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Observed and predicted future changes of total organic carbon in the lake Päijänne catchment (southern Finland): Implications for water treatment of the Helsinki metropolitan area

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Lake Päijänne (1083 km^2) is the main drinking-water source for more than one million people of the Helsinki metropolitan area and the lake is important also for fisheries and recreation. We carried out a detailed study on observed and modelled future changes of total organic carbon (TOC) in this large lake catchment (26 459 km^2), and assessed the implications for current water treatment processes. Concentrations of TOC/COD_{Mn} in the lake and its sub-catchments increased during the period 2000–2014 (COD_{Mn} was used as a TOC proxy in the statistical analysis because of long-term data availability). Stepwise multiple regression analysis on the relationships between COD_{Mn}, water quality parameters, air temperature and runoff in selected 18 catchments indicated that the explaining variables are site-specific and that the observed recent changes are mainly due to a combination of the simultaneously interacting factors of climate and atmospheric deposition. Linear regression analysis revealed no relationships between COD_{Mn} increases and land-use related factors or specific catchment characteristics. A catchment-scale dynamic model system (VEMALA) was used to predict future concentrations and fluxes of TOC, using three different climate change scenarios. TOC concentrations were predicted to decrease by 19% in the Dry scenario and increase by 13% in the Wet scenario by the end of the century. The current treatment processes in the city of Helsinki can likely meet the challenges set by climate change in form of changed raw water TOC and quality. Integrated carbon (C) balance calculations indicated large changes in future C fluxes and lake retention time. These changes would markedly affect several key ecosystem processes such as transport of organically bound nutrients to sea areas and the importance of surface waters in the overall landscape C budgets.

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Introduction

Lakes are active processors and collectors of carbon (C) and thus have proved to be quantitatively important within the terrestrial C cycle (Kortelainen *et al*. 2004, Cole *et al*. 2007, McGovan *et al*. 2015). Globally, the loss of terrestrial organic carbon to rivers is equivalent to 10% of the net ecosystem production on land (Schlesinger 1991), and is therefore an important part of the global C budget. Increases in concentrations of organic carbon (analysed as dissolved organic carbon (DOC) or total organic carbon (TOC)) have been observed in surface waters over large areas in Europe (e.g. Evans *et al*. 2005, Vuorenmaa *et al*. 2006, Monteith *et al*. 2007) and North America (Monteith *et al*. 2007, Couture *et al*. 2012). Many different processes have been suggested as likely main causes including climate and hydrology (Freeman *et al*. 2001, Sarkkola *et al*. 2009, Räike *et al*. 2012, Lepistö *et al*. 2014), decreased acid and sea-salt deposition (Vuorenmaa *et al*. 2006, Monteith *et al*. 2007, Evans *et al*. 2012), and land-use changes (Armstrong *et al*. 2010, Yallop *et al*. 2010). Combined effects, acting at different time-scales, have also been suggested (Roulet and Moore 2006, Clark *et al*. 2010, Finstad *et al*. 2016, Räike *et al*. 2016).

Various modelling tools have been developed for prediction of future changes in DOC/TOC concentrations and fluxes. Approaches include statistically based neural network modelling, indicating increasing C-fluxes in a climate change situation in both Canadian rivers (Clair and Ehrman 1998) and Finnish headwater streams (Holmberg *et al*. 2006). Dynamic simulation models simulating the C dynamics of forest soils, including the production and transport of DOM (dissolved organic matter) on the basis of soil hydrological processes and sorption/de-sorption reactions, have also been developed. Such models include DyDOC (Tipping *et al*. 2005) and INCA-C (Futter *et al*. 2009, Holmberg *et al*. 2014, Lepistö *et al*. 2014), and they have been applied to soils and catchments in northern environments to predict impacts of climate change and deposition scenarios, as well as effects of manipulation experiments. Weyhenmeyer *et al*. (2016) recently presented an approach where a numerical model for spatial variation of absorbance (a_{420}) was used to predict impacts of a worst-case climate scenario for Sweden until 2030. Lakes with a long-term mean water retention time between one and three years were predicted to be particularly vulnerable to climate-change induced browning. Hanson *et al*. (2011) used a coupled hydrodynamic water quality model to study how DOC recalcitrance, in combination with the processing capacity of lakes, controlled the fate of DOC loads to lakes. The VEMALA model (Huttunen *et al*. 2016) simulates runoff and water quality and has specifically been developed for Finnish conditions including large, lake-rich watersheds. The VEMALA model was therefore chosen as a modelling tool for this study.

The observed and potential future DOC changes have many consequences. Organic matter derived from terrestrial sources can play a major role in the food webs of humic lakes, and changes in flux of DOC from the land to surface waters may alter the base of the aquatic food web and affect lake ecology (Salonen *et al*. 1992). Brownification has been detected to decrease unsaturated fatty acid content in phytoplankton, which may lead to lower nutritional quality of fish for human consumption (Taipale *et al*. 2016). Changes in DOC also affect water transparency and thus the growing conditions for phytoplankton. Most mercury (Hg), a potentially toxic metal in the aquatic environment, is associated with DOC. Increased surface water DOC may lead to higher fluxes of Hg and increased risk to humans and the environment (Ravichandran 2004, Poste *et al*. 2015). Rates of recovery from air pollution induced acidification may also be affected by increasing DOC (Evans *et al*. 2005, Wright *et al*. 2006).

Lakes and rivers are also main sources of drinking water in many countries, including Finland. The increases in DOC are a challenge for many water works as removal of colour and DOM are often essential parts of water treatment to comply with national and EU drinking water quality regulations (Tryland *et al*. 2011, Ledesma *et al*. 2012). Recently there have been major increases in water colour and DOC in many forest lakes that serve as drinking water reservoirs in the southern part of Norway. Colour of raw water reaching waterworks have doubled and in some cases even tripled (Hongve *et al*. 2004, Tryland *et al*. 2011).

Given the potential expectation of reduced raw-water quality under environmental change, drinking water treatment plants face considerable uncertainty. The future challenges in drinking water treatment related to potentially rising concentrations of DOC include increases in filter cycles, greater consumption of chemicals, and a reduction in treatment capacity (Eikebrokk *et al*. 2004). The main processes for removal of organic substances and water colour are coagulation and filtration, ozonation/biofiltration, and membrane filtration (Odegaard *et al*. 1999). Although the main purposes of these water treatment processes are to improve the physical quality of the raw water, they also function as hygienic process barriers (Tryland *et al*. 2011). Higher DOC in drinking water can be a human health issue since DOC reacts with the chlorine, used in some drinking water treatment processes as a disinfectant, producing potentially carcinogenic trihalomethanes (Chow *et al*. 2003).

Lake Päijänne (1083 km^2) is the main drinking water source for more than one million people in the metropolitan area of the city of Helsinki, south Finland. Moreover, the lake has an important role in recreational and professional fisheries, recreational use and tourism. The aims of this study were to:

- quantify the TOC/COD_{Mn} changes in different parts of the lake Päijänne watershed,
- analyze the reasons for the observed recent increases in TOC,
- predict impacts of climate changes on future TOC concentrations using the regional-scale dynamic model VEMALA, and
- assess the implications of observed and predicted future TOC changes on drinking water treatment processes for the Helsinki metropolitan area.

Material and methods

Site description

Lake Päijänne is Finland's second largest lake with a surface area of 1083 km^2 (Table 1). It is also the deepest lake in Finland, with maximum and average depths of 95.3 m and 16.2 m, respectively. The volume of the lake is 18.1 km^3 and water residence time 2.5 years. The drainage area of the lake is 26 459 km^2, and the lake drains into the Gulf of Finland via the Kymijoki. Most of the catchment is covered with forests on mineral soil (56%). The proportions of agricultural land and built areas are 7% and 4%, respectively. About 14 and 19% of the catchment is covered with peatlands and surface waters, respectively (Table 1).

