

1 CDOM variations in Finnish lakes and rivers between 1913 and 2014

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7

8 *Abstract*

9 In lakes and rivers, the concentrations of dissolved organic carbon (DOC) and coloured dissolved
10 organic matter (CDOM) are closely related. We analysed three large spectrophotometer data sets
11 of Finnish inland waters from the years 1913–1914, 1913-1931 and 2014 for long-term changes
12 in optical properties. The first data set consists of absorption spectra in the band 467-709 nm of
13 212 filtered water samples, the second one contains 11-19 years of data for seven rivers, and the
14 third one contains 153 sites with high resolution spectra over the band 200-750 nm. These data
15 sets were supplemented with more recent monitoring data of DOC. The sites represent typical
16 optical inland water types of northern Europe. The results did not show any consistent large-scale
17 changes in CDOM concentrations over the 101-year time period. The statistics of the absorption
18 coefficients in 1913 and 2014 were almost identical, at 467 nm they were $1.9 \pm 1.0 \text{ m}^{-1}$ in 1913
19 and $1.7 \pm 1.2 \text{ m}^{-1}$ in 2014), and the shape of the CDOM absorption spectrum was unchanged,
20 proportional to $\exp(-S \cdot \lambda)$, $S = 0.011 \text{ nm}^{-1}$ and λ is wavelength. Catchment properties, primarily
21 lake and peat-land percentages, explained 50% of the variation of CDOM concentration in the
22 lakes, and hydrological conditions explained 50 % of the variation of CDOM in the rivers. Both

23 illustrate the importance of catchments and hydrology to CDOM concentrations of boreal inland
24 waters.

25

26 *Introduction*

27 In natural waters, in addition to the pure water itself, the optically active substances (OAS) are
28 coloured dissolved organic matter (CDOM; also called chromophoric dissolved organic matter),
29 chlorophyll *a*, and suspended matter. All these OAS absorb light, while chlorophyll *a* and
30 suspended matter also scatter light. When water samples are filtered, only CDOM remains. For
31 higher CDOM concentrations, shorter wavelengths of sunlight are absorbed more and the peak
32 wavelength of the light spectrum is shifted towards brown. This is how the colour of natural
33 waters, the degree of brownification, is connected to CDOM, or “yellow substance” as it has
34 often been called in early literature (Hutchinson, 1957). Because of its influence on the optical
35 properties of water, CDOM has an important role in the heat budget, water usability, and
36 biological production of inland waters. In addition, CDOM may to some extent also support the
37 growth of bacteria (Tranvik, 1988; Tilonen et al., 1992; Steinberg et al., 2006) and algae (Arvola
38 and Tilonen, 1998), and further influence the nutrition of higher trophic levels as well (Jones et
39 al. 1999; Jansson et al., 2007; Taipale et al., 2016). Studies also suggest that CDOM may affect
40 algal growth indirectly through its direct toxic effects and complexing metals (e.g. Nagai et al.,
41 2006), and by changing the quantity and quality of photosynthetically active radiation (Eloranta
42 1978; Karlsson et al. 2009).

43

44 Dissolved organic carbon (DOC) is closely related to CDOM (Jones, 1992; Karlsson et al., 2009;
45 Arvola et al., 2014). DOC and CDOM are known to be sensitive, in particular, to changes in the

46 land-cover including topography and land use in the drainage basin (Kortelainen and Saukkonen,
47 1998; Weyhenmeyer and Karlsson, 2009; Arvola et al. 2016), and to hydrological conditions
48 (Erlandsson et al., 2008; Arvola et al., 2010). But also other factors such as changes in air
49 temperature (Freeman et al., 2001), atmospheric carbon dioxide (Freeman et al., 2004) and
50 sulphur concentration, together with consequent changes in soil buffering capacity and ionic
51 strength (Monteith et al., 2007), have been suggested to influence DOC and CDOM levels.
52 Additionally, light absorption properties of lake water and its CDOM concentration can also be
53 influenced by ferric iron (Xiao et al., 2013).

54
55 The longest (>100 years) historical data series of optical properties of natural waters concern the
56 depth of visibility or the Secchi depth, which is merely an index of water clarity and difficult to
57 measure accurately and repeatedly. More recent field observations have suggested that during the
58 last 10-40 years DOC concentration and water colour have increased in vast areas of Europe and
59 North America (Monteith et al., 2007; Sobek et al., 2007). At the same time also increasing iron
60 concentrations in surface waters have been reported from Europe (Xiao et al., 2013; Sarkkola et
61 al., 2013). These recent increases seem to be rather consistent, but reliable and over half a century
62 long data series of DOC and CDOM have unfortunately been missing. Only indirect data series
63 with relatively low accuracy, such as lake sediments (Cunningham et al., 2011), are longer than
64 50 years, and, therefore, it has not been known how the optical properties of inland waters have
65 changed over longer periods of time.

66
67 In this paper we present results based on accurate absorbance measurements of two snapshot field
68 campaigns and monthly river samples from 1913 and 2014. Our results show that the present

69 CDOM concentrations of Finnish lakes and rivers are surprisingly similar to those a century ago.
70 The old data sets of Witting (1914a, 1914b) and Holmberg (1935) are unique because at that time
71 the first photometers had just recently been produced, and according to our knowledge nobody
72 had yet applied these instruments for any similar large-scale field study on optical properties of
73 inland waters.

