https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

Biogeosciences
Discussions
Open Access
EGU

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

Yan Chang[1*], Moritz Müller[2], Ying Wu[1], Shan Jiang[1], Wan wan Cao[1], Jian guo Qu[1], Jing ling Ren[3], Xiaona Wang [1], En ming Rao[3], Xiao lu Wang[1], Aazani Mujahid[4], Mohd Fakharuddin Muhamad[2], Edwin Sia Sien Aun[2], Faddrine Holt Ajon Jang[2], Jing Zhang[1]

[1] State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai 200062, China
[2] Faculty of Engineering, Computing and Science Swinburne, University of Technology, Sarawak 93350, Malaysia
[3] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China
[4] Faculty of Resource Science and Technology, University Malaysia Sarawak, Sarawak 93350, Malaysia

Correspondence to:

Yan Chang

Email: ychang@sklec.ecnu.edu.cn

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

Biogeosciences Discussions

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.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

78 is accumulated and stored in dome-shaped peat swamps (Gonzalez et al., 2006,
79 Vesper et al., 2008; Clark and Johnson, 2008). In a global study, Fernández-
80 Martínez and Charlet (2009) summarized that the concentrations of Se in soils
81 generally ranged from about 0.01 to 2 mg kg^{-1} and averaged about 0.44 mg
82 kg^{-1}. Gonzalez et al. (2006) reported Se concentrations of up to 28 mg kg^{-1} in
83 peatland in Switzerland and from 0.9 to 2.2 mg kg^{-1} in peat cores in Spain. High
84 spatial variability has been found in dissolved Se concentrations in runoff from
85 peatlands at regional scales, with concentrations of up to 13 nmol L^{-1} being
86 observed in northern Minnesota, US (Clausen and Brooks, 1983), and from
87 0.38 to 5 nmol L^{-1} in the Krycklan catchment, Sweden (Lidman et al., 2011).
88 Although these various studies did not report different species of Se, the organic
89 form of Se is probably more important than inorganic forms in runoff from
90 peatland. An understanding of Se speciation may therefore be important for
91 determining the bioavailability of Se that is transported from land to oceans.
92 The chemical behaviour of Se in estuarine mixing plays an important role
93 in overall geochemical cycling. From their investigation into dissolved Se
94 species in various estuaries, Chang et al. (2016) found that Se was controlled
95 by biological, physical, and redox processes in the estuaries; non-conservative
96 processes resulting from phytoplankton uptake; absorption by suspended
97 particles; and regeneration of particulate organic selenide in the water. Thus far,
98 the behaviour of Se in estuaries has been studied mainly in the temperate zone
99 of the northern hemisphere (between 20°N and 60°N) (Measures and Burton,
100 1978; Takayanagi and Wong, 1984; Van der Sloot et al., 1985; Cutter, 1989a;
101 Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati, 1998; Yao et al.,
102 2006; Chang et al., 2016). Wide spatial and temporal variations have been
103 reported in total dissolved Se concentrations in runoff from high-latitude
104 peatlands (Clausen and Brooks, 1983; Lidman et al., 2011). The behaviour of
105 Se in tropical organic-rich estuaries, however, is still poorly understood. It is

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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)

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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 TDSe concentrations were determined in carbon-

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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.

2.4 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 $p < 0.05$.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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 ($p > 0.05$).

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

maximum in the coastal areas, whereas DOSe concentrations were higher in the delta-plain 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-plain distributaries than in the upper reach (Fig. 2g and h). DOSe/TDSe ratios were high in the delta-plain 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).

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

290 3.2.2 Peat-draining rivers and estuaries

291 In the Maludam estuary, DISe concentrations were extremely low (near or
292 below the detection limits) in the freshwater reach and were around 0.3 nmol
293 L^{-1} near the sea in both seasons (Fig. 4a). DISe concentrations followed similar
294 patterns in the Sebuyau, Simunjan, and Samunsam rivers and were lower in
295 the river than in the area closer to the sea. DISe concentrations ranged from
296 0.12 to 0.35 nmol L^{-1} in the Sematan and Lundu and showed little seasonal
297 variation (Fig. 4b–e). Se(IV) and Se(VI) concentration are not presented but
298 were even lower than those of DISe and commonly lay below the detection limit,
299 especially in the freshwater reaches. In the Maludam estuary, DOSe
300 concentrations ranged from 1.5 to 4 nmol L^{-1} and increased with distance
301 downstream in the freshwater area to the river mouth and then decreased
302 towards the sea (Fig. 4f). DOSe concentrations in the Sebuyau estuary ranged
303 from around 1.3 to 3.8 nmol L^{-1} and followed a similar trend to those in the
304 Maludam estuary (Fig. 4g). In the Simunjan and Samunsam estuaries, DOSe
305 concentrations decreased in a seaward direction in both seasons (Fig. 4i and
306 j). In the Sematan and Lundu estuaries, DOSe concentrations ranged from 0.42
307 to 2.5 nmol L^{-1}, were slightly lower than those in the blackwater rivers, and
308 decreased in a seaward direction. DOSe/TDSe ratios were between 0.8 and
309 almost 1 in the freshwater reaches of the Maludam, Sebuyau, Simunjan, and
310 Samunsam estuaries, indicating that DOSe was the only (or dominant) species
311 in the freshwater of the blackwater rivers. DOSe/TDSe ratios were between 0.6
312 and 0.9 in the Sematan and Lundu, indicating that more than half of the Se was
313 still present in the form of DOSe in those rivers and estuaries with limited
314 peatland cover (Fig. 4l). As TDSe is the sum of the DISe and DOSe
315 concentrations, and DOSe generally dominated in the sampled rivers and
316 estuaries, the distributions of TDSe and DOSe were similar (Fig. 4m–q). TDSe,

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

317 DISe, and DOSe concentrations did not differ between seasons in the Maludam,
318 Sebuyau, Samunsam, Sematan or in the Rajang (p > 0.05). In the Simunjan
319 estuaries, DOSe concentrations ranged from around 1.8 to 5.7 nmol L^{-1} in
320 March and were significantly higher than those in September (p < 0.05); TDSe
321 concentrations in this river also differed between the two seasons. The limited
322 seasonal variations in the Se species in the rivers and estuaries sampled in this
323 study may reflect the La Niña conditions that caused high precipitation and high
324 discharge rates in Malaysia in 2017 (Jiang et al., 2019).

325 Plots of DISe concentration against salinity show a positive linear
326 regression between DISe and salinity in the Maludam, Sebuyau, and
327 Samunsam estuaries (p < 0.05) in both seasons, but not in the Sematan estuary
328 (p > 0.05), where DISe concentrations in the freshwater and marine water
329 endmembers were similar in both seasons (Fig. 5a–d). The salinities varied little,
330 either between the two seasons in the Simunjan and Lundu estuaries or in the
331 Sebuyau estuary in September, and therefore Se concentration–salinity
332 relationships were not examined. As shown in Fig. 4f and g, DOSe
333 concentrations in the freshwater parts of the Maludam and Sebuyau rivers
334 varied widely and increased downstream, so the geographical location nearest
335 to the river mouth with a salinity of <1 was selected as the freshwater
336 endmember in the linear mixing models. A negative linear correlation was
337 observed between DOSe concentration and salinity (p < 0.05) in the Maludam,
338 Sebuyau, and Samunsam estuaries for both seasons, but DOSe concentrations
339 did not vary significantly with salinity (p > 0.05) in the Sematan estuary (Fig.
340 5e–h). TDSe concentrations were also negatively correlated with salinity (p <
341 0.05) in the Maludam, Sebuyau, and Samunsam estuaries but not in the
342 Sematan Estuary (Fig. 5i–l). DOSe/TDSe ratios in the Maludam and
343 Samunsam estuaries were almost 1 when salinity was less than 10 and
344 decreased to around 0.8 as salinity increased. In the Sebuyau estuary, the

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

345 DOSe/TDSe ratio decreased from nearly 1 to 0.8 along the salinity gradient (Fig.
346 5m–o). In the Sematan estuary, DOSe/TDSe ratios remained at around 0.9
347 along the salinity gradient and varied widely in the coastal area in March but did
348 not follow any clear pattern in September (Fig. 5p).
349 Generally, relationships between the Se species and salinity fell into three
350 groups. In the blackwater estuaries (the Maludam, Sebuyau, and Samunsam),
351 DISe concentrations were positively correlated with salinity; DOSe and TDSe
352 concentrations were negatively correlated with salinity. In the Rajang estuary,
353 which has a large area of peatland in its delta area, DISe increased with salinity
354 but behaved non-conservatively and was removed in the brackish water;
355 whereas DOSe and TDSe decreased with salinity, behaved non-conservatively,
356 and were added during estuarine mixing (Fig. 3). In the Sematan estuary, TDSe,
357 DOSe, and DISe behaved non-conservatively and showed little change during
358 estuarine mixing (Fig. 5).

