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Spatial and temporal variations in coloured dissolved organic matter in large and shallow Estonian waterbodies

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Spatial and temporal variations in coloured dissolved organic matter (CDOM) were studied in two large, shallow and eutrophic Estonian lakes (Peipsi and Võrtsjärv), and in the CDOM-rich Pärnu Bay (in the Gulf of Riga, Baltic Sea). The concentration of CDOM, determined by its absorption coefficient at wavelength λ = 380 nm, ranged from 4.17 to 22.3 m^{-1} in Peipsi, from 3.96 to 15.7 m^{-1} in Võrtsjärv and from 2.24 to 32.9 m^{-1} in Pärnu Bay. The amount of CDOM was spatially variable in all investigated waterbodies. It was highest in the coastal/onshore areas and in the estuaries of the main rivers. It usually decreased from spring towards autumn, and the seasonal patterns were most distinct in the onshore areas. In standing water bodies, the short-term dynamics of discharges had a more significant effect on CDOM concentration in onshore areas than in offshore areas, where the influence of the discharges became visible over a longer period. The results suggest that in large and shallow water bodies the share of the allochthonous component in the CDOM pool decreases towards offshore areas. The impact of CDOM discharged into the inflowing rivers reaches further from shores if the ratio of the catchment area to the volume of the standing water body (C/V) is larger. The influence of precipitation on CDOM absorption proved to be insignificant.

Introduction

Most of the organic matter pool in aquatic systems is dissolved organic matter (DOM), the remainder consisting of particulate forms (Wetzel 2001). The size limit used to differentiate DOM from particulate organic matter is around 0.45 μm. DOM can be divided into two categories: non-humic and humic substances (Aiken *et al*. 1985, Thurman 1985). Non-humic substances are labile, relatively easily utilized and degraded by microorganisms, so their concentrations in the water are low (Wetzel 2001). In contrast, humic substances are refractory (they can stay in environment for years) and give a yellow-brown colour to natural waters (Thurman 1985, McKnight and Aiken 1998). Humic substances are formed during the decay of algal and plant material, mainly of vascular plants that are modified by microbial metabolism. This fraction of DOM is usually called coloured dissolved organic matter (CDOM), also referred to as chromophoric dissolved organic matter, gelbstoff or yellow substance, and in the boreal region it constitutes up to 90% of DOM (Thurman 1985).

Waters with high CDOM concentrations are usually associated with catchments with a high percentage of peat and organic soils. Catchments with organic soils typically export between 10 and 300 kg ha^{-1} yr^{-1} dissolved organic carbon (DOC) (Jonsson *et al*. 2006, Jennings *et al*. 2010). In forested catchments, CDOM is mainly produced in the upper forest floor; deciduous litter is an important source of CDOM and colour in runoff and soil water (Zsolnay 1996, Hongve 1999). In Europe, organic soils are mostly found in the colder, wetter regions of the west and north (Jennings *et al*. 2010).

CDOM may be transported to streams as surface flow, subsurface lateral flow (interflow) or groundwater inputs. It may also reach surface water directly through precipitation (Hejzlar *et al*. 2003). Both the production and transport of CDOM are highly influenced by several factors: climate, anthropogenic atmospheric deposition, land-use and in-lake processes (NORDTEST 2003). The climatic aspect mainly comprises the effects of temperature and soil moisture on different decomposition processes, solar radiation, and changes in the flushing of DOM from catchments related to changes in precipitation and timing of snowmelt (Jennings *et al*. 2010).

CDOM plays a significant role in aquatic ecosystems and has an impact on the colour and quality of the water (Kirk 1983, Dera 1992, Lindell and Rai 1994). It modifies the optical properties of the water by absorbing both visible (from 400 to 700 nm) and ultraviolet (from 280 to 400 nm) radiation. This leads to a decrease in the depth to which light penetrates the water column (Kirk 1996, Huovinen *et al*. 2000). Light absorption by CDOM decreases exponentially toward longer wavelengths (Kirk 1996). CDOM competes with phytoplankton and other aquatic plants for the capture of available light energy. The poorer light conditions and narrower euphotic zone caused by high CDOM levels in a water body may possibly decrease primary production; at the same time, CDOM protects aquatic organisms against harmful UV radiation (Kirk 1980, Jones and Arvola 1984, Davies-Colley and Vant 1987, Arvola *et al*. 1999). It may also strengthen the thermal stratification of water bodies (Münster and Chróst 1990). In addition, the organic acids in CDOM may cause the naturally low pH in freshwaters (Lydersen 1998, Kortelainen 1999), and its photochemical and biological degradation consumes oxygen in lakes (Lindell and Rai 1994).