74

75 *Material and methods*

76 In 1913–1914 Witting (Witting, 1914b) collected water samples for spectrophotometer
77 measurements at 212 sites in Finnish inland waters (**Fig. 1; see Table 1**). Filtered samples were
78 used for the measurements. Witting (Witting, 1914b) obtained reliable spectra for 208 out of his
79 212 sites in the summer 1913; in summer 2014 we repeated the measurements at 153 sites. For
80 the final data set (see Table 1) we used data from the sites, which were sampled and analysed
81 both in 1913 and 2014. The total number of sampling sites was then 151. In addition, there were
82 12 sampling sites, which could not be well-defined as either a lake or a river, and therefore, for
83 the separate analysis of lakes and rivers, the number of combined sampling sites was 139.
84 Witting (Witting, 1914a) provided also monthly data from summer 1913 to summer 1914 from
85 six river mouths (Table 1). Based on these two data sets (Witting1913 and Witting1913-14) and
86 our data from 2014, we assessed the net changes in the CDOM abundance and CDOM absorption
87 spectra that have taken place during this 101-year period. The original Witting's data and our
88 2014 data are abbreviated as W1913 and W2014 data, respectively.

89

90 The third historical data set we analysed was given by Holmberg (1935), with seven rivers
91 draining into the Bay of Bothnia, the northernmost basin of the Baltic Sea (Tables 1 and 2). This

92 data was taken in order to better understand the temporal variability of CDOM, which is
93 necessary when results based on snapshot sample sets are interpreted. Holmberg (1935) measured
94 absorbance of water once a month at six different wavelengths between 451-681 nm. Her data
95 comprised of 11 (1921-1931) to 19 (1913-1931) years of measurements, and therefore her data
96 set provides additional information on the temporal variation of CDOM between Witting's case
97 and ours. Finally, more recent data sets on TOC of the Finnish Environment Institute (SYKE)
98 were collected for the same purpose (Table 1). Those data include 15 river sites and 36 lake sites,
99 and covers the time period from 1995 to 2014. The TOC values were converted to CDOM values
100 using a conversion factor obtained from the data set of Lake Pääjärvi (see Table 1). For the 51
101 sites the 95% confidence interval (CI) was calculated, and then the corresponding CI was also
102 estimated for these sites of W1913 and W2014 data. The aim was to better understand the
103 variation of CDOM between different summer seasons in the study sites. The site selection was
104 random except that all major rivers draining into the Baltic Sea were included. We assumed that
105 CDOM variation would be similar today to what it was 101 years ago.

106
107 Supplementary data sets on hydrological conditions of river basins as well as on land-use of lakes
108 and rivers were also collected (Table 1). In addition, in August 2014 we determined the
109 absorbance properties of 30 small lakes in the vicinity of the Lammi Biological Station to obtain
110 an independent data set for calculating a conversion factor for CDOM based on the absorbance
111 measurements at 467 nm instead of 420 nm (for details, see below).

112

113 **Absorption measurements**

114 Absorption of a light beam in natural waters follows Beer's law: the intensity of light decreases
115 with distance proportional to the absorption coefficient $a = a(\lambda)$, where λ is wavelength. This
116 coefficient depends on the concentrations of optically active substances and is here defined as the
117 inverse of the distance where the light intensity has decreased to 1/10 of its original intensity. The
118 absorption spectrum of a filtered water sample can be written as

119

$$120 \quad a(\lambda) = a_w(\lambda) + a_y(\lambda_0) \exp[-S(\lambda - \lambda_0)] + a_R(\lambda) \quad (1)$$

121

122 where a_w is the absorption coefficient of pure water (Smith & Baker, 1981), $a_y(\lambda_0)$ is the CDOM
123 absorption coefficient at $\lambda_0 \sim 400$ nm, with λ_0 as a reference wavelength, $S \sim 0.01 \text{ nm}^{-1}$ is the
124 shape factor of the CDOM absorption spectrum, and a_R is the residual. The residual is due to
125 leakages in filtering, colloids, and errors in the measurement system itself. Here the residual is
126 taken as noise, and the reference wavelength is $\lambda_0 = 420$ nm according to the standards used in
127 many countries (Keskitalo & Salonen, 1994; Weyhenmeyer 2008).

128

129 Witting's (Witting, 1914b; Witting, 1914a) sampling sites were distributed all over Finland from
130 south to north and east to west. Sample bottles were sent to local field assistants, who took
131 samples at or close to a fixed date, and who then sent the bottles to Helsinki for the analyses. In
132 2014 local people and organisations also helped in sampling, and sent the samples kept in cold
133 and dark to the laboratory of Lammi Biological Station where the absorbance spectra were
134 measured.

135

136 **CDOM and water colour**

137 The colour of the water, B (unit mg Pt L⁻¹), can be estimated from the absorption curve of a given
 138 spectrophotometer using a calibration formula. Here we take

139

$$140 \quad B = F \cdot a_y(420 \text{ nm}) \quad (2)$$

141

142 where F is a conversion factor ($F = 33.762 \cdot A_{420\text{nm}} + 0.0633$ mg Pt L⁻¹ m⁻¹) based on the calibration
 143 curve of absorbance ($A_{420\text{nm}}$) against Pt-Co standards (APHA). In limnology the colour quantity
 144 B is widely used and therefore shown here in the figures. It transforms to absorption coefficient
 145 just by dividing by the calibration factor as shown in Eq. (2).

146

147 The CDOM absorption spectrum (see Eq.1) has three parameters: λ_0 , $a_y(\lambda_0)$ and S . Two of them
 148 are independent providing the CDOM level and shape of the absorption spectrum. The reference
 149 wavelength is chosen, and the absorption at this reference wavelength is proportional to the
 150 CDOM concentration. The shape parameter is estimated from the absorption curve
 151 independently. It can also be obtained from literature.