359 **3.3 Mixing experiments**

360 To simulate the behaviour of selenium species in different organic matter
361 conditions, simple mixing experiments without suspended particles were
362 conducted in the laboratory using water from the Rajang and Maludam
363 estuaries. The results of these laboratory mixing experiments are shown in Fig.
364 6. DISe concentrations were lower in the Maludam estuary than in the Rajang,
365 whereas DOSe concentrations were higher. The TML obtained when the river
366 and seawater components were mixed showed that when suspended particles
367 were excluded, there was a near-linear increase in DISe concentration with
368 salinity in the Rajang estuary, which indicates a marine source of DISe (Fig. 6a).
369 In the Maludam estuary, DISe concentrations also increased with salinity, but
370 the measured values were lower than the theoretical values, with removal rates
371 of 52% to 74%, indicating intense removal during mixing with marine water (Fig.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

372 6a). In contrast to DISe, there was a near-linear decrease in DOSe
373 concentration with salinity in both the Rajang and Maludam estuaries, indicating
374 riverine sources of DOSe (Fig. 6b). In the Rajang estuary, TDSe showed a near-
375 linear decrease along the salinity gradient. While in the Maludam estuary, TDSe
376 concentrations decreased with salinity (Fig. 6c), with the measured values
377 being lower than the theoretical values, indicating removal processes at high
378 salinity (>16), mainly due to the removal of DISe (Fig. 6c). In the Maludam
379 estuary, DOSe/TDSe ratios ranged from nearly 1 to 0.8 in the mixing
380 experiments, indicating that DOSe was the major species of TDSe, with ratios
381 close to 1 when the salinity was less than 15, confirming the *in situ* results (Fig.
382 6d).
383

384 # 4. Discussion

385 ## 4.1 Se speciation in freshwater

386 Considerable variation was observed in Se speciation between the studied
387 rivers. DISe concentrations in the blackwater rivers (Maludam, Simunjan,
388 Sebuyau, and Samunsam) were lower than, or close to, the detection limits
389 (0.0063 nmol L^{-1}) in the freshwater, and DOSe (from 1.3 to 5.7 nmol L^{-1})
390 dominated TDSe in both seasons (Fig. 3). DISe concentrations were slightly
391 higher (from 0.12 to 0.25 nmol L^{-1}) and DOSe concentrations (1.0 to 2.7 nmol
392 L^{-1}) lower in the freshwater of the Rajang and Sematan rivers than in the
393 blackwater rivers (Fig. 7). TDSe concentrations in the sampled rivers were
394 comparable with those measured in other rivers worldwide (between 0.2 and
395 6.4 nmol L^{-1}); however, in contrast to our findings, DISe generally dominates in
396 other rivers (Cutter, 1989b; Conde and Sanz Alaejos, 1997; Pilarczyk et al.,
397 2019). The limited data available show that DOSe concentrations in rivers

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

398 worldwide range from <0.02 to 0.82 nmol L^{-1} (Takayanagi and Wong, 1984;
399 Wang and Shy, 1995; Cutter and Cutter, 2001, 2004). In the blackwaters of the
400 Orinoco in South America, TDSe concentrations were found to range from 0.07
401 to 0.25 nmol L^{-1} (Yee et al., 1987). Although they did not analyse DOSe
402 fractions directly, Yee et al. (1987) assumed that DOSe was likely to constitute
403 about 10%–15% of the total Se, a much lower value than the DOSe proportions
404 observed in peat-draining rivers in Sarawak.

405 The behaviour of Se in the environment is complex, as it can exist in
406 multiple oxidation states and as organic species (Conde and Sanz Alaejos,
407 1997). As shown in Fig. 7a–d, DISe concentrations were positively correlated
408 with the DO concentrations and pH values in the freshwaters of the studied
409 rivers. Se(IV)/Se(VI) ratios represent the relative proportions of Se(IV) and
410 Se(VI) in DISe. Se(IV)/Se(VI) ratios increased as DO concentrations and pH
411 values increased in March, indicating that the proportion of Se(IV) in DISe
412 increased as DO and pH increased. Species of Se are very sensitive to redox
413 conditions and pH values (Sharma et al., 2015). Sorption to solid surfaces
414 (including metallic oxides, hydroxides, and clays) is also a pH-dependent
415 process, with substantial sorption of Se(IV) and Se(VI) occurring at pH values
416 of 4 to 6 and negligible sorption under more alkaline conditions (pH > 8)
417 (BarYosef and Meek, 1987; Balistrieri and Chao, 1987; Papelis et al., 1995;
418 Sharma et al., 2015). Se(VI) adsorption onto solid surfaces is weaker than that
419 of Se(IV) (Balistrieri and Chao, 1987; Zhang and Sparks, 1990; Seby et al.,
420 1998). Thus, adsorption of Se(IV) and Se(VI) by metal oxyhydroxides and clays
421 when pH is between 4 and 6 may help to explain the low DISe concentrations
422 in the sampled freshwater, and DISe concentrations and Se(IV)/Se(VI) ratios
423 might be expected to increase as pH increases.

424 Peat has a high content of natural organic matter, which also plays an
425 important role in Se speciation (Tam et al. 1999; Li et al., 2017). Martin et al.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

(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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

454 humification index (HIX, which represents the humification degree of dissolved
455 organic matter) and the sum of the humic-like CDOM components (C1, C2, C3,
456 and C4) ($p < 0.05$) (data from Zhou et al., 2019) in the freshwater of the studied
457 rivers (Fig. 7f and g). These results indicate that DOSe in Sarawak may be
458 associated with dissolved humic substances, which is consistent with the
459 findings of Zhang and Moore (1996), who reported that substantial amounts of
460 dissolved Se in natural waters were associated with organic matter. Gustafsson
461 and Johnsson (1992, 1994) found that a high proportion of the Se(IV) added to
462 humic lake water was adsorbed by humic substances in the form of Se(IV) to
463 metal–humic complexes, which is similar to phosphate adsorption by iron–
464 humic complexes. A study of Finnish lakes has also shown that about half of
465 the TDSe was present in humic substances, whereas DISe represented
466 between 12% and 24% of the TDSe (Wang et al., 1995). However, the
467 mechanisms behind the interactions between Se and dissolved organic ligands
468 are still poorly understood. Three hypotheses have been proposed to explain
469 organic-matter-mediated retention of Se, as follows: 1) direct complexation of
470 organic matter with Se, 2) indirect complexation via Se-cation–organic-matter
471 complexes, or 3) microbial reduction and incorporation into amino acids,
472 proteins, and natural organic matter (Winkel et al., 2015). Depending on the
473 type of binding, Se may be easily mobilized (e.g., through adjusting pH) or
474 immobilized (e.g., by covalent incorporation to organic matter) (Winkel et al.,
475 2015). However, there is ambiguity about the molecular structure and species
476 of Se that bind to organic matter, and further work is needed to identify the
477 mechanisms by which Se is bound to, and released from, organic matter.
478

