Eesti Maaülikool
Estonian University of Life Sciences

DISSOLVED ORGANIC MATTER AND ITS ECOLOGICAL ROLE IN LARGE AND SHALLOW WATER BODIES

LAHUSTUNUD ORGAANILINE AINE JA SELLE ÖKOLOOGILINE TÄHTSUS SUURTES MADALATES VEEKOGUDES

KAIRE TOMING

A Thesis
for applying for the degree of Doctor of Philosophy in Hydrobiology

Väitekiri
Filosoofiadoktori kraadi taotlemiseks hüdrobioloogia erialal

Tartu 2013

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LIST OF ORIGINAL PUBLICATIONS

The present thesis is based on the following papers, which are referred to by Roman numerals in the text. The papers are reproduced with the kind permission of the publishers.

I **Toming, K.**, Arst, H., Paavel, B., Laas, A., Nõges, T. 2009. Spatial and temporal variations in coloured dissolved organic matter in large and shallow Estonian waterbodies. Boreal Environment Research, 14(6): 959–970.

II **Toming, K.**, Tuvikene, L., Vilbaste, S., Agasild, H., Viik, M., Kisand, A., Feldmann, T., Martma, T., Jones, R.I., Nõges, T. Contributions of autochthonous and allochthonous sources to dissolved organic matter in a large, shallow, eutrophic lake with a highly calcareous catchment. Limnology and Oceanography, submitted.

III **Toming, K.**, Nõges, P., Arst, H., Kõiv, T. & Nõges, T. 2013. Long-term changes of the underwater light field in large shallow lakes Peipsi and Võrtsjärv, North-East Europe. Proceedings of the Estonian Academy of Sciences, accepted.

IV Paavel, B., Arst, H., Metsamaa, L., **Toming, K.** & Reinart, A. 2011. Optical investigations of CDOM-rich coastal waters in Pärnu Bay. Estonian Journal of Earth Sciences, 60(2): 102–112.

V Nõges, T., Arst, H., Laas, A., Kauer, T., Nõges, P. & **Toming, K.** 2011. Reconstructed long-term time series of phytoplankton primary production of a large shallow temperate lake: the basis to assess the carbon balance and its climate sensitivity. Hydrobiologia, 667(1): 205–222.

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KT – Kaire Toming; HA – Helgi Arst; TN – Tiina Nõges; BP – Birgot Paavel; AL – Alo Laas; RJ – Roger I. Jones; LT – Lea Tuvikene; SV – Sirje Vilbaste; MV – Malle Viik; TK – Toomas Kõiv; PN – Peeter Nõges; TKa – Tuuli Kauer; LM – Liisa Metsamaa; + – other authors; * – co-workers.

ABBREVIATIONS

a	absorption coefficient
A/V ratio	catchment area/lake volume ratio
a_{250}:a_{365}	absorption ratio
a_{CDOM}	absorption coefficient of CDOM
Al-DOM	allochthonous dissolved organic matter
Au-DOM	autochthonous dissolved organic matter
b	scattering coefficient
BOD_7	biological oxygen demand
c	spectral beam attenuation coefficient
$c(\lambda)$	beam attenuation coefficient of the water at wavelength λ
$c_d(\lambda$	beam attenuation coefficient of the distilled water at wavelength λ
CDOM	coloured dissolved organic matter
$c_f(\lambda)$	beam attenuation coefficient of the filtered water at wavelength λ
Chl *a*	pigment chlorophyll *a*
CO_2	carbon dioxide
CO_3^{2-}	carbonate ion
$\mathrm{COD}_{\mathrm{Mn}}$	chemical oxygen demand
C_{ph}	concentrations of chlorophyll *a* and phaeophytin *a*
C_s	concentration of total suspended matter

DC	total dissolved carbon
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
DOM	dissolved organic matter
DW	dry weight
$E_{\mathrm{d,PAR}}$	downwelling irradiance for PAR region
$E_{\mathrm{d,PAR}}(-0)$	downwelling irradiance for PAR region just below the water surface
$E_{\mathrm{d,PAR}}(z)$	downwelling irradiance for PAR region at depth z
E_{mix}	mean light availability in the mixed layer
E_{u}	upwelling irradiance
FI	fluorescence index
HCO_3^-	bicarbonate ion
ISO	International Organization for Standardization
K_{d}	diffuse attenuation coefficient
$K_{\mathrm{d,PAR}}$	diffuse attenuation coefficient for PAR region
LP	station of Lake Peipsi
Inflow	main inflow of Lake Võrtsjärv
n	number of samples
NAO	North Atlantic Oscillation
O_2	oxygen
OAS	optically active substances
Outflow	outflow of Lake Võrtsjärv

PAR	photosynthetically available radiation
PB	station of Pärnu Bay
PhB	wet weight biomass of phytoplankton
SD	standard deviation
SE	standard error
SI	stable isotopes
Sta.	station
SUVA_{254}	specific UV absorbance
UV	ultra violet
WT	water temperature
$z_{1\%}$	depth of the euphotic zone
Z_{avg}	mean depth of the lake
z_{mix}	depth of the mixed water layer
z_{SD}	Secchi depth
λ	wavelength

1. INTRODUCTION

Our home planet, the Earth is covered by many water bodies (oceans, seas, lakes, rivers etc), that have not only different size and shape but also the composition of the water medium varies between different water bodies as well as within the same water body in spatial and temporal scales. The substances in water affect its transparency, productivity, food webs and finally the ecological quality of aquatic systems. The main constituents are inorganic nitrogen, phosphorus and carbon compounds, mineral particles, plankton organisms that contain different pigments (e.g. chlorophyll *a*), and dissolved organic matter (DOM). The three last mentioned attenuate solar radiation affecting the underwater light field (DOM makes it via its 'coloured component', CDOM). In turn, the underwater light field influences the growth of photosynthetic organisms (e.g. phytoplankton, macrophytes). The present work focuses on one of the most important constituents in aquatic medium – DOM.

About 90% of the organic matter in most aquatic systems is DOM and the rest forms the pool of particulate organic matter (Wetzel 2001). DOM plays a significant role in the carbon and energy cycle of water bodies and as the main source of energy for microbial metabolism (Münster & Chróst 1990; Tranvik 1992) it can have a broad effect on food chains and on the proportions of auto- and heterotrophic processes. CDOM is one of the optically active substances which modifies the optical properties of the water and influence the underwater light field by absorbing both visible (from 400 to 700 nm) and ultraviolet (from 280 to 400 nm) radiation.

The role of DOM in ecological and biogeochemical processes depends on its source and composition. Autochthonous DOM (Au-DOM) is produced in the pelagic and littoral zones of the lake by phytoplankton and other photosynthetic organisms and it consists mainly of non-humic substances, e.g. monomeric sugars, carboxylic acids, amino acids, alditols (Bertilsson & Jones 2003), that are labile and easily utilized or degraded by microorganisms (Thurman 1985). Allochthonous DOM (Al-DOM) is transported from the catchment area, primarily originates from vascular plants and soil organic matter, and consists mainly of humic substances having high molecular weight, brownish colour and being refractory to decomposition (Thurman 1985). The composition and sources of DOM in an aquatic ecosystem may vary spatially and temporally (Finlay & Kendall 2007). In lakes, the relative importance of allochthonous sources should increase with decreasing lake trophy (Jones 1992; Grey *et al.* 2000). In many lakes, especially within the cool boreal region, net ecosystem production is negative (lakes release carbon, Cole *et al.* 2000; Jansson *et al.* 2007), suggesting that appreciable Al-DOM runoff from the catchments increases the respiration within the lake ecosystem to a level that exceeds photosynthetic carbon sequestration by phytoplankton and aquatic plants.

The chemical composition of DOM is very variable and difficult to determine. Different methods have been used to analyse DOM, such as UV–visible and fluorescence spectroscopy (McKnight *et al.* 2001), biomarkers as lipids, amino acids, lignin compounds, lipid acids (Canuel *et al.* 1995; Goni & Thomas 2000), pyrolysis–gas chromatography/mass spectrometry (Wickland *et al.* 2007) and also stable isotopes, that have become increasingly popular in recent years in investigating the sources of DOM (Hood *et al.* 2005; Tank *et al.* 2011).

Many studies have considered the origin and the variability of DOM in humic lakes or in rather deep water bodies with relatively clear water while the information from large, shallow and eutrophic water bodies is scarce and the present study aims to fill this gap.

2. REVIEW OF THE LITERATURE

2.1. DOM in aquatic ecosystems

2.1.1. The composition of DOM

About 90% of the organic matter in most aquatic systems is DOM (passes through 0.2–0.7-μm pore size filters) and the rest forms the pool of particulate organic matter (Wetzel 2001). The role of DOM in ecological and biogeochemical processes depends on its composition and source. The DOM can be viewed as a mixture of plant, microbial and animal products in various stages of decomposition (Wetzel 2001) consisting of heterogeneous mixture of organic compounds. DOM includes elements such as carbon (45–60%), oxygen (25–45%), hydrogen (4–7%), nitrogen (2–5%) and 0.5–5% other elements (Thurman 1985; MacCarthy 2001). DOM can be divided into two categories: non-humic and humic substances (Aiken *et al.* 1985; Thurman 1985). Non-humic substances include carbohydrates, proteins, peptides, amino acids, fats, waxes, resins, pigments and other low-molecular weight organic substances. Generally, these substances are labile and relatively easily utilized and degraded by microorganisms (degradation rate from minutes to months) and therefore the concentrations of these substances are low in water (Wetzel 2001). Previous studies have shown that non-humic substances correlate positively with both nutrients and biological activity while the humic substances correlate negatively with nutrients and positively with biological degradation (Thomas 1997). Humic substances have a medium to high molecular weight, they are refractory (can stay in environment for years) and give a brownish colour to the water. Humic substances constitute the largest fraction (up to 80–90%) of natural organic matter in waters (Thurman 1985; Aiken *et al.* 1985) and they are generally divided into three groups according to solubility: humic acids, fulvic acids and humin (McDonald *et al.* 2004). Chromophore-containing compounds of DOM contribute significantly to the total light absorption in the water and its optically active fraction is usually called coloured DOM (CDOM), also referred to as chromophoric DOM, gelbstoff or yellow substance, and in boreal region it constitutes up to 90% of DOM (Thurman 1985).

2.1.2. The origin of DOM

There are two major sources of DOM in aquatic ecosystems. Au-DOM is produced in the pelagic and the littoral zone of the lake by phytoplankton and other photosynthetic organisms, mostly in the growing season and it consists mainly of non-humic substances. Al-DOM is transported from the catchment area and its inflow is generally highest during flooding periods, for example spring snowmelt (McKnight *et al.* 1997; 2001). Al-DOM primarily originates from vascular plants and soil organic matter consisting mainly humic substances. Al-DOM is extensively modified by microbial metabolism on its way towards recipient lakes (Wetzel 2001) and therefore its concentration and composition is strongly influenced by watershed characteristics like geomorphology, hydrologic regime, land cover and land use (Jaffe *et al.* 2008). Changes in catchment area that increase Al-DOM input to lakes can greatly affect the structure and functioning of ecosystems and cause problems in lake management (Carpenter & Pace 1997).

Generally, the composition and sources of DOM in a given aquatic ecosystem may vary spatially and temporally (Finlay & Kendall 2007). In rivers and streams DOM is derived mainly from allochthonous sources while in lakes Au-DOM prevails and the relative importance of allochthonous sources should increase with decreasing lake trophy (Jones 1992; Grey *et al.* 2000). Although, in many lakes, especially within the cool boreal climate region, net ecosystem production is often negative (Cole *et al.* 2000; Jansson *et al.* 2007), suggesting that the allochtonous organic matter runoff from the catchments increases the respiration rate of the lake ecosystem to a level that exceeds photosynthetic carbon sequestering by phytoplankton and aquatic plants.

2.1.3. The role of DOM

DOM as a major pool of dissolved organic carbon (DOC) plays a significant role in the carbon and energy cycle of lakes and as the main source of energy for microbial metabolism it can have a broad effect on food chains and on the proportions of auto- and heterotrophic processes (Tranvik 1992). DOM also has an influence on nutrient retention and release and on the mobility of metals (De Haan 1992). High concentration of organic acids in DOM gives naturally low pH to the water of humic lakes (Kortelainen 1999) and the photochemical degradation of DOM decreases oxygen concentration (Lindell & Rai 1994).

CDOM is one of the optically active substances (OAS) in water competing with phytoplankton and other aquatic plants for the capture of available light energy. The poorer light climate and narrower euphotic zone caused by high CDOM may possibly decrease primary production; at the same time, CDOM protects aquatic organisms against harmful UV radiation (Kirk 1980; Jones & Arvola 1984; Davies-Colley & Vant 1987; Arvola *et al.* 1999). It may also strengthen the thermal stratification of water bodies (Münster & Chróst 1990).

2.1.4. Methods for DOM analysis

The chemical composition of DOM is very variable and difficult to determine, because DOM in natural water bodies is not identifiable as a distinct molecule, but it is a rather indeterminate mixture of dissolved organic substances (Dera 1992). Different methods have been used to analyse DOM, such as UV–visible and fluorescence spectroscopy (McKnight *et al.* 2001), biomarkers such as lipids, amino acids, lignin compounds, lipid acids (Canuel *et al.* 1995; Goni & Thomas 2000), pyrolysis–gas chromatography/mass spectrometry (Wickland *et al.* 2007) and also stabile isotopes (Hood *et al.* 2005; Tank *et al.* 2011).

SI ratios ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) have become increasingly popular in recent years for assessing sources and transformations of organic matter in pelagic food webs (Grey *et al.* 2000; Jones *et al.* 2001; Palmer *et al.* 2001). For this approach to be successful, the isotopic compositions of potential source materials for DOM and of the DOM itself should differ markedly. In practice, SI ratios of DOM sources in freshwaters may show substantial overlap, being influenced by multiple biogeochemical, physical, and physiological processes (Phillips & Gregg 2003; Finlay & Kendall 2007) that complicate the estimation of source contributions. Moreover, the isotopic ranges for organic matter sources in a certain water body are much smaller than those reported in a global literature survey (Finlay & Kendall 2007). Therefore SI data are best used together with complementary methods. For instance, Hood *et al.* (2005) combined SI data with ancillary data such as elemental analyses and catchment discharge in a Rocky Mountains stream. Tank *et al.* (2011) measured DOM fluorescence and absorption in addition to SI to obtain a comprehensive assessment of DOM sources and transformations in a lake-rich region (Mackenzie Delta) in the Canadian Arctic.

$\delta^{13}C$ values for Al-DOM and for Au-DOM depend on the isotopic signatures of DOM precursor materials. The average $\delta^{13}C$ value of C_3 plants and soil organic matter (Al-DOM precursor materials) is around −27‰ in northern latitudes (Finlay & Kendall 2007). Reported values for $\delta^{13}C$ of freshwater aquatic plants and algae (Au-DOM precursor materials) are more variable and less predictable ranging from about −47‰ to −8‰, with values typically falling in the range of −30‰ to −20‰ (Finlay 2004; Vuorio *et al.* 2006; Finlay & Kendall 2007). This variability arises from: the physiological diversity of aquatic autotrophs and the large variation in the concentrations and SI ratios of dissolved inorganic carbon (DIC) in freshwater systems (Finlay & Kendall 2007).

2.2. CDOM and underwater light field

As mentioned before, CDOM as one of the OAS is an important component of water ecosystems having an impact on the water colour and quality. Applicable analytical methods for determining CDOM in water have been developed, but it is extremely difficult to determine individual organic compounds therein. Many researchers have shown that optical determination of CDOM has distinct advantages over chemical analytic techniques (Bricaud *et al.* 1981; Davies-Colley & 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). The light attenuation coefficient of CDOM, $c^{*}_{f}(\lambda)$ can be considered as the sum of the absorption coefficients of CDOM, $a_{\mathrm{CDOM}}(\lambda)$ and the scattering/absorption coefficients of colloids, $b(\lambda)$ (extremely small particles penetrated through the filter). The contribution of colloids is small in comparison to the total attenuation coefficient of light for CDOM (Bricaud *et al.* 1981; Davies-Colley & Vant 1987). For filtered water $b(\lambda)$ is small and $c^*_f(\lambda)$ can be considered approximately equal to $a_{\mathrm{CDOM}}(\lambda)$ in the water.

Light absorption in water is the sum of contributions due to pure water and OAS (phytoplankton, tripton and CDOM). Although water itself contributes to the absorption of light, the optical properties of turbid water bodies depend largely on suspended particles and dissolved substances (Scheffer 2004). In lakes on peaty catchments CDOM can play the most important role in light absorption giving a dark brownish colour to the water. CDOM absorbs strongly in the UV and blue regions of the spectrum and its absorption capacity decreases exponentially toward longer wavelengths (Kirk 1996).

The underwater light field in lakes, one of the main prerequisites for phytoplankton primary production, results from incident solar radiation (depends on solar altitude, meteorological conditions, time) and the optical properties of water (Kirk 1994). The absorption of light by different OAS, i.e. tripton, phytoplankton and CDOM, leads not only to the attenuation of irradiance with depth but also to the change of its spectral composition. The concentrations of OAS in water can vary by several orders of magnitude (Kirk 1994; Paavel *et al.* 2008) with relative contributions of various OAS differing both seasonally and over the range of different types of natural waters (Zhang *et al.* 2007). In large and shallow water bodies the influence of resuspended sediment particles on the underwater light field is remarkable in comparison with that in deeper lakes (Zhang *et al.* 2007).

The decrease of irradiance with depth in an optically homogenous water column is exponential, but theoretically this law is strictly correct only in case of monochromatic radiation (Dera 1992; Arst *et al.* 2000). For photosynthesis and growth of aquatic plants the quantum irradiance in photosynthetically active region (PAR, 400-700 nm) is of primary interest. In many limnological studies the diffuse attenuation coefficient over the PAR band ($K_{\mathrm{d,PAR}}$) is used to describe the vertical decrease of irradiance in the water column (Paavel *et al.* 2006; Zhang *et al.* 2007; Paavel *et al.* 2008; Reinart & Pedusaar 2008). If underwater PAR irradiance at different depths is measured, the average $K_{\mathrm{d,PAR}}$ for a water column can be estimated using the least square fit of the irradiance vs. depth ($K_{d,PAR}$ is the slope of this exponential regression). $K_d(\lambda)$ and $K_{d,PAR}$ also allow to estimate the depth of the euphotic zone ($z_{1\%}$), spectral and average for PAR region, respectively (Wetzel 2001; Arst 2003).

If besides $K_{d,PAR}$ also the incoming irradiance just below the water surface ($E_{d,PAR}(z=-0)$), is known, we can calculate the downwelling underwater irradiance at depth z ($E_{d,PAR}(z)$). However, a database containing only $K_{d,PAR}$ can be used for estimation the relative values of the irradiance at different depths as well as the seasonal and long-term changes of water transparency. The water layer above the compensation point in which the rate of photosynthesis and respiration become equal, is called the euphotic layer. Its lower border is often defined as the penetration depth of 1% of the subsurface irradiance ($z_{1\%}$). In shallow water bodies the value of $z_{1\%}$ allows to estimate the illuminated bottom area, which is an important parameter for the growth of macrophytes (Scheffer 2004). The average light availability in the mixed water layer (E_{mix}) is the actual value to which phytoplankton is adapted and is biologically more relevant than individual light intensities in different water layers (Phlips *et al.* 1995).

3. AIMS AND HYPOTHESIS OF THE STUDY

The thesis focuses on DOM in eutrophic large and shallow water bodies (coastal areas, large lakes) and the main **aims** of the study are to:

- estimate the range of temporal and spatial variability of DOM (**I, II**);
- trace the origin and estimate the proportion of allochthonous and autochthonous DOM (**I, II**);
- assess the controlling factors of DOM variability and origin (**I, II**);
- estimate the impact of CDOM on underwater light attenuation (**III, IV**);
- assess the factors driving long term changes of underwater light field (**III, V**).

The key **hypotheses** tested in the study are:

- DOM values and the proportions of autochthonous and allochthonous fractions vary spatially and temporally being influenced by climatic and environmental characteristics, *e.g.* river discharges, precipitation, biomass of primary producers, water level, temperature and nutrient concentrations (**I, II**);
- CDOM is one of the main factors controlling the underwater light attenuation in large and shallow water bodies (**III, IV**);
- long-term changes of underwater light field correspond to eutrophication history and changes in water levels of large and shallow water bodies (**III, V**).

4. MATERIALS AND METHODS

4.1. Study area

Studies were conducted in Lake Võrtsjärv (**I, II, III, V**), in Lake Peipsi (**I, III**) and in Pärnu Bay (**I, IV**). All three water bodies (Fig. 1) belong to the southern Boreal forest zone and are important for fisheries and recreation. Basic features of the study water bodies are shown in Table 1.

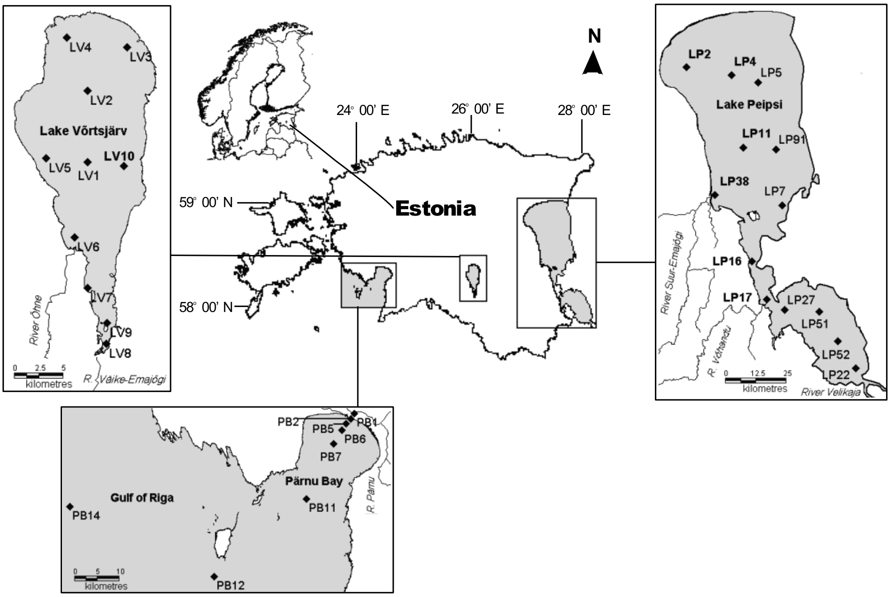

Figure 1. Study area.

4.1.1. Lake Võrtsjärv

Lake Võrtsjärv is large, shallow and eutrophic lake in Central Estonia, well mixed by the surface waves and currents (Table 1, Fig.1). Macrovegetation occupies about 19% of its total area (Nõges *et al.* 2010a). Lake Võrtsjärv with its large catchment area has a larger A/V ratio (4.1 m^{-1} at mean water level) than other well-studied large and shallow lakes like Peipsi (1.9 m^{-1}) or Balaton (2.7 m^{-1}), and much larger than large, deep lakes like Ontario (0.046 m^{-1}), Ladoga (0.08 m^{-1}), Onega (0.18 m^{-1}), and Vänern

(0.27 m^{-1}) (ILEC World Lake Database, http://www.ilec.or.jp/database/index/idx-lakes.html). Võrtsjärv catchment comprises arable land and grassland 45.3%, forest 46.1% (mixed forest 24.4%, coniferous forest 15.0%, and deciduous forest 6.7%), wetland 0.6%, bog 0.4% and marsh 0.1% (Toming *et al.* 2009). The catchment is in carbonate terrain and DIC is the dominant form of aquatic C as is typical of temperate regions and boreal forests in carbonate terrain due to high soil respiration, carbonate weathering, and groundwater flow (Tranvik *et al.* 2009). A specific feature of Võrtsjärv is the large natural climate-related variability of water level, which causes up to a 3-fold difference in its water volume and A/V ratio (Nõges *et al.* 2010b). The lake is covered by ice for an average 184 days (November–April). The flow regimes of the inflowing rivers are natural, and discharges usually peak in April. The northern and central area of Võrtsjärv is plankton-dominated, where the large width, strong impacts of winds and currents and eroded bottom sediments make it inappropriate for macrophytes. In contrast, the sheltered and narrow southern part of the lake has fine-grained sediments and is macrophyte-dominated. Also the influence of inflows is strongest in this part of the lake. To get complementary information, lower course of the largest inflow (the River Väike Emajõgi) and the upper course of the outflow (the River Suur Emajõgi) of Lake Võrtsjärv were also studied in paper **II**. All-year-round monthly hydrochemical and hydrobiological monitoring started in Lake Võrtsjärv in 1961 (Nõges *et al.* 2001).

4.1.2. Lake Peipsi

Lake Peipsi, the fourth largest lake in Europe, is located in the eastern part of Estonia (Table 1, Fig. 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). Peipsi is large, shallow eutrophic and polymictic water body, well mixed by the surface waves and currents. It is interconnected with Lake Võrtsjärv by the River Emajõgi running from Võrtsjärv into Peipsi. The water level of Lake Peipsi is unregulated and has a natural variability (mean annual range 1.15 m), which is strongly associated to the changes of North Atlantic Oscillation (Nõges *et al.* 2010c). Peipsi is ice-covered usually for four months a year. The shallowness of the lake and the wave-induced resuspension of bottom sediments contribute to the formation of high seston concentrations and high turbidity.

4.1.3. Pärnu Bay

Pärnu Bay is a shallow water basin in the northeastern Gulf of Riga (Table 1, Fig. 1), which could be divided into an inner and an outer basin. The inner part has approximate measures of 13 km × 14 km, an area of about 190 km^2 and the maximum depth of 7.6 m. The outer part extends down to the southern tip of Kihnu Island, having an area of about 500 km^2 and the maximum depth of about 15 m. The quality of water and quantity of nutrients in Pärnu Bay depend on the inflow of fresh water from rivers and on the intrusion of water from the Gulf of Riga due to changes in wind direction and water level. Nutrient concentrations in Pärnu Bay are higher than the average level in the Gulf of Riga, as it is a relatively isolated strip of sea. The Pärnu River accounts for approximately 80% of the inflow to Pärnu Bay, bringing annually 2 km^3 of fresh water to the bay, although the volume of the inner basin is only 1 km^3 (Suursaar & Tenson 1998). The average river flow rate is 64 $m^3\ s^{-1}$, which varies considerably during the year. Due to this fact the salinity of water in Pärnu Bay is low, only 3.5‰ in comparison with the salinity of 4.5-6‰ of the Gulf of Riga (Tervisekaitseinspektsioon 2009). The characteristic bay bottom type is fine sand, with only occasional stony areas. Due to the effect of waves and currents the water always contains particles of soft bottom sediments. Additional suspended matter is brought also by the Pärnu River waters. More specifically, large quantities of peat dust are directed to ditches and to the Sauga River and from there to the Pärnu River with drainage water from peat excavation areas. Peat dust reaches the bay also in the course of loading unpacked peat at the mouth of the river.

Table 1. Basic features of the studied water bodies.

Water body	Lake Võrtsjärv	Lake Peipsi	Pärnu Bay
Location (N/E)	57°50’-58°30’/ 25°35’-26°40’	57°51’-59°01’/ 26°57’-28°10’	58°05’-58°23’/ 24°06’-24°35’
Area (km^2)	270	3 555	690
Catchment area (km^2)- A	3104	10 207	8532
Arable land & grassland (% of A)	45.3	40.6	31.4
Forest (% of A)	46.1	47.0	49.9
Volume (km^3) – V	0.75	5.37	5.17
A/V	4.1	1.9	1.65
Mean depth (m)	2.8	7.1	7.5
Maximum depth (m)	6	15.3	15

4.2. Sampling and data

Depth-integrated (**I, II, III, V**) or surface layer (0.2 m, **IV**) water samples were collected with a standard water sampler once per month at selected sampling stations (Fig. 1) during the ice-free period of the year in 2002-2007 in Peipsi (**I, III)**, 2002-2007 in Võrtsjärv (**I, III, V)** and 2005-2007 in Pärnu Bay (**I, IV**) or throughout the year in 2008-2010 in Võrtsjärv (**II)**. Water samples were stored in polyethylene bottles in the dark at 4 °C and analysed within 12 hours. The polyethylene bottles were washed with distilled water and flushed with lake water prior to sampling.

The beam attenuation coefficient of unfiltered (**III, IV, V**) and filtered (**I, IV**) water, absorption at wavelengths 250, 254, 365 nm (**II**), concentration of DIC (**II**), DOC (**II**), Chl *a* (**IV**), phaeophytin *a* (**IV**) and total suspended matter (**IV**), carbon stable isotope ratio (δ^{13}C) of DIC and DOM (**II**) and FI (**II**) were measured from the water samples.

SI samples of phytoplankton were collected with the plankton net (mesh size 145 μm) in 2008- 2010 from Sta. 10 in Lake Võrtsjärv (**II**). SI samples of dominant macrophytes (*Phragmites australis* (Cav.) Trin. ex Steud. and *Nuphar lutea* (L.) Sibth. and Smith) were collected during the vegetation period in 2008 from Sta. 8 in Lake Võrtsjärv (**II**). For more details see paper **II**.

Daily discharges of the River Väike Emajõgi (**I, II**), the River Õhne (**I**), the River Emajõgi (**I**), the River Võhandu (**I**) and the River Pärnu (**I**), daily precipitation (**I, II**), water level (**I, II**), salinity (**I,** only in Pärnu Bay), BOD_7 (**I**), COD_{Mn} (**I, III**), water colour (**III**), WT (**II**), pH (**II**), O_2 (**II**), Secchi depth (**I, III**), concentrations of Chl *a* (**II, III**), total number of bacteria (**II**) and biomasses and composition of phytoplankton (**I, II, III**) were measured as part of the state monitoring programme and 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.

4.3. Sample analysis and methods

4.3.1. Beam attenuation coefficients c(λ) and cf(λ)

Beam attenuation coefficients of filtered water ($c_f(\lambda)$, **I**) or unfiltered water ($c(\lambda)$, **III, IV, V**) were measured at 280–800 nm with a Hitachi U1000 (**IV**) or Hitachi U-3010 (**I, III, V**) dual-beam spectrophotometer, using distilled water as the reference.

The attenuation coefficients of light were obtained as:

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

$$c_f^*(\lambda) = c_f(\lambda) - c_d(\lambda) \quad (2)$$

where $c_d(\lambda)$ is the beam attenuation coefficient of distilled water at wavelength (λ) (m^{-1}). For more detailed descriptions see papers **I** and **III**.

4.3.2. Absorption coefficient a_{CDOM}

To describe the spatial and temporal variations of DOM in water bodies we used CDOM (the optically measurable component of the DOM). Using optical methods, the concentration of CDOM in water is expressed in terms of its attenuation or absorption coefficient at a given wavelength (see paragraph 2.2). We chose the absorption coefficient, a_{CDOM} at wavelength λ = 380 nm (**I, IV**). The measured values of $c^*_{\mathrm{f}}(\lambda)$ can be used to calculate a_{CDOM}. Still the values of $c^*_{\mathrm{f}}(\lambda)$ are not identical to the a_{CDOM} because very small particles (colloids) may pass through the filter (see paragraph 2.2). 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):

$$a_{\mathrm{CDOM}}(\lambda) = c^*_{\mathrm{f}}(\lambda) - c^*_{\mathrm{f}}(\lambda_{\mathrm{R}})(\lambda_{\mathrm{R}}/\lambda)^{g} \tag{3}$$

where $c^*_{\mathrm{f}}(\lambda)$ and $c^*_{\mathrm{f}}(\lambda_{\mathrm{R}})$ were obtained using dual-beam spectrophotometer at wavelength λ and at some reference wavelength (λ_{R}), respectively, and g is a parameter describing the contribution of scattering by colloids to $c^*_{\mathrm{f}}(\lambda)$. For more details see paper **I** and **IV.**

4.3.3. Diffuse attenuation coefficient $K_{\mathrm{d,PAR}}$

The model described by Arst *et al.* (2002) and Arst (2003) allowed to correct the values of $c(\lambda)$ for forward scattering, and differentiate $c(\lambda)$ to its two components, absorption coefficient, $a(\lambda)$ and scattering coefficient, $b(\lambda)$. Then, using the formulae developed by Kirk (1984, 1994), the $K_{\mathrm{d}}(\lambda)$ spectra and $K_{\mathrm{d,PAR}}$ values and corresponding irradiance profiles were calculated for the period of 2002-2007 for Peipsi (**III**) and Võrtsjärv (**III, V**). To extend the $K_{\mathrm{d,PAR}}$ data series for earlier periods (1964-2001 for Võrtsjärv and 1983-2001 for Peipsi), lake-specific backward stepwise multi-component regression models were developed on the basis of monitored Chl *a*, PhB, Z_{SD}, $\mathrm{COD}_{\mathrm{Mn}}$, and water colour. The two latter variables served as proxies for the CDOM. For more detailed descriptions see paper **III**.

4.3.4. Irradiance characteristics

Incoming irradiance (MJ m^{-2} month^{-1}) for the observation periods was measured at actinometric stations of Tõravere (58°16' N, 26°26' E, about 20 km from Võrtsjärv) and Tiirikoja (on the northern coast of Peipsi, 58°51' N, 26°57' E). These data together with corresponding values of

$K_{d,PAR}$ allowed to roughly estimate the variation of underwater light field (**III**). $E_{d,PAR}(z)$ was calculated according to the following formula (Dera 1992; Arst 2003):

$$E_{d,PAR}(z) = E_{d,PAR}(z = -0)\exp(-K_{d,PAR}z) \tag{4}$$

where z is measured in m and $K_{d,PAR}$ in m^{-1}. $E_{d,PAR}(z=-0)$ is the downwelling irradiance just under the water surface (immediately after refraction). By rough estimation $E_{d,PAR}(z=-0) = 0.934*E_{d,PAR}(z=0)$, since it is supposed that reflection coefficient from water surface is approximately 0.066 (Jerlov 1976).

We calculated $z_{1\%}$ from $K_{d,PAR}$ as:

$$z_{1\%} = -\ln(0.01)/K_{d,PAR} \tag{5}$$

For calculating E_{mix} (Phlips *et al.* 1995), we first derived an integral (ζ) from irradiance values over depth in the range from $z=0$ to $z=z_{mix}$:

$$\zeta = \int_0^{z_{mix}} E_{d,PAR}(z = -0)\exp(-K_{d,PAR}z)dz \tag{6}$$

According to its definition, $E_{mix} = \zeta/z_{mix}$. It leads to the following equation:

$$E_{mix} = \frac{E_{d,PAR}(z = -0)}{K_{d,PAR}z_{mix}}\left[1 - \exp(-K_{d,PAR}z_{mix})\right], \tag{7}$$

where E_{mix} is in the same units as $E_{d,PAR}(-0)$. In lakes Võrtsjärv and Peipsi, water is typically mixed down to the bottom, therefore z_{mix} was taken equal to Z_{avg} of the lake. For more details see paper **III.**

4.3.6. Chl-*a*, phaeophytin-*a* and total suspended matter

For Chl-*a* and phaeophytin-*a* assessment, water (0.5-1 litres) was passed through Whatman GF/F filters (**IV**) and the pigments were extracted from the filters with 90% ethanol at 75°C for 5 minutes. Absorption spectra of the extracts at 400-800 nm were measured spectrometrically before and after acidification with dilute hydrochloride acid. The determined absorbance values were converted respectively to Chl-*a* and phaeophytin-*a* concentrations (ISO 10260, 1992 (E)). For the sake of simplicity, the sum of concentrations is abbreviated to C_{ph}.

Suspended solid concentration C_s (**IV**) was measured gravimetrically after filtration of water through pre-weighed and pre-combusted (103–105 C for 1 h) filters (ESS method 340.2, 1993).

4.3.7. DOC and DIC concentrations

For determination of DIC and DOC concentrations (**II**), water samples were filtered through precombusted (3 h at 500 °C) Whatman GF/F glass microfiber filters and the carbon content of the filtrate was measured by TOC-VCPH analyzer (detection limit 4 μg L^{-1}; Shimadzu, Japan) or, after April 2009, by the TOC cuvette tests (detection limit 2 mg L^{-1}; Hach Lange, Germany). Both methods conform to European standard method (BS EN 1484: 1997). In both methods, DOC concentration was determined as the difference between total dissolved carbon and dissolved inorganic carbon (DOC=DC-DIC). For more details see paper **II.**

4.3.8. Fluorescence index

McKnight *et al.* (2001) introduced a spectrofluorometrical method for qualitative estimation of the origin of the precursor material of DOM. Terrestrially derived DOM in natural waters is characterized by lower fluorescence index (FI) values (ca 1.4) than the DOM of predominantly microbial origin (ca 1.9). FI was determined as the ratio of the emission intensity at a wavelength of 450 nm to the emission intensity at 500 nm, obtained with an excitation of 370 nm (McKnight *et al.* 2001) using fluorescence spectrophotometer Hitachi 2500 (**II**). Prior to the fluorimetric measurements, water was filtered through Millipore Millex-LCR 0.45 μm pore size filter.

4.3.9. SUVA$_{254}$ and a_{250}:a_{365}

Absorptions of the filtrate at wavelengths of 250, 254 and 365 nm were measured by UV-Vis spectrophotometer (Lambda 35, Perkin Elmer Shelton, USA) in a 1-cm quartz cuvette (**II**). Measured absorbances were used to calculate a_{250}:a_{365} and SUVA$_{254}$ (L mg C^{-1} m^{-1}). SUVA$_{254}$ was obtained by dividing the absorbance at 254 nm (m^{-1}) by the concentration of DOC in mg C L^{-1} (Weishaar *et al.* 2003). SUVA$_{254}$ is used as an index of the aromatic nature of DOM: its values > 4 indicate highly hydrophobic and aromatic DOM, while the values < 3 indicate hydrophilic and less aromatic DOM (Peuravuori & Pihlaja 2007). a_{250}:a_{365} has been used as an indicator of the proportion of fulvic and humic acids in DOM – the increasing value reflects decreasing aromaticity (Egeberg *et al.* 2002; Peuravuori & Pihlaja 2007) and, thus, increasing proportion of the autochthonous or microbiologically decomposed DOM (Strome & Miller 1978). For more details see paper **II.**

4.3.10. Stable isotopes

Stable isotope ratios are expressed in parts per thousand (‰) using the δ notation where $\delta = [(^{13}C/^{12}C_{sample})/(^{13}C/^{12}C_{reference})-1] \times 1000$.