152

153 The 2014 data contains the absorption coefficient at the standard wavelength $\lambda_0 = 420$ nm, and in
 154 the Witting data (1913–1914) the shortest wavelength was $\lambda_1 = 467$ nm. The ratio $a_y(\lambda_0)/a_y(\lambda_1)$ in
 155 2014 was used to estimate the absorption at λ_0 in the Witting data. The ratio averaged to $1.829 \pm$
 156 0.0003 , and the coefficient of determination (equal to the square of the correlation coefficient or
 157 the ratio of explained variance to total variance) was $R^2 = 0.988$. For the river data of Holmberg
 158 (1935) the CDOM calculations were done as in the case of Witting except that the wavelength of

159 452 nm (the real band was 451-453 nm) was used instead of 467 nm to obtain the absorption at
160 420 nm. In the reference Evo lakes (Table 1; for more information about the lakes, see Arvola et
161 al., 2010) the absorbance ratio $a_y(420 \text{ nm})/a_y(450 \text{ nm})$ averaged to 1.48 ± 0.0005 with a
162 coefficient of determination $R^2 = 0.997$. The results of the data set of Holmberg were then
163 compared with total organic carbon (TOC) determinations of the HERTTA data archive of the
164 Finnish Environment Institute (<https://wwwp2.ymparisto.fi/scripts/hearts/welcome.asp>; see Table
165 [1](#)). However, the TOC results (mg C L^{-1}) were first converted to CDOM values (mg Pt L^{-1}) by
166 using a factor of 8.7, which, in turn, was calculated based on the TOC and colour (using 420 nm
167 wavelength) measurements of Lake Pääjärvi. The samples were taken from the uppermost 5 m
168 water layer during August-September in 2000-2016 (TOC vs. CDOM; $R = 0.792$, $n=33$).

169
170 The light absorption spectra of filtered water samples consist of the superposition of pure water
171 and CDOM absorption spectra. The pure water spectrum is well known (Smith and Baker, 1981)
172 and for CDOM an exponentially decaying shape $\exp(-S \cdot \lambda)$ is usually employed as shown in Eq.
173 (1). To examine whether the absorption curves of the two data sets have similar shape, the two
174 shortest wavelengths of Witting data, $\lambda_1 = 467 \text{ nm}$ and $\lambda_2 = 504 \text{ nm}$, were considered. The ratio
175 of the CDOM absorption coefficients at these wavelengths, $a_y(\lambda_1)/a_y(\lambda_2)$, averaged to 1.45 in
176 1913 and 1.44 in 2014, and the correlation coefficients between $a_y(\lambda_1)$ and $a_y(\lambda_2)$ were 0.994 and
177 0.995. The similarity extended to longer wavelengths as well (**Fig. 2**). It should be noted that the
178 pure water absorption spectrum (Smith and Baker, 1981) has been excluded from the graphs in
179 Fig. 2.

180

181 **Measurement techniques**

182 Before the measurements of Witting (Witting, 1914b; Witting, 1914a), the samples were filtered
183 with a hardened Schleicher & Schülls #575 ½ filter. Then the water was put into 25 cm
184 (sometimes 12 cm for darker waters or longer wavelengths) glass tubes closed at both ends. A
185 similar 2 cm long reference tube was used to eliminate the reflection of the glass and water
186 borders. The measurements were made using a spectrophotometer designed by König and
187 Martens (Martens and Grünbaum, 1903), with band widths of 4 and 5 nm at the wavelengths of
188 467 and 504 nm, respectively, while in longer wavelengths the bandwidths were from 8 nm (at
189 551 nm) up to 16 nm (at 709 nm). Twelve (or 16 in the outer parts of the spectrum)
190 measurements were made at every wavelength. In 2014 the water samples were analysed at
191 Lammi Biological Station, University of Helsinki. The spectrophotometer (Shimadzu UV-2100)
192 provided the deviation of the absorption spectra from its clean water reference,
193 $a'(\lambda) = a(\lambda) - a_w(\lambda)$, and the spectral coverage was 200–750 nm with 0.5 nm spectral resolution.
194 The accuracy of the absorption coefficient was 0.1–0.2 m⁻¹. The samples were measured before
195 and after filtration through Whatman GF/C glass fibre filters within a few days (at most two
196 weeks) after sampling, in the same way as the measurements in 1913 by Witting (Witting,
197 1914b). Equally with Witting (1914a, b) and our samples from 2014, the results of Holmberg
198 (1935) represent absorption of filtered water samples.

199
200 In 2014 the samples were measured again 4-8 weeks after their samplings, and it was seen that
201 the long duration of the preservation did not decrease the absorbance values more than 17%
202 ($R^2=0.973$). After sampling the samples were kept in a dark and cold (4-5°C) place until they
203 were measured. We came to the conclusion that although the filters used were different in 1913–
204 1914 from those in 2014, this has no significant influence on the results.

205
 206 According to Witting (Witting, 1914b), the standard error of the laboratory measurement of the
 207 absorption coefficient was $\sim 10^{-2} \text{ m}^{-1}$. This is quite small, around 1 % for most water samples. For
 208 a finite bandwidth, the exponential decay rate causes a bias in that the representative wavelength
 209 is a little shorter than the central band wavelength. By direct calculation it is evident that for a
 210 bandwidth less than 5 nm the error is less than 1%. In August 2014 we measured absorbance at
 211 420, 467 and 504 nm wavelengths from 30 surface water samples of small lakes situating nearby
 212 the Lammi Biological Station (Arvola et al., 2010). The wavelengths of 467 and 504 nm
 213 explained 99.3% and 94.5% of the variation of the absorbance at 420 nm among the lakes
 214 according to the linear regression, which demonstrates the accuracy of the used method for
 215 estimating the CDOM concentration.