479 **4.2 Behaviour of DISe during estuarine mixing**

480 As shown in Figures 3 and 5, DISe concentrations increased as salinity

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

481 increased in the Rajang, Maludam, Sebuyau, and Samunsam estuaries. These
482 reversed concentration–salinity relationships contrast with those reported for
483 other estuaries (Measures and Burton, 1978; Takayanagi and Wong, 1984; Van
484 der Sloot et al., 1985; Cutter, 1989a; Guan and Martin, 1991; Hung and Shy,
485 1995; Abdel-Moati, 1998; Yao et al., 2006; Chang et al., 2016). Laboratory
486 mixing experiments conducted using water from the Rajang and Maludam
487 rivers also revealed that DISe concentration increased as salinity increased (Fig.
488 6a). During estuarine mixing, DISe has been shown in some other studies to
489 behave conservatively (R^2 > 0.9), with concentrations decreasing along a
490 salinity gradient in the estuaries of the Scheldt (Van der Sloot et al., 1985), Test
491 (Measures and Burton, 1978), Rhone (Guan and Martin, 1991), and James
492 (Takayanagi and Wong, 1984) rivers. DISe has also been shown to behave
493 non-conservatively, with concentrations decreasing along the salinity gradient
494 in the Changjiang estuary (Chang et al., 2016), Zhujiang estuary (Yao et al.,
495 2006), Mex Bay (Abdel-Moati, 1998), San Francisco Bay (Cutter, 1989a), and
496 Kaoping and Erhjen estuaries (Hung and Shy, 1995). The marine endmember
497 of the DISe concentrations in the sampled estuaries (salinity > 31) was 0.30
498 nmol L^{-1} (range: 0.12 to 0.47 nmol L^{-1}), encompassing or close to the values
499 reported for surface water in the South China Sea (around 0.38 nmol L^{-1},
500 Nakaguchi et al., 2004) and the Pacific (mean of 0.24 nmol L^{-1}, range: 0.02 to
501 0.69 nmol L^{-1}) (Cutter and Bruland, 1984; Sherrard et al., 2004; Mason et al.,
502 2018). The salinity-related increases in DISe in a seaward direction indicate
503 that the patterns of distribution of DISe in the Rajang, Maludam, Sebuyau, and
504 Samunsam estuaries are controlled mainly by conservative mixing of ocean-
505 derived DISe. Nitrate behaves in a similar way in the Dumai River estuary
506 (Sumatra, Indonesia), another tropical blackwater river (Alkhaitb and
507 Jennerjahn, 2007). The Maludam, Sebuyau, Samunsam, and Simunjan rivers
508 are peat-draining rivers, and most of the coastal areas in the Rajang delta are

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

509 also covered by peat; thus, DISe in the black-water estuaries and in the Rajang
510 may have been mainly ocean derived.
511 In the Rajang estuary, DISe was removed in March and was added in
512 September during estuarine mixing (Fig. 3g and j). DISe removal rates of
513 between 52% and 74% were calculated for Maludam River water in the
514 laboratory mixing experiments (Fig. 6a). At low salinity, DISe concentrations
515 were slightly scattered around the linear mixing model for the Maludam and
516 Samunsam rivers (Fig. 5c and 4c). The Rajang River drains mineral soils in its
517 upper reaches, and peatland is found only in the delta surrounding the
518 distributaries (Staub et al., 1994, 2000). In the distributary channels, DOC
519 concentrations reached around 240 μmol L^{-1}, almost double the concentrations
520 further upstream, indicating large inputs of organic matter from peat. High DOC
521 concentrations (between 3100 and 4400 μmol L^{-1}) have also been reported for
522 the Maludam River (Martin et al., 2018). As discussed above, organic matter
523 can immobilize Se(IV) and Se(VI). Laboratory studies have shown that Se(IV)
524 can be adsorbed by peat and that 60% of the adsorbed Se(IV) can be desorbed
525 upon exposure of the solid phase to seawater (Kharkar et al., 1968). Selenium
526 may have been added to the Rajang estuary in September via release of Se(IV)
527 from peat in brackish waters. Other studies have reported removal of the humic
528 fractions of DOM, colloidal iron, and phosphorus by flocculation in the river–sea
529 mixing zones (Eckert and Sholkovitz, 1976; Forsgren et al., 1996; Asmala et al.,
530 2014). Some of the DISe may exist in colloidal form in natural water
531 (Takayanagi and Wong, 1984), and DISe may be removed by flocculation. In
532 peat-draining estuaries, ocean-derived DISe may be adsorbed to peat and may
533 be associated with DOM, which is then converted to DOSe and/or flocculated
534 to particulate Se.
535

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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 *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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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 ($S_{275\text{-}295}$, 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 $S_{275\text{-}295}$ (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–

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

589 C5 components in the Rajang estuary were also almost 10 times lower than
590 those in the Maludam estuary (Martin et al., 2018; Zhou et al., 2019), indicating
591 that, depending on the geochemical setting, the concentration and molecular
592 weight distribution of DOM in the Rajang estuary were unlike those in the
593 Maludam. $S_{275\text{-}295}$ is inversely related to the mean molecular weight of DOM
594 (Helms et al., 2008), and $SUVA_{254}$ is positively related to the aromaticity of DOM
595 (Weishaar et al., 2003). These correlations suggest that DOSe was associated
596 closely with high-molecular-weight and highly aromatic DOM in the Maludam
597 estuary. Also, DOSe concentrations were strongly and positively correlated with
598 the humic-like C3 component (data from Zhou et al., 2019) during estuarine
599 mixing in the two seasons (Fig. 8h). As reported by Zhou et al. (2019), the C3
600 components derived corresponded to aromatic and black carbon compounds
601 with high molecular weight. The positive correlation between DOSe and the C3
602 component (Fig. 8g) also indicates that DOSe fractions are associated with
603 high-molecular-weight aromatic DOM in the Maludam estuary (Fig. 9). Kamei-
604 Ishikawa et al. (2008) investigated the binding between Se(IV) and humic acid
605 in a laboratory study and found that the Se remaining in solution was associated
606 with the dissolved humic acid fractions, and those authors' ultrafiltration
607 experiments suggested that 50% to 60% of these Se–humic acid associates
608 had high molecular weights (>10 kDa). Bruggeman et al. (2007) studied the
609 interactions between Se(IV) and humic substances in aqueous sediment
610 extracts and found that consistent with our findings, over 70% of the original
611 Se(IV) was associated with high molecular weights (>30 kDa). Gustafsson and
612 Johnsson (1994) reported that forest soil fixed 10% of added Se(IV) into low-
613 molecular-weight fractions of the humic substances by means of microbial
614 reductive preferential incorporation.

615 In the Maludam estuary, DOSe/DOC ratios were negatively correlated with
616 C2/C1 ratios (Fig. 8j), indicating that compared to bulk DOM, the DOSe

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

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,

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

672 indicating terrestrial sources. In the delta area of the Rajang River, where
673 peatland dominates, DISe concentrations increased with salinity, and DOSe
674 concentrations generally decreased with salinity but increased in the middle
675 parts of the estuary. In the Maludam, DOSe fractions may be associated with
676 high-molecular-weight peatland-derived aromatic and black carbon compounds
677 and may photodegrade to more bioavailable forms once transported to
678 oligotrophic coastal waters, where they may promote productivity.
679

680 ## 6. Author contribution

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

688 ## 7. Competing interests

689 The authors declare that there is no conflict of interesting.

690 ## 8. Acknowledgements

691 This study was kindly supported by the Newton-Ungku Omar Fund
692 (NE/P020283/1), Natural Science Foundation of China (41806096), China
693 Postdoctoral Science Foundation (2018M630416; 2018M632062), MOHE
694 FRGS 15 Grant (FRGS/1/2015/WAB08/SWIN/02/1), Overseas Expertise
695 Introduction Project for Discipline Innovation (B08022), SKLEC Open Research

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

Fund (SKLEC-KF201610) and Scientific Research Foundation of SKLEC (2017RCDW07). The authors thank the Sarawak Forestry Department and the Sarawak Biodiversity Centre for permission to conduct collaborative research in Sarawak waters under permit numbers NPW.907.4.4(Jld.14)-161, Park Permit No WL83/2017, and SBC-RA-0097-MM. Lukas Chin and the SeaWonder crew are acknowledged for their support during the cruises. Technical support from Dr Patrick Martin and Dr Gonzalo Carrasco at Nanyang Technological University during the cruises is gratefully acknowledged.