For DIC δ^{13}C analyses from lake water, Labco 12 mL vials for were prepared sampling in the laboratory. 4 drops of phosphoric acid (ca. 4 μL) were placed in the empty 12 mL screw top vials. After sealing the vials with septa, all vials were flushed with pure helium. The water samples (0.5 mL) were injected to vials in the field using gastight, disposable syringes. δ^{13}C from the CO$_2$ in the headspace of each vial was analysed within 90 days at the Institute of Geology at Tallinn University of Technology, Estonia using a Thermo Fisher Scientific Delta V Advantage mass spectrometer and GasBench II.

For DOM SI analyses (**II**), 100-200 mL of the Whatman GF/F (pre-combusted at 500 °C, 3 hours) filtrate was freeze-dried (Heto PowerDry LL3000, ca 48 hours). Prior to δ^{13}C assessment (two replicates, ca 3 mg dry weight each) the dried material was held for 24 hours in concentrated HCl fumes to remove inorganic C from samples and then re-dried for 1 hour at 60 °C.

For phytoplankton SI assessment (**II**), dominant species (mainly the diatoms *Aulacoseira* spp.) were separated from fresh samples by repeated sedimentation in the laboratory. In the summer period floating cyanobacteria (mainly *Limnothrix planctonica* (Wołoszyńska) Meffert, and *Limnothrix redekei* (Van Goor) Meffert) were collected from the surface of the phytoplankton sample and included in the bulk dominant phytoplankton sample. For more details see paper **II.**

For macrophyte SI assessment (**II**), the collected material was gently cleaned from periphyton, dried at 60 °C overnight, pulverized and stored as a ground powder. Two replicates (ca 1.5 mg DW each) were prepared for SI analyses.

SI analyses of organic matter were carried out at the University of Jyväskylä, Finland with a Carlo-Erba Flash 1112 series Elemental Analyzer connected to a DELTAplus Advantage IRMS (Thermo Finnigan). The reference materials used (IAEA standard NBS-22) were secondary standards of known relation to the international standard (Pee Dee belemnite). The analyses were run using dried and homogenized potato leaves as an internal laboratory working standard. Instrument precision was ±0.2‰. The standard deviation between replicates was normally within 0.2‰ (**II**).

4.4. Data analysis

To examine the spatial dissimilarities in CDOM (**I**), the sampling points of different water bodies were grouped by non-metric multidimensional scaling (MDS) using the software package PRIMER, version 5 (Clarke & Gorley 2001; Clarke & Warwick 2001). The spatial similarity of CDOM absorption among groups of sampling points was subsequently tested for significance by analysis of similarity (ANOSIM) using the same software package. For description of the ANOSIM see paper **I.**

The software Statistica 7.0 or 8.0 (StatSoft, Inc. 2004, StatSoft, Inc. 2007) was applied to analyze the data (**I, II, III**). Spearman's Rank Order correlation was used to find relationship between indices (**I, II, III**). The nonparametric Kolmogorov-Smirnov (K-S) test was used to compare the differences of the measured parameters in different sampling stations (**II**). The significance level to indicate differences and relationships was set at $p<0.05$.

Two source mixing model (Fry 2006) was used to assess the contribution of river water DOM and primary producers (phytoplankton or macrophytes) to lake-water DOM in Lake Võrtsjärv (**II,** Eq. 2 and 3).

5. RESULTS AND DISCUSSION

5.1. Temporal and spatial variability of DOM

5.1.1. Spatial variability of DOM

CDOM values (a_{CDOM}, see paragraph 4.3.2) that are usually strongly correlated with DOC concentrations (Kortelainen 1993; Kallio 1999) were used to describe the spatial and temporal variations of DOM in studied water bodies.

CDOM were generally higher in the southern basins of Peipsi than in the northern basin (Fig. 1a in **I**). 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. In Võrtsjärv, the values of CDOM were fairly similar in different parts of the lake, with the exception of the southernmost part close to the discharge of the River Väike Emajõgi, where the values were usually higher than in other parts of the lake (Fig. 1b in **I**). In Pärnu Bay, the values of CDOM varied several fold within the sampling transect, clearly decreasing with increasing distance from the mouth of the River Pärnu towards the open part of the Gulf of Riga (Fig. 1c in **I**).

Analysis of the spatial distribution of CDOM absorption revealed that CDOM values were always highest near the river mouths (**I**). The spatial differences were connected with the river discharges in Peipsi, especially in the southern parts of the lake. Based on the river flow rates and catchment areas, three main rivers discharge into Peipsi: the River Velikaja, the River Emajõgi and the River Võhandu, all flowing 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 values in the southern lake areas. That also applies to station LP38, which is situated close to the mouth of the River Emajõgi. The high discharge rate and high values of CDOM in this large river could be considered the main reasons for the high CDOM values 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 values there. 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 Al-DOM (**I**).

The spatial dissimilarity among the water bodies investigated was highest in Pärnu Bay (**I**). 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 & Del Vecchio 2002; Chen *et al.* 2002). Significant negative correlations between CDOM and salinity at stations PB7 and PB11 in Pärnu Bay (Table 3 in **I**) confirm the strong influence of the freshwater on CDOM values.

5.1.2. Temporal variability of DOM

In Peipsi the values of CDOM ranged from 4.17 m^{-1} (sampling point LP4 in October 2003) to 22.3 m^{-1} (sampling point LP17 in March 2007, **I**). In general, CDOM absorption decreased slightly from spring to autumn, usually showing the highest values in April and May (Fig. 2a). The CDOM values increased somewhat again in October, 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. In the southern area of Peipsi, CDOM was significantly positively correlated with the average daily discharge of the River Emajõgi measured 1-4 weeks earlier (Table 4 in **I**). 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. COD_{Mn} (can be used as proxy for the CDOM) in the water of the Rivers Emajõgi and Võhandu was significantly correlated with the discharges of both rivers ($r = 0.43$ and $r = 0.64$, $p < 0.05$, respectively). The mean COD_{Mn} values of the rivers Emajõgi and Võhandu were respectively 13.3 and 10.4 mgO L^{-1}.

At the offshore sampling point in Võrtsjärv (Sta. 10) the values of CDOM ranged from 3.96 to 15.7 m^{-1} (**I**). As in Peipsi, CDOM generally decreased towards autumn and the maximum values were usually obtained during April and May (Fig. 2b). In Võrtsjärv, CDOM was positively correlated with the lake's water level (Table 3 in **I**). We obtained statistically significant ($p < 0.05$) correlations between CDOM at offshore Sta. 10 in Võrtsjärv and the average daily discharges of the rivers Väike Emajõgi and Õhne measured 1-4 weeks earlier (Table 4 in **I**). Also, there were significant relationships between the COD_{Mn} values in Väike Emajõgi (mean 9.23 mgO L^{-1}) and Õhne (mean 14.59 mgO L^{-1}) and the discharges of the same rivers (respectively $r = 0.43$ and $r = 0.62$, $p < 0.05$).

In Pärnu Bay both the lowest and highest values of CDOM were observed in 2007: 2.24 m^{-1} (in August at sampling point PB12) and 32.9 m^{-1} (in April at sampling point PB1, **I**). Generally, the values of CDOM absorption decreased from April to September (Fig. 2c). The temporal variation of CDOM at the sampling points situated near the mouth of the River Pärnu (PB1, PB2 and PB5) was markedly higher than at the open sea sampling points (PB11 and PB12). Spearman correlation showed a good correspondence between the CDOM in Pärnu Bay and discharges of the river in the transect from the mouth of the River Pärnu towards to the open water area. The discharges of the River Pärnu were measured 2-4 weeks earlier than the CDOM (Table 4 in **I**). The COD_{Mn} values in the River Pärnu were much higher (mean 17.3 mgO L^{-1}) than those in the other rivers (Emajõgi, Võhandu, Õhne, Väike Emajõgi) giving a significant correlation with the discharge ($r = 0.63$, $p < 0.05$).

Temporal variations of CDOM in the lakes and bay followed more or less the pattern of CDOM in their main inflows (Fig. 2). In the inflows, however, CDOM followed the dynamics/seasonality of precipitation while that was not evident in the lakes and bay (Table 4 in **I**).

We found considerable evidence that discharges from the rivers determine the values of CDOM in lake and bay areas close to the river mouths (**I**). In Peipsi, the strongest correlation (r = 0.82, $p < 0.05$) 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 River Võhandu, were not correlated with the discharge of this river (Table 4 in **I**). These sampling points are situated in Lämmijärv, which receives its waters largely from Lake Pihkva where the largest inflow, the River Velikaya discharges; the much smaller River Võhandu seems to make only a minor contribution to the CDOM value in southern parts of Peipsi. The close correlation between CDOM in Lämmijärv and the discharge of the Emajõgi (Table 4 in **I**) should be considered occasional and most probably caused by the close correlation of 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 values but with a time lag of 2-4 weeks (Table 4 in **I**). In Võrtsjärv, CDOM at the offshore station correlated significantly with discharges 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 A/V ratio (4.1), so the influence of the rivers reaches open water areas more quickly and strongly than in Peipsi, where the A/V ratio is only 1.9. However, in Pärnu Bay, where the A/V ratio is 1.65, the impact of the discharge of the River Pärnu reached quite far into the open water area fairly quickly. This could most probably be attributed to the high CDOM values in this river, which exceeds the CDOM values in the main rivers of the Peipsi and Võrtsjärv catchments. However, the A/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, CDOM was also positively correlated with the water level (Table 3 in **I**) that is unregulated and has a natural variability strongly associated with the changes of NAO winter 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 values and more variation in CDOM during spring. CDOM values are generally positively related to discharge in Estonian rivers. In the two major rivers in the Lake Võrtsjärv catchment, water colour and COD_{Mn} (often used as proxies of CDOM) 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 (**I**).

Within-year changes in precipitation and runoff may affect both organic matter production and transport processes (Evans *et al.* 2005). Temporal variation of CDOM values in the studied lakes and bay followed the discharge patterns of the main inflowing rivers (see Fig. 2), that corresponds well to published observations (Bricaud *et al.* 1981; Clair *et al.* 1999; Chen *et al.* 2002). CDOM values were lower in summer, probably because of the lower discharge. However, we did not study the importance of photobleaching or microbial consumption while other authors have shown that photobleaching combined with microbial consumption might also cause a summer decline of CDOM in surface waters (Vodacek *et al.* 1997; Whitehead *et al.* 2000; Blough & Del Vecchio 2002).

According to our results (**I**), precipitation seasonality was not correlated with CDOM in the lakes and 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 positive correlation between the precipitations and DOM concentrations in the streams discharging from the peaty and forested areas, where stronger runoff increases DOM discharge from the upper organic-rich soil horizons (Arvola *et al.* 2004; Laudon *et al.* 2004). However, precipitation and runoff are not always very closely correlated due to the variations in evaporation processes and soil moisture levels (Pandžić & Trninić 1999-2000).

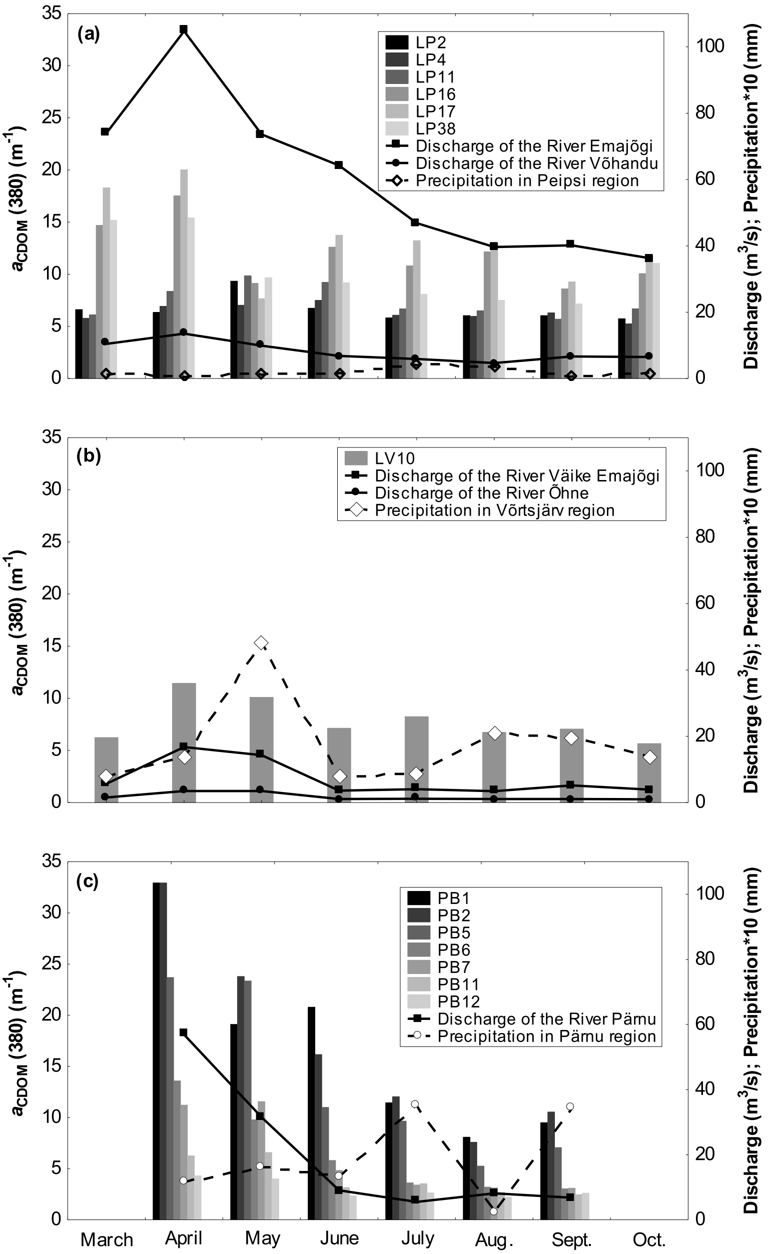

Figure 2. Temporal variation of a_{CDOM} in Peipsi (a), in Võrtsjärv (b) and in Pärnu Bay (c) averaged over the observation periods: 2002-2007 (a); 2003-2007 (b); 2005-2007 (c) at the indicated sampling points. The daily mean discharges of the rivers Emajõgi (a), Võhandu (a), Väike Emajõgi (b), Õhne (b) and Pärnu (c) as well as the daily mean precipitation in the regions of Peipsi (a), Võrtsjärv (b) and Pärnu Bay (c) measured one week before CDOM measurements are also shown.

5.2. The origin of DOM and the contributions of allochthonous and autochthonous fractions

5.2.1. The origin of DOM

DOM δ^{13}C values varied from –28.4‰ (Sta. 10 in August 2010) to –25.4‰ (inflow in February 2010) in Lake Võrtsjärv and the mean values (Table 1 in **II**) in the Inflow and the nearby southern lake site were significantly higher than those from the central lake and the outflow (Fig. 3; Table 2 in **II**). This indicates a difference between lake and river DOM due to different primary producers and the level of terrestrial influence. It also reflects changes in DOM due to photochemical and microbial processes, and sedimentation.

While bulk parameters and single biomarker compounds may not individually be adequate for identifying specific sources of organic matter, it might be possible to identify the likely sources of organic matter to an aquatic system when these indices are assessed together (Canuel *et al.* 1995; Countway *et al.* 2007). In Võrtsjärv we used multiple tracers to provide best estimates of the origin of DOM (**II**). DOC concentration was variable, and higher in-lake DOC concentrations coincided both with higher inputs from the catchment after snowmelt and with higher primary production, making it impossible to estimate the origin of DOM based on DOC concentrations. Use of $SUVA_{254}$ values (dependent on DOC concentrations) to draw conclusions about the origin of DOM needs also to take into account that in shallow eutrophic lakes carbon concentration can be largely determined by both the runoff from catchment area and by lake productivity. The absorption ratio a_{250}:a_{365} appeared to be a useful method for estimating the source of DOM in Võrtsjärv. FI values between 1.42 and 1.61 (Table 1 in **II**) showed that fulvic acids are of mainly allochthonous origin in Lake Võrtsjärv. Relatively high FI values from our study (Table 1 in **II**) support previous results by other authors that in those freshwaters where DOM is derived primarily from autochthonous algal and microbial precursor material, fulvic acids generally account for a lower proportion of the DOM compared to water bodies where DOM is derived from plants and soil organic matter (Hood *et al.* 2005).

Au-DOM is produced mainly by phytoplankton in Võrtsjärv (especially in the northern and central part), which has relatively low primary production of littoral and bottom macrophytes. The reed belt and other macrophytes cover only 18.8% of the lake area (Feldmann & Nõges 2001) and the contribution of macrophytes to the total primary production in this lake has been estimated to be about 15% (Nõges *et al.* 2003). Furthermore, Cremona *et al.* (subm.) found that, unlike several other eutrophic and shallow lakes, the contribution of macrophytes to the Lake Võrtsjärv C budget was low (only 5%). Therefore, we can assume that there are two main potential sources of DOM in the northern and central part of Lake Võrtsjärv: phytoplankton as an autochthonous part and river water DOM as an allochthonous part (Fig. 7 in **II**). At Sta. 10, where phytoplankton is the dominant primary producer, the mean δ^{13}C of phytoplankton was –28.7‰ (minimum –30.5‰ and maximum –26.8‰; *n*=16). The mean δ^{13}C value for *Phragmites australis* was –26.4‰ (minimum –28.3‰ and maximum –24.2‰; *n*=3) and for *Nuphar lutea* -26.5‰ (minimum –28.6‰ and maximum –25.4‰; *n*=6) in the southern part of Lake Võrtsjärv where macrophytes are the dominant primary producers (**II**).

Against our expectations, δ^{13}C signatures of Au-DOM in Võrtsjärv were lower than those of the allochthonous riverine DOM (**II**). As the isotope signatures of the precursors of Au-DOM, phytoplankton and other seston, were also relatively low in Lake Võrtsjärv, this was presumably the cause of ^{13}C-depleted Au-DOM. Phytoplankton δ^{13}C value is determined by the physiology of algae, and by the availability and isotopic composition of different forms of DIC (Xu *et al.* 2007). In Võrtsjärv DIC δ^{13}C is already rather low (Table 1 in **II**), while $^{12}CO_2$ is incorporated preferentially in photosynthesis (Laws *et al.* 1997; Popp *et al.* 1998). If phytoplankton uses already ^{13}C-depleted DIC to synthesize even more ^{13}C-depleted organic matter, the DOM originating from such phytoplankton should also have low δ^{13}C values. The negative correlation between δ^{13}C of DOM and FI values and a_{250}:a_{365} (Table 3 in **II**) supports our contention that in Võrtsjärv Al-DOM has higher δ^{13}C values than autochthonous material.

Based on the high pH values (Table 1 in **II**), HCO_3^- is the main component of DIC in Lake Võrtsjärv and its inflowing rivers. Lower DIC concentrations in the lake center and outflow during summer (Table 1, Fig. 4a in **II**) might be the result of precipitation of carbonates, as well as uptake of CO_2 or even HCO_3^- by photosynthetic organisms (Barešić *et al.* 2011). Bade *et al.* (2004) reported that δ^{13}C values of DIC varied broadly among 72 lakes from diverse regions (from –31‰ to +2.6‰), while seasonal variation within most lakes was smaller. In Võrtsjärv $\delta^{13}C$ signatures of DIC were within this range varying from –14.5‰ to –3.56‰ (Table 1 in **II**), although spatially and seasonally variable (Fig. 4b in **II**). Values of DIC $\delta^{13}C$ in the Inflow were more negative than in the lake center and outflow (Table 1, Fig. 4b in **II**), especially in summer. According to Barešić *et al.* (2011), dissolution of carbonate minerals with $\delta^{13}C$ around 0‰ and oxidation of soil organic matter ($\delta^{13}C$ around −28‰) in the catchment area might increase the concentration of HCO_3^- and saturate river water with CO_2 leading to decreased $\delta^{13}C$ values of DIC. A downstream increase in $\delta^{13}C$ values of DIC is mainly due to the fractionation effect during both CO_2 degassing and calcite precipitation. During the warm part of the year, preferential removal of ^{12}C by the photosynthetic activity of aquatic plants and the evaporation of water (both emphasised by temperature increase) result in more positive $\delta^{13}C$ values of DIC compared with winter. In the main lake at Sta. 10, the very strong relationship between $\delta^{13}C$ of DIC and Chl *a* concentration (Fig. 4c in **II**) suggested that photosynthetic uptake of DIC was the main process causing the marked seasonal variation in $\delta^{13}C$ values of DIC. Jones *et al.* (2001) showed a positive correlation between $\delta^{13}C$ of DIC and Chl *a* in deep oligotrophic soft-water lake Loch Ness, but it is remarkable that the same strong relationship can be found in highly alkaline Võrtsjärv. In our study, seasonal variation of $\delta^{13}C$ of DIC was highest in the lake center at Sta. 10 while only minor seasonal variation occurred in the Inflow and at the southern lake site close to it. Probably at these sites the processes like microbial respiration and carbonate weathering that produce ^{13}C-depleted DIC (Finlay 2003) were more in balance throughout the year with the evasion and photosynthetic uptake of CO_2 that can increase $\delta^{13}C$ value of DIC. Winter $\delta^{13}C$ values of DIC at the lake outflow were much higher than at the lake center (Fig. 4b in **II**). This can be explained by the warmer and heavier lake water that disturbs the formation of ice cover at the outflow. Thus the outflow is usually ice-free in winter allowing evasion of excess CO_2 which increases the $\delta^{13}C$ value of the remaining DIC.

Seasonally DOM $\delta^{13}C$ values were lower from May to September, during the active growing season when Au-DOM should prevail and higher from October to April when Al-DOM should dominate (Fig. 3). A Kolmogorov-Smirnov test confirmed that the differences of $\delta^{13}C$ values between those two periods were statistically significant for all sampling stations ($p<0.05$). After ice break in April, increasing WT, light and nutrient availability lead to intensive primary production, increasing Chl *a* concentration and pH (**II**). Therefore, a higher proportion of Au-DOM in the whole DOM pool starting from April might be expected. Our study revealed that in the central part of Lake Võrtsjärv the proportion of Au-DOM did increase together with rising WT, Chl *a* and pH (Table 3 in **II**) reflecting increasing autotrophy of the ecosystem. A high frequency metabolism study by Laas et al. (2012) revealed the prevalence of net autotrophy in Võrtsjärv from early spring until August or September whereas during the rest of the year heterotrophy prevailed.

Intensive primary production in spring decreases the dissolved CO_2 concentration and increases the $\delta^{13}C$ value of the DIC pool. The phytoplankton community in mid- and late summer might start to be limited by availability of dissolved CO_2 that would lead to declining isotopic discrimination and production of ^{13}C-enriched organic matter (Xu *et al.* 2007). In fact, $\delta^{13}C$ values of phytoplankton and DOM in Võrtsjärv were low during the active growing season (from April to September), and in high alkalinity Võrtsjärv the DIC pool is probably high enough to avoid depletion of dissolved CO_2 to levels that would limit phytoplankton growth. In lakes with high DIC inputs from the catchment area the in-lake metabolism might play only a minor role in determining the amount of dissolved CO_2 (Tranvik *et al.* 2009), and that is presumably the case in Võrtsjärv which receives a substantial DIC loading from its catchment area. Cremona *et al.* (subm.) also suggested that primary production is mostly using inflowing DIC in Võrtsjärv.

Al-DOM comes to Võrtsjärv mainly from the watershed. Nevertheless, only during summer did Al-DOM in the inflows of Võrtsjärv have the typical low terrestrial $\delta^{13}C$ signature (around –27‰) expected based on other studies (Finlay 2004; Finlay & Kendall 2007). Furthermore, Amiotte-Suchet *et al.* (2007) showed that the isotopic composition of stream DOC should be lower than that of its soil sources, because of isotopic fractionation that makes leached stream DOC more ^{13}C-depleted than the soil organic matter. Thus, $\delta^{13}C$ values of DOM could have been expected to be even more negative in the River Väike Emajõgi than the values for soil organic matter (around –27‰). However, Amiotte-Suchet *et al.* (2007) also showed that this ^{13}C depletion is smaller in coniferous catchments than in deciduous catchments, and coniferous forest characterizes 17% and mixed forest 34% of land use in the River Väike Emajõgi catchment. Additionally, Piirsoo *et al.* (2012) showed that DOM in the inflows of Lake Võrtsjärv is not totally terrestrial, but was of rather low aromaticity, dominated by fulvic acids, and had only a very small contribution of ketonic and quinic structures. Only in a few cases, usually in early spring or late autumn, did humic acids with higher aromaticity predominate in DOM of the inflows. In our study, mean values of $SUVA_{254}$ remained under 4 at the Inflow, also indicating that DOM in the Inflow is not totally terrestrial.

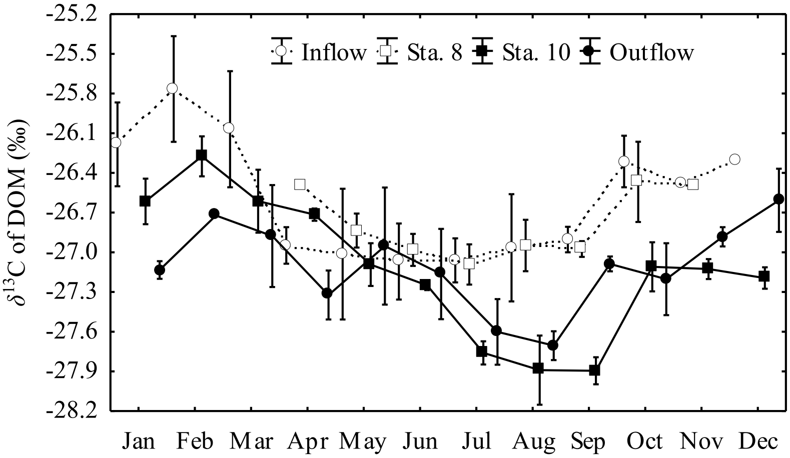

Figure 3. Mean (± SE) monthly values of δ^{13}C of dissolved organic matter (DOM) in the main inflow, outflow, at the southern (Sta. 8) and central (Sta. 10) sampling stations of Lake Võrtsjärv in 2008-2010.

5.2.3. Contributions of autochthonous and allochthonous sources to DOM

Cremona *et al.* (subm.) found that the contribution of carbon inflow from the catchment to the total influx of carbon was very high in Lake Võrtsjärv; in 2009-2011 DOC inflow varied from 1683 to 144 500 kg C day^{-1} and the mean gain of DOC was 64 219 kg C day^{-1} and mean loss of DOC was 50 282 kg C day^{-1}. The mean annual phytoplankton primary production of Võrtsjärv was 218 g C m^{-2} in 2009 (Nõges *et al.* 2011), of which the dissolved fraction formed up to 37% (Nõges 1999). From those data and the DOC loading data (Cremona *et al.* subm), we can see that phytoplankton-derived DOC (21 778 200 kg C y^{-1}) and DOC loading from inflows, atmosphere and macrophytes (27 058 180 kg C y^{-1}) were almost equivalent in Võrtsjärv in 2009.

We used a simple mixing model to assess river water DOM (Al-DOM) contribution to lake water DOM and found that Al- DOM contributed an average 81% (SD=18%) from October to April and 68% (SD=17%) from May to September of lake water DOM in the northern and central part of Lake Võrtsjärv (**II**). It was not possible to obtain similar estimates for the macrophyte-rich southern part of Lake Võrtsjärv because isotope signatures of the two main source materials of DOM (river water DOM and macrophytes) overlapped. Thus, our mixing model calculations indicated that Al-DOM prevailed in the total DOM pool in Võrtsjärv, even during periods of high primary production. This shows that, even in highly productive lakes, labile Au-DOM is rapidly degraded by microorganisms and thus contributes little to the instantaneous in-lake DOM pool (Tranvik *et al.* 2009). The low share of Au-DOM in Võrtsjärv might also reflect some loss of the Au-DOM to the sediment or its transport out from the lake. Cremona *et al.* (subm.) showed that Võrtsjärv is exporting carbon to downstream ecosystems during periods of high algal productivity.

Easily degradable Au-DOM may lead to peaks in bacterial abundance (Tank *et al.* 2011). In Võrtsjärv two peaks in bacterial abundance occurred (Fig. 3b in **II**), during vernal and late summer and autumn phytoplankton blooms, when there should be a large release of labile DOM into the water column. Consequently, we can assume that bacteria acts as a sink for Au-DOM, as has been shown for systems in which primary productivity is dominated by phytoplankton (Kritzberg *et al.* 2006) or macrophytes (Tank *et al.* 2011), promoting the prominence of Al-DOM in forming the in-lake DOM pool. Tank *et al.* (2011) showed that organic matter from macrophytes is largely absent from the bulk DOM pool indicating that the flux of this DOM into bacterial biomass may also be extremely rapid.

Refractory Al-DOM, which accumulates and is degraded over longer timescales (Stedmon & Markager 2005) seems not to benefit bacterioplankton because relatively fresh allochthonous material did not boost the bacterioplankton in spring (Fig. 3b in **II**). Kisand and Nõges (2004) also found that the degradation of such compounds might be of less importance in Võrtsjärv since the residence time of the lake is relatively short (1 year). Cremona *et al.* (subm.) showed that Võrtsjärv may belong to the group of mixotrophic lakes, where both allotrophy and autotrophy are potential energy sources. Our results from Võrtsjärv, in which Al-DOM generally represents a high proportion of the measured DOM concentration, illustrate that the composition of the instantaneous DOM pool in a lake does not necessarily reflect the functional importance of its various sources. More labile Au-DOM, with high turnover and hence smaller contribution to the total DOM pool, can still have a major influence on the lake ecosystem.

5.3. Light attenuation and underwater light field

5.3.1. Light attenuation and CDOM

Correct measurement of light attenuation *in situ* requires sophisticated and relatively expensive equipment and is easily disturbed by high surface waves that occur frequently on large lakes; therefore these data are rare in historical data sets. Empirical regressions potentially enable estimation of light attenuation if the concentrations of detritus, inorganic suspended matter and chlorophyll are measured, but often only the latter is available in the datasets (Scheffer 2004). The long-term datasets that were available for lakes Võrtsjärv and Peipsi included Chl *a*, PhB, Z_{SD}, COD_{Mn} and water colour. The two latter variables served as proxies for the CDOM.

In Võrtsjärv Chl *a* described 71% of the variation of $K_{d,PAR}$ and was used for long-term calculations of $K_{d,PAR}$ (**III, V**) that in turn enabled the reconstruction of long-term time series of primary production (**V**), euphotic depth ($z_{1\%}$, **III**) and the mean light intensity in the mixed layer (E_{mix}, **III**). The mean Chl *a* was relatively high and varied over a wide range (Table 1 in **III**). Among OAS, Chl *a* is one of the main components that together with total suspended matter and CDOM determines the optical properties of water.

In Peipsi Z_{SD} accounted for 76% of the variation in $K_{d,PAR}$ and was used for long-term calculations of $K_{d,PAR}$ (**III**). Similar strong relationships with similar coefficients of the power function formulae were found by Arst *et al.* (2008) for 21 Estonian and Finnish lakes. The relationship between $K_{d,PAR}$ and Z_{SD} is strongly dependent on lake type because scattering has a stronger effect on Z_{SD} than on the vertical light attenuation (Wetzel 2001). For instance, a lake in which turbidity is mainly caused by suspended clay particles which scatter rather than absorb, will have a lower light attenuation than a lake with the same Z_{SD} in which the turbidity is mainly due to phytoplankton (Scheffer 2004). The high correlation between $K_{d,PAR}$ and Z_{SD} in Peipsi could be attributed to a presumably stronger effect of algal blooms on optical properties of water compared to suspended mineral particles. In much shallower Võrtsjärv stronger resuspension of sediments brings more mineral particles into the water column affecting strongly the optical properties of water.

COD_{Mn} and water colour as proxies for CDOM appeared to be less important than Chl *a* or Z_{SD} in describing the variation of $K_{d,PAR}$ in both lakes (**III**). It certainly does not mean that CDOM has a marginal effect on light attenuation, but due to the narrow seasonal range of COD_{Mn} and water colour, their impact on variation in light climate turned out weaker than that of PhB and Chl *a*, which both vary over a wide range. Still the positive relationship between $K_{d,PAR}$ and Z_{avg} and the negative relationship between E_{mix} and $Z_{avg,}$ appearing in spring in Võrtsjärv and in inshore areas of Peipsi (Table 4 in **III**) was likely caused by poorer light conditions due to higher concentrations of DOM, since the concentration of DOM is usually high at high water levels in April and May (Toming *et al.* 2009). Furthermore, according to Reinart & Nõges (2003) and Reinart *et al.* (2004) up to 53% of light attenuation in the PAR region can be attributed to CDOM in lakes Peipsi and Võrtsjärv. In Võrtsjärv where $K_{d,PAR}$ was calculated from Chl *a* for most of the period, it could not account directly for CDOM, however an adaptive response resulting in an increase in Chl *a* in response to deeper mixing in darker water could be inferred. The negative correlation between $K_{d,PAR}$ and Z_{avg} in summer and autumn months (Table 4 in **III**) was obvious evidence of the increasing impact of sediment resuspension during seasonally lowest water levels that carried freshly sedimented algae and Chl *a* back into the water column. According to Nõges *et al.* (2003), PhB in Võrtsjärv is significantly higher in years of low water level. The decreasing E_{mix} with increasing Chl *a* in summer reveals the greater relative role of phytoplankton in light attenuation during this time of the year compared to spring and autumn.

According to the results (**IV**), the main factor influencing the light attenuation in Pärnu Bay was CDOM which overshadows the relationships between the radiation characteristics and organic/inorganic particles. Surprisingly weak relationship between the C_{ph} and C_s could probably be explained by significant contribution of mineral particles in the total suspended matter. As mentioned before, the River Pärnu brings large amounts of CDOM into the bay from the surrounding peat excavation areas, which makes the water close to the river inflow brownish and usually less transparent than the water in deeper parts of Pärnu Bay. That spatial behaviour of the $K_{\mathrm{d,PAR}}$ had almost similar pattern — decrease from the north-eastern part of the bay towards its south-western part.

5.3.2. Underwater light field

Long-term variations of underwater irradiance are controlled by human impact, climate change and water level fluctuations. The eutrophication of Estonian lakes from agricultural and point sources accelerated since the 1950s (Heinsalu *et al.* 2007; Heinsalu & Alliksaar 2009), and culminated in the 1970s and 1980s (Ott & Kõiv 1999). As a large portion of these nutrients was accumulated in lake sediments and is still supporting high primary productivity of lakes, the decreased pollution loads and use of fertilizers has not caused a corresponding improvement in the bio-optical properties of water. Even on the contrary – we can see the increase in the reconstructed $K_{\mathrm{d,PAR}}$ series for Võrtsjärv and inshore areas of Peipsi (**III**). The situation is somewhat better in offshore areas of Peipsi, where the influences of the river discharges and sediment resuspension are smaller (Toming *et al.* 2009).

Lake depth has a very pronounced impact on the light climate experienced by algae, and thus for their growth rates and realized biomass (Scheffer 2004). Since algal cells are dispersed throughout the mixed layer, the light they experience depends not only on the $K_{\mathrm{d,PAR}}$ but also on z_{mix}, which in most shallow lakes is the entire water column (Scheffer 2004). Oliver (1981) showed that the threshold level of E_{mix} for light limitation of phytoplankton standing crop is 3.5 mol m^{-2} day^{-1}. Similarly, some other authors have estimated that the range at which light availability is the major factor in controlling the phytoplankton growth is 0.9–4.0

mol m^{-2} day^{-1} (Geddes 1984), 2.0–3.5 mol m^{-2} day^{-1} (Phlips *et al.* 1995) and 0.24–3.9 mol m^{-2} day^{-1} (Reinart & Pedussaar 2008). Minimum E_{mix} values (Table 4 in **III**) were below the critical threshold in Peipsi in autumn (0.6–0.7 mol m^{-2} day^{-1}) and in Võrtsjärv throughout the year (0.3–2.8 mol m^{-2} day^{-1}) showing that phytoplankton in these lakes could be light limited and this issue is more critical in Võrtsjärv. A comparison of Figs. 2b, 4b, and 5b in **III** gives a good example of the predominant role of the water level in determining the light climate in Võrtsjärv. E_{mix} reached its highest values in low water years in the 1960s and in 1996 and the minimum in 1978, the year of the highest water level (**III**). Remarkably the water was most transparent in 1978 and the low E_{mix} can be fully attributed to the high water level in this year. A large change in phytoplankton composition took place at that time with two highly shade tolerant species appearing among dominants (Nõges *et al.* 2010c). The leading role of water level in the formation of light conditions for phytoplankton can be seen also in the general increase of E_{mix} since the 1970s, which has occurred despite increasing $K_{d,PAR}$ and which can be explained by the decrease in water levels.