Many studies have considered the absorption of light by CDOM in geographically diverse waters (Kirk 1996, Vodacek *et al*. 1997, Kallio 1999, Aas 2000, Boss *et al*. 2001, Siegel *et al*. 2002, Blough and Del Vecchio 2002, Osburn and Morris 2003, Zepp 2003, Sipelgas *et al*. 2003). It has been shown that physical, chemical and biological processes might all influence the spatial and temporal variability and optical properties of CDOM. Nevertheless, most of these water bodies are rather deep with relatively clear water. The factors controlling the spatial and seasonal distribution of CDOM and its influence on the aquatic ecosystem in shallow and eutrophic water bodies are still poorly investigated.

The main objective of our study was to analyse the patterns of spatial and temporal variability in CDOM concentration in shallow and relatively turbid water bodies, and the reasons for these patterns. In addition to two Estonian lakes, Peipsi and Võrtsjärv, we also studied Pärnu Bay (in the Gulf of Riga, Baltic Sea). We chose Pärnu Bay because it is strongly influenced by the inflow from the Pärnu River, which carries a high concentration of CDOM. Among the factors causing variations in CDOM, special attention was paid to the impact of precipitation and freshwater inflows from the rivers.

Materials and methods

Study sites

Lake Peipsi is located in the eastern part of Estonia (Fig. 1 and Table 1), on the border of Estonia and Russia, and consists of three basins: the largest and deepest northern basin (Peipsi), the middle narrow basin (Lämmijärv), and the southern basin (Pihkva). Võrtsjärv is situated in the central part of Estonia (Fig. 1 and Table 1). The Pärnu Bay is situated in south-western Estonia (Fig. 1 and Table 1) and can be divided into an inner and outer basins. The inner basin is strongly influenced by the inflow from the Pärnu

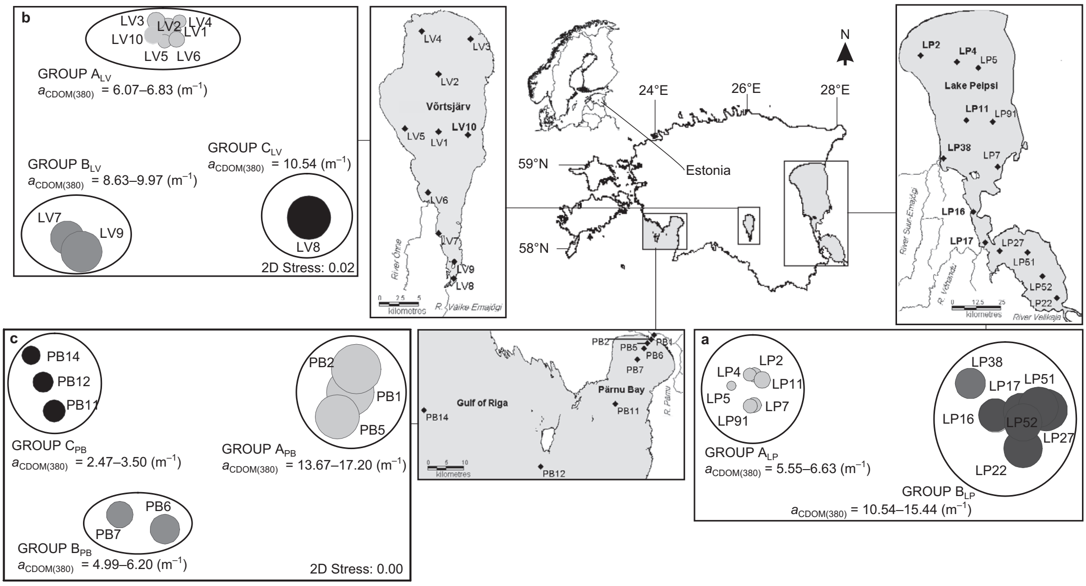

Fig. 1. Study sites (regularly sampled stations are marked in bold) and non-metric multidimensional scaling (MDS) ordination plots of a_{CDOM}(380) sampled at the indicated sampling points in (**a**) Peipsi from March/April to October/November (2002–2007), (**b**) Võrtsjärv in August (2003–2007), and (**c**) Pärnu Bay from April to October (2005–2007). The plots are superimposed on circles with diameters proportional to the average a_{CDOM}(380) (m^{-1}) during observation periods representing the spatial dissimilarity of CDOM.

River (Table 1). In our study the data from both basins were considered (including one station in the Gulf of Riga). All three waterbodies are eutrophic and they belong to the southern boreal forest zone (Table 2). The flow regime of the inflowing rivers is natural, and discharges usually peak in April. In addition, the studied waterbodies are important for fisheries and recreation.

Data collection

The concentration of CDOM was determined by its effect on light absorption by water. Many previous studies have shown that this optical approach has distinct advantages over analytical chemical techniques (Bricaud *et al*. 1981, Davies-Colley and Vant 1987, Dera 1992). Using optical methods, the concentration of CDOM in water is expressed in terms of its attenuation or absorption coefficient at a given wavelength in the UV or visible regions (mostly in the wavelength range 380–440 nm).