9. References

Abdel-Moati, M. A. R.: Speciation of Selenium in a Nile Delta Lagoon and SE Mediterranean Sea Mixing Zone, Estuarine Coastal & Shelf Science, 46, 621-628, 1998.

Alkhatib, M., Jennerjahn, T., and Samiaji, J.: Biogeochemistry of the Dumai River estuary, Sumatra, Indonesia, a tropical black‐water river, Limnology & Oceanography, 52, 2410-2417, 2007.

Apte, S., Howard, A., Morris, R., and McCartney, M.: Arsenic, antimony and selenium speciation during a spring phytoplankton bloom in a closed experimental ecosystem, Marine Chemistry, 20, 119-130, 1986.

Asmala, E., Bowers, D. G., Autio, R., Kaartokallio, H., and Thomas, D. N.: Qualitative changes of riverine dissolved organic matter at low salinities due to flocculation, Journal of Geophysical Research: Biogeosciences, 119, 1919-1933, 2014.

Baines, S. B., and Fisher, N. S.: Interspecific differences in the bioconcentration of selenite by phytoplankton and their ecological implications, Marine Ecology Progress Series, 213, 1-12, 2001.

Balistrieri, L. S., and Chao, T. T.: Selenium Adsorption by Goethite, Soil Science Society of America Journal, 51:5, 1987.

Bar-Yosef, B., and Meek, D.: Selenium sorption by kaolinite and montmorillonite, Soil Science, 144, 11-19, 1987.

Bergquist, B., and Boyle, E.: Iron isotopes in the Amazon River system: weathering and transport signatures, Earth and Planetary Science Letters, 248, 54-68, 2006.

Bruggeman, C., Maes, A., and Vancluysen, J.: The interaction of dissolved Boom Clay and Gorleben humic substances with selenium oxyanions

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

(selenite and selenate), Applied Geochemistry, 22, 1371-1379, 2007.

Chang, Y., QU, J.G., Zhang, R.F., Zhang J.: Determination of inorganic selenium speciation in natural water by sector field inductively coupled plasma mass spectrometry combined with hydride generation, Chinese Journal of Analysis Chemistry, 42: 753–758, 2014. (in Chinese with an English abstract)

Chang, Y., Zhang, J., Qu, J., Zhang, G., Zhang, A., and Zhang, R.: The behavior of dissolved inorganic selenium in the Changjiang Estuary, Journal of Marine Systems, 154, 110-121, 2016.

Chang, Y., Zhang, J., Qu, J. Q., and Xue, Y.: Precise selenium isotope measurement in seawater by carbon-containing hydride generation-Desolvation-MC-ICP-MS after thiol resin preconcentration, Chemical Geology, 471, 65-73, 2017.

Clark, S. K., and Johnson, T. M.: Effective isotopic fractionation factors for solute removal by reactive sediments: a laboratory microcosm and slurry study, Environmental Science & Technology, 42, 7850-7855, 2008.

Clausen, J. C., and Brooks, K. N.: Quality of runoff from Minnesota peatlands: I. A Characterization, Water Resources Bulletin, 19, 769-772, 1983.

Conde, J. E., and Alaejos, M. S.: Selenium Concentrations in Natural and Environmental Waters, Chemical Reviews, 28, 1979-2004, 1997.

Cutter, G. A., and Bruland, K. W.: The Marine Biogeochemistry of Selenium: A Re-Evaluation, Limnology & Oceanography, 29, 1179-1192, 1984.

Cutter, G. A.: The estuarine behaviour of selenium in San Francisco Bay, Estuarine, Coastal and Shelf Science, 28, 13-34, 1989a.

Cutter, G. A.: Freshwater systems, Occurrence and Distribution of Selenium. CRC Press, Boca Raton, Florida, 243, 1989b.

Cutter, G. A., and Cutter, L. S.: Behavior of dissolved antimony, arsenic, and selenium in the Atlantic Ocean, Marine Chemistry, 49, 295-306, 1995.

Cutter, G. A., and Cutter, L. S.: Sources and cycling of selenium in the western and equatorial Atlantic Ocean, Deep Sea Research Part II Topical Studies in Oceanography, 48, 2917-2931, 2001.

Cutter, G. A., and Cutter, L. S.: Selenium biogeochemistry in the San Francisco Bay estuary: changes in water column behavior, Estuarine Coastal & Shelf Science, 61, 463-476, 2004.

De Temmerman, L., Waegeneers, N., Thiry, C., Du, L. G., Tack, F., and Ruttens, A.: Selenium content of Belgian cultivated soils and its uptake by field crops and vegetables, Science of the Total Environment, 468–469, 77-82, 2014.

Eckert, J., and Sholkovitz, E.: The flocculation of iron, aluminium and humates from river water by electrolytes, Geochimica et Cosmochimica Acta, 40, 847-848, 1976.

Fernández-Martínez, A., and Charlet, L.: Selenium environmental cycling and bioavailability: a structural chemist point of view, Reviews in Environmental

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

Science and Bio/Technology, 8, 81-110, 2009.

Ferri, T., and Sangiorgio, P.: Voltammetric study of the interaction between Se (IV) and dissolved organic matter in environmental aqueous matrices, Analytica chimica acta, 385, 337-343, 1999.

Floor, G. H., Iglesías, M., Román-Ross, G., Corvini, P. F., and Lenz, M.: Selenium speciation in acidic environmental samples: application to acid rain–soil interaction at Mount Etna volcano, Chemosphere, 84, 1664-1670, 2011.

Forsgren, G., Jansson, M., and Nilsson, P.: Aggregation and sedimentation of iron, phosphorus and organic carbon in experimental mixtures of freshwater and estuarine water, Estuarine, Coastal and Shelf Science, 43, 259-268, 1996.

González A, Z. I., Krachler, M., Cheburkin, A. K., and Shotyk, W.: Spatial distribution of natural enrichments of arsenic, selenium, and uranium in a minerotrophic peatland, Gola di Lago, Canton Ticino, Switzerland, Environmental science & technology, 40, 6568-6574, 2006.

Guan, D. M., and Martin, J. M.: Selenium distribution in the Rhône delta and the Gulf of Lions, Marine Chemistry, 36, 303-316, 1991.

Gustafsson, J., and Johnsson, L.: Selenium retention in the organic matter of Swedish forest soils, Journal of Soil Science, 43, 461-472, 1992.

Gustafsson, J. P., and Johnsson, L.: The association between selenium and humic substances in forested ecosystems—laboratory evidence, Applied Organometallic Chemistry, 8, 141-147, 1994.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnology and Oceanography, 53, 955-969, 2008.

Hung, J., and Shy, C.: Speciation of dissolved Selenium in the Kaoping and Erhjen Rivers and Estuaries, southwestern Taiwan, Estuaries, 18, 234-240, 1995.

Jiang, S., Müller, M., Jin, J., Wu, Y., Zhu, K., Zhang, G.S., Mujahid, A., Muhamad, M., Fakharuddin, M., Edwin, S., Jang, A., Zhang, J.: Dissolved inorganic nitrogen in a tropical estuary at Malaysia : transport and transformation. Biogeosciences Discuss, 2019. https://doi.org/10.5194/bg-2019-7

Kamei-Ishikawa, N., Tagami, K., and Uchida, S.: Sorption kinetics of selenium on humic acid, Journal of Radioanalytical and Nuclear Chemistry, 274, 555-561, 2007.