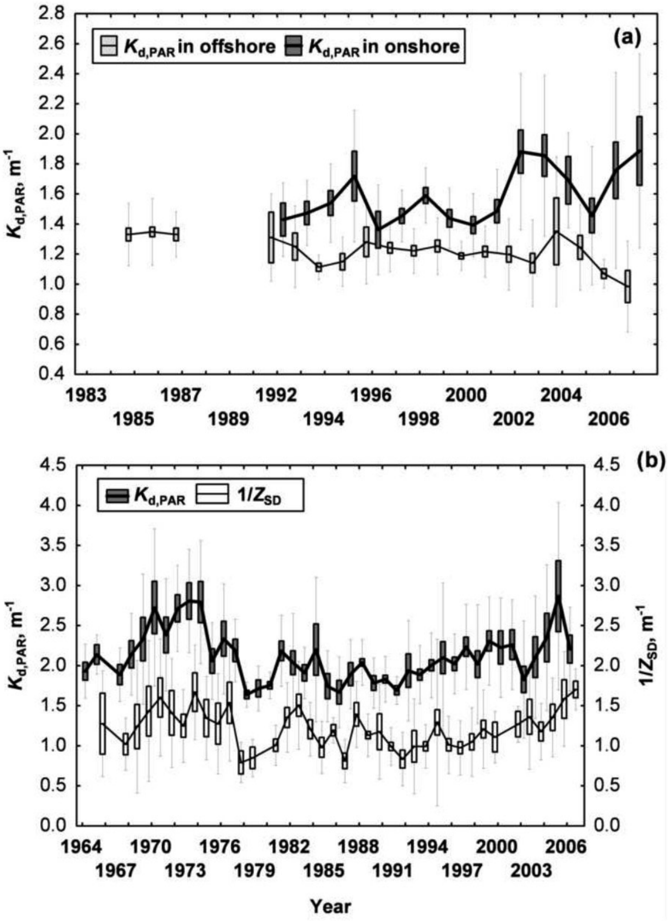

Figure 4. Long-term changes of the yearly average values of the diffuse attenuation coefficient ($K_{d,PAR}$, m^{-1}) in ice-free period (a) in Lake Peipsi in offshore (LP2, LP4, LP11) and inshore (LP16, LP17, LP38) sampling points in 1983-2007 and (b) in Lake Võrtsjärv in 1964-2007. The reciprocal of Secchi depth ($1/Z_{SD}$) is also shown for Võrtsjärv. ± SE is shown as vertical boxes and ± SD as vertical lines.

6. CONCLUSIONS

1. The discharges from the main rivers were mainly responsible for CDOM spatial variability and its high values in the coastal/onshore areas in all studied large and shallow water bodies (**I**).

2. CDOM values were highest in spring and lowest in autumn with most distinct seasonal pattern in onshore areas close to the river mouths. The impact of the riverine CDOM in lakes and in the bay increased together with the ratio of the catchment area to the lake/bay volume (**I**).

3. Contrary to our prediction, in Lake Võrtsjärv Au-DOM had lower δ^{13}C values than Al-DOM. This is a consequence of low δ^{13}C values of DIC, phytoplankton and other seston in this lake (**II**).

4. With increasing water level the proportion of Al-DOM and the heterotrophy of the ecosystem of Võrtsjärv increased; with increasing water temperature the proportion of Au-DOM increased and the autotrophy of the ecosystem enhanced (**II**).

5. According to the DOM δ^{13}C values, the average proportion of Al-DOM in Võrtsjärv was 68% during the active growing season (May-September) and 81% in October-April. The high share of Al-DOM indicates rapid degradation of Au-DOM in the lake ecosystem and illustrates that the composition of the instantaneous DOM pool in a lake does not necessarily reflect the functional importance of its various sources (**II**).

6. The main factor controlling the light attenuation in the Pärnu Bay was CDOM, which overshadowed the impact of organic/inorganic particles (**IV**). The latter played the main role in Peipsi and Võrtsjärv (**III**).

7. The reconstructed time series of diffuse attenuation coefficient ($K_{\mathrm{d,PAR}}$), based on regressions with optically active substances, enabled the reconstruction of long-term time series of primary

production (**V**), euphotic depth ($z_{1\%}$, **III**) and the mean light intensity in the mixed layer (E_{mix}, **III**), which corresponded to the eutrophication history and changes in water levels of studied water bodies (**III**).

8. E_{mix} values below the critical threshold showed that in Peipsi phytoplankton was likely light limited in autumn and in Võrtsjärv throughout the year (**III, V**).

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SUMMARY IN ESTONIAN

Lahustunud orgaaniline aine ja selle ökoloogiline tähtsus suurtes madalates veekogudes

Meie koduplaneedil Maa on palju erinevaid veekogusid (ookeanid, mered, järved, jõed), mis ei erine ainult suuruse ja kuju, vaid ka vee koostise poolest. Veekeskkonnas on palju aineid, mille sisaldus on veekoguti erinev ning varieerub ruumiliselt ja ajaliselt ka ühe veekogu piires. Vees sisalduvad ained mõjutavad muuhulgas vee läbipaistvust, produktiivsust ja toiduahelaid ning seega kogu veeökosüsteemi seisundit.

Eriti mitmekomponendiline on vee koosseis järvedes ja kaldavetes. Peamised lisaained veekogudes on anorgaanilised lämmastiku-, fosfori- ja süsinikuühendid, mineraalsed ja orgaanilised osakesed, mitmesuguseid pigmente (nt klorofülli) sisaldavad planktoniorganismid ja lahustunud orgaaniline aine (DOM). Viimased kolm on optiliselt aktiivsed ained, mis nõrgendavad vette jõudvat päikesekiirgust ja mõjutavad veealust valgusvälja (DOM-i puhul teeb seda tema nn värvuskomponent CDOM). Valgusväli omakorda mõjutab fotosünteesivate organismide (nt fütoplankton, suurtaimed) kasvu ja arengut. Käesolev töö keskendub ühele tähtsamale veekeskkonnas sisalduvale ainele – DOM-ile.

Umbes 90% veeökosüsteemide orgaanilisest ainest on DOM ja ülejäänu moodustab partikulaarne orgaaniline aine (Wetzel 2001). DOM mängib olulist rolli veekogude süsiniku- ja energiaringes. Olles mikroobse ainevahetuse peamine energiaallikas (Münster ja Chróst 1990, Tranvik 1992), on DOM-il suur mõju veekogu toiduahelatele ning auto- ja heterotroofsete protsesside osakaalule. Nagu eespool mainitud on DOM-i värvuskomponent (CDOM) üks optiliselt aktiivsetest ainetest, mis muudab vee optilisi omadusi ning mõjutab veealust valgusvälja, neelates nii nähtavat kiirgust (400–700 nm) kui ka UV-kiirgust (280–400 nm).

DOM-i roll ökoloogilistes ja biogeokeemilistes protsessides sõltub tema päritolust ja koostisest. Autohtoonset DOM-i (Au-DOM) toodavad veekogude litoraalses ja pelaagilises osas fütoplankton ja muud fotosünteesivad organismid ning see koosneb peamiselt mittehumiinainetest, mis on labiilsed ning kergesti lagundatavad ja kasutatavad mikroorganismide poolt (Thurman 1985). Allohtoonne

DOM (Al-DOM) transporditakse veekokku valgalalt ning ta pärineb peamiselt soontaimedest ja mulla orgaanilisest osast, koosnedes enamjaolt humiinainetest, mis on suure molekulmassiga, pruunika värvusega ning raskesti lagundatavad (Thurman 1985). DOM-i koosseis ja päritolu võivad ühe veekogu piires erineda nii ruumiliselt kui ka ajaliselt (Finlay ja Kendall 2007). Allohtoonsete allikate suhteline tähtsus peaks järve troofsuse langedes suurenema (Jones 1992, Grey *et al.* 2000). Paljudes järvedes, eriti jahedates boreaalsete piirkondade järvedes on ökosüsteemi koguproduktsioon negatiivne (järved vabastavad süsinikku) (Cole *et al.* 2000, Jansson *et al.* 2007). See näitab, et Al-DOM-i sissevool valgalalt suurendab järvesisest hingamist sedavõrd, et see ületab süsiniku sidumise fotosünteesi käigus.

DOM-i keemiline koostis on väga varieeruv ning seda on keeruline kindlaks määrata. Analüüsimiseks on kasutatud erinevaid meetodeid: UV-, nähtava kiirguse ja fluorestsentsspektroskoopiat (McKnight *et al.* 2001); biomarkereid (lipiidid, aminohapped, ligniiniühendid, rasvhapped) (Canuel *et al.* 1995, Goni ja Thomas 2000); pürolüüs-gaaskromatograafiat või mass-spektromeetriat (Wickland *et al.* 2007); ka stabiilseid isotoope, mis on muutunud viimastel aastatel üha populaarsemaks DOM-i päritolu uuringutes (Hood *et al.* 2005, Tank *et al.* 2011).

Paljud uuringud on käsitlenud DOM-i päritolu ja varieeruvust humiinsetes või suhteliselt selgeveelistes ja sügavamates veekogudes, kuid teave suurte madalate eutrofeerunud veekogude kohta on puudulik ja käesolev doktoritöö püüab seda lünka täita.

Doktoritöö keskendubki DOM-i uurimisele suurtes madalates eutroofsetes veekogudes ja selle peamisteks eesmärkideks oli:

- hinnata DOM-i ruumilist ja ajalist varieeruvust (**I, II**);
- uurida DOM-i päritolu ning hinnata allohtoonse ja autohtoonse DOM-i osakaalusid (**I, II**);
- hinnata, millised tegurid mõjutavad DOM-i varieeruvust ja päritolu (**I, II**);
- hinnata CDOM-i mõju valguse nõrgenemisele vees (**III, IV**);
- hinnata, millised tegurid mõjutavad veealuse valgusvälja pikaajalisi muutusi (**III, V**).

Töö peamised hüpoteesid olid:

- DOM-i kontsentratsioon ning autohtoonse ja allohtoonse DOM-i osakaal varieerub nii ajaliselt kui ka ruumiliselt, mõjutatuna klimaatilistest ja keskkonnateguritest, nt jõgede vooluhulgad, sademed, primaarprodutsentide biomass, veetase, temperatuur, toiteainete kontsentratsioonid (**I, II**);
- CDOM on üks peamistest teguritest, mis mõjutab veealuse valguse nõrgenemist suurtes madalates veekogudes (**III, IV**);
- veealuse valgusvälja pikaajalised muutused on kooskõlas suurte madalate veekogude eutrofeerumise ajaloo ning veetaseme muutustega (**III, V**).

Töö tulemusena leiti järgmist.

- Peamiste sissevoolude vooluhulgad mõjutasid enim CDOM-i ruumilist varieeruvust järvedes ja lahes ning põhjustasid CDOM-i kõrgemaid väärtusi ranniku- ning kaldalähedastes piirkondades (**I**).
- CDOM-i väärtused järvedes ja lahes olid kõrgeimad kevadel ja madalaimad sügisel ning taoline muster joonistus eriti selgelt välja kalda- ja rannikulähedastes piirkondades, mis olid sissevoolude lähedal. Jõgedest pärineva CDOM-i mõju tõusis valgala pindala ja veekogu ruumala suhte suurenemisel (**I**).
- Vastupidiselt eeldatule olid Võrtsjärves autohtoonse DOM-i δ^{13}C-väärtused madalamad kui allohtoonsel DOM-il. See oli tingitud lahustunud anorgaanilise süsiniku (DIC), fütoplanktoni ja muu sestoni madalates δ^{13}C väärtustest järves (**II**).
- Kõrgema veetasemega kaasnes Võrtsjärves allohtoonse DOM-i osakaalu suurenemine ja ökosüsteemi muutumine heterotroofsemaks; veetemperatuuri tõusuga suurenes autohtoonse DOM-i osakaal ning ökosüsteem muutus autotroofsemaks (**II**).
- DOM-i δ^{13}C-väärtuste alusel oli allohtoonse DOM-i keskmine osakaal Võrtsjärves vegetatsiooniperioodil (mai-september) 68% ning oktoobrist aprillini 81%. Allohtoonse DOM-i suur osakaal viitab autohtoonse DOM-i intensiivsele kasutamisele järve ökosüsteemis ning näitab, et erinevate allikate osakaal järvesiseses

DOM-is ei ole otseselt seotud nende funktsionaalse tähtsusega ökosüsteemis (**II**).

- CDOM oli peamine tegur, mis mõjutas valguse nõrgenemist Pärnu lahes, varjutades orgaaniliste ja anorgaaniliste osakeste mõju (**IV**), mis omakorda oli oluline Peipsis ja Võrtsjärves (**III**).
- Valguse difuusse nõrgenemise koefitsiendi ($K_{d,PAR}$) aegread, mis arvutati regressioonidest optiliselt aktiivsete ainetega, võimaldasid taastada primaarproduktsiooni (**V**), eufootilise sügavuse ($z_{1\%}$, **III**) ning järvevee segunenud kihi keskmise valgustatuse (E_{mix}, **III**) aegread, mis muutusid kooskõlas uuritavate veekogude eutrofeerumise ajaloo ning veetaseme muutustega (**III, V**).
- E_{mix}-väärtused, mis jäid alla fütoplanktonile vajalikku kriitilist piiri, näitasid, et valgus oli fütoplanktoni kasvu limiteerivaks teguriks Peipsi järves sügisel ning Võrtsjärves kogu aasta vältel (**III**).

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I

ORGINAL PUBLICATIONS

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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 $\lambda = 380$ 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.* 2009). 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.* 2009).

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.* 2009).

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

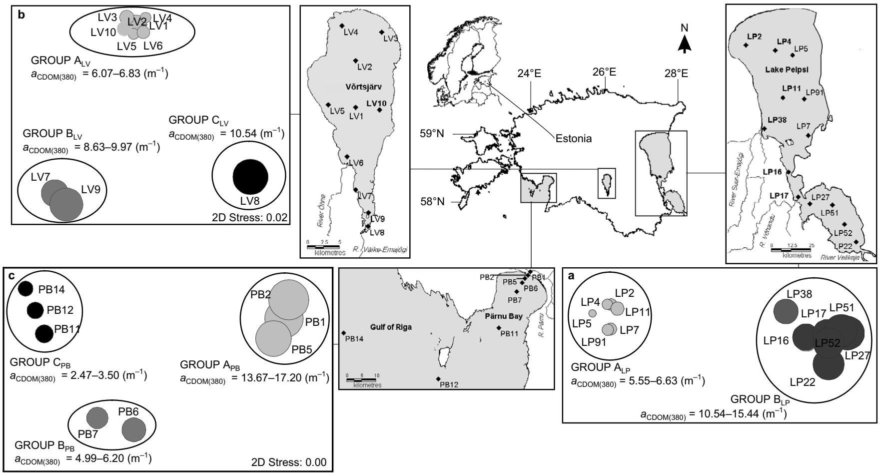

Fig. 1. Study sites (regularly sampled stations are marked in bold) and non-metric multidimensional scaling (MDS) ordination plots of $a_{\mathrm{CDOM}}(380)$ sampled at the indicated sampling points in (**a**) Peipsi from March/April to October/November (2002–2007), (**b**) Võrtsjärv in August (2003–2007), and (**c**) Pärnu Bay from April to October (2005–2007). The plots are superimposed on circles with diameters proportional to the average $a_{\mathrm{CDOM}}(380)$ (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	2003–2007	108	63
Võrtsjärv	270	2.8	4.1	Väike Emajõgi	84	1273	8.6			
				Õhne	94	573	2.6	2005–2007**	78	67
Pärnu Bay	690	7.5	1.65	River	144	6690	20.0			

* 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:

$$c^*_{\mathrm{f}}(\lambda) = c_{\mathrm{f}}(\lambda) - c_{\mathrm{d}}(\lambda) \tag{1}$$

where $c_{\mathrm{f}}(\lambda)$ is the beam attenuation coefficient of the filtered water at wavelength (λ) and $c_{\mathrm{d}}(\lambda)$ is the beam attenuation coefficient of distilled water at wavelength (λ) (all in m^{-1}). The value of $c^*_{\mathrm{f}}(\lambda)$ 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):

$$a_{\mathrm{CDOM}}(\lambda) = c^*_{\mathrm{f}}(\lambda) - c^*_{\mathrm{f}}(\lambda_{\mathrm{R}})(\lambda_{\mathrm{R}}/\lambda)^{g} \tag{2}$$

where $c^*_{\mathrm{f}}(\lambda)$ and $c^*_{\mathrm{f}}(\lambda_{\mathrm{R}})$ 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 $c^*_{\mathrm{f}}(\lambda)$. 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 (m²)	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, $\mathrm{COD}_{\mathrm{Mn}}$, 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, version 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

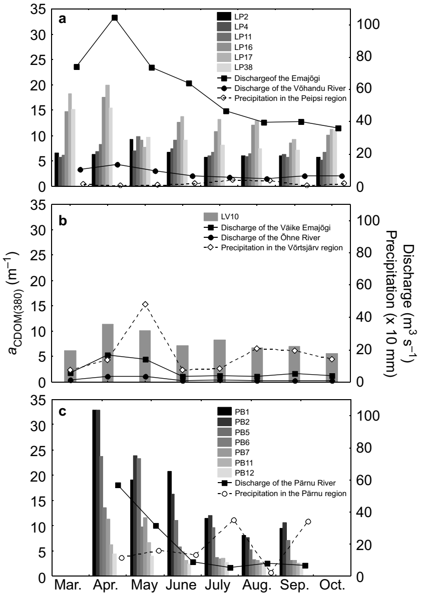

Fig. 2. Temporal variation of a_{CDOM} in (**a**) Peipsi, (**b**) Võrtsjärv, and (**c**) Pärnu Bay averaged over the observation periods at the indicated sampling points. The daily mean discharges of the rivers (**a**) Emajõgi and Võhandu, (**b**) Väike Emajõgi and Õhne; and (**c**) Pärnu, as well as 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), $a_{\mathrm{CDOM}}(380)$ 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). $\mathrm{COD_{Mn}}$ 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 $\mathrm{COD_{Mn}}$ values of the rivers Emajõgi and Võhandu were 13.27 and 10.37 mgO $\mathrm{l^{-1}}$, 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 $a_{\mathrm{CDOM}}(380)$ 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 $\mathrm{COD_{Mn}}$ (mean 9.23 mgO $\mathrm{l^{-1}}$) and the discharges of the Väike Emajõgi ($r = 0.428$, $p < 0.05$) and between the $\mathrm{COD_{Mn}}$ (mean 14.59 mgO $\mathrm{l^{-1}}$) and the discharges of the Õhne River ($r = 0.622$, $p < 0.05$).

Spearman correlation showed a good correspondence between $a_{\mathrm{CDOM}}(380)$ 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 $a_{\mathrm{CDOM}}(380)$ 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 River 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, $a_{\mathrm{CDOM}}(380)$ 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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II

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CONTRIBUTIONS OF AUTOCHTHONOUS AND
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Contributions of autochthonous and allochthonous sources to dissolved organic matter in a large, shallow, eutrophic lake with a highly calcareous catchment.

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Running head: The origin of dissolved organic matter

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Abstract

We traced the origins of dissolved organic matter (DOM) in the large, shallow, eutrophic Lake Võrtsjärv in Estonia. Võrtsjärv allochthonous DOM (Al-DOM) had higher δ^{13}C values than autochthonous DOM (Au-DOM). The δ^{13}C of inflow DOM varied from –28.2‰ to –25.4‰ (mean –26.7‰) and in-lake DOM varied from –28.4‰ to –26.1‰ (mean –27.2‰). Low stable isotope (SI) signatures of Au-DOM were caused by relatively ^{13}C-depleted values of its precursors (mainly phytoplankton) with mean δ^{13}C of –28.9‰. SI signatures of dissolved inorganic carbon (DIC) in the inflows and in the lake were also relatively low (from –15.1‰ to –3.28‰). SI values of DOM were lower during the active growing season from May to September and higher from October to April, with the corresponding estimated average proportions of Al-DOM 68% and 81%. The proportion of

Al-DOM decreased with increasing water temperature, chlorophyll *a*, and pH and increased with increasing water level and concentration of yellow substances and DIC. The high proportion of Al-DOM in Võrtsjärv shows that, even in this highly productive ecosystem, the labile Au-DOM produced is rapidly utilized and degraded by microorganisms and thus makes a relatively small contribution to the instantaneous in-lake DOM pool. The low proportion of Au-DOM may also reflect loss of some Au-DOM to the sediment by transport out from the lake.

Introduction

Dissolved organic matter (DOM) plays a significant role in the carbon and energy cycle of lakes and, as the main source of energy for microbial metabolism, it can have a broad effect on food chains and on the balance between autotrophic and heterotrophic processes (Tranvik 1992). The role of DOM in ecological and biogeochemical processes depends on its source and composition. Autochthonous DOM (Au-DOM) is produced in the pelagic and littoral zones of the lake by phytoplankton and other photosynthetic organisms and it consists mainly of non-humic substances, e.g. monomeric sugars, carboxylic acids, amino acids, alditols (Bertilsson and Jones 2003), that are labile and easily utilized or degraded by microorganisms (Thurman 1985). Allochthonous DOM (Al-DOM) is transported from the catchment area, primarily originates from vascular plants and soil organic matter, and consists mainly of humic substances having high molecular weight, brownish color and being refractory to decomposition (Thurman 1985). The composition and sources of dissolved organic matter (DOM) in an aquatic ecosystem may vary spatially and temporally (Finlay and Kendall 2007). In lakes, the relative importance of allochthonous sources should increase with decreasing lake trophy (Jones 1992; Grey et al. 2000). In many lakes, especially within the cool boreal region, net ecosystem production is negative (Cole et al. 2000; Jansson et al. 2007), suggesting that appreciable Al-DOM runoff from the catchments increases the respiration within the lake ecosystem to a level that exceeds photosynthetic carbon sequestration by phytoplankton and aquatic plants.

The chemical composition of DOM is very variable and difficult to determine. Stable isotope (SI) ratios ($\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$) have become increasingly popular in recent years for assessing sources and transformations of DOM and the pathways of carbon in pelagic food webs (Grey et al. 2000; Jones et al. 2001; Palmer et al. 2001). For this approach to be successful, the isotopic compositions of potential source materials for DOM and of the DOM itself should differ markedly. In practice, SI ratios of DOM sources in freshwaters may show substantial overlap, being influenced by multiple biogeochemical, physical, and physiological processes (Finlay and Kendall 2007) that complicate the estimation of source contributions (Phillips and Gregg 2003). Moreover, the isotopic ranges for organic matter sources in a certain water body are much smaller than those reported in a global literature survey (Finlay and Kendall 2007). Therefore SI data are best used together with complementary methods. For instance, Hood et al. (2005) combined SI data with ancillary data such as elemental analyses and catchment discharge in a Rocky Mountains stream. Tank et al. (2011) measured DOM fluorescence and absorption in addition to SI to obtain a comprehensive assessment of DOM sources and transformations in a lake-rich region (Mackenzie Delta) in the Canadian Arctic.

$\delta^{13}C$ values for Al-DOM and for Au-DOM depend on the isotopic signatures of DOM precursor materials. The average $\delta^{13}C$ value of C_3 plants and soil organic matter, the Al-DOM precursor materials, is around −27‰ in northern latitudes (Finlay and Kendall 2007). Reported values for $\delta^{13}C$ of freshwater aquatic plants and algae (Au-DOM precursor materials) are more variable and less predictable ranging from about −47‰ to −8‰, with values typically falling in the range of −30‰ to −20‰ (Finlay 2004; Vuorio et al 2006;

Finlay and Kendall 2007). This variability arises from the physiological diversity of aquatic autotrophs (Finlay and Kendall 2007) and the large variation in the concentrations and SI ratios of dissolved inorganic carbon (DIC) in freshwater systems (Finlay and Kendall 2007). The ratio of ^{13}C to ^{12}C in DIC is influenced by several major processes that alter the input or output of either isotope (Bade et al. 2004). Inputs include atmospheric CO_2, respiration of organic matter, surface water and groundwater inflow of dissolved CO_2 and alkalinity, calcite dissolution, and methane oxidation; the losses include evasion of CO_2, calcite precipitation, photosynthetic uptake, and water outflow (Bade et al. 2004).

Lake studies of DOM sources have mainly focused on humic waterbodies (Tranvik 1998; Jonsson et al. 2001), and information from eutrophic lakes, as well as from large and shallow lakes, is scarce. We therefore used $\delta^{13}C$ values of DIC, DOM, and DOM precursors (phytoplankton, macrophytes, river water DOM) together with the DOM fluorescence index (FI), specific ultraviolet absorption ($SUVA_{254}$), and the absorption ratio (a_{250}:a_{365}) to provide better resolution for tracing the origin of DOM in large, shallow and eutrophic Lake Võrtsjärv, Estonia. Our study was part of a larger project aiming to estimate the role of autochthonous and allochthonous organic matter in the carbon budget of this lake in order to answer the question of whether Lake Võrtsjärv is a net heterotrophic (carbon-emitting) or net autotrophic (carbon-sequestering) system. The main objectives of our study were to assess the origin of DOM and estimate the proportion of Al-DOM and Au-DOM in a large shallow eutrophic lake by using $\delta^{13}C$ analyses and complementary methods. Based on the highly eutrophic status of Lake Võrtsjärv and on the fact that it receives about three times more DIC than DOC from its highly calcareous catchment (Pall et al. 2011), a rather high proportion of Au-DOM might be expected. However, considering that the lake is very shallow and its volume compared to the catchment area is rather small, we still hypothesized a rather large proportional contribution of Al-DOM, with strong spatial and temporal variation due to the seasonality of riverine inflows, phytoplankton development and meteorological conditions.

Methods

Study site and sampling.

Lake Võrtsjärv (57º50’-58º30’ N and 25º35’-26º40’ E) is a large, shallow, eutrophic lake in central Estonia (Fig.1). The lake area is 270 km^2, volume (V) 0.75 km^3, mean depth 2.8 m, maximum depth 6 m, and catchment area (A) 3104 km^2, and macrovegetation occupies about 19% of the total area (Nõges et al. 2010a). The water column is well mixed by surface waves and currents. The renewal of water takes 240–384 days, and can differ markedly between dry and rainy years (Jaani 1990). Lake Võrtsjärv with its large catchment area has a larger A:V ratio (4.1 m^{-1} at mean water level) than other well-studied large and shallow lakes like Peipsi (1.9) or Balaton (2.7), and much larger than large, deep lakes like Ontario (0.046), Ladoga (0.08), Onega (0.18), and Vänern (0.27) (International Lake Environment Committee Foundation World Lake Database, http://www.ilec.or.jp/database/index/idx-lakes.html). The Võrtsjärv catchment comprises arable land and grassland 45.3%, forest 46.1% (mixed forest 24.4%, coniferous forest 15.0%, and deciduous forest 6.7%), wetland 0.6%, bog 0.4%, and marsh 0.1% (Toming et al. 2009). The catchment is in carbonate terrain and DIC is the dominant form of aquatic C (Table 1) as is typical of temperate regions and boreal forests in carbonate terrain due to high soil respiration, carbonate weathering, and groundwater flow (Tranvik et al. 2009). A specific feature of Võrtsjärv is the large natural climate-related variability of water level, which causes up to a 3-fold difference in its water volume and A:V ratio (Nõges et al. 2010b). The lake is covered by ice for an average 184 days (November–April). The flow regimes of the inflowing rivers are natural, and discharges usually peak in April.

Plankton dominates the northern and central area of Võrtsjärv, where the large width, strong effect of winds and currents and eroded bottom sediments make it inappropriate for macrophytes. In contrast, the sheltered and narrow southern part of the lake has fine-grained sediments and is macrophyte-dominated. Also the influence of inflows is strongest in this part of the lake. Therefore, separate sampling was carried out for the northern and central part (Sta. 10) and for the southern part (Sta. 8). To obtain complementary information, the lower course of the largest inflow (inflow) and the upper course of the outflow (outflow) were also sampled.

Depth-integrated water samples for the analyses of stable isotopes, DOM concentration and fluorescence index (FI) were collected monthly from February 2008 to December 2010. Sta. 8 was not sampled during the ice cover from November to March. Water samples for DIC δ^{13}C were collected monthly from 2009 to 2010 and for DOM ultraviolet absorption in 2010. Water samples were stored in polyethylene bottles in the dark at 4°C and analysed within 12 hours. The polyethylene bottles were washed with distilled water and flushed with lake water prior to sampling.

Phytoplankton samples for SI were collected with a plankton net (mesh size 145 μm) four times in 2008 (May, June, September, and October), five times in 2009 (May, June, August, September, and October), and nine times in 2010 (twice each in May, July and October and once each in June, August and September) from Sta. 10.

SI samples of dominant macrophytes (*Phragmites australis* (Cav.) Trin. ex Steud. and *Nuphar lutea* (L.) Sibth. and Smith) were collected four times (in May, July, August, September, and October) during the vegetation period in 2008 from Sta. 8. The floating leaves, emergent leaves and submerged stems and leaves were used for SI analyses.

Daily discharges of the River Väike Emajõgi, daily precipitation, water level, water temperature, pH, O_2, concentrations of chlorophyll *a* (Chl *a*), colored dissolved organic matter (CDOM), total number of bacteria, biomasses and composition of phytoplankton were measured as part of the state monitoring programme. These data were obtained from the Information Centre of the Estonian Ministry of Environment and from the Estonian Meteorological and Hydrological Institute.

Water temperature and concentration of dissolved oxygen were measured in situ using a portable dissolved oxygen meter Marvet Junior 2000 (Elke Sensor), and pH with a portable meter ProfiLine pH 3210 (WTW Wissenschaftlich-Technische Werkstätten GmbH).

For Chl *a* (mg m^{-3}), 0.1–1 l of water was passed through Whatman GF/F glass microfiber filter and concentrations were measured spectrophotometrically (Edler 1979) at a wavelength of 665 nm from 96% ethanol extracts of the filters.

The amount of CDOM was characterized by its concentration (mg L^{-1}) using the following equation (Højerslev 1980, Mäekivi and Arst 1996, Sipelgas et al. 2003):

$$C_{CDOM} = \frac{c^*_f(\lambda)}{\exp(-S(\lambda-\lambda_0))a^*_{CDOM}(\lambda_0)} \qquad (1)$$

where $a^*_{\mathrm{CDOM}}(\lambda_0)$ is the specific absorption coefficient of DOM, which numerical value at $\lambda_0 = 380$ nm was 0.565 L m^{-1} mg^{-1} (Højerslev 1980), *S* is the slope parameter equal to 0.017 nm^{-1} (Mäekivi and Arst 1996, Kallio 1999, Sipelgas et al. 2003), and $c^*_f(\lambda)$ was taken from spectrometric reading at $\lambda = 380$ nm.

The total number of bacteria was determined by fluorescence microscopy at x1000 magnification (Leica DM RB) on DAPI-stained 0.22 mm black membrane filters (Osmonics Inc., Livermore, CA) according to Porter and Feig (1980). Filters contained material obtained from volumes of 1–5 mL of fixed subsamples. At least 400 cells were determined per filter.

Phytoplankton samples were preserved with acidified Lugol solution and composition was identified and biovolumes determined with an inverted microscope at 400 magnifications using the Utermöhl (1958) technique. Phytoplankton biomass (g m^{-3}) was calculated from cell numbers and geometry.

Sample analysis.

DOC and DIC concentrations.

For determination of DIC and DOC concentrations, water samples were passed through precombusted (3 h at 500 °C) Whatman GF/F glass microfiber filters and the carbon content of the filtrate was measured with a Total Organic Carbon (TOC)-VCPH analyzer (detection limit 4 μg L^{-1}; Shimadzu) or, after April 2009, by the TOC cuvette tests (detection limit 2 mg L^{-1}; Hach Lange). Both methods conform to European standard methods (BS EN 1484: 1997). In the TOC-VCPH analyzer, the samples were combusted at 680°C to convert total dissolved carbon (DC) components to CO_2 which was detected with a non-dispersive infrared gas analyser (NDIR). The Dr. Lange TOC cuvette tests (LCK 380) involved wet chemical oxidative digestion followed by photometric determination of the CO_2. The organic compounds were oxidized during two hours at 100°C in the thermostat LT 200 (Hach Lange). The CO_2 from the digestion cuvette passed through a gas-permeable membrane into an indicator cuvette and the resulting color change was measured and evaluated with Hach Lange spectrophotometer (DR 2800). For DIC concentration, carbonates were converted to carbon dioxide by acidifying the sample, and detected with the NDIR in the TOC-V_{CPH} analyser, or measured photometrically in the case of the LCK 380 test. In both methods, DOC concentration was determined as the difference between total dissolved carbon and dissolved inorganic carbon (DOC=DC-DIC). Results from the two methods were also intercalibrated for one month samples as well as for standard solutions, and it was found that there was a non systematic difference less than 10% in dissolved carbon results.

Fluorescence spectroscopy.

The method of McKnight et al. (2001) was used for qualitative estimation of the origin of the precursor material of DOM, whereby terrestrially-derived DOM in natural waters is characterized by lower fluorescence index (FI) values (ca 1.4) than DOM of predominantly microbial origin (ca 1.9). FI was determined as the ratio of the emission intensity at a wavelength of 450 nm to the emission intensity at 500 nm, obtained with an excitation of 370 nm (McKnight et al. 2001) using a Hitachi 2500 fluorescence spectrophotometer. Prior to the fluorimetric measurements, water was filtered through a Millipore syringe-driven filter unit with 0.45 μm pore size filter (Millex-LCR 0.45 μm)

UV spectroscopy.

Before absorbance measurements all samples were filtered through pre-combusted (3 h at 500°C) Whatman GF/F filters and the material remaining in the water was considered to be dissolved. Absorption of the filtrate at wavelengths of 250, 254 and 365 nm was measured by UV-Vis spectrophotometry (Lambda 35, Perkin Elmer Shelton) in a 1-cm quartz cuvette. Measured absorbances were used to calculate the absorption ratio (a_{250}:a_{365}) and specific UV absorbance ($SUVA_{254}$, L mg C^{-1} m^{-1}). $SUVA_{254}$ was obtained by dividing the absorbance at 254 nm (m^{-1}) by the concentration of DOC in mg C L^{-1} (Weishaar et al. 2003). $SUVA_{254}$ is used as an index of the aromatic nature of DOM: values > 4 indicate highly hydrophobic and aromatic DOM, while values < 3 indicate hydrophilic and less aromatic DOM (Karanfil et al. 2003; Peuravuori and Pihlaja 2007). The ratio a_{250}:a_{365} has been used as an indicator of the proportion of fulvic and humic acids in DOM, as higher values reflect lower aromaticity (Egeberg et al. 2002; Peuravuori and Pihlaja 2007) and thus a higher proportion of autochthonous or microbiologically-decomposed DOM (Strome and Miller 1978).

Stable isotopes.

For DIC δ^{13}C analyses from lake water, Labco 12 mL vials for were prepared sampling in the laboratory. 4 drops of phosphoric acid (ca. 4 μL) were placed in the empty 12 mL screw top vials. After sealing the vials with septa, all vials were flushed with pure helium. The water samples (0.5 mL) were injected to vials in the field using gastight, disposable syringes. δ^{13}C from the CO_2 in the headspace of each vial was analysed within 90 days using a Thermo Fisher Scientific Delta V Advantage mass spectrometer and GasBench II.

For DOM SI analyses, 100-200 mL of the Whatman GF/F (pre-combusted at 500°C, 3 hours) filtrate was freeze-dried (Heto PowerDry LL3000, ca 48 hours). Prior to δ^{13}C assessment (two replicates, ca 3 mg dry weight each) the dried material was held for 24 hours in concentrated HCl fumes to remove inorganic C from samples and then re-dried for 1 hour at 60°C.

For phytoplankton SI assessment, dominant species (mainly the diatoms *Aulacoseira* spp.) were separated from fresh samples by repeated sedimentation in the laboratory. In the summer period floating cyanobacteria (mainly *Limnothrix planctonica* (Wołoszyńska) Meffert, and *Limnothrix redekei* (Van Goor) Meffert) were collected from the surface of the phytoplankton sample and included in the bulk dominant phytoplankton sample. Separated phytoplankton was collected on 300 or 500 μm mesh plankton net and rinsed with distilled water. Finally, the collected material was sorted manually under a dissection microscope to remove detrital particles and zooplankton. The sorted subsamples were dried on aluminium foil at 60°C, transferred into tin capsules (ca 1.5 mg dry weight each) and packed for SI analyses.

For macrophyte SI assessment, the collected material was gently cleaned from periphyton, dried at 60°C overnight, pulverized and stored as a ground powder. Two replicates (ca 1.5 mg dry weight each) were prepared for SI analyses.

SI analyses of organic matter were carried out with a Carlo-Erba Flash 1112 series Elemental Analyzer connected to a DELTAplus Advantage IRMS (Thermo Finnigan). Results are given using the δ notation where $\delta = [(^{13}C{:}^{12}C_{sample})/(^{13}C{:}^{12}C_{reference})-1] \times 1000$, expressed in parts per thousand (‰). The reference material used (International Atomic Energy Agency standard, NBS-22) was a secondary standard of known relation to the international standard (Pee Dee belemnite). The analyses were run using dried and homogenized potato leaves as an internal laboratory working standard. Instrument precision was ±0.2‰. The standard deviation between replicates was normally within 0.2‰.

Data analysis.

The software Statistica 8.0 (StatSoft 2007) was applied to analyze the data. The nonparametric Kolmogorov-Smirnov (K-S) test was used to compare the differences in δ^{13}C of DOM from different sampling stations (inflow, Sta. 8, Sta. 10, outflow). Spearman's Rank Order correlation was used to test relationships between indices. The significance level to indicate differences and relationships was set at $p<0.05$.

