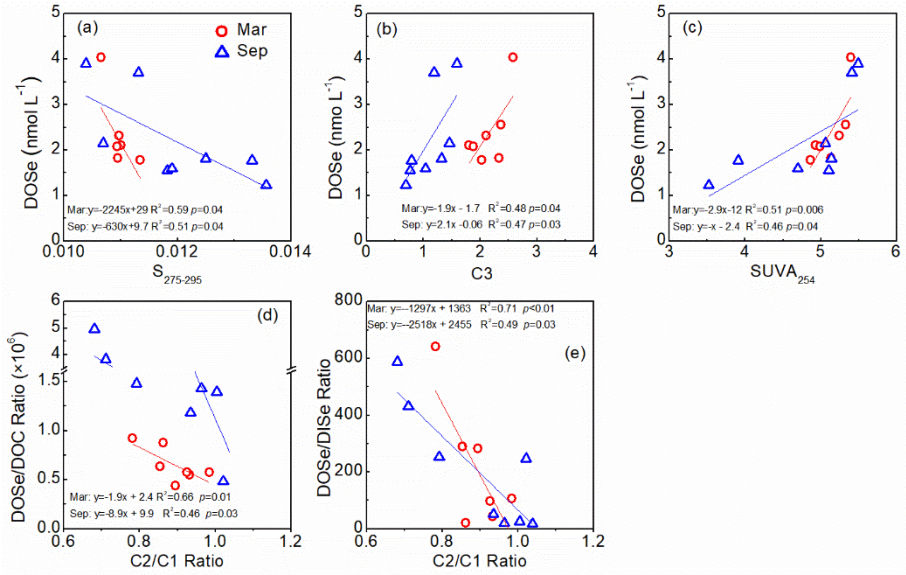
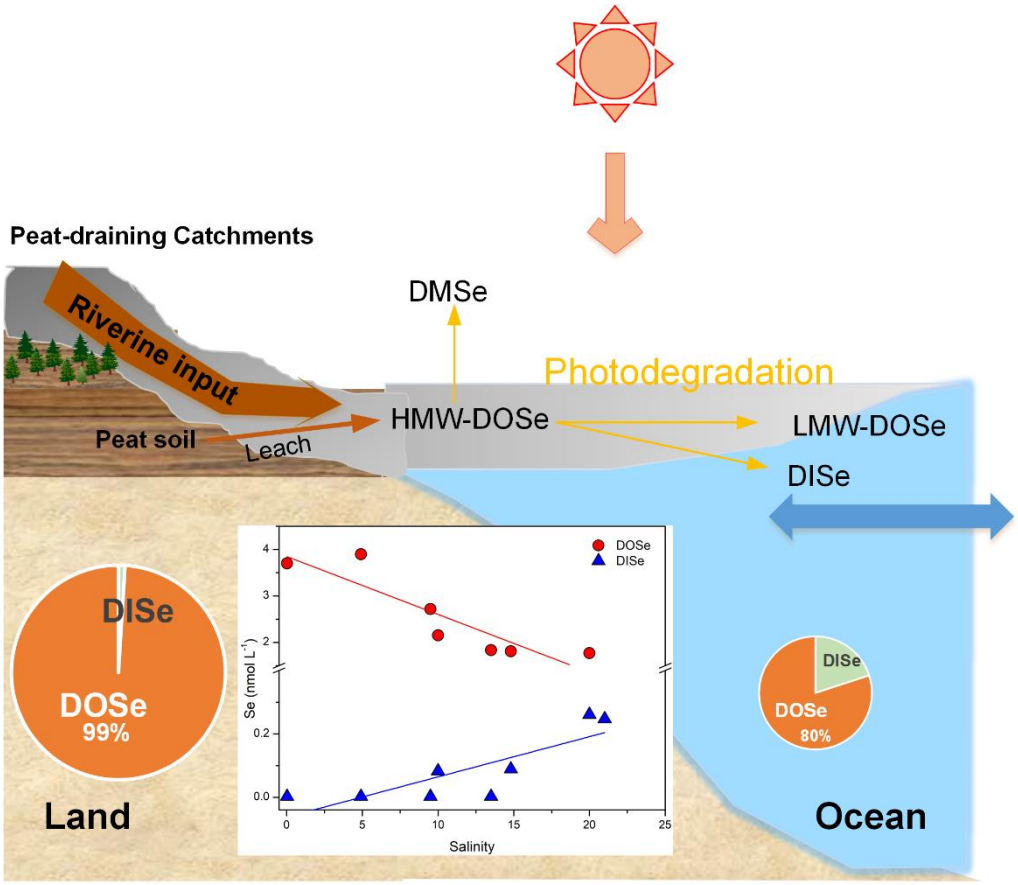


Figure 5. Relationships between DOSe concentrations and $S_{275-295}$, C3 components and $SUVA_{254}$, DOSe/DOC ratio and C2/C1 component ratios, and DOSe/DISe ratios and C2/C1 component ratios in the Rajang and Maludam estuaries. The $S_{275-295}$, $SUVA_{254}$, C1, C2, and C3 components are from Martin et al. (2018) and Zhou et al. (2019) from the same cruises.

764



765

766 Figure 6. Conceptual diagram of the behaviour of Se species in the Maludam
767 estuary. HMW, LMW, and DMSe represent high molecular weight, low
768 molecular weight, and dimethyl selenide, respectively.