Kamei-Ishikawa, N., Nakamaru, Y., Tagami, K., and Uchida, S.: Sorption behavior of selenium on humic acid under increasing selenium concentration or increasing solid/liquid ratio, Journal of environmental radioactivity, 99, 993-1002, 2008.

Kang, Y., Yamada, H., Kyuma, K., Hattori, T., and Kigasawa, S.: Selenium in

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

soil humic acid, Soil Science and Plant Nutrition, 37, 241-248, 1991.

Kharkar, D. P., Turekian, K. K., and Bertine, K. K.: Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans, Geochimica et Cosmochimica Acta, 32, 285-298, 1968.

Li, L., Ren, J.-L., Yan, Z., Liu, S.-M., Wu, Y., Zhou, F., Liu, C.-G., and Zhang, J.: Behavior of arsenic in the coastal area of the Changjiang (Yangtze River) Estuary: Influences of water mass mixing, the spring bloom and hypoxia, Continental Shelf Research, 80, 67-78, 2014.

Li, Z., Liang, D., Peng, Q., Cui, Z., Huang, J., and Lin, Z.: Interaction between selenium and soil organic matter and its impact on soil selenium bioavailability: a review, Geoderma, 295, 69-79, 2017.

Lidman, F., Mörth, C.-M., Björkvald, L., and Laudon, H.: Selenium dynamics in boreal streams: the role of wetlands and changing groundwater tables, Environmental science & technology, 45, 2677-2683, 2011.

Lobanov, A. V., Hatfield, D. L., and Gladyshev, V. N.: Eukaryotic selenoproteins and selenoproteomes, Biochim Biophys Acta, 1790, 1424-1428, 2009.

Long, J. A., Large, R. R., Lee, M. S. Y., Benton, M. J., Danyushevsky, L. V., Chiappe, L. M., Halpin, J. A., Cantrill, D., and Lottermoser, B.: Severe selenium depletion in the Phanerozoic oceans as a factor in three global mass extinction events, Gondwana Research, 36, 209-218, 2016.

Long, S. M.: Sarawak coastal biodiversity: a current status, Kuroshio Science, 8, 71-84, 2014.

Martin, P., Cherukuru, N., Tan, A. S., Sanwlani, N., Mujahid, A., and Müller, M.: Distribution and cycling of terrigenous dissolved organic carbon in peatland-draining rivers and coastal waters of Sarawak, Borneo, Biogeosciences, 15, 6847-6865, 2018.

Mason, R. P., Soerensen, A. L., Di Mento, B. P., and Balcom, P. H.: The global marine selenium cycle: Insights from measurements and modeling, Global Biogeochemical Cycles, 32, 1720-1737, 2018.

Measures, C. I., and Burton, J. D.: Behaviour and speciation of dissolved selenium in estuarine waters, Nature, 273, 293-295, 1978.

Miller, W. L., and Moran, M. A.: Interaction of photochemical and microbial processes in the degradation of refractory dissolved organic matter from a coastal marine environment, Limnology and Oceanography, 42, 1317-1324, 1997.

Moore, S., Evans, C. D., Page, S. E., Garnett, M. H., Jones, T. G., Freeman, C., Hooijer, A., Wiltshire, A. J., Limin, S. H., and Gauci, V.: Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes, Nature, 493, 660, 2013.

Mueller, D., Bange, H. W., Warneke, T., Rixen, T., Mueller, M., Mujahid, A., and Notholt, J.: Nitrous oxide and methane in two tropical estuaries in a peat-

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

dominated region of northwestern Borneo, Biogeosciences (BG), 13, 2415-2428, 2016.

Nakaguchi, Y., Mitsuhashi, Y., Kitahata, K.-i., Fujita, A., Sumiyoshi, A., and Kawai, Y.: Selenium speciation in the eastern tropical and subtropical South Pacific Ocean, Science and Technology, 21, 25-33, 2008.

Opsahl, S., and Benner, R.: Photochemical reactivity of dissolved lignin in river and ocean waters, Limnology and Oceanography, 43, 1297-1304, 1998.

Papelis, C., Brown Jr, G. E., Parks, G. A., and Leckie, J. O.: X-ray absorption spectroscopic studies of cadmium and selenite adsorption on aluminum oxides, Langmuir, 11, 2041-2048, 1995.

Pilarczyk, B., Tomza-Marciniak, A., Pilarczyk, R., Marciniak, A., Bąkowska, M., and Nowakowska, E.: Selenium, Se, in: Mammals and Birds as Bioindicators of Trace Element Contaminations in Terrestrial Environments, Springer, 301-362, 2019.

Sa'adi, Z., Shahid, S., Ismail, T., Chung, E.-S., and Wang, X.-J.: Distributional changes in rainfall and river flow in Sarawak, Malaysia, Asia-Pacific Journal of Atmospheric Sciences, 53, 489-500, 2017.

Schiavon, M., Ertani, A., Parrasia, S., and Dalla Vecchia, F.: Selenium accumulation and metabolism in algae, Aquatic Toxicology, 189, 1-8, 2017.

Séby, F., Potin-Gautier, M., Giffaut, E., and Donard, O.: Assessing the speciation and the biogeochemical processes affecting the mobility of selenium from a geological repository of radioactive wastesto the biosphere, Analusis, 26, 193-198, 1998.

Sharma, V. K., McDonald, T. J., Sohn, M., Anquandah, G. A., Pettine, M., and Zboril, R.: Biogeochemistry of selenium. A review, Environmental chemistry letters, 13, 49-58, 2015.

Sherrard, J. C., Hunter, K. A., and Boyd, P. W.: Selenium speciation in subantarctic and subtropical waters east of New Zealand: trends and temporal variations, Deep Sea Research Part I: Oceanographic, 51, 491-506, 2004.

Staub, J., and Gastaldo, R.: Seasonal sediment transport and deposition in the Rajang River delta, Sarawak, East Malaysia, Sedimentary Geology, 133, 249-264, 2000.

Staub, J. R., and Esterle, J. S.: Peat-accumulating depositional systems of Sarawak, East Malaysia, Sedimentary Geology, 89, 91-106, 1994.

Stubbins, A., Niggemann, J., and Dittmar, T.: Photo-lability of deep ocean dissolved black carbon, Biogeosciences, 9, 1661-1670, 2012.

Takayanagi, K., and Wong, G. T.: Organic and colloidal selenium in southern Chesapeake Bay and adjacent waters, Marine Chemistry, 14, 141-148, 1983.

Takayanagi, K., and Wong, G. T. F.: Total selenium and selenium (IV) in the James River estuary and southern Chesapeake Bay, Estuarine Coastal &

