CDOM variations in Finnish lakes and rivers between 1913 and 2014

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Abstract

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

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

Introduction

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

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

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

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

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

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

Material and methods

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

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

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

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

Absorption measurements

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

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

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

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

CDOM and water colour

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

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

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

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

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

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

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

Measurement techniques

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

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

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206 According to Witting (Witting, 1914b), the standard error of the laboratory measurement of the
207 absorption coefficient was ~10^{-2} 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

219

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

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

224

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

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

Results

CDOM absorption

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

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

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

Rivers

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

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

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

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

Dependence of CDOM on external factors

Using the SYKE and Witting river data sets, the seasonal variation of CDOM was examined. In 1913-1914 the CDOM values of large rivers varied seasonally rather similarly as in 2014. The coefficient of variation (%) varied between 12 and 38 in 1913-1914 and between 7 and 65 in 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 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 $$CDOM = 6.883 \cdot field\% + 8.112 \cdot forest+peat\% - 7.258 \cdot urban+open\% - 59.567 \quad (5)$$
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 km^2 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

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

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

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

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

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533 Table 1. Metadata information on the data sets used for the analysis.
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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
[2)] For the lake,s see Arvola et al. 2010.
[3)] For the lake, see Jennings et al. 2012.

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541 Table 2. River discharge (m^3 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
Tornio	207	242	425	205
Kemi	282	409	457	193
Simo	9.7	33	28	27
Ii	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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Table 3.Stepwise multiple linear regression results between CDOM of the sampling sites of the three southernmost largest river basins (Kokemäenjoki, Kymijoki and Vuoksi; Data source: Witting2014) and their catchment properties (Lake or river area, Lake%, Peat% of land-area, Peat% of water area and Upstream catchment area).

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				Alpha	0.05		
	df	SS	MS	F	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

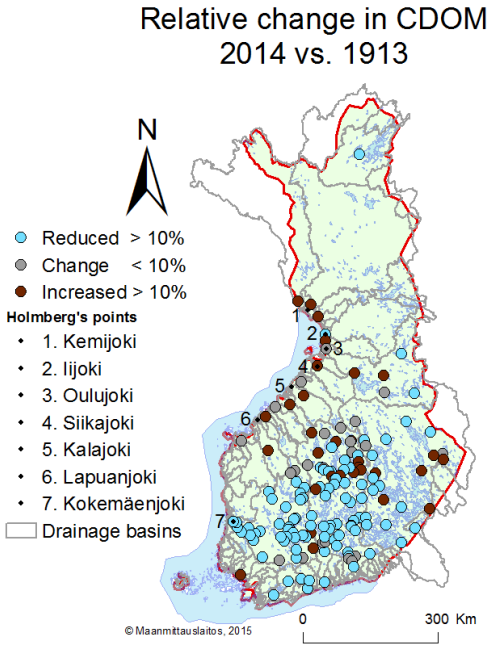

Fig. 1. Location of the sampling sites in 2014. Blue and brown colours indicate more than 10% decreasing or increasing CDOM values in 2014 relative to 1913. See also Table 1.

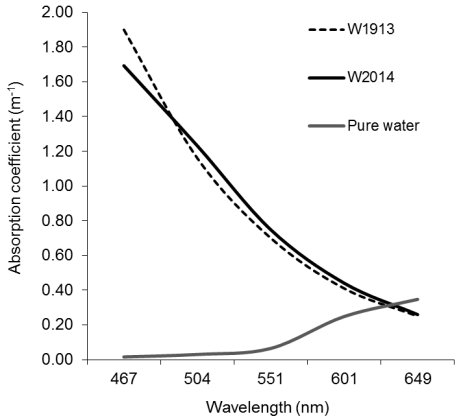

Fig. 2. The CDOM absorption spectra of samples taken in 1913 and 2014. Also shown are the fits for the exponential absorption curve, $a_y(\lambda_0)\exp[-S\cdot(\lambda-\lambda_0)]$, for the 1913 and 2014 data.