We used a two-source mixing model (Fry 2006; Eqs. 2 and 3) to assess the contribution of river water DOM and primary producers (phytoplankton or macrophytes) to lake-water DOM.

$$f_1=(\delta_{SAMPLE}-\delta_{SOURCE2})/(\delta_{SOURCE1}-\delta_{SOURCE2}), \qquad (2)$$

where f_1 is contribution of source 1 in sample, δ_{SAMPLE} is $\delta^{13}C$ value of DOM in Lake Võrtsjärv, $\delta_{SOURCE1}$ is $\delta^{13}C$ value of DOM in inflow and $\delta_{SOURCE2}$ is $\delta^{13}C$ value of phytoplankton at Sta. 10 or $\delta^{13}C$ value of macrophyte at Sta. 8. The contribution of source 2 (f_2) is calculated by Eq. 2.

$$f_2=1-f_1 \qquad (3)$$

Results

Environmental characteristics.

The discharge of the River Väike Emajõgi (Fig. 2) was highest in early spring (mean value 29.9 $m^3 s^{-1}$) being influenced by snowmelt; there was also a smaller peak in late autumn (mean value 18.7 $m^3 s^{-1}$). Lake water level showed a similar trend, while precipitation and WT were usually higher in summer and autumn.

O_2 and pH in the southern lake area (Sta. 8) were lower than in the center (Sta. 10) and at the outflow (Table 1) where pH and O_2 were higher due to intensive primary production, especially in summer. During the vegetation period the lowest oxygen concentrations occurred in July and August; in winter 2010 low oxygen values (around 5 mg L^{-1}) were measured at Sta. 10.

Chl *a* concentration was high in the phytoplankton-dominated lake center and in the outflow (corresponding mean values 35.3 mg m^{-3} and 26.5 mg m^{-3}, Table 1). Chl *a* concentration started to increase already in early spring and remained high until the late autumn (Fig. 3). Chl *a* values were lower in the southern lake and inflow (mean value 13.5 mg m^{-3} and 6.53 mg m^{-3} respectively, Table 1) where macrophytes dominated. In the inflow and at the southern lake station Chl *a* values increased later in spring and decreased earlier in autumn than at the lake center and outflow (Fig. 3). The phytoplankton community was mostly formed by cyanobacteria (*Limnothrix planctonica* and *Limnothrix redekei*), especially in summer and autumn, and by diatoms (*Aulacoseira* spp.) which prevailed in spring at Sta. 10. The abundance of bacterioplankton at the lake center was highest in March and in August (Fig. 3).

DIC concentrations and $\delta^{13}C$ of DIC.

DIC concentrations in the inflow and at the southern lake station were seasonally rather stable and higher than at the lake center and outflow where DIC also decreased during the ice-free period (Table 1, Fig. 4a).

$\delta^{13}C$ of DIC was low and stable in the inflow and at the southern lake site (Fig. 4b). At the lake center $\delta^{13}C$ of DIC was lowest in winter when the lake was ice-covered, and increased rapidly after ice-break in April (Table 1, Fig. 4b). $\delta^{13}C$ values of DIC in the outflow were 7-8‰ higher than in the inflow in winter, but in summer the two sites had similar values. $\delta^{13}C$ of DIC increased significantly with increasing Chl *a* (inflow $r = 0.67$, $p < 0.05$; Sta. 8 $r = 0.62$, $p < 0.05$; Sta. 10 $r = 0.93$, $p < 0.001$), with a particularly strong relationship evident at Sta. 10 (Fig. 4c).

DOC concentrations.

DOC concentrations varied during the study period at all sampling stations (Table 1) being somewhat higher in spring during the high water period and also in autumn (Fig. 5a) when Chl *a* concentration also reached its maximum. The mean DOC concentration was lowest, though with highest variation, at the lake center.

SUVA$_{254}$, a_{250}:a_{365} and fluorescence index

SUVA$_{254}$ varied from 1.90 in the outflow to 5.22 in the inflow (Table 1). Rather low mean values of SUVA$_{254}$ at the lake center and outflow (Table 1) indicate that hydrophilic and less aromatic Au-DOM prevailed in the central and northern part of Võrtsjärv.

Increasing values of absorption ratio (a_{250}:a_{365}) reflected decreasing aromaticity of DOM along the gradient from the inflow towards the outflow (Table 1). a_{250}:a_{365} was higher and thus the proportion of the autochthonous or microbiologically decomposed DOM was larger at the central lake site and in the outflow from July to August and September (Fig. 5b). FI values (Fig. 5c, Table 1) showed that fulvic acids in Võrtsjärv were mainly of allochthonous origin

δ^{13}C of DOM and its precursors.

DOM δ^{13}C values varied from –28.4‰ (Sta. 10 in August 2010) to –25.4‰ (inflow in February 2010) and the mean values (Table 1) in the inflow were significantly higher than those from the central lake and the outflow (Table 2). Seasonally DOM δ^{13}C values were lower from May to September, during the active growing season when Au-DOM should prevail and higher from October to April when Al-DOM should dominate (Fig. 6). A Kolmogorov-Smirnov test confirmed that the differences of δ^{13}C values between those two periods were statistically significant for all sampling stations ($p<0.05$).

There was a statistically significant negative correlation between SI signature of DOM and both a_{250}:a_{365} and FI, but no correlation with DOC-dependent SUVA$_{254}$ (Table 3). High values of WT, precipitation, δ^{13}C of DIC, Chl *a* and pH (characteristic of the active growing season) also correlated negatively with DOM δ^{13}C (Table 3). In contrast, high water level, CDOM and DIC concentration correlated positively with δ^{13}C of DOM. We found no significant relationships of DOM δ^{13}C with oxygen content and bacterioplankton in Lake Võrtsjärv.

There are two main potential sources of DOM in the northern and central part of Lake Võrtsjärv: phytoplankton as an autochthonous part and river water DOM as an allochthonous part (Fig. 7). At Sta. 10, where phytoplankton was the dominant primary producer, the mean δ^{13}C of phytoplankton was –28.7‰ (minimum –30.5‰ and maximum –26.8‰; *n*=16). We used a simple mixing model to assess river water DOM (Al-DOM) contribution to lake water DOM and found that Al- DOM contributed an average 81% (SD=18%) from October to April and 68% (SD=17%) from May to September of lake water DOM in the northern and central part of Lake Võrtsjärv. It was not possible to obtain similar estimates for the macrophyte-rich southern part of Lake Võrtsjärv because isotope signatures of the two main source materials of DOM (river water DOM and macrophytes) overlapped. The mean δ^{13}C value for *Phragmites australis* was –26.4‰ (minimum –28.3‰ and maximum –24.2‰; *n*=3) and for *Nuphar lutea* -26.5‰ (minimum –28.6‰ and maximum –25.4‰; *n*=6) in the southern part of Lake Võrtsjärv.

Discussion

While bulk parameters and single biomarker compounds may not individually be adequate for identifying specific sources of organic matter, it might be possible to identify the likely sources of organic matter to an aquatic system when these indices are assessed together (Canuel et al. 1995; Countway et al. 2007). In Võrtsjärv we used multiple tracers to provide best estimates of the origin of DOM. DOC concentration was variable, and higher in-lake

DOC concentrations coincided both with higher inputs from the catchment after snowmelt and with higher primary production, making it impossible to estimate the origin of DOM based on DOC concentrations. Use of $SUVA_{254}$ values (dependent on DOC concentrations) to draw conclusions about the origin of DOM needs to take into account that in shallow eutrophic lakes carbon concentration can be largely determined by both the runoff from catchment area and by lake productivity. The absorption ratio a_{250}:a_{365} appeared to be a useful method for estimating the source of DOM in Võrtsjärv. FI values between 1.42 and 1.61 (Table 1) showed that fulvic acids are of mainly allochthonous origin in Lake Võrtsjärv. Relatively high FI values from our study (Table 1) support previous results by other authors that in those freshwaters where DOM is derived primarily from autochthonous algal and microbial precursor material, fulvic acids generally account for a lower proportion of the DOM compared to water bodies where DOM is derived from plants and soil organic matter (Hood et al. 2005).

DOM $\delta^{13}C$ values in the central part of Võrtsjärv and in the outflow were considerably lower than those in the inflow and the nearby southern lake site (Fig. 6). This indicates a difference between lake and river DOM due to different primary producers and the level of terrestrial influence. It also reflects changes in DOM due to photochemical and microbial processes, and to sedimentation. These results confirm that Võrtsjärv is an active site for transport, transformation, and storage of considerable amounts of carbon received from the catchment area (Pall et al. 2011, Cremona et al. 2013), as has been shown for other lakes (Tranvik et al. 2009).

Au-DOM is produced mainly by phytoplankton in Võrtsjärv, which has relatively low primary production of littoral and bottom macrophytes. The reed belt and other macrophytes cover only 18.8% of the lake area (Feldmann and Nõges 2001) and the contribution of macrophytes to the total primary production in this lake has been estimated to be about 15% (Nõges et al. 2003). Furthermore, Cremona et al. (2013) found that, unlike several other eutrophic and shallow lakes, the contribution of macrophytes to the Lake Võrtsjärv C budget was low (only 5 %). Carbon biomass estimates from Zingel et al. (2007) showed that filamentous phytoplankton and bacteria were the most important reservoirs of the living carbon biomass in Võrtsjärv.

Against our expectations, $\delta^{13}C$ signatures of Au-DOM in Võrtsjärv were lower than those of the allochthonous riverine DOM. As the isotope signatures of the precursors of Au-DOM, phytoplankton and other seston, were also relatively low in Lake Võrtsjärv (mean $\delta^{13}C$ for phytoplankton was –28.9‰), this was presumably the cause of ^{13}C-depleted Au-DOM. Phytoplankton $\delta^{13}C$ value is determined by the physiology of algae, and by the availability and isotopic composition of different forms of DIC (Xu et al. 2007). In Võrtsjärv DIC $\delta^{13}C$ is already rather low (Table 1), while $^{12}CO_2$ is incorporated preferentially in photosynthesis (Laws et al. 1997; Popp et al. 1998). If phytoplankton uses already ^{13}C-depleted DIC to synthesize even more ^{13}C-depleted organic matter, the DOM originating from such phytoplankton should also have low $\delta^{13}C$ values. The negative correlation between $\delta^{13}C$ of DOM and FI values and a_{250}:a_{365} (Table 3) supports our contention that in Võrtsjärv Al-DOM has more positive $\delta^{13}C$ values than autochthonous material.

Based on the high pH values (Table 1), HCO_3^- is the main component of DIC in Lake Võrtsjärv and its inflowing rivers. Lower DIC concentrations in the lake center and outflow during summer (Table 1, Fig. 4a) might be the result of precipitation of carbonates, as well as uptake of CO_2 or even HCO_3^- by photosynthetic organisms (Barešić et al. 2011). Bade et al. (2004) reported that $\delta^{13}C$ values of DIC varied broadly among 72 lakes from diverse regions (from –31‰ to +2.6‰), while seasonal variation within most lakes was smaller. In Võrtsjärv

$\delta^{13}C$ signatures of DIC were within this range varying from −14.5‰ to −3.56‰ (Table 1), although spatially and seasonally variable (Fig. 4b).

Values of DIC $\delta^{13}C$ in the inflow were more negative than in the lake center and outflow (Table 1, Fig. 4b), especially in summer. According to Barešić et al. (2011), dissolution of carbonate minerals with $\delta^{13}C$ around 0‰ and oxidation of soil organic matter ($\delta^{13}C$ around −28‰) in the catchment area might increase the concentration of HCO_3^- and saturate river water with CO_2 leading to decreased $\delta^{13}C$ values of DIC. A downstream increase in $\delta^{13}C$ values of DIC is mainly due to the fractionation effect during both CO_2 degassing and calcite precipitation. During the warm part of the year, preferential removal of ^{12}C by the photosynthetic activity of aquatic plants and the evaporation of water (both emphasised by temperature increase) result in more positive $\delta^{13}C$ values of DIC compared with winter. In the main lake at Sta. 10, the very strong relationship between $\delta^{13}C$ of DIC and Chl *a* concentration (Fig. 4c) suggested that photosynthetic uptake of DIC was the main process causing the marked seasonal variation in $\delta^{13}C$ values of DIC. Jones et al. (2001) showed a positive correlation between $\delta^{13}C$ of DIC and Chl *a* in deep oligotrophic low alkalinity lake Loch Ness, but it is remarkable that the same strong relationship can be found in high alkalinity Võrtsjärv. In our study, seasonal variation of $\delta^{13}C$ of DIC was highest in the lake center at Sta. 10 while only minor seasonal variation occurred in the inflow and at the southern lake site close to it. Probably at these sites the processes like microbial respiration and carbonate weathering that produce ^{13}C-depleted DIC (Finlay 2003) were more in balance throughout the year with the evasion and photosynthetic uptake of CO_2 that can increase $\delta^{13}C$ value of DIC.

Winter $\delta^{13}C$ values of DIC at the lake outflow were much higher than at the lake center (Fig. 4b). This can be explained by the warmer and heavier lake water that disturbs the formation of ice cover at the outflow. Thus the outflow is usually ice-free in winter allowing evasion of excess CO_2 which increases the $\delta^{13}C$ value of the remaining DIC.

After ice break in April, increasing WT, light and nutrient availability lead to intensive primary production, increasing Chl *a* concentration and pH. Therefore, a higher proportion of Au-DOM in the whole DOM pool starting from April might be expected. Our study revealed that in the central part of Lake Võrtsjärv the proportion of Au-DOM did increase together with rising WT, Chl *a* and pH (Table 3) reflecting increasing autotrophy of the ecosystem. A high frequency metabolism study by Laas et al. (2012) revealed the prevalence of net autotrophy in Võrtsjärv from early spring until August or September whereas during the rest of the year heterotrophy prevailed.

Intensive primary production in spring decreases the dissolved CO_2 concentration and increases the $\delta^{13}C$ value of the DIC pool. The phytoplankton community in mid- and late summer might start to be limited by availability of dissolved CO_2 that would lead to declining isotopic discrimination and production of ^{13}C-enriched organic matter (Xu et al. 2007). In fact, $\delta^{13}C$ values of phytoplankton and DOM in Võrtsjärv were low during the active growing season (from April to September), and in high alkalinity Võrtsjärv the DIC pool is probably high enough to avoid depletion of dissolved CO_2 to levels that would limit phytoplankton growth. In lakes with high DIC inputs from the catchment area the in-lake metabolism might play only a minor role in determining the amount of dissolved CO_2 (Tranvik et al. 2009), and that is presumably the case in Võrtsjärv which receives a substantial DIC loading from its catchment area. Cremona et al. (2013) also suggested that primary production is mostly using inflowing DIC in Võrtsjärv.

Al-DOM comes to Võrtsjärv mainly from the watershed. Nevertheless, only during summer did Al-DOM in the inflows of Võrtsjärv have the typical low terrestrial $\delta^{13}C$

signature (around –27‰) expected based on other studies (Finlay 2004; Finlay and Kendall 2007). Furthermore, Amiotte-Suchet et al. (2007) showed that the isotopic composition of stream DOC should be lower than that of its soil sources, because of isotopic fractionation that makes leached stream DOC more ^{13}C-depleted than the soil organic matter. Thus, δ^{13}C values of DOM could have been expected to be even more negative in the River Väike Emajõgi than the values for soil organic matter (around –27‰). However, Amiotte-Suchet et al. (2007) also showed that this ^{13}C depletion is smaller in coniferous catchments than in deciduous catchments, and coniferous forest characterizes 17% and mixed forest 34% of land use in the River Väike Emajõgi catchment. Additionally, Piirsoo et al. (2012) showed that DOM in the inflows of Lake Võrtsjärv is not totally terrestrial, but was of rather low aromaticity, dominated by fulvic acids, and had only a very small contribution of ketonic and quinic structures. Only in a few cases, usually in early spring or late autumn, did humic acids with higher aromaticity predominate in DOM of the inflows. In our study, mean values of $SUVA_{254}$ remained under 4 at the inflow, also indicating that DOM in the inflow is not totally terrestrial.

Cremona et al. (2013) found that the contribution of carbon inflow from the catchment to the total influx of carbon was very high in Lake Võrtsjärv; in 2009-2011 DOC inflow varied from 1683 to 144 500 kg C day^{-1} and the mean gain of DOC was 64 219 kg C day^{-1} and mean loss of DOC was 50 282 kg C day^{-1}. The mean phytoplankton primary production of Võrtsjärv was 218 g C (m^{2})$^{-1}$ in 2009 (Nõges et al. 2011), of which the dissolved fraction formed up to 37% (Nõges 1999). From those data and the DOC loading data (Cremona et al. 2013), we can see that phytoplankton-derived DOC (21 778 200 kg C y^{-1}) and DOC loading from inflows, atmosphere and macrophytes (27 058 180 kg C y^{-1}) were almost equivalent in Võrtsjärv in 2009.

However, our mixing model calculations indicated that Al-DOM prevailed in the total DOM pool in Võrtsjärv, even during periods of high primary production. This shows that, even in highly productive lakes, labile Au-DOM is rapidly degraded by microorganisms and thus contributes little to the instantaneous in-lake DOM pool (Tranvik et al. 2009). The low share of Au-DOM in Võrtsjärv might also reflect some loss of the Au-DOM to the sediment or by transport out from the lake. Cremona et al. (2013) showed that Võrtsjärv is exporting carbon to downstream ecosystems during periods of high algal productivity.

Easily degradable Au-DOM may lead to peaks in bacterial abundance (Tank et al. 2011). In Võrtsjärv two peaks in bacterial abundance occurred (Fig. 3b), during vernal and late summer and autumn phytoplankton blooms, when there should be a large release of labile DOM into the water column. Consequently, we can assume that bacteria acts as a sink for Au-DOM, as has been shown for systems in which primary productivity is dominated by phytoplankton (Kritzberg et al. 2006) or macrophytes (Tank et al. 2011), promoting the prominence of Al-DOM in forming the in-lake DOM pool. Tank et al. (2011) showed that organic matter from macrophytes is largely absent from the bulk DOM pool indicating that the flux of this DOM into bacterial biomass may also be extremely rapid.

Refractory Al-DOM, which accumulates and is degraded over longer timescales (Stedmon and Markager 2005) seems not to benefit bacterioplankton because relatively fresh allochthonous material did not boost the bacterioplankton in spring (Fig. 3b). Kisand and Nõges (2004) also found that the degradation of such compounds might be of less importance in Võrtsjärv since the residence time of the lake is relatively short (1 year). Cremona et al. (2013) showed that Võrtsjärv may belong to the group of mixotrophic lakes, where both allotrophy and autotrophy are potential energy sources. Our results from Võrtsjärv, in which Al-DOM generally represents a high proportion of the measured DOM concentration, illustrate that the composition of the instantaneous DOM pool in a lake does not necessarily reflect the functional importance of its various sources. More labile Au-DOM, with high turnover and hence smaller contribution to the total DOM pool, can still have a major influence on the lake ecosystem.

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Tables

Table 1. The mean, minimum (min) and maximum (max) values of δ^{13}C of dissolved organic matter (DOM) and of dissolved inorganic carbon (DIC), specific ultraviolet absorption (SUVA$_{254}$), absorption ratio (a_{250}:a_{365}), fluorescence index (FI) of DOM, concentrations of DIC and of dissolved organic carbon (DOC), absorption of colored DOM (CDOM), pH, water temperature (WT), dissolved O_2, and chlorophyll *a* (Chl *a*) in the main inflow (inflow), outflow, the southern part (Sta. 8) and the central part (Sta. 10) of Lake Võrtsjärv. *n* = number of samples, - no data.

		DOM $\delta^{13}C$ (‰)	DIC $\delta^{13}C$ (‰)	$SUVA_{254}$ (L mg C^{-1} m^{-1})	a_{250}:a_{365}	DOM FI	DIC (mg L^{-1})	DOC (mg L^{-1})	CDOM (m^{-1})	pH	WT (°C)	O_2 (mg L^{-1})	Chl *a* (mg m^{-3})
inflow	mean	-26.7	-13.3	3.61	5.52	1.517	44.9	17.3	-	7.84	9.16	8.8	6.53
	min	-28.2	-15.1	2.35	4.79	1.42	25.5	4.80	-	7.62	0.20	4.6	0.16
	max	-25.4	-11.3	5.22	6.24	1.61	56.0	27.6	-	8.10	24.8	13.0	26.0
	n	29	19	12	12	24	34	34	-	37	38	38	33
Sta. 8	mean	-26.8	-13.1	3.29	5.39	1.517	45.3	18.9	12.9	7.74	14.3	8.34	13.5
	min	-27.3	-14.5	2.36	5.06	1.42	34.0	14.3	5.90	7.05	5.80	6.68	2.68
	max	-26.1	-12.0	4.05	6.17	1.60	55.0	27.2	21.4	8.04	20.1	10.3	46.5
	n	20	13	12	12	16	21	21	21	12	8	8	21
Sta. 10	mean	-27.2	-8.97	2.97	6.40	1.516	35.5	16.8	9.68	8.26	7.38	11.0	35.3
	min	-28.4	-14.1	2.39	5.07	1.46	21.5	7.83	5.28	7.54	0.95	4.64	1.14
	max	-26.1	-3.56	3.43	7.86	1.56	54.6	32.7	17.64	8.97	19.3	14.95	79.6
	n	34	22	12	12	21	29	31	37	37	30	30	37
outflow	mean	-27.1	-6.49	2.69	6.98	1.521	35.0	17.1	-	8.42	8.88	12.0	26.5
	min	-28.1	-9.09	1.90	6.10	1.46	27.6	9.80	-	7.72	0.2	8.40	1.55
	max	-26.4	-3.28	3.60	8.12	1.60	45.8	21.6	-	8.90	26.0	16.0	59.9
	n	27	20	12	12	23	34	34	-	34	35	35	33

Table 2. Results of the nonparametric Kolmogorov-Smirnov test of differences between sampling stations for δ^{13}C values of DOM. Significant *p*-values are shown; ns = not significant.

	δ^{13}C DOM
Sta. 8 vs inflow	ns
Sta. 8 vs 10	0.05
Sta. 8 vs outflow	ns
Sta. 10 vs inflow	0.03
Sta. 10 vs outflow	ns
inflow vs outflow	0.01
inflow+ Sta. 8 vs Sta. 10+outflow	0.005

Table 3. Spearman correlation between average values of $\delta^{13}C$ of DOM in Lake Võrtsjärv (Sta. 8 and Sta. 10) and other measured parameters. *See* Table 1 for symbols of other indices. Precip.- precipitation (mm), Disch.– discharge (m^3 s^{-1}), W. level– water level (m a.s.l), Bacter.– bacterioplankton (10^6 cells m L^{-1}). Significant ($p<0.05$) *r*-values are shown; ns = not significant.

	WT	Precip.	Disch.	W. level	DOC	$SUVA_{254}$	$a_{250}:a_{365}$	CDOM	O_2	pH	Chl *a*	Bacter.	DOM FI	DIC	DIC $\delta^{13}C$
DOM $\delta^{13}C$	-0.50	-0.49	ns	0.60	ns	ns	-0.64	0.54	ns	-0.61	-0.68	ns	-0.45	0.45	-0.59

Figures

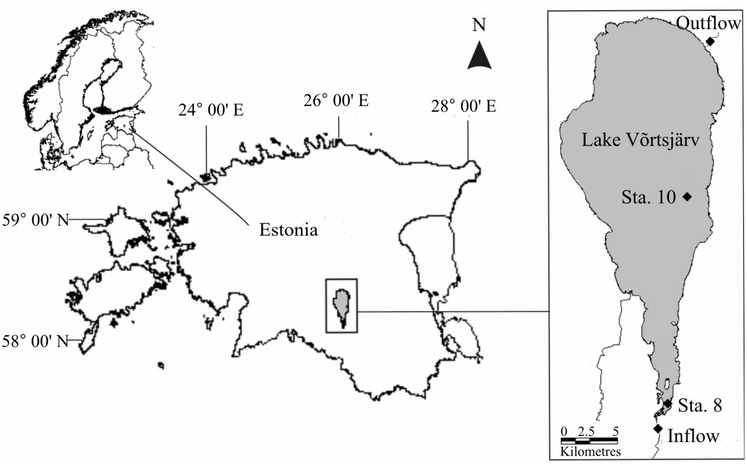

Fig. 1. Location of the study site. Sampling stations in the lower course of the River Väike Emajõgi (inflow), in Lake Võrtsjärv (Sta. 8 and Sta.10), and in the upper course of the River Emajõgi (outflow) are shown.

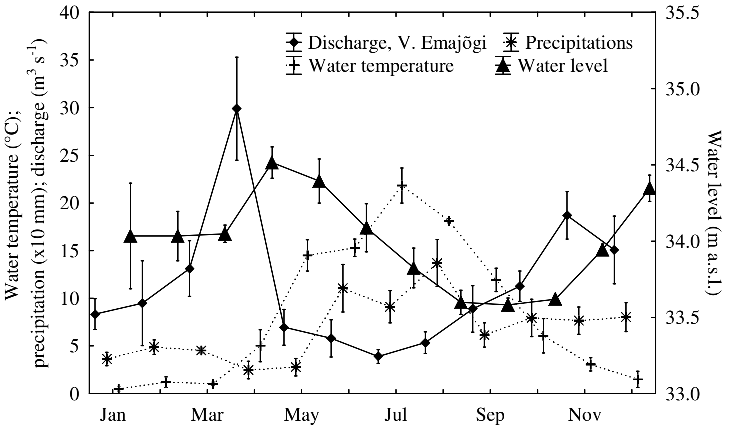

Fig. 2. Mean (± SE) monthly values of water level in Lake Võrtsjärv, precipitation at the nearby Tõravere meteorological station, discharge of the River Väike Emajõgi and lake water temperature at the central sampling station (Sta. 10) in 2008-2010. a.s.l.- above sea level.

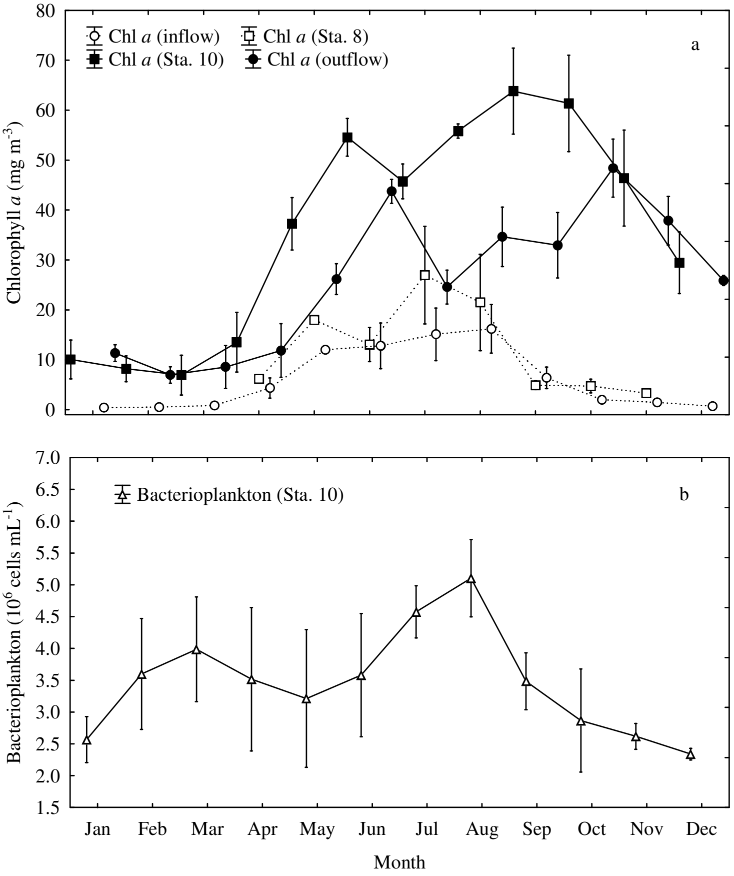

Fig.3. (a) Mean (± SE) monthly values of chlorophyll *a* (Chl *a*) concentration in the main inflow (inflow), outflow, at the southern (Sta. 8) and central (Sta. 10) sampling stations of Lake Võrtsjärv, and (b) the mean (± SE) monthly abundance of bacterioplankton at Sta. 10 in 2008-2010.

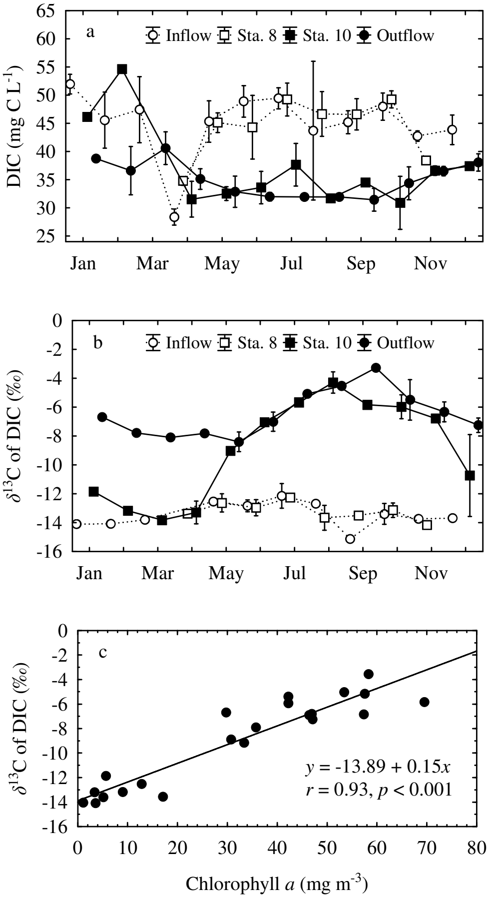

Fig. 4. Mean (± SE) monthly values of (a) dissolved inorganic carbon (DIC) concentration in 2008-2010 and (b) δ^{13}C of DIC in 2009-2010 in the main inflow (inflow), outflow, at the southern (Sta. 8) and central (Sta. 10) sampling stations of Lake Võrtsjärv. (c) Relationship between δ^{13}C value of DIC and chlorophyll *a* concentration in Lake Võrtsjärv (Sta. 10).

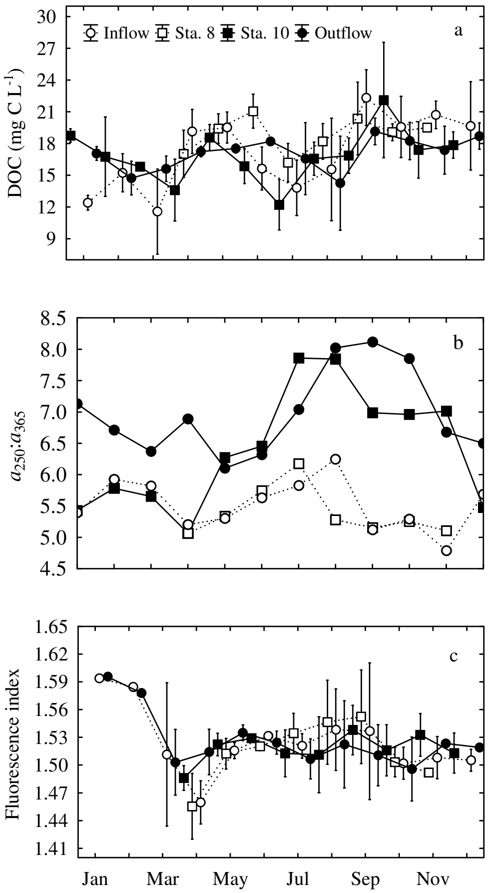

Fig. 5. Mean (± SE) monthly values of (a) dissolved organic carbon (DOC) concentration in 2008-2009 and of (b) a_{250}:a_{365} and (c) fluorescence index in 2010 in the main inflow (inflow), outflow, at the southern (Sta. 8) and central (Sta. 10) sampling stations of Lake Võrtsjärv.

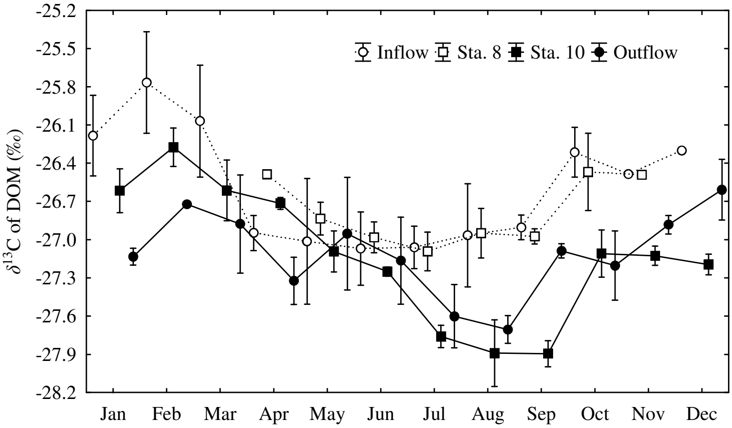

Fig. 6. Mean (± SE) monthly values of δ^{13}C of dissolved organic matter (DOM) in the main inflow (inflow), outflow, at the southern (Sta. 8) and central (Sta. 10) sampling stations of Lake Võrtsjärv in 2008-2010.

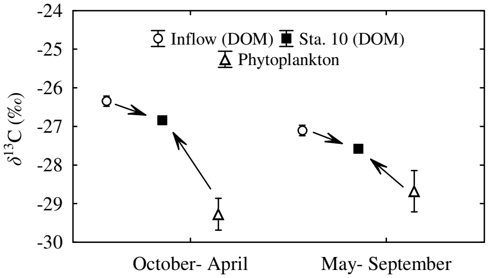

Fig. 7. Mean (± SE) values of δ^{13}C of dissolved organic matter (DOM) in the main inflow (inflow) and at the Lake Võrtsjärv central sampling station (Sta. 10), and of phytoplankton δ^{13}C at Sta. 10 during low (October-April) and high (May-September) vegetation.

III

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Reconstruction of long-term changes of the underwater light field in large shallow lakes Peipsi and Võrtsjärv, North-East Europe

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Abstract

The main objective of our study was to reconstruct the multi-decadal changes of the underwater light field in two large, shallow and polymictic Estonian lakes Võrtsjärv and Peipsi in order (i) to assess the potential role that light limitation could have on phytoplankton growth in the past and (ii) to have an insight to the factors driving underwater light climate in shallow turbid lakes in the long term. We reconstructed the long-term variations of the diffuse attenuation coefficient of water ($K_{\mathrm{d,PAR}}$) in the photosynthetically active region (PAR, 400-700 nm) partly based on measured beam attenuation spectra and partly using regression analysis. From $K_{\mathrm{d,PAR}}$ we calculated the depth of the euphotic zone ($z_{1\%}$) and the mean light availability in the mixed layer (E_{mix}). The reconstructed time series of these bio-optical parameters gave a plausible picture of the long-term development of light conditions in the two lakes studied, which was in accordance with their eutrophication history and changes in water levels. Better light availability in both lakes generally coincided with the years of low water level, and more distinctly in the shallower Võrtsjärv. E_{mix} values revealed a likely light limitation in Peipsi in autumn and in Võrtsjärv throughout the year.

Key words*:* large shallow lakes, underwater light climate, diffuse attenuation coefficient, seasonal and long-term changes

Introduction

The underwater light field in lakes, one of the main prerequisites for phytoplankton primary production, results from incident solar radiation which depends on solar altitude, meteorological conditions, and time and the optical properties of water (Kirk 1994). The absorption of light by different optically active substances (OAS), i.e. tripton, phytoplankton and coloured dissolved organic matter (CDOM), leads not only to the attenuation of irradiance with depth but also to the change of its spectral composition. The concentrations of OAS in water can vary by several orders of magnitude (Kirk 1994; Paavel *et al.* 2008) with relative contributions of various OAS differing both seasonally and over the range of different types of natural waters (Zhang *et al.* 2007). In large and shallow lakes the influence of resuspended sediment particles on the underwater light field is greater in comparison with that in deeper lakes (Zhang *et al.* 2007).

The attenuation of light caused by the sum of OAS present in the water can be described mainly by three different metrics of light attenuation: the Secchi depth (Z_{SD}), the beam attenuation coefficient of light determined from water samples (c), and the diffuse attenuation coefficient of light in the water body (K_d). A more detailed description of the underwater irradiance could be obtained from vertical profiles at different wavelengths (λ). The main characteristic of these profiles is the spectral diffuse attenuation coefficient, $K_d(\lambda)$ (Dera 1992; Kirk 1994; Arst 2003). The decrease of irradiance with depth in an optically homogenous water column is exponential, but theoretically this law is strictly correct only in the case of monochromatic radiation (Dera 1992; Arst *et al.* 2000). For photosynthesis and growth of aquatic plants the quantum irradiance in the photosynthetically active region (PAR, 400-700 nm) is of primary interest. In many limnological studies the diffuse attenuation coefficient over the PAR band ($K_{d,PAR}$) is used to describe the vertical decrease of irradiance in the water column (Paavel *et al.* 2006; Zhang *et al.* 2007; Paavel *et al.* 2008; Reinart and Pedusaar 2008). If underwater PAR irradiance at different depths is measured, the average $K_{d,PAR}$ for a water column can be estimated using the least square fit of the irradiance vs. depth ($K_{d,PAR}$ is the slope of this exponential regression). $K_d(\lambda)$ and $K_{d,PAR}$ also allow estimation of the depth of the euphotic zone ($z_{1\%}$), spectral and average for the PAR region, respectively (Wetzel 2001; Arst 2003).

When the value of incoming irradiance just below the water surface, $E_{d,PAR}(z=-0)$, is known in addition to $K_{d,PAR}$, the downwelling underwater irradiance at depth z, $E_{d,PAR}(z)$, can also be calculated. However, a database containing only $K_{d,PAR}$ can be used for estimating the relative values of the irradiance at different depths as well as the seasonal and long-term changes of water transparency. The water layer above the compensation point in which the rate of photosynthesis and respiration become equal, is called the euphotic layer. Its lower boundary is often defined as the penetration depth of 1% of the subsurface irradiance ($z_{1\%}$). In shallow lakes the value of $z_{1\%}$ allows estimation of the illuminated bottom area, which is an important parameter for the growth of macrophytes. The average light availability in the mixed water layer (E_{mix}) is the actual value to which phytoplankton is adapted and is biologically more relevant than individual light intensities in different water layers.