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

899 Shelf Science, 18, 113-119, 1984.
900 Tam, S.-C., Johnson, S. A., and Graham, A.: The effect of organic structures on
901 pentachlorophenol adsorption on soil, Water, Air, and Soil Pollution, 115,
902 337-346, 1999.
903 Torres, J., Pintos, V., Domínguez, S., Kremer, C., and Kremer, E.: Selenite and
904 selenate speciation in natural waters: interaction with divalent metal ions,
905 Journal of solution chemistry, 39, 1-10, 2010.
906 Vandermeulen, J., and Foda, A.: Cycling of selenite and selenate in marine
907 phytoplankton, Marine Biology, 98, 115-123, 1988.
908 Van der Sloot, H. Vd., Hoede, D., Wijkstra, J., Duinker, J. C., and Nolting, R. F.:
909 Anionic species of V, As, Se, Mo, Sb, Te and W in the Scheldt and Rhine
910 estuaries and the Southern Bight (North Sea), Estuarine Coastal & Shelf
911 Science, 21, 633-651, 1985.
912 Vesper, D. J., Roy, M., and Rhoads, C. J.: Selenium distribution and mode of
913 occurrence in the Kanawha Formation, southern West Virginia, USA,
914 International Journal of Coal Geology, 73, 237-249, 2008.
915 Vriens, B., Ammann, A. A., Hagendorfer, H., Lenz, M., Berg, M., and Winkel, L.
916 H.: Quantification of methylated selenium, sulfur, and arsenic in the
917 environment, PlOS one, 9, e102906, 2014.
918 Wang, D., Alfthan, G., Aro, A., Mäkelä, A., Knuuttila, S., and Hammar, T.: The
919 impact of selenium supplemented fertilization on selenium in lake
920 ecosystems in Finland, Agriculture, Ecosystems & Environment, 54, 137-
921 148, 1995.
922 Wang, Z., and Gao, Y.: Biogeochemical cycling of selenium in Chinese
923 environments, Applied Geochemistry, 16, 1345-1351, 2001.
924 Wang, X. N., Wu, Y., Bao, H.Y., Gan, S.C., Zhang, J.: Sources, Transport, and
925 Transformation of Dissolved Organic Matter in the Large River System-
926 Illustrated by the Changjiang River, China, Journal of Geophysical
927 Research: Biogeosciences (under review)
928 Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., and
929 Mopper, K.: Evaluation of specific ultraviolet absorbance as an indicator of
930 the chemical composition and reactivity of dissolved organic carbon,
931 Environmental science & technology, 37, 4702-4708, 2003.
932 Winkel, L. H., Vriens, B., Jones, G. D., Schneider, L. S., Pilonsmits, E., and
933 Bañuelos, G. S.: Selenium cycling across soil-plant-atmosphere interfaces:
934 a critical review, Nutrients, 7, 4199-4239, 2015.
935 Wit, F., Müller, D., Baum, A., Warneke, T., Pranowo, W. S., Müller, M., and Rixen,
936 T.: The impact of disturbed peatlands on river outgassing in Southeast Asia,
937 Nature communications, 6, 10155, 2015.
938 Wrench, J., and Measures, C.: Temporal variations in dissolved selenium in a
939 coastal ecosystem, Nature, 299, 431, 1982.
940 Yao, Q. Z., Zhang, J., Qin, X. G., Xiong, H., and Dong, L. X.: The behavior of

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

941 selenium and arsenic in the Zhujiang (Pearl River) Estuary, South China
942 Sea, Estuarine Coastal & Shelf Science, 67, 170-180, 2006.
943 Yee, H., Measures, C., and Edmond, J.: Selenium in the tributaries of the
944 Orinoco in Venezuela, Nature, 326, 686, 1987.
945 Zhang, P., and Sparks, D. L.: Kinetics of selenate and selenite
946 adsorption/desorption at the goethite/water interface, Environmental
947 Science & Technology, 24, 1848-1856, 1990.
948 Zhang, Y., and Moore, J. N.: Selenium fractionation and speciation in a wetland
949 system, Environmental science & technology, 30, 2613-2619, 1996.
950 Zhou, Y., Martin, P., and Müller, M.: Composition and cycling of dissolved
951 organic matter from tropical peatlands of coastal Sarawak, Borneo,
952 revealed by fluorescence spectroscopy and PARAFAC analysis,
953 Biogeosciences Discuss, https://doi.org/10.5194/bg-2018-508, 2019.
954
955

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

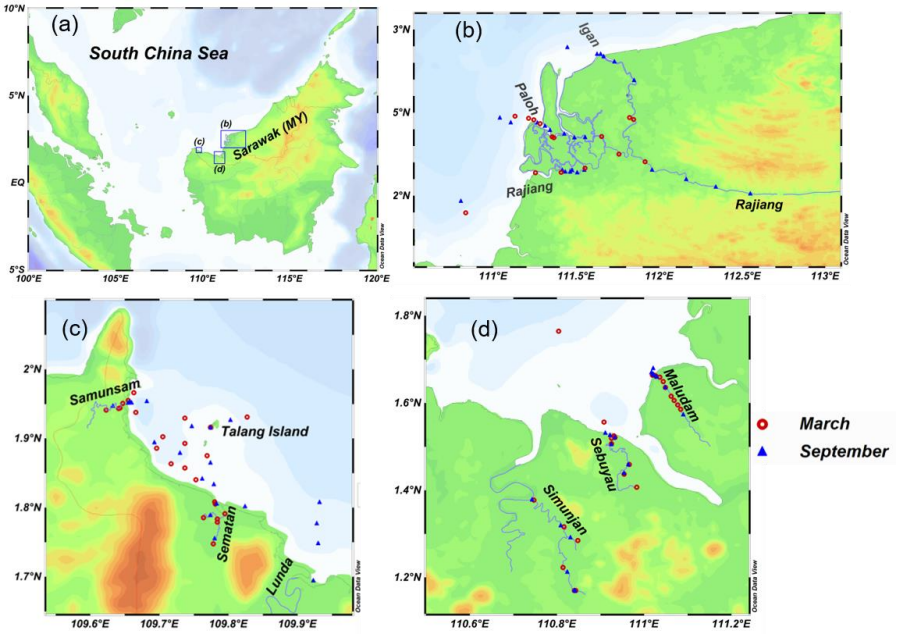


Figure 1. (a) Map of the study area showing the location of Sarawak on the island of Borneo. Blue boxes with letters indicate the areas shown in panels b–d. (b–d) Station locations for the Rajang River (b), the Samunsam, Sematan, and Lunda rivers (c), and the Maludam, Sebuyau, and Simunjan rivers (d)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

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

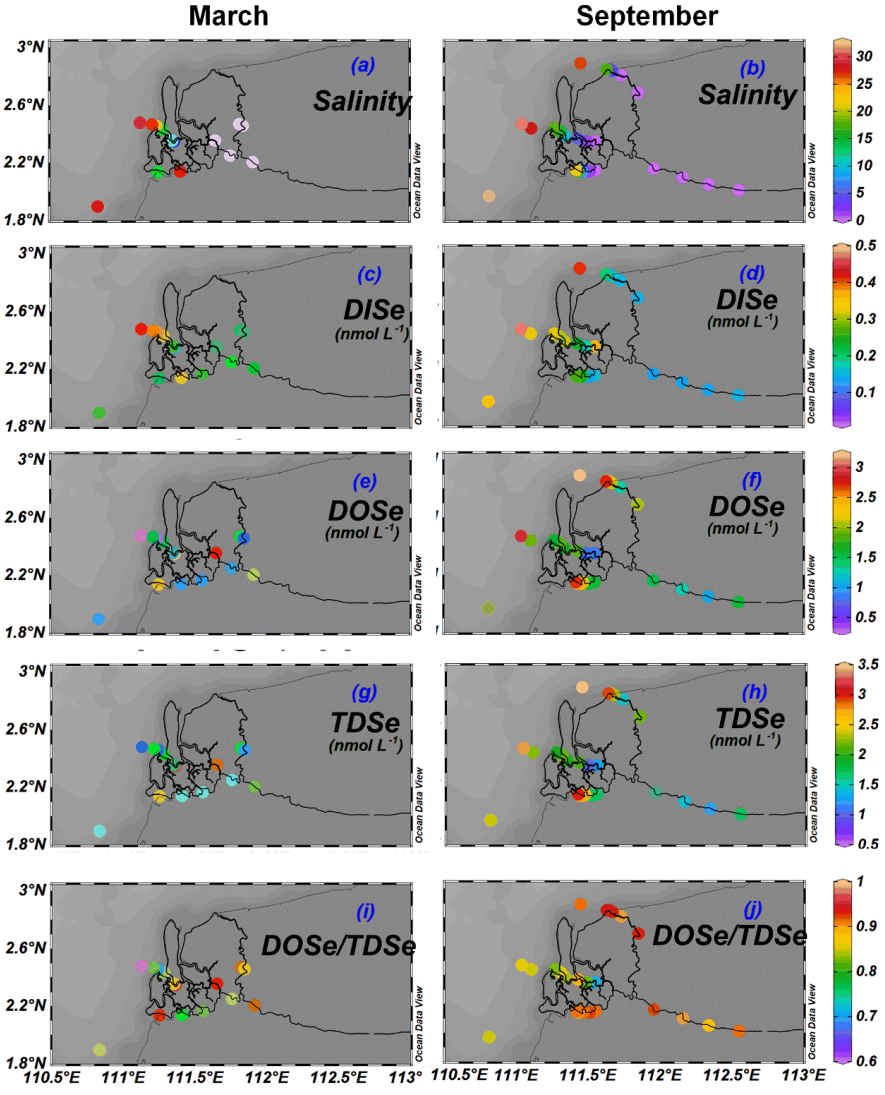


Figure 2. Distributions of salinity, of DISe, DOSe, and TDSe concentrations, and of DOSe/TDSe ratio in surface waters of the Rajang estuary in March and September 2017. All distribution plots were made with Ocean Data View (2019).