Water samples were collected once per month at selected stations during the ice-free periods (from March/April to October/November) of the years 2002–2007 in Peipsi, 2003–2007 in Võrtsjärv, and 2005–2007 in Pärnu Bay (Fig. 1 and Table 1). In general, the water layer studied was about 1.5–2 times thicker than the corresponding Secchi depth. However, as all the waterbodies were unstratified, the results obtained from the 'integrated' water samples represent the average values of parameters in these layers. The data from the regularly sampled stations were used to analyse the temporal and spatial variations in CDOM, and the relationships among the variability in CDOM absorption, biomass of phytoplankton, biochemical oxygen demand (BOD_7), water level, salinity (only in Pärnu Bay), precipitation and discharges from surrounding rivers. Data from samples from the other stations were also used for spatial analyses. The relationship between discharge and chemical oxygen demand by permanganate (COD_{Mn}) in the rivers of the watershed was also investigated.

Water samples were stored in plastic bottles in the dark at 4 °C and received no treatment until the analyses were conducted (maximum 12 hours). Prior to sampling, the plastic bottles

Table 1. Some general data on the water bodies in our study area, observation periods and number of samples. *C*/*V* = the ratio of catchment area (*C*) to lake volume (*V*).

Water body	Area (km²)	Mean depth (m)	*C*/*V*	Main inflows (rivers)	Total length (km)	River basin area (km²)	Average inflow (m^3 s^{-1})	Observation period	Total number of samples	The number of samples from the regularly visited stations
Lake Peipsi	3555	7.1	1.9	Velikaja	430	25200	150.0	2002–2007	227	161
				Emajõgi*	100	9960	67.3			
				Võhandu*	162	1420	8.5			
Võrtsjärv	270	2.8	4.1	Väike Emajõgi	84	1273	8.6	2003–2007	108	63
				Õhne	94	573	2.6			
Pärnu Bay	690	7.5	1.65	River	144	6690	20.0	2005–2007**	78	67

* Main inflows on Estonian territory.
** 2005 only in April and May.

had been washed with distilled water and flushed with lake water. Before optical measurements, all samples were filtered through pre-combusted (500 °C, 3 hours) Whatman GF/F filters and the material remaining in the water was considered to be dissolved. For optical characterization of CDOM, the beam attenuation coefficient of the filtered water was measured at 380–440 nm with a Hitachi U-3010 dual-beam spectrophotometer, using distilled water as the reference:

$$c^*_f(\lambda) = c_f(\lambda) - c_d(\lambda) \quad (1)$$

where $c_f(\lambda)$ is the beam attenuation coefficient of the filtered water at wavelength (λ) and $c_d(\lambda)$ is the beam attenuation coefficient of distilled water at wavelength (λ) (all in m^{-1}). The value of $c^*_f(\lambda)$ is not identical to the absorption coefficient of CDOM (a_{CDOM}) because very small particles (colloids) may pass through the filter. To obtain the true values of the spectra of a_{CDOM} we made the following correction (Bricaud *et al*. 1981, Aas 2000, Sipelgas *et al*. 2003):

$$a_{CDOM}(\lambda) = c^*_f(\lambda) - c^*_f(\lambda_R)(\lambda_R/\lambda)^g \quad (2)$$

where $c^*_f(\lambda)$ and $c^*_f(\lambda_R)$ were obtained using the Hitachi U-3010 at wavelength λ and at some reference wavelength (λ_R), respectively, and g is a parameter describing the contribution of scattering by colloids to $c^*_f(\lambda)$. Different publications have used g values equal to 0, 1 or 2 (Aas 2000, Arst 2003, Sipelgas *et al*. 2003). We set λ_R to a

Table 2. Catchment characteristics of the water bodies.

	Lake Peipsi*	Võrtsjärv	Pärnu Bay
Catchment area (m^2)	10207	3104	8532
Arable land and grassland (%)	40.6	45.3	31.4
Forest (%), including	47.0	46.1	49.9
deciduous forest	9.5	6.7	10.3
coniferous forest	18.4	15.0	16.4
mixed forest	19.1	24.4	23.2
Wetland (%)	0.4	0.6	0.5
Marsh (%)	1.6	0.1	0.4
Bog (%)	1.3	0.4	5.1
Other (%)	9.2	7.6	12.7

* Land use on Estonian part of the catchment area of Lake Peipsi.

value of 700 nm and g to a value of 1 (Davies-Colley and Vant 1987). To describe the spatial and temporal variations of CDOM in waterbodies we set the wavelength λ to a value of 380 nm in the computation of a_{CDOM} in Eq. 2.

The daily discharges of the main rivers, daily precipitation, biomass of phytoplankton, BOD_7, COD_{Mn}, water level and salinity were measured as part of the state-monitoring programme. These data were obtained from the Information Centre of the Estonian Ministry of Environment, the Estonian Meteorological and Hydrological Institute, the Centre for Limnology, and the Estonian Marine Institute, University of Tartu.