216
 217 Absorption ratios γ for different wavelengths have been estimated by linear regression from $a(\lambda_1)$
 218 $= \gamma \cdot a(\lambda_2)$, giving

$$220 \quad \gamma = \frac{\sum a(\lambda_1)a(\lambda_2)}{\sum a(\lambda_1)^2}, s_\gamma = \sqrt{\frac{1}{\sum a(\lambda_1)^2}} \cdot s[a(\lambda_1)] \quad (3)$$

221
 222 where s stands for the standard deviation and the sums are taken over the available data pairs. For
 223 the shape factor S in the CDOM absorption law, the minimum variance estimator is

$$225 \quad S = \frac{1}{\lambda_2 - \lambda_1} \log \left[\frac{1}{n} \sum_{k=1}^n \frac{a_y^{(k)}(\lambda_2)}{a_y^{(k)}(\lambda_1)} \right] \quad (4)$$

226
227
228 For statistical analyses non-transformed original data sets were used with SigmaPlot 12.5 and
229 Real Statistics software. Parametric tests were applied if possible. Linear regression models were
230 used for calculating the relationships between CDOM and land-coverage, including land-use,
231 characteristics of the catchment areas.

232

233

234 *Results*

235

236 **CDOM absorption**

237 In both 1913 and 2014 data sets, the best fits (see Eq. 4) for the shape factor in the exponential
238 CDOM absorption law produced the estimate of $S = 0.011 \text{ nm}^{-1}$, with an accuracy of 0.001 nm^{-1}
239 ($S = 0.0109 \pm 0.0015 \text{ nm}^{-1}$ in 1913 and $S = 0.0106 \pm 0.0025 \text{ nm}^{-1}$ in 2014). Consequently, the
240 CDOM absorption spectra of 1913 and 2014 data were similar in shape, both estimates of S were
241 within the range reported in inland waters (Bukata et al., 1995; Arst, 2003; Arst et al., 2008). In
242 1913 the mean CDOM absorption coefficient of the study lakes was 1.9 m^{-1} at $a_y(467 \text{ nm})$ and in
243 2014 it was 1.7 m^{-1} (**Table 1**).

244

245 As CDOM absorption is proportional to CDOM concentration we compared the concentrations
246 between different sites, and thus the ratio of the 1913 and 2014 absorption provides the relative
247 change in the CDOM concentrations. The mean CDOM absorption spectrum had a slightly
248 higher level in 1913 than in 2014 (**Fig. 2**), although there was no significant overall change

249 between the two data sets ($p > 0.05$, t -test; **Fig. 3**). When the CDOM results of the sampling sites
250 are plotted against each other, the results indicate no common change in the river sites while in
251 the lake data CDOM levels were mostly lower in 2014 than in 1913 (t -value=5.046, $p < 0.00001$,
252 $n=98$; **Fig. 4**), a result, which was contrary to our expectations. In 69% of the lakes (25 of 36
253 lakes) the change was considered statistically significant because the estimated 95% confidence
254 intervals did not overlap, and in 84% of those a higher CDOM concentration was obtained in
255 1913 than in 2014. Respectively, in 11 of 15 rivers (73%) the difference in CDOM was
256 statistically significant, and in 64% of them a higher CDOM concentration was measured in 2014
257 than in 1913. Altogether, in less than one third of the lakes and rivers no significant change in
258 CDOM was observed.

259

260 **Rivers**

261 The results show that rivers draining to the Bay of Bothnia, the northernmost basin of the Baltic
262 Sea had highly variable CDOM concentrations both in 1913–1914 and in 2014 (**Fig. 5**). The
263 values were mostly higher in 2014. Among the six largest rivers of Finland (River Tornionjoki,
264 R. Kemijoki, R. Oulujoki, R. Kokemäenjoki, R. Kymijoki and R. Vuoksi) the absorbance values
265 at 467 nm varied between 1.0–1.8 m^{-1} in 1913–1914 and between 0.8–2.2 m^{-1} in 2014, and the
266 respective colour values were between 62–113 mg Pt L^{-1} in 1913–1914 and between 49–136 mg
267 Pt L^{-1} in 2014. From these, Rivers Torniojoki, Kemijoki and Oulujoki flow to the Bay of Bothnia,
268 Kokemäenjoki flows to the Sea of Bothnia, and Rivers Kymijoki and Vuoksi flow to the Gulf of
269 Finland, the last one through Lake Ladoga.

270

271 When all the sampling sites except those in river mouths of the four southernmost river basins

272 (i.e. Oulujoki, Kokemäenjoki, Kymijoki and Vuoksi) were considered, the mean colour values in
273 1913 varied between 109-148 mg Pt L⁻¹ and in 2014 between 85-113 mg Pt L⁻¹. The only river
274 basin with significantly lower CDOM values in 2014 compared to 1913–1914 was Kokemäenjoki
275 river basin ($p=0.002$, Mann-Whitney Rank Sum Test; see also **Fig. 6**). Among the rivers which
276 discharge to Bothnian Sea, Kokemäenjoki was the only one where the absorbance values were
277 distinctly lower than in the long-term data set by Holmberg (1935), while in three of them,
278 namely in Lapuanjoki, Kalajoki and Lestijoki the absorbance values were higher in 2014 than in
279 the old data sets (**Fig. 7**).

