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 limit, 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 those reported for other small rivers, 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 diatoms (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.

78 Thus far, the behaviour of Se in estuaries has been studied mainly in the

79 temperate zone of the northern hemisphere (between 20°N and 60°N)

80 (Measures and Burton, 1978; Takayanagi and Wong, 1984; Van der Sloot et al.,

81 1985; Cutter, 1989a; Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati,

82 1998; Yao et al., 2006; Chang et al., 2016). The behaviour of Se in tropical

83 estuaries, however, is still poorly understood.

84 In the high-latitude peatland-draining rivers, dissolved Se concentrations

85 are spatially variable, with concentrations of up to 13 nmol L^{-1} being observed

86 in northern Minnesota, US (Clausen and Brooks, 1983), from 0.38 to 5 nmol L^{-1}

87 in the Krycklan catchment, Sweden (Lidman et al., 2011) and from 0.25 to 1.25

88 nmol L^{-1} in the lakes and rivers of western Siberian (Pokrovsky et al., 2018).

89 Although these various studies did not report different species of Se (Clausen

90 and Brooks, 1983; Lidman et al., 2011; Pokrovsky et al., 2018), the DOSe is

91 probably the dominated species in peatland-draining river. In the open ocean,

92 DOSe was assumed mainly associate with soluble peptides with low molecule

93 weight in surface waters and were relatively refractory (Cutter and Cutter, 1995;

94 2004). Substantial amounts of dissolved Se also are known to be associated

95 humic substances, Gustafsson and Johnsson (1994) assumed that Se was

96 preferentially incorporated into low molecular weight humic substances

97 fractions by means of microbial reductive incorporation, while Kamei-Ishikawa

98 et al. (2008) found that Se associated with high molecular weights humic acid

99 fractions. The current paucity of information on DOSe characteristics and its

100 export by tropical peat-draining rivers remains a major gap in our understanding

101 of Se biogeochemical cycling. Highest concentrations of dissolved organic

102 carbon (DOC) globally were reported in tropical peat-draining rivers in Borneo

103 (Moore et al., 2013; Wit et al., 2015). More works of Se in the fluvial systems of

104 this region are therefore needed to provide an improved understanding of the

105 biogeochemical processing of Se and the associations with organic matter.

106   To the best of our knowledge, the present study is the first analysis of the

107   distribution and behaviour of dissolved species of Se in seven rivers and

108   estuaries in western Borneo (Sarawak, Malaysia, Southeast Asia). We

109   hypothesize that the DOSe is the major species in those peatland-draining

110   rivers which mainly from peat soils and sizable Se from peatland is delivered to

111   the coastal areas. The main objectives of the study were to 1) evaluate the fate

112   of dissolved Se species in peatland-draining estuaries; 2) characterize the

113   DOSe fractions; and 3) estimate the magnitude of Se fluxes delivered from to

114   coastal ocean. The results of this study should contribute to an improved

115   understanding of how Se behaves in tropical peat-draining rivers and estuaries.

116   2. Materials and methods

117   2.1 Study areas and sample collection

118   Sarawak, Malaysia's largest state, is in the northwest of the island of

119   Borneo, Malaysia (Müller et al., 2016). Sarawak has a tropical climate, with a

120   mean annual air temperature at the capital Kuching of 26.1 °C (Müller et al.,

121   2016). Rainfall is abundant throughout the year but is pronounced during the

122   northeastern monsoon, which occurs between November and February (wet

123   season). The period from May to September, before the southwestern monsoon,

124   constitutes the dry season (Sa'adi et al., 2017). About 12% of the coastal area

125   of western Sarawak is covered by peatlands, of which approximately 41% has

126   been converted to palm plantations (Müller et al., 2016).

127   Two sampling campaigns were conducted in peat-draining rivers and

128   estuaries in Sarawak in 2017. The first was at the end of the northeastern

129   monsoon (from 4 to 12 March 2017, just after the wet season), and the second

130   was shortly before the beginning of the southwestern monsoon (from 4 to 17

131   September 2017, in the dry season) (Fig. 1). Six rivers, namely, the Rajang,

132 Maludam, Simunjan, Sebuyau, Sematan, and Samunsam, were sampled in

133 March and September, and the Lundu River was sampled only in September

134 (Fig. 1). The physio-geographical parameters of sampled river basins are

135 summarized in Table 1. Four of the rivers (the Maludam, Simunjan, Sebuyau,

136 and Samunsam) drain catchments with high peatland coverages and are known

137 as blackwater rivers, whereas the Sematan and Lundu drain catchments with

138 high proportions of mineral soils (Table 1).The Rajang River drains mineral soils

139 in its upper reaches (Staub et al., 2000) but, at Sibu, branches into multiple

140 distributary channels (the Igan, Paloh, and Rajang) that flow from north to south

141 through land covered with thick peat (Staub et al., 2000) (Fig. 1). Water samples

142 were collected from a boat. As the boat moved forward, surface water was

143 collected upstream and to the side of the boat into an acid-cleaned polyethylene

144 bottle attached to the end of a plastic pole sampler (3–4 m long). Water

145 temperature, salinity, pH, and dissolved oxygen (DO) concentrations were

146 measured *in situ* using a portable multifunction water-quality meter (AP–2000,

147 Aquaread Company, Britain) at the time of sample collection. Water samples

148 were filtered within 12 h of collection through pre-cleaned 0.4 μm filters

149 (Nuclepore) at a laminar air flow cleanbench (Class 100). The filtrates were

150 placed in acid-cleaned polyethylene bottles and were frozen and stored until

151 analysis.