569 Data sources: W1914 and W2014.

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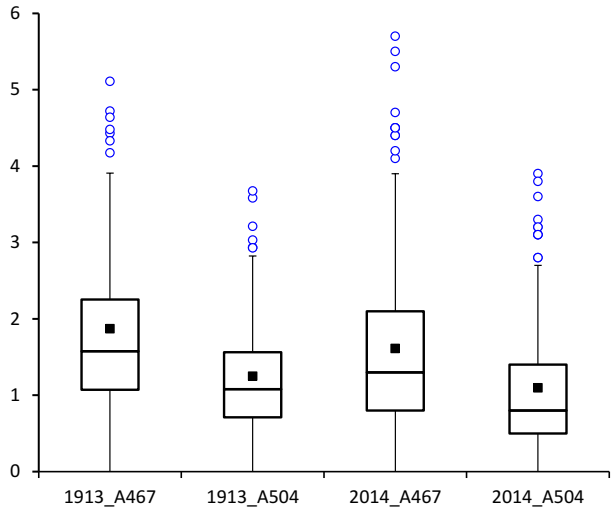

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575 Fig. 3. Box plot statistics of W1913 and W2014 sites for the absorption coefficients (m^{-1}) at the

576 wavelengths of 467 nm and 504 nm. n =151.

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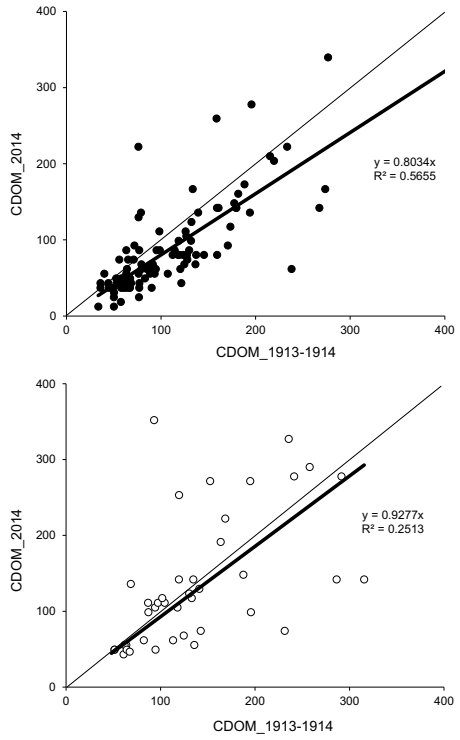

Fig. 4. CDOM plots for lakes (top; n=99) and rivers (bottom; n=41) in 1913-1914 and 2014. The equality relationship lines (thin) and linear regression lines (thick) are also given. The CDOM unit is absorbance (m^{-1}). Data sources: W1913 and W2014.

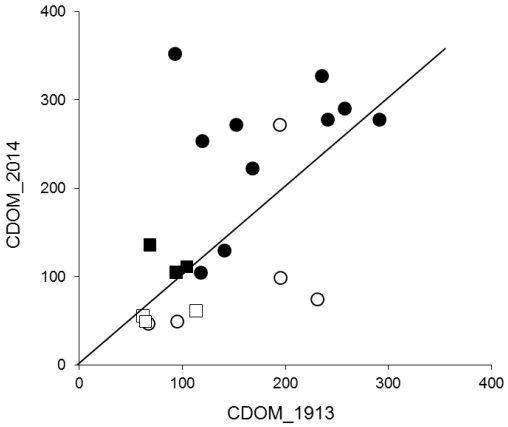

Fig. 5. CDOM plots for rivers draining into the Bay of Bothnia (black dots and squares), and into the Gulf of Bothnia, Gulf of Finland and Lake Ladoga (white dots and squares) in 1913 and