280
281 In general, the results are consistent with those based on the time series of data (see **Fig. 6**).
282 When the data sets of Holmberg and SYKE (**Table 1**) were compared with each other, the latter
283 CDOM concentrations were statistically (t -test with unequal variances) significantly ($p<0.05$)
284 higher in five of the six rivers discharging into the Bay of Bothnia. However, it has to be noted
285 that the CDOM concentrations of both data sets were on average 32 to 21% lower than those of
286 Witting and our measurements in 2014. This demonstrates that inter-annual variability in CDOM
287 has to be considered carefully when the CDOM results of inland waters are analysed and
288 interpreted.

289 290 **Dependence of CDOM on external factors**

291 Using the SYKE and Witting river data sets, the seasonal variation of CDOM was examined. In
292 1913-1914 the CDOM values of large rivers varied seasonally rather similarly as in 2014. The
293 coefficient of variation (%) varied between 12 and 38 in 1913-1914 and between 7 and 65 in
294 2014 (see also **Fig. 4**), and no significant correlation between discharge and CDOM was

295 obtained. The 45 year long hydrological and CDOM data base (1971-2015) of the Finnish
296 Environment Institute from the three northernmost rivers of the Baltic Sea, Tornionjoki,
297 Kemijoki and Simojoki, showed that in August discharge explained on average 53% ($p < 0.001$) of
298 the variation of CDOM, while similar data from River Kokemäenjoki and River Kymijoki did not
299 show any significant relationship between discharge and CDOM ($p > 0.1$). In the largest river
300 basin, River Vuoksi, the relationship was significant ($p = 0.033$) as in the northernmost rivers. The
301 differences in the relationship between the river basins may be explained by their specific
302 hydrological and drainage conditions. For example, lakes cover a greater areal proportion of river
303 basins in the south, where water levels usually fluctuate less than in the north. Although year
304 1913 was a little warmer than an average year and precipitation was low, especially in July, and
305 June 2014 was cool and rainy and July 2014 was warm and sunny, prior to the samplings in 1913
306 and 2014 hydrological conditions, with a few exceptions, were within the normal range of the
307 long-term variability (**Table 2**).

308
309 W2014 CDOM values of 14 larger rivers (drainage basins $> 3000 \text{ km}^2$) draining to the Baltic Sea
310 (for more information about the rivers, see Räike et al. 2012) was analysed together with their
311 terrestrial land-use data (field%, forest+peat%, urban+open% of the catchment) by multiple
312 regression analysis, the following statistically significant equation ($F = 7.327$, $p = 0.00695$) was
313 received:

314
315
$$\text{CDOM} = 6.883 \cdot \text{field}\% + 8.112 \cdot \text{forest+peat}\% - 7.258 \cdot \text{urban+open}\% - 59.567 \quad (5)$$

316
317

318 The results showed that only forest+peat% (t -value= 3.775, p =0.00363) and field% (t -value
319 =2.966, p =0.0141) were statistically significant factors, while urban+open% did not (t -value= -
320 1.483, p =0.169). Together the variables explained 69% of the variation (F =7.327, p =0.00695) of
321 CDOM among the rivers.

322
323 When the variability of W2014 CDOM values of 47 lakes larger than 10 km² were analysed
324 together with their basic bathymetric and land-coverage information (lake area, elevation above
325 sea level, neighbouring catchment area, total upstream catchment area, peat% of the neighbouring
326 catchment, peat% of the total upstream catchment, lake% of neighbouring catchment, and lake%
327 of total upstream catchment) by multiple regression analysis, lake elevation (F =9.524, p =0.004)
328 and lake% of the total upstream catchment area (F =11.188, p =0.002) were the only statistically
329 significant variables, and together they explained 46% of the CDOM variability among the lakes
330 (**Table 3**).

331
332 A more detailed examination of the data showed that the CDOM values changed most clearly
333 within the Kokemäenjoki (Sea of Bothnia) and Kymijoki (Gulf of Finland) river basins, where
334 the decrease in the CDOM median values was statistically significant (Mann-Whitney Rank Sum
335 Test: Kokemäenjoki, p =0.002; Kymijoki, p =0.019). Within the Vuoksi (south) and Oulujoki (Bay
336 of Bothnia) drainage basins no significant changes were observed (t -test results: Vuoksi,
337 p =0.477, df =42; Oulujoki, p =0.475, df =6).

338

339

340 *Discussion*

341 The present results of absorption spectra of lake and river water samples did not show any major
342 consistent change in the CDOM concentration from the year 1913 to 2014 in Finnish inland
343 waters. This does not mean that the optical properties of lakes and rivers remained stable
344 throughout the whole period. Rather the results further showed that on the seasonal and inter-
345 annual scales the CDOM concentrations have varied in a wide range, although in the long,
346 centennial run no overall changes in CDOM concentrations have taken place. In shorter, decadal
347 time scales the CDOM concentrations have varied, likely for several reasons: due to organic
348 waste waters produced by paper and pulp industry, changes in the land-use, and, in particular,
349 peat draining for agriculture, forestry and energy purposes (Rantakari et al., 2004; Mattsson et al.,
350 2005; Temnerud et al., 2014). Peat draining was extremely intensive in vast areas in Finland
351 during a relatively short period, from the middle of 1960s until the end of 1980s. During that time
352 window nearly 80% of all peatland areas in southern and central Finland were drained (Tattari et
353 al., 2015), a fact, which had important consequences to the hydrological conditions in many
354 catchments as well as the transport of organic matter out of them. Another potential factor, which
355 may have influenced recent CDOM concentrations in vast areas in Finland, is sulphate
356 deposition, which increased after the Second World War and then rapidly declined since the
357 middle of 1980s (Niemi et al., 2004; Vuorenmaa, 2007).