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

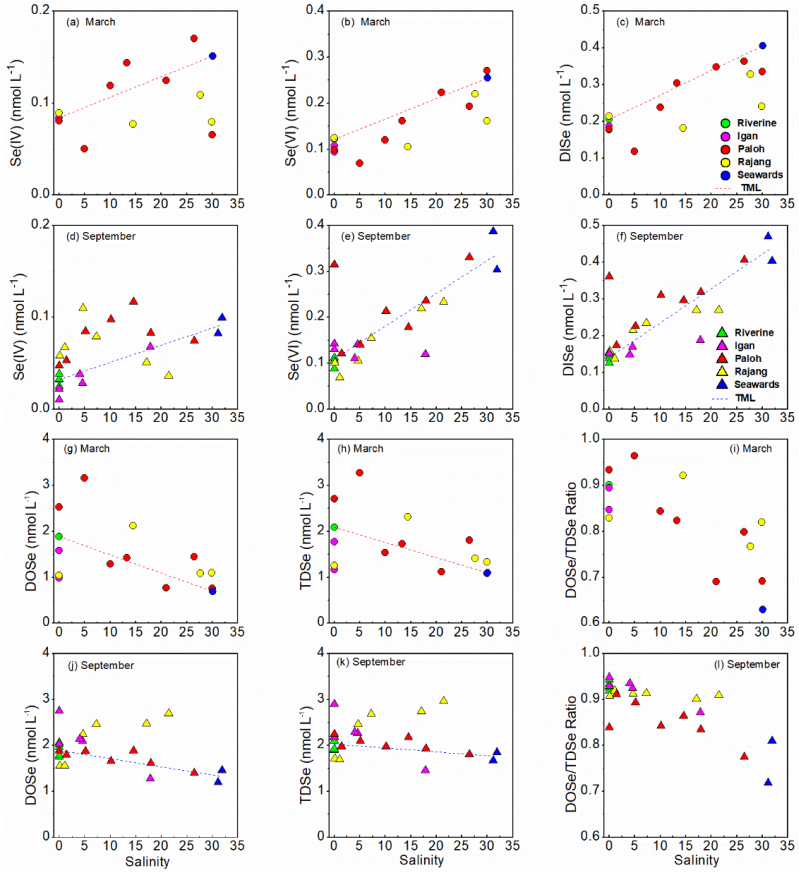
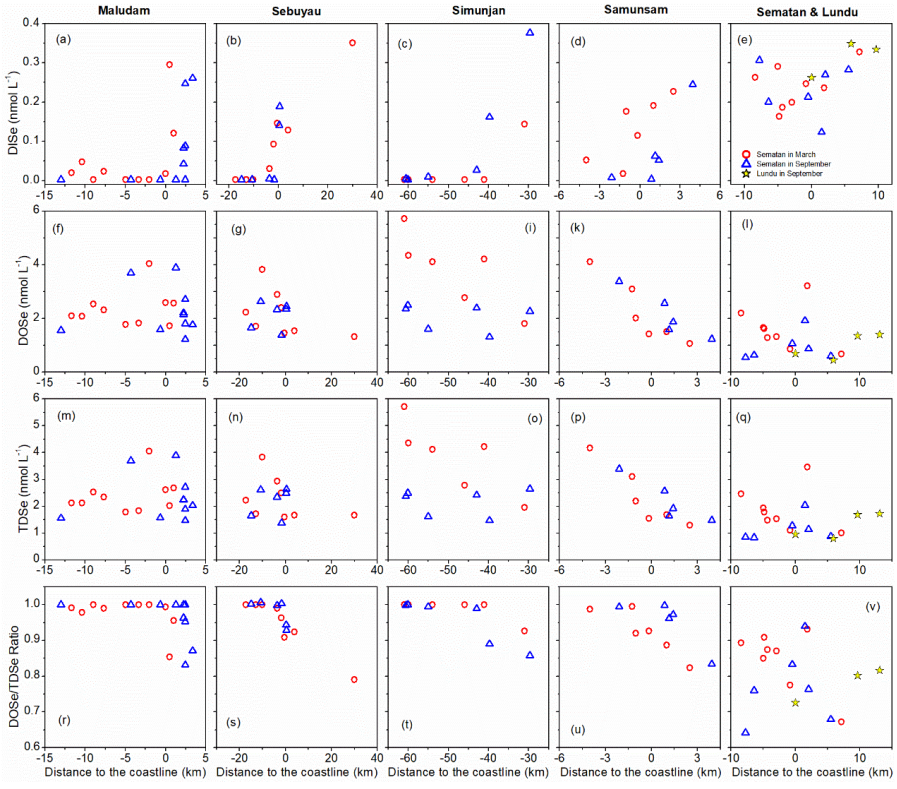


Figure 3. Relationships between Se(IV) (a, d), Se(VI) (b, e), DISe (c, f), DOSe (g, j), and TDSe (h, k) concentrations, and DOSe/TDSe ratio (i, l) with salinity in the Rajang and three Rajang tributaries (Igan, Lassa, and Rajang) in March and September 2017. TML refers to the theoretical mixing line, which was defined using two endmembers: freshwater in the riverine system and seawater.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

978



979

980 Figure 4. DISe, DOSe, and TDSe concentrations and DOSe/TDSe ratio along
981 the Maludam, Sebuyau, Simunjan, Samunsam, Sematan, and Lunda
982 estuaries in March and September 2017.