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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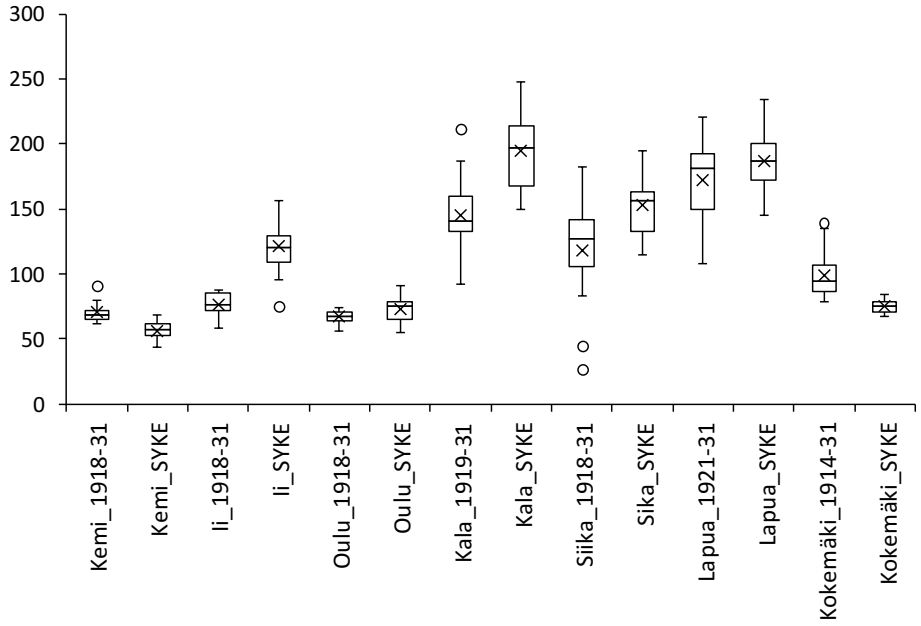

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598 Fig. 6. Box plot of historical and current CDOM concentrations (mg Pt L^{-1}) of rivers draining into
599 the Bay of Bothnia and the Sea of Bothnia according to the data sets of Holmberg (1935) for
600 1913-1931 and Finnish Environment Institute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

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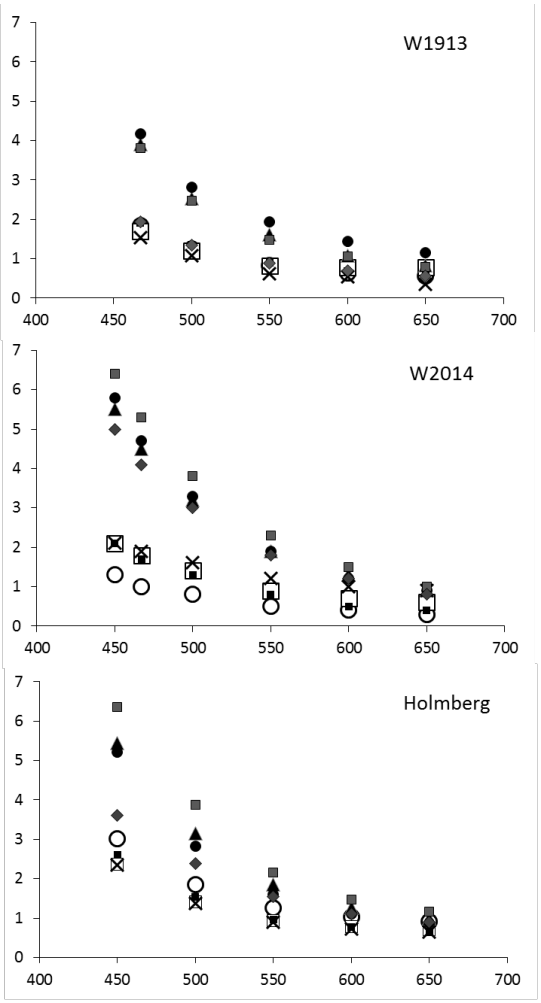

Fig. 7. The CDOM absorption (m^{-1}) spectra of eight rivers (the same as in Fig. 6, plus river Lestijoki) sampled in 1913, 2014 and 1914-1931. The markers indicate following rivers: black square=Iijoki, grey square=Lapuanjoki, white square=Oulujoki, black dot=Kalajoki, white circle=Kokemäenjoki, diamond=Lestijoki,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