358
359 The impact of anthropogenic factors can be overlapping, and the response of catchments, rivers
360 and lakes regarding CDOM concentrations may vary, for example, due to their specific properties
361 and different delays. Therefore, the impact of anthropogenic factors may be difficult to
362 distinguish from other factors. In the analyzed data set, landscape properties and changes in land-
363 use, in particular, explained best the observed variations in CDOM concentrations between the

364 sampling sites and between the geographical areas. This is in-line with the idea that catchment
365 properties, including land-use, and hydrological conditions are the key controlling drivers of
366 CDOM in boreal inland waters (see also Arvola et al., 2016). In that sense peat draining for
367 forestry farming and using turf for an energy source may be outstandingly important, because of
368 their wide distribution and intensity. According to the statistics of Tattari et al. (2015) the
369 drainage percentage has been especially high in those drainage basins flowing into the Bay of
370 Bothnia, where higher CDOM values were measured in 2014 than in 1913. An interesting
371 question is how CDOM concentrations are influenced by summer temperature, and length and
372 quality of ice season (Salonen et al., 2009), which have changed in Finland (Jylhä et al., 2014).
373

374 In conclusion, the results indicate that no uniform large-scale change in CDOM concentrations
375 has taken place in inland waters in Finland during the 101 year time period 1913-2014. Also the
376 form of the CDOM absorption spectrum described by the shape factor in the exponential decay
377 law has not changed. The data sets indicate that CDOM concentrations in lakes and rivers are
378 influenced by multiple factors, including the nature of the catchments such as lake percentage and
379 peatland coverage, both also affecting iron concentrations in inland surface waters as well as
380 man-made stressors such as drainage and excavation of peatlands. The results suggest that
381 hydrological conditions are responsible mostly for the inter-annual and seasonal variations in
382 CDOM and no overall long-term change in the annual mean river discharges has been observed
383 (Korhonen and Kuusisto, 2007).

384
385 Finally, it needs to be emphasized that the historical studies made by Witting and Holmberg were
386 carefully planned, organized, analysed, and documented, and thus they provide an extremely

387 good basis to investigate long-term changes of optical properties in inland waters. The difference
388 with filters and spectrophotometers was considered insignificant in regard to the results. With the
389 large number of sample sites, the outcome of the statistical analysis becomes reliable, and as such
390 the results support our knowledge of long-term changes in the optical properties of Finnish inland
391 waters as well as factors influencing their CDOM concentrations. These data can be used in
392 management of lakes and rivers, and to learn how to project the present state to conditions in
393 future climate.

394
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401

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 527 iron to light absorption by chromophoric dissolved organic matter. Limnology and
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Table 1. Metadata information on the data sets used for the analysis.

Principal data	Year	N of sites	N of measurements	Type of CDOM data	Abbreviation	Source
Witting1913	1913	212	151	Lake and river	W1913	Witting 1915a
Witting1913-14	1913-1914	6	60	River, monthly	W1913-14	Witting 1915b
Witting2014	2014	153	151	Re-sampled Witting1913	W2014	This paper
Holmberg	1914-1931	7	1372	River, monthly	Holmberg	Holmberg 1935
Supplementary data						
SYKE/Baltic Sea rivers	1971-2014	21		River CDOM, weekly-monthly	SYKE_River	HERTTA data base ¹
SYKE/Lake	1995-2014	36		Lake CDOM, monthly	SYKE_Lake	HERTTA data base ¹
SYKE/Hydrology	1911-2014	10		River discharge, daily	SYKE_Hydrology	HERTTA data base ¹
Evo lakes	2014	30		Lake absorbance 200-750 nm	EVO	Unpublished ²
Lake Pääjärvi	2000-2014	1		Lake CDOM and DOC, monthly	Pääjärvi	Unpublished ³
Land-use of Witting lakes and rivers	2014	87		Land-coverage and land-use	SYKE_Land-use	HERTTA data base ¹

¹<https://wwwp2.ymparisto.fi/scripts/hearts/welcome.asp>

²For the lake,s see Arvola et al. 2010.

³For the lake, see Jennings et al. 2012.

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Table 2. River discharge ($\text{m}^3 \text{s}^{-1}$) in August in 1913-1914 (Witting) and 2014 (SYKE). Also long-

542 term (LT; mostly the time period since 1911 until 2014 with a few minor gaps) means and
 543 standard deviations (SD) are given. The LT data has been collected from the Finnish
 544 Environment Institute's HERTTA data archive (see Table 1).

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	1913-14	2014	LT mean	LT SD
Tomio	207	242	425	205
Kemi	282	409	457	193
Simo	9.7	33	28	27
li	64	80	122	67
Kiiminki	20	22	25	20
Kala	1.9	9.5	16	20
Lesti	2.8	4.7	6.7	6.3
Kokemäki	184	105	161	84
Kymi	327	98	191	112
Vuoksi	691	662	622	113

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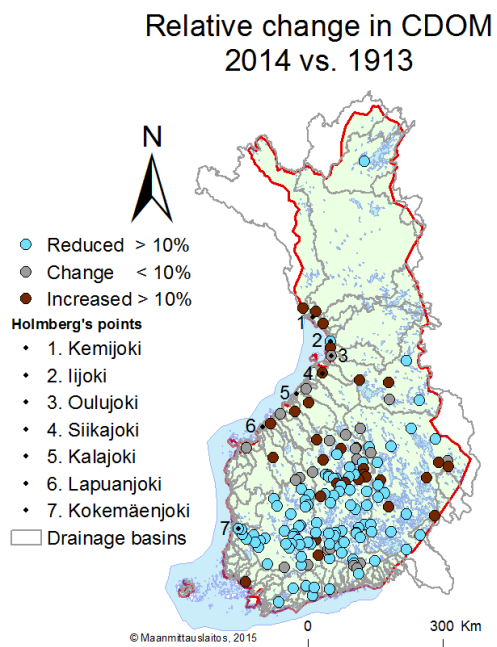
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550
 551 Table 3. Stepwise multiple linear regression results between CDOM of the sampling sites of the
 552 three southernmost largest river basins (Kokemäenjoki, Kymijoki and Vuoksi; Data source:
 553 Witting2014) and their catchment properties (Lake or river area, Lake%, Peat% of land-area,
 554 Peat% of water area and Upstream catchment area).
 555