Statistical analysis

To examine the spatial dissimilarities in CDOM, the sampling points in different waterbodies were grouped by non-metric multidimensional scaling (MDS) using the software package PRIMER ver. 5 (Clarke and Gorley 2001, Clarke and Warwick 2001). The spatial similarity of CDOM absorption among groups of sampling points was subsequently tested for significance with an analysis of similarity (ANOSIM) using the same software package. ANOSIM provides a way of testing the statistical significance of a difference between two or more groups of sampling units. A statistical parameter R, generated by ANOSIM, is a relative measure of the separation between *a priori*-defined groups. A value of 0 indicates no difference among the groups (similarities between and within groups are approximately the same), while a value of 1 indicates that all samples within a group are more similar to each other than to any sample from a different group.

Correlation analyses to identify the possible reasons for spatial and temporal dissimilarity in CDOM were performed using the Spearman rank correlation coefficient (software STATISTICA 7.0, StatSoft Inc. 2004).

Results

Spatial variation in CDOM

MDS and ANOSIM analyses (227 samples from 13 sampling points) showed that the CDOM concentration in the southern basins of Peipsi (sampling points LP16, LP17, LP22, LP27, LP51, LP52) was generally higher than in the northern basin (sampling points LP2, LP4, LP5, LP7, LP11, LP91, Fig. 1a; $R = 1$, $p < 0.05$). There was only one exception, sampling point LP38 in the northern basin, where the CDOM values varied much more than at the other points and were closer to those of the southern basins. Therefore, the MDS (Fig. 1) and the ANOSIM test placed sampling point LP38 in group B_{LP} (southern basins) and not in group A_{LP}, which comprises the stations in the northern basin ($R = 1$, $p < 0.05$). Phytoplankton biomass (PhB) and BOD_7 in Peipsi were positively correlated with CDOM at the open lake stations LP2, LP4 and LP11 (Table 3), although the correlation between PhB and CDOM was not significant ($p > 0.05$).

In Võrtsjärv (108 samples from 10 sampling points), the values of $a_{\mathrm{CDOM}}(380)$ were fairly similar in different parts of the lake, with the exception of the southernmost part close to the discharge of the Väike Emajõgi (sampling points LV7, LV8, LV9), where the values were usually higher than in other parts of the lake. MDS analysis divided the sampling points into three groups (Fig. 1b). Group A_{LV} comprised sampling points LV1, LV2, LV3, LV4, LV5, LV6 and LV10 and group B_{LV} sampling points LV7 and LV9. Group

Table 3. Spearman correlation coefficients of $a_{\mathrm{CDOM}}(380)$ with phytoplankton biomass (PhB), BOD_7, water level and salinity at indicated sampling stations. Values set in boldface are significant at $p < 0.05$.

	LP2, LP4, LP11	LP16, LP17, LP38	LV10	PB7	PB11	PB12
PhB *vs.* a_{CDOM}	0.19	–0.20	**–0.31**	0.45	–0.04	**0.83**
BOD_7 *vs.* a_{CDOM}	**0.48**	0.22	–0.26	–	–	–
Water level *vs.* a_{CDOM}	–	–	**0.73**	–	–	–
Salinity *vs.* a_{CDOM}	–	–	–	**–0.88**	**–0.96**	–0.71

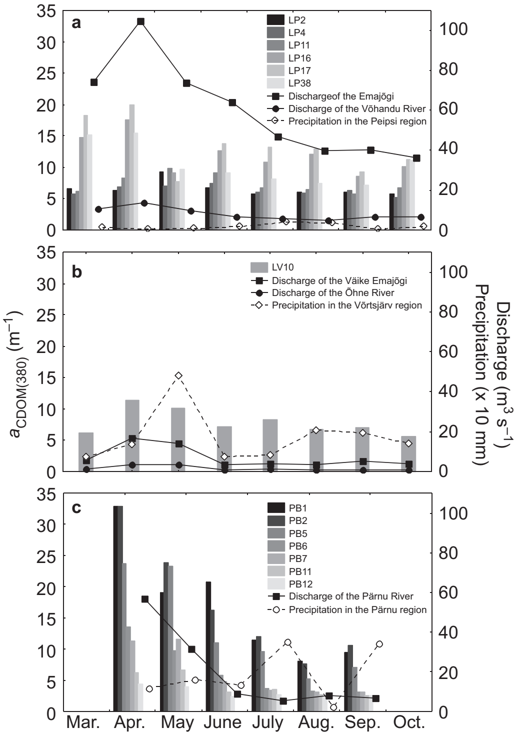

Fig. 2. Temporal variation of a_{CDOM} in (**a**) Peipsi, (**b**) Võrtsjärv, and (**c**) Pärnu Bay averaged over the observation periods at the indicated sampling points. The daily mean discharges of the rivers (**a**) Emajõgi and Võhandu, (**b**) Väike Emajõgi and Õhne; and (**c**) Pärnu, as well as the daily mean precipitation in the (**a**) Peipsi, (**b**) Võrtsjärv and (**c**) Pärnu Bay regions were measured one week before CDOM measurements.