983

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

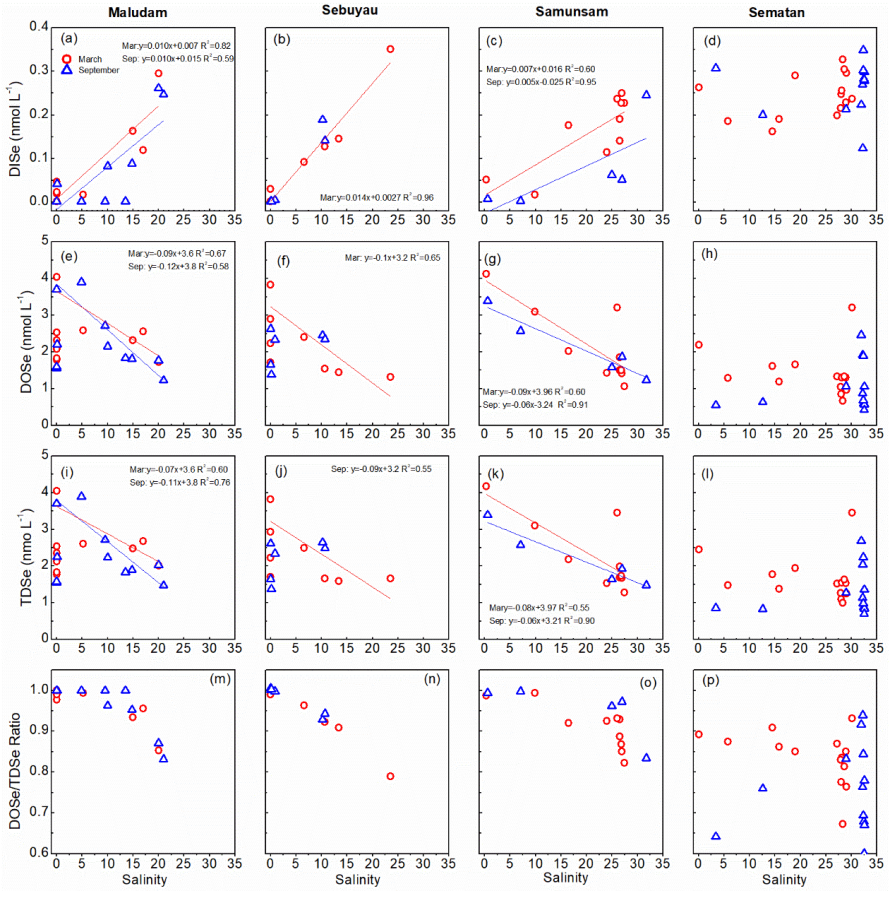
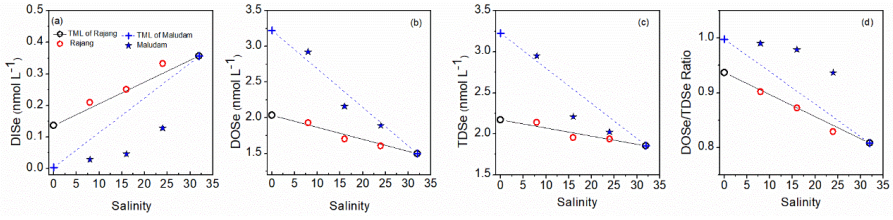


Figure 5. Relationships between DISe, DOSe, and TDSe concentrations and DOSe/TDSe ratio with salinity in the Maludam, Sebuyau, Samunsam, and Sematan estuaries. Red circles and blue triangles represent data for March and September 2017, respectively.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

992



993

994 Figure 6. Results of laboratory mixing experiments showing variation in DISe,
995 DOSe, and TDSe concentrations and DOSe/TDSe ratio as a function of
996 salinity using filtered riverine water from the Rajang and Maludam rivers and
997 filtered coastal seawater. TML refers to theoretical mixing line.

998

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

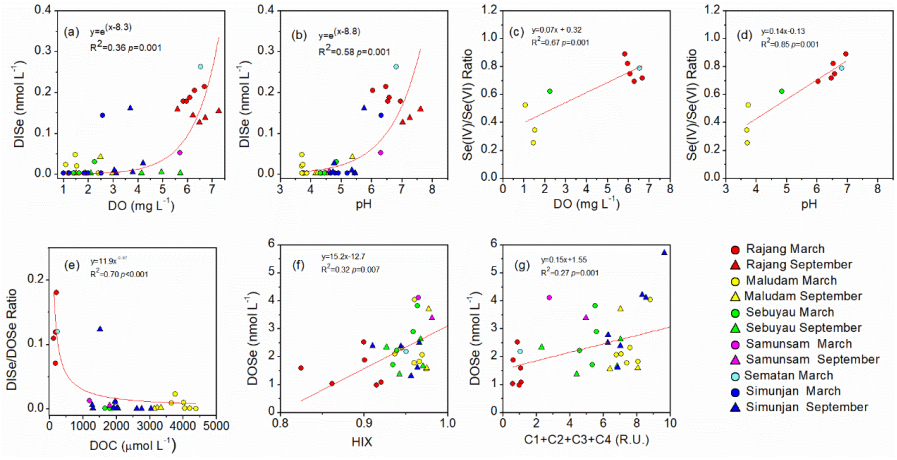


Figure 7. Relationships between (a, b) DISe concentrations and DO and pH values, (c, d) Se(IV)/Se(VI) ratios and DO and pH values, and (e–g) DOSe concentrations with the humification index (HIX) and the sum of humic-like CDOM components (C1, C2, C3, and C4) in freshwater (Salinity < 1) for the Rajang, 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.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

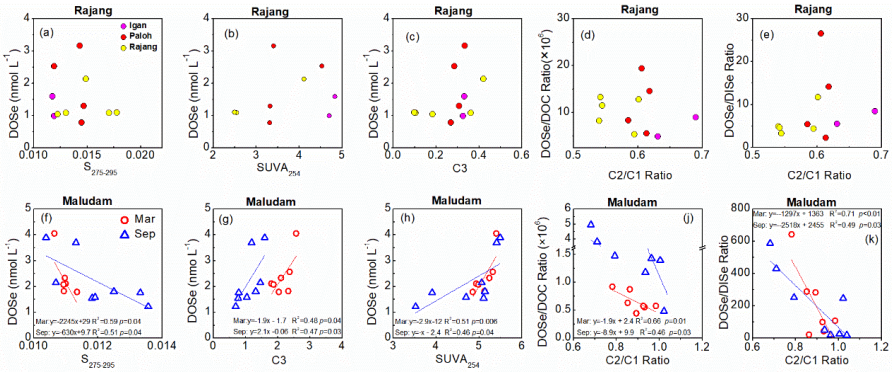


Figure 8. Relationships between DOSe concentrations and $S_{275-295}$, C3 components and $SUVA_{254}$, DOSe/DOC ratio and C2/C1 component ratios, and DOSe/DISe ratios and C2/C1 component ratios in the Rajang and Maludam estuaries. The $S_{275-295}$, $SUVA_{254}$, C1, C2, and C3 components are from Martin et al. (2018) and Zhou et al. (2019) from the same cruises.

https://doi.org/10.5194/bg-2019-233
Preprint. Discussion started: 5 August 2019

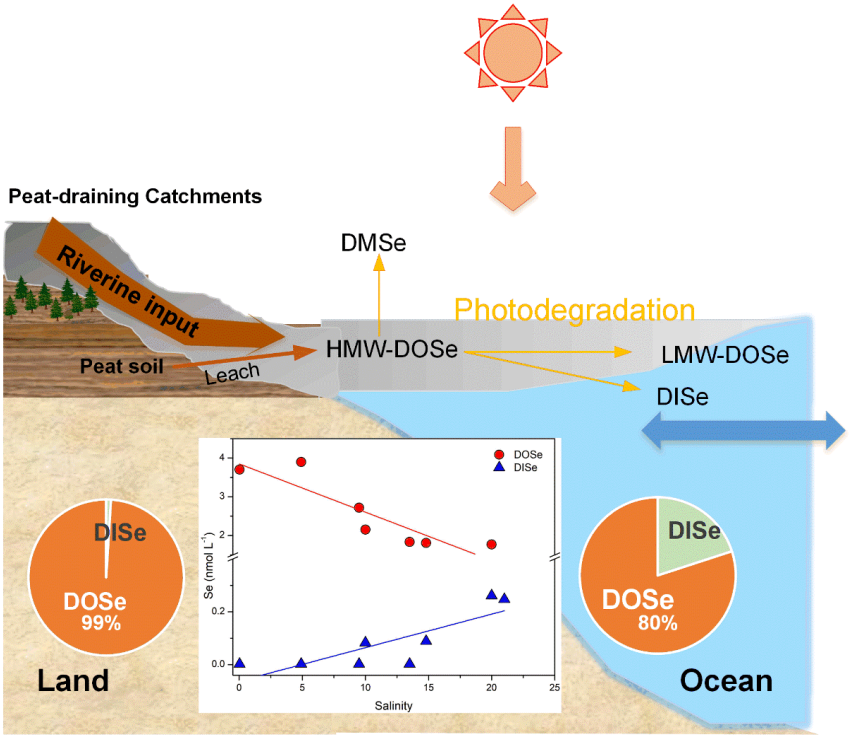


Figure 9. Conceptual diagram of the behaviour of Se species in the Maludam estuary. HMW, LMW, and DMSe represent high molecular weight, low molecular weight, and dimethyl selenide, respectively.