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Jonna Kuha

Automated Water Quality Monitoring of Humic Lakes by Using the Optical Properties of Water

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ABSTRACT

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Automated water quality monitoring (AWQM) is becoming increasingly common in lakes worldwide. The history of AWQM is relatively short and standard calibration procedures for the measured variables are largely yet to be established. The use of optical AWQM sensors, developed in oceanic environments, raises new questions on the diverse effects which humic compounds may have on the automated optical measurements in inlands waters. The focus of this thesis was to characterize the effects of coloured dissolved organic matter (CDOM) on optical *in situ* measurements of organic matter (OM) and chlorophyll (Chl) in lakes with varying humic content, and to use AWQM data as a part of traditional monitoring and independently to study current topics in limnology; weather-related episodic events on lake mixing and the effect of hypolimnetic oxygenation (HLO) on the nutrient conditions in a humic lake. The data were collected from AWQM stations on lakes in Finland and Ireland and involved both AWQM and discrete data from open water season. The study on the quality of CDOM revealed that OM fluorometers represented the humic content in water column reliably. However, OM fluorometers did not detect changes in the quality of OM. *In situ* Chl fluorometer was affected by background OM. The effect was less important when OM remained at constant level. Effects of weather-related episodic events on lake mixing and on Chl-patterns studied with AWQM showed Finnish lakes to face multiple short-lived mixing events during stratified period. The Chl-a content in the lakes varied accordingly. A case study conducted on Jyväsjärvi showed that HLO had a significant effect on the temperature structure of the lake but had little long-term effect on its trophic status.

Keywords: Automated monitoring; chlorophyll a; coloured dissolved organic matter; dissolved oxygen; episodic events; fluorescence; temperature.

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original papers, which will be referred to in the text by their Roman numerals I–IV.

I had a significant contribution in planning and data collection and executing all studies. Planning the studies was mainly done together with JK (I–IV), MJ (II, III), ER (I), EdE (I) and EJ (I). Data collection and sample analysis was done together with ER (I), EdE (I), EJ (I), MN (I) and TR (I). AWQM data were collected and analysed as a joint project with co-authors of III and IV. I was responsible for writing the preliminary manuscripts. All papers were finalized with the co-authors.

I Kuha J., Ryder E., de Eyto E., Jennings E., Nieminen M., Roiha T. & Karjalainen J. 2016. How does the changing composition of dissolved organic matter (DOM) impact on the use of *in situ* single-wavelength FOM sensors? Manuscript.

II Kuha J., Järvinen M. & Karjalainen J. 2016. Use of single-wavelength fluorometers for *in situ* chlorophyll monitoring of humic lakes. Manuscript.

III Kuha J., Arvola L., Hanson P.C., Huotari J., Huttula T., Juntunen J., Järvinen M., Kallio K., Ketola M., Kuoppamäki K., Lepistö A., Lohila A., Paavola R., Vuorenmaa J., Winslow L.A. & Karjalainen J. 2016. Response of boreal lakes to episodic weather-induced events. Manuscript.

IV Kuha J., Palomäki A., Keskinen T. & Karjalainen J. 2016. Negligible effect of hypolimnetic oxygenation on the trophic state of Lake Jyväsjärvi, Finland. *Limnologica* 58: 1–6.

ABBREVIATIONS

AU	arbitrary units
AWQM	automated water quality monitoring
CDOM	coloured or chromophoric dissolved organic matter
Chl	chlorophyll
Chl-a	chlorophyll-a
C1–C5	PARAFAC components 1–5
ΔDO	hypolimnetic DO consumption rate, mg l^{-1} d^{-1}
DO	dissolved oxygen
DOC	dissolved organic carbon
DOM	dissolved organic matter
EEM	excitation-emission matrix
F_{max}	maximum fluorescence intensity, RU
FOM	fluorescent organic matter
GF/C	glass fibre filter, average pore size 1.2 µm
GPP	gross primary production, mg O_2 l^{-1} d^{-1}
H	heat content, J
HLO	hypolimnetic oxygenation by pumping oxygen rich surface water to the hypolimnion
HOx	hypolimnetic oxygenation
in situ	on site measurement
NEP	net ecosystem production, mg O_2 l^{-1} d^{-1}
OFF	HLO off
OM	organic matter
ON	HLO on
PARAFAC	parallel factor analysis
PCA	principal component analysis
PC1	principal component 1
PC2	principal component 2
peak C	F_{max} of EEM region; excitation 350–370 nm / emission 430–450 nm
ρ	temperature coefficient for FOM sensors
R	ecosystem respiration, mg O_2 l^{-1} d^{-1}
RFU	relative fluorescence unit
RFU_{20}	relative fluorescence unit in reference temperature of 20 °C
RP	event return period, days
RU	Raman units
RU_{wl}	Raman units at FOM sensor wavelength
S	Schmidt stability index, kJ cm^{-2}
TN	total nitrogen, µg l^{-1}
TP	total phosphorus, µg l^{-1}
U_{10}	wind speed at 10 meters height, m s^{-1}

1 INTRODUCTION

1.1 Need for AWQM

Freshwater lakes provide numerous important ecosystem services, such as drinking water, fisheries, and recreation. It is likely that these services will come increasingly under stress in future (Aylward *et al.* 2005, Kratz *et al.* 2006). Non-linear dynamics in lake ecosystems (Carpenter *et al.* 2011) coupled with complex physical and biological processes (Hamilton and Schladow 1997) require monitoring on adequate temporal and spatial scales to develop knowledge on lake ecosystem processes and functioning. Sudden phenomena, such as mixing events and short-lived algal blooms, can affect bio-chemical processes and higher organisms of the lake (Carpenter *et al.* 2015) but may remain outside the detection limit of traditional monitoring. Abrupt changes in lake ecosystems are often driven by weather-related events (Jennings *et al.* 2012, Crockford *et al.* 2014). Due to their short-term nature, they are difficult to study with conventional water sampling. Variability in ecological systems affects the general public and raises a need for careful consideration of lake management by policy makers (Williamson *et al.* 2014). Modern tools, such as AWQM are needed to observe this variability (Benson *et al*. 2009).

New developments in sensor and network technology promise advances in how high-frequency data can be collected *in situ* (Porter *et al.* 2005, Benson *et al*. 2009). Research groups around the world are interested in increasing the amount of data (Porter *et al.* 2005, Meinson *et al.* 2016). Physical and biological processes in lakes, for example effects of circulation patterns on nutrient cycling, metabolism and algal blooms, have been under comprehensive study during the past decades (Hamilton *et al.* 2014, Meinson *et al.* 2016). Building new hypothesis and understanding previously unknown phenomena becomes possible by using AWQM as a part of traditional research or as a tool of its own (Williamson *et al.* 2014).