C_{LV} consisted of only LV8, the nearest sampling point to the discharge of the Väike Emajõgi. The ANOSIM test confirmed that the CDOM values in LV8 were more similar to one another than to the values from other sampling points ($R = 1, p < 0.05$). At the regularly sampled offshore station LV10, CDOM was negatively correlated with PhB as well as with BOD_7 (Table 3).

In Pärnu Bay (78 samples from eight sampling points), the values of $a_{CDOM}(380)$ varied several fold within the sampling transect, clearly decreasing with increasing distance from the mouth of the Pärnu River towards the open part of the Gulf of Riga. MDS analysis distinguished three different groups (Fig. 1c) and the ANOSIM test showed statistically significant differences among those groups ($R = 1, p < 0.05$). CDOM was significantly negatively correlated with salinity at stations PB7 and PB11; a significant positive correlation between CDOM and PhB appeared only at the furthest offshore station, PB12 (Table 3).

Temporal variation of CDOM

In Peipsi, the values of $a_{CDOM}(380)$ ranged from 4.17 m^{-1} (sampling point LP4 in October 2003) to 22.33 m^{-1} (sampling point LP17 in March 2007). In general, CDOM absorption decreased slightly from spring to autumn (Fig. 2a), usually showing the highest values in April (sampling points LP16, LP17 and LP38) and May (sampling points LP2 and LP11). The CDOM values increased somewhat again in October (sampling points LP11, LP16, L17 and LP38), most probably because of high precipitation and increased river discharge during autumn in 2003 and 2004. Temporal variation was usually higher at the sampling points situated near the river mouths (Emajõgi and Võhandu) or near the shoreline, e.g. at LP16, LP17 and LP38.

At the offshore sampling point in Võrtsjärv (LV10) the values of $a_{CDOM}(380)$ ranged from 3.96 to 15.68 m^{-1}. As in Peipsi, CDOM generally decreased towards autumn and the maximum values were usually obtained during April and May. The five year (2003–2007) average values of CDOM were 11.44 m^{-1} in April and 10.09 m^{-1} in May (Fig. 2b). In Võrtsjärv, $a_{CDOM}(380)$ was positively correlated with the lake's water level (Table 3).

In Pärnu Bay, both the lowest and highest values of $a_{CDOM}(380)$ were observed in 2007: 2.24 m^{-1} (in August at sampling point PB12) and 32.94 m^{-1} (in April at sampling point PB1). Generally, the values of CDOM absorption decreased from April to September, as in the other two water bodies investigated (Fig. 2c). The temporal variation of CDOM at the sampling points situated near the mouth of the Pärnu River (PB1, PB2 and PB5) was markedly higher than at the open sea sampling points (PB11 and PB12).

The impact of discharge and precipitation on CDOM concentration

In the southern area of Peipsi (stations LP38, LP17 and LP16), $a_{CDOM}(380)$ was significantly positively correlated with the average daily discharge of the Emajõgi measured one to four weeks earlier (Table 4). This correlation was strongest ($r = 0.822$, $p < 0.05$) at sampling point LP38, which is situated very close to the river mouth. The average river discharges two, three and four weeks prior to measurements of CDOM in the lake were most strongly correlated with CDOM absorption at the open lake stations (LP2, LP4 and LP11). COD_{Mn} in the water of the rivers Emajõgi and Võhandu was significantly correlated with the discharges of both rivers ($r = 0.428$ and $r = 0.638$, $p < 0.05$, respectively). The mean COD_{Mn} values of the rivers Emajõgi and Võhandu were 13.27 and 10.37 mgO l^{-1}, respectively.

Correlations between CDOM at sampling points LP16 and LP17 and the discharge of the Võhandu River were predominantly insignificant (Table 4) although these points are close to the mouth of the Võhandu River.

We obtained statistically significant ($p < 0.05$) correlations between $a_{CDOM}(380)$ at offshore station LV10 in Võrtsjärv and the average daily discharges of the rivers Väike Emajõgi and Õhne measured one to four weeks earlier (Table 4). Also, there were significant correlations between the COD_{Mn} (mean 9.23 mgO l^{-1}) and the discharges of the Väike Emajõgi ($r = 0.428$, $p < 0.05$) and between the COD_{Mn} (mean 14.59 mgO l^{-1}) and the discharges of the Õhne River ($r = 0.622$, $p < 0.05$).