152 **2.2 Analytical methods**

153 The Se(IV), DISe, and TDSe concentrations were determined in carbon-

154 containing plasma using a hydride generation (HG) system (Hydride FAST, ESI)

155 combined with a sector field inductively coupled plasma–mass spectrometry

156 (ICP–MS) instrument, as outlined in the operationally defined hydride

157 generation-based speciation analysis methods described by Chang et al. (2014,

158 2017). Selenium was measured at $m\ z^{-1}$ = 82 with low resolution. By adding

159 methane (2 ml min^{-1}) to the carbon-containing plasma, Se sensitivity was

160 increased and spectral interference was suppressed, which improved the

161 detection limits. Briefly, Se(IV) at an acidity of 2 mol l^{-1} HCl was reacted with

162 NaBH$_4$ to produce hydrogen selenide and then quantified using HG–ICP–MS.

163 Se(VI) was quantitatively reduced to Se(IV) by heating a sample acidified with

164 3 mol l^{-1} HCl to 97 °C for 75 min and then quickly cooling to room temperature

165 using an ice-water bath. The steps used to determine Se(IV) were then followed

166 to obtain the concentration of DISe. The reduction recoveries ranged from 95%

167 to 103%. The Se(VI) concentration was calculated as the difference between

168 DISe and Se(IV). The total dissolved selenium (TDSe) concentrations were

169 determined using the same method as for DISe, following ultraviolet digestion

170 (Li et al., 2014). The concentration of DOSe was calculated as the difference

171 between the TDSe and DISe concentrations (DOSe = TDSe − DISe). Detection

172 limits for Se(IV), DISe, and TDSe were 0.0025, 0.0063, and 0.0097 nmol l^{-1},

173 respectively. The accuracy of the methods was tested with standard solutions,

174 and Se(IV) GSBZ 50031-94, Se(VI) GBW10032, selenocysteine GBW10087,

175 and selenomethionine GBW10034 showed differences within 3.0%, 0.7%, 1.6%,

176 and 1.4%, respectively.

177 **2.3 The calculation of TDSe flux and yield**

178   TDSe fluxes (Q) transported to the ocean were estimated according the

179 following equation:

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

181 Where C is the mean concentration of TDSe at the fresh endmember of the

182 river (salinity < 1), and V is the river water discharge. Riverine TDSe yield is the

183 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 peatlands 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

208 (Table 1, Fig. 2). Student's t-test results showed that the concentrations of

209 TDSe, DISe and DOSe did not differ between the wet and dry seasons in the

210 sampled rivers and estuaries ($p > 0.05$), which may reflect the La Niña

211 conditions that caused high precipitation and high discharge rates in Malaysia

212 in 2017 (Jiang et al., 2019).

213 In the Rajang estuary, Se(IV), Se(VI) and DISe concentrations were high

214 in the coastal areas, whereas DOSe concentrations were higher in the

215 distributaries than in the upper reach in both seasons (Fig. S3). DOSe/TDSe

216 ratios were high in the distributaries and decreased in a seaward direction to

217 around 0.7 (Fig. S3). In the Maludam estuary, DISe concentrations were

218 extremely low (near or below the detection limit) in the freshwater reach and

219 increased towards the sea, whereas the DOSe concentrations decreased in a

220 seaward direction in both seasons (Fig. S4). DISe and DOSe concentrations

221 followed similar patterns in the Sebuyau, Simunjan, Samunsam, Sematan and

222 Lundu estuaries (Fig. S4). Se(IV) and Se(VI) concentration are not presented

223 but were even lower than those of DISe and commonly lay below the detection

224 limit, especially in the freshwater reaches. As TDSe is the sum of the DISe and

225 DOSe concentrations, and DOSe generally dominated in the sampled rivers

226 and estuaries, the distributions of TDSe and DOSe were similar (Fig S4). The

227 DOSe/TDSe ratios were between 0.8 and almost 1 in the Maludam, Sebuyau,

228 Simunjan, and Samunsam estuaries as salinity < 1, indicating that DOSe was

229 the only (or dominant) species in the freshwater of the blackwater rivers. The

230 DOSe/TDSe ratios were between 0.6 and 0.9 in the Sematan and Lundu,

231 indicating that more than half of the Se was still present in the form of DOSe in

232 those rivers and estuaries with high proportions of mineral soils (Fig. S4).

233 **3.3 Se species relationship with salinity**

234 Variation in Se species concentrations along a salinity gradient in the three

235   tributaries (the Igan, Lassa, and Rajang) of the Rajang Estuary in March and

236   September are shown in Fig. 3. Theoretical mixing lines (TMLs) were

237   developed using two endmembers, namely, a freshwater endmember in the

238   freshwater reach of the Rajang River and a marine endmember with a salinity

239   of >30. DISe concentrations increased with salinity and, compared with the TML,

240   DISe removals were observed in the Rajang branches in March, and DISe

241   additions were observed in the upper reaches of the Rajang and Paloh

242   branches (Fig. 3a, 3b). DOSe concentrations decreased with salinity and were

243   much higher than the TML in the Rajang and upper Paloh branches in both

244   March and September and in the Igan Branch in September (Fig. 3e, 3f). TDSe

245   concentrations in the mixing zone of the Rajang and Igan branches were also

246   higher than the TML (Fig. 3i, 3j).

247   Plots of DISe concentration against salinity show a positive linear

248   regression between DISe and salinity in the Maludam, Sebuyau, and

249   Samunsam estuaries ($p < 0.05$) in both seasons, but not in the Sematan estuary

250   ($p > 0.05$), where DISe concentrations in the freshwater and marine water

251   endmembers were similar in both seasons (Fig. 3, Fig. S5). The salinities varied

252   little, either between the two seasons in the Simunjan and Lundu estuaries or

253   in the Sebuyau estuary in September, and therefore Se concentration–salinity

254   relationships were not examined. As shown in Fig. 3j and 3h, DOSe

255   concentrations in the freshwater parts of the Maludam and Sebuyau rivers

256   varied widely and increased downstream, so the geographical location nearest

257   to the river mouth with a salinity of <1 was selected as the freshwater

258   endmember in the linear mixing models. A negative linear correlation was

259   observed between DOSe concentration and salinity ($p < 0.05$) in the Maludam,

260   Sebuyau, and Samunsam estuaries for both seasons, but DOSe concentrations

261   did not vary significantly with salinity ($p > 0.05$) in the Sematan estuary (Fig. 3

262   and Fig. S5). TDSe concentrations were also negatively correlated with salinity

263 ($p < 0.05$) in the Maludam, Sebuyau, and Samunsam estuaries but not in the

264 Sematan Estuary (Fig.3 and Fig. S5).

265   Generally, relationships between the Se species and salinity fell into three

266 groups. In the blackwater estuaries (the Maludam, Sebuyau, and Samunsam),

267 DISe concentrations were positively correlated with salinity; DOSe and TDSe

268 concentrations were negatively correlated with salinity (Fig. 3). In the Rajang

269 estuary, DISe increased with salinity but behaved non-conservatively and was

270 removed in the brackish water region; whereas DOSe and TDSe decreased

271 with salinity, behaved non-conservatively, and were added during estuarine

272 mixing (Fig. 3). In the Sematan estuary, TDSe, DOSe, and DISe behaved non-

273 conservatively and showed little change during estuarine mixing (Fig. 3).

274 **3.4 Correlation between Se species with DO, pH and DOM**

275   For the freshwaters (S < 1) of the studied rivers, DISe concentrations were

276 positively correlated with the DO concentrations and pH values, and the

277 DISe/DOSe ratio was negatively related to DOC concentration (data from

278 Martin et al., 2018; Fig. 4a, 4b). DOSe concentrations correlated positively with

279 the humification index (HIX) and the sum of the humic-like chromophoric

280 dissolved organic matter (CDOM components, C1, C2, C3, and C4) ($p < 0.05$)

281 (data from Zhou et al., 2019) (Fig. 4c, 4d).

282   In the Maludam Estuary, DOSe concentrations were negatively correlated

283 with the CDOM spectral slope from 275 to 295 nm ($S_{275-295}$) and were positively

284 correlated with the humic-like C3 component and specific UV absorbance at

285 254 nm ($SUVA_{254}$) during estuarine mixing in both seasons (data from Martin et

286 al., 2018; Zhou et al., 2019, Fig. 5a-c). In addition, DOSe/DOC and DOSe/DISe

287 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 are 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)

314 associated with humic and fulvic substances appear to be responsible for the
315 immobilization of inorganic Se (Kang et al., 1991; Zhang and Moore, 1996;
316 Wang and Gao, 2001). The DISe/DOSe ratios negatively related with DOC
317 concentrations (Fig. 4c). DO, pH, and DOC concentrations of the water
318 probably contributed to the observed variations in Se species, and the acidic,
319 low-oxygen, and organic-rich blackwater rivers were not a suitable environment
320 for DISe.

321 During estuarine mixing, reversed DISe concentration–salinity
322 relationships were observed in the Rajang, Maludam, Sebuyau, and
323 Samunsam estuaries (Fig. 3, Fig S5), which contrasts with those reported for
324 other estuaries (Measures and Burton, 1978; Takayanagi and Wong, 1984; Van
325 der Sloot et al., 1985; Cutter, 1989a; Guan and Martin, 1991; Hung and Shy,
326 1995; Abdel-Moati, 1998; Yao et al., 2006; Chang et al., 2016). The marine
327 endmember of the DISe concentrations in the sampled estuaries (salinity > 31)
328 was 0.30 nmol L^{-1} (range: 0.12 to 0.47 nmol L^{-1}), encompassing or close to the
329 values reported for surface water in the South China Sea (around 0.38 nmol
330 L^{-1}, Nakaguchi et al., 2004) and the Pacific (mean of 0.24 nmol L^{-1}, range: 0.02
331 to 0.69 nmol L^{-1}) (Cutter and Bruland, 1984; Sherrard et al., 2004; Mason et al.,
332 2018). The salinity-related increases in DISe in a seaward direction indicate
333 that the patterns of distribution of DISe in those peat-draining estuaries are
334 controlled mainly by conservative mixing of ocean-derived DISe. In addition,
335 DISe was removed in March but was added in September in the Rajang estuary.
336 Laboratory studies have shown that Se(IV) can be adsorbed by peat and that
337 60% of the adsorbed Se(IV) can be desorbed upon exposure of the solid phase
338 to seawater (Kharkar et al., 1968). DISe may have been added to the Rajang
339 estuary in September via release of Se(IV) from peat in brackish waters. Other
340 studies have reported removal of the humic fractions of DOM, colloidal iron, and
341 phosphorus by flocculation in the river–sea mixing zones (Eckert and Sholkovitz,

342 1976; Forsgren et al., 1996; Asmala et al., 2014). Some of the DISe may exist

343 in colloidal form in natural water (Takayanagi and Wong, 1984), and DISe may

344 be removed by flocculation. In peat-draining estuaries, ocean-derived DISe

345 may be adsorbed to peat and may be associated with DOM, which is then

346 converted to DOSe and/or flocculated to particulate Se.

347 In contrast to DISe, DOSe concentrations were high in the rivers and

348 decreased in a seaward direction as salinity increased (Fig. 3, Fig S5). DOSe

349 has been shown to behave non-conservatively in other estuaries, with

350 concentrations decreasing along salinity gradients or with mid-estuarine input

351 (Cutter, 1989a; Guan and Martin, 1991; Hung and Shy, 1995; Abdel-Moati,

352 1998). DOSe concentrations in the estuaries studied in Sarawak were higher

353 than those reported in other estuaries (0.1 to 2.5 nmol L^{-1}) (Cutter, 1989a; Guan

354 and Martin, 1991; Hung and Shy, 1995; Abdel-Moati, 1998). The marine

355 endmember of the DOSe concentrations in the sampled estuaries (salinity >31)

356 ranged from 0.42 to 2.91 nmol L^{-1} (mean: 1.32 nmol L^{-1}) and exceeded those

357 in surface water of the South China Sea (mean: 0.20 nmol L^{-1}, range: 0.33 to

358 0.14 nmol L^{-1}, Nakaguchi et al., 2004) and the Pacific (mean: 0.36 nmol L^{-1},

359 range: 0.01 to 0.67 nmol L^{-1} (Cutter and Bruland, 1984; Sherrard et al., 2004;

360 Mason et al., 2018). The high DOSe concentrations in coastal waters in

361 Sarawak (S > 30) suggest a significant contribution from terrigenous DOSe. In

362 the distributary channels of Rajang, there are large inputs of organic matter

363 from peat, thus higher DOSe concentrations than the TML values be expected

364 in most of the brackish waters (Fig. 3).

365 **4.2 Character of the DOSe fractions**

366 Coal deposits in Kanawha County in the USA have been interpreted as a

367 dome-shaped peat swamp, analogous to those in Malaysia. Coal Se contents

368 reached 10.7 mg/kg, and sequential extraction results showed that the

369   concentrations of the organically bound fraction were the highest (Vesper et al.,

370   2008). It is therefore expected that organic matter that is solubilized and

371   leached from peat would cause Se concentrations to increase, and therefore

372   leaching from Se-rich peat soils is inferred to be the major source of DOSe in

373   our sampled rivers. Moreover the peat-draining rivers demonstrated a linear

374   relationship between DOSe concentrations and HIX and humic-like CDOM

375   components (Fig. 4d, 4e) indicating that DOSe may be associated with

376   dissolved humic substances. In addition, DOSe correlated with $S_{275-295}$ and

377    $SUVA_{254}$ (Fig. 5a, 5c) suggesting that DOSe was associated closely with high-

378   molecular-weight and highly aromatic DOM. In addition, the positive

379   correlations between DOSe and the humic-like C3 component (Fig. 5b), i.e.

380   aromatic and black carbon compounds, suggest a strong association of DOSe

381   to these high molecular weight DOM (Fig. 6). Pokrovsky et al. (2018) also found

382   that Se was transported in the form of high molecular weights organic aromatic-

383   rich complexes from peat to the rivers and lakes in the Arctic. Bruggeman et al.

384   (2007) and Kamei-Ishikawa et al. (2008) both found that 50% to 70% of Se(IV)–

385   humic substances associates had high molecular weights (>10 kDa), consistent

386   with our findings.

387   During the estuarine mixing, the negatively correlation between

388   DOSe/DOC and DOSe/DISe ratios with C2/C1 ratios which is enhanced by

389   photodegradation (Wang et al., 2019; Fig. 5d, 5e), indicating that compared to

390   bulk DOM, the DOSe fractions were more susceptible to photodegradation, and

391   that DOSe was probably photodegraded to DISe. As suggested by Martin et al

392   (2018) that most photochemical transformations of DOM in Sarawak likely take

393   place after DOM reaches the sea. Thus, photodegradation plays an important

394   role in DOSe processing once transported to offshore, and DOSe might contain

395   a significant photoreactive fraction that facilitates photodegradation of DOSe

396   into lower mean molecular weights or gaseous Se or photomineralization to

397   DISe (Fig. 6). Considerable amounts of Se may be volatilized when

398   methylselenide compounds form (Lidman et al., 2011). A field study found that

399   volatile species of Se were naturally emitted from peatland at concentrations of

400   around 33 nmol L^{-1} (Vriens et al., 2015). As a result of the method used in the

401   present study, volatile methylselenide compounds in the DOSe fractions may

402   not have been detected, so DOSe may have been underestimated. In future

403   work, particular attention should be given to methylselenide. Studies have

404   shown that photodegradation of DOM results in a range of bioavailable products

405   (Miller and Moran, 1997). Peatland-derived DOSe might be degraded to a lower

406   molecular weight or DISe in the coastal areas, both of which are bioavailable

407   for phytoplankton and may stimulate their growth, and thereby impact the

408   marine animals via food chain. The photoreactive DOSe fractions are probably

409   transported across the marginal sea and circulated globally. Given that the

410   bioavailability and biogeochemical cycling of the peatland-derived DOSe

411   fractions may differ from those of peptides produced *in situ* by phytoplankton in

412   the ocean, the impact on coastal and open ocean ecosystems should be

413   evaluated in the future.

414   **4.3 TDSe flux**

415   Information on the biogeochemistry of peat-draining rivers is scare, and so

416   their possible quantitative significance for the oceanic TDSe budget is

417   unexplored as yet. The TDSe flux was estimated to be 16 × 10^3 and 0.044 ×

418   10^3 kg yr^{-1} for Rajang and Maludam, respectively (Table 2). On a global scale,

419   the TDSe delivered from Rajang were less than those large rivers including

420   Changjiang, Amozon, Zhujiang, Orinoco and St.Lawrence River, but exceeded

421   other small rivers reported so far (Table 2). The TDSe delivered by Rajang and

422   Maludam contributed nearly 1% of the total riverine TDSe input to the ocean

423   with only 0.3% of freshwater discharge (Nriagu, 1989; Milliman and Farnsworth,

424 2013). The TDSe yields for Rajang and Maludam were just below the second

425 largest river Changjiang and the polluted Scheldt River, but exceed the other

426 rivers (Table 2). The magnitude of DOSe yields obtained from Rajang and

427 Maludam was one to two orders of degree higher than those in other reported

428 rivers (Table 2). This indicates that the numerous small blackwater rivers

429 draining from peatland are very efficient TDSe and DOSe sources for the

430 coastal waters. The roughly estimated TDSe flux from tropical peatland

431 (439,238 km^2, Page et al., 2011) could be around 120×10^3 kg yr^{-1}, which were

432 nearly 35% of the current total riverine TDSe flux, based on average TDSe yield

433 from Rajang and the Maludam (0.27 kg km^{-2} yr^{-1}). On a global perspective,

434 TDSe export from peat-draining rivers is quantitatively more significant than

435 previously thought. It can be expected that increasing anthropogenic disturbing

436 of peat can release a great amount of Se to rivers, and then transported to the

437 coastal areas. The impact of peatland derived Se to the ecosystem should

438 receive more attention in future studies.

5. Conclusion

440 To the best of our knowledge, this is the first study of seasonal variations

441 in Se speciation in peat-draining rivers and estuaries in Southeast Asia.

442 Contrary to the results from studies elsewhere, DOSe, not DISe, was the major

443 species in the peat-draining rivers and estuaries of Sarawak, Malaysia.

444 Contrary to our expectations, reversed DISe concentration–salinity

445 relationships were observed in those estuaries, indicating a marine origin, while

446 DOSe concentrations decreased with salinity, indicating terrestrial sources. The

447 DOSe fractions may be associated with high-molecular-weight peatland-

448 derived aromatic and black carbon compounds. The DOSe yields in the

449 peatland-draining rivers were one or even two orders of magnitude higher than

450 other reported rivers. The TDSe flux delivered by the peat-draining rivers

451 ==exceeded other small rivers==, and it is quantitatively more significant than
452 previously thought. The impact of the sizable Se from increasing anthropogenic
453 disturbing of peat to the ecosystem should be evaluated in the future.
454

6. Data availability

456 The datasets used and/or analysed in this study are available from the
457 corresponding author on reasonable request.

7. Author contribution

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

8. Competing interests

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

9. Acknowledgements

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710   Biogeosciences, 16, 2733–2749, 2019.

711

712

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

714   for not available.)

River Names	Total Basin [a]	Runoff (km^3 yr^{-1})	Peatland cover (%) [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

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

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

717   [c] Cited Müller et al., 2016

718   Table 2 Overview of the TDSe concentrations and DOSe/TDSe ratios in the river and the magnitude of riverine TDSe flux and TDSe

719   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

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

721   [b] The data were DISe species.

722   [c] The DOSe were not measured.

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724

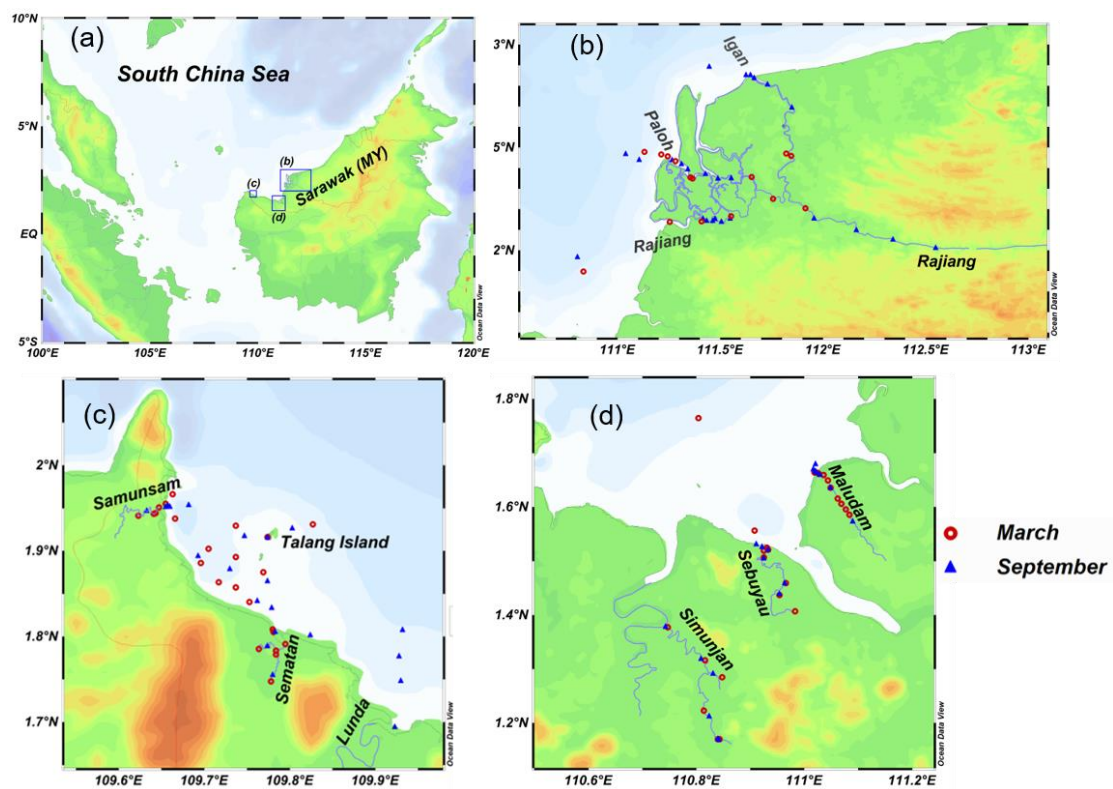
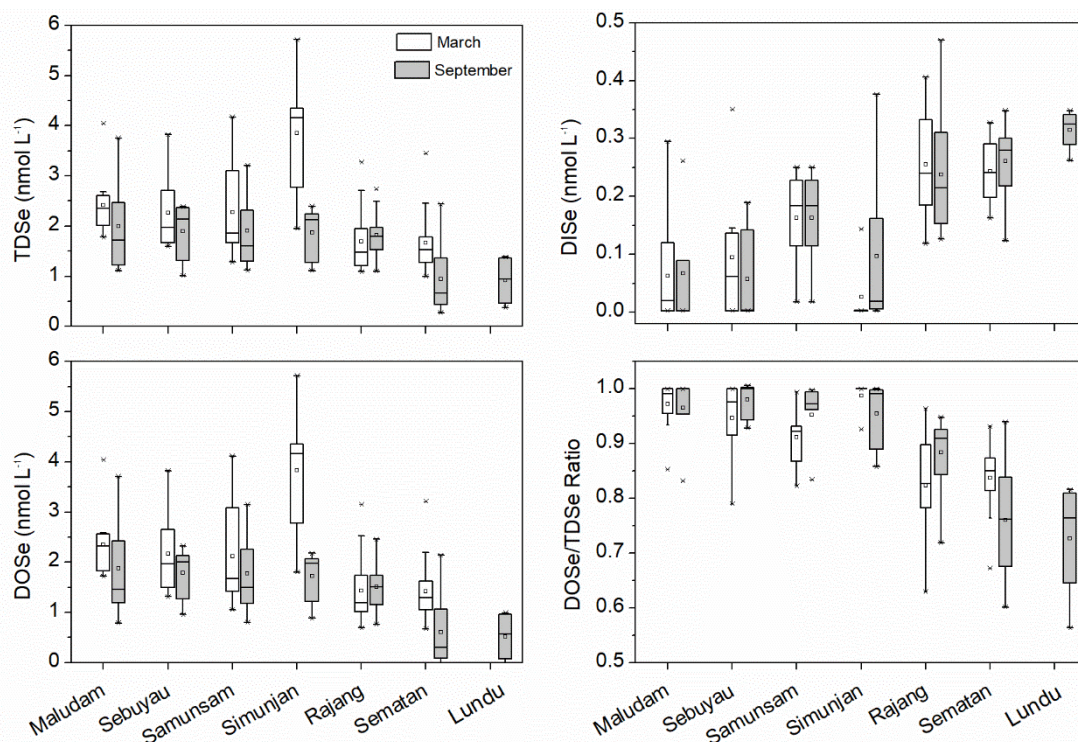



Figure 1. (a) Map of the study area showing the location of Sarawak on the island of Borneo. Blue boxes with letters indicate the areas shown in panels b–d. (b–d) Station locations for the Rajang River (b), the Samunsam, Sematan, and Lunda rivers (c), and the Maludam, Sebuyau, and Simunjan rivers (d)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

732

733 Figure 2 The box plot of TDSe, DISe and DOSe concentration and

734 DOSe/TDSe ratio in the sampled rivers and estuaries in Malaysia in March

735 and September 2017, respectively. In the plot of the upper panel, the ends of

736 the box and the ends of the whiskers, and the line across each box represent

737 the 25th and 75th percentiles, the fifth and 99th percentiles, and the median,

738 respectively; the open square indicates the mean value.

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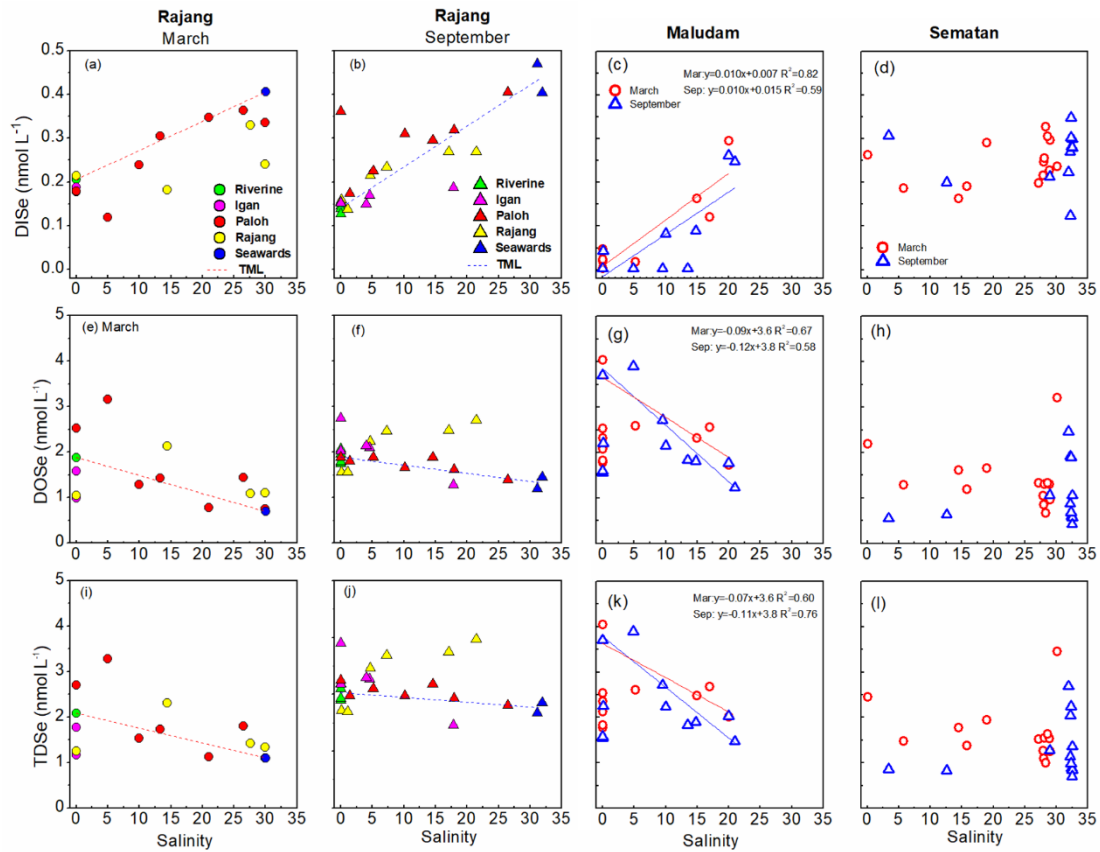
741 Figure 3. Relationships between DISe (a - d), DOSe (e - h), and TDSe (i - l)

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

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

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

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

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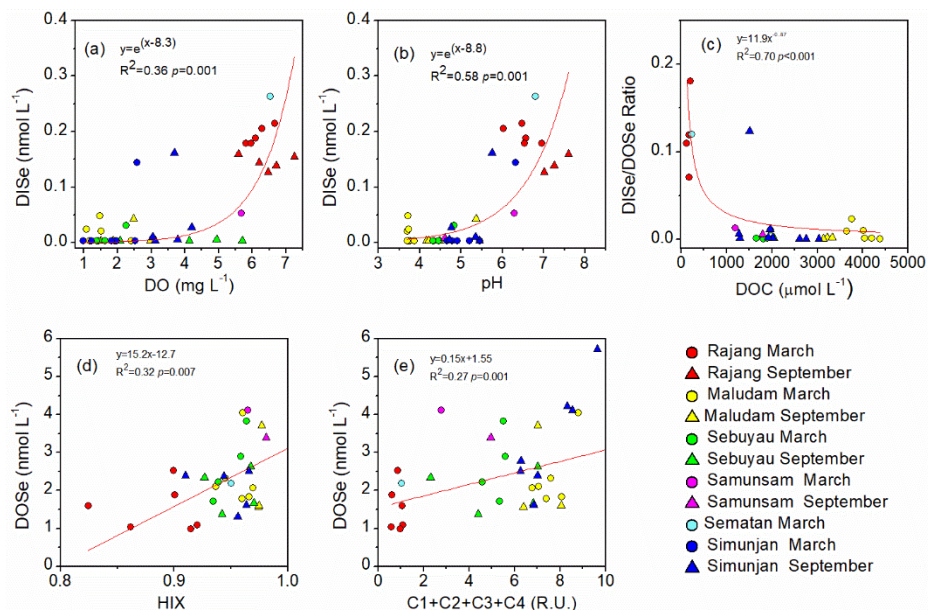
747

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

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

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

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

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

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

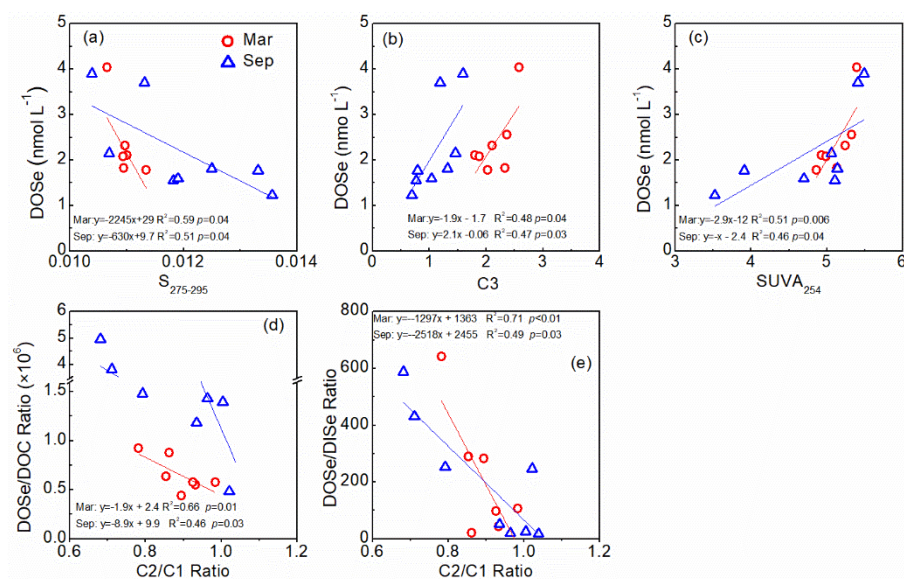
754 from Zhou et al. (2019) from the same cruises. DO concentrations and pH

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

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

757 September.

758

759

760 Figure 5. Relationships between DOSe concentrations and $S_{275-295}$, C3

761 components and $SUVA_{254}$, DOSe/DOC ratio and C2/C1 component ratios,

762 and DOSe/DISe ratios and C2/C1 component ratios in the Rajang and

763 Maludam estuaries. The $S_{275-295}$, $SUVA_{254}$, C1, C2, and C3 components are

764 from Martin et al. (2018) and Zhou et al. (2019) from the same cruises.

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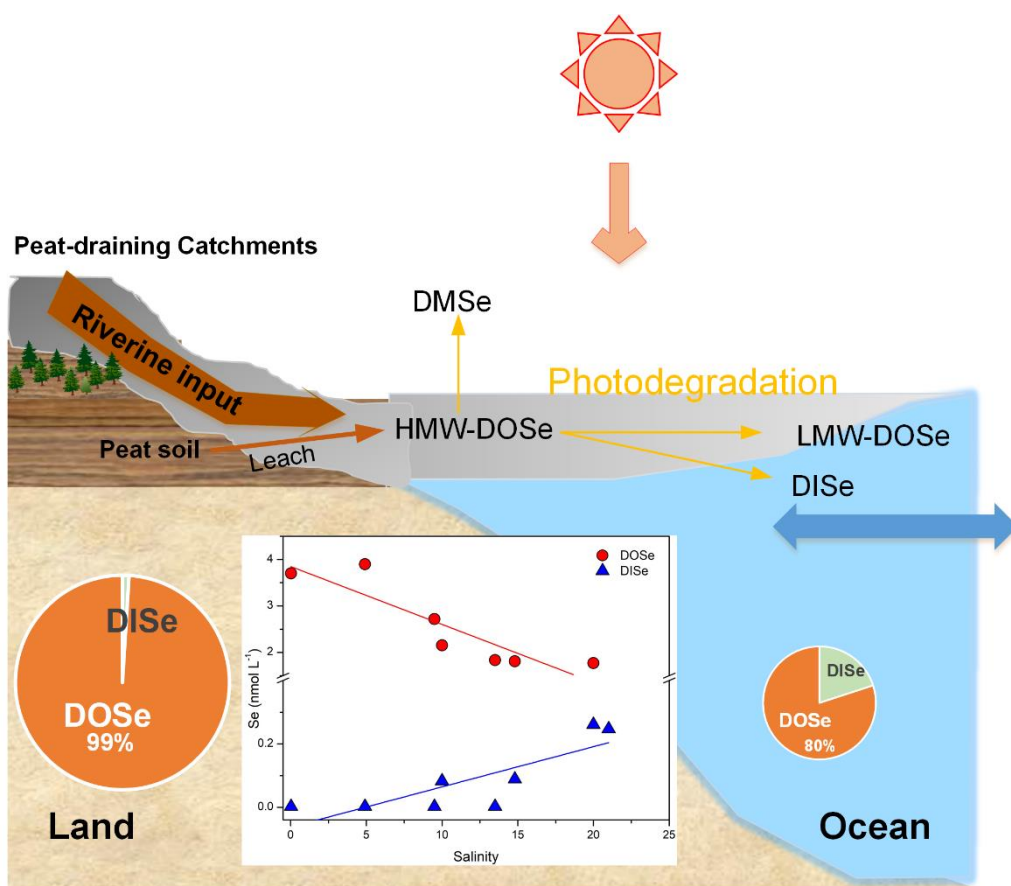
767

768   Figure 6. Conceptual diagram of the behaviour of Se species in the Maludam

769   estuary. HMW, LMW, and DMSe represent high molecular weight, low

770   molecular weight, and dimethyl selenide, respectively.