The main goal of the present study is to assess the potential role that light limitation could have had on phytoplankton growth in the past and to gain insight into the factors driving the underwater light climate in shallow turbid lakes in the long term. The topic of our work is very important to understanding the ecology and functioning of lakes ecosystems. Studies focused on long term data provide relevant information on the efficiency of management and restoration efforts in lakes impacted by human activities;, as well as providing insights about the factors and processes stabilizing alternative ecological states. To reconstruct the characteristics of the underwater light field ($K_{d,PAR}$, E_{mix} and $z_{1\%}$) we used data on phytoplankton, hydrochemistry and Secchi depth collected from 1964 to 2007 in eutrophic Lake Võrtsjärv and from 1982 to 2007 in mesotrophic/eutrophic Lake Peipsi. Both lakes are large, shallow and well-mixed (Fig.1).

Materials and Methods

Study sites

Lakes Peipsi (57º51'-59º01' N and 26º57'-28º10' E) and Võrtsjärv (57º50'-58º30' N and 25º35'-26º40' E) are large, shallow eutrophic and polymictic water bodies, well mixed by the surface waves and currents (Fig.1). The lakes are interconnected by the River Emajõgi flowing from Võrtsjärv into Peipsi. Lake Peipsi (3555 km^2), the fourth largest lake in Europe, is located in the eastern part of Estonia, on the border between Estonia and Russia, and consists of three basins: the largest and deepest northern basin Peipsi *sensu stricto*, the middle narrow basin Lämmijärv, and the southern basin Pihkva. The mean depth of the lake is 7.1 m and maximum depth 15.3 m. The mean water residence time is about two years. Lake Võrtsjärv (surface area 270 km^2, mean depth 2.8 m, maximum depth 6 m) is situated in the central part of Estonia. The retention time of water in Võrtsjärv is approximately one year, but may differ greatly between dry and rainy years (Jaani 1990).

The water levels of both lakes are unregulated and have found by applying a natural variability strongly associated with the changes in the North Atlantic Oscillation (NAO, Nõges *et al.* 2010a). The mean annual range of water level fluctuations is 1.4 m in Võrtsjärv and 1.15 m in Peipsi. The lakes are ice-covered usually for four months a year. The shallowness of the lakes and the wave-induced resuspension of bottom sediments contribute to the formation of high seston concentrations and high turbidity. Mean Z_{SD} in Peipsi is about 2 m and in Võrtsjärv less than 1 m. Therefore, among OAS, an important part of light in the PAR region, additionally to absorbance by humic substances and phytoplankton pigments, is scattered by suspended particles. The ratio of catchment area to lake volume (Ohle's index, C/V) is much higher in Võrtsjärv than in Peipsi, a sign of the larger effect of the catchment on Võrtsjärv's metabolism. All-year-round monthly hydrochemical and hydrobiological monitoring started in Võrtsjärv in 1961 (Nõges *et al.* 2001). Wet weight biomass of phytoplankton (PhB) and species composition data are available since 1964 and data on chlorophyll *a* concentrations (Chl *a*) since 1982. In Peipsi phytoplankton and Chl *a* measurements started in 1983. Spectral beam attenuation coefficients were recorded at monthly intervals in water samples of both lakes in 2002 – 2007. The detail on methods for Chl *a*, beam attenuation spectra and other parameters is given below. *In situ* $K_{d,PAR}$ measurement data from the lakes were not used firstly because of their scarcity and secondly because of their noisy character due to often high waves on those large lakes. In these conditions, we considered $K_{d,PAR}$, calculated from the measured beam attenuation spectra more reliable.

Calculations of $K_{d,PAR}$ from beam attenuation spectra

For the years 2002-2007 for which measured beam attenuation spectra were available, we calculated $K_{d,PAR}$ from $K_d(\lambda)$ using a model developed by Arst *et al.* (2002) and Arst (2003). This model was elaborated using 70 spectra of diffuse attenuation coefficient, measured *in situ* in 18 Estonian and Finnish lakes and corresponding results of the beam attenuation coefficient spectra determined from water samples in the laboratory (altogether 885 individual points). Based on measured $c(\lambda)$ spectra the model determines the ratio $A = b(\lambda_r)/c(\lambda_r)$, where $b(\lambda_r)$ is the scattering coefficient. The reference wavelength $\lambda_r = 580$ nm was chosen. The value of A was computed as a function of water sample measurement results:

$$A = f[c(400), c^*_f(400), c(580)] \qquad (1)$$

where $c^*_f(400)$ is the attenuation coefficient of filtered water at 400 nm. The final values of $b(580)$ and $c(580)$ were found applying the iteration method (Arst *et al.* 2002; Arst 2003). Then the spectra of $b(\lambda)$ in the range of 400-700 nm were found using the power law (Herlevi *et al.* 1999, Arst 2003). Knowing $b(\lambda)$ and $c(\lambda)$ we calculated the spectra of $K_d(\lambda)$ according to the formulae by Kirk (1984, 1994). Regression between the measured and modelled values of

$$K_d(\lambda,\text{meas}) = 1.0023 K_d(\lambda,\text{calc}), \text{ with } r = 0.96, p < 0.005 \;\; n = 70 \qquad (2)$$

showed a sufficient fit allowing to use the model in further calculations.

To obtain $K_{d,PAR}$, needed for the long-term reconstruction of the light field, we calculated from $K_d(\lambda)$ the vertical profiles of spectral underwater irradiance, which were integrated over the PAR region. Building a regression between the vertical profile of the PAR irradiance, $E_{d,PAR}(z)$ and z we found $K_{d,PAR}$ for each individual case.

Depth-integrated water samples were collected monthly during the ice-free period from March to November from one sampling point in Võrtsjärv and from six sampling points in Peipsi (Fig. 1). Samples were stored in plastic bottles in the dark at 4 °C without any treatment until analyses (for maximum 12 hours). The beam attenuation coefficient of water, $c(\lambda)$, was measured with a Hitachi U-3010 dual-beam spectrophotometer over the region of 280-800 nm using distilled water as the reference:

$$c(\lambda) = c*(\lambda) + c_d(\lambda) \qquad (3)$$

where $c^*(\lambda)$ is the reading of the Hitachi U-3010 spectrophotometer and $c_d(\lambda)$ is the beam attenuation coefficient of distilled water at the wavelength λ (all in m^{-1}).

The model described by Arst *et al.* (2002) and Arst (2003) allows for correction of the values of $c(\lambda)$ for forward scattering, and for differentiation $c(\lambda)$ into its two components, the absorption coefficient, $a(\lambda)$ and the scattering coefficient, $b(\lambda)$. Then, using the formulae developed by Kirk (1984, 1994), the $K_d(\lambda)$ spectra and $K_{d,PAR}$ values and corresponding irradiance profiles were calculated for the period of 2002-2007.

Extending the $K_{d,PAR}$ data series for earlier periods

To extend the $K_{d,PAR}$ data series for earlier periods (1964-2001 for Võrtsjärv and 1983-2001 for Peipsi), we developed lake-specific backward stepwise multi-component regression models for calculating $K_{d,PAR}$ from the Chl *a*, phytoplankton biomass (PhB), Secchi depth (Z_{SD}), permanganate oxygen demand (COD_{Mn}), and water colour data collected from both lakes at weekly to monthly intervals during the whole study period (Table 1). The two latter variables served as proxies for CDOM. The backward stepwise method used in this study, starts with all variables in the regression model and successively removes the variable with the smallest F-to-remove statistic, provided that this is less than the threshold value for F-to-remove. Regression assumes that variables have normal distributions. The box plots and the probability plots of the residuals and Kolmogorov-Smirnov test were used to check for normality. To avoid collinearity we omitted predictor variables if they were highly correlated with other predictor variables that remain in the model.

Phytoplankton samples were preserved with formaldehyde (until 1994) or acidified Lugol's solution (since 1995). Phytoplankton composition was identified and biovolumes determined in Goryajev's counting chamber (until 1994) or by an inverted microscope at 400X magnification using the Utermöhl (1958) technique (since 1995). Intercalibration did not reveal any significant differences between these counting methods (Nõges *et al.* 2003). PhB (g m^{-3}) was calculated from cell numbers and geometry.

For Chl *a* (mg m^{-3}), 0.1–1 l of water was filtered through filters of 0.7 µm pore size and concentrations were measured spectrophotometrically (Edler 1979) at a wavelength of 665 nm from 90% acetone (until 1995), 96% ethanol (since 1996) or both (1996) extracts of the filters. There were no remarkable differences in the extraction efficiency of these two solvents (Nõges and Solovjova 2000). In years 1964-1981, Chl *a* was not monitored in Võrtsjärv and the values were calculated from PhB (g m^{-3}) using the regression obtained from the data of 1982–2007 (Eq. 4).

$$\text{Chl } a = 1.30\text{PhB} + 10.9 \qquad (4)$$

$r^2 = 0.57, p < 0.001, N = 438$

Z_{SD} (m) was measured with a 30 cm diameter Secchi disk. COD_{Mn} (mgO l^{-1}) and water colour by Pt/Co scale (or Apha-Hazen scale) were measured as part of the State Monitoring Programme and data were obtained from the Information Centre of the Estonian Ministry of Environment.

Determination of irradiance characteristics

Incoming irradiance (MJ m^{-2} $month^{-1}$) for the observation periods was measured at actinometric stations of Tõravere (58°16' N, 26°26' E, about 20 km from Võrtsjärv) and Tiirikoja (on the northern coast of Peipsi, 58°51' N, 26°57' E). These data together with corresponding values of $K_{d,PAR}$ allowed us to roughly estimate the variation of underwater light field during the observation period. We calculated $E_{d,PAR}(z)$, according to the following formula (Dera 1992; Arst 2003):

$$E_{d,PAR}(z) = E_{d,PAR}(z = -0)\exp(-K_{d,PAR}z) \qquad (5)$$

where z is measured in m and $K_{d,PAR}$ in m^{-1}. $E_{d,PAR}(z=-0)$ is the downwelling irradiance just under the water surface (immediately after refraction). By rough estimation $E_{d,PAR}(z=-0) = 0.934E_{d,PAR}(z=0)$, since it is supposed that reflection coefficient from water surface is approximately 0.066 (Jerlov 1976).

We calculated $z_{1\%}$ from $K_{d,PAR}$ as:

$$z_{1\%} = -\ln(0.01) / K_{d,PAR} \qquad (6)$$

For calculating E_{mix} (Phlips et al. 1995), we first derived an integral (ζ) from irradiance values over depth in the range from z=0 to z= z_{mix}:

$$\zeta = \int_{0}^{z_{mix}} E_{d,PAR}(z = -0)\exp(-K_{d,PAR}z)dz \qquad (7)$$

According to its definition, $E_{\mathrm{mix}} = \zeta / z_{\mathrm{mix}}$. It leads to the following equation:

$$E_{mix} = \frac{E_{d,PAR}(z = -0)}{K_{d,PAR}z_{mix}}\left[1 - \exp(-K_{d,PAR}z_{mix})\right], \qquad (8)$$

where E_{mix} is in the same units as $E_{\mathrm{d,PAR}}(z=-0)$. In lakes Võrtsjärv and Peipsi, water is typically mixed down to the bottom, therefore z_{mix} was taken equal to Z_{avg} of the lake (Table 1).

For calculating E_{mix} we converted energy units (MJ m^{-2} day^{-1}) into quantum units (mol m^{-2} day^{-1}) according to the relationship 1 J m^{-2} s^{-1} = 4.61 μmol m^{-2} s^{-1} in air (Reinart *et al.* 1998; Reinart and Pedusaar 2008).

Data analysis

The software Statistica 8.0 (StatSoft, Inc. 2007) was applied to analyze the data. Spearman's Rank Order correlation was used to find relationship between indices. The significance level to indicate relationships was set at $p<0.05$.

Results

$K_{\mathrm{d,PAR}}$ estimates from OAS, their proxies and from Z_{SD}

The best stepwise multiple regression model for $K_{\mathrm{d,PAR}}$ included Z_{SD} as the only independent variable for Peipsi and Chl *a* as only independent variable for Võrtsjärv (Table 2). The best fit for $K_{\mathrm{d,PAR}}$ was achieved with Chl *a* by linear relationship and with Z_{SD} by a power function (Table 2).

Long-term changes of $K_{\mathrm{d,PAR}}$, $z_{1\%}$, and E_{mix}

In Peipsi (1983-2007) the $K_{\mathrm{d,PAR}}$ values in the inshore sampling points (LP16, LP17, LP38) were usually about 20% higher and more variable than in the offshore sampling points (LP2, LP4, LP11) (Fig. 2a, 3a, Table 3). Low $K_{\mathrm{d,PAR}}$ values were characteristic of the whole lake in the beginning of the 1990s (e.g., on average 1.1 m^{-1} offshore and 1.4 m^{-1} inshore in 1993). Since that, $K_{\mathrm{d,PAR}}$ developed several peaks in the inshore areas reaching highest mean values of about 1.9 m^{-1} in 2002, 2003, and 2007. In offshore areas, the peaks remained much lower (the annual mean value reaching a maximum of 1.4 m^{-1} in 2004) and lagged behind the inshore peaks by one or two years. The relationship between $K_{\mathrm{d,PAR}}$ and Z_{avg} was statistically significant ($p<0.05$) in the inshore and non-significant in the offshore areas of Peipsi (Table 4). $K_{\mathrm{d,PAR}}$ will increase when there are high Z_{avg} in spring or low Z_{avg} in summer and autumn in inshore areas (Table 4).

Being a function of $K_{\mathrm{d,PAR}}$, the euphotic depth varied in from 1.8 to 4.6 in inshore areas and from 2.1 to 7.0 m in offshore areas of Peipsi with corresponding average values of 3.0 and 3.8 m (Fig. 4a, Table 3). The ratio varied from 0.23 to 0.49 in the inshore and from 0.25 to 0.86 in the offshore areas. In offshore areas E_{mix} decreased with increasing Z_{avg} in summer whereas no significant correlations with E_{mix} were found in the inshore areas (Fig 5a, Table 4). The relationship between E_{mix} and Chl *a* was non-significant, although the trend was clearly different for the spring and summer/autumn data (Table 4).

In Võrtsjärv (1964-2007) $K_{d,PAR}$ was continuously much higher than in Peipsi with annual mean values exceeding 2.0 for most of the time (Table 3). The period of highest $K_{d,PAR}$ values in Võrtsjärv in the beginning of the 1970s (on average 2.8 m^{-1} in 1973, Fig. 2b) was followed by a decline in the 1980s. As a result of a new growing since 1987, especially in summer and autumn, $K_{d,PAR}$ reached a peak in 2006 equal to those of the 1970s. In Võrtsjärv both long-term and seasonal changes of $K_{d,PAR}$ and $1/Z_{SD}$ followed a similar trend (Fig. 2b, 3b). The correlation between $K_{d,PAR}$ and Z_{avg} was significant and identical to the inshore area of Peipsi (Table 4).

The euphotic depth varied in Võrtsjärv from 1.1 to 5.2 m (Fig. 4b) having an average value of 2.3 m, which was slightly smaller than the long-term mean depth of the lake (2.8 m). E_{mix} had its annual maximum value (8.25 mol m^{-2} d^{-1}) in the beginning of the study period (1964), the minimum level in late 1970s and a slightly increased since that time (Fig. 5b). E_{mix} decreased with increasing Chl *a* over summers, and with increasing Z_{avg} over springs (Table 4).

In both lakes highest $K_{d,PAR}$ values occurred in summer and autumn (Fig. 3a,b; Table 3). Also the interannual ranges were largest in summer and autumn values whereas the spring values were much more stable. In the shallower sites (Võrtsjärv and inshore area of Peipsi), $K_{d,PAR}$ increased with decreasing water levels (expressed as Z_{avg}) in the summer and autumn series, and was positively correlated in the spring series (Table 4) whilst no significant correlation was found between $K_{d,PAR}$ and water level in offshore areas of Peipsi. In Võrtsjärv the general long-term dynamics of the euphotic depth followed the water level changes (r=0.33, p<0.05, n=361), but not in Peipsi (Fig. 4). E_{mix} was always much lower in Võrtsjärv than in Peipsi. In both lakes E_{mix} values were much higher in spring and summer than in autumn (Table 3).

Discussion

Correct measurement of light attenuation *in situ* requires sophisticated and relatively expensive equipment and is easily disturbed by high surface waves that occur frequently on large lakes; therefore these data are rare in historical data sets. Empirical regressions potentially enable estimation of light attenuation if the concentrations of detritus, inorganic suspended matter and chlorophyll are measured, but often only the latter is available in the datasets (Scheffer 1998). The long-term datasets that were available for lakes Võrtsjärv and Peipsi included Chl *a*, PhB, Z_{SD}, COD_{Mn} and water colour.

In Võrtsjärv Chl *a* described 71% of the variation of $K_{d,PAR}$ and was used for long-term calculations (Table 2). The mean Chl *a* was relatively high and varied over a wide range (Table 1). Among OAS, Chl *a* is one of the main components that together with total suspended matter and dissolved organic matter determines the optical properties of water.

In Peipsi Z_{SD} accounted for 76% of the variation in $K_{d,PAR}$ (Table 2) and was used for long-term calculations. Equally strong relationships with similar coefficients of the power function formulae were found by Arst *et al.* (2008) for 21 Estonian and Finnish lakes. The relationship between $K_{d,PAR}$ and Z_{SD} is strongly dependent on lake type because scattering has a stronger effect on Z_{SD} than on the vertical light attenuation (Wetzel 2001). For instance, a lake in which turbidity is mainly caused by suspended clay particles which scatter rather than absorb, will have a lower light attenuation than a lake with the same Z_{SD} in which the turbidity is mainly due to phytoplankton (Scheffer 1998).

The high correlation between $K_{d,PAR}$ and Z_{SD} in Peipsi could be attributed to a presumably stronger effect of algal blooms on optical properties of water compared to suspended mineral particles. In much shallower Võrtsjärv stronger resuspension of sediments brings more mineral particles into the water column affecting strongly the optical properties of water.

COD_{Mn} and water colour as proxies for CDOM appeared to be less important than Chl *a* or Z_{SD} in describing the variation of $K_{d,PAR}$ in both lakes. It certainly does not mean that CDOM has a marginal effect on light attenuation, but due to the narrow seasonal range of COD_{Mn} and water colour, their impact on variation in light climate turned out weaker than that of PhB and Chl *a*, which both vary over a wide range. Still the positive relationship between $K_{d,PAR}$ and Z_{avg} and the negative relationship between E_{mix} and $Z_{avg,}$ appearing in spring in Võrtsjärv and in inshore areas of Peipsi (Table 4) was likely caused by poorer light conditions due to higher concentrations of dissolved organic matter, since the concentration of dissolved organic matter is usually high at high water levels in April and May (Toming *et al.* 2009). Furthermore, according to Reinart and Nõges (2003) and Reinart et al. (2004) up to 53% of light attenuation in the PAR region can be attributed to CDOM in lakes Peipsi and Võrtsjärv (Reinart and Nõges 2003; Reinart *et al.* 2004). In Võrtsjärv where $K_{d,PAR}$ was calculated from Chl *a* for most of the period, it could not account directly for CDOM, however an adaptive response resulting in an increase in Chl *a* in response to deeper mixing in darker water could be inferred. The negative correlation between $K_{d,PAR}$ and Z_{avg} in summer and autumn months (Table 4) was obvious evidence of the increasing impact of sediment resuspension during seasonally lowest water levels that carried freshly sedimented algae and Chl *a* back into the water column. According to Nõges et al. (2003), PhB in Võrtsjärv is significantly higher in years of low water level. The decreasing E_{mix} with increasing Chl *a* in summer reveals the greater relative role of phytoplankton in light attenuation during this time of the year compared to spring and autumn.

Long-term variations of underwater irradiance are controlled by human impact, climate change and water level fluctuations. The eutrophication of Estonian lakes from agricultural and point sources accelerated since the 1950s (Heinsalu *et al.* 2007; Heinsalu and Alliksaar 2009), and culminated in the 1970s and 1980s (Ott and Kõiv 1999). As a large portion of these nutrients was accumulated in lake sediments and is still supporting high primary productivity of lakes, the decreased pollution loads and use of fertilizers has not caused a corresponding improvement in the bio-optical properties of water. Even on the contrary – we can see the increase in the reconstructed $K_{d,PAR}$ series for Võrtsjärv and inshore areas of Peipsi. The situation is somewhat better in offshore areas of Peipsi, where the influences of the river discharges and sediment resuspension are smaller (Toming *et al.* 2009).

Lake depth has a very pronounced impact on the light climate experienced by algae, and thus for their growth rates and realized biomass (Scheffer 1998). Since algal cells are dispersed throughout the mixed layer, the light they experience depends not only on the $K_{d,PAR}$ but also on z_{mix}, which in most shallow lakes is the entire water column (Scheffer 1998). Oliver (1981) showed that the threshold level of E_{mix} for light limitation of phytoplankton standing crop is 3.5 mol m^{-2} day^{-1}. Similarly, some other authors have estimated that the range at which light availability is the major factor in controlling the phytoplankton growth is 0.9–4.0 mol m^{-2} day^{-1} (Geddes 1984), 2.0–3.5 mol m^{-2} day^{-1} (Phlips *et al.* 1995) and 0.24–3.9 mol m^{-2} day^{-1} (Reinart and Pedussaar 2008). Minimum E_{mix} values (Table 4) were below the critical threshold in Peipsi in autumn (0.6–0.7 mol m^{-2} day^{-1}) and in Võrtsjärv throughout the year (0.3–2.8 mol m^{-2} day^{-1}) showing that phytoplankton in these lakes could be light limited and this issue is more critical in Võrtsjärv. A comparison of Figs. 2b, 4b, and 5b gives a good example of the predominant role of the water level in determining the light climate in Võrtsjärv. E_{mix} reached its highest values in low water years in the 1960s and in 1996 and the minimum in 1978, the year of the highest water level. Remarkably the water was most transparent in 1978 and the low E_{mix} can be fully attributed to the high water level in this year. A large change in phytoplankton composition took place in at that time with two highly shade tolerant species appearing among dominants (Nõges *et al.* 2010b). The leading role of water level in the formation of light conditions for phytoplankton can be seen also in the general increase of E_{mix} since the 1970s, which has occurred despite increasing $K_{d,PAR}$ and which can be explained by the decrease in water levels.

Conclusions

Reconstruction of the diffuse attenuation coefficient ($K_{d,PAR}$) based on regressions with optically active substances or their proxies offers a good approach for calculating the euphotic depth ($z_{1\%}$) and the mean light intensity in the mixed layer (E_{mix}), which are crucial parameters for understanding the light conditions for phytoplankton and aquatic macrophytes and indispensable for modelling primary production.

The reconstructed time series of $K_{d,PAR}$, $z_{1\%}$, and E_{mix} gave a plausible picture of the long-term development of light conditions in the two lakes studied, which was in accordance with their eutrophication history and changes in water levels.

The dependence of bio-optical parameters on water quality and lake levels differed by seasons and sites. In the shallower sites, $K_{d,PAR}$ increased with decreasing water levels in the summer and autumn, which could be attributed to intensified resuspension in low water, and was positively correlated with water level in the spring series, likely due to more dissolved organic matter contained in high flood waters. In offshore areas of Peipsi $K_{d,PAR}$ remained independent from water level.

The analysis showed the more important role of water level changes compared to changes of $K_{d,PAR}$ in determining E_{mix} in the shallower Võrtsjärv. In this lake a general increase of E_{mix} occurring since the 1970s, despite increasing $K_{d,PAR}$, could be explained by the decrease in water levels. E_{mix} is a crucial parameter for phytoplankton photosynthesis and for identifying light limitation. Minimum E_{mix} values remaining below the critical threshold showed that in Peipsi phytoplankton was likely light limited in autumn and in Võrtsjärv throughout the year.

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Summary in Estonian

Veealuse valgusvälja pikaajaliste muutuste taastamine suurtes ja madalates Kirde Euroopa järvedes (Peipsi ja Võrtsjärv)

Kaire Toming, Peeter Nõges, Helgi Arst, Toomas Kõiv, Tiina Nõges

Meie töö peamine eesmärk oli taastada veealuse valgusvälja mitme aastakümne pikkused muutused kahes suures, madalas ja polümiktilises Eesti järves- Võrtsjärves ja Peipsi järves, et (a) hinnata valguse limitatsiooni mõju fütoplanktoni kasvule minevikus ning (b) vaadelda, mis mõjutavad veealust valgusvälja madalates segunenud järvedes pikal ajaskaalal. Me rekonstrueerisime vee difuusse nõrgenemise koefitsiendi ($K_{\mathrm{d,PAR}}$) pikaajalise varieeruvuse fotosünteetiliselt aktiivses spektri piirkonnas (PAR, 400-700 nm) kasutades nii mõõdetud kiirguse nõrgenemise spektreid kui ka regressioon analüüsi. $K_{\mathrm{d,PAR}}$-st arvutasime omakorda eufootilise tsooni sügavuse ($z_{1\%}$) ning järvevee segunenud kihi keskmise valguse kättesaadavuse (E_{mix}). Eelpool nimetatud bio-optiliste parameetrite rekonstrueeritud aegread andsid tõepärase pildi pikaajalistest valgustingimuste muutustest Peipsi ja Võrtsjärves, mis oli kooskõlas eutrofeerumise ajaloo ja veetaseme varieerumisega nimetatud järvedes. Veealused valgustingimused olid üldiselt paremad madalaveelistel aastatel. E_{mix} väärtused näitasid, et Peipsi järves on valgus suurema tõenäosusega limiteerivaks teguriks sügisel ning Võrtsjärves kogu aasta jooksul.

Tables

Table 1. Mean phytoplankton biomass (PhB), chlorophyll *a* (Chl *a*), COD_{Mn}, water colour, Secchi depth (Z_{SD}), average water depth (Z_{avg}) and standard deviations (SD) in lakes Võrtsjärv and Peipsi during the observation periods indicated. *N* is the number of samples.

	Peipsi, offshore (sampling points LP2, LP4, LP11)			Peipsi, inshore (sampling points LP16, LP17, LP38)			Võrtsjärv		
	Mean+/-SD	*N*	Obs. period	Mean+/- SD	*N*	Obs. period	Mean+/- SD	*N*	Obs. period
PhB , g m^{-3}	7.21 ± 6.13	223	1983-2007	11.0 ± 9.78	230	1964-2007	14.9 ± 14.4	639	1964-2007
Chl *a*, mg m^{-3}	18.8 ± 12.7	352	1983-2007	30.0 ± 28.6	215	1982-2007	29.8 ± 20.6	432	1982-2007
COD_{Mn}, mgO l^{-1}	29.3 ± 17.4	218	1992-2007	35.1 ± 8.46	175	1968-2007	11.5 ± 3.7	303	1968-2007
Water colour, Pt-Co°	34.8 ± 9.03	224	1992-2007	62.4 ± 23.9	177	1964-2007	55.9 ± 18.8	206	1964-2007
Z_{SD}, m	1.88 ± 0.78	337	1985-2007	1.30 ± 1.51	199	1968-2007	1.0 ± 0.5	428	1968-2007
Z_{avg}, m	9.32 ± 1.24	246	1983-2007	7.59 ± 1.20	130	1964-2007	2.55 ± 0.44	569	1964-2007

Table 2. Regression formulas describing the relationships between K_{dPAR}, m^{-1} and phytoplankton biomass (PhB, g m^{-3}), chlorophyll *a* (Chl *a*, mg m^{-3}), and Secchi depth (Z_{SD}, m) in lakes Võrtsjärv and Peipsi for the period of 2002-2007; in all cases $p < 0.001$.

		Peipsi				Võrtsjärv			
y	x	Relationship	SE	r^2	*N*	Relationship	SE	r^2	*N*
$K_{d,PAR}$	Chl *a*	$y = 0.02x + 0.998$	0.32	0.59	137	$y = 0.03x + 1.07$	0.59	0.71	43
$K_{d,PAR}$	PhB	$y = 0.05x + 1.04$	0.36	0.48	143	$y = 0.05x + 1.47$	0.80	0.27	43
$K_{d,PAR}$	Z_{SD}	$y = 1.72x^{-0.546}$	0.30	0.76	163	$y = 1.73x^{-0.803}$	0.63	0.59	43

Table 3. Mean, minimum and maximum values of the diffuse attenuation coefficient ($K_{\mathrm{d,PAR}}$, m^{-1}), average light availability in the mixed layer (E_{mix}, mol m^{-2} day^{-1}), depth of the euphotic zone ($z_{1\%}$, m) and the ratio between euphotic zone and the average water depth ($z_{1\%}/Z_{\mathrm{avg}}$) in offshore (LP2, LP4, LP11) and inshore (LP16, LP17, LP38) sampling points of Peipsi in 1983-2007 and in Võrtsjärv in 1964-2007. *N* is the number of samples. Spring is defined as March, April, and May; summer as June, July, and August; fall as September, October, and November.

Lake	**Season**	$K_{\mathrm{d,PAR}}$			E_{mix}			$z_{1\%}$		
		Mean	Min/Max	*N*	Mean	Min/Max	*N*	Mean	Min/Max	*N*
Peipsi	Spring	**1.11**	0.65/1.72	27	**11.6**	6.77/18.1	25	**4.33**	2.67/7.03	27
offshore	Summer	**1.22**	0.96/2.23	41	**14.1**	7.02/22.4	39	**3.84**	2.06/4.81	41
	Fall	**1.38**	1.00/1.72	36	**3.92**	0.73/11.7	36	**3.39**	2.67/4.60	36
	AVER.	**1.24**	0.65/2.23	104	**9.72**	0.73/22.4	100	**3.81**	2.06/7.03	104
Peipsi	Spring	**1.35**	1.03/1.70	19	**11.2**	6.33/15.7	18	**3.50**	2.71/4.46	19
inshore	Summer	**1.66**	1.25/2.52	33	**11.7**	5.56/16.2	29	**2.87**	1.82/3.67	33
	Fall	**1.64**	1.18/2.60	30	**3.73**	0.55/11.3	30	**2.92**	1.77/3.90	30
	AVER.	**1.58**	1.03/2.60	82	**8.48**	0.55/16.2	77	**3.03**	1.77/4.46	82
Võrtsjärv	Spring	**1.67**	0.88/3.10	119	**5.66**	2.31/11.6	119	**2.91**	1.48/5.22	119
	Summer	**2.27**	1.12/4.19	123	**6.50**	2.78/11.7	123	**2.15**	1.10/4.10	123
	Fall	**2.46**	1.53/3.96	119	**1.83**	0.29/4.97	119	**1.97**	1.16/3.01	119
	AVER.	**2.14**	0.88/4.19	361	**4.68**	0.29/11.7	361	**2.34**	1.10/5.22	361

Table 4. Spearman correlation coefficients for the relationship between average light availability in the mixed layer (E_{mix}, mol m^{-2} day^{-1}) and phytoplankton biomass (PhB, g m^{-3}), chlorophyll *a* (Chl *a*, mg m^{-3}) and average water depth (Z_{avg}, m) and between average water depth (Z_{avg}, m) and depth of the euphotic zone ($z_{1\%}$, m) and diffuse attenuation coefficient ($K_{\mathrm{d,PAR}}$, m^{-1}) in the offshore (LP2, LP4, LP11) and inshore (LP16, LP17, LP38) sampling points of Peipsi in 1983-2007 and in Võrtsjärv in 1964-2007. Correlation analyses were performed on a seasonal basis. Spring is defined as March, April, and May; summer as June, July, and August; fall as September, October, and November. *N* is the number of samples and correlation coefficients in bold type indicate $p < 0.05$.

Lake	**Season**	**E_{mix} vs Chl *a***			**E_{mix} vs Z_{avg}**			**$K_{\mathrm{d,PAR}}$ vs Z_{avg}**		
		r	*p*	*N*	*r*	*p*	*N*	*r*	*p*	*N*
Peipsi	Spring	0.16	0.45	24	-0.32	0.12	25	0.14	0.49	27
offshore	Summer	-0.26	0.13	36	**-0.47**	0.00	36	0.05	0.78	41
	Fall	-0.31	0.07	35	-0.12	0.47	36	0.06	0.71	36
Peipsi	Spring	0.15	0.56	18	-0.40	0.09	18	**0.46**	0.05	19
inshore	Summer	-0.22	0.23	31	-0.12	0.52	31	**-0.45**	0.01	33
	Fall	-0.26	0.17	29	-0.02	0.93	30	**-0.36**	0.05	30
Võrtsjärv	Spring	-0.16	0.08	119	**-0.36**	0.00	119	**0.19**	0.04	119
	Summer	**-0.64**	0.00	123	0.06	0.48	123	**-0.41**	0.00	123
	Fall	-0.14	0.12	119	-0.15	0.08	119	**-0.28**	0.00	119

Figures

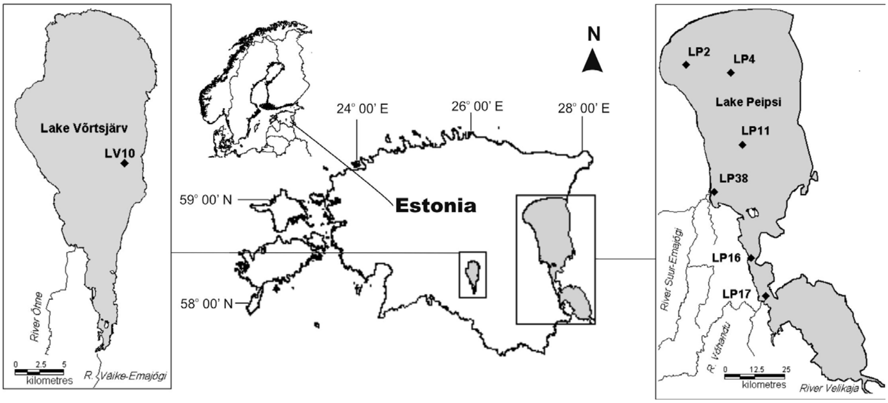


Fig. 1 Location map of Lake Peipsi and Lake Võrtsjärv. Sampling points for beam attenuation coefficient measurements and long-term monitoring are indicated with symbols LV10, LP2, LP4, LP11, LP16, LP17 and LP38.

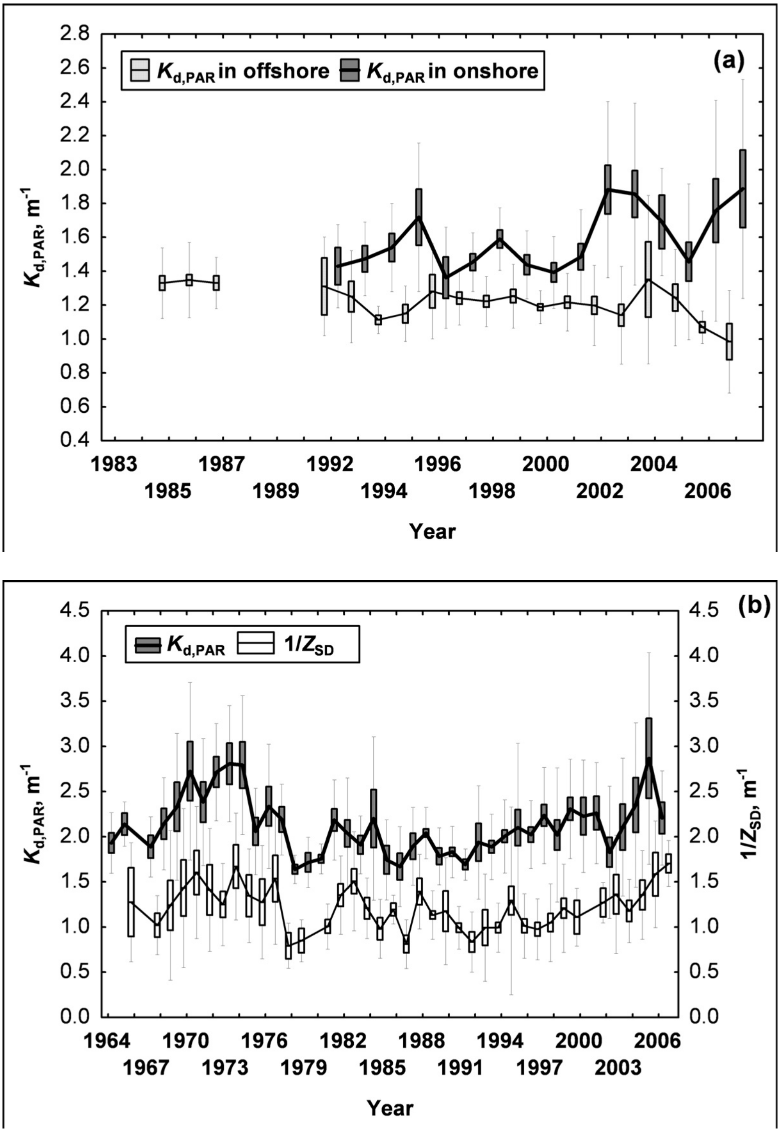


Fig. 2 Long-term changes of the yearly average values of the diffuse attenuation coefficient ($K_{d,PAR}$, m^{-1}) for the ice-free period in (a) in offshore (LP2, LP4, LP11) and inshore (LP16, LP17, LP38) sampling points of Peipsi in 1983-2007 and (b) in Võrtsjärv in 1964-2007. The reciprocal of Secchi depth ($1/Z_{SD}$) is also shown in Võrtsjärv. Standard error is shown as vertical boxes and standard deviation as vertical lines.