Spearman correlation showed a good correspondence between $a_{CDOM}(380)$ in Pärnu Bay and discharges of the river in the transect from the mouth of the Pärnu River towards the open

Table 4. Spearman correlation coefficients between $a_{CDOM}(380)$ and average daily discharge and precipitation measured one to four weeks before a_{CDOM} measurements. The a_{CDOM} values for the ice-free period (2002–2007 for Peipsi, 2003–2007 for Võrtsjärv, 2005–2007 for Pärnu Bay) at the indicated stations were correlated with: the discharges of the rivers Emajõgi, Võhandu, Väike Emajõgi, Õhne and Pärnu; and precipitation in the Peipsi, Võrtsjärv and Pärnu Bay regions. Values set in boldface are significant at $p < 0.05$.

	Emajõgi						Õhne	Pärnu						
	LP2	LP4	LP11	LP16	LP17	LP38	LV10	PB1	PB2	PB5	PB6	PB7	PB11	PB12
1 day	0.35	0.24	0.10	**0.59**	**0.61**	**0.82**	**0.54**	0.57	**0.74**	**0.69**	**0.78**	**0.87**	0.57	**0.94**
1 weeks	0.35	0.31	0.16	**0.56**	**0.57**	**0.76**	**0.62**	0.54	**0.74**	**0.66**	**0.86**	**0.92**	0.64	0.49
2 weeks	**0.40**	**0.39**	0.26	**0.62**	**0.56**	**0.74**	**0.65**	**0.82**	**0.88**	**0.73**	**0.90**	**0.96**	**0.86**	0.66
3 weeks	**0.44**	**0.45**	0.33	**0.60**	**0.54**	**0.71**	**0.64**	**0.82**	**0.88**	**0.81**	**0.94**	**0.88**	**0.86**	0.66
4 weeks	**0.45**	**0.50**	**0.39**	**0.63**	**0.54**	**0.67**	**0.68**	**0.82**	**0.88**	**0.80**	**0.94**	**0.86**	**0.86**	0.66
	Võhandu						Väike Emajõgi							
	LP2	LP4	LP11	LP16	LP17	LP38	LV10							
1 day	–0.05	–0.19	–0.26	0.23	0.36	**0.63**	**0.53**							
1 weeks	–0.10	–0.17	–0.32	0.22	0.42	**0.57**	**0.58**							
2 weeks	–0.06	–0.13	–0.27	0.25	0.44	**0.57**	**0.63**							
3 weeks	–0.02	–0.05	–0.18	0.29	0.39	**0.52**	**0.69**							
4 weeks	0.01	0.00	–0.10	0.33	0.43	**0.43**	**0.71**							
	Precipitation													
	LP2	LP4	LP11	LP16	LP17	LP38	LV10	PB1	PB2	PB5	PB6	PB7	PB11	PB12
1 day	0.20	0.06	0.34	0.27	0.41	0.13	–0.08	–0.20	–0.20	–0.22	–0.42	–0.30	–0.61	–0.13
1 weeks	–0.19	–0.23	–0.20	0.17	0.36	0.09	0.12	0.00	0.07	–0.11	–0.43	–0.60	–0.04	0.60
2 weeks	–0.23	–0.26	**–0.42**	0.00	0.03	–0.09	0.21	–0.54	–0.48	–0.41	**–0.71**	**–0.82**	–0.64	–0.14
3 weeks	–0.24	–0.24	**–0.44**	0.17	0.19	–0.08	**0.32**	–0.64	–0.60	–0.56	**–0.73**	**–0.80**	–0.68	–0.26
4 weeks	–0.24	–0.15	**–0.40**	0.11	0.11	–0.08	0.25	**–0.82**	–0.64	**–0.60**	**–0.64**	**–0.68**	–0.54	–0.37

water area (stations PB1, PB2, PB5, PB6, PB7 and PB11). The discharges of the Pärnu River were measured two to four weeks earlier than the CDOM (Table 4). The COD_{Mn} values in the Pärnu River were much higher (mean 17.26 mgO l^{-1}) than those in the other rivers (Emajõgi, Võhandu, Õhne, Väike Emajõgi) giving a significant correlation with the inflows ($r = 0.629$, $p < 0.05$).

Temporal variations in CDOM in the standing water bodies studied followed more or less the pattern of the main discharges (Fig. 2). Unlike discharges, however, CDOM did not follow the dynamics/seasonality of precipitation; also, there was no significant positive correlation between $a_{CDOM}(380)$ and the average daily precipitation measured one to four weeks before the CDOM observation (Table 4).

Discussion

Spatial variation of CDOM

Analysis of the spatial distribution of CDOM absorption revealed that CDOM values were always highest near the river mouths. The spatial differences were connected with the locations of the river inflows in Peipsi, especially in the southern parts of the lake. The three main rivers discharging into Peipsi are the Velikaja, Emajõgi and Võhandu (Table 1), and all of them discharge into the southern part of the lake. The high CDOM values in the southern basins (Pihkva and Lämmijärv) could be explained by the strong influence of the forested and peaty catchments of the rivers Velikaja and Võhandu. Variations in the amount and properties of DOM in standing water bodies reflect variations in watershed land use, which determines the DOM concentration in the discharging rivers. High DOM concentrations in rivers are usually associated with drainage from peaty and shallow upland soils (NORDTEST 2003). The southern basins of Peipsi are also much shallower and smaller (Pihkva, 708 km^2, mean depth 3.8 m; Lämmijärv 236 km^2, mean depth 2.5 m) than the northern basin (2611 km^2, mean depth 8.3 m) and therefore CDOM exported from the catchment makes a highly significant contribution to the CDOM concentration in the southern lake areas. That also applies to station LP38, which is in the northern basin but groups with the stations of the southern basins. LP38 is situated close to the mouth of the Emajõgi. The high discharge rate (Table 1) and high concentration of DOM in this large river could be considered the main reasons for the high CDOM concentration at station LP38. However, as LP38 is situated in the southern part of the northern lake basin, discharge from the CDOM-rich southern basins also contributes to the formation of a high CDOM concentration there.

The share of autochthonous production of CDOM generally increases in offshore areas (Kowalczuk 1999, Kahru and Mitchell 2001, Twardowsky and Donaghay 2001, Blough and Del Vecchio 2002, Chen *et al*. 2002, Nelson and Siegel 2002), where primary production by phytoplankton should be mostly responsible for producing labile DOM, which is an indirect source of CDOM. CDOM itself is produced by bacteria using organic matter derived from phytoplankton (Rochelle-Newall *et al*. 1999). Twardowsky and Donaghay (2001) showed that the CDOM formed in association with phytoplankton primary production might be 10% or less of the total CDOM absorption in coastal areas, but in the open ocean this fraction may account for nearly all the absorption by dissolved materials.

In our study we found no significant correlation between CDOM and phytoplankton biomass in Peipsi; their correlation coefficient was highest at the open lake stations LP2, LP4 and LP11 (Table 3). BOD_7, which is an indirect measure of autochthonous organic matter, was significantly positively correlated with CDOM values at the open lake stations. Thus, autochthonous DOM seems to contribute more to total DOM in the northern open part of the lake than in the southern area, where the DOM is mostly allochthonous, discharged into the lake by the large inflowing rivers.

In Võrtsjärv, CDOM differed spatially only in the southern area of the lake. As in Peipsi, the discharge of the main river seemed to play a major role here, indicating the importance of allochthonous DOM. CDOM was negatively correlated with phytoplankton biomass as well as with BOD_7 at off-shore station LV10 (Table 3), indicating that the contribution of autochthonous DOM was insignificant. In Võrtsjärv, the share of allochthonous CDOM was greater than in Peipsi, most probably because of the higher catchment area to lake volume ratio (Ohle's index, C/V in Table 1), which is a sign that the catchment has a large effect on lake metabolism (Thomas 1997, Smal *et al*. 2005). However, further studies are needed to confirm these conclusions.

The spatial dissimilarity among the water bodies investigated was highest in Pärnu Bay. A strong onshore-offshore gradient of CDOM absorption similar to that observed in Pärnu Bay has been shown to be typical of coastal waters owing to the influence of significant terrestrial discharges (Blough and Del Vecchio 2002, Chen *et al*. 2002, 2004). Significant negative correlations between CDOM and salinity at stations PB7 and PB11 in Pärnu Bay (Table 3) confirm the strong influence of the freshwater on CDOM concentrations. A significant positive correlation between CDOM and PhB appeared at the far offshore station PB12, where the correlation of CDOM with salinity was non-significant. That suggests that at greater distances from the river mouth, allochthonous CDOM becomes less important as the salinity increases; CDOM values decrease and autochthonous CDOM becomes more important (Del Vecchio 2002, Rochelle-Newall and Fisher 2002).

The impact of discharge and precipitation on temporal variation in CDOM concentration

We found considerable evidence that discharges from rivers determine the concentrations of CDOM in lake areas close to the river mouths. In Peipsi, the strongest correlation ($r = 0.822$, $p < 0.05$) between the discharge of the Emajõgi and CDOM absorption in the lake occurred at sampling point LP38 with no time lag. LP38 is situated very close to the mouth of the Emajõgi so it is not surprising that the short-term influence of the river is most significant here. However, CDOM values at sampling points LP16 and LP17, which are situated close to the mouth of the Võhandu, were not correlated with the discharge of this river (Table 4). These sampling points are situated in Lämmijärv, which receives its waters largely from Lake Pihkva where the largest inflow, the Velikaya River, discharges; the much smaller Võhandu River seems to make only a minor contribution to the CDOM concentration in southern parts of the lake. The close correlation between CDOM in Lämmijärv and the discharge of the Emajõgi (Table 4) should be considered occasional and most probably caused by the high correlation between the discharges of the rivers Velikaya and Emajõgi. At the open lake stations in Peipsi (LP2, LP4 and LP11), river discharge also contributed to the CDOM concentration but with a time lag of two to four weeks (Table 4). In Võrtsjärv, CDOM at the offshore station correlated significantly with discharge both on the sampling day and one week prior to sampling; however, this correlation was strongest after a four-week time lag. Võrtsjärv is a very shallow lake with a high C/V ratio (4.1), so the influence of the rivers reaches open water areas more quickly and strongly than in Peipsi, where the C/V ratio is only 1.9. However, in Pärnu Bay, where the C/V ratio is 1.65, the impact of the discharge of the Pärnu River reached quite far into the open water area fairly quickly. This could most probably be attributed to the high CDOM concentration in this river, which exceeds the CDOM values in the main rivers of the Peipsi and Võrtsjärv catchments. Also, the C/V ratio is not such a straightforward index in an open bay as it is in lakes, so it should be interpreted with some caution.

In Võrtsjärv, $a_{CDOM}(380)$ was also positively correlated with the lake's water level (Table 3). This water level is unregulated and has a natural variability strongly associated with changes in the North Atlantic Oscillation (NAO) index. Warm and wet winters related to a positive winter NAO cause higher water levels in spring because the discharge of the rivers increases (Nõges 2004), which also brings about higher concentrations and more variation in CDOM during spring. CDOM concentration is generally positively related to discharge in Estonian rivers. In the two major rivers in the Võrtsjärv catchment, water colour and COD_{Mn} (often used as proxies of CDOM concentration) were positively related to discharge throughout the year (Nõges *et al*. 2007). Our analysis also showed that the values of COD_{Mn} in the water of the rivers Emajõgi, Võhandu, Väike Emajõgi and Õhne were positively correlated with discharges.

Within-year changes in precipitation and runoff may affect both organic matter production and transport processes (Evans *et al*. 2005). In our study, temporal variation of CDOM concentration in the standing water bodies studied followed the discharge patterns of the main inflowing rivers (*see* Fig. 2). The strong correlation between CDOM and river discharge agrees with previous observations (Bricaud *et al*. 1981, Clair *et al*. 1999, Chen *et al*. 2002). CDOM concentrations were lower in summer, probably because the discharges decrease. We did not investigate the importance of photobleaching or microbial consumption in our study. Many authors have shown that photobleaching combined with microbial consumption may result in a decline of the CDOM in surface waters (Vodacek *et al*. 1997, Whitehead *et al*. 2000, Blough and Del Vecchio 2002).

According to our results, seasonal precipitation was not correlated with CDOM in the lakes or the bay. This confirms the statement of Chen *et al*. (2002) that precipitation has only a minor direct effect on the CDOM values in surface waters. However, other studies have shown a strong correlation between the intensity of precipitation and DOM concentration, mainly in the discharges from the peaty and forested sites, where increased runoff leads to a higher DOM discharge from the upper parts of the soil profile, which is rich in organic matter (Arvola *et al*. 2004, Laudon *et al*. 2004). Precipitation influences the moisture level of soils, so it could modify the processes that regulate the soil organic matter pool and carbon fluxes (including DOM dynamics) from the catchment (NORDTEST 2003). Presumably, this connection depends on conditions, and in some cases precipitation and runoff are not necessarily very closely correlated (*see* Fig. 2). The difference in precipitation and discharge dynamics might be connected to variations in evaporation processes and soil moisture levels (Pandžić and Trninić 1999–2000).

Conclusions

Our study revealed that CDOM concentrations were highest in the coastal/onshore areas, and the discharges of the main rivers were mainly responsible for the spatial variability in CDOM in all the large and shallow water bodies studied. The CDOM concentration was highest in spring and lowest in autumn and the seasonal patterns were most distinct at onshore areas. Temporal variation in CDOM was strongly correlated with discharges from the main rivers, but this relationship became weaker with increasing distance from the river mouth area towards to the open part of a standing water body.

The short-term dynamics of the discharges had a more significant influence on the CDOM concentrations in standing water bodies in onshore than in offshore areas; in offshore areas, the influence of the discharges became more important over a longer period.

In the offshore areas of Lake Peipsi and Pärnu Bay, it could be assumed that autochthonous DOM contributes significantly to the total DOM pool because CDOM is positively correlated with phytoplankton production and biochemical oxygen demand. In these water bodies the C/V ratio was much smaller than in the very shallow Võrtsjärv, where the above-mentioned relationship was lacking and allochthonous DOM was assumed to dominate throughout the lake.

We found indirect evidence that the share of the allochthonous component in the DOM pool decreases towards offshore areas in large and shallow water bodies. The impact of the DOM discharged in the inflowing rivers reaches farther from the shores if the ratio of the catchment area to the volume of the standing water body (C/V) is larger.

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