Sub-catchments, point sources and water quality data

Lake Päijänne has been monitored intensively for decades. Eighteen water quality monitoring sites representing different sub-catchments, were selected for this study. Ten of them are lake sites and eight are river sites, and all are monitored for water quality by the Finnish Environment Institute (SYKE), in co-operation with regional Centres for Economic Development, Transport and the Environment. Catchment area and land cover were determined for each site, based on national databases of SYKE. Land cover was divided

Table 1. Main characteristics of lake Päijänne and its catchment.

Lake	
Location	61°29´N, 25°26´E
Area (km^2)	1083
Average depth (m)	16.2
Maximum depth (m)	95.3
Volume (km^3)	18.1
Water residence time (years)	2.5
P_{tot} (μg l^{-1}, 1 m depth)	7.7
N_{tot} (μg l^{-1}, 1 m depth)	500
TOC (mg l^{-1}, 1 m depth)	7.6
Colour (mg Pt l^{-1}, 1 m depth)	25
Catchment	
Area (km^2)	26459
Forests (%)	56
Agricultural land (%)	6.6
Built area (%)	4.1
Peatlands (%)	14
Water (%)	19
Mean air temp. (°C, 1981–2010)	3.6
Annual precipitation (mm, 2014)	581
Annual runoff (mm, 2014)	253

into five classes and their shares expressed as percentages: peatland (open and forested peatlands, Peat%), upland forests (Forest%), agricultural fields (Field%), built-up areas (Built%), and water (Water%). The land-cover data were derived from the national CORINE land cover (CLC2012) database (20 × 20-m grids), except for Field% and Built%. In the national CORINE database, Peat% was based on the topographical database of the National Land Survey of Finland. Peat% includes areas where peatland vegetation dominates and the thickness of the peat layer is at least 30 cm. Field% was obtained from the field plot register owned by the Agency for Rural Affairs (Mavi). Built% was derived from the urban-layer database of SYKE.

Several municipal and industrial plants are located in the lake Päijänne catchment, and in addition also many peat production areas (especially in the northern parts). Three pulp and paper industrial complexes located in different parts of the lake's catchment and the city of Jyväskylä (133 000 inhabitants) are the largest point source loaders. Point source load data were collected from a database of SYKE. DOC or TOC is not included in the monitoring programmes of the point source loaders, but they measure BOD and COD_{Cr}. BOD (biochemical oxygen demand) is a proxy for easily degradable organic matter, whereas COD_{Cr} (chemical oxygen demand) is a proxy for refractory organic matter.

The area of the sub-catchments varied between 10 and 26 459 km^2 (mean 6170 km^2; *see* Table 2). The proportions of upland forests in the sub-catchments varied between 25% and 76% (mean 55%), Field% between 0% and 18% (mean 6%), and Peat% between 0% and 39% (mean 17%). Water areas covered 4%–23% (mean 15%) of the catchments. Built% included urban or industrial areas, road networks, and aggregate extraction sites, accounted for 2%–51% (Table 2).

The studied period covered the years 2000–2014. Water samples were taken 56–165 times during that period from the different sites. The samples were analysed with accredited methods in the laboratories of the regional centres and SYKE (Vuorenmaa *et al*. 2014). Chemical oxygen demand (COD_{Mn}) was determined titrimetrically following oxidation with $KMnO_4$ according to the Finnish Standard (SFS 3036). TOC was determined by UV-persulfate oxida-

Table 2. Area and land cover of the 18 selected sub-catchments of the study. Locations of the sites are shown in Fig. 3.

ID#		Catchment area km^2	Agricultural fields (%)	Upland forests (%)	Peatlands (%)	Built areas (%)	Water (%)
River sites							
16	Aittokoski 3300	3077	7.4	55	25	3.2	9.2
12	Haapakoski 4100	17658	6.4	56	17	3.4	17
15	Häränvirta 3400	6254	4.9	58	17	2.6	18
11	Kalkkistenkoski 4800	26459	6.6	56	14	4.1	19
13	Kapeenkoski 3500	9587	5.8	57	19	2.9	15
17	Koivujoki 15300	206	6.6	53	24	2.6	14
18	Nuoramoinen 4600	1738	7.2	59	9.0	4.0	21
14	Vanajanjoki 54	38	3.9	61	13	3.0	20
Lake sites							
4	Kangastakunen	10	0	76	11	3.6	8.5
9	Konnevesi 64	5602	6.0	53	17	3.3	21
7	Kuuhankavesi 42	46	9.7	55	25	6.5	4.1
1	Majutvesi 010	58	18	59	5.2	11	7.0
10	Pieksänjärvi 020	52	3.7	38	20	20	19
2	Päijänne 675	1936	6.1	65	15	4.3	9.2
5	Päijänne 69	18091	6.4	56	17	3.7	17
3	Päijänne 71	19268	6.4	56	16	3.8	17
6	Vesijärvi, Lankiluoto 10	29	0.3	25	0.1	51	23
8	Pääjärvi 256	968	5.9	48	39	2.1	5.2

tion followed by IR gas measurements or using a high-temperature oxidation. In Finnish surface waters the relative proportion of particulate organic carbon is minor (< 6%, Mattsson *et al*. 2005, < 3%, Kortelainen *et al*. 2006a), and therefore COD_{Mn} and TOC are the standard water-quality variables used for determining organic carbon concentrations in routine water-quality monitoring programmes. TOC values are thus considered to be essentially equivalent to DOC in Finnish conditions. COD_{Mn} usually correlates well with TOC concentration (Kortelainen 1993, Sarkkola *et al*. 2009, Räike *et al*. 2012), and is often used as a proxy for TOC/DOC, especially in Finland, Norway and Sweden.

Much more long-term data was available for COD_{Mn} than for TOC in the lake Päijänne data set, and therefore COD_{Mn} samples were used in the statistical analyses. For comparisons and combining of the data sets, the following formula of Kortelainen (1993) based on randomly selected Finnish lakes was used:

$$TOC = 0.675COD_{Mn} + 1.94, r^2 = 0.92, n = 975 \quad (1)$$

Statistical analyses

Trends in concentration were analysed with the seasonal Kendall test, which is simple, robust and can cope with missing values and values below a detection limit, and it includes seasonality (Hirsch *et al*. 1982, 1991). The magnitude of statistically significant trends was estimated according to the seasonal Kendall slope estimator (Hirsch *et al*. 1982). Trends were computed with the Multitest ver. 5 visual basic program (www.ida.liu.se/divisions/stima/research/Software/index.en.shtml)), which also takes into account serial correlation (Libiseller and Grimwall 2002).

The relationships between COD_{Mn}, water quality parameters (pH, alkalinity, SO_4, water temperature), air temperature and runoff in the 18 sub-catchments were studied with stepwise linear multiple regression analysis. Data from the period 2000–2014 were used in statistical analyses and some variables were ln-transformed to achieve normality. The multiple regression models were selected on the basis of explanation power and mutual correlation between the explaining variables, excluding models with a variance inflation factor exceeding five. The sites had to have a minimum of 30 samples to be included in the multiple regression analysis. The stepwise multiple regression analyses were performed using SAS® 9.3 (SAS Intitute).

Modelling of future changes

The VEMALA model system (Huttunen *et al*. 2015, 2016) was used to predict future concentrations and fluxes of TOC for the study catchment. VEMALA is a novel, national scale, operational modelling and assessment system that simulates runoff and water quality on a daily time-step for all Finnish watersheds. The simulation of large, lake-rich watersheds (a special characteristics of Finland), has been given special attention in the model development. A detailed description of the model system and calibration procedures is given in Huttunen *et al*. (2015, 2016), and only some key features are here summarized.

VEMALA was developed using the operational watershed simulation and forecasting system (WSFS), which has been developed at SYKE since the 1980s. Since the year 2005, two modelling systems have been in use: WSFS (operational watershed simulation and forecasting system) and WSFS-VEMALA (new nutrient loading model, here VEMALA). Both models use a similar hydrological model. A comprehensive spatial description of the catchments has been created using a basic simulation unit for the hydrological model at the third order sub-catchment (average size of about 60 km^2). The model is divided further into fourth order sub-catchments for each lake larger than 1 ha. Organic carbon processes in VEMALA are modelled using a concentration–flow relationship (Huttunen *et al*. 2016).

The terrestrial TOC loading model is based on a non-linear regression between concentration and daily simulated runoff. Daily simulated runoffs are divided into 5 classes in order to represent the non-linearity of the relationship: r_1 (0–1 mm d^{-1}), r_2 (1–3 mm d^{-1}), r_3 (3–6 mm d^{-1}), r_4 (6–10 mm d^{-1}) and r_5 (> 10 mm d^{-1}). The daily

TOC concentrations in runoff flowing from mineral soil areas are calculated as follows:

$$c_{\mathrm{daily,m}} = \frac{r_1 c_{1,\mathrm{m}} + r_2 c_{2,\mathrm{m}} r_3 c_{3,\mathrm{m}} r_4 c_{4,\mathrm{m}} r_5 c_{5,\mathrm{m}}}{r} C_{\mathrm{f,mineral}} \quad (2)$$

where $c_{\mathrm{daily,m}}$ is the daily TOC concentrations for mineral soil land area, respectively, taking into account the concentration of each runoff class: $c_{1,\mathrm{m}}$, $c_{2,\mathrm{m}}$, $c_{3,\mathrm{m}}$, $c_{4,\mathrm{m}}$, $c_{5,\mathrm{m}}$. A similar equation is used for simulation of daily concentrations from peat-soil land areas, and peat- and mineral-soil distribution is used to estimate TOC concentration leaving the sub-catchment. $C_{\mathrm{f,mineral}}$ is the scaling factor for scaling mean annual TOC concentration ($c_{\mathrm{ANNUAL\_SIM}}$) to match mean annual TOC concentrations from observations, ($c_{\mathrm{ANNUAL\_OBS}}$). The relationship between the observed mean annual TOC concentration in streams ($c_{\mathrm{ANNUAL\_OBS}}$) and peat soil percentage in the catchment (Peat%), which is based on concentration data from Kortelainen *et al*. (2006a), is calculated as follows:

$$c_{\mathrm{ANNUAL\_OBS}} = 0.32\mathrm{Peat\%} + 5.2 \quad (3)$$

COD_{Mn} observations were transformed into surrogate observations for TOC according to the formula of Kortelainen (1993: eq. 1), except for the largest lakes (with long residence time) and their outflow streams where TOC was assumed to equal COD_{Mn}. VEMALA simulations of TOC specific leaching vary between 2 and 15 t km^{-2} year^{-1} depending on the peat-soil percentage in the sub-catchment.

The VEMALA model was calibrated in two steps. First, the catchment parameters characterizing daily TOC concentration–flow relationship were calibrated to minimize the difference between observed and simulated TOC concentrations in rivers for sub-catchment 14_6 (Saarijärvi) consisting of 54 3rd-level sub-catchments. In this calibration 540 parameters (10 parameters for each 3rd-level sub-catchment) were received. VEMALA model involves high amount of calibrated parameters, which requires TOC concentration observation data for calibration. When observation data for a particular 3rd-level sub-catchment are lacking, the model parameters are estimated from the data for the next sub-catchment downstream. However, the concentration–flow relationship is quite stable over the larger spatial areas, and therefore one parameter set calculated as the mean value of each parameter for 54 sub-catchments was used (also reducing the amount of calibrated parameters). The same parameter set was then used for all other sub-catchments, with the consideration that mean concentration-flow parameters are representing the other parts of Päijänne catchment. Saarijärvi sub-catchment was chosen because of high percentage of peat soils, providing the possibility to calibrate and validate concentration–flow parameters for peat soil dominated catchments. After that, the catchment parameters were set unchanged, and second a lake parameter characterizing C loss from lakes was calibrated using all observations from lakes.

Only one parameter was calibrated for each 3rd-level sub-catchment, i.e. C loss from lake's surface and sedimentation (k_rate). The daily C loss and sedimentation parameter is dependent on the air temperature. The k_rate value was calibrated to vary from 0.001 (largest lakes) to 0.005 (smallest lakes). A total of 291 lake parameters were calibrated for Päijänne catchment, which covers 26 459 km^2. For this size of lake-rich catchment the conceptual calibrated VEMALA model is in our view more appropriate than process-based models. A justification for the use of calibrated lake parameter is that the calibrated value of the k_rate parameter corresponded with Kortelainen *et al*. (2006b) findings that C losses per surface area unit were significantly higher in small lakes compared with large lakes.

Comparison between observed [TOC] values and [TOC] values calibrated with the VEMALA model for the lowest part of lake Päijänne for the period 1992–2015 is shown in Fig. 1. The goodness of the model was evaluated by ability to simulate mean, maximum and minimum TOC concentrations within reasonable limits compared with observed values. Observed and simulated mean [TOC] differed by only 1% (observed 6.38 mg l^{-1} and simulated 6.28 mg l^{-1}). Simulated range of concentration variation was lower in model predictions than in observations. Maximum simulated TOC concentration was 7.4 mg l^{-1}, but observed was 8.4 mg l^{-1}. TOC concentrations were slightly overestimated, well simulated and underestimated for the peri-

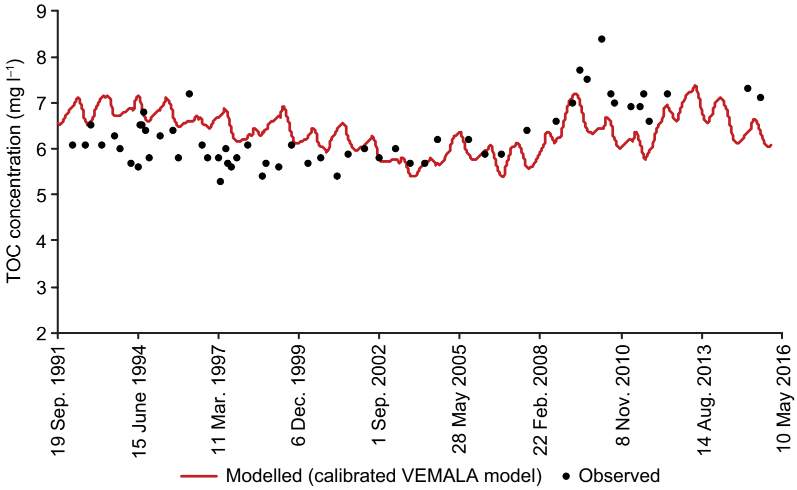


Fig. 1. Comparison between observed and modelled [TOC] values for the lowest part of lake Päijänne (Päijänne 76) for the period 1992–2015. Observed TOC values were derived from COD_{Mn} measurements.

ods 1991–2002, 2003–2009 and 2010–2015, respectively (Fig. 1). After high TOC inputs (98×10^3 t year^{-1}) during the wet year 2008, both observed and simulated TOC concentrations were rising. After that, the observed [TOC] remained higher than mean concentration, but the simulated concentrations fluctuated more depending on input fluctuations.

Three climate scenarios were used in this study. All scenarios use the emission scenario A1B, in which greenhouse gas emissions are rather high in the first part of the century and start to decrease from 2050 onwards (Nakićenović and Swart 2000). One of the climate scenarios used was Mean A1B, which is an average scenario calculated from 19 global climate models for Finland by the Finnish Meteorological Institute (Ruosteenoja *et al*. 2007). The other two scenarios were from Regional Climate Models (RCMs) obtained from the ENSEMBLES data base (van der Linden and Mitchell 2009). The scenarios were HIRHAM-ARPEGE-A1B (referred to as the "Dry" scenario since the precipitation increase is small) and RCA3-HadCM3-A1B (referred to as the "Wet" scenario since the precipitation increase is large). These two scenarios were selected from a larger ensemble of RCM scenarios to represent the uncertainty associated with climate change. Precipitation increase by 2040–2069 as compared with that in 1971–2000 was 11.5% in the Mean A1B scenario, 4.7% in the dry scenario and 16.2% in the wet scenario. Corresponding temperature increases were 3.2, 2.6 and 2.5 °C, respectively. The calibrated VEMALA model was used to simulate TOC concentrations and budgets for the present day and future conditions (1991–2100), using these climate change scenarios.

Water treatment processes

Helsinki Region Environmental Services Authority (HSY) is the largest drinking-water producer in Finland and it provides drinking water to the Helsinki metropolitan area. In Helsinki, HSY has two water-treatment plants (WTP), Pitkäkoski and Vanhakaupunki, which use water from lake Päijänne as their raw water. The raw water is transported to the treatment plants through the 120-km-long Päijänne water tunnel drilled in bedrock (construction was completed in 1982). The tunnel enables for a raw-water flow of 10 m^3 s^{-1} (annual flow 94 million m^3). The water-treatment process at both WTPs consists of the same steps: ferric sulphate coagulation, flocculation, horizontal sedimentation, rapid sand filtration, ozone disinfection, two-step activated carbon filtration, UV and chloroamine disinfection and pH adjustment.

The majority of TOC, 65%, is removed in the coagulation, sedimentation and sand filtration parts of the process. The following ozonation process breaks down DOM that is still present in the water and at the same time destroys viruses and other pathogens. As DOM is broken into smaller compounds, it becomes easier for microbes to use as nutrient. In the two-step activated-carbon filtration water flows through two activated carbon filters: the first works as a biological filter and the second as a physical filter. Of the remaining TOC, some 30% is removed in this step of the process. The main purpose of UV-disinfection is to control microbes that are released during the preceding activated filtration. Chloroamine disinfection is used to maintain good water quality in the distribution network. Adjusting pH is important in different parts of the process so that the conditions for different process parts are optimal. In the final pH adjustment, pH is raised to 8.5 to make the water less corrosive.

Results and discussion

Observed changes in COD_{Mn}/TOC concentrations

Median COD_{Mn} concentrations at the lake stations in the different sub-catchments varied between 4.9 and 25.5 mg l^{-1} (5.2–19.2 mg l^{-1} TOC calculated with Eq. 1), and at the river stations between 5.9–17 mg l^{-1} (5.9–13.4 mg l^{-1} TOC) (Fig. 2). Most of the water draining into the lake enters from the north. Concentrations were lower in the southern part of the lake mainly due to in-lake mineralization and sedimentation processes. In northern lakes, DOC is efficiently removed by microbial and photochemical degradation (Schindler *et al.* 1997, Vähätalo *et al.* 2010).

Since our focus was on studying the recent increases (and potential future changes), and its implications for water use, the year 2000 was selected as the starting point for the statistical trend analysis of the data from the different sub-catchments. The slope for the change in [COD_{Mn}] was positive for all the selected 18 sub-catchments and varied between 0.13 and 0.33 mg l^{-1} year^{-1} at the stations where the change was statistically significant ($p < 0.05$). The %change during the study period varied between 18% and 47% (Fig. 2).

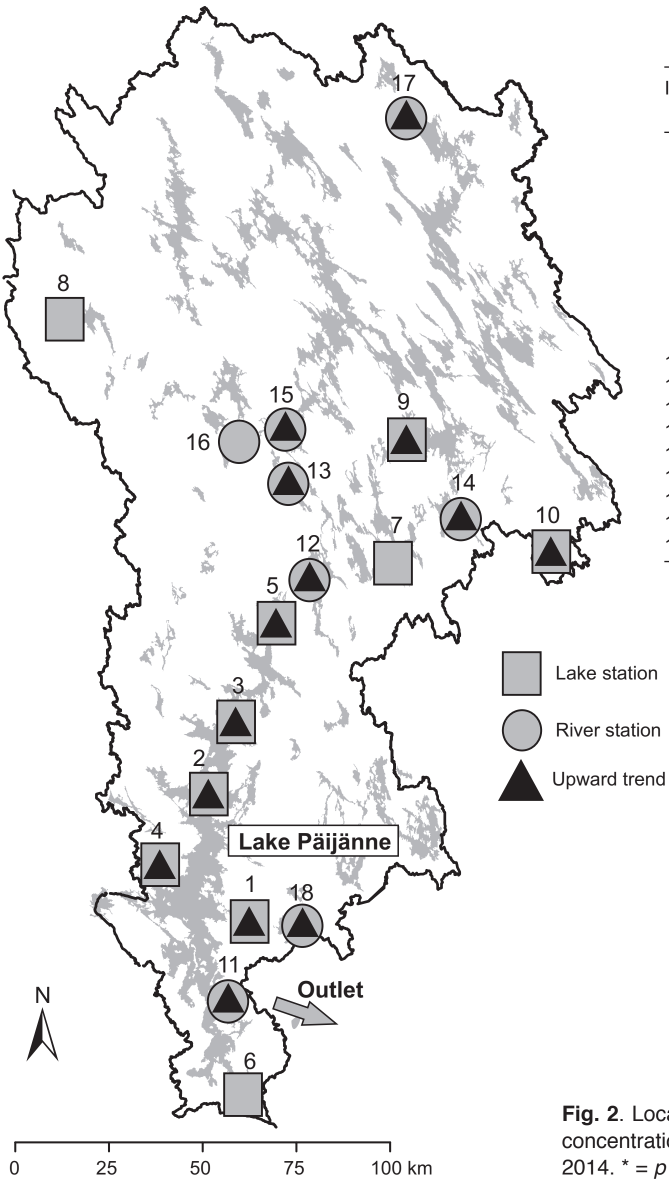
In general, the long-term change in COD_{Mn}/TOC in lake Päijänne showed U-shaped pattern (Fig. 3).

COD_{Mn} concentrations decreased from 1975 to 1995 mainly due to decreased point source loading, and clear increase started approximately in mid-2000s. The BOD_7 and COD_{Cr} loads originating from point sources in 2013 were 878 t and 11 800 t, respectively. In 2013, the three pulp and paper industrial complexes were responsible for 70% and 89% of BOD_7 and COD_{Cr} point-source load, respectively. During the last three decades, point-source loads of BOD and COD_{Cr} decreased markedly in the lake Päijänne catchment area as well as in other parts in Finland (Räike *et al.* 2012), mainly due to improved wastewater treatment. BOD loading has decreased since 1975 by 98%. Rapid decline in COD_{Cr} load had been observed before the year 1995, after which much slower decrease occurred (Räike *et al.* 2012).

Also TOC concentrations in raw water of the Päijänne tunnel measured by HSY showed an increase, and are currently at a higher level than in the beginning of the measurement period (Fig. 4). There is a gap in the monitoring data due to a repair of the tunnel in 2008.

As summarized above, many different processes could potentially explain the observed changes in TOC/COD_{Mn} concentrations. Impacts of multiple factors are accentuated in very large basins like lake Päijänne with varying land-use, and affected by changes in those factors occurring at different spatial scales. Instead of searching for a single overwhelming factor, more attention has recently been paid to the fact that there might be several factors acting together (Roulet and Moore 2006, Lepistö *et al.* 2008, Sarkkola *et al.* 2009), and that the relative importance of different factors may be scale-dependent (Clark *et al.* 2010). The factor that clearly is not causing the recently observed increase in organic matter in lake Päijänne is wastewater loading, since reported point source loading observations indicate steady decrease (Räike *et al.* 2012). Without this decrease, the observed increase in TOC/COD_{Mn} in the surface waters would likely have been even larger.

Linear regression analysis revealed no relationships between COD_{Mn} increases and land-use related factors or specific catchment characteristics at the selected 18 sub-catchments (Fig. 5). Finnish flat topography and cold climate are favourable for DOC production and peatlands



Id	*n*	Median (mg l^{-1})	Slope (mg l^{-1} a^{-1})	Change (%)
1	57	6.9	0.15**	32
2	85	8.9	0.19**	32
3	76	7	0.17**	37
4	66	11.1	0.2	
5	74	8.3	0.16**	29
6	83	4.9	0.04	
7	56	15.6	0	
8	59	25.5	0.2	
9	77	6.4	0.20**	47
10	65	11.7	0.25*	32
11	165	5.9	0.14***	36
12	117	9	0.13**	22
13	117	11.5	0.14**	18
14	80	8	0.23***	44
15	117	6.4	0.17***	40
16	121	17	0.25	
17	59	13	0.33**	38
18	58	6.6	0.19**	43

Fig. 2. Locations of the sampling sites, median COD_{Mn} concentrations and COD_{Mn} trends between 2000 and 2014. * = $p < 0.05$, ** = $p < 0.01$, *** = $p < 0.001$.

have been shown to be the major source of riverine DOC in Finland (Arvola *et al*. 2004, Mattsson *et al*. 2005, Räike *et al*. 2012). Draining of peatlands affected DOC export in many areas in Finland (Heikkinen 1994), although according to Alasaarela and Heinonen (1984), long-term patterns in COD_{Mn} could not be linked to peatland drainage. Besides peatland draining, forest management practices such as clear-cutting and ditching temporarily enhance leaching of DOC to surface waters (Kortelainen and Saukkonen 1998, Nieminen 2004).

According to the stepwise multiple regression analysis, the variation in COD_{Mn} was to some extent explained by pH, alkalinity and SO_4 concentration in three sub-catchments (Table 3). At one river site, runoff explained 47% of the variation in COD_{Mn}. The explaining power of the models varied between 9% and 64% (*see* Table 3). When the data from all sub-catchments were combined and used in the analysis, alkalinity, pH, SO_4 and water temperature explained 71% of the variation in COD_{Mn} (*see* Table 3). Because not all explaining variables were avail-

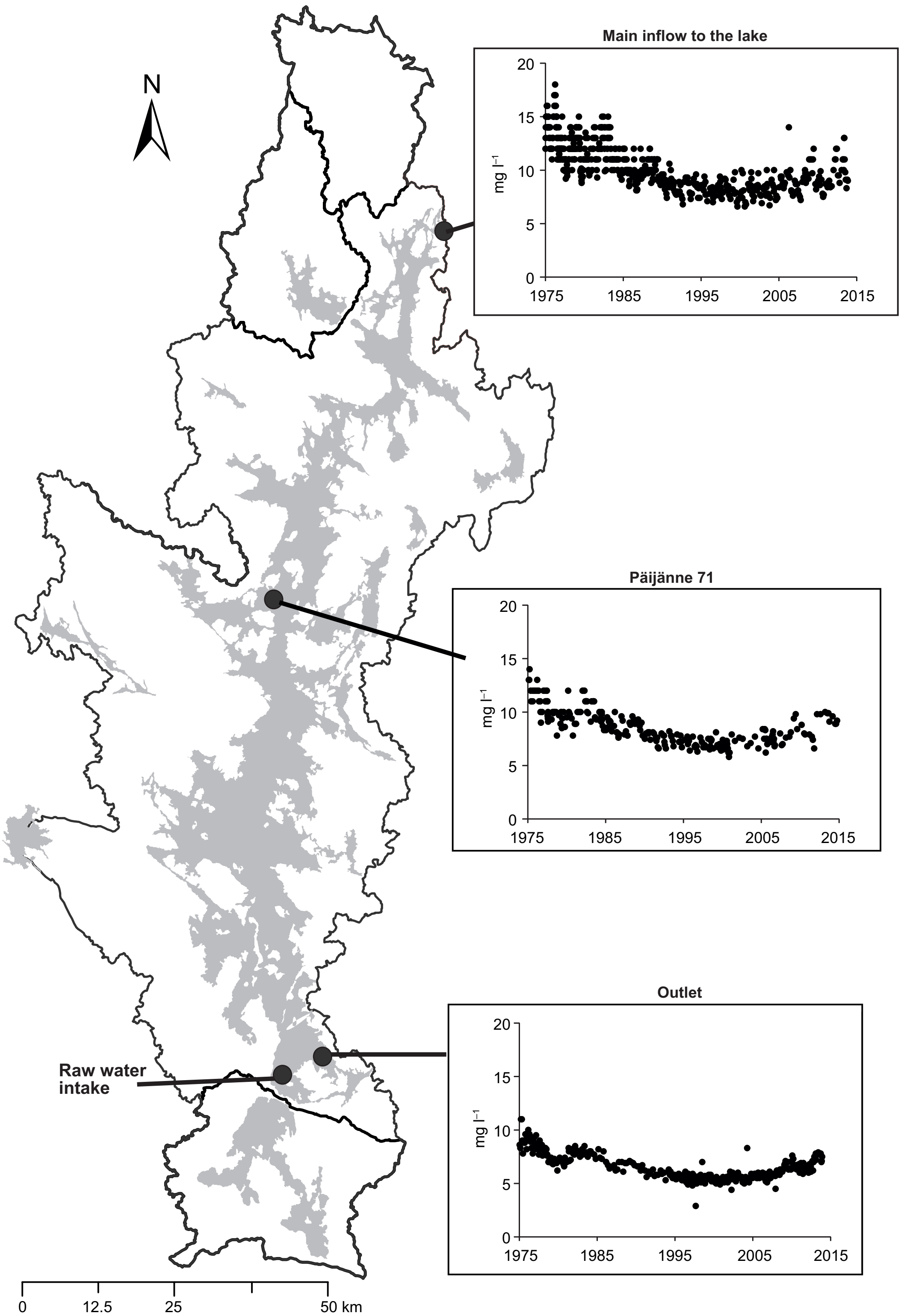


Fig. 3. Long-term (1975–2014) development of COD_{Mn} concentration at three selected stations in lake Päijänne. The location of the raw-water intake is also shown.

Fig. 4. TOC concentrations in the Päijänne Tunnel in 2000–2015.

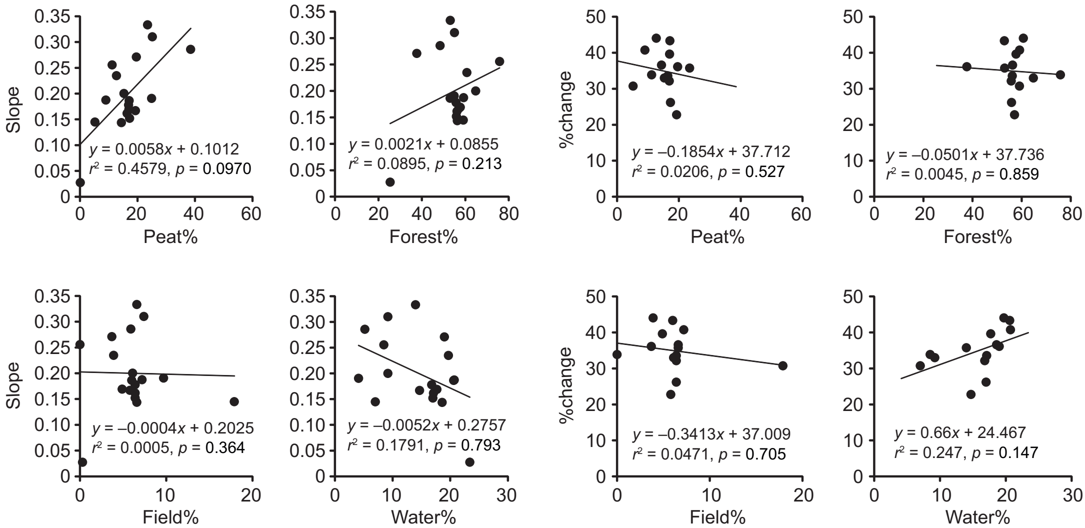


Fig. 5. Statistical relationships between land-use characteristics, trend slopes and %changes in the 18 sub-catchments. Data for individual catchments are presented in Table 2 and Fig. 3. Note that all dependencies are statistically insignificant (all p values > 0.05).

able for 14 sub-catchments, the analysis was also carried out without alkalinity and SO_4. In this analysis, the explaining powers of the models were 64% and 38%, respectively (*see* Table 3).

Hydrological factors play a major role in determining organic matter fluxes, also in Finland (e.g. Lepistö *et al*. 2008, Räike *et al*. 2012, Lepistö *et al*. 2014), and the importance of runoff was indicated also at one of the inflowing-river sites at Päijänne (Table 3). The water-residence time in lake Päijänne is 2.5 years (Table 1), which tends to damp the effect of hydrological factors at all the lake sites and lake outlet (site Kalkkistenkoski, *see* Table 3).

In many studies, the increase in the river and lake water DOC and TOC concentrations has been linked to the decrease in the amount of acid atmospheric deposition (Vuorenmaa *et al*. 2006, Monteith *et al*. 2007, Erlandsson *et al*. 2011). The fact that SO_4 was included into the multiple regression equations with a negative coefficient (Table 3) indicates influence of acid deposition changes on COD_{Mn} concentrations. TOC in natural waters is both a natural background source of acidity and a pH buffer in low alkalinity waters, and therefore affects the acid–base balance (Kortelainen *et al*. 1989). The observed TOC/COD_{Mn} changes could thus also partly explain the role of alkalinity and pH in the equations.

Several studies in Finland have recently investigated trends in organic carbon. Vuorenmaa *et al*. (2006) studied trends in TOC concentrations in the period 1987–2003 in 13 small forest lakes. Decreasing SO_4 deposition and improved acid–base status in soil due to the recovery from acidification increased mobilization of organic acids and TOC. There was little evidence that the long-term increasing trend in TOC concentrations was related to long-term changes in runoff. The study of Sarkkola *et al*. (2009) used mixed-model approach in headwater streams in eastern Finland and identified stream water temperature, precipitation and peatland percentage to be the most important variables explaining annual and most of seasonal TOC concentrations. The atmospheric deposition of SO_4, NH_4, and NO_3 decreased significantly during the studied period, but no significant link with TOC concentration was found in this low deposition area. Räike *et al*. (2012) studied changes in TOC fluxes in the period 1975–2010 using the data from 29 Finnish river basins. They found increasing normalized TOC fluxes in 8 river basins, decreasing in 7 basins, and no trends in 14 basins. Inter-annual variation in TOC export was high and controlled mainly by hydrological changes. There was no overall trend in annual water flow, although winter flow showed slight increase in northern Finland. In another study, Räike *et al*. (2016) concluded that even if TOC concentrations were commonly increasing in those 29 river basins, it was not clearly reflected in TOC export trends. This was because changes in water flow affected TOC export to the sea. Lepistö *et al*. (2014) showed that seasonal and long-term patterns in TOC in the large northern Simojoki basin were controlled primarily by changes in soil frost, seasonal precipitation, drought and runoff. Almost 50-year monitoring and INCA-C modelling in this study demonstrated that climate, not forestry, controlled TOC fluxes.

In agreement with previous studies (Roulet and Moore 2006, Lepistö *et al*. 2008, Sarkkola *et al*. 2009) we could thus not identify a dominating single factor causing the observed TOC/COD_{Mn} changes in the large lake Päijänne catchment, which can be expected to be better buffered against changes than smaller lakes or rivers. The effects of multiple factors are accentuated in very large basins like Päijänne, and it seems evident that the observed recent changes were here mainly due to a combined effect of several factors of climate and atmospheric deposition. The influence of changes in land-use-related factors seemed to be less important.

Prediction of future changes in TOC concentrations

The mean TOC concentration in 2001–2010 at the Päijänne-Asikkalanselkä station was 5.8 mg l^{-1}. According to the VEMALA model simulations with the three different climate

Table 3. Multiple linear regression equations for predicting COD_{Mn} at 4 sampling sites with sufficient data, and for the combined data set including all 18 sites (all relations are significant at $p < 0.001$). Alkalinity (ALK), pH, SO_4, water temperature, air temperature and runoff are used as explaining variables. For sites ($n = 14$) that did not have enough data from all the explaining variables equations were not created. Locations of the sites are shown in Fig. 3. The site Kalkkistenkoski is the outlet of lake Päijänne.

ID#			r^2	n
	River sites			
11	Kalkkistenkoski 4800	$\ln(COD_{Mn}) = 3.5 + 0.68\ln(ALK) – 0.35\ln(SO_4)$	0.09	154
17	Koivujoki 15300	$\ln(COD_{Mn}) = 4.7 – 0.38\ln(ALK) – 0.41pH$	0.49	36
18	Nuoramoinen 4600	$\ln(COD_{Mn}) = 2.0 + 0.12\ln(Runoff)$	0.47	38
	Lake site			
4	Kangastakunen	$\ln(COD_{Mn}) = 6.4 – 0.55pH – 0.43\ln(SO_4)$	0.64	79
	All sites[1]	$\ln(CODMn) = 8.7 + 0.39\ln(ALK) – 0.69\ pH – 0.66\ln(SO_4) + 0.01watertemp$	0.71	389
	All sites[2]	$\ln(COD_{Mn}) = 5.2 – 0.30pH – 0.57\ln(SO_4)$	0.64	393
	All sites[3]	$\ln(COD_{Mn}) = 7.0 – 0.70pH + 0.01watertemp$	0.38	1501

1) Data from all 18 sites: alkalinity, SO_4, pH, water temperature, air temperature and runoff used as explaining variables.

2) Data from all 18 sites: SO_4, pH, water temperature, air temperature and runoff used as explaining variables.

3) Data from all 18 sites: pH, water temperature, air temperature and runoff used as explaining variables.

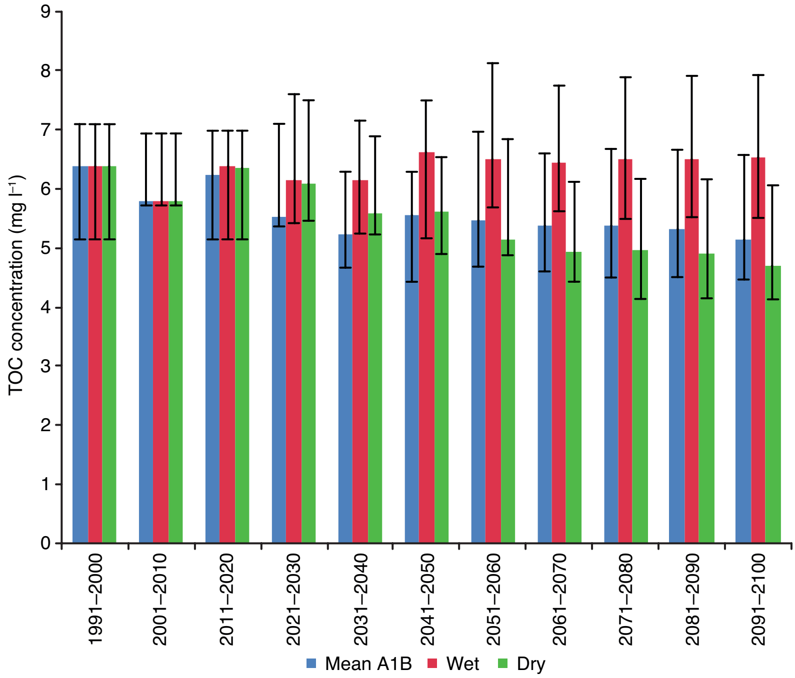


Fig. 6. VEMALA model predictions of TOC concentrations for the Päijänne-Asikkalanselkä station for the period 1991–2100, according to three climate change scenarios (Mean A1B, Wet, Dry). Mean values with daily minimum and maximum concentrations (whiskers) are shown.

change scenarios (Mean A1B, Wet, Dry; Ruosteenoja *et al*. 2007, van der Linden and Mitchell 2009), large changes in TOC concentrations are not expected. TOC concentrations were predicted to decrease by 11% (to 5.15 mg l^{-1}) in the Mean A1B scenario and by 19% (to 4.69 mg l^{-1}) in the Dry scenario by 2091–2100 (Fig. 6). In the Mean A1B scenario despite increased inflow discharge (23%) there will also be increased outflow (26%) from the lake.

The residence time in lake Päijänne will decrease in the Mean A1B scenario by about 19% by the end of the century (from 894 days 2001–2010 to 726 in 2091–2100; *see* Table 4), because of the increase in runoff. Accordingly, in the Wet scenario the residence time will decrease considerably, by 36% (from 894 days 2001–2010 to 573 in 2091–2100), but in the Dry scenario the residence time will practically remain the same. The water and material balance between inflow, outflow water and loading is determining the TOC concentrations of the lake. The other process reducing the TOC concentrations in the lake is increased C loss through outgassing and sedimentation (for the Mean A1B scenario from 26.4 × 10^3 t $year^{-1}$ 2001–2010 to 32.3 × 10^3 t $year^{-1}$ in 2091–2100; *see* Table 4). If the TOC balance in the lake is positive then there will be an increase in TOC concentration. In the Wet scenario, TOC would increase by 13% by the end of the century (Fig. 6), due to the considerably higher inflow: runoff would increase considerably (by 61%) as well as inflow loading (by 70%) by 2100. Due to the increase in TOC outflow (by 86%) and C loss through outgassing and sedimentation (by 45%), the TOC balance is not changing remarkably (Fig. 7), and therefore the TOC concentration would increase only by 13%. Due to the assumptions in deriving the climate scenarios (*see* Material and methods) some differences among different modelled periods are predicted (Fig. 6).

Predictions of TOC leaching in VEMALA are based on a concentration–flow relationship (Eq. 2), and the model includes simplified in-lake processes (*see* Huttunen *et al*. 2015, 2016). Those process formulations are supported by the multiple regression analysis which identified runoff and lake water temperature as predicting variables (Table 3). Also the studies of Räike *et al*. (2012) and Lepistö *et al*. (2014) showed the importance of runoff for controlling interannual variation in TOC export in Finnish rivers. VEMALA is based on the WSFS operational hydrological flood forecasting modelling system, and therefore runoff processes are very well quantified. An effort was also made in the present study to use real measured data from Finnish lakes (Kortelainen *et al*. 2006b) for estimation of the C loss parameter in the VEMALA model. We did not consider omission of atmospheric deposition related processes in the VEMALA modelling to be a major source of error in the predictions. Although the multiple regression analysis (Table 3) indicated some effect of decreasing acid deposition (decreasing SO_4), this decline levelled off (Vuorenmaa *et al*. 2017), and only small changes were also predicted in the future for Finland (Gauss *et al*. 2016).

Simulated mean annual TOC concentration leached from land areas is related to peat and mineral soil distribution in VEMALA, which should account for some of the effect of land-use characteristics (Fig. 5). The overall results of VEMALA are also supported by detailed C process modelling (Holmberg *et al*. 2014, *see* below). It should also be recognized that Päijänne is a very large complex catchment (26 459 km^2) and in this type of large-scale modelling, a balance has to be reached between data availability, complexity of the model formulations, and computational efficiency. Consequently, some simplifications are therefore necessary at this spatial scale.

VEMALA was also used to construct an integrated TOC balance for lake Päijänne in the present situation and assuming the three climate change scenarios for the period 2091–2100 (Fig. 7). Those calculations clearly showed the need for understanding the interactions among the main processes regulating lake C concentrations and fluxes.

Even though VEMALA is based on a simplified model structure, similar modelling results have been obtained also using a much more process-oriented model system applied to an intensively studied small Finnish research catchment (area 30 ha). Holmberg *et al*. (2014) applied a novel model chain using HBV, INCA-C and MyLake to simulate runoff, snow dynamics, ice cover, soil moisture, lake thermal stratification and in-lake DOC concentrations in Valkea-Kotinen, a headwater lake in a forest-covered boreal catchment in southern Finland. One of the most comprehensive ecosystem data sets is available for this site (Rask *et al*. 2014). Impact response surfaces (IRSs) were constructed with 63 combinations of changes in temperature (–2 to +14 °C) and precipitation (–10% to +50%). Using this approach, slightly decreasing (–6%) in-lake DOC concentrations were predicted, primarily due to decreased terrestrial runoff, as well as longer water residence times and greater opportunity for organic carbon processing in the lake. Other studies also indicated climatic regulation of C-mineralization processes in Finnish lakes (Rantakari and Kortelainen 2005, Hari *et al*. 2008, Forsius *et al*. 2010). Studies in North

Table 4. VEMALA model simulations of C loss from lake's surface and sedimentation ($\times 10^3$ t year^{-1}) and residence time (days) for the three climate change scenarios (Mean A1B, Wet, Dry) for different time periods.

	C loss from lake's surface and sedimentation			Residence time		
	Mean A1B	Wet	Dry	Mean A1B	Wet	Dry
1991–2000	27.6	27.6	27.6	878	878	878
2001–2010	26.4	26.4	26.4	894	894	894
2011–2020	30.2	31.7	31.0	760	732	745
2021–2030	24.9	28.2	26.2	903	770	833
2031–2040	26.0	30.5	25.6	901	728	886
2041–2050	29.1	33.3	26.8	782	642	824
2051–2060	28.7	32.7	24.8	797	661	901
2061–2070	29.2	33.2	25.0	775	643	892
2071–2080	29.9	34.2	25.5	772	637	894
2081–2090	30.7	35.3	25.9	756	619	880
2091–2100	32.3	38.3	26.0	726	573	873

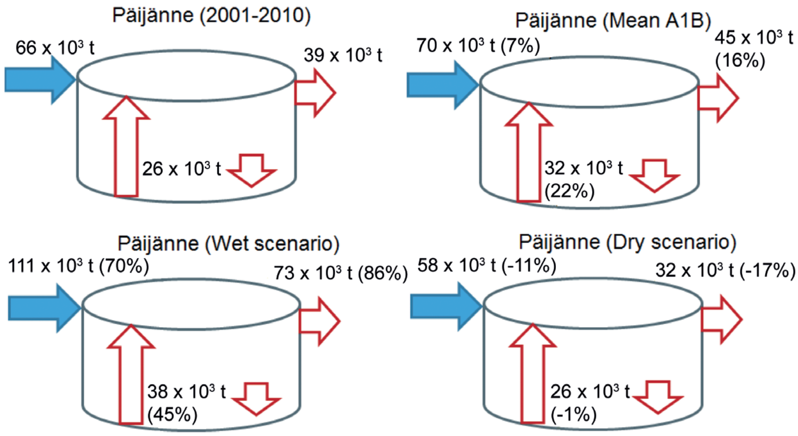


Fig. 7. Integrated TOC balance for lake Päijänne in present situation (2001–2010) and assuming the three climate change scenarios for the period 2091–2100. Percentages show the proportional change in relation to the period 2001–2010. The VEMALA model was used for the calculations.

America showed the hydrologic residence time to be one of the key factors in determining the fate of DOC in lakes, together with the recalcitrance of the DOC and lake temperature (Hanson *et al*. 2011). It was shown that relatively small changes in residence time can cause large shifts in the proportion of lake DOC that is exported rather than mineralized. The proportional water area of the catchment (Water%), which also indicates residence time, predicts rather well TOC retention in Finnish freshwaters (Räike *et al*. 2016). Also Rantakari *et al*. (2004) and Mattson *et al*. (2005) found that the percentage of water area in the catchment is an important regulator of TOC concentrations. Furthermore, this factor can regulate the molecular composition of DOM (Kothawala *et al*. 2014).

According to the MyLake model predictions for lake Päijänne (Forsius *et al*. 2013), temperature stratification during summer would last longer and the thermocline would be deeper at the end of the century in the climate change scenario A1B. Temperature in the topmost layer (epilimnion) would be 2–3 °C higher than at present. In winter, there would not be permanent ice cover every year, and the lake is expected to freeze and melt several times in the course of the same winter. It thus seems evident that future climate change will emphasize the role of lakes in landscape-scale carbon and nutrient cycling, lead to changes in greenhouse gas emissions from the lake surfaces (*see* Table 4 and Fig. 7), and affect lake biota in many ways.

Implications for water treatment

According to the VEMALA model results, the TOC concentration in lake Päijänne would increase slightly by 2100 only in the Wet scenario (Fig. 6). The seasonal variation in TOC concentration, on the other hand, would increase in all scenarios. Earlier melting periods in winter and spring, reduced the role of the spring runoff peak, and higher temperature and precipitation in autumn increased the role of the autumn export peak. Similar results were obtained by Rantakari *et al*. (2010) for small headwater streams. These effects will further add to the altered seasonal dynamics of TOC and TON (total organic nitrogen) along the hydrological pathways (Mattsson *et al*. 2015). Greater seasonal variation may affect the HSY water treatment process mostly in terms of adjusting doses of chemicals so as to keep the water quality excellent. Compared with the predicted potential slight increase in TOC concentration or increase in seasonal variation, the possible changes in quality of DOM would be of more concern, because HSY's water treatment process is designed to treat water that consists mainly of hydrophobic organics. If the DOM quality changes to more hydrophilic, treatment process will not be able to remove DOM as effectively as nowadays.

An increase in TOC concentration in Wet scenario is mainly because of greatly increased leaching (Fig. 7). The VEMALA model results suggest that the residence time in lake Päijänne decreases in the Mean A1B scenario by 19%

and in the Wet scenario by 36% by the end of the century (Table 4). Studies conducted in Lake Mälaren in Sweden, showed clear relationship between residence time and hydrophobicity of DOM (Köhler *et al*. 2013). With short residence time in-lake processes have less time to process DOM, resulting in DOM of more hydrophobic character. When residence time increases DOM becomes consequently more hydrophilic. Lakes with longer water residence time are thus expected to contain a greater proportion of hydrophilic DOM (Köhler *et al*. 2013), which is more resistant to removal by conventional drinking water treatment processes.

Modelled decrease in residence time in lake Päijänne particularly in the Wet scenario (Table 4) means that quality of DOM will change to more hydrophobic when it reaches HSY's raw-water extraction point. On the other hand, assuming the climate change scenario A1B, the temperature in the topmost layer of lake Päijänne is expected to increase by 2–3 °C (Forsius *et al*. 2013). This would enhance the in-lake mineralization processes, and would likely counteract some of the effect of decreased retention time on DOM quality. Also the study of Hanson *et al*. (2011) pointed out the complex interactions between residence time, lake temperatures and DOC quality in regulating the lake DOC concentrations and fluxes.

From the water treatment point of view, it thus seems that the changes in surface water DOM concentration and quality can be dealt with, at least in the case of HSY water treatment processes. TOC concentration is expected to increase slightly by 2100 only if precipitation increases significantly. At the same time DOM is expected to become slightly more hydrophobic, as residence time in lake Päijänne decreases, making the organics easier to remove by coagulation. These results would suggest that HSY's current treatment processes are able to meet the challenges set by climate change in form of changed raw-water TOC concentration and quality, and that no major improvements to the treatment processes due to those changes are likely needed.

Conclusions

There was clear evidence of increasing concentrations of TOC/COD_{Mn} in lake Päijänne and its sub-watersheds during the studied period 2000–2014. The slope for the change in COD_{Mn} was positive at all the selected 18 sub-catchments and change was statistically significant at a majority (n = 13) of those stations. Also the concentrations in the raw-water intake increased during this period. The long-term changes (1975–2014) in organic matter concentrations showed a U-shaped pattern, caused by large decrease in point-source loadings during earlier decades, followed by increases since the mid-2000s. Recent increases in DOC have been documented in many previous studies in Finland and other countries in the northern hemisphere.

There has been a long-term scientific debate regarding the causes for the observed DOC/TOC increases, and processes related to changing climatic conditions (hydrological processes and temperature), atmospheric deposition, and land-use have all been suggested as likely causes. We could not identify a dominating single factor causing the observed recent changes in the lake Päijänne watershed, and it seemed that the changes are mainly due to a combined impact of climate and atmospheric deposition. The influence of changes in land-use related factors seemed to be less important. The impacts of multiple drivers are accentuated in very large basins like Päijänne.

The lake DOC concentrations are determined by a complex system consisting of the water and material balance between inflow, outflow water and loading, as well as in-lake regulating processes of mineralization, sedimentation and outgassing. The VEMALA model simulations with three quite different climate change scenarios, indicated that large changes in organic matter concentrations are not likely, and even decreasing concentrations were predicted in two of the scenarios. However, particularly regarding the Wet scenario, the integrated C balance calculations (Fig. 7) indicated potentially great changes in C fluxes and lake retention time, having a large impact of several key ecosystem processes such as transport of organically bound nutrients to sea areas and the importance of surface waters in the overall landscape C budgets. The VEMALA model results are generally supported by applications of more detailed C process models, applied to intensively studied small research catchments in Finland.

Since large increases in average concentrations of organic carbon are not expected in lake Päijänne, major difficulties for the water treatment processes are not foreseen. Also the fact that the retention time of the lake was predicted to decrease (particularly in the Wet scenario), likely causing the organic matter to be more hydrophobic and easier to remove, points to the fact that treatment process can cope with the expected changes. The greatest concerns regarding the water treatment process are probably related more to changes in seasonal variation (including frequency of extreme events) and quality of the organic matter, than the changes in long-term average concentrations.

Uncertainties remain regarding the reasons for the observed TOC/COD_{Mn} changes, process descriptions in our modelling systems, as well as in the future climate change scenarios. The uncertainties regarding precipitation changes in the scenarios are larger than for temperature, which is a particular concern for hydrologically based catchment models. Since the C processes in these catchment-lake systems are inherently complex and important for a number of central ecosystem processes and water use, further work in this field is clearly still needed.

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