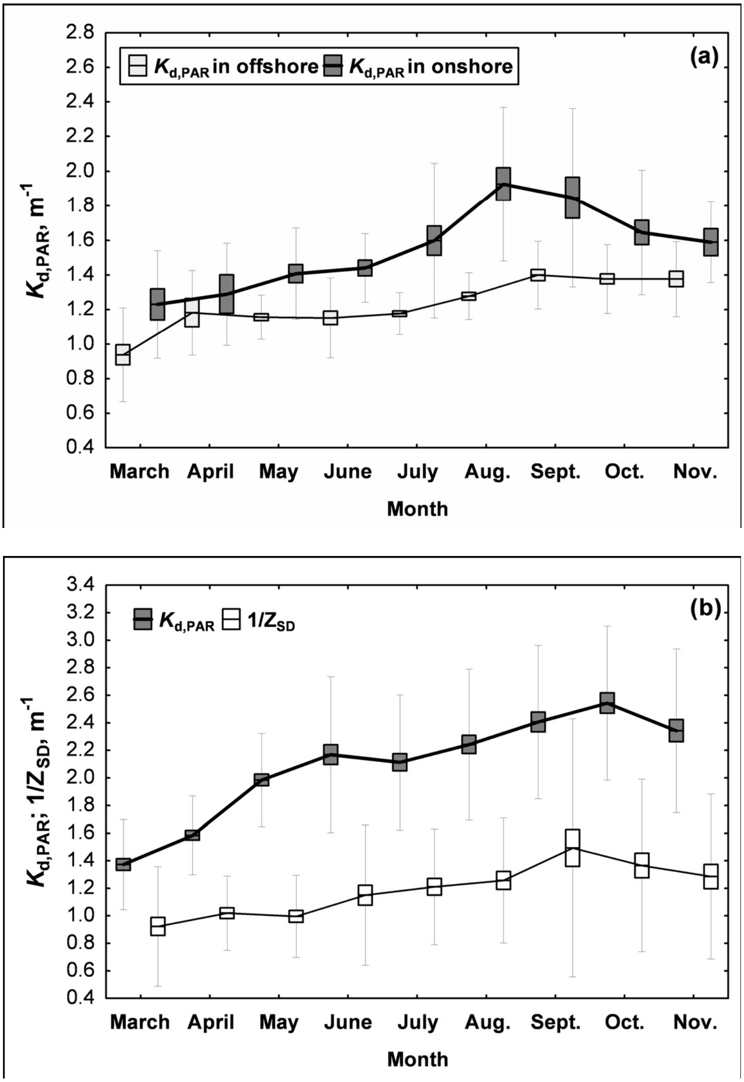


Fig. 3 Seasonal distribution of the monthly averages of the diffuse attenuation coefficient ($K_{d,PAR}$, m^{-1}) for the ice-free period in (a) in offshore (LP2, LP4, LP11) and inshore (LP16, LP17, LP38) sampling points of Peipsi in 1983-2007 and (b) in Võrtsjärv in 1964-2007. The reciprocal of Secchi depth ($1/Z_{SD}$) is also shown in Võrtsjärv. Standard error is shown as vertical boxes and standard deviation as vertical lines.

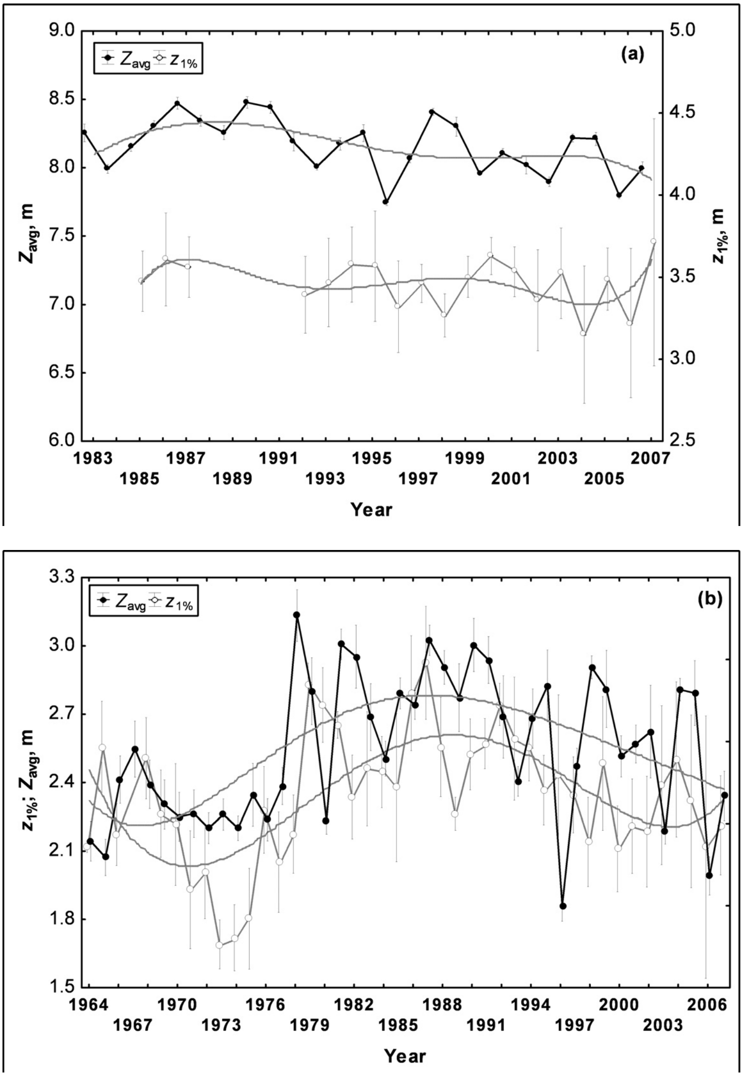
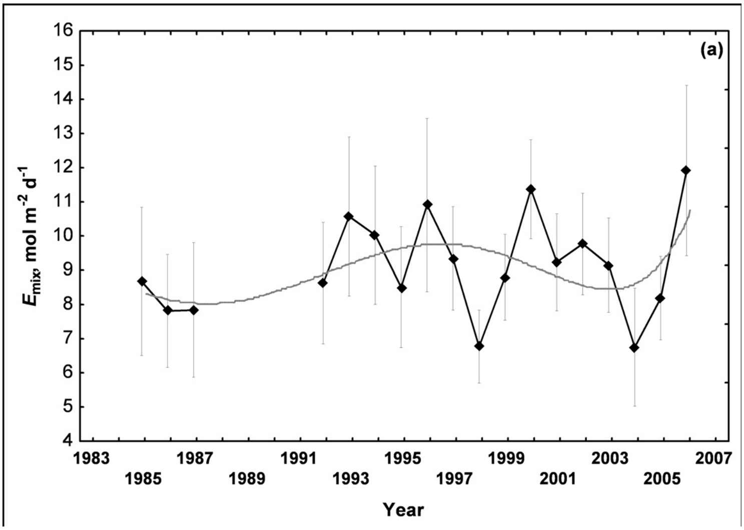


Fig. 4 Long-term changes of the yearly averages values of the water depth (Z_{avg}, m) and depth of the euphotic zone ($z_{1\%}$, m) for the ice-free period (a) in Peipsi in 1983-2007 and (b) in Võrtsjärv in 1964-2007. Standard errors are shown as vertical lines and polynomial trends as grid lines.



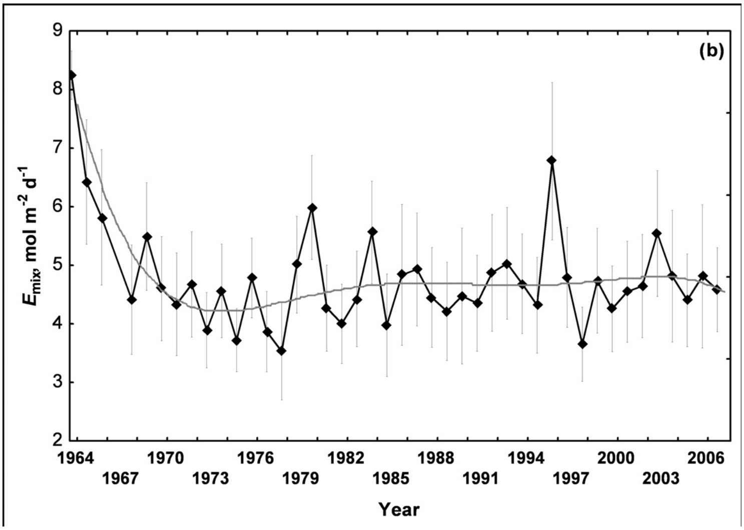


Fig. 5 Long-term changes of the average light availability in the mixed layer (E_{mix}, mol m^{-2} d^{-1}) for the ice-free period (a) in Peipsi in 1983-2007 and (b) in Võrtsjärv in 1964-2007. Standard errors are shown as vertical lines and polynomial trends as grid lines.

IV

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Optical investigations of CDOM-rich coastal waters in Pärnu Bay

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Abstract. Pärnu Bay in the Eastern Baltic Sea was chosen for studying the spatial-temporal variability of water parameters as an optically complex and semi-enclosed coastal area. The water properties of Pärnu Bay are influenced by the town of Pärnu with its 70 000 inhabitants and by the high inflow from the Pärnu River. The in situ database was collected during the ice-free period of 2006–2007 (11 sampling stations, 10 series of field trips). According to the results, the main factor influencing the light attenuation in the water was coloured dissolved organic matter (CDOM) which overshadows the relationships between the radiation characteristics and organic/inorganic particles. In April and May, when the freshwater discharge of the Pärnu River was highest, the values of $a_{\mathrm{CDOM}}(380)$ were between 4.6 and 31.8 m^{-1}, while in September they varied only within 2.52–10.2 m^{-1}. The concentrations of chlorophyll *a* (including its metabolite phaeophytin *a*) generally ranged from 4 to 12 mg m^{-3} but during algal blooms they rapidly increased to 31.8 mg m^{-3}. The temporal and spatial irregularity of suspended matter concentrations was caused by the loading of unpacked peat at the Pärnu River mouth as well as by undulation and ship traffic in Pärnu Bay. MODIS level 1 data with 250 m resolution were used for illustrative comparison of spatial and temporal variations in the water properties in Pärnu Bay and the Gulf of Riga. An attempt to perform the quantitative analysis with the purpose of estimating the concentrations of different optically significant substances separately gave statistically incorrect results.

Key words: coastal waters, underwater light field, diffuse attenuation coefficient, optically active substances, remote sensing.

INTRODUCTION

Nowadays problems connected with the estimation of the ecological state of seas and inland waters have become especially topical due to increasing industrial and human impact on the aquatic environment. For a comprehensive survey of some water body complex investigations consisting of chemical, hydrophysical, optical and biological measurements are necessary. However, rather essential conclusions may be drawn also on the basis of a certain group of in situ measurements: quite often the complex of data, containing the concentrations of optically significant substances (phytoplankton, coloured dissolved organic matter (CDOM) and suspended matter) as well as the incoming irradiance and diffuse attenuation coefficient, has been collected. These data enable also determination of the underwater irradiance, which is an important factor in forming the phytoplankton productivity. Optical measurements yield information on temporal and spatial variation in optically significant substances, including certain kinds of water pollution.

The advances in ocean colour remote sensing over the decades have made it possible to use remote sensing imagery to produce maps of productivity in the world oceans (Platt & Sathyendranath 1988). Considering the seas and coastal waters, the daily MODIS (onboard the Aqua platform) overpass covers the whole of the Baltic Sea area, which makes it very operative for environmental monitoring. The MODIS/Aqua Level 1 (Top of Atmosphere, TOA) and Level 2 images (including atmospherically corrected water-leaving radiance and chlorophyll *a* concentration) with 250 m spatial resolution are freely available. The MODIS standard algorithm for the diffuse attenuation coefficient of seawater at 490 nm, $K_{\mathrm{d}}(490)$, has been developed using the ratio of water-leaving radiances at 490 and 555 nm (Austin & Petzold 1981; Mueller 2000). $K_{\mathrm{d}}(490)$ gives more accurate results in the Baltic Sea than chlorophyll standard algorithms (Darecki & Stramski 2004; Kratzer et al. 2008). The values of $K_{\mathrm{d}}(490)$ are influenced by all absorbing substances in the water including CDOM, which is often the dominant absorbing compound in these bands.

However, coastal waters are optically complex, characterized by a large variability of optically significant constituents resulting from different biological, chemical and physical processes. This leads to difficulties in the interpretation of satellite data in coastal and inland waters due to several technical and methodological limitations (spatial, spectral and radiometric resolution of the instrument, and the determination of atmospheric correction in multicomponental waters).

Many Estonian coastal regions and inland waters are under strong human impact, and the Baltic is a rather polluted internal sea. The nature of the bays is often influenced by the inflow of rivers that bring along large quantities of CDOM. Small and semi-enclosed Pärnu Bay (in the Eastern Baltic Sea) is under the influence of the town of Pärnu with its 70 000 inhabitants and the high inflow from the Pärnu River. This causes the low transparency of Pärnu Bay water. The bay has been investigated in situ for some years, but the majority of investigations have been conducted in the sphere of hydrology and biology. In the present study the optically complex Pärnu Bay was chosen for in situ measurements with the aim of comprehensive investigation of the temporal-spatial variability of the optical properties of water. We considered it also as a test site for assessing the possibilities of developing remote sensing algorithms for this kind of water. For building and testing a model for interpretation of remote sensing data, however, simultaneous in situ measurements of optically significant substances and radiation characteristics in the water body are needed.

Besides, in situ measurement data have their own, independent value. Firstly, the satellite sensor cannot describe the water state in the conditions of cloudy weather. Secondly, the signal coming into the sensor originates from the surface layer, which is only 20–40 cm thick in case of turbid waters (Secchi disk depth below 0.5 m) (Arst 2003). For this reason the in situ data on the vertical profiles of optically significant substances and underwater irradiance are indispensable.

A database describing the variability of the bio-optical water parameters in Pärnu Bay (and partly in the Gulf of Riga) was collected during 2006–2007 (11 sampling stations, 10 series of field trips). Several correlation relationships between optically significant substances and radiation characteristics were investigated.

MATERIAL AND METHODS

Description of Pärnu Bay

Pärnu Bay is a shallow water basin in the northeastern Gulf of Riga (Fig. 1), which could be divided into an inner and an outer basin. The inner part has approximate measures of 13 km × 14 km, an area of about 190 km^2 and the maximum depth of 7.6 m. The outer part extends down to the southern tip of Kihnu Island, having an area of about 500 km^2 and the maximum depth of about 15 m.

The quality of water and quantity of nutrients in Pärnu Bay depend on the inflow of fresh water from rivers and on the intrusion of water from the Gulf of Riga due to changes in wind direction and water level. Nutrient concentrations in Pärnu Bay are higher than the average level in the Gulf of Riga, as it is a relatively isolated strip of sea. However, in comparison with the general situation of Estonian coastal waters, the bay water has a high quantity of phosphate and a particularly high quantity of nitrogen compounds – consequently, predominantly the environment, which is suitable for primary productivity limited by phosphorus and the light conditions (Tervisekaitseinspektsioon 2009).

The Pärnu River accounts for approximately 80% of the inflow to Pärnu Bay, bringing annually 2 km^3 of fresh water to the bay, although the volume of the inner basin is only 1 km^3 (Suursaar & Tenson 1998). The average river flow rate is 64 m^3 s^{-1}, which varies considerably during the year. Maximum rates remain in

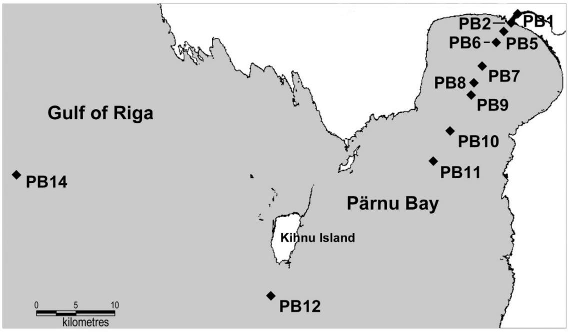

Fig. 1. Pärnu Bay as part of the Gulf of Riga in the Baltic Sea (the mouth of the Pärnu River is also shown). The sampling stations are marked by dark diamonds.

the range of 220–330 $m^3\ s^{-1}$, but minimum rates are approximately 100 times smaller – in the range of 3.5 to 4.7 $m^3\ s^{-1}$ (BERNET 2000). Due to this fact the salinity of water in Pärnu Bay is low, only 3–5 in comparison with the salinity of 4.5–6 of the Gulf of Riga (Tervisekaitseinspektsioon 2009).

The characteristic bay bottom type is fine sand, with only occasional stony areas. Due to the effect of waves and currents the water always contains particles of soft bottom sediments. Additional suspended matter is brought also by the Pärnu River waters. More specifically, large quantities of peat dust are directed to ditches and to the Sauga River and from there to the Pärnu River with drainage water from peat excavation areas. Peat dust reaches the bay also in the course of loading unpacked peat at the mouth of the river.

Measurement methods

Optical monitoring of Pärnu Bay and the Gulf of Riga was carried out at 11 sampling stations (Table 1 and Fig. 1) during the ice-free period in 2006–2007. The study programme involved both in situ measurements and collection of water samples for subsequent laboratory analyses.

Water samples were collected from the surface layer (0.2 m) with a standard water sampler and stored in the dark and cold for less than 7 h before filtering. The concentrations of chlorophyll *a* and phaeophytin *a* were analysed in duplicate by filtration of water samples (0.5–1 L) through Whatman GF/F-filters. Pigments were extracted from the filters in 90% ethanol at 75 °C for 5 min and measured spectrometrically, both before and after acidification with dilute hydrochloride acid (ISO 1992). Eventually, the determined absorbance values were converted, respectively, to chlorophyll *a* and phaeophytin *a* concentrations. For the sake of simplicity, the sum of concentrations is from now on abbreviated to C_{ph}. The concentration of total suspended matter, C_{s}, was measured gravimetrically after filtration of the same amount of water through pre-weighed and pre-combusted (103–105 °C for 1 h) filters (ESS 1993). The attenuation coefficients of light, $c^*(\lambda)$ and $c_{\mathrm{f}}^*(\lambda)$, were determined, respectively, from unfiltered and filtered water samples. The variable $c^*(\lambda)$ was obtained as the difference $c(\lambda) - c_{\mathrm{d}}(\lambda)$, where $c(\lambda)$ and $c_{\mathrm{d}}(\lambda)$ are the beam attenuation coefficients for natural and distilled water, respectively.

Table 1. Sampling stations in Pärnu Bay (field trips were carried out from April to September in 2006–2007)

Station	Latitude N, °	Longitude E, °	Number of trips
PB1	58.386	24.489	8
PB2	58.376	24.476	9
PB5	58.367	24.457	10
PB6	58.354	24.442	10
PB7	58.326	24.410	9
PB8	58.306	24.392	2
PB9	58.293	24.388	1
PB10	58.251	24.342	2
PB11	58.216	24.305	8
PB12	58.059	24.952	7
PB14	58.2	23.4	3

Both fresh and saline waters contain also varying concentrations of dissolved organic material (DOM), the optically active fraction of which, known as CDOM, plays a great role in the attenuation of irradiance in the water. Due to the fact that in natural waters CDOM is a rather indeterminate mixture of dissolved organic substances, it is extremely difficult to determine individual organic compounds therein by analytical methods (Dera 1992). In the present study the amount of CDOM was characterized by its absorption coefficient at 380 nm, $a_{\mathrm{CDOM}}(380)$. Unfortunately, with spectrometers such as Hitachi U1000 we cannot directly measure $a_{\mathrm{CDOM}}(\lambda)$, but attenuation coefficient spectra of filtered water, $c^*_{\mathrm{f}}(\lambda)$. The variable $c^*_{\mathrm{f}}(\lambda)$ is not identical to $a_{\mathrm{CDOM}}(\lambda)$ because some very small inorganic particles and colloids also pass through the filter and the water may remain a scattering medium even after filtration. However, the differences are small, about 2–8% (Sipelgas et al. 2003).

The depth profiles of planar downwelling irradiance ($q_{\mathrm{d}}(z)$) in the water column were measured using a LI-192 SA sensor (LI-COR, Inc., 1984). This device has an almost ideal quantum response over 400–700 nm (photosynthetically active region of the spectrum, PAR). We used the results of the underwater quantum irradiance for estimating the widely used diffuse attenuation coefficient, K_{d}(PAR) (Dera 1992; Kirk 1994; Arst 2003). The coefficient K_{d}(PAR) characterizes the averaged (over a water column) vertical decrease in natural light in the PAR. For these calculations irradiance values were plotted against depth (for the 0.1–3 m layer) and K_{d}(PAR) was found as the exponent of the least-squares regression line through these point.

A semi-empirical model described in Arst et al. (2002) and Arst (2003) allows estimation of the spectra of the diffuse attenuation coefficient, $K_{\mathrm{d}}(\lambda)$, on the basis of measured $c^*(\lambda)$. From these results the spectra of the attenuation depth ($z_{\mathrm{att}}(\lambda)$) can be determined using the relationship $z_{\mathrm{att}}(\lambda) = 1/K_{\mathrm{d}}(\lambda)$. This parameter shows the thickness of the surface layer from which 90% of radiation received by satellite sensors originates. Precisely, the spectral values of z_{att} are needed due to remote sensing sensors working in separate wavebands.

RESULTS

In situ and laboratory measurements

The minimum and maximum values of the optical characteristics measured in Pärnu Bay in 2006 and 2007 are presented in Table 2. The spatial variations in optically active substances (except for total suspended matter, whose concentrations are connected with ship traffic, i.e. resuspensions of sediments form the bottom) measured in the transect from the Pärnu River mouth towards the open parts of Pärnu Bay are shown in Fig. 2. Some examples on the seasonal change in C_{ph}, C_s and $a_{CDOM}(380)$ for stations PB5 and PB11 in Pärnu Bay during 2007 are shown in Fig. 3. The spectral distributions of the attenuation depth at two stations, PB5 and PB12, are described in Fig. 4.

Our database showed both spatial and temporal variation in the water properties in Pärnu Bay. The Pärnu River brings large amounts of CDOM into the bay from the surrounding peat excavation areas, which makes the water close to river inflow brownish and usually less transparent than the water in deeper parts of Pärnu Bay. At the present study typical Secchi depth values near the coast (between stations PB1 and PB6) were below 1 m, while in the outer basin and in the Gulf of Riga z_{SD} was always higher than 1.4 m (Table 2). That spatial behaviour of the optical parameters $c^*(\mathrm{PAR})$ and $K_d(\mathrm{PAR})$ had an almost similar pattern – decrease from the northeastern part of the bay towards its southwestern part. The concentrations of C_{ph} generally ranged from 4 to 12 mg m^{-3}, however, during the vernal algal bloom in April 2007 the exceptional maximums (25.5–31.8 mg m^{-3}) were observed at stations PB6, PB7, PB11 and PB12 (Fig. 2A). The amount of suspended matter in the water was mostly between 8 and 14 g m^{-3}. Extremely high values of C_s (from 23.2 to 49.0 g m^{-3}) at stations PB5–PB7 were influenced by the loading of unpacked peat at the mouth of the river on 2 August 2007. However, the variations in the concentration of total suspended matter were also caused by ship traffic, i.e. resuspension of sediments form the bottom. As expected, there was also a very pronounced decrease in CDOM from the river mouth towards the offshore stations in Pärnu Bay and the Gulf of Riga. In April and May, when freshwater discharge by the Pärnu River was highest, the values of $a_{CDOM}(380)$ were between 4.6 and 31.8 m^{-1}, while in September $a_{CDOM}(380)$ varied only from 2.52 to 10.2 m^{-1} (Fig. 2B).

The seasonal behaviour of water parameters at different stations was to some extent even opposite (Fig. 3). The higher vernal $a_{CDOM}(380)$ values at station PB5 compared to those at offshore station PB11 resulted from intensive inflow from the Pärnu River to the bay. The chlorophyll *a* (including its metabolite phaeophytin *a*) concentration at both stations increased towards late summer, however, at station PB11 intensive algal bloom occurred also in April. During spring and summer the concentrations of the total suspended matter at station PB5 varied generally between 4.7 and 5.6 g m^{-3}, but by the beginning of September the value of C_s had risen up to 13.5 g m^{-3}. The slightly higher values of C_s (10.2 g m^{-3}) on 20 June 2007 were caused by yacht racing in the transect PB1–PB6. In the Pärnu Bay outer basin the concentrations of total suspended matter were somewhat higher – from 8.6 to 12.7 g m^{-3}.

In order to estimate the values and variability of the attenuation depth z_{att}, first the $K_d(\lambda)$ spectra were

Table 2. Minimum and maximum values of water characteristics measured in Pärnu Bay during the ice-free period in 2006–2007. The denotation *N* in the last row is the number of individual results of each water parameter

Station	z_{SD}, m	$c^*(\mathrm{PAR})$, m^{-1}	$K_d(\mathrm{PAR})$, M^{-1}	C_{ph}, mg m^{-3}	C_s, g m^{-3}	$a_{CDOM}(380)$, m^{-1}
PB1	0.6–1.6	3.0–6.5	1.4–2.3	5.7–12.4	3.9–10.9	7.8–31.8
PB2	0.6–1.2	3.2–6.5	1.6–2.3	6.7–17.6	3.8–14.1	7.5–31.8
PB5	0.5–1.5	3.1–6.5	1.1–2.0	6.6–15.1	3.7–26.7	5.5–31.4
PB6	0.4–1.5	3.3–4.6	0.8–1.8	5.2–31.8	9.9–49.0	2.9–14.1
PB7	0.8–1.7	1.7–5.6	0.8–1.9	2.6–30.4	8.7–23.2	2.2–11.4
PB8	1.5	1.5–3.7	0.8–1.0	2.8–6.6	9.4–11.2	2.2–5.0
PB9	1.7	2.8	0.78	2.7	8.9	4.2
PB10	2	1.8–2.0	0.83	2.1–6.7	9.4–9.8	2.4–4.0
PB11	1.3–3.1	1.0–2.5	0.5–1.6	1.5–25.5	8.0–14.7	2.3–5.8
PB12	1.5–3.5	0.8–2.1	0.6–1.2	5.6–28.2	7.8–13.4	2.3–3.9
PB14	2.3–4.3	0.8–1.4	–	3.2–12.0	7.4–17.5	2.1–2.6
N	58	60	33	67	67	65

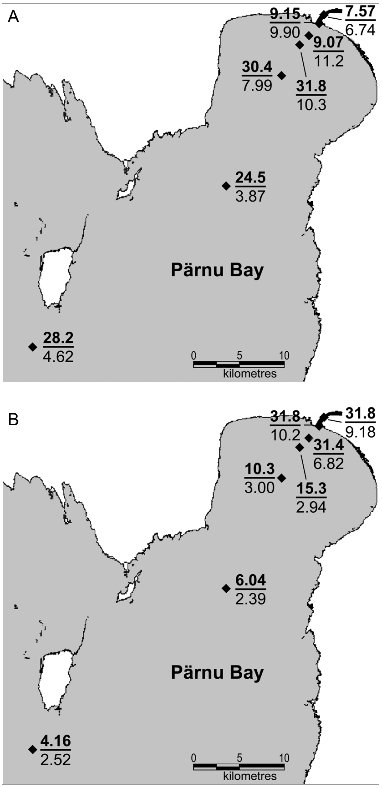

Fig. 2. Spatial variation in optical parameters in Pärnu Bay (upper numbers are the results obtained on 27 April 2007, the lower numbers those obtained on 5 September 2007): (A) for C_{ph}, (B) for $a_{CDOM}(380)$.

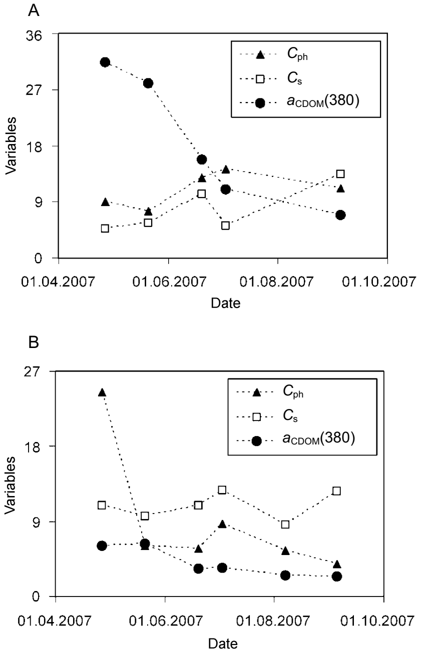

Fig. 3. Variation in chlorophyll *a* (including phaeophytin *a*), suspended matter and CDOM during 2007: (A) station PB5, (B) station PB11.

calculated from measured $c^*(\lambda)$ by using a semi-empirical model described in Arst et al. (2002). Subsequently, the corresponding attenuation depth spectra were determined by using the relationship $z_{att}(\lambda) = 1/K_d(\lambda)$. Our computation results for stations PB5 and PB12 (respectively, in the fluvial region and in the Gulf of Riga) are shown in Fig. 4. The data of $z_{att}(\lambda)$ permit us to draw some important conclusions about the possibilities of using optical remote sensing. We can see that at station PB12 remote sensing yields information from the surface layer down to 2.3 m, but at station PB5 only from the upper 0.34–0.8 m (Fig. 4). As the thickness of the informative layer varies also with wavelength, the colour indices and other water optical parameters of remote sensing spectra would be most effective if they were chosen at the wavelengths corresponding to maximum values of attenuation depth.

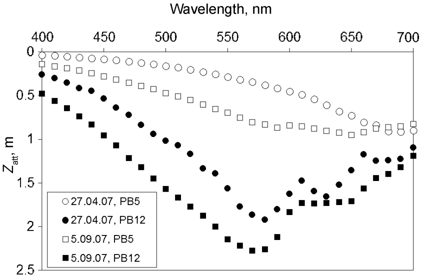

Fig. 4. Spectral variation in the attenuation depth in two stations (PB5 and PB12) in April and September 2007.

Table 3. Values of $K_d(490)$ (in m^{-1}) determined in the region of Pärnu Bay from in situ measurements in 2006–2007. The stations where the number of field trips was less than 6 were left out

Date	Station						
	PB1	PB2	PB5	PB6	PB7	PB11	PB12
31.05.2006	3.83	3.78	3.62	2.24	–	–	–
20.06.2006	–	3.24	1.91	1.90	1.60	0.77	–
31.07.2006	6.44	–	2.28	1.99	1.09	–	–
24.04.2007	7.11	7.32	7.20	3.55	2.46	1.53	1.06
21.05.2007	–	6.72	6.43	3.10	2.70	1.75	0.88
20.06.2007	4.22	4.17	3.63	2.15	2.53	0.93	0.79
3.07.2007	2.44	2.52	2.43	1.85	1.52	1.33	1.29
5.08.2007	2.16	2.42	2.78	–	1.13	0.92	0.70
5.09.2007	2.22	2.63	2.35	1.98	1.89	1.31	0.69

As is known, the MODIS standard algorithm for the diffuse attenuation coefficient of seawater at 490 nm ($K_d(490)$) is widely used for describing the spatial variation in the water properties. Table 3 shows the results of in situ measurements of $K_d(490)$ at most of the sampling stations.

Regression analysis

We used a linear regression program Microsoft Data Analysis. The determination of coefficients and significance of various combinations of parameters are presented in Table 4. It turned out that for $c^*(\mathrm{PAR})$ vs z_{SD} and $K_d(\mathrm{PAR})$ vs z_{SD} the best regression was nonlinear:

$$c^*(\mathrm{PAR}) = 3.72 z_{\mathrm{SD}}^{-1.02}, \quad (1)$$

where $R^2 = 0.793$ and $p < 0.0001$;

$$K_{\mathrm{d}}(\mathrm{PAR}) = 1.48 z_{\mathrm{SD}}^{-0.75}, \quad (2)$$

where $R^2 = 0.655$ and $p < 0.0001$.

According to the results, the main factor influencing the light attenuation in water was CDOM. It overshadows the relationships between the radiation characteristics and organic/inorganic particles. A surprisingly weak relationship between the concentrations of C_{ph} and C_s could probably be explained by a significant contribution of mineral particles in the total suspended matter. There were some additional negative regressions, all containing the suspended matter mentioned above (C_s vs a_{CDOM}, $c^*(\mathrm{PAR})$ vs C_s and $K_d(\mathrm{PAR})$ vs C_s). The reason for this is temporal and spatial irregularity of C_s, caused by loading unpacked peat at the mouth of the Pärnu River, undulation and ship traffic.

Due to the facts that ocean colour sensors SeaWiFS and MODIS provide $K_d(490)$ as standard Level 2 product (http://oceancolor.gsfc.nasa.gov/) and this parameter is also widely used for describing the water properties, we studied its regressions with $a_{CDOM}(380)$, C_{Chl} and C_s (all obtained from in situ measurements in 2006–2007). The numerical values of $K_d(490)$ were calculated from measurements of $c^*(490)$ by using a special model developed in Arst et al. (2002). The results of the regression analysis are presented in Tables 5 and 6. For recognition of the cases with negative correlation in these tables the values of R are presented (instead of R^2). Despite the small number of regression points, these results allow of some useful conclusions. It is clear that in Pärnu Bay the values of $K_d(490)$ are strongly influenced by CDOM that overshadows the actual relationship between $K_d(490)$ and C_{ph}. In some cases it has led even to negative correlation coefficients for $K_d(490)$ vs C_{ph} (Tables 5 and 6). These results support the opinion that (a) in CDOM-rich coastal waters the spatial distribution of $K_d(490)$ allows determination of the corresponding values of $a_{CDOM}(380)$ with high accuracy and (b) in these waters $K_d(490)$ is unsuitable for estimating C_{ph} and C_s. However, in case of remote sensing measurements we can derive $a_{CDOM}(380)$ from $K_d(490)$ only when the satellite values of $K_d(490)$ are reliable enough.

MODIS level 1 data with 250 m resolution were used for illustrative comparison of spatial and temporal variations in the water properties in Pärnu Bay and the Gulf of Riga (Fig. 5). According to these results, the water properties in Pärnu Bay are very variable and differ markedly from those in the open area of the Gulf of Riga. Obviously, optically significant substances vary in higher levels inside the bay and all relative concentrations are decreasing outside the Pärnu Bay area. An attempt to perform quantitative analysis with the purpose of estimating the concentrations of different optically active substances separately gave statistically incorrect results.

DISCUSSION

We compared our in situ measurement data with some others (different time periods, different sampling stations). In Arst et al. (1993, 1994) three field trips to the Pärnu Bay inner basin (8 sampling stations) were carried out in May, June and October in 1991. During summer months the values of C_{chl} were in the range of 3.9–12.9 mg m^{-3}. This means that generally the chlorophyll concentrations were in a good accordance with the present study, but due to the vernal algal bloom in April in 2007 our maximum values of C_{chl} were much higher. In the present study the concentration of suspended matter ranged from 3.7 to 49 g m^{-3} (all measurements), while on 6 June 1991 the values of C_{s} were between 11 and 38 g m^{-3}. This fact proves once more the temporal and spatial irregularity of suspended matter, which is influenced by undulation and ship traffic in the bay. Similarly to our investigation, the beam attenuation coefficient decreased from the river mouth towards the open parts of Pärnu Bay, but the absolute values of c^*_{PAR} were noticeably higher (at stations close to the coast even up to 20 m^{-1}). This implies increase in the water transparency from the year 1991 to 2007.

Another database for describing the bio-optical properties of Pärnu Bay on 5–6 June 2001 is also available (L. Sipelgas, pers. comm. 2002). The measurements were carried out at two depths (0 and 2 m) at 10 stations over the whole Pärnu Bay (from the mouth of the Pärnu River to the station with the coordinates 58°10′N and 24°17′E). The values of C_{chl}, C_{s}, c^*(PAR) and $a_{\mathrm{CDOM}}(380)$ varied, respectively, in the ranges 28–133 mg m^{-3}, 4.4–14.4 g m^{-3}, 2.7–9.4 m^{-1} and 5.3–20.5 m^{-1}. Extraordinarily high chlorophyll *a* concentrations, mainly at the stations in the inner basin of the bay, were obviously caused by strong phytoplankton bloom. Secchi depth varied between 0.75 and 2.5 m and K_{d}(PAR) from 0.8 to 2.1 m^{-1}. The results lead to a conclusion that during the past decades the optical properties of Pärnu Bay have been almost unchanged, however, the comparison is complicated due to a large variability of these properties in time and space.

For comparison of the results obtained in the river mouth areas in Pärnu Bay with those from the other water bodies we chose the Kymijoki and Porvoonjoki estuaries (both rivers discharge into the Gulf of Finland). However, we had a rather small database collected on 9 and 12 August 2005 as well as on 13–14 June 2006. In the Kymijoki the measurements were carried out in a transect, which starts with the coordinates 60°27′N and 26°28′E and ends at the station with coordinates 60°23′N and 26°33′E. In the Porvoonjoki the respective coordinates were 60°22′N and 25°40′E, and 60°20′N and 25°38′E. As expected, a pronounced decrease in CDOM from the river mouths towards the offshore stations was observed also in Finnish estuaries. In August 2005 the values of $a_{\mathrm{CDOM}}(380)$ were between 3.7 and 7.4 m^{-1} in the Porvoonjoki, while in the Kymijoki the $a_{\mathrm{CDOM}}(380)$ varied only from 5.2 to 6.4 m^{-1}. In June 2006 the absorptions by CDOM in both estuaries were in the range 5.9–11.3 m^{-1}. According to these values, Finnish estuaries, are to some extent different from Pärnu Bay. They are less ‘yellow’ (the maximum of $a_{\mathrm{CDOM}}(380)$ differs about 2.5 times). However, sometimes similar values of $a_{\mathrm{CDOM}}(380)$ were observed: in June 2006 Pärnu Bay gave $a_{\mathrm{CDOM}}(380)$ between 2.4 and 12.6 m^{-1}, in June 2005 in the Porvoonjoki estuary this variation was 5.9–11.3 m^{-1}. Except for the phytoplankton blooms, the chlorophyll concentration in Pärnu Bay was generally below 12 mg m^{-3}. At the stations of the estuary of the Porvoonjoki it was considerably higher (in June 2006 from 8.7 to 30.4 mg m^{-3} and in August 16.2–19.9 mg m^{-3}). In the Kymijoki estuary the values of C_{ph} varied between 10.2 and 14.2 mg m^{-3}. The amount of suspended matter in the water was almost similar in all three regions – in Pärnu Bay the values of C_{s} were mostly between 8 and 14 g m^{-3} and in Finnish estuaries they ranged from 8.1 to 17.5 g m^{-3}.

The ENVISAT satellite, which carries the medium resolution imaging spectrometer (MERIS) sensor, was launched on 1 March 2002. The MERIS sensor characteristics have been developed according to optically complex water properties, making it the first sensor for monitoring the multicomponental waters. MERIS (like other earth observation satellite sensors) has high measurement frequencies, passing over the regions of interest each day and greatly increasing the chances of obtaining useful cloud-free images. The full resolution (~300 m) data provide the high spatial resolution available from a satellite sensor, whereas new developments for optically complex (Case-2 Regional, Boreal Lakes, Eutrophic Lakes) processors are still going on. The new processors have additional products such as downwelling irradiance attenuation coefficient, absorption coefficients of phytoplankton, CDOM, and a coefficient of all particles after bleaching and scattering (Doerffer & Schiller 2008). To illustrate spatial variation in water properties, MERIS image from 6 July 2002, which is a good example for characterizing the situation in Pärnu Bay, is presented in Fig. 6. Using MERIS standard products, we can observe very complex spatial distribution of the water properties, which could not be visualized by in situ measurements. Clearly visible is a highly turbid water area (Fig. 6 top left) flowing out of the bay. This feature is notable on the suspended matter and CDOM products, but not on the algal_2 product. The high amount of CDOM in Pärnu Bay overshadows the signal of chlorophyll *a*, which leads to invalid reflectances used for calculating chlorophyll *a* product algal_2. As different times of measurements and different parameters were used, the quantitative comparison of Figs 5 and 6 is impossible. However, in both figures the multi-coloured Pärnu Bay region, different from that in the open part of the Gulf of Riga, is clearly seen.

Kutser et al. (2009) analysed the results of remote sensing investigations by a satellite sensor Advanced Land Imager (ALI) in the eastern part of the Baltic Sea.

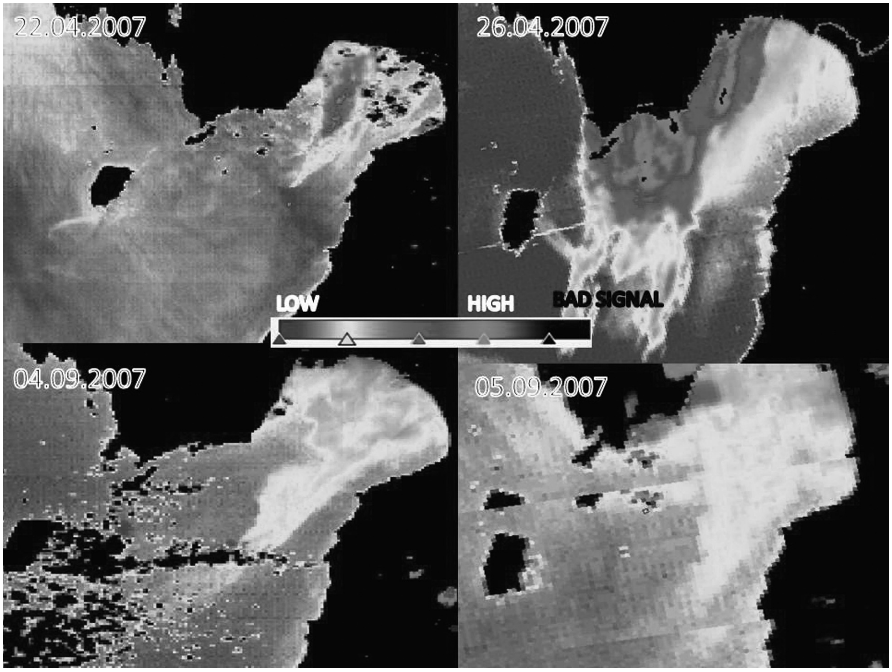

Fig. 5. MODIS Aqua 250 m resolution images over Pärnu Bay showing the spatial variation in the mixture of the three optically significant substances (CDOM, phytoplankton and suspended matter). Bad signal is defined as quality mask over land and clouds.

Table 4. Determination coefficients (R^2) and significance (p) of the linear regressions obtained for several bio-optical parameters of Pärnu Bay

Regression	R^2	p	Comments
C_{ph} vs C_s	0.077	0.028	
C_{ph} vs a_{CDOM}	0.022	0.247	
C_s vs a_{CDOM}	0.268	<0.0001	Negative
c^*(PAR) vs C_{ph}	0.035	0.143	
c^*(PAR) vs C_s	0.029	0.188	Negative
c^*(PAR) vs a_{CDOM}	0.662	<0.0001	
K_d(PAR) vs C_{ph}	0.110	0.084	
K_d(PAR) vs C_s	0.029	0.386	Negative
K_d(PAR) vs a_{CDOM}	0.568	<0.0001	
c^*(PAR) vs K_d(PAR)	0.745	<0.0001	

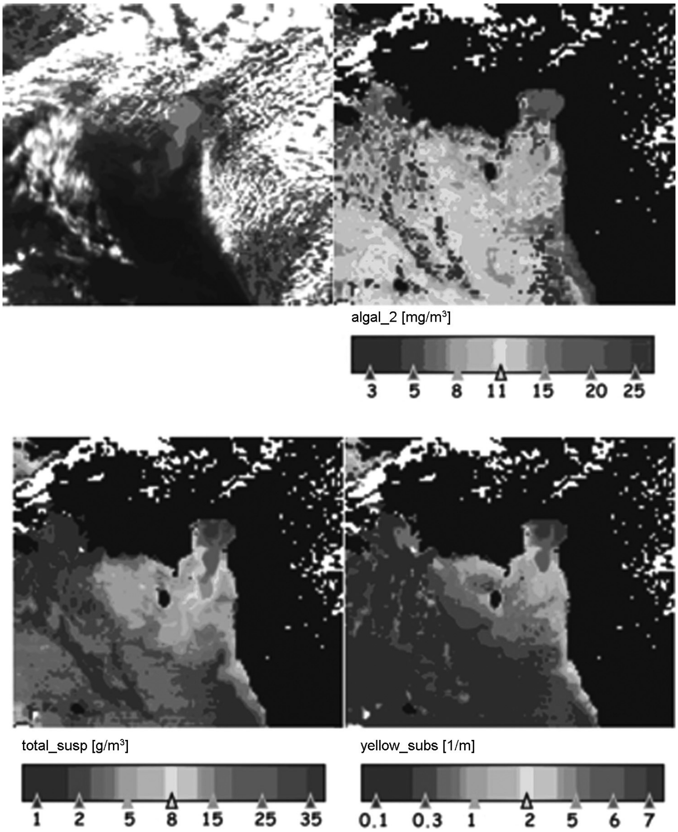

Fig. 6. MERIS L1 image (top left) and three water products for chlorophyll *a* in multicomponential waters (algal_2), suspended matter (total_susp) and CDOM (yellow_subs) on 6 July 2002 in Pärnu Bay.

Table 5. Correlation characteristics ($K_d(490)$ vs different optically significant substances) obtained at sampling stations PB5, PB7 and PB11 in 2006–2007. The station PB5 is located close to the shore (near the pier), PB7 in the central part of Pärnu Bay and PB11 in the western part of the bay, close to the Gulf of Riga

Regression	PB5, $N = 9$		PB7, $N = 8$		PB11, $N = 7$	
	R	p	R	p	R	p
$K_d(490)$ vs $a_{CDOM}(380)$	0.971	<0.0001	0.792	0.019	0.799	0.031
$K_d(490)$ vs C_{Chl}	–0.176	0.650	0.618	0.102	0.486	0.268
$K_d(490)$ vs C_s	–0.491	0.180	0.683	0.062	0.244	0.597

Table 6. Correlation characteristics ($K_d(490)$ vs different optically significant substances) obtained on 27 April 2007 and 5 September 2007 in Pärnu Bay (all stations together)

Regression	27.04.2007		05.09.2007	
	R	p	R	p
$K_d(490)$ vs $a_{CDOM}(380)$	0.999	<0.0001	0.794	0.01
$K_d(490)$ vs C_{Chl}	–0.897	0.006	0.741	0.022
$K_d(490)$ vs C_s	–0.874	0.01	0.366	0.419

The conclusion was that optical properties of the Baltic Sea are dominated by CDOM. Strong absorption of light by CDOM at shorter wavelengths is probably the main reason why standard chlorophyll *a* retrieval algorithms fail in the Baltic Sea. Thus, according to this study, CDOM dominates not only in Pärnu Bay, but also in many coastal regions of the Baltic.

CONCLUSIONS

During the ice-free period in 2006–2007 Pärnu Bay was characterized by marked spatial and seasonal variation in the water properties. A very pronounced decrease in CDOM occurred from the river mouth towards the offshore stations in Pärnu Bay and the Gulf of Riga. In April and May, when freshwater discharge of the Pärnu River was highest, the $a_{\mathrm{CDOM}}(380)$ values were between 4.6 and 31.8 m^{-1}, whilst in September $a_{\mathrm{CDOM}}(380)$ varied only from 2.52 to 10.2 m^{-1}. Phytoplankton contributed to light attenuation of seawater primarily during algal bloom periods, when C_{ph} increased rapidly from its general values of 4–12 mg m^{-3} to its vernal peak of 25.5–31.8 mg m^{-3}. The temporal and spatial irregularity of C_{s} was caused by the loading of unpacked peat at the mouth of the Pärnu River as well as by undulation and ship traffic in the bay.

The results of correlation analysis (data obtained in situ) showed that the main factor influencing light attenuation in the water is CDOM. It overshadows the relationships between the radiative characteristics and organic/inorganic particles. In some cases it has led even to negative correlation coefficients for $K_{\mathrm{d}}(490)$ vs C_{ph}.

Due to the variability of the water properties, Pärnu Bay seems to be an interesting subject of investigations by optical remote sensing. However, in summer the spectral values of the attenuation depth in the inner basin of the bay were mostly below 1 m (especially in the blue–green region of the spectrum) and only in autumn the values $z_{\mathrm{att}}(\lambda) > 1.5$ m were observed. Also the values of $K_{\mathrm{d}}(490)$ that are often used in satellite results analysis are strongly influenced by CDOM, which overshadows the actual relationship between $K_{\mathrm{d}}(490)$ and C_{ph}.

The main conclusions concerning the interpretation of the satellite data in CDOM-rich coastal waters are: (a) the spatial distribution of $K_{\mathrm{d}}(490)$ allows determination of the corresponding values of $a_{\mathrm{CDOM}}(380)$ with a high accuracy; (b) in these waters $K_{\mathrm{d}}(490)$ is unsuitable for estimating C_{Chl} and C_{s}. However, in case of remote sensing measurements we can derive $a_{\mathrm{CDOM}}(380)$ from $K_{\mathrm{d}}(490)$ only when the satellite values of $K_{\mathrm{d}}(490)$ are reliable enough. Thus, the remote sensing investigation of Pärnu Bay is still problematic and new algorithms are necessary.

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Optilised mõõtmised lahustunud orgaanilise aine rikastes Pärnu lahe rannikuvetes

Birgot Paavel, Helgi Arst, Liisa Metsamaa, Kaire Toming ja Anu Reinart

Veekogu omaduste ajalis-ruumilise muutlikkuse uurimise objektiks oli Pärnu laht, mis on optiliselt keerukas, vähese veeläbipaistvusega ja osaliselt suletud rannikuala Läänemere idaosas. Pärnu lahte mõjutab nii Pärnu linnaelanike tekitatav antropogeenne koormus kui ka tugev vee sissevool Pärnu jõest. Aastate 2006–2007 jäävabal perioodil koguti *in situ* mõõtmiste teel arvestatava suurusega andmebaas Pärnu lahe optiliste omaduste kohta (11 mõõtejaama, 10 seeriat välitöid). Saadud tulemused näitavad vee parameetrite olulist ajalis-ruumilist muutlikkust. Veealuse valgusvälja formeerumisel oli suurim tähtsus värvilisel lahustunud orgaanilisel ainel (VLOA), mis varjutas kiirguskarakteristikute seoseid vees sisalduva fütoplanktoni ja heljumiga. Selgesti joonistus välja VLOA kontsentratsiooni vähenemine alates Pärnu jõe suudmealast suunaga Liivi lahele. Aprillis-mais ületasid VLOA neeldumiskoefitsiendi ($a_{\mathrm{VLOA}}(380)$) väärtused jõesuudme läheduses 30 m^{-1}, septembris olid need väärtused vahemikus 2,52–10,2 m^{-1}. Harilikult oli fütoplanktoni kontsentratsioon vahemikus 4–12 mg m^{-3}, kuid veeõitsengute perioodil olid need väärtused mõnes mõõtmisjaamas kuni 31 mg m^{-3}. Vees sisalduva heljumi puhul esines selle kontsentratsioonide märgatav ruumiline ja ajaline irregulaarsus, mille põhjustas osaliselt turba laadimine alustele ning elav laevaliiklus Pärnu lahes. Pärnu lahe ja sellega külgneva Liivi lahe omaduste illustreerimiseks kasutati satelliitandmeid (MODIS level 1 lahutusvõimega 250 m).

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PRIMARY RESEARCH PAPER

Reconstructed long-term time series of phytoplankton primary production of a large shallow temperate lake: the basis to assess the carbon balance and its climate sensitivity

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Abstract Aiming at building the carbon budget for further climate change impact research in the large and shallow northern temperate Lake Võrtsjärv, the present paper focuses on reconstructing the full phytoplankton primary production (PP) data series for the lake for the period of 1982–2009 covered by disconnected measurements, and testing the uncertainties involved both in the PP measurements and bio-optical modelling. During this 28-year period, in situ PP was measured in Võrtsjärv in 18 years with ^{14}C-assimilation technique. We reconstructed the full time series using a semi-empirical PP simulation model based on continuously measured PAR irradiance and interpolated values of monthly measured chlorophyll *a* (C_{chl}). The modelling results, which proved highly reliable during the calibration phase, correlated rather weakly with the annual PP estimates for the 18 years, which were based on 2-h incubations at midday, 1–2 times per month. Being based on continuous irradiance data, the modelled PP can be considered more reliable than the sparse measurements, especially for short to medium term studies. We demonstrate that in the long-term, the bio-optical method can be biased if changes in water colour or

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water level alter the light climate causing adaptive responses in the cellular chlorophyll content of light-limited phytoplankton.

Keywords Phytoplankton · Primary production · Võrtsjärv · Shallow eutrophic lake · Modelling · Light limitation

Introduction

Phytoplankton primary production (PP) represents the major synthesis of organic matter in aquatic systems giving start to the food chains and forming the basis of the ecological pyramid. The amount of primarily synthesised organic matter indicates the trophic state of a waterbody, while the efficiency of its subsequent transformation in food chains results in a higher or lower fish production, and in a poorer or better water quality. Lakes are sites of intensive carbon processing, although often disregarded in models of the global carbon cycle due to their small percentage of the Earth's surface area (Sobek et al., 2006). Several recent studies have demonstrated that lakes are significant sources of carbon dioxide and methane to the atmosphere (Huttunen et al., 2003; Jonsson et al., 2003; Cole et al., 2007), and that they simultaneously bury more organic carbon in their sediments than the entire ocean (Downing et al., 2008). Hence, lakes turn out to be disproportionately important sites of carbon cycling relative to their small areal extent. Lakes and reservoirs act as sentinels by providing signals that reflect the influence of climate change in their much broader catchments (Williamson et al., 2008, 2009). In the context of global warming caused by the increase of greenhouse gases, it is important to know the role of each ecosystem type in the global carbon budget. It has been increasingly acknowledged that in many lakes, first of all in those located in cool-climate forested boreal regions, the heterotrophic processes are dominating over autotrophic ones turning the lakes into CO_2 sources (Algesten et al., 2003; Sobek et al., 2003). To study the carbon metabolism of a lake, the first and the basic step would be the estimation of the amount of carbon fixed by the ecosystem. The importance of PP studies is impressively reflected in publication statistics of ISI Web of Science (ISI WoS), which showed that lake primary production has been analysed in ca. 1400 publications since 1990 with an increasing average yearly rate from ca. 60 until year 2000 to ca. 80 afterwards. The annual citation rate of these papers has exponentially increased from about 100 in 1992 to nearly 3000 in 2009, resulting on average 17 citations per item. However, to understand climate sensitivity of the carbon metabolism, long-term changes of primary production need to be known. As stated already by Jassby et al. (1990), interannual changes of primary production remain one of the least investigated areas in limnology and this situation has not much improved during the last 20 years. The query on 'long term lake primary production' resulted in only in 126 publications in ISI WoS database since 1990. The average citation rate of one publication was 26 showing the high importance of the studies on this field.

The present paper is the first step of the large-scale assessment of the carbon metabolism of Lake Võrtsjärv, a large and very shallow lake, the largest one remaining fully within the borders of Estonia. Its catchment area makes up 7% of Estonian territory and, thus, contributes significantly to Estonian natural CO_2 budget. Our aim was to summarise the long-term primary production measurements in Võrtsjärv in order to receive reliable daily, monthly and annual estimates of this parameter as the starting point in the lake's carbon balance calculations. The results will provide further basis for long-term studies of the ecosystem metabolism and its climate sensitivity.

Study site and dominant primary producers

Lake Võrtsjärv (58°16′N 26°02′E) is located in Central Estonia. With a surface area of 270 km^2 and a catchment area of 3374 km^2 (including the lake), it is the country's second largest lake. Võrtsjärv is shallow and polymictic with a maximum depth of 6 m and a mean depth of 2.8 m. The lake is eutrophic (OECD, 1982) characterised by the following annual mean concentrations: TP 54 $\mu g\ l^{-1}$, total nitrogen (TN) 1.6 $mg\ l^{-1}$, C_{chl} 24 $\mu g\ l^{-1}$ and has an average Secchi depth of 1.1 m (Tuvikene et al., 2004; Nõges et al., 2007). The water retention time is about 1 year and lake is ice-covered for more than 4 months (average 135 days) of the year. The unregulated water level has an annual mean amplitude of 1.4 m, the absolute range of 3.1 m, and exhibits a long-term periodicity with a period length of 20–30 years. The minimum and maximum water levels correspond to a 1.4-fold difference in the lake area, a 2.3-fold difference in the mean depth and a 3.2-fold difference in the water volume (Nõges et al., 2003).

Within the 50 km^2 (19% of the lake area at mean water level) covered by aquatic macrophytes 35 km^2 is accounted for by submerged, 12 km^2 by emergent and 3 km^2 by floating-leaved macrophytes (Feldmann & Mäemets, 2004). The earlier dominance of *Potamogeton perfoliatus* L. among submerged macrophyte is by now overtaken by *Myriophyllum spicatum* L.

Cyanobacteria compose the bulk (up to 95%) of the phytoplankton biomass during the ice-free period from May to October. The beginning of our study period coincided with a break through of two new dominants, *Limnothrix redekei* (van Goor) Meffert and *L. planktonica* (Wolosz.) Meffert. Both species are slow growing and highly shade tolerant that gives them an advantage in turbid waters. Seasonally *L. redekei* starts its growth earlier and reaches the biomass maximum in June while *L. planctonica* has its maximum usually in September–October. *L. redekei* reached its maximum in the years 1988–1990 forming on average more than 60% of filamentous cyanobacteria. By now, its share has decreased to an average of 20%. *L. planktonica*, which started to increase also in 1980s, became the main phytoplankton dominant since 1995 often building up more than 80% of the total biomass.

The lake underwent a rapid eutrophication during 1970s and 1980s. Since that, despite a considerable decrease in external nutrient loadings, the internal loading modulated by the long-term cyclic water levels has still prevented any significant decline in nutrient concentrations of the lake (Nõges & Kisand, 1999; Nõges et al., 2007, 2010c).

Materials and methods

PP measurements

Phytoplankton primary production (PP) in Võrtsjärv has been measured in situ with ^{14}C-assimilation technique (Steeman-Nielsen, 1952) in 1982–1984, 1989, 1991, 1993–1998, 2000, 2003–2009. PP has been measured mainly during ice-free periods from April to October with weekly to monthly intervals. In 1983, 1984, 1991 and 1995, PP was measured also in winter under the ice. The applied methodology and the detailed results have been published in a number of earlier papers (Nõges & Nõges, 1998; Nõges et al., 1998, 1999; Nõges, 1999b; Kisand et al., 2001; Kisand & Nõges, 2004; Agasild et al., 2007; Zingel et al., 2007). In situ PP (mg C m^{-3} h^{-1}) was measured at six different depths in the lake in two parallels. After incubation, the water was acidified to pH <2 with 0.5 N HCl to remove the remaining inorganic ^{14}C (Niemi et al., 1983; Hilmer & Bate, 1989; Lignell, 1992), after which the radioactivity of the sample was measured with a scintillation counter (LSC RackBeta 1211, Wallac, Finland) using external standardisation for decays per minute (DPM) calculations and Optiphase 'HiSafe 3' scintillation cocktail (Wallac, Finland). PP was calculated according to the standard formula (Nielsen & Bresta, 1984). Non-photosynthetic carbon fixation was measured in dark vials and subtracted from the light assimilation. Integral PP values (PPint) were calculated by integrating measured PP values over depth. We used 2-h incubations around midday, which measure rather the gross production (Vollenweider & Nauwerck, 1961). The daily gross PP (PP_{day}) was calculated using an equation relating day-long series of short incubations to hourly PP at midday (PP_{hour}), and the day length (DL) found for Lake Võrtsjärv (Nõges & Nõges, 1998):

$$PP_{day} = PP_{hour} / \left(0.230 - 890 \times 10^{-5} \times DL\right); \quad R^2 = 0.66,\ P < 0.01. \tag{1}$$

We used two options to calculate annual PP values from the measurements. For years when PP was measured monthly or more frequently from April to October (1983, 1989, 1991, 1994, 1995–1997, 2000, 2004), we integrated the measured daily PP values over the time to achieve the yearly values. If not measured, the under-ice PP was assumed to be zero. For years when PP was measured only from May to August, we calculated yearly PP values from the average daily PP in May–August, which formed on average 0.55% of the yearly PP as calculated from the more complete data (Table 1).

Chlorophyll *a* and phytoplankton biomass

Phytoplankton abundance was measured as chlorophyll *a* concentration (C_{chl}, mg m^{-3}), and phytoplankton biomass on each occasion of PP

Table 1 Average daily, monthly and annual depth-integrated primary production of phytoplankton (PP_{int}) in Võrtsjärv measured and modelled in 1982–2009

Month	Daily PP_{int} (mg C m^{-2} day^{-1})						Monthly PP_{int} (g C m^{-2} $month^{-1}$)			
	Measured			Modelled			Measured		Modelled	
	AVG	*n*	SD	AVG	*n*	SD	AVG	% of annual	AVG	% of annual
January	24	9	16	3	28	14	0.7	0.4	0.1	0.0
February	40	8	35	0	28	0	1.1	0.5	0.0	0.0
March	183	12	169	14	28	52	5.7	2.8	0.4	0.2
April	516	28	395	352	28	276	15.5	7.6	10.6	5.3
May	1021	46	560	1077	28	250	31.7	15.5	33.4	16.6
June	1299	47	784	1299	28	378	39.0	19.1	39.0	19.4
July	1174	44	648	1235	28	274	36.4	17.8	38.3	19.1
August	1009	47	493	1088	28	173	31.3	15.3	33.7	16.8
September	557	40	316	852	28	267	16.7	8.2	25.6	12.7
October	359	35	247	492	28	115	11.1	5.4	15.2	7.6
November	482	20	889	130	28	90	14.4	7.1	3.9	1.9
December	28	10	21	13	28	25	0.9	0.4	0.4	0.2
Annual mean	558			546[a]			17		17	
Apr.–Nov. mean	848			816			25		25	
May–Aug. mean	1126			1175			35		36	
Annual PP_{int}, g C m^{-2} $year^{-1}$							205		200[a]	

In the modelling approach, the under-ice PP_{int} was assumed to be zero. The measured PP_{int} from December to March when the lake is generally frozen, constituted about 4% of the annual PP_{int}. As the mean values are based on different numbers of measurements (*n*) over the years, the table does not seek a strict comparison between the months, but is rather a condensed way of presenting the data

[a] Correction for under-ice production not applied

measurements. For C_{chl} analysis, plankton was collected on Whatman glass fibre filters (GF/F), pigments were extracted with 90% acetone (in 1982–2000) or 96% ethanol (since 2001), analysed spectrophotometrically, and calculated according to Lorenzen (1967). No statistically significant differences between the acetone and ethanol extractions were found for Võrtsjärv (Nõges & Solovjova, 2000).

Phytoplankton biomass (B, g m^{-3}) and the taxonomic composition were determined by microscopic counting and measuring the algae. Details of the methods are given in Nõges et al. (2010a).

PP modelling

In parallel with in situ measurements, long-term PP was estimated using an integral version of the semi-empirical model elaborated by Arst et al. (2008). The model used as input variables chlorophyll concentration, C_{chl}, the incoming irradiance, and the diffuse attenuation coefficient. We calculated C_{chl} values for each day by linearly interpolating the measured values. The irradiance and the diffuse attenuation coefficient were integrated over PAR region, correspondingly, q_{PAR}(inc), and $K_{d,PAR}$. As no spectral irradiance data was available for the whole period, we could not use the slightly better performing (Arst et al., 2008) spectral version of this model.

Incident global radiation, Q, was measured by the Estonian Institute of Hydrology and Meteorology (EMHI) at Tõravere (58°15′55N, 26°27′58″E), ca. 30 km from the eastern shore of Võrtsjärv. Before the year 2000, the values of Q were derived from direct and diffuse solar radiation, measured, correspondingly, with Janishevsky actionometer AT-50, and Janishevsky pyranometer model M-115M (Kondratyev, 1965). We calculated the incident photosynthetically active radiation, q_{PAR}(inc), as $0.436 * Q$. Since the year 2000, q_{PAR}(inc) was measured directly with the irradiance quantum sensor Li-COR 190SA (Li-COR Biosciences).

Since, there were only few in situ measurements of $K_{\mathrm{d,PAR}}$ available for Võrtsjärv, we calculated its values from spectral beam attenuation coefficients, $K_{\mathrm{d}}(\lambda)$, measured from water samples using the model of Arst et al. (2002). Monthly depth-integrated samples were collected in 2002–2007 from one sampling point in Võrtsjärv, stored in plastic bottles in the dark at 4°C without any treatment until analyses (for maximum 12 h).

We extended $K_{\mathrm{d,PAR}}$ data series for the whole study period (1982–2009) using the regression with monitored chlorophyll *a* concentration (Eq. 2):

$$K_{\mathrm{d,PAR}} = 0.03C_{\mathrm{chl}} + 1.07 \quad \left(R^2 = 0.73,\ P < 0.001\right) \tag{2}$$

The PP computing system based on the integral model (Arst et al., 2008) gives the values of $\mathrm{PP}_{\mathrm{int}}$ in mg C m^{-2} h^{-1}, and calculates the daily values by summing up the hourly values. However, our database contained mostly the daily sums of incident irradiance, which we could not use directly in our computing system. Dividing the daily sum of q_{PAR}(inc) by the day length (DL) we found the average hourly q_{PAR}(inc, av) for each day, which enabled us to calculate the corresponding average hourly $\mathrm{PP}_{\mathrm{int}}$ for each day. Multiplying this by DL gave us the daily sum of $\mathrm{PP}_{\mathrm{int}}$.

We compared the two calculation options for daily $\mathrm{PP}_{\mathrm{int}}$ values during a special study in Võrtsjärv in 2009. From May to August, we recorded the incident global irradiance (Q) using Yanishevsky pyranometer (Kondratyev, 1965) placed on the roof of a building close to the coastal station in Võrtsjärv. We took q_{PAR}(inc) equal to 0.436 * Q(inc). The q_{PAR}(inc) readings taken each 2 min allowed to compute the hourly averages. There were 12 in situ measurements of C_{chl} and $K_{\mathrm{d,PAR}}$ within this period (more frequently than usually) that improved the reliability of the interpolated values. Using these data we calculated hourly PP profiles and $\mathrm{PP}_{\mathrm{int}}$ values. By summing up these values we calculated the daily values referred further as $\mathrm{PP}_{\mathrm{int}}$(model). For long-term PP modelling, we could use only the average daily q_{PAR}(inc) values from EMHI, and the corresponding $\mathrm{PP}_{\mathrm{int}}$ values are referred further as $\mathrm{PP}_{\mathrm{int}}$(appr). We used the regression formulae relating these two series during this 4-month study to make corrections in all $\mathrm{PP}_{\mathrm{int}}$ values calculated on the basis of daily sums of incident irradiance.

Mean water column irradiance based on Secchi depth and water level

As we suspected that part of the C_{chl} changes in the long-term data might have occurred as an adaptive response of phytoplankton to a variable strength of light limitation due to changing water colour and/or depth (i.e. not directly related to PP dynamics as supposed by the model), we calculated another $K_{\mathrm{d,PAR}}$ value from its regression with the Secchi depth (S)

$$K_{\mathrm{d,PAR}} = 1.698\ \mathrm{S}^{-0.767} \quad \left(R^2 = 0.56,\ P < 0.001\right) \tag{3}$$

and applied that in the Lambert–Beer's law

$$I_z = I_0 \cdot \mathrm{e}^{(-K_{\mathrm{d,PAR}} \cdot Z)} \tag{4}$$

where I_z is the fraction of incident light at the surface (I_0) reaching the depth Z. Taking I_0 equal to 100% and the mean depth of the lake for Z (a variable depending on the largely fluctuating water level), we calculated the average irradiance in the mixed water column (I_{mix}; %) according to Riley (1957)

$$I_{\mathrm{mix}} = \frac{I_0 \cdot (1 - \mathrm{e}^{-K_{\mathrm{d,PAR}} \cdot Z})}{K_{\mathrm{d,PAR}} \cdot Z} \tag{5}$$

assuming that in Võrtsjärv the mixing depth increases simultaneously with the mean depth of the lake.

Results

Measured primary production

According to the 18-year measurements, the mean daily integrated PP was 558 mg C m^{-2} day^{-1} with monthly means changing from about 25 mg C m^{-2} day^{-1} in December and January to nearly 1300 mg C m^{-2} day^{-1} in June (Table 1). The scatter of single daily measurements in each month was rather large characterised by standard deviations (SD) making up from 49 to 184% of the monthly mean values. The daily PP was relatively most variable in November and March due to the onset and ending of the ice season. The maximum chlorophyll specific production rate at light saturation varied from 0.1 to 14.7 mg C mg C_{chl}^{-1} h^{-1} being on average 2.06 ± 1.72 mg C mg C_{chl}^{-1} h^{-1}.

The mean daily PP from May to August formed on average 0.55% of the annual PP. We used this ratio to

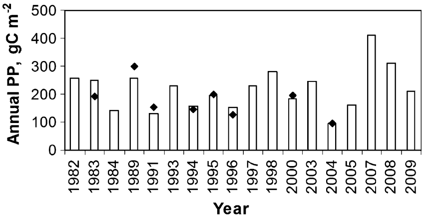


Fig. 1 Annual phytoplankton primary production estimates calculated as the integral over the ice-free period (*dots*), and from the average daily PP values in May–August assuming its correspondence to 0.551% of the yearly PP (*columns*)

calculate the annual PP for years with incomplete data coverage. For the years to which both methods were applied, the integrated values corresponded well to the calculated values (Fig. 1).

PP had a pronounced seasonality in Võrtsjärv, with two-third of the annual PP produced during one-third of the year from May to August. The monthly PP in June (39 g C m^{-2} $month^{-1}$) exceeded the average monthly PP (17 g C m^{-2} $month^{-1}$) by a factor more than two. The measured annual average pelagic PP in Võrtsjärv was 205 g C m^{-2}. In the long-term, the measured PP had no significant trend either over single months or in the annually integrated values.

Modelled primary production

Modelled versus measured primary production profiles

The vertical profiles of measured and modelled PP corresponded generally well with each other (Fig. 2). Also the modelled integral PP (PP_{int}, mg C m^{-2} h^{-1}) values that were computed by integrating vertical PP profiles over depth, were in good concordance with the measured PP_{int} values. For example, the profiles represented in Fig. 2, gave measured PP_{int} values of 102 and 211 mg C m^{-2} h^{-1}, and modelled PP_{int} values of 113 and 223 mg C m^{-2} h^{-1}, respectively.

Comparison of the two calculation options for daily PP_{int}

The relationship between the two integral primary production estimates computed from hourly irradiances over the day (PP_{int}(mod)) and the daily sums of irradiance (PP_{int}(appr)) was strong with a determination coefficient R^2 higher than 0.94 (Fig. 3). The regression formulae were slightly different for the two chlorophyll ranges, $C_{chl} < 35$ mg m^{-3} and $C_{chl} \geq 35$ mg m^{-3}, for which different algorithms were used in the model (Arst et al., 2008). We corrected all results of PP_{int} according to these formulae.

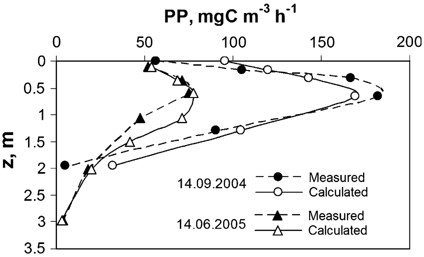


Fig. 2 Comparison of measured and modelled PP profiles in Võrtsjärv on 14.09.2004 and 14.06.2005 characterised by the respective C_{chl} values of 70 and 40 mg m^{-3}, q_{PAR}(inc) values of 1300 and 1003 μmol m^{-2} s^{-1}, and $K_{d,PAR}$ values of 2.5 and 2.2 m^{-1}

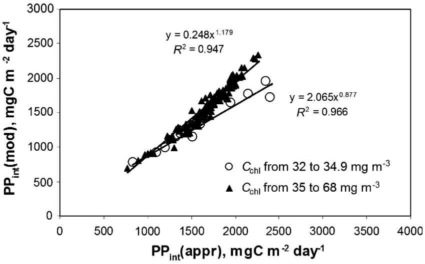


Fig. 3 Regression between the two integral primary production estimates for Võrtsjärv computed using hourly irradiances over the day (PP_{int}(mod)) and daily sums of irradiance (PP_{int}(appr)) for the days from May to August 2009 when C_{chl} was measured. Due to different algorithms in the model for $C_{chl} < 35$ mg m^{-3} and for $C_{chl} > 35$ mg m^{-3} (Arst et al., 2008), separate correction formulae were derived for these ranges

Modelled versus measured primary production time series

We calculated PP_{int}(mod) in total for 6011 ice-free days in the 28-year period from 1982 to 2009. The

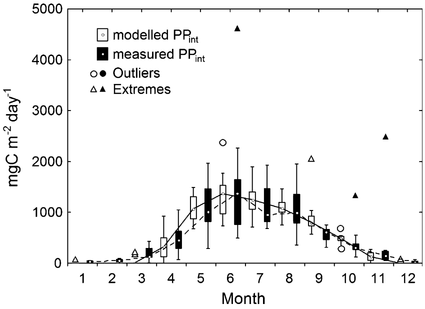


Fig. 4 Variation of measured (*black*) and modelled (*white*) daily primary production in Võrtsjärv in different months over the period 1982–2009. *Boxes* represent the median and quartiles, whiskers show the non-outlier range

median values of modelled and measured daily PP_{int} values were quite close in different months but the variation of the modelled values was smaller than that of the measured values (Fig. 4; Table 1).

The average annual pelagic PP_{int}(mod) in 1982–2009 was 200 g C m^{-2} $year^{-1}$ (Table 1). Considering approximately 4% underestimation of annual PP_{int} due to ignoring the under-ice production, the modelled average annual PP_{int} in Võrtsjärv would be 208 (min. 144, max. 306) g C m^{-2} $year^{-1}$, which is very close to the average of the measured values (205 g C m^{-2} $year^{-1}$). The yearly average volumetric PP (the ratio of the annual areal PP_{int}(mod) to the mean depth of the lake) was 80 (min. 48, max. 148) g C m^{-3} $year^{-1}$ (Table 2).

For the 18 years when PP_{int} was both measured and modelled, the results were significantly correlated ($R^2 = 0.32$, $P = 0.015$) (Fig. 5), the modelled daily PP_{int}, however, exhibited significant linear increasing trends in all ice-free months over the whole study period (Fig. 6) while no trend was detected in the measured PP values. A trial to detrend the modelled PP_{int} values did not improve the relationship with measured values and was given up.

The increase in modelled PP_{int} was caused by the strong significant trends in C_{chl}, one of the important input parameters, occurring from May to December over the whole study period (Fig. 7). The slope of the long-term chlorophyll trendline increased towards autumn and reached its maximum in September–October indicating the season in which the biggest changes in C_{chl} took place.

The mean light intensity within the water column (I_{mix}) calculated from Secchi depth and water level, showed a bell-shape change over the years (Fig. 8A) with average light conditions for phytoplankton improving over 1980s and deteriorating again since the first half of 1990s. The percentage of chlorophyll in the total phytoplankton biomass (Chl% *B*) had opposite dynamics with an increasing trend since the beginning of 1990s (Fig. 8B).

Total carbon fixation in the lake

For the assessment of total PP of the lake and its long-term changes, we further used the modelled PP values. Multiplying the annual areal phytoplankton PP by the average lake area in each year, we got an estimate of 56 559 (min. 41 013, max. 77 064) tonnes of carbon fixed annually by phytoplankton primary production in Võrtsjärv. Considering the estimations that phytoplankton contributes 79% and macrophytes with their epiphyton 21% to the total PP in Võrtsjärv (Nõges et al., 2010b), the total annual whole-lake carbon fixation of Võrtsjärv resulted in 71 268 (min. 51 679, max. 97 107) tonnes (Table 2).

Discussion

In the global context, Võrtsjärv occupies by its annual primary production a medium position among the World lakes for which data on PP are available (Table 3; Fig. 9).

Annual areal PP of Võrtsjärv is very close to that of the other large and shallow lake close by, Lake Peipsi, but is also similar to the PP of much deeper large temperate lakes, such as Erie and Ontario. According to the data presented in Table 3, the annual PP of 63 World's lakes was significantly negatively correlated with latitude ($R^2 = 0.23$, $n = 63$, $P < 0.001$). The strong effect of latitude (Lat) on lake productivity was stressed also by Håkanson & Boulion (2002) and Boulion (2003). They showed a strong and significant decrease in phytoplankton primary production with increasing Lat, a relationship that could be successfully used to predict PP of inland waters. They found that 60% of the variation of annual PP could be explained by Lat according to linear equation: $PP = -130 * Lat + 8453$ and even 74% using the exponential equation: $PP = 647461 * \exp(-4.29 * TranLat)$ where

Table 2 Modelled annual primary production of Võrtsjärv

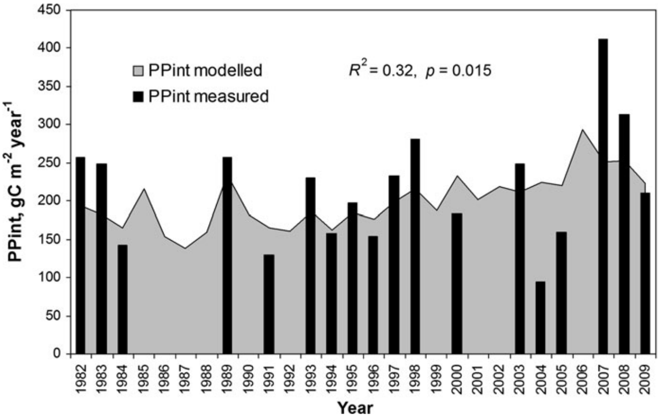
Year	Areal pelagic PP, ice-free ($g\ C\ m^{-2}\ y^{-1}$)	Areal pelagic PP, annual[a] ($g\ C\ m^{-2}\ y^{-1}$)	Lake mean depth (m)	Volumetric pelagic PP, annual[a] ($g\ C\ m^{-3}\ y^{-1}$)	Lake area (km^2)	Annual phytoplankton PP in the lake (Tonnes $C\ y^{-1}$)	Annual total PP in the lake[b] (Tonnes $C\ y^{-1}$)
1982	194	202	2.97	68	283	57062	71902
1983	182	190	2.66	71	273	51675	65115
1984	165	171	2.53	68	268	45931	57876
1985	216	225	2.75	82	275	61975	78094
1986	154	161	2.75	58	276	44273	55787
1987	138	144	3.00	48	284	41013	51679
1988	160	167	2.93	57	282	46978	59196
1989	234	244	2.81	87	278	67775	85402
1990	182	189	3.00	63	284	53796	67788
1991	166	173	2.98	58	283	48888	61602
1992	160	167	2.72	61	274	45843	57766
1993	186	194	2.38	81	263	50907	64147
1994	162	169	2.61	65	271	45760	57661
1995	185	193	2.71	71	274	52948	66719
1996	176	184	1.88	98	245	45100	56829
1997	199	207	2.38	87	263	54384	68529
1998	216	225	2.83	79	278	62682	78985
1999	188	196	2.80	70	277	54245	68353
2000	232	242	2.50	97	267	64635	81446
2001	202	211	2.55	82	269	56609	71332
2002	219	228	2.60	88	270	61575	77590
2003	211	220	2.17	101	255	56192	70806
2004	225	234	2.82	83	278	65053	81972
2005	219	229	2.84	80	279	63743	80321
2006	294	306	2.06	148	252	77064	97107
2007	251	262	2.36	111	262	68638	86489
2008	252	263	2.83	93	278	73149	92174
2009	223	232	2.98	78	283	65745	82844
Average	200	208	2.66	80	272	56559	71268
Min	138	144	1.88	48	245	41013	51679
Max	294	306	3.00	148	284	77064	97107
StDev	35	37	0.29	20	10	9504	11976

[a] Corrected for the 4% of under-ice production

[b] Corrected for the 21% of macrophyte and epiphyton production (Nõges et al., 2010b)

$TranLat = (90/(90 - Lat))^{0.5}$. Data presented in Table 3 showed somewhat weaker relationship also with the transformed values ($R^2 = 0.36$, $n = 63$, $P < 0.001$). Annual PP of Lake Võrtsjärv calculated according to the above described formulae of Håkanson & Boulion (2002) and Boulion (2003) on the basis of Lat and TranLat gave the corresponding values of 880 and 480, which overestimate the real PP in the lake fourfold and twice, accordingly. Basing on this simple comparison, it is evident that besides global large-scale estimations, the direct measurements and local modelling are indispensable to calculate the carbon budget and to understand lake metabolism. Figure 9 shows, however, that Võrtsjärv is located rather close to the

Fig. 5 Measured and modelled annual primary production in Võrtsjärv in years from 1982 to 2009



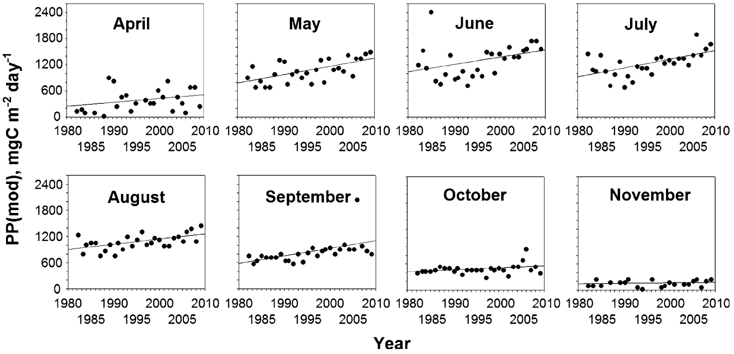


Fig. 6 Modelled daily primary production in Võrtsjärv during ice-free months over the study period of 1982–2009. *Straight lines* show linear trends (R^2 from 0.02 to 0.38, $P < 0.05$)

nutrient-saturated production boundary determined by Lat, where light limitation has the leading role. Theoretically, its productivity could increase if the relative proportion of chlorophyll among optically active substances (Chl, yellow substance and suspended solids) would increase. On average, these three components account almost equally for light attenuation in Võrtsjärv (Nõges, 2000).

Our measured PP database covers only 18 years while several other data series from Võrtsjärv started already in 1960s and by now cover a nearly 50-year time period. In order to fill the gaps in measurements and, potentially, to extend the PP data to the whole period of existing biological and chemical data, we selected the modelling approach. The bio-optical model developed for Võrtsjärv, which calculates primary production as a function of chlorophyll and light was a good descriptor for both volumetric and integral PP (Arst et al., 2008) giving strong and highly significant ($R^2 = 0.9$, $P < 0.0001$) correlations between synchronously measured and modelled PP. At daily and monthly scales, the modelled PP values, as based on real sums of irradiance, should be more accurate than the measured values which

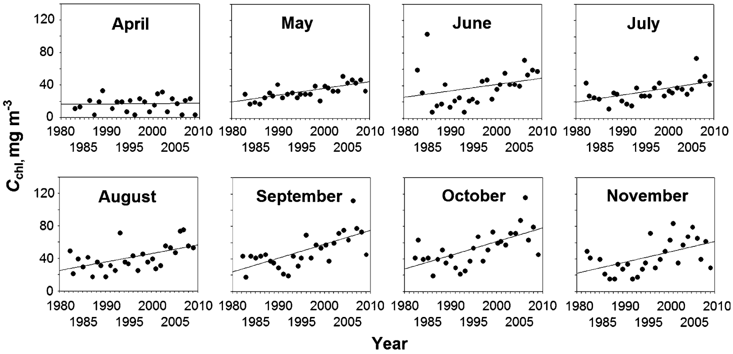


Fig. 7 Concentration of chlorophyll a (C_{chl}) in Võrtsjärv by months over the study period of 1982–2009. *Straight lines* show linear trends (since May, R^2 from 0.08 to 0.46, $P < 0.05$)

capture the light conditions of a couple of midday hours in single days only and introduce a large uncertainty to the daily estimates. The high daily and monthly variation of measured PP_{int} values (Fig. 4) show that the calculation of monthly average PP_{int} based on one or two measured daily values only, could give strongly erroneous estimates.

There are two interrelated possible explanations for the long-term stability of the measured PP on the background of increasing C_{chl}: (1) that the increase in C_{chl} was an adaptive response of phytoplankton to a deterioration of light conditions and (2) that some other factor caused the succession of dominating species having different rates of chlorophyll specific photosynthesis. Adaptation of phytoplankton to deteriorating light levels may include photoacclimation of existing species or, if exposure to dim light is prolonged, also succession of species in the favour of more shade tolerant ones. A simple strategy to survive sub-optimal light conditions is to increase the cellular content of light-harvesting pigments in order to maintain productivity (Falkowski & Owens, 1980; Dubinsky & Stambler, 2009; Yacobi & Zohary, 2010). Phytoplankton species differ largely by their ability to increase cellular chlorophyll content (Johnsen & Sakshaug 2007). Experiments with *Limnothrix redekei* (Foy & Gibson, 1982), the species that dominated in Võrtsjärv in the beginning of our study period, showed the species ability to more than triple its cellular chlorophyll content under low light doses. In Võrtsjärv the long-term increase in cellular chlorophyll content observed in autumn was much smaller but still significant and covered the period from 1988 onward during which the proportion of *L. planctonica* among dominants was continuously increasing.

In order to explain the increase of C_{chl} by a deterioration of light conditions, the latter has to be shown. Besides the underwater light climate calculations based on Secchi depth (Fig. 8A), also some other arguments suggest that light conditions have changed over the years: (1) although it seems a circular argument, the significant increase in C_{chl} itself (Fig. 7) must have had an effect on light conditions and, hence, the increase in C_{chl} could be caused by self-shading of phytoplankton; (2) a comparison of historical beam attenuation measurements from 1913 (Mühlen, 1918) with those from 2000 to 2001, Reinart & Nõges (2004) found that the absorption at 453 nm has significantly increased and therefore amount of dissolved organic matter in water may be higher nowadays than it was in the beginning of century. Given the general "browning" trends in many lakes over the northern hemisphere (Jennings et al., 2010), an increase of humic matter content in Võrtsjärv over a longer period cannot be excluded. An increase in water colour coinciding with high water levels in 1978–1979 has been suggested as the main cause for the earlier switching of phytoplankton dominants from *Planktolyngbya limnetica* (Lemm.) J. Komárková-Legnerová to *Limnothrix redekei* (Nõges et al., 2010a; Tuvikene et al., 2010); (3) chemical

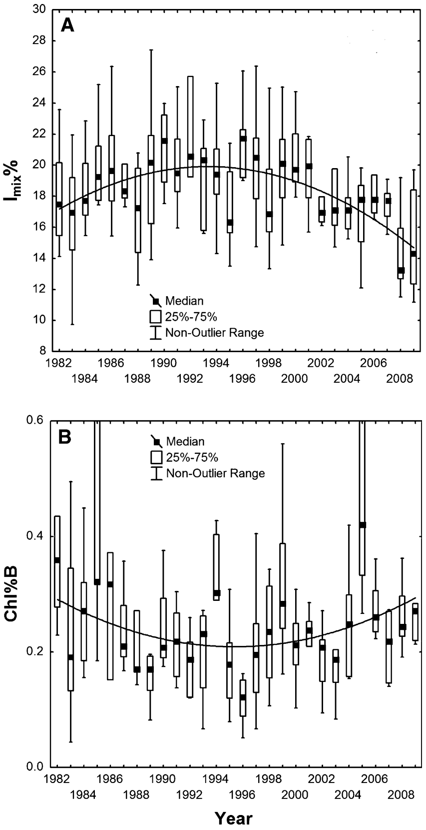


Fig. 8 Long-term adaptive response of phytoplankton to changing light conditions in Võrtsjärv. **A** Average solar irradiance in the mixed water column as the fraction of incident irradiance at the water surface during ice-free period; **B** percentage of chlorophyll *a* in total phytoplankton biomass during the ice-free period. *Curves* show the quadratic fitting line

oxygen demand COD_{Mn}, a common proxy for dissolved organic matter (DOM), was significantly lower in the period 1968–1977 compared with that in 1998–2008 and had a highly significant increasing trend within both periods (Tuvikene et al., 2010). Potassium permanganate, a much milder oxidizer compared to the more often used potassium dichromate, is highly sensitive to variations in dissolved organic matter, including humic substances (Xia et al., 2005). A correlations analysis between limnological variables in 102 Estonian lakes (Milius & Starast, 1999) found the strongest correlation among all analysed 14 variables between COD_{Mn} and water colour ($r = 0.97$) that allows using COD_{Mn} as a proxy for water colour.

As a conclusion, an increase in C_{chl} and a decrease in chlorophyll specific production rate in response to deteriorated light conditions is the most likely explanation to the different long-term trends in modelled and measured PP.

Figure 7 shows that in the long-term, there was a breaking point in the trend of the C_{chl} series in the beginning of 1990s and that the biggest increase in C_{chl} has taken place in autumn. A comparison of these changes with the biomass dynamics of *Limnothrix planctonica* in Fig. 10 (Nõges et al., 2004, updated) show a striking correspondence suggesting strongly that the C_{chl} change was caused by the emerging new dominant. Both *Limnothrix* species are considered true shade tolerants (Chomérat et al., 2007; Padisák et al., 2009) and occupy generally a similar niche in turbid polymictic lakes. Both species contain besides chlorophylls also phycocyanin, an additional photosynthetic pigment that has been shown as one of the main advantages in cyanobacteria in competition for light in turbid environments (Tilzer, 1987). The only major autecological difference between the two species in Võrtsjärv was expressed in their different seasonality and this may be the key to the observed inconsistency between C_{chl} and PP changes. The biomass of *L. planctonica* increases steadily during the vegetation period and, in the absence of major loss mechanisms, builds up a considerable standing stock by autumn. This standing stock is characterised by high C_{chl} which simulates a higher PP(mod) for this period as seasonal or species specific differences in chlorophyll specific productivity are not included in PP model. It leads to some change of the specific absorption coefficients of the phytoplankton that was not taken into account in the model, which used the algorithm by Bricaud et al. (1995). The late autumn biomass was characterised also by higher cellular chlorophyll content that explains the positive trend in C_{chl}/B ratio over the period when the proportion of *L. planktonica* increased in the phytoplankton community, i.e. since the early 1990s. This smooth succession of dominants

Table 3 Phytoplankton primary productivity (PP) of some individual lakes in g C m^{-2} y^{-1}

Lake name	Latitude	PP	Reference
Verkhneye, Schirmacher Oasis, Antarctica	68.6	0.6	Kaup (1994)
Mexcut L1, USA	39.0	1.3	Dodson et al. (2000)
Long, USA	40.1	1.5	Dodson et al. (2000)
Latnjajaure, Swedish Lappland	68.4	2.7	Dodson et al. (2000)
LaCaldera, Spain	37.1	3.4	Dodson et al. (2000)
Char, USA	74.7	4.1	Dodson et al. (2000)
Toolik, USA	68.6	5.5	Dodson et al. (2000)
Imikpuk, Alaska	71.3	8.4	Dodson et al. (2000)
Watts Lake, Vestfold Hills, Antarctica	68.6	10	Heath (1988)
Onega, Russia (May-Oct)	61.5	11	Syarki & Tekanova (2008)
Great Bear Lake, Canada	66.0	18	De Vooys (1979)
Lake 239 ELA, Canada	49.7	21	Dodson et al. (2000)
Eckarfjärden, Sweden	60.4	24	Andersson & Kumblad (2006)
Tahoe, Sierra Nevada, USA	39.1	36	De Vooys, 1979
Great Slave Lake, Canada	61.7	37	De Vooys (1979)
Lawrence, USA	42.4	41	Dodson et al. (2000)
Mirror, USA	43.9	47	Dodson et al. (2000)
Superior, USA	47.7	60	De Vooys, (1979)
Paul, USA	46.2	60	Dodson et al. (2000)
Huron, USA	44.8	85	De Vooys (1979)
Biwa, Japan	35.3	88	Dodson et al. (2000)
Little Rock, USA	46.0	91	Dodson et al. (2000)
Superior, USA	47.7	94	Sterner (2010)
Washington	47.6	96	Dodson et al. (2000)
Gull, USA	42.4	102	Dodson et al. (2000)
Trek, USA	43.1	110	Hoffmann & Dodson (2005)
Baikal, Russia	53.5	113	De Vooys (1979)
Sparkling, USA	46.0	134	Dodson et al. (2000)
Michigan, USA	44.0	145	De Vooys (1979)
Crystal, USA	46.0	149	Dodson et al. (2000)
Trout, USA	46.1	153	Dodson et al. (2000)
Constance, Lower Basin, Switzerland	47.7	164	De Vooys (1979)
Krankesjön, Sweden (May-Sept)	55.7	166	Blindow et al. (2006)
Thonotosassa, USA	28.0	166	Dodson et al. (2000)
Acton, USA	39.6	181	Dodson et al. (2000)
Ontario, USA	43.7	185	De Vooys (1979)
Plusssee, Germany	54.2	187	Dodson et al. (2000)
Memphremagog, Canada	45.1	197	Hoffmann & Dodson (2005)
Hall, USA	47.8	200	Hoffmann & Dodson (2005)
Peipsi, Estonia/Russia	58.7	200	Nõges et al. (2001)
Võrtsjärv, Estonia	58.3	208	Present study
Erie, USA	42.2	240	De Vooys (1979)
Fish, USA	43.2	292	Dodson et al. (2000)
Buckeye, USA	43.1	310	Hoffmann & Dodson (2005)

Table 3 continued

Lake name	Latitude	PP	Reference
Mendota, USA	43.1	342	Dodson et al. (2000)
Monona, USA	43.1	343	Dodson et al. (2000)
Wingra, USA	43.1	345	Dodson et al. (2000)
Wintergreen, USA	42.4	369	Dodson et al. (2000)
IJssel, The Netherlands	52.6	400	De Vooys (1979)
Börringesjön, Sweden (May-Sept)	55.5	413	Blindow et al. (2006)
Nakuru, Africa	0.4	467	De Vooys (1979)
St. George, USA	44.0	548	Dodson et al. (2000)
Suwa, Japan	36.0	557	Dodson et al. (2000)
Tjeukemeer, Netherlands	52.1	567	Hoffmann & Dodson (2005)
Highway, USA	43.1	572	Hoffmann & Dodson (2005)
Portage, USA	43.2	575	Hoffmann & Dodson (2005)
Ziegler, USA	43.2	605	Hoffmann & Dodson (2005)
Kasumigaura, Japan	36.2	608	Dodson et al. (2000)
Kinneret, Israel	32.8	619	Dodson et al. (2000)
Lanao, Philippines	8.8	621	Dodson et al. (2000)
Valencia, Venezuela	10.1	821	Dodson et al. (2000)
Clear, California, USA	39.1	913	De Vooys (1979)
MadMetro2B, USA	43.0	1300	Dodson et al. (2000)

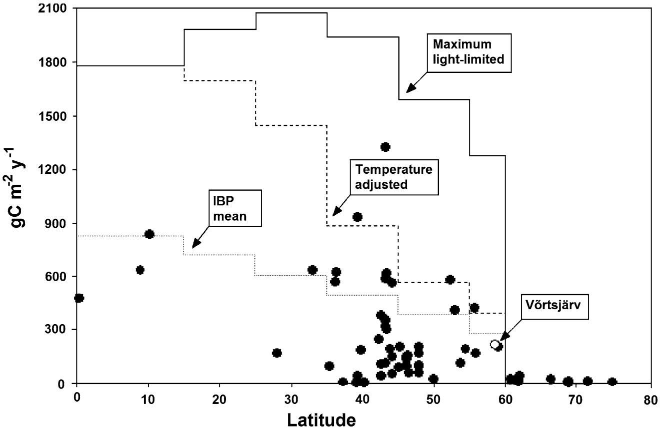


Fig. 9 Latitudinal trends in primary production (PP) redrawn from Lewis (1996) and combined with data on single lakes presented in Table 3. *Top line*: modelled maximum PP for nutrient-saturated conditions if there was no thermal gradient with latitude (the latitudinal trends can be traced mainly to latitudinal gradients in minimum monthly solar irradiance); *middle line*: the same adjusted for the temperature effect on optimum photosynthesis rate (Q_{10} about 2); *bottom line*: empirical mean of measurements within the International Biological Program. According to this scheme, Võrtsjärv is located very close to light limitation boundary

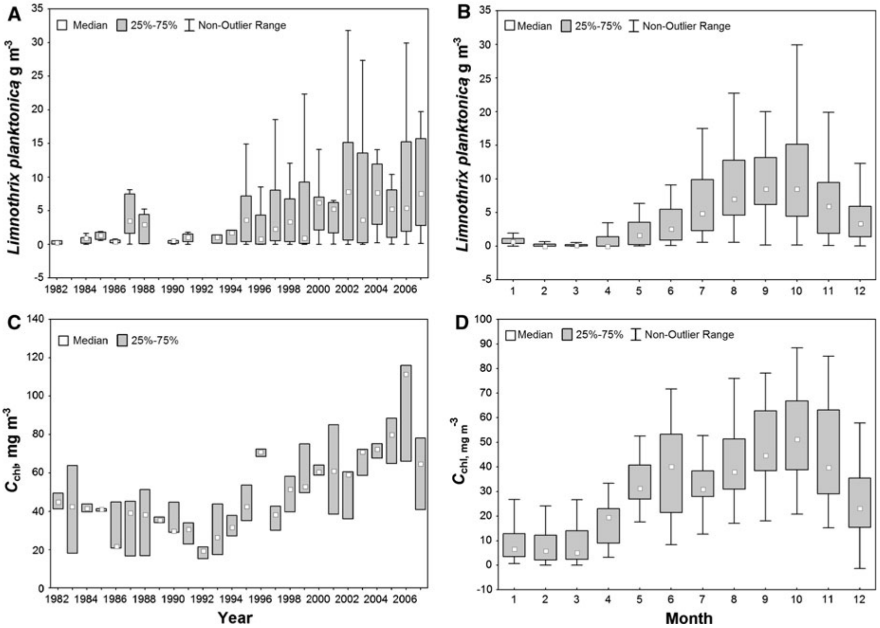


Fig. 10 Long-term (**A**) and average seasonal dynamics (**B**) of *L. planctonica* biomass in Võrtsjärv (modified from Nõges et al., 2004) compared to long-term autumn C_{chl} in September–December (**C**) and average seasonal changes of C_{chl} (**D**) over the study period 1982–2009

could explain the absence of any significant trend in annual PP values.

Still the question remains, what caused the succession between the two *Limnothrix* species. Resource limited conditions favour the species which has even a small advantage in exploiting the limiting resource. Building up a higher biomass by extending the growth period towards autumn may be a clear advantage in light-limited conditions. The earlier dominant and present subdominant *L. redekei* reaches its biomass peak in June but in summer its gas vacuoles collapse and the cells autolyse. The regular collapse of gas vacuoles in *L. redekei* in summer is a very common phenomenon not only in Võrtsjärv but has been mentioned also for Edebergsee, where trichomes with no or only small gas vacuoles dominated at high light intensities (Meffert & Krambeck, 1977). Such collapse has not been described in *L. planctonica*, which has much smaller gas vacuoles *per se*. A study of the filament length structure in the two *Limnothrix* species (Nõges, 1999) suggested the selective sedimentation of longer filaments of *L. redekei* with collapsed gas vacuoles as the main loss factor of this species in summer. A CCA analysis for 44-year data on species composition and environmental variables (Nõges et al., 2010a) showed that in Võrtsjärv *L. redekei* was favoured by increasing water level and *L. planktonica* by increasing temperatures in summer and autumn. Trend analysis for the period 1961–2004 (Nõges, 2009) revealed a highly significant ($P < 0.01$) upward trend for water temperature in August with a significant ($P < 0.05$) stepwise increase in 1989. Hence, we suppose that the initial breakthrough of *Limnothrix* species in early 1980s was caused by the sudden deterioration of light conditions following a water level increase in 1978/1979 (Nõges & Järvet, 1995; Nõges et al., 2010a; Tuvikene et al., 2010) while the consequent gradual increase of the proportion of

L. planktonica could be more related to the late summer warming trend.

The relationship between the annual PP_{int} values, based on measurements and modelling found in this paper ($R^2 = 0.32$) is much weaker compared with the $R^2 = 0.9$ reported in Arst et al. (2008). However, in Arst et al. (2008) the results were obtained from 2-h measurement series of PP with full (without breaks) complex of initial data for model calculations, that is not so for long-term estimations. In general, there can be a number of errors included both in the modelling and the measured data.

Excluding other methodological errors potentially included in the ^{14}C technique for measuring PP (see overview by Marra, 2002), the sources of error in summarising the measured data are included in the depth integration of the discrete vertical measurements, the extrapolation of the PP values around noon to the whole day (Richardson, 1991), but the major source of errors is included in the interpolation of the highly variable but infrequently measured daily PP values. The latter is largely avoided by modelling in which we used the true monthly mean values of daily irradiances and only the values of C_{chl}, a less variable parameter compared to PP, were interpolated between discrete measurements.

Conclusions

- Our aim was to summarise the long-term primary production measurements in Võrtsjärv in order to receive reliable daily, monthly and annual estimates of this parameter as the first step in the lake's carbon balance calculations. The results will provide further basis for long-term studies of the ecosystem metabolism and its climate sensitivity.
- According to the long-term annual PP (208 ± 27 g C m^{-2} y^{-1}) Võrtsjärv is located rather close to the nutrient-saturated production boundary determined by latitude where light limitation has the leading role. This assignment is supported by the phytoplankton composition dominated by eutrophic highly shade tolerant cyanobacteria species from the genus *Limnothrix.*
- The semi-empirical primary production model based on continuous irradiance (PAR) measurements and interpolated values for chlorophyll concentration and light attenuation coefficient simulated sufficiently well the interannual changes in PP.
- Increasing trend in the long-term PP(mod) series (induced by increasing C_{chl}) was not supported by measured PP. This controversy can be explained by an adaptive increase in the cellular C_{chl} content in phytoplankton in response to deteriorated light conditions, and the change of dominating species from *Limnothrix redekei* to *L. planctonica.* The latter is characterised by a seasonally later biomass peak in Võrtsjärv and lower chlorophyll specific productivity not taken into account in the model.
- We consider the developed PP model a useful tool for filling the gaps in the measured data and potentially extending the PP data series over periods for which other biological and chemical data are available. The model can be improved, however, by including seasonal and species specific correction factors to the chlorophyll specific productivity.

Acknowledgments The study was supported by Estonian target funding project SF 0170011508, by grants 5594, 7156 and 7600 from Estonian Science Foundation, by 7th EU Framework Programme, Theme 6 (Environment including Climate Change) project REFRESH (Adaptive strategies to Mitigate the Impacts of Climate Change on European Freshwater Ecosystems, Contract No.: 244121), and by the Doctoral School of Earth Sciences and Ecology created under the auspice of European Social Fund.

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CURRICULUM VITAE

I. General

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Education: 1988–2000 Haljala Gymnasium

2000–2004 University of Tallinn, BSc in biology

2004–2006 University of Tartu, MSc in hydrobiology

2006–2012 Estonian University of Life Sciences, PhD studies in hydrobiology

Professional employment:

2012–present Centre for Limnology, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, researcher (0.5)

2012–present Department of Remote Sensing and Marine Optics, Estonian Marine Institute, Faculty of Science and Technology, University of Tartu, researcher (0.5)

2005–2011 University of Tartu, Faculty of Science and Technology, Estonian Marine Institute, University of Tartu, insenier

II. Scientific activity

Research interests: Particulate and dissolved organic matter and the carbon cycle in aquatic ecosystems.

Grants and projects:

01.01.12–31.12.15 Estonian Science Foundation grant ETF9102, Modelling of Lake Võrtsjärv food webs, carbon cycle and impacts of the climate, senior personnel.

01.01.12–31.12.14 Project SLOMI12010T, Observatory of Estonian aquatic environment', researcher.

01.01.08–31.12.13 Target financed project SF0170011s08, Will climate change alter the relative importance of catchment and in-lake processes in the carbon balance of shallow lakes?, PhD student.

01.01.08–31.12.11 Estonian Science Foundation grant ETF7600, Is Lake Võrtsjärv an autotrophic or heterotrophic system? The role of autochthonous and allochthonous organic matter in the budget of a large shallow lake, senior personnel.

01.04.08–31.12.10 Project EMP1, Improving Satellite Remote Sensing Products for Large Lakes, senior personnel.

01.01.07–31.12.10 Estonian Science Foundation grant ETF7156, Modelling long-term primary production of turbid lakes on the example of lakes Võrtsjärv and Harku, senior personnel.

01.01.05–31.12.10 Target financed project SF0712699s05, Optics and remote sensing of coastal and inland waters, PhD student.

01.01.04–31.12.07	Estonian Science Foundation grant ETF5738, Impact of climate change on ecosystems of large shallow lakes, mediated by the altered inflow of substances, senior personnel.
01.01.03–31.12.07	Target financed project SF0362480s03, Impact of climatic change on shallow lake ecosystems, PhD student.

Publications:

Toming, K., Tuvikene, L., Vilbaste, S., Agasild, H., Viik, M., Kisand, Feldmann, T., Martma, T., Jones, R.I., Nõges, T. Contributions of autochthonous and allochthonous sources to dissolved organic matter in a large, shallow, eutrophic lake with a highly calcareous catchment. Limnology and Oceanography, submitted.

Toming, K, Arst, H., Kõiv, T., Nõges, T. 2013. Long-term changes of the underwater light field in large shallow lakes Peipsi and Võrtsjärv, North-East Europe. Proceedings of the Estonian Academy of Sciences, accepted.

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Olenina, I., Wasmund, N., Hajdu, S., Iveta, J., Gromisz, S., Kownacka, J., Toming, K., Vaiciūtė, D., Olenin, S. 2010. Assessing impacts of invasive phytoplankton: the Baltic Sea case. Marine Pollution Bulletin, 60(10), 1691 - 1700.

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Thesis of the international conferences:

Kauer, T., Toming K., Arst H., Nõges, T. 2012. Underwater Light Field and Phytoplankton Primary Production in Different Types of Lakes, Ocean Optics 2012, Glasgow, Scotland, 8-12 October.

Toming, K., Tuvikene, L., Vilbaste, S., Agasild, H., Viik, M., Kisand, A., Nõges, T., Jones, R.I. 2012. How δ^{13}C values reflect the origin of organic matter in a large, shallow lake with a calcareous catchment, ISOECOL 8th- International Conference on Applications of Stable Isotope Techniques to Ecological Studies, Brest, France, 20-24 August.

Arst, H., Paavel, B., Reinart, A., Toming, K., Kutser, T. 2009. Investigations of the CDOM rich Pärnu Bay in situ and remote sensing measurements, 7th Baltic Sea Science Congress, Tallinn, Estonia, 17-21 August.

Jaanus, A., Andersson, A., Olenina, I., Toming, K., Kaljurand, K. 2009. Phytoplankton community change in different Baltic sub-basins during 1990 -2008. 7th Baltic Sea Science Congress, Tallinn, Estonia, 17-21 August.

Toming, K. Tuvikene, L., Agasild, H., Kisand, A., Nõges, T., Jones, R. I. 2009. Variation of autochthonous and allochthonous dissolved organic matter in large and shallow Lake Võrtsjärv, 12th Nordic-Baltic IHSS Symposium, Tallinn, Estonia, 14-17 June.

Kisand, A., Ott, K., Tõnno, I., Tuvikene, L., Toming, K., Nõges, T. 2009. Fluorescent Properties of Sediment Pore Water in River Õhne and Lake Võrtsjärv, Estonia, 12th Nordic-Baltic IHSS Symposium, Tallinn, Estonia, 14-17 June.

Agasild, H., Salujõe, J., Toming, K., Nõges, T., Jones, R. I. 2009. Within-lake variability in carbon and nitrogen stable isotope signatures of zooplankton in large shallow Lake Võrtsjärv (Estonia), 12th Nordic-Baltic IHSS Symposium, Tallinn, Estonia, 14-17 June.

Toming, K, Arst, H., Kõiv, T., Nõges, T. 2008. Long-term changes of the underwater light field in large shallow lakes Peipsi and Võrtsjärv, North-East Europe, Shallow Lakes, Uruguay, 23-28 November.

Arst, H., Paavel, B., Metsamaa, L., Toming, K., Reinart, A., Alikas, K., Kutser, T. 2008. Optical investigations and remote sensing of CDOM-rich coastal waters. In: Proceedings of the XIX Ocean Optics Conference: XIX Ocean Optics Conference; Tuscany, Italy, 6-10 October.

Toming, K, Arst, H., Nõges, T., Paavel, B., Laas, A. 2007. Spatial and temporal variation of coloured dissolved organic matter in Estonian large water bodies. Fifth Symposium for European Freshwater Sciences (SEFS-5), Palermo, Sicily, 8-13 July.

Jaanus, A., Hällfors, S., Kaljurand, K., Lips I., Toming, K. 2006. Selection of potential phytoplankton indicator species for monitoring Baltic coastal waters. Research and management of eutrophication in coastal ecosystems – an international symposium, Nyborg, Denmark, 20-23 June.

Toming, K., Lips, I., Lips, U. 2005. Use of ships of opportunity to detect and understand short time summer phytoplankton blooms. ASLO Conference: A pilgrimage through global aquatic sciences, Santiago de Compostela, Spain, 21- 26 June.

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Töökogemus:

2012–praeguseni	Limnoloogiakeskus, Põllumajandus- ja Keskkonnainstituut, Eesti Maaülikool, teadur (0.5)
2012–praeguseni	Kaugseire ja mereoptika osakond, Eesti Mereinstituut, Loodus- ja tehnoloogiateaduskond, Tartu Ülikool, teadur (0.5)
2005–2011	Eesti Mereinstituut, Loodus- ja tehnoloogiateaduskond, Tartu Ülikool, laborant

II. Teadustegevus

Peamised uurimisvaldkonnad: Partikulaarne ja lahustunud orgaaniline aine ning süsinikuringe veeökosüsteemides.

Grandid ja projektid:

01.01.12–31.12.15	Eesti Teadusfondi grant ETF9102, Võrtsjärve toiduahelate, süsinikuringe ja kliimamõju modelleerimine, põhitäitja.
01.01.12–31.12.14	Projekt SLOMI12010T, Eesti veekeskkonna observatoorium, teadur.
01.01.08–31.12.13	Sihtfinantseeritud projekt SF0170011s08, Kas kliimamuutus muudab valgala- ja järvesiseste protsesside osakaalu madala järve süsinikubilansis?, doktorant.
01.01.08–31.12.11	Eesti Teadusfondi grant ETF7600, Kas Võrtsjärv on valdavalt auto- või heterotroofne süsteem? Autohtoonse ja allohtoonse orgaanilise aine vahekord suure madala järve ainebilansis, põhitäitja.
01.04.08–31.12.10	Projekt EMP1, Satelliitide tulemite parandamine kasutamiseks suurte järvede kaugseires, põhitäitja.
01.01.07–31.12.10	Eesti Teadusfondi grant ETF7156, Häguste järvede primaarproduktsiooni mudelarvutused pikkade aegridadena Võrtsjärve ja Harku järve näitel, põhitäitja.
01.01.05–31.12.10	Sihtfinantseeritud projekt SF0712699s05, Ranna- ja sisevete optika ning kaugseire, doktorant.
01.01.04–31.12.07	Eesti Teadusfondi grant ETF5738, Kliimamuutuste mõju suure madala järve ökosüsteemile ainete sissekande muutuste kaudu, põhitäitja.
01.01.03–31.12.07	Sihtfinantseeritud projekt SF0362480s03, Kliimamuutuste mõju madalate järvede ökosüsteemile, doktorant.

Publikatsioonide loetelu:

Toming, K., Tuvikene, L., Vilbaste, S., Agasild, H., Viik, M., Kisand, Feldmann, T., Martma, T., Jones, R.I., Nõges, T. Contributions of autochthonous and allochthonous sources to dissolved organic matter in a large, shallow, eutrophic lake with a highly calcareous catchment. Limnology and Oceanography, esitatud.

Toming, K, Arst, H., Kõiv, T., Nõges, T. 2013. Long-term changes of the underwater light field in large shallow lakes Peipsi and Võrtsjärv, North-East Europe. Proceedings of the Estonian Academy of Sciences, vastu võetud.

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Olenina, I., Wasmund, N., Hajdu, S., Iveta, J., Gromisz, S., Kownacka, J., Toming, K., Vaiciūtė, D., Olenin, S. 2010. Assessing impacts of invasive phytoplankton: the Baltic Sea case. Marine Pollution Bulletin, 60(10), 1691 - 1700.

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Rahvusvaheliste konverentside teesid:

Kauer, T., Toming K., Arst H., Nõges, T. 2012. Underwater Light Field and Phytoplankton Primary Production in Different Types of Lakes, Ocean Optics 2012, Glasgow, Šotimaa, 8.-12. oktoober.

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