1.2 Current AWQM and its limitations

Frequent time-series data is irreplaceable in designing environmental models for lakes and their catchment areas. However, well-designed AWQM networks have to be established to accomplish accurate data collection (Meinson *et al.* 2016). Instrument management is a key task in AWQM. This includes deployment, configuration, and calibration (Porter *et al.* 2012, Campbell *et al.* 2013). Location design and maintenance plan are also important. Researchers working with the AWQM should be familiar with the functioning and character of the study area to be able to best assess the quality of the data (O'Flynn *et al.* 2010).

To reduce the costs of AWQM it is essential to know whether simple parameters, such as temperature, DO, pH and conductivity that can be measured *in situ*, provide sufficient information for monitoring purposes (Becq 1994). The most important water quality parameters in terms of human health are not yet automatically monitored, i.e. variables associated with ecotoxicology and metals. Many automatically measured water quality parameters are indirect measures of the target variable. The use of optics in AWQM has gained popularity due to low cost and low power requirements of LED-light-based *in situ* fluorometers (Ryder *et al.* 2012, Meinson *et al.* 2016). At present, fluorescence *in situ* measurements include detection of algal pigments; Chl-a, phycocyanin and phycoerythrin, or oil spills, and measurements of FOM and turbidity, for example.

1.3 Optical AWQM in humic lakes

Commercially available submersible fluorometers are becoming increasingly common in AWQM of inland waters (Watras *et al.* 2011, Downing *et al.* 2012, Ryder *et al.* 2012, Meinson *et al.* 2016). Brought in from oceanic environments, the use of optical sensors in inland waters is challenging because of the high concentrations of CDOM. A problem well documented in the coastal research (Goldman *et al.* 2013) and remote monitoring (Carder *et al.* 1989), humic substances in water interfere with optical measurements (Leppä *et al.* 1995, Proctor and Roesler 2010, Zeng and Li 2015). Calibration procedures for using *in situ* optical sensors in inland water are yet to be established.

Calibration of *in situ* Chl fluorometers for water OM content is an essential procedure when interpreting data measured in humic lakes since OM can cause high background fluorescence to optical Chl-a monitoring (Leppä *et al.* 1995, Beutler *et al.* 2001, Proctor and Roesler 2010, Zeng and Li 2015). Relatively little is known about the variation in OM background fluorescence and the effects it has on *in situ* Chl fluorescence measurements (Proctor and Roesler 2010). Interpretation of *in situ* Chl data is not straightforward as the efficiency of Chl fluorescence is also species dependent (Strain 1951, Seppälä and Balode 1998, Richardson *et al.* 2010, Lawrenz and Richardson 2011) and affected by the physiological state of phytoplankton (Williams and Bridges 1964). Also several environmental variables can affect the measurements (Strickland 1968, Marra 1997, Kruskopf and Flynn 2006, Serra *et al.* 2009).

Considering the fact that aquatic OM is more labile than previously thought (Bianchi *et al.* 2004), FOM sensors can provide supplementary information to the OM dispersion in water (Ryder *et al.* 2012). Developed from submersible chlorophyll fluorometers (Lorenzen 1966) and based on measuring fluorescent OM (FOM) at single-wavelength pair around humic peak C (Coble 1996), OM fluorescence can be calibrated to DOM or DOC concentration (Watras *et al.* 2011). Characterization of DOM pool in laboratory can be conducted with EEM spectroscopy. EEM contains a lot of information and the technique has been frequently used in aquatic studies of DOM (Jaffé *et al.* 2008). Comparison of field and laboratory optical measurements of OM is not straightforward. Water samples are filtered (DOM) and measured at a constant temperature in laboratory for DOM fluorescence (Baker 2005), whereas *in situ* FOM sensors measure also the fluorescence of particulate and colloidal OM. *In situ* FOM measurements are also affected by the temperature changes in the measured environment. Further, laboratory optical DOM is corrected for inner-filter effect but *in situ* measurements are affected by the concentration (Watras *et al.* 2011, Coble *et al.* 2014). Recently, calibration procedures for *in situ* FOM monitoring have been established for some environmental variables (temperature, concentration, turbidity; Saraceno *et al.* 2009, Watras *et al.* 2011, Downing *et al.* 2012) but question remains how much the quality of DOM affects these measurements (Ryder *et al.* 2012, Lee *et al.* 2015).

1.4 Objectives

This thesis aims to provide new knowledge on processing of fluorescence optical sensor data from boreal inland waters with varying humic content. It also uses high-frequency AWQM data in currently relevant topics of limnology, on its own and as a part of traditional monitoring by focusing especially on the following main questions, aims and hypotheses:

Firstly, this thesis aimed to characterize the humic content in boreal lakes with PARAFAC modelling and study the effects of changing DOM pool on *in situ* single-wavelength OM fluorometer measurements (I). The hypothesis was that humic content of lakes can be reliably measured with FOM sensors. However, changes in the quality of DOM affect the *in situ* OM measurements.

Second hypothesis was that AWQM and *in situ* Chl fluorometers provide an efficient means to monitor Chl also in freshwaters where OM may interfere with the optical measurements. Changes in the amount of background producing OM can cause error in the calibration of Chl fluorometers for Chl-a concentration. However, Chl fluorometer readings can be corrected to remove OM interference. Calibration of Chl fluorometers for OM is necessary in humic waters. To test this *in situ* Chl fluorescence was monitored in lakes with varying humic content and different calibrations performed for OM correction (II).

Third aim of the thesis was to use high-frequency AWQM data to study influence of episodic weather-related events on physico-chemical conditions and biology of the lakes in Finland (III). Finnish lakes are generally considered well stratified but the strength of the response depends on the characteristics of the lake as well as the strength of the forcing factor. Hypothesis was that strong weather fronts passing Finland give a coherent response in the studied lakes but the impact depends in particular upon lake morphometry and thermal structure.

The last aim of this thesis was to use AWQM as a part of more traditional monitoring to help reveal the effects of hypolimnetic oxygenation on water quality of Lake Jyväsjärvi, Finland (IV). Hypolimnetic oxygenation was assumed to improve deep water DO conditions, but also impact temperature and nutrient conditions in the lake.

2 MATERIAL AND METHODS

2.1 Study lakes and instrumentation

For this study, AWQM and discrete (i.e. manually sampled) data were collected from 10 Finnish lakes (Table 1) and Lough Feeah located in the north-western Ireland (Ryder *et al.* 2012). The Finnish lakes are dimictic with the exception of shallow and polymictic Pyhäjärvi. Lough Feeagh is a warm monomictic lake with no ice-cover in winter. The lakes represent a wide range of surface area (from 2 to 1050 km^2) and maximum depth (from 8 to 95 m). The trophic status of the lakes varies from oligotrophic to eutrophic and water colour from clear to humic (Table 1).

Lough Feeagh and Finnish lakes Jyväsjärvi, Konnevesi, Pallasjärvi, Pyhäjärvi, Päijänne, Vanajavesi, Vesijärvi and Yli-Kitka had pelagic AWQM stations during the study period (Table 2). The two most humic lakes, Alvajärvi and Ruokojärvi did not have AWQM stations and were monitored with the multiparameter sonde of Konnevesi AWQM station as a handheld unit during individual sampling occasions (I, II). The same multiparameter sonde was also used on lakes Jyväsjärvi, Vanajavesi and Vesijärvi to study the operation of single-wavelength Chl and OM fluorometers attached to the sonde (I, II).

Water quality variables measured with AWQM included water temperature (I–IV), DO (III, IV), Chl fluorescence (II, III) and OM fluorescence (I, II) (Table 2). Meteorological variables, air temperature and wind speed, were measured on AWQM stations or on shore of the Finnish study lakes (Table 2). Wind speed data were calibrated to reference height of 10 meters (U_{10}) to minimize the effect of station location (III). Maximum wind speed and maximum mean daily wind speed were calculated (expressed as difference from the seasonal mean wind speed for each site) to investigate the effects of weather-related episodic events on lakes (III).

A case study conducted on Jyväsjärvi included AWQM data profiles of water temperature and DO (IV) during years 2008–2014. Profiles were measured with Aanderaa 3835 and a DMU08 (AFRISO–EURO–INDEX, Güglingen, Germany) pressure sensor. Temperature and DO measurements were supplemented with Thermochron 1922L -dataloggers and YSI6600V2-4 profile measurements in case of instrument malfunction (IV).

TABLE 1 Limnological characteristics of the study lakes and the use of lake data in the original papers of this thesis. Data source: Finnish Environmental Institute, SYKE and Marine Institute, Ireland. TP = total phosphorus, Chl-a = chlorophyll-a. Lough Feeagh water colour transformed to permanent glass colour standard (Anon. 1995) by multiplying spectrophotometric values with 0.6.

Lake	Lat	Lon	Mean Chl-a µg l^{-1}	Area km^2	Mean TP µg l^{-1}	Max depth m	Mean colour mg Pt l^{-1}	Data usage
Alvajärvi	62° 18′ N	25° 43′ E	16.5	2.0	29	17	80	I, II
Jyväsjärvi	62° 14′ N	25° 46′ E	10.8	3.1	25	25	70	I−IV
Konnevesi	62° 37′ N	26° 36′ E	4.2	190.3	6	57	25	I, II, IV
Lough Feeagh	53° 56′ N	9° 34′ E	1.3	4.1	11	46	49	I
Pallasjärvi	68° 01′ N	24° 12′ E	2.1	17.0	5	36	13	IV
Pyhäjärvi	61° 01′ N	22° 17′ E	7.2	155.0	20	26	17	IV
Päijänne	62° 09′ N	25° 47′ E	5.9	1050.0	13	95	29	IV
Ruokojärvi	62° 15′ N	27° 18′ E	10.6	4.6	30	8	109	I, II
Vanajavesi	61° 90′ N	24° 13′ E	16.0	166.3	24	24	50	I, II, IV
Vesijärvi	61° 30′ N	25° 35′ E	9.6	107.5	27	40	10	I, II, IV
Yli-Kitka	66° 07′ N	28° 39′ E	3.9	237.0	9	41	30	IV

2.2 Sensor calibration

Intercalibration of the *in situ* OM fluorometers were conducted on lakes Jyväsjärvi and Lough Feeagh (I) and these sensors were also calibrated to water temperature (Watras *et al*. 2011) (I). Temperature calibrated OM fluorometer data from Finnish lakes were used in the Chl fluorometer calibration study to comprehend water colour measurements by *in situ* monitoring (II).

Automatically monitored Chl fluorescence data from the study lakes were transformed to Chl-a concentration with individual calibration equations and using laboratory measurements of Chl-a and cyanobacteria counts established in monitoring campaigns of the lakes (III).

TABLE 2 Instrumentation for the automatically measured (A) water temperature (Temp), dissolved oxygen (DO), chlorophyll fluorescence (Chl) and organic matter fluorescence (OM) in the study lakes. Manual measurements (M) were done with a multiparameter sonde. Meteorological stations (MET) were situated on monitoring stations or near the shore of the study lakes.

Lake	MET	Meas.	Temp	DO	Chl	OM
Alvajärvi		M	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	Cyclops-7 Turner Designs Inc. Sunnyvale CA,USA
Jyväsjärvi	Vantage Pro2 Davis Inst. Co. Hayword, CA, USA	A	Thermochron 1922L Express Thermo San Jose CA, USA	Aanderaa 3835 Aanderaa Data Inst. Bergen, NO		Cyclops-7 Turner Designs Inc. Sunnyvale CA,USA
Konnevesi	a-Weather a-Lab Ltd. Keuruu, FIN	A	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	Cyclops-7 Turner Designs Inc. Sunnyvale CA,USA
Lough Feeagh		A	Hydrolab DataSonde 5X OTT MESSTECHNIK GmbH & Co Kempten, Germany			SeaPoint SeaPoint Sensors Inc. Brentwood NH, USA
Pallasjärvi	uSonic Pt100 TG-4100 Elmshorn, DE	A	Tinytag Aquatic 2 Metek GmbH Gemini Data Loggers Chichester, UK			
Pyhäjärvi	WXT510 Vaisala Co. Helsinki, FIN	A	Marvet Helox13-25 Elke Sensor Oy Tallinn, EST	Marvet Helox13-25 Elke Sensor Oy Tallinn, EST	MicroFlu Trios Rastede, DE	
Päijänne	Vantage Pro2 Davis Inst. Co. Hayword, CA, USA	A	TSIC50x IST AG Ebnat-Kappel, CH	4175C Aanderaa Data Inst. Bergen, NO		
Ruokojärvi		M	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	YSI6600V2-4 YSI Inc. Yellow Springs OH,USA	Cyclops-7 Turner Designs Inc. Sunnyvale CA,USA
Vanajavesi	WMO station 02863 FIN	A	YSI600 YSI Inc. Yellow Springs OH, USA	YSI600 YSI Inc. Yellow Springs OH, USA	YSI600 YSI Inc. Yellow Springs OH, USA	
Vesijärvi	WXT520 Vaisala Co. Helsinki, FIN	A	NTC WTW GmbH Weilheim, DE	FDO700IQ WTW GmbH Weilheim, DE	MicroFlu Trios Rastede, DE	
Yli-Kitka	DS18B20 Vaisala Co. Helsinki, FIN	A	T100, EHP Tekniikka Ltd. Oulu, FIN	Hach-Langen LDO Berlin, DE		

2.3 Sampling and supplementary data

Water samples of Chl-a, water colour and DOM were collected during open water season from the study lakes simultaneously with the fluorometer measurements in the calibration studies (I, II). Lough Feeagh was sampled monthly from surface (1 m) for OM fluorometer calibration (I). Lakes Alvajärvi, Jyväsjärvi, Konnevesi, Ruokojärvi, Vanajavesi and Vesijärvi were sampled for Chl and OM fluorometer calibration from surface and selected depths during individual sampling occasions (I, II). The samples were kept in cool and dark until analysis. Additional Chl-a and water colour data from Hertta-database (Finnish Environment Institute, SYKE) were used for the calibration of Chl fluorometer in Konnevesi (II). Additional data of temperature and DO from Pallasjärvi and Päijänne (III) and temperature, DO and nutrients from Jyväsjärvi (IV) were also collected from Hertta-database.

2.4 Analytical methods

Water samples were filtered for DOM analysis with 0.22 µm cellulose acetate filters (Finland) or glass fibre filters (GF/C) (Ireland) (I). Filtered water samples were analysed for UV absorbance and EEM fluorescence (I) (n = 90). EEM data was corrected for inner-filter effect, machine-specific variation and background fluorescence of water to water Raman units (RU) with UV absorbance of the sample and MilliQ water (I). A PARAFAC model (Murphy *et al.* 2011, 2013) was built from the DOM samples of this study and additional freshwater data collected in Finland (I) (n = 925). Intensities of Peak C (Coble 1996) and the OM fluorometer representative wavelengths were picked from corrected EEM data.

Water colour was measured with a spectrophotometer (Shimadzu UV-1800 UV-VIS spectrophotometer) at 420 nm from filtered (GF/C) water samples collected in Finland (II). Data is presented as Platinum cobalt concentration, mg Pt l^{-1} (Anon. 1995). These water samples were also analysed for Chl-a concentration by cold ethanol extraction (overnight in the dark) after filtration of 0.5–1 l of sample water through GF/C glass fibre filters. Absorbance of Chl-a was measured with Shimadzu UV-1800 spectrophotometer at wavelengths 665 and 750 nm (II).

To estimate the effects of episodic mixing events in lakes with AWQM, surface water temperatures were examined for continuous drop in temperature for over two days to indicate surface water mixing. For all the observed mixing events an RP was determined to define the re-occurrences of the mixing events (III).

Estimates of GPP, R and NEP were determined using the surface DO data from AWQM station of Konnevesi by the open water method (Odum 1956) using an R package 'LakeMetabolizer' (III). Hypolimnetic DO data from the Finnish AWQM stations was investigated for mixing of DO from the upper water column (complete, substantial or no renewal) (III). During the case study on Lake Jyväsjärvi hypolimnetic DO consumption was indicated as ΔDO for the multi-year AWQM data (IV).

Seasonal maximum of S (Schmidt 1928, Idso 1973) was determined for the Finnish study lakes (III) and H (Wetzel and Likens 2000) for the case study conducted on Lake Jyväsjärvi (IV). Thermocline was considered to exist when a vertical temperature gradient exceeding 1 °C m^{-1} was observed in the profiles measured on the Finnish AWQM stations.

Statistical methods included descriptive statistics, *t*-test, curve fitting, linear and log-linear regressions, calculations of modelling efficiency (ME) and mean absolute percentage error (MEA, %), metabolism modelling, PCA and PARAFAC models. Tests were conducted using statistical programs Microsoft Excel (14.0), SPSS (22.0), Matlab (R2014a) and R (package 'LakeMetabolizer', version 3.2.2.). Results with $p < 0.05$ were reported significant.

3 RESULTS AND DISCUSSION

3.1 DOM quality and *in situ* FOM measurements

The current study (I) used PARAFAC modelling to discriminate DOM quality components in one Irish and six Finnish lakes with varying humic content. Five components were identified from the model built from a larger dataset of 925 samples collected from boreal lakes and streams (I). Three of the components (C1–C3) had humic-like character. According to Openfluor library of fluorescent DOM (Murphy *et al.* 2014), these components are generally considered to be terrestrial in origin (Stedmon *et al.* 2007, Fellman *et al.* 2010, Osburn *et al.* 2012, Shutova *et al.* 2014). Components C4 and C5 had protein-like character. Free proteins in aquatic environment are often considered to originate from biological activity and described as autochthonous DOM (Murphy *et al.* 2006, 2011).

Components C1 and C2 represented the major contribution of the overall fluorescence of DOM, C2 being the most abundant component found in all the studied Finnish lakes (Fig. 1). Component C1 was the most abundant component in the Irish Lough Feeagh. Component C3 ranged from 8.7 % to 14.0 % across all sites. Components C4 and C5 were represented in small proportions throughout the study lakes (Fig. 1).

When analysed with PCA, PARAFAC components pooled into two groups, with PC1 and PC2 scores of 61.4 % and 19.0 %, respectively (I). PC2 separated C4 most notably from other components with high PC2 loading of 0.9. Other PARAFAC components gained PC2 loadings from -0.26 to 0.18. PC1 of this group of components varied between 0.17 and 0.36, C4 being the only component with negative (-0.02) PC1 loading (I). Therefore, PC2 was associated largely with the abundance of component C4, which had a protein-like character, whereas PC1 was associated with terrestrial components C1–C3. This analysis highlighted that autochthonous DOM has distinct patterns in the study lakes, not strongly related to terrestrial DOM.

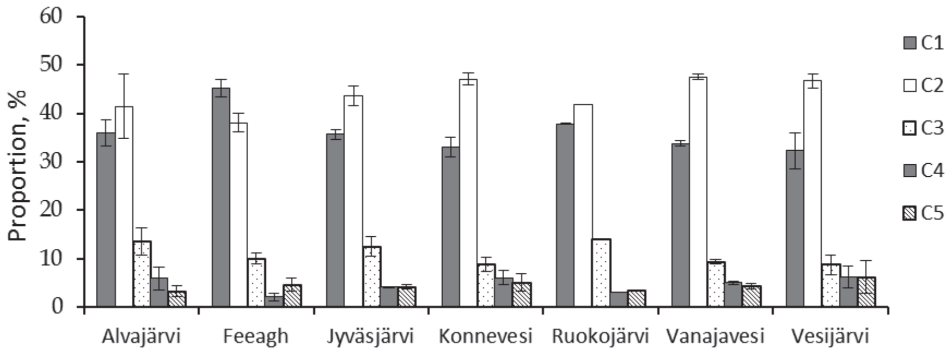

FIGURE 1 Proportions (%, mean ± SD) of fluorescence emission maxima of PARAFAC components C1–C5 in the study lakes.

When temperature-calibrated *in situ* measurements of OM by single-wavelength FOM sensors (RFU_{20}) in the study lakes and corresponding laboratory measurements at sensor wavelength (RU_{wl}), determined from laboratory EEM data, were compared to the F_{max} of Peak C measured in the laboratory, a significant relationship between both measures ($p < 0.001$, $R^2 = 0.95$, n = 90 for both) was found (I).

Since Peak C is considered to consist of humic-like DOM of terrestrial origin (Coble *et al.* 2014, Arellano and Coble 2015) and is often found in great proportion in many type of humic waters, a good detection of humic-like substances by the FOM sensors can be expected in most cases. Many studies have reported fairly good representativeness when FOM sensor data have been transformed to other OM concentration measures, such as DOC (Saraceno *et al.* 2009, Watras *et al.* 2011, Downing *et al.* 2012, Ryder *et al.* 2012, Lee *et al.* 2015). However, when humic substances are broken down by UV and microbial activity, also the optical structure of humic substances starts to change (Coble *et al.* 2014). This may alter the relationship between *in situ* sensors and DOM concentration. The single-wavelength FOM sensors used in this study seemed to represent the original idea behind the sensor operation principle, Peak C intensity (Coble *et al.* 2014), regardless of the DOM quality changes in the study lakes.

In cases where autochthonous DOM becomes dominant, FOM sensors most likely will lack the ability to observe the total DOM pool. FOM sensor measuring at the wavelengths representing autochthonous DOM fractions have been tested in sewage water monitoring, where the role of autochthonous DOM is substantial (Baker *et al.* 2015). Despite the rapid development in fluorometer applications the *in situ* measurements of FOM still lack the ability to scan comprehensive image of DOM composition.

3.2 Measurements of *in situ* Chl in humic lakes

Multiparameter sonde YSI6600V2-4 recorded water temperature, Chl and OM fluorescence from 6 Finnish lakes (II). Chl fluorescence varied from 0.20 to 2.37 RFU and temperature corrected OM fluorescence from 0.21 to 2.51 RFU_{20}. Corresponding laboratory measurements of Chl-a and water colour varied between 0.5–17.4 µg l^{-1} and 17–208 mg Pt l^{-1}, respectively (II).

Linear regression models between laboratory Chl-a concentrations and *in situ* Chl and OM fluorometer data, and water colour (Table 3 in II) provided reasonable approximation between the measured and predicted Chl-a (Fig. 1 in II). Models 2 and 3, where Chl-a concentration was adjusted with humic content of water provided better approximations of Chl-a concentration than model 1 adjusted only with laboratory Chl-a concentrations (Fig. 2 in II).

When measured on a single lake, the change in water colour may not have such a significant impact on the Chl fluorometer data as between lakes. This of course depends largely on the scale of variation in water colour of an individual lake on both spatial and temporal scales. For example, profile of Chl fluorescence measured in humic Vanajavesi (Fig. 2a, water colour 81–89 mg Pt l^{-1}) shows higher background fluorescence throughout the water column compared to clear water lake Konnevesi (Fig. 2b, water colour 58–64 mg Pt l^{-1}).

The results (II) showed that calibrating Chl fluorescence for water colour improves the interpretation of Chl fluorescence data markedly. Proctor and Roesler (2010) did a comprehensive study on *in situ* Chl monitoring data and found OM composition among several other environmental factors to affect Chl fluorometer calibration, and stated also that OM quantity would be more important than OM quality. Goldman *et al.* (2013) showed a significant overestimation of Chl concentration with increased OM concentration in estuary waters. A Finnish study by Leppä *et al.* (1995) found high background fluorescence caused by water colour in their *in situ* Chl fluorescence measurements conducted in SE Finland. Contradictory results have also been reported by Kring *et al.* (2014) where DOM (Suwannee river fulvic acid standard) had no effect on Chl fluorescence.

The paper II aimed to solve issues in sensor deployment with simple variables for *in situ* AWQM. Water quality variables such as Chl-a and colour are easily monitored, cost effective measures for *in situ* fluorometer calibration and the calibration procedures presented in the paper can be used in both AWQM and discrete monitoring of Chl fluorescence.

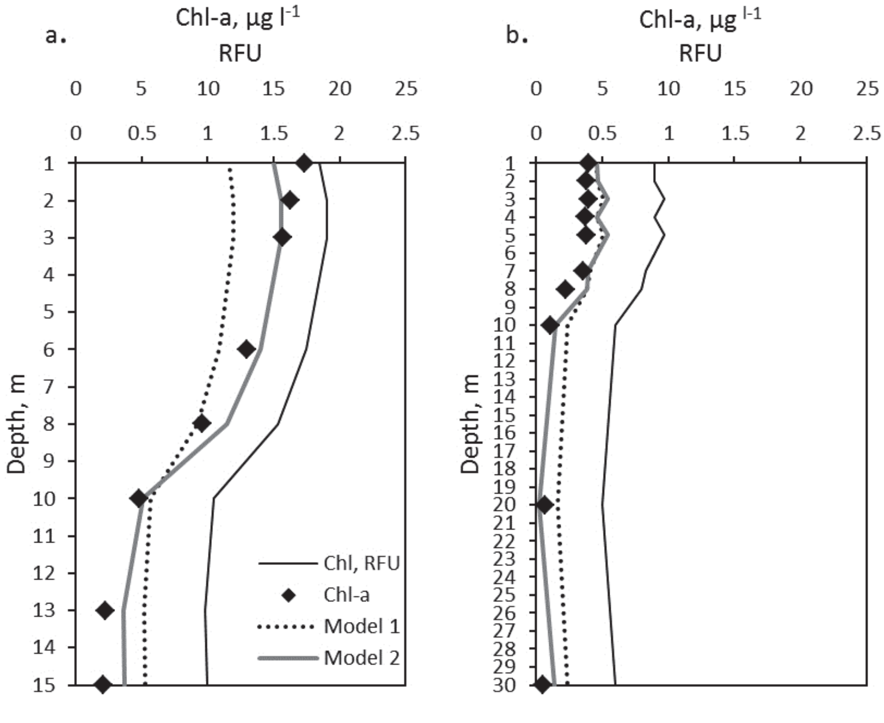

FIGURE 2 Profiles of observed Chl-a concentration (black diamond), Chl fluorescence (RFU) and Chl-a concentrations estimated with different calibration models (II) in a) humic Vanajavesi and b) clear water Konnevesi in July 2013.

3.3 Episodic events studied with AWQM

Altogether 50 weather-related episodic events were recorded on the AWQM stations in Finland (III). Two to four of the events were considered as high disturbance events on each site (i.e. decrease in surface water temperature > 2 °C). These strong impact events were recorded on each lake within few days from each other during the highest wind speeds and the lowest air temperatures (III). The synchrony in the timing of the events could be expected, since the mixing is most likely driven by strong Atlantic Ocean weather systems that are capable to cross the whole country (Heino 1994).

In summer 2013 (June–August) weather-related water column mixing was monitored automatically on all 8 study lakes. During the high-disturbance event in June 2013, no full overturn was observed in any of the study lakes. A month later, high-disturbance mixing caused lakes Yli-Kitka and Pyhäjärvi to mix completely in July (III). The high-disturbance event recorded on the lakes did not cause full overturn in any of the study lakes. The third mixing event in early August led to warming of deeper waters, but no complete mixing in any of the study lakes was observed. At the time of the mixing, Pyhäjärvi had not yet recovered from the July mixing event. Lakes Yli-Kitka and Pyhäjärvi had the lowest recorded seasonal Schmidt's stability index (S), 85 and 18 kJ cm^{-2}, respectively.

Data from other study years from lakes Konnevesi, Vesijärvi and Pyhäjärvi (June, July and August) showed a similar monthly high disturbance mixing pattern, as in 2013. During these events, Pyhäjärvi mixed completely. Full overturn also occurred twice on the lake without any significant temperature change in the surface water (III). During the high disturbance mixing wind speed maximums from 2.8 to 20.7 m s^{-1} were typically recorded on the study lakes with air temperature decreases from 1.7 to 15.3 °C, respectively.

When all 50 events that caused surface water temperature drop in the study lakes for at least two days were measured, no significant relationship between surface water temperature drop and event maximum wind speed was found. However, there was a positive relationship between the water temperature decrease and maximum daily wind speed ($R^2 = 0.352$, $n = 50$, $p = 0.012$) and decrease in air temperature ($R^2 = 0.446$, $n = 50$, $p = 0.001$) during the mixing events. Similarly, return period (RP) calculated for the events did not show a significant relationship with the maximum wind speed but a positive relationship with both maximum mean daily wind speed ($R^2 = 0.121$, $p = 0.014$, $n = 50$) and air temperature decrease ($R^2 = 0.310$, $n = 50$, $p < 0.001$) was found. The RP of high disturbance events varied from 20 to 92 d, which is typical to stratified lakes in Europe (Jennings *et al.* 2012).

Wind speeds recorded during the mixing events were relatively low compared to the ones recorded in other mixing studies (Jennings *et al.* 2012, Klug *et al.* 2012) but resulted in similar mixing patterns. This might be a cause from relative high resistance of the study lakes to external forcing. Finnish lakes in particular are known to have strong stability (Kuusisto 1981), especially deep and humic lakes (e.g. Bowling and Salonen 1990). It is notable though that even when high wind speeds are measured, the response in lake stratification can be relatively short-lived (Klug *et al.* 2012). Changes in the stratification are mainly determined by lake characteristics as more prone effects are likely to occur in shallow clear water lakes (Boehrer and Schultze 2008, Arvola *et al.* 2010).

Seasonal S varied from 18 to 1125 kJ cm^{-2} in the study lakes with lowest values for Pyhäjärvi and highest for Päijänne. However, highest post-event temperature differences between epi- and hypolimnion were measured in Jyväsjärvi, where seasonal S maximum reached 258 kJ cm^{-2}. Jyväsjärvi is the smallest of the automatically monitored lakes (Table 1) and had the highest depth to surface area –ratio and water colour (III; Fig. 4).

Notable chemical/biological responses can occur even after moderate mixing events (Jennings *et al.* 2012). This can inject oxygen and heat into the deeper water layers, and the resulting nutrient upwelling from the hypolimnion (Jennings *et al.* 2012, Solomon *et al.* 2013, Crockford *et al*. 2014) can cause sudden algal blooms (Kallio 1994). The 50 recorded mixing events resulted in a complete renewal in hypolimnetic DO reserve only in lakes Yli-Kitka and

Pyhäjärvi. In Pyhäjärvi DO deficit was evident even after short stratified periods (III).

Chl-a concentration varied between 1.4 and 20 µg l^{-1} in the studied lakes. In all four lakes with *in situ* Chl monitoring, seasonal Chl-a maximum was recorded within days from each other, and was possibly launched by the major mixing event in July 2013. In Vanajavesi Chl-a remained at a constant level prior to the second mixing event recorded in July after which the average Chl-a increased from 12.1 to post-event average of 16.4 µg l^{-1}. In Pyhäjärvi, two distinct Chl-a maxima were recorded additional to the July maximum (13.3 µg l^{-1}), in early June (11.0 µg l^{-1}) and end of August (10.5 µg l^{-1}). Similar pattern could be found in Vesijärvi, yet the Chl-a concentrations were low (III). In Konnevesi, Chl-a concentration remained low during the season, but a constant increase towards the end of summer was visible in AWQM data (III). Mean daily NEP (GPP-R) in Konnevesi remained low, varying between -0.3 and 0.2 mg O_2 l^{-1} d^{-1} with seasonal average close to zero. Highest NEP was recorded in the beginning of summer and towards the end of stratification in 2013.

Mixing events are known to dilute Chl-a to deeper water layers, hence the drop in surface water Chl-a concentration can sometimes be observed (MacIntyre *et al.* 2009). Mixing can also change the community composition of phytoplankton (Wilhelm and Adrian 2008, Cottingham *et al.* 2015), generally favoring diatoms (Reynolds 2006). The high early summer Chl-a peak recorded in Pyhäjärvi is known to originate from diatoms (Kallio *et al.* 2010). The synchronized Chl-a maximum recorded mid-summer on all studied lakes could have resulted from upwelling of accumulated hypolimnetic nutrients. Nutrients were not monitored in this study, but after a long stratified period mixing is known to be an important fertilizer for all phytoplankton production (Huisman *et al.* 1999, Crockford *et al.* 2014).

3.4 AWQM and traditional monitoring – a case study on lake restoration

During AWQM, the duration of summer stratification in Lake Jyväsjärvi was on average 1.8 months shorter when the lake was mixed with HLO than without HLO (IV). Hypolimnetic temperature increased during the stratified period on average 0.092 and 0.011 °C d^{-1} in HLO ON and HLO OFF years, respectively. Maximum heat content (H) in the lake was not affected by HLO (420–450 J), but an average drop of 55 kJ cm^{-2} in S was observed between HLO ON and HLO OFF summers. The maximum heat content under ice varied (40–67 J) regardless of the HLO, but a slow increasing pattern was observed when HLO was not operational in winter.

During the stratified period average ΔDO was 0.093 and 0.082 mg l^{-1} d^{-1} in ON and OFF summers and 0.032 and 0.056 mg l^{-1} d^{-1} in ON and OFF winters. In summer, as the stratified period continued longer in OFF years, DO concentrations eventually fell below 2 mg l^{-1} in the hypolimnion. In winter, HLO broke down the under ice stratification completely leading to homogeneous DO distribution in the lake. According to AWQM data, hypolimnetic DO saturation under ice varied between 46–83 % and 26–93 % in ON and OFF winters.

The effects of HLO on temperature and DO conditions were similarly also observed with the long-term traditional water quality monitoring data. In the hypolimnion, deviations from the observed trends of water temperature and DO differed significantly (Table 1 in IV) between ON and OFF years in both summer and winter observations; in OFF years DO was lower and hypolimnetic water temperature lower in winters and higher in summers than in ON years (IV). Oxygenation methods based on mechanical mixing, such as HLO, are known to have a strong impact on hypolimnetic water temperatures (Lappalainen 1994, Grochowska and Gawrońska 2004, Salmi *et al.* 2014) which was also the case in IV.

Even though the temperature and DO in Jyväsjärvi was largely affected by HLO, the long-term monitoring data showed negligible effects of HLO on Chl-a, TP and TN (IV). In accordance with the re-oligotrophication process of Jyväsjärvi (Salonen *et al.* 2005), concentrations of Chl-a and TP followed the decreasing trend observed during 1992–2010, prior to the shutdown of HLO. Epilimnetic N decreased significantly when HLO was not in use (IV). However, an increase in TN was observed in hypolimnion in winter without HLO.

Different HOx methods in general are relaying on an assumption that by maintaining the oxic conditions in hypolimnion and sediment overlaying water HOx would decrease the sediment phosphorus release, based on the classical outcome in the studies of Mortimer (1941, 1942). Nor did Mortimer or the followed studies on the subject assume sediment processes to be that simple. The P binding capacity of sediment is higher in oxic conditions but the sediment processes are more complex beyond the anoxic–oxic interface. Release of phosphorus from the sediment is controlled by its amount, quality and transformation, among other chemical factors (Gächter and Müller 2003, Hupfer and Lewandowski 2008, Gantzer *et al.* 2009, Bryant *et al.* 2010, Horppila *et al.* 2015, Orihel *et al.* 2015).

In Jyväsjärvi, HLO had substantial effect on hypolimnetic temperature and DO conditions, but no effect on Chl-a or nutrients (IV). The gradual decrease in external nutrient loading after enhanced land and waste water management policies (Salonen *et al.* 2005) is more likely to be the cause of the enhanced water quality in the lake.

4 CONCLUSIONS

This thesis highlighted the importance of calibration procedures when using AWQM in humic lakes. Measurements of OM fluorescence with single-wavelength fluorometers showed that even when the DOM pool is represented very well by peak C fluorescence (Coble 1996), the FOM sensors do not detect changes in OM quality. This is good news in terms of sensor usage for DOM/DOC quantity estimations but leaves out the ability to record changes in the quality of DOM that have a key role in food-web energy pathways and hence the productivity in lakes (Jones 1992, Tranvik 1992, Battin *et al.* 2009). The current calibration procedures established for the single-wavelength OM fluorometers are important since water temperature and turbidity are known to have an impact on the *in situ* measurements of OM (Saraceno *et al.* 2009, Watras *et al.* 2011, Downing *et al.* 2012, Ryder *et al.* 2012, Lee *et al.* 2015).

When *in situ* single-wavelength Chl fluorometer was tested in lakes with variable humic content, the relationship between Chl fluorescence and Chl-a concentration was significant. By adding a factor representing the humic content of the water body, Chl-a representativeness of the sensor increased substantially. When within lake calibration was conducted, water humic content was less significant. Monitoring bulk Chl fluorescence overestimates Chl-a in low concentrations but underestimates it in higher concentrations. However, despite the masking effect by OM, the variation in Chl-a could still be detected from the raw data. Calibrated high-frequency Chl fluorescence data combined with other AWQM variables enabled to study the effects of short-lived physical phenomena, such as weather-induced mixing events that may have long-lasting effects in the lake ecosystems.

In the future, more frequent and possibly more severe weather-events are expected for northern latitudes (Brönnimann *et al.* 2012, Hov *et al.* 2013). Understanding the effects of the predicted change is highly relevant. Without high-frequency monitoring short-term changes induced by episodic events may remain unnoticed. In this thesis, AWQM was used to demonstrate and quantify the frequency and magnitude of current weather-events and their impacts on different Finnish lakes.

Even relatively simple AWQM measurements (such as water temperature and DO) can aid the traditional research as part of a case study or long-term monitoring. Basic variables can increase knowledge on sudden phenomena and help interpret the discrete monitoring data. In this thesis AWQM was used as part of a restoration study of Jyväsjärvi, where HLO had been conducted for decades. High-frequency water temperature data were able to reveal the large impact HLO had on the lake mixing and temperature regimes. More importantly AWQM revealed the negligible effect of HLO on the nutrients.

Long-term data are important in water quality monitoring and lake status assessment. At current state AWQM campaigns are mostly designed to answer individual scientific questions without established standard procedures for AWQM. Data are also often infrequent and lack local and global comparability. The field of AWQM is expanding fast and the tools for better and more efficient data collection have to be established now. Currently, guidelines and metadatabases are being developed under grass-root organizations such as GLEON (Global Lake Ecological Observatory Network) and Netlake (Networking Lake Observatories in Europe) to further aid the development of AWQM. In the future, more emphasis has to be put into research of short-term variations, since they are the ultimate hotspots for ecosystem functioning (Jentsch *et al.* 2007).

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YHTEENVETO (RÉSUMÉ IN FINNISH)

Humusjärvien automaattinen seuranta veden optisten ominaisuuksien avulla

Vuosikymmenien ajan vedenlaadun arviointi on perustunut muutaman kerran vuodessa tapahtuvaan manuaaliseen vesinäytteenottoon ja laboratoriomittauksiin. Näytteenottojen välillä tapahtuneita ilmiöitä ei ole havaittu tai niiden syy-seuraussuhteita on ollut vaikea jäljittää. Viime vuosina automaattinen mittaaminen on tullut tukemaan perinteistä näytteenottoa tuottamalla jatkuvatoimisesti tietoa vesistöjemme tilasta. Mittausvälin tihenemisen myötä tuotetun tiedon määrä on kasvanut huomattavasti.

Automaattinen mittaaminen asettaa tutkijoille kuitenkin haasteita: yksinkertaisten suureiden avulla pyritään selvittämään luonnon monimutkaisia prosesseja. Laboratoriomittauksia varten vuosien saatossa kehitettyjä standardeja ja kalibrointikäytäntöjä vastaavat menetelmät puuttuvat kuitenkin vielä lähes täysin automaattisesta vesistöseurannasta.

Uusia mittalaitteita kehitetään myös jatkuvasti lisää. Pääosin optiseen mittaukseen perustuvien uusien laitteiden käyttö sisävesillämme asettaa jatkuvatoimiselle mittaukselle toisenlaisia haasteita kuin merialueilla, joilla jatkuvatoiminen seuranta on saanut alkunsa. Humuspitoisissa sisävesissämme optista mittausta häiritsee vedessä liukoisina tai partikkeleina olevat yhdisteet, eivätkä mittaustulokset ole välttämättä suoraan vertailtavissa järvien välillä. Humuksen määrä ja laatu vaihtelevat järvillä ja siten monien laitteiden, kuten fluoresenssiin perustuvien levän määrän mittareiden tulosten vertailukelpoisuus heikkenee. Humuksen vaikutus mittauksiin on erilaista eri järvillä. Uusilla mittausmenetelmillä on kuitenkin mahdollista kerätä tietoa ilmiöistä, joita ei aiemmin ole voitu tutkia. Sisävesien jatkuvatoiminen seuranta tarjoaa uusia mahdollisuuksia, mutta myös haasteita.

Väitöskirjan ensimmäisen osatyön (I) tarkoituksena oli selvittää, miten humuksen laatu vaikuttaa tämän orgaanisen aineksen määrän mittaamiseen yksiaallonpituuksisella fluoresenssianturilla luonnonoloissa (*in situ*). Orgaanisen aineksen laatua mitattiin laboratoriossa optisella EEM-tekniikalla, jossa liuenneen orgaanisen aineksen fluoresenssi määritetään usealla eri aallonpituusparilla. Automaattisessa järviseurannassa orgaanisen aineksen määrää mittaava *in situ* -fluorometri on suunniteltu mittaamaan vain yhtä aallonpituusaluetta, joka edustaa maaperästä tulevia humusaineita. Orgaanisen aineksen optiset ominaisuudet vaihtelevat kuitenkin humuksen laadun mukaan ja voivat siten vaikuttaa humuksen määrän arviointiin *in situ* -tekniikalla. Tulokset osoittivat, että orgaanisen aineksen määrää voitiin arvioida *in situ* -mittausten avulla luotettavasti tutkimusjärvillä. Laajempi orgaanisen aineksen optisen laadun tutkimus osoitti, että orgaanisen aineksen laatu vaihteli kuitenkin huomattavasti järvien välillä, mutta *in situ* -fluorometrilla tätä vaihtelua ei voitu havaita (I).

Järviaineistosta määritettiin EEM-tekniikalla viisi optisesti erilaista orgaanisen aineksen komponenttia, joista kolme oli peräisin valuma-alueen maaperän humusaineista. Nämä kolme komponenttia esiintyvät suomalaisissa hu-

musvesissä runsaimpina. Vaikka orgaanisen aineksen määrää voidaan arvioida luotettavasti *in situ* -menetelmillä, sen laatua ei voida vielä mitata jatkuvatoimisesti. Orgaanisen aineksen laadulla on usein määrää merkittävämpi rooli järviekosysteemeissä hiilen ja ravinteiden kierrossa. Automaattisten mittausten kalibrointi veden lämpötilalla ja muilla ympäristömuuttujilla, kuten veden sameudella, orgaanisen aineksen määrän lisäksi on tärkeä toimenpide *in situ* -mittauksia tehtäessä.

Yksiaallonpituuksisella fluorometrillä pyrittiin mittaamaan myös levän määrää kuvaavan a-klorofyllin (Chl-a) runsautta humuspitoisilla tutkimusjärvillä (II). Kaupallisesti saatavilla olevat *in situ* –Chl -fluorometrit on alun perin suunniteltu käytettäväksi merialueilla, joilla humuspitoisuudet pysyvät suhteellisen alhaisina. Orgaaninen aines aiheuttaa kuitenkin virhettä jatkuvatoimisessa Chl-a-mittauksessa humuspitoisissa vesistöissä sammuttamalla vedessä sekä fluorometrin lähettämää että levien signaalivaloa. Osatyössä II pyrittiin määrittämään humuksen tausta-arvolle sekä Chl-a-pitoisuudelle yhteinen malli, jota käyttämällä Chl-fluorometritulosten luotettavuutta voitaisiin parantaa. Laboratoriossa mitatun Chl-a-pitoisuuden ja Chl-fluorometrin tuottaman vasteen välillä havaittiin selkeä yhteys. Lisäämällä malliin humuspitoisuutta kuvaava veden väriluku tulosten yhdenmukaisuus kasvoi. Chl-arvon korjaukseen käytettiin myös jatkuvatoimisella fluorometrillä mitattua orgaanisen aineksen määräarviota jolloin humuksen aiheuttama harha voitiin huomioida paremmin jatkuvatoimisessa mittauksessa.

Tulosten perusteella levien määrää voidaan arvioida varsin luotettavasti jatkuvatