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## **Relationships between dissolved black carbon and dissolved organic matter in streams**

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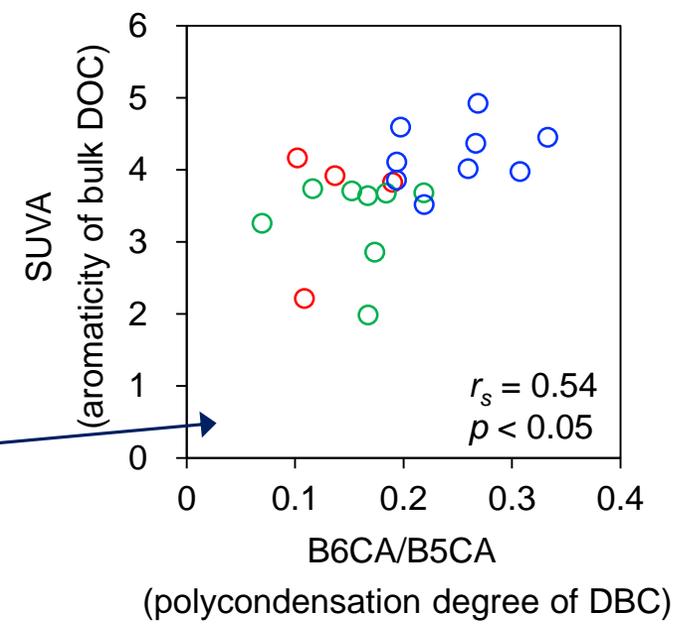
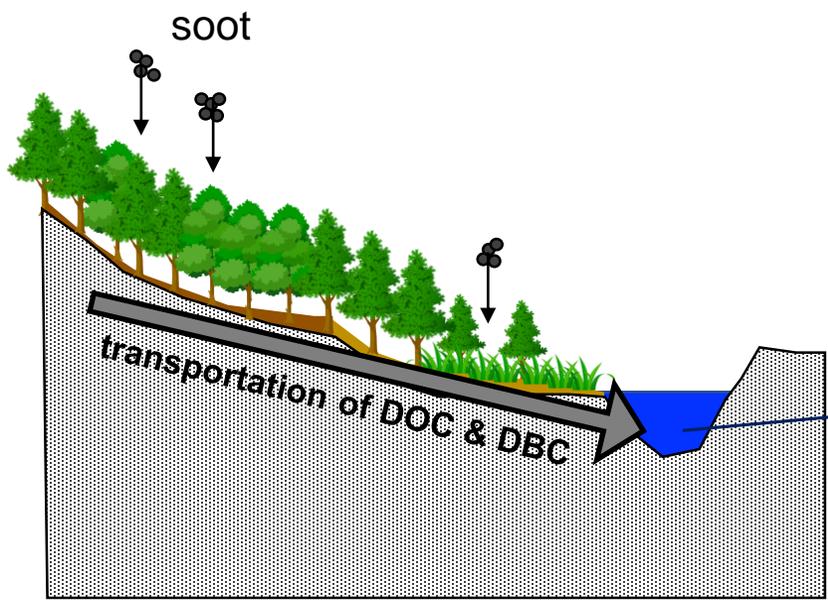
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## **Highlights**

- Stream DBC, in which the catchment was unaffected by fire, was studied
- Atmospheric deposition of BC to the catchment is predominant source of stream DBC
- DBC concentration was linearly correlated with DOC concentration
- The degree of DBC polycondensation was correlated with bulk DOC quality
- Mobilization mechanism from soil to stream was similar between DBC and DOC



13 **Abstract**

14 Black carbon (BC) is a pyrolyzed product derived from incomplete combustion. A major  
15 fraction of BC produced by landscape fires is initially deposited onto onsite soils.  
16 Atmospheric deposition of soot is known to be an important source of soil BC, especially in  
17 watersheds that are not affected by landscape fires. The transport of the dissolved fraction  
18 of oxidized BC in soil, defined as dissolved black carbon (DBC), to streams is considered  
19 one of the important loss pathways of BC in soil, but the mechanism is not well  
20 documented. We measured the quantity and quality of DBC, determined by a  
21 benzenepolycarboxylic acid method, and the quantitative and qualitative parameters of bulk  
22 dissolved organic matter (DOM) in streams in Hokkaido, northern Japan, whose  
23 catchments were not affected by landscape fire for at least 110 years. DBC with relatively  
24 low polycondensed signatures occurred in the streams, irrespective of differences in  
25 watershed characteristics and seasons, suggesting that atmospheric deposition of soot into  
26 the catchment is probably a major source of stream DBC. The DBC concentration was  
27 linearly related to the dissolved organic carbon (DOC) concentration, irrespective of the  
28 differences in watershed characteristics and seasons. Furthermore, the polycondensation  
29 degree of DBC was observed to correlate with the qualitative parameters of bulk DOM.  
30 Such quantitative and qualitative relationships between DBC and bulk DOM imply that the  
31 transfer mechanism from soils to streams of soot-derived polycondensed DBC is linked  
32 with that of higher plant-derived, high-molecular-weight aromatic DOM.

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35

36 **Keywords**

37 dissolved black carbon; dissolved organic matter; streams; soot; mobilization

38

## 39 **1. Introduction**

40 Black carbon (BC) is a pyrolyzed product derived from incomplete combustion during  
41 biomass burning as well as fossil fuel combustion and includes soot, charcoal, and slightly  
42 charred biomass (Masiello, 2004). BC is chemically heterogeneous but has a high carbon  
43 content and condensed aromatic structures (Hedges et al., 2000; Masiello, 2004; Wonizak  
44 et al., 2020). Although BC produced under low charring temperatures, e.g., levoglucosan, is  
45 highly water soluble and biodegradable (Myers-Pigg et al., 2015), the major fraction of BC  
46 with polycyclic aromatic structures is considered to be resistant to biodegradation for at  
47 least thousands of years (Masiello and Druffel, 1998). The majority of biomass is  
48 completely oxidized to CO<sub>2</sub> during a landscape fire, including wildfires, deforestation fires  
49 and agricultural burns, while 5–15% of the biomass is converted to BC (Santín et al., 2016).  
50 A recent study estimated that 2.2 PgC of CO<sub>2</sub> is emitted into the atmosphere, and 0.26 PgC  
51 of biomass carbon is converted to BC by annual landscape fires (Jones et al., 2019a). In  
52 addition, 0.002–0.029 PgC yr<sup>-1</sup> of BC was estimated to be emitted into the atmosphere  
53 globally by fossil fuel combustion and biomass burning (Bond et al., 2013). This BC is  
54 eventually deposited on the land or ocean and impacts biogeochemical cycles as well as  
55 ecosystems (Mari et al., 2014; 2019).

56 A part of BC produced during landscape fires is emitted to the atmosphere mainly as  
57 soot, but the major fraction of BC is initially deposited onto onsite soils mainly as charcoal  
58 (Kuhlbusch, 1998; Santín et al., 2016). Otherwise, BC is redistributed to stream corridors  
59 or transported to rivers as particulate BC with overland flow (Wagner et al., 2015; Cotrufo  
60 et al., 2016). The riverine flux of particulate BC is found to be primarily controlled by  
61 erosion (Wagner et al., 2015; Cotrufo et al., 2016, Coppola et al., 2018). The annual global

62 flux of riverine particulate BC to the ocean was estimated to be 0.017 to 0.037 PgC  
63 (Coppola et al., 2018), which is equivalent to 6.5 to 14.2% of 0.26 PgC, the annually  
64 produced BC by landscape fires (Jones et al., 2019a).

65 As BC incorporated in soils ages, BC becomes water soluble due to the introduction of  
66 oxygen- and nitrogen-containing functionalities (Knicker, 2011). The soluble fraction of  
67 BC in soil pore water is known to be exported to rivers (Hockaday et al., 2006; 2007). The  
68 long-term effects of slash and burn activities on the riverine export of dissolved BC (DBC,  
69 having condensed aromatic structures, detected by a benzenepolycarboxylic acid (BPCA)  
70 method), have been demonstrated (Dittmar et al., 2012). On the other hand, it has been  
71 pointed out that anthropogenic BC, associated with soot, is the most prominent source of  
72 DBC in glacial rivers (Stubbins et al., 2012; Ding et al., 2015). It has also been documented  
73 that BC atmospherically deposited onto vegetation is transferred to soil by throughflow and  
74 stemflow (Stubbins et al., 2017; Wagner et al., 2019b), and soot-derived BC deposited in  
75 watersheds is reported to be exported to rivers as DBC (Wang et al., 2016; Jones et al.,  
76 2017; 2019b). The relationships between riverine DBC parameters and land use variables  
77 showed that riverine DBC is generally less polycondensed in anthropogenically disturbed  
78 areas of the watershed, namely, urban and agricultural areas (Roebuck et al., 2018a). It was  
79 estimated that 0.027 PgC of DBC is transported annually to the global ocean (Jaffé et al.,  
80 2013). The flux has been updated to 0.018 PgC yr<sup>-1</sup> (Jones et al., 2020). The riverine DBC  
81 flux is ~10% of the annual BC production by landscape fires (Jones et al., 2019a) and is  
82 one order of magnitude larger than the annual atmospheric deposition of BC to the ocean  
83 (~0.002 PgC) (Santín et al., 2016); therefore, the transport of DBC from the soil to rivers is  
84 a key factor shaping the distributional pattern of BC on the Earth's surface. However, it

85 should be noted that a recent study, which determined the  $\delta^{13}\text{C}$  of riverine and oceanic  
86 BPCA, revealed that oceanic DBC does not predominantly originate from rivers (Wagner et  
87 al., 2019a).

88 Recent studies have reported the coupling of the spatial distribution of dissolved  
89 organic carbon (DOC) and DBC in fluvial systems with global (Jaffé et al., 2013), regional  
90 (Ding et al., 2015; Stubbins et al., 2015) and different catchment scales (Ding et al., 2013;  
91 2014; Güereña et al., 2015). Jaffé et al. (2013) suggested that the coupling of DOC and  
92 DBC is possibly due to the same diagenetic processes driving the release of DOC and DBC  
93 from soils or the ability of DOC as a mobilizing agent of DBC through hydrophobic  
94 interactions. On the other hand, decoupling of DOC and DBC was observed for temporal  
95 variations in both parameters for streams and large rivers (Wang et al., 2016; Roebuck et  
96 al., 2018b; Bao et al., 2019). Such decoupling of the two parameters was explained by  
97 different source contributions, in particular anthropogenic sources (Wang et al., 2016;  
98 Roebuck et al., 2018b), or by the delayed recovery of soil pore water DBC stocks relative  
99 to pore water DOC stocks following rainfall (Jones et al., 2019b). As such, factors  
100 controlling DBC export from soil to rivers have not been well constrained (Wagner et al.,  
101 2018).

102 This study measured DBC in streams with different types of watershed characteristics  
103 in a transitional area from a cool-temperate zone to a boreal zone in Hokkaido, northern  
104 Japan. An important aspect of the watershed compared with other studies is fire history.  
105 The watershed was not affected by landscape fire for at least 110 years, and therefore, a  
106 major source of stream DBC is probably soot deposited in the catchment rather than  
107 charcoal produced by landscape fire. The bulk dissolved organic matter (DOM) parameters

108 and their optical proxies were analyzed together with DBC quality and quantity determined  
109 using the BPCA method. The main purpose of this study was to assess the DBC export  
110 from the soil to the stream in a watershed not affected by landscape fires for the last 110  
111 years. To achieve this purpose, we evaluated the quantitative and qualitative relationships  
112 between the parameters DBC and bulk DOM and clarified the linkage between the  
113 transport mechanisms of DBC and bulk DOM.

114

## 115 **2. Materials and methods**

### 116 **2.1. Study site**

117 The studied streams are located in Hokkaido University's Uryu Experimental Forest  
118 (UREF), northern Hokkaido, Japan (Fig. 1). UREF is a part of the North Hokkaido  
119 Experimental Forest, a core site of the Japan Long Term Ecological Research Network  
120 (JaLTER). The climate is characterized by cold temperatures (minimum temperature is ca. -  
121 35°C) and heavy snowfall (200 cm or greater of maximum snowpack depth) in winter with  
122 a 4.2°C mean annual air temperature and 1467 mm mean annual precipitation (Ozawa et  
123 al., 2001). Stream discharge reaches its maximum during spring snowmelt (Ogawa et al.,  
124 2006), and the plant-growing season is restricted to a short summer (June to September)  
125 (Seki et al., 2010). Vegetation in the forest area is characterized by a cool-temperate mixed  
126 forest composed of natural broad-leaved deciduous hardwood and evergreen coniferous  
127 species with dense Sasa dwarf bamboo as understory vegetation (Ogawa et al., 2006; Seki  
128 et al., 2010). Stream water samples were collected from the Dorokawa River (D),  
129 Butokamabetsu River (B), and Akaishi River (A) in the UREF (Fig. 1). The watersheds of  
130 the Dorokawa and Butokamabetsu Rivers are almost all natural forest areas, but that of the

131 Akaishi River is partly in pastureland for dairy cattle farming (Hino et al., 2006). The  
132 upstream Dorokawa River is covered by natural forest, while there are several types of  
133 wetlands, i.e., spruce-swamp forests, open mire, and riparian wetlands, downstream  
134 (Ogawa et al., 2006).

135 There has been no record of landscape fire around the studied watershed since the  
136 establishment of the UREF in 1901. The UREF is located approximately 70 km and 160  
137 km north of Asahikawa (population, 0.4 million) and Sapporo (population, 2 million),  
138 respectively (Fig. 1). Hokkaido is known to be affected by the long-range transport of BC  
139 from eastern Eurasia to the outflow region (Zhu et al., 2019). Therefore, atmospheric  
140 deposition of soot produced by fossil fuel combustion and biomass burning in Hokkaido  
141 and/or eastern Eurasia are probable major sources of BC in the UREF.

142

## 143 **2.2. Field observations and sampling**

144 Stream water samples for DBC analysis were collected from sites D, B, and A on 10  
145 June 2011, 24 October 2011, 24 January 2012, 17 April 2012, and 10 September 2012.  
146 Additionally, water samples were collected from tributaries of the Dorokawa River, whose  
147 watersheds were covered by forest (DF) and wetlands (DW) (Fig. 1), on 24 October 2011,  
148 24 January 2012, 17 April 2012, and 10 September 2012. Approximately 10 L of water was  
149 collected in an acid-cleaned tank. Just after sampling, a water sample was transferred to the  
150 laboratory and filtered through a precombusted (450°C, 3 h) Whatman GF/F filter (0.7 µm  
151 nominal pore size), and the pH of the filtrate was adjusted to 2 with HCl. The acidified  
152 filtrate was then immediately subjected to solid-phase extraction (SPE) (1 g, Bond Elut  
153 PPL, Agilent Technologies). The SPE cartridge was immediately dried under a N<sub>2</sub> stream,

154 and the organic matter adsorbed on the SPE resin was eluted by methanol, according to  
155 Dittmar et al. (2008). The eluate was poured into a glass vial with a Teflon-lined cap and  
156 then stored in the dark in a freezer.

157 The separate water sample was also collected in an acid-cleaned 250 ml polypropylene  
158 bottle for bulk DOM analysis. The sample was filtered using a precombusted Whatman  
159 GF/F filter. The pH of filtrate was not changed. DOC concentration, fluorescence spectrum,  
160 and absorbance spectrum were measured just after filtration, while samples for total  
161 dissolved nitrogen (TDN) and nutrient ( $\text{NO}_3^- + \text{NO}_2^-$ , and  $\text{NH}_4^+$ ) analyses were stored in the  
162 dark in a freezer. Samples for bulk DOM analysis were generally collected biweekly from  
163 June 2011 to October 2012, and then, DOC concentrations were determined.

164 Precipitation data observed at the headquarter office of UREF were obtained from the  
165 JaLTER Database (<http://db.cger.nies.go.jp/JaLTER/>, Metadata ID: JaLTER-Hokkaido-  
166 Kita.16.9). Stream discharge was calculated from the recorded water level and the H-Q  
167 curve obtained at site D of the Dorokawa River and site B of the Butokamabetus River  
168 (Ogawa et al., 2006). Stream discharge was not determined during winter due to river  
169 freezing.

170

### 171 **2.3. Chemical analysis**

172 DBC analysis was performed by the BPCA method according to Dittmar (2008) with  
173 some modifications. In 2020, the methanol eluate that had been stored in a freezer in the  
174 dark, corresponding to 0.3 to 1.5 L of original water, was transferred into 2 mL glass  
175 ampoules and dried on a centrifugal vacuum evaporator (CVE-3000, EYELA) at 50°C.  
176 Then, 0.5 mL of concentrated  $\text{HNO}_3$  was added to the ampoule, and the ampoule was

177 flame-sealed and kept in an oven at 170°C for 6 h according to Nakane et al. (2017). After  
178 oxidation, HNO<sub>3</sub> was evaporated to dryness in a centrifugal vacuum evaporator at 50°C.  
179 The oxidation residue in the ampoules was redissolved in 0.2 mL of mobile phase A (4 mM  
180 tetrabutylammonium bromide, 50 mM sodium acetate, and 10% MeOH) to quantify  
181 BPCAs, namely, benzenepentacarboxylic acid (B5CA) and benzenhexacarboxylic acid  
182 (B6CA), using high-performance liquid chromatography (HPLC) with a photodiode array  
183 detector (1260 Infinity, Agilent). Analytical conditions of reverse-phase HPLC with mobile  
184 phases A and B (MeOH) were based on Dittmar (2008). Benzenetricarboxylic acids  
185 (B3CA) and benzenetetracarboxylic acids (B4CA) were not determined in this study  
186 because these compounds were shown to be produced from molecules with no condensed  
187 aromatic functionalities, such as lignin (Kappenberg et al., 2016; Bostick et al., 2018).

188 The DBC concentration was estimated from the BPCA concentrations using equation  
189 (1) based on Stubbins et al. (2015).

$$190 \quad [\text{DBC}] = 12.01 \times 0.0891 \times ([\text{B6CA} + \text{B5CA}])^{0.9175} \quad (1)$$

191 The units of [DBC] and [BPCAs] were µgC L<sup>-1</sup> and nM, respectively. The molar ratio of  
192 B6CA to B5CA (B6CA/B5CA) was calculated as the polycondensation degree of DBC  
193 (Stubbins et al., 2015; Marques et al., 2017). The analytical error determined with replicate  
194 analyses (*n*=4) of a sample from a stream in the UREF was 5.0% and 4.1% for the DBC  
195 concentration and the B6CA/B5CA ratio, respectively.

196 The DOC concentration was determined by a high-temperature catalytic oxidation  
197 method (TOC-V<sub>CSH</sub>, Shimadzu). A standard curve with a series of glucose solutions  
198 determined daily was used for calibration.

199 Absorbance analysis of DOM was carried out using a spectrophotometer (UV-1800,  
200 Shimadzu) with a 1 cm cuvette. The absorbance spectrum was determined from 250 to 800  
201 nm at 0.5 nm intervals under a medium scan speed. The absorbance spectrum of the sample  
202 was baseline-corrected by subtracting average values ranging from 700 to 800 nm from the  
203 entire spectrum. The Napierian absorption coefficient at 254 nm,  $a_{254}$  ( $\text{m}^{-1}$ ), was reported as  
204 a quantitative parameter of chromophoric DOM (CDOM). Specific UV absorbance  
205 (SUVA) was calculated by dividing the Decadic absorbance at 254 nm,  $A_{254}$  ( $\text{m}^{-1}$ ), by the  
206 DOC concentration ( $\text{mg L}^{-1}$ ) (Weishaar et al., 2003). The  $S_R$  value, the ratio of the spectral  
207 slope parameter ( $S$ ) obtained from the two regions, 275 to 295 nm ( $S_{275-295}$ ) and 350 to 400  
208 nm ( $S_{350-400}$ ), was calculated according to Helms et al. (2008).

209 Excitation-emission matrix (EEM) fluorescence was determined with a fluorometer  
210 (FluoroMax-4, Horiba) according to Tanaka et al. (2014) with some modifications. Forty-  
211 one emission scans from 290 to 550 nm taken at 2-nm intervals were acquired for  
212 excitation wavelengths between 250 and 450 nm at 5-nm intervals. The bandpass was set to  
213 5 nm for both excitation and emission monochromators, and the integration time was set to  
214 0.1 seconds. The fluorescence spectra were acquired in S/R mode. Several postacquisition  
215 steps were involved in the correction of the fluorescence spectrum, including inner filter  
216 correction with absorbance spectrum, instrumental bias correction, and the subtraction of  
217 the EEM of Milli-Q water (Murphy et al., 2010). The fluorescence unit was converted to a  
218 Raman unit (RU) with a water Raman peak (excitation=350 nm) of Milli-Q water analyzed  
219 daily (Lawaetz and Stedmon, 2009). The fluorescence index was calculated as the ratio of  
220 fluorescence intensities at 470 nm and 520 nm emissions at 370 nm excitation according to  
221 Cory and McKnight (2005). Parallel factor analysis (PARAFAC) was conducted in

222 MATLAB (Mathworks, Natick, MA) using the DOMFluor toolbox (Stedmon and Bro,  
223 2008) with 205 EEMs collected from streams in the UREF watersheds. A four-component  
224 model was validated according to Stedmon and Bro (2008). Following Coble (2007), C1,  
225 C2, and C3 (Fig. S1) were assigned as humic-like components, and C4 (Fig. S1) was  
226 identified as a protein-like component.

227 TDN and nutrient ( $\text{NO}_3^- + \text{NO}_2^-$ , and  $\text{NH}_4^+$ ) concentrations were determined using a  
228 continuous flow analyzer (Hansen and Koroleff, 1999) with a built-in wet oxidation system  
229 by potassium persulfate (QuAatro, Bran+Luebbe Analytics). The dissolved organic  
230 nitrogen (DON) concentration was determined by subtracting the inorganic nutrient  
231 concentrations from the TDN concentration. The C/N ratio of bulk DOM was calculated as  
232 the molar ratio of DOC concentration to DON concentration.

233

#### 234 **2.4. Statistical analysis**

235 The differences in DBC parameters, i.e., the DBC contribution of DOC (DBC/DOC, %)  
236 and the B6CA/B5CA ratio, among watersheds were examined. The Shapiro-Wilk test  
237 indicated that the DBC parameters in the three watersheds followed a normal distribution  
238 (Table S1). However, due to the small number of samples, we used a nonparametric  
239 Wilcoxon rank sum test as well as a parametric t-test for the comparison of DBC  
240 parameters. Spearman's rank correlation coefficient and Kendall's rank correlation  
241 coefficient were determined between DBC and the bulk DOM parameters. The results of  
242 Kendall's rank correlation test can be found in Supplementary Tables and Figures.  
243 Spearman's rank correlation coefficient and Kendall's rank correlation coefficient were also  
244 determined for DBC and DOC vs. discharge and precipitation. The precipitation data

245 obtained from April to October were used for the correlation analyses to eliminate snowfall.  
246 Since many values of precipitation were 0 during the observation of DOC, correlation  
247 coefficients were not determined between DOC and precipitation. A confidence level ( $\alpha$ ) of  
248 95% was used for all statistics. The Wilcoxon rank sum test, t-test, Spearman's rank  
249 correlation test, and Kendall's rank correlation test were carried out with R (version 3.5.1).

250

### 251 **3. Results**

#### 252 **3.1. Temporal variability of DOC and DBC in streams**

253 Figure 2 shows temporal variations in the DOC concentration, DBC concentration, and  
254 B6CA/B5CA ratio value at sites D, B, and A with precipitation and stream discharge. The  
255 DOC concentration at site D, which was partly covered by wetlands, ranged from 1.0 to 5.4  
256 mgC L<sup>-1</sup> (Fig. S2). The concentrations were generally higher than those at site B (0.5–4.8  
257 mgC L<sup>-1</sup>), where the watershed was covered by natural forest, and site A (0.8–7.1 mgC L<sup>-1</sup>),  
258 where the watershed was used for pastureland (Fig. S2). The DOC concentrations at site A  
259 tended to be slightly higher than those at site B. Temporal variations in the DOC  
260 concentration were similar among the three sites. Stream discharge showed a broad  
261 maximum with some spikes in the spring due to snowmelt. The DOC concentration was not  
262 high during snowmelt (Fig. 2) and was not significantly correlated with stream discharge  
263 ( $p=0.18$ ,  $n=25$  for site D;  $p=0.70$ ,  $n=25$  for site B; Spearman's rank correlation; Fig. S3).  
264 Peaks of the DOC concentration were observed on 15 August 2011 and 10 September  
265 2012. Both peaks corresponded to small peaks of stream discharge with precipitation (Fig.  
266 2 and Fig. S3).

267 The DBC concentrations at the three sites were highest on 10 September 2012 when the  
268 DOC concentrations peaked (Fig. 2). The DBC concentrations at site D (0.052–0.304 mgC  
269 L<sup>-1</sup>) were always higher than those at sites B (0.026–0.166 mgC L<sup>-1</sup>) and A (0.033–0.129  
270 mgC L<sup>-1</sup>), while the concentrations were similar between sites B and A throughout the  
271 observations (Fig. S4). The DBC concentration was not significantly correlated with stream  
272 discharge ( $p=0.42$ ,  $n=4$  for site D;  $p=0.92$ ,  $n=4$  for site B, Spearman's rank correlation; Fig.  
273 S5) or precipitation ( $p=0.33$ ,  $n=4$  for site D;  $p=0.75$ ,  $n=4$  for site B;  $p=0.33$ ,  $n=3$  for site A;  
274 Spearman's rank correlation; Fig. S6). The B6CA/B5CA ratio values ranged from 0.19 to  
275 0.31, from 0.10 to 0.19, and from 0.12 to 0.22 at sites D, B, and A, respectively (Fig. 2 and  
276 Fig. S4). The B6CA/B5CA ratio value was always highest at site D and lowest at site A,  
277 except on 24 October 2011. The ratios at the three sites did not show a clear trend on 10  
278 September 2012 when the DBC concentration was highest, even though the ratios at sites B  
279 and A on that observation day were highest. The ratio was not significantly correlated with  
280 stream discharge ( $p=0.92$ ,  $n=4$  for site D;  $p=0.75$ ,  $n=4$  for site B; Spearman's rank  
281 correlation; Fig. S5) or precipitation ( $p=0.75$ ,  $n=4$  for site D;  $p=0.33$ ,  $n=4$  for site B;  $p=1$ ,  
282  $n=3$  for site A; Spearman's rank correlation; Fig. S6).

283 Figure 3 shows the relationships between the DBC concentration and DOC  
284 concentration as well as  $a_{254}$  for all samples collected from all sites (i.e., sites D, B, A, DF,  
285 and DW). The DBC and DOC concentrations were linearly correlated for all samples  
286 ( $[\text{DBC}] = 0.054 \times [\text{DOC}] - 0.022$ ,  $r^2=0.95$ ,  $p<0.01$ ,  $n=21$ ). On the other hand, DBC/DOC  
287 (%) was significantly different between the wetland area ( $4.8 \pm 0.7\%$  for D and DW) and  
288 forest area ( $4.3 \pm 0.5\%$  for B and DF) and pastureland area ( $3.5 \pm 0.9\%$  for A) ( $p<0.05$  for t-  
289 test and Wilcoxon rank sum test; Table S2 and Fig. S7). The contribution was not

290 significantly different between the forest area and pastureland area ( $p=0.49$  and  $0.57$  for t-  
291 test and Wilcoxon rank sum test, respectively; Table S2 and Fig. S7). The DBC  
292 concentration was also linearly correlated with  $a_{254}$  ( $[DBC] = 0.0053 \times [a_{254}] - 0.0065$ ,  
293  $r^2=0.97$ ,  $p<0.01$ ,  $n=21$ ) and with humic-like components ( $p<0.01$ ) but not with a protein-  
294 like component ( $p=0.08$ ) obtained by EEM-PARAFAC (Fig. S8).

295

### 296 **3.2. Relationships among qualitative parameters of DBC and bulk DOM**

297 The polycondensation degree of DBC, as determined by the B6CA/B5CA ratio, was  
298 significantly different between the wetland area ( $0.25 \pm 0.05$  for D and DW) and forest area  
299 ( $0.16 \pm 0.05$  for B and DF) and pastureland area ( $0.13 \pm 0.04$  for A) ( $p<0.01$  for t-test and  
300 Wilcoxon rank sum test; Table S2 and Fig. S7). The ratio was not significantly different  
301 between the forest area and pastureland area ( $p=0.43$  and  $0.46$  for t-test, respectively; Table  
302 S2 and Fig. S7).

303 The relationships among the qualitative parameters of DBC and bulk DOM were  
304 determined for all samples collected from all sites (Fig. 4, Table S3, and Fig. S9).  
305 DBC/DOC (%) was significantly positively correlated with SUVA, i.e., the ratio of CDOM  
306 to DOC ( $r_s=0.74$ ,  $p<0.01$ ,  $n=21$ , Spearman's rank correlation). A significant positive  
307 correlation was also evident between DBC/DOC and B6CA/B5CA ( $r_s=0.67$ ,  $p<0.01$ ,  $n=21$ ,  
308 Spearman's rank correlation). DBC/DOC was also significantly correlated with  $S_R$  ( $r_s=-$   
309  $0.66$ ,  $p<0.01$ ,  $n=21$ , Spearman's rank correlation) and the C/N of bulk DOM ( $r_s=0.53$ ,  
310  $p<0.05$ ,  $n=21$ , Spearman's rank correlation) but not with the fluorescence index ( $p=0.07$ ,  
311  $n=21$ , Spearman's rank correlation) (Fig. S9). The B6CA/B5CA ratio value was  
312 significantly positively correlated with the C/N of bulk DOM ( $r_s=0.60$ ,  $p<0.01$ ,  $n=21$ ,

313 Spearman's rank correlation) and SUVA ( $r_s=0.54$ ,  $p<0.05$ ,  $n=21$ , Spearman's rank  
314 correlation) but was negatively correlated with  $S_R$  ( $r_s=-0.51$ ,  $p<0.05$ ,  $n=21$ , Spearman's rank  
315 correlation) and fluorescence index ( $r_s=-0.66$ ,  $p<0.01$ ,  $n=21$ , Spearman's rank correlation).  
316 The B6CA/B5CA ratio value was also significantly correlated with the DBC concentration  
317 ( $r_s=0.68$ ,  $p<0.01$ ,  $n=21$ , Spearman's rank correlation), DOC concentration ( $r_s=0.66$ ,  $p<0.01$ ,  
318  $n=21$ , Spearman's rank correlation), and  $a_{254}$  ( $r_s=0.69$ ,  $p<0.01$ ,  $n=21$ , Spearman's rank  
319 correlation) (Fig. S9).

320

## 321 **4. Discussion**

### 322 **4.1. Stream DBC characteristics and its origin**

323 The DBC contribution to the DOC (%) ranged from  $3.5\pm 0.9\%$  for pastureland to  
324  $4.8\pm 0.7\%$  for wetlands in streams of the UREF watersheds and was smaller than the  
325  $10.6\pm 0.7\%$  global average (Jaffé et al., 2013). DBC contributions have recently been  
326 determined to significantly differ among biomes (Jones et al., 2020), and the contributions  
327 observed in streams in the UREF watersheds were similar to those in temperate forests  
328 ( $4.4\pm 2.5\%$ ) and boreal forests ( $5.4\pm 1.1\%$ ) (Jones et al., 2020).

329 It has been documented that DBC is produced from not only fresh charcoal but also old  
330 charcoal (Abiven et al., 2011; Wagner et al., 2017), and DBC has been continuously  
331 released into rivers for a long time through the degradation of historically accumulated soil  
332 BC (Dittmar et al., 2012; Marques et al., 2017). It is possible that an ancient forest fire  
333 event contributed to the DBC in the studied streams, even though the sites were unburned  
334 for at least 110 years.

335 Recent studies have indicated that atmospheric deposition of BC to watersheds is a  
336 source of DBC in soil water (Santos et al., 2017) as well as riverine DBC (Jones et al.,  
337 2017; 2019b). It has also been documented that BC atmospherically deposited onto  
338 vegetation is transferred to riverine catchments by throughflow and stemflow (Stubbins et  
339 al., 2017; Wagner et al., 2019b). It is interesting to note that recent studies have suggested  
340 that the DBC derived from soot is less polycondensed than that from charcoal produced by  
341 a wildfire (Ding et al., 2015; Roebuck et al., 2018a; Coppola et al., 2019). Ding et al.  
342 (2015) reported that the DBC in the water soluble fraction extracted from atmospheric dust  
343 was less polycondensed than wildfire-derived DBC, and Roebuck et al. (2018a) suggested  
344 that atmospheric deposition of soot or polyaromatic hydrocarbons contributed to the less  
345 polycondensed DBC signature in streams in the urban area of the Altamaha watershed. A  
346 negative relationship between the polycondensation degree, namely, B6CA/B5CA, in  
347 riverine DBC and the fossil fuel BC deposition rate integrated in corresponding  
348 subcatchments was also found in the Amazon River (Coppola et al., 2019). The  
349 B6CA/B5CA ratio of the DBC observed in streams in the UREF watersheds was generally  
350 lower than that of the DBC in an area of the Amazon River subcatchment (B6CA/B5CA of  
351 0.26), which is the most affected by the atmospheric deposition of BC produced by fossil  
352 fuel combustion in addition to charcoal produced by landscape fires. The B6CA/B5CA  
353 ratio of the DBC in streams of the UREF was also generally lower than the ratio of the  
354 water-soluble fraction extracted from atmospheric dust (B6CA/B5CA of 0.32, Ding et al.,  
355 2015). Additionally, the DBC concentration was not significantly correlated with  
356 precipitation for the UREF watersheds (Fig. S6), implying that soot and DBC in  
357 precipitation are unlikely to contribute directly to DBC in the streams. These pieces of

358 evidence suggest that atmospheric deposition of soot on the soil of the catchment and  
359 subsequent mobilization and transport of soot-derived BC to the stream are probably the  
360 major sources of DBC in the UREF watersheds.

361

#### 362 **4.2. Factors controlling DBC export from soils to streams**

363 The DOC and DBC concentrations were not significantly correlated ( $p>0.05$ ) with  
364 stream discharge (Fig. 2, Figs. S3 and S5). Positive relationships between river (stream)  
365 discharge and DOC concentration (e.g., Holmes et al., 2008; Wilson et al., 2013) and DBC  
366 concentration (Dittmar et al., 2012; Stubbins et al., 2015; Wagner et al., 2015), indicative of  
367 flushing of high levels of DOC and DBC from upper soil horizons under high flow  
368 conditions, have often been observed. On the other hand, in addition to the discharge,  
369 antecedent moisture conditions were determined to control the DOC concentration under  
370 high flow conditions (Inamdar et al., 2008; Oswald and Branfireun, 2014). The different  
371 effects of antecedent precipitation on riverine DOC and DBC concentrations due to the  
372 quick and slow rebound of porewater DOC and DBC concentrations after precipitation,  
373 respectively, were also noted for the Amazon River (Jones et al., 2019b). In our study, two  
374 spikes of DOC concentration were found in the small peaks of discharge with precipitation  
375 events after relatively long nonprecipitation periods (Fig. 2). These results suggest that  
376 spikes in the DOC and DBC concentrations observed in the UREF watersheds were  
377 possibly affected by antecedent precipitation. Further observations are needed to determine  
378 the factors controlling temporal variations in DOC and DBC concentrations in the UREF  
379 watersheds.

380 The DBC concentration was linearly related to the DOC concentration, irrespective of  
381 differences in seasons and watershed characteristics (Fig. 3a), even though the DBC/DOC  
382 (%) was different among the watersheds with different characteristics. Linear relationships  
383 between the two parameters have also been observed from the watershed scale to the global  
384 scale (Jaffé et al., 2013; Ding et al., 2013; 2014; 2015; Stubbins et al., 2015; Wagner et al.,  
385 2015). On the other hand, decoupling of the DBC concentration and DOC concentration,  
386 probably due to the different source contributions, particularly anthropogenic source  
387 contributions (Wang et al., 2016; Roebuck et al., 2018b), or the divergent effects of soil  
388 properties, temperature, rainfall, and aerosol deposition (Bao et al., 2019; Jones et al.,  
389 2019b), has also been reported. Interestingly, it has been pointed out that charcoal in soils  
390 supplies DBC to channels at baseflow, and atmospherically deposited soot contributes as an  
391 additional source of riverine DBC during high-flow regimes (Roebuck et al., 2018b; Jones  
392 et al., 2019b). Such a shift in DBC sources to channels was suggested to be a reason for  
393 seasonal decoupling of DOC and DBC (Roebuck et al., 2018b; Jones et al., 2019b). The  
394 major source of DBC in the stream in the UREF watersheds during the baseflow as well as  
395 spikes of the discharge was possibly mobilization from the soot deposited on the soil in the  
396 watersheds but was not direct contribution of soot and DBC in precipitation (Fig. S6).  
397 Therefore, the reason for the linear relationship between the DBC and DOC concentrations  
398 observed in this study might be the result of the coupled transport of soot-derived DBC and  
399 DOC from the soil to the stream.

400 The DBC/DOC (%) and B6CA/B5CA ratio values in streams with wetlands in the  
401 watersheds were significantly higher than those in streams in which watersheds were  
402 completely covered by forests and partly covered by pastureland (Fig. S7). In addition, a

403 positive correlation was evident between the two parameters (Fig. 4b). A significant  
404 positive correlation was also observed between DBC/DOC and B6CA/B5CA in small  
405 watersheds in the southeastern part of China and was considered a result of  
406 photodegradation of DBC (Bao et al., 2019). The streams observed in this study were near  
407 headwater regions that are heavily forested (Fig. 1), suggesting that a process other than  
408 photodegradation must be causing changes in DBC/DOC and B6CA/B5CA in this study.

409       Roebuck et al. (2018a) found that the DBC concentration and BPCA ratio in river water  
410 were positively correlated with wetland coverage but were negatively correlated with urban  
411 land use in the Altamaha River, a large subtropical watershed. Such relationships were  
412 considered to be the result of changes in the DBC sources along the river from fire-derived  
413 charcoal in wetlands to fossil fuel combustion-derived soot in urban areas (Roebuck et al.,  
414 2018a). Since the major source of DBC in the UREF watersheds is probably soot deposited  
415 on the soil of the watershed, the differences in the source may not solely account for the  
416 differences in DBC/DOC and B6CA/B5CA among the watersheds in the UREF. Kothawala  
417 et al. (2012) showed that larger aromatic compounds can be preferentially adsorbed in  
418 mineral-rich soils. Thus, a fraction having relatively highly polycondensed DBC mobilized  
419 from soot deposited onto soil may be preferentially retained in mineral-rich soils in forested  
420 and pastureland areas, resulting in a lower polycondensation degree of riverine DBC in  
421 forested and pastureland areas than in wetland areas.

422       The linear relationship between the DBC concentration and DOC concentration has  
423 been interpreted as the result of similar diagenetic processes driving the release of DOC and  
424 DBC from soils or intermolecular associations between DOC and DBC through  
425 hydrophobic interactions (Jaffé et al., 2013). In addition to the linear relationship between

426 the two parameters, we found significant correlations between the polycondensation degree  
427 of DBC (B6CA/B5CA) and the qualitative parameters of bulk DOM in the UREF  
428 watersheds (Fig. 4). SUVA is positively related to the aromaticity of DOM (Weishaar et al.,  
429 2003), while  $S_R$  is negatively related to the molecular weight of DOM (Helms et al., 2008).  
430 Therefore, positive and negative correlations between B6CA/B5CA and SUVA and  $S_R$ ,  
431 respectively, indicate that the environmental dynamics of polycondensed DBC are similar  
432 to those of high-molecular-weight aromatic DOM. The polycondensation degree of DBC  
433 was also positively correlated with the C/N of bulk DOM but negatively correlated with the  
434 fluorescence index of bulk DOM. A high value of C/N and a low value of the fluorescence  
435 index indicate a higher plant origin of DOM (McKnight et al., 1997; 2001). In conclusion,  
436 the qualitative relationships between DBC and DOC observed in this study indicate that the  
437 transfer mechanism from soils to streams, namely, the release and subsequent adsorption  
438 and desorption processes, is similar between DBC derived from soot deposited on soil and  
439 higher plant-derived, high-molecular-weight aromatic DOM. This conclusion is supported  
440 by the significant positive correlation between SUVA and DBC/DOC (Fig. 4a).

441 The results of controlled DBC leaching experiments using charcoal and wildfire-  
442 influenced soil samples did not determine the effect of DOM as a mobilizing agent through  
443 hydrophobic interactions (Wagner et al., 2017). Wagner et al. (2017) also determined the  
444 octanol-water partition coefficients of modeled DBC and noted that a considerable portion  
445 of the DBC pool that has been quantified in aquatic environments is not truly dissolved.  
446 Knowledge of “DBC speciation” will help to better understand the biogeochemical  
447 mechanisms that control the transfer of BC from soils to streams. The soot from urban dust  
448 probably releases more DBC than charcoal produced from onsite soils, since the

449 polycondensation degree of DBC dissolved from soot is lower than that from charcoal  
450 (Ding et al., 2015). Therefore, the soot/charcoal ratio in soils is possibly a factor that  
451 controls the mobility of DBC and shapes the coupling/decoupling of riverine DBC and  
452 DOC. DBC leaching experiments with charcoal as well as soils affected by atmospheric  
453 deposition of soot may clarify specific mechanisms of DBC leaching from various types of  
454 BC in soils.

455

## 456 **5. Conclusions**

457 This study investigated the quantitative and qualitative relationships among DBC and DOC  
458 in streams in a transitional area from a cool-temperate zone to a boreal zone in which  
459 catchments were not affected by landscape fire for at least 110 years. The relatively low  
460 polycondensation degree of DBC found in this study implies that atmospherically deposited  
461 soot on the soil in the catchment, which can preferentially release poorly polycondensed  
462 DBC, is an important source of riverine DBC and is one of the important processes in the  
463 global BC cycle. A strong linear relationship was found between the DOC and DBC  
464 concentrations, irrespective of the differences in watershed characteristics and seasons.

465 Furthermore, qualitative relationships were evident between DBC and bulk DOM. These  
466 quantitative and qualitative relationships suggest that for landscapes with dominant inputs  
467 of soot-derived BC, the transfer mechanisms of natural DOC and DBC are closely linked,  
468 while this linkage for wildfire charcoal-derived DBC has been shown to be more complex.

469

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476

477

478 **Author contributions**

479 Y.Y. contributed to the design of the research. Y.Y., N.Y., and H.S. conducted field  
480 observations and water sampling. D.K. and N.Y. performed experiments in the laboratory.  
481 Y.Y., D.K., and N.Y. analyzed the results. Y.Y. prepared the manuscript with inputs from  
482 H.S.

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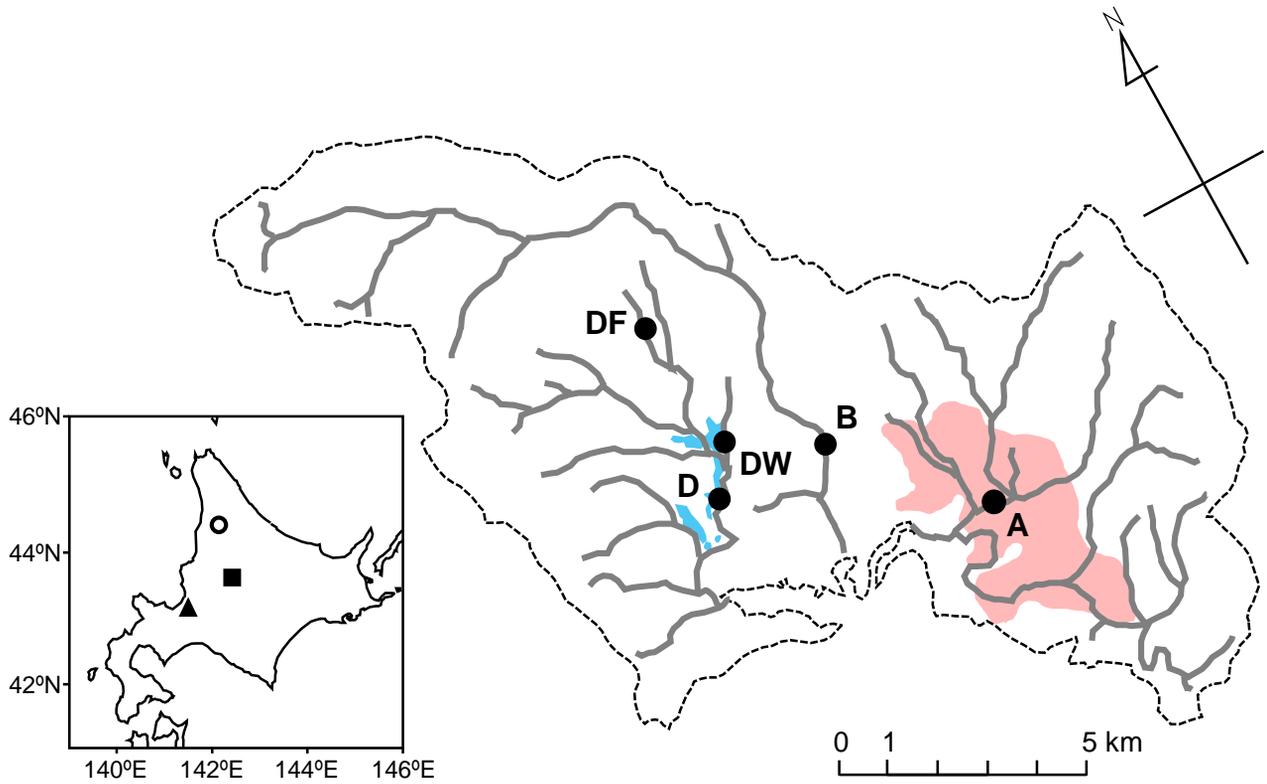


Figure 1. Map of the sampling sites and their watersheds. Blue and red shadows in watersheds indicate wetlands and pastureland, respectively. Open circle, closed triangle, and closed square represent Hokkaido University's Uryu Experimental Forest (UREF), Sapporo, and Asahikawa, respectively. D, B, and A represent sampling sites of the Dorokawa River, Butokamabetsu River, and Akaishi River, respectively. DF and DW represent sampling sites of tributaries of the Dorokawa River, whose watersheds were covered by forest and wetlands, respectively.

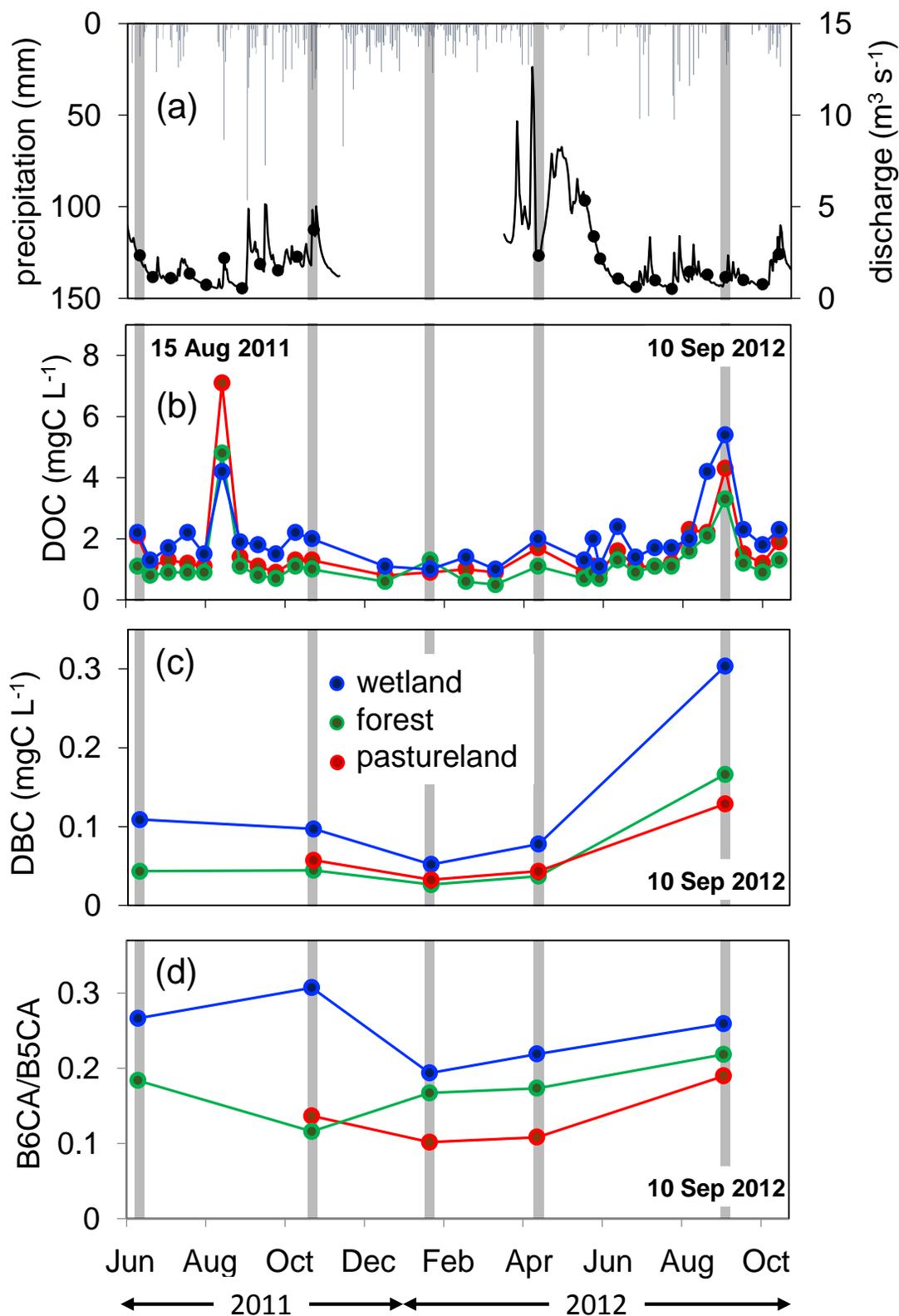


Figure 2. Temporal variations in precipitation (a); stream discharge at the Butokamabetsu River site (B) (a); DOC concentration at the Dorokawa River (D), B, and Akaishi River sites (A) (b); DBC concentration at sites D, B, and A (c); and B6CA/B5CA at sites D, B, and A (d). Black closed circles on stream discharge (a) and gray hatches in all panels (a–d) indicate sampling days of DOC and DBC, respectively. Blue, green, and red symbols indicate D (wetland), B (forest), and A (pastureland) sites, respectively.

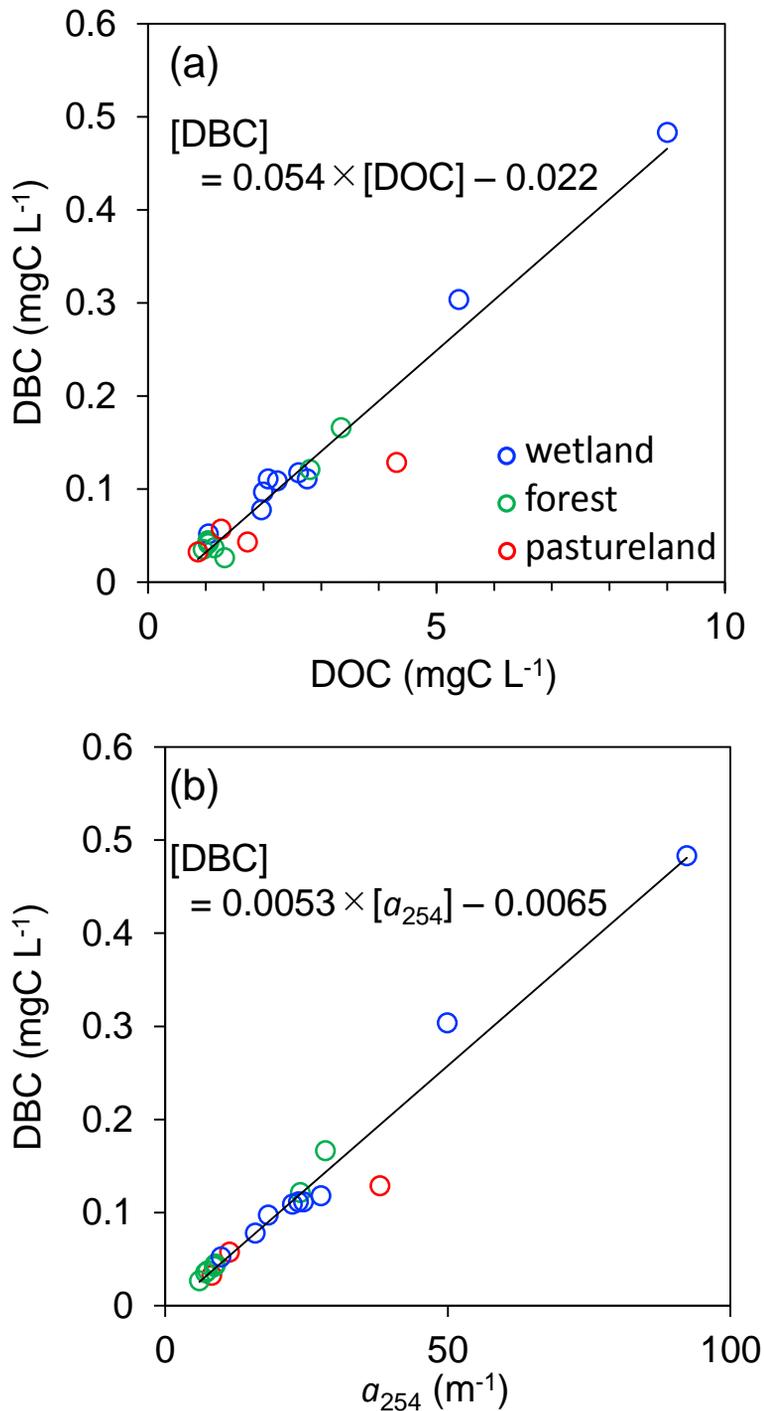


Figure 3. Relationships between DBC concentration and DOC concentration (a) and  $a_{254}$  (b) for all samples collected from all sites. For the DBC–DOC regression (a), standard error of the slope = 0.003; standard error of the intercept = 0.009;  $r^2 = 0.95$ ;  $n = 21$ ;  $p < 0.01$ . For the DBC– $a_{254}$  regression (b), standard error of the slope = 0.0002; standard error of the intercept = 0.0066;  $r^2 = 0.97$ ;  $n = 21$ ;  $p < 0.01$ . Blue, green, and red symbols indicate the wetland area (Dorokawa River and wetland tributary of Dorokawa River), forest area (Butokamabetsu River and forested tributary of Dorokawa River), and pastureland area (Akaishi River), respectively.

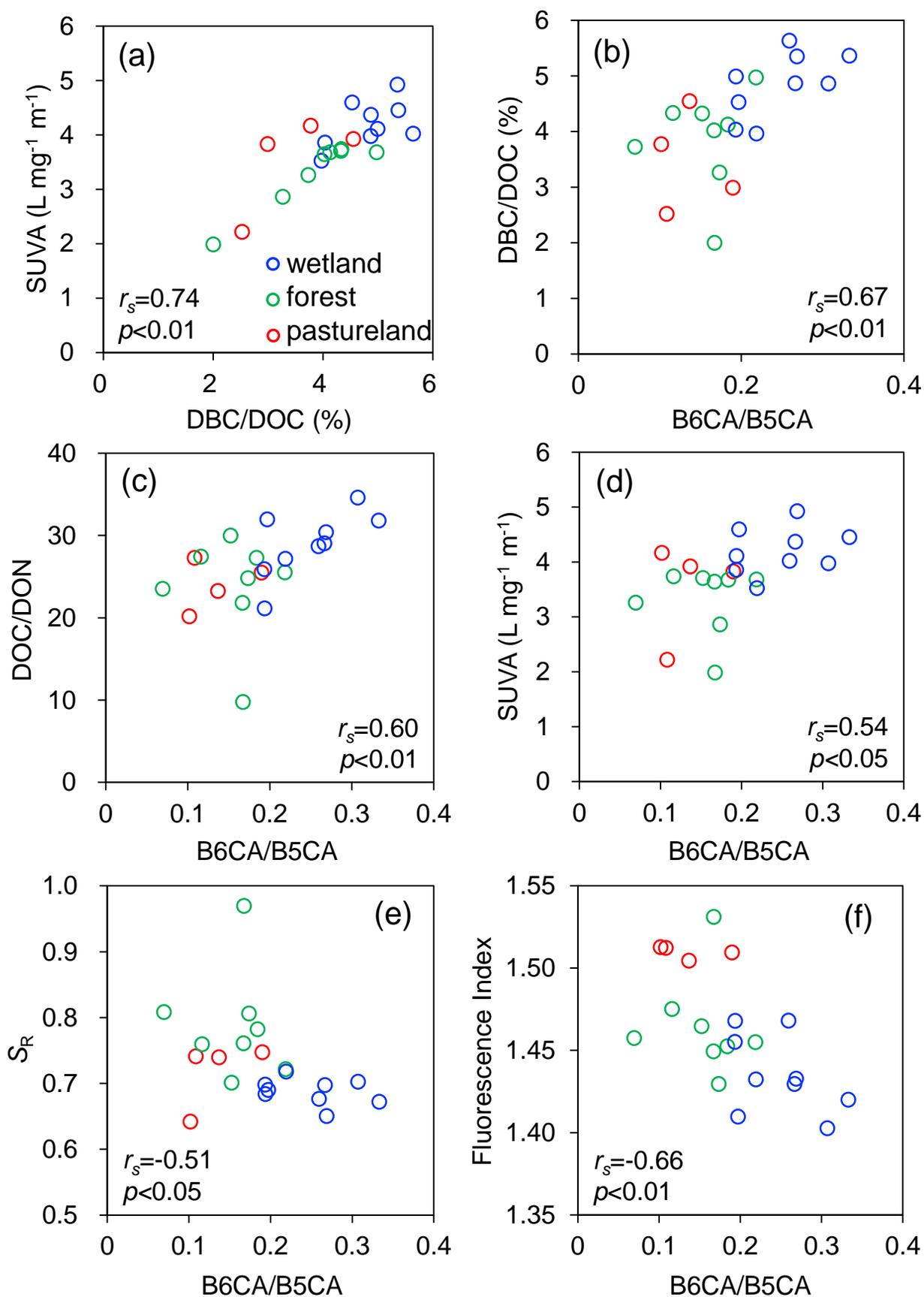


Figure 4. Relationships among qualitative parameters of DBC and bulk DOM. SUVA vs. DBC/DOC (a), DBC/DOC vs. B6CA/B5CA (b), DOC/DON vs. B6CA/B5CA (c), SUVA vs. B6CA/B5CA (d),  $S_R$  vs. B6CA/B5CA (e), and fluorescence index vs. B6CA/B5CA (f).  $r$  and  $p$  values are the results of Spearman's rank correlation test. A confidence level ( $\alpha$ ) of 95% was used. Blue, green, and red symbols indicate the wetland area (Dorokawa River and wetland tributary of Dorokawa River), forest area (Butokamabetsu River and forested tributary of Dorokawa River), and pastureland area (Akaishi River), respectively.