OVERALL FIT							
Multiple R	0.695		AIC	626.31			
R Square	0.483		AICc	627.09			
Adjusted R Square	0.463		SBC	635.99			
Standard Error	42.50						
Observations	83						
ANOVA							
	df	SS	MS	Alpha F	0.05 p-value	sig	
Regression	3	133244	44415	24.591	2.45E-11	yes	
Residual	79	142686	1806				
Total	82	275930					
	coeff	std err	t stat	p-value	lower	upper	vif
Intercept	185.48	14.93	12.426	2.85E-20	155.772	215.195	
Peat% of land-area	1.487	0.542	2.745	0.00749	0.409	2.565	1.056
Upstream catchment area	-0.0012	0.001	-2.098	0.0391	-0.0022	-5.9E-05	1.030
Lake%	-5.270	0.752	-7.010	7.16E-10	-6.766	-3.77359	1.030

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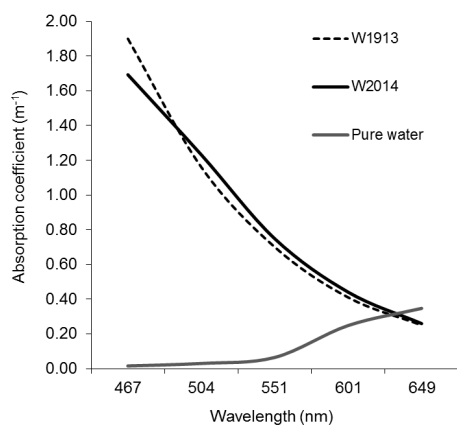
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560 Fig. 1. Location of the sampling sites in 2014. Blue and brown colours indicate more than 10%

561 decreasing or increasing CDOM values in 2014 relative to 1913. See also Table 1.

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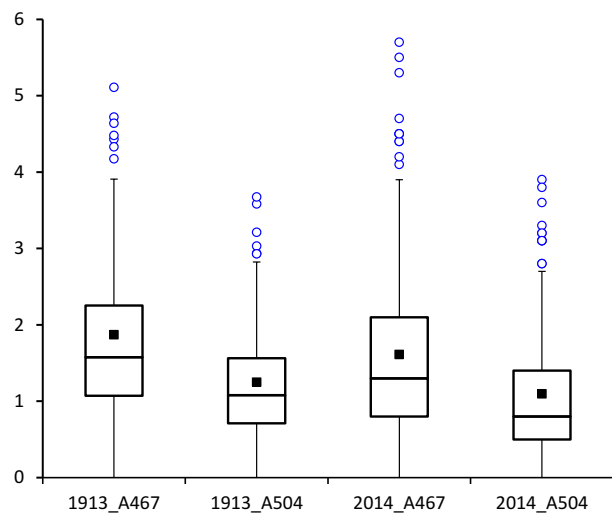
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567 Fig. 2. The CDOM absorption spectra of samples taken in 1913 and 2014. Also shown are the fits

568 for the exponential absorption curve, $a_y(\lambda_0) \exp[-S \cdot (\lambda - \lambda_0)]$, for the 1913 and 2014 data.

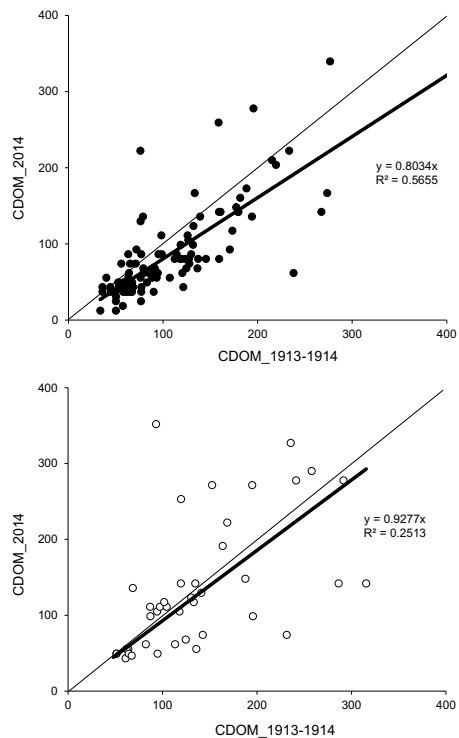
569 Data sources: W1914 and W2014.

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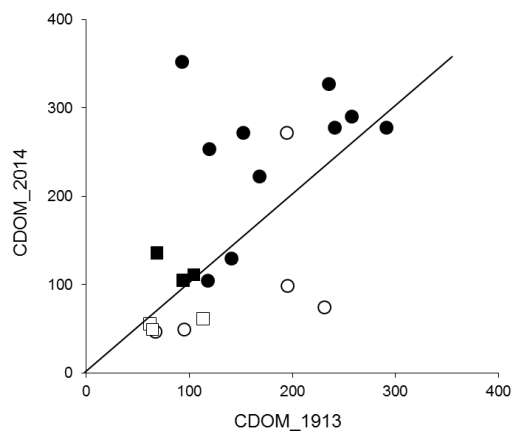
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575 Fig. 3. Box plot statistics of W1913 and W2014 sites for the absorption coefficients (m^{-1}) at the
576 wavelengths of 467 nm and 504 nm. $n = 151$.

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 581 Fig. 4. CDOM plots for lakes (top; n=99) and rivers (bottom; n=41) in 1913-1914 and 2014. The
 582 equality relationship lines (thin) and linear regression lines (thick) are also given. The CDOM
 583 unit is absorbance (m^{-1}). Data sources: W1913 and W2014.

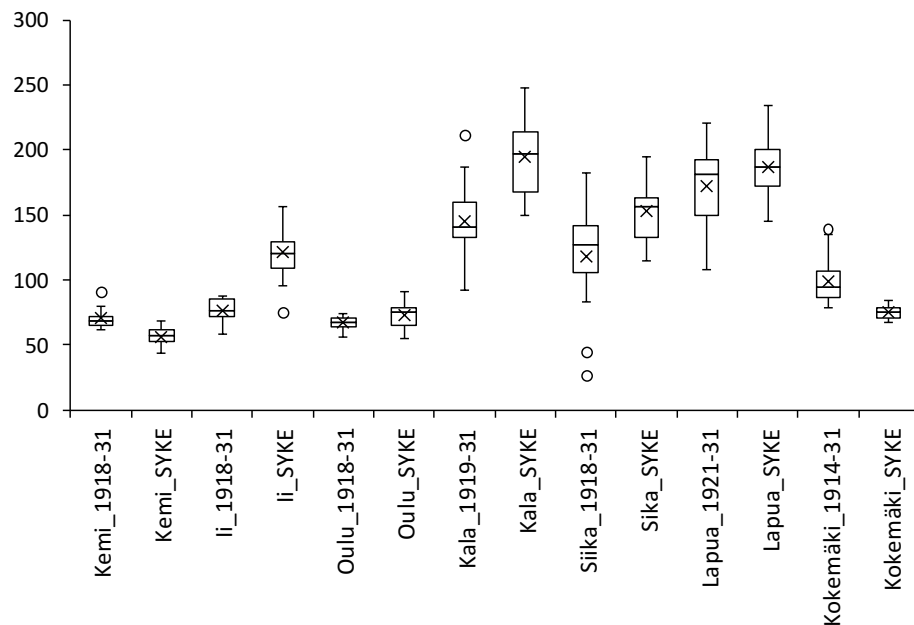
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 589 Fig. 5. CDOM plots for rivers draining into the Bay of Bothnia (black dots and squares), and into
 590 the Gulf of Bothnia, Gulf of Finland and Lake Ladoga (white dots and squares) in 1913 and

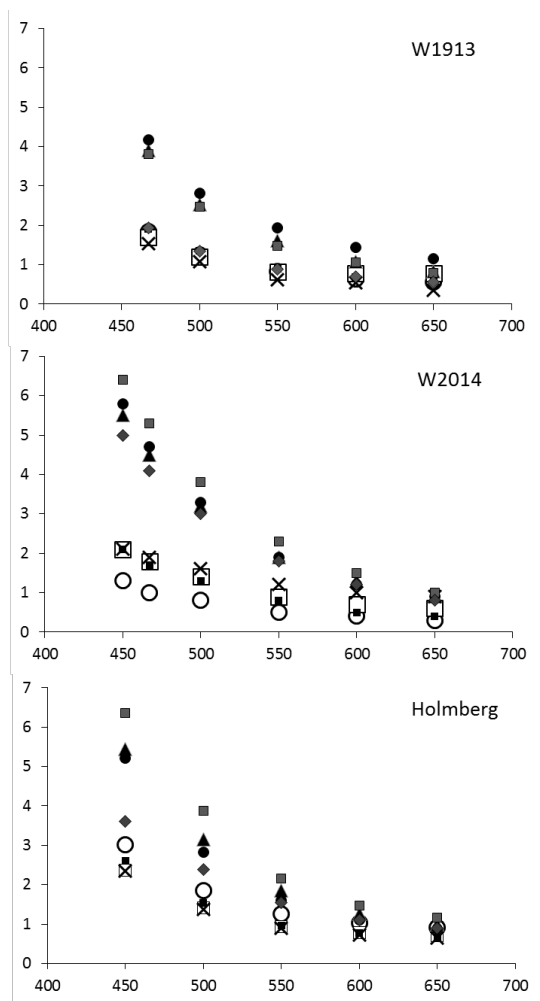
591 2014. The equality relationship is also given. The CDOM unit is mg Pt L^{-1} . The largest rivers
 592 (Tornionjoki, Kemijoki, Oulujoki, Kokemäenjoki, Kymijoki and Vuoksi) are marked by squares.
 593 Data sources: W1913 and W2014.

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 598 Fig. 6. Box plot of historical and current CDOM concentrations (mg Pt L^{-1}) of rivers draining into
 599 the Bay of Bothnia and the Sea of Bothnia according to the data sets of Holmberg (1935) for
 600 1913-1931 and Finnish Environment Institute (SYKE) for 1995-2014.

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 606 Fig. 7. The CDOM absorption (m⁻¹) spectra of eight rivers (the same as in Fig. 6, plus river
 607 Lestijoki) sampled in 1913, 2014 and 1914-1931. The markers indicate following rivers: black
 608 square=Iijoki, grey square=Lapuanjoki, white square=Oulujoki, black dot=Kalajoki, white
 609 circle=Kokemäenjoki, diamond=Lestijoki, triangle=Siikajoki, and x=Kemijoki. Data sources, see
 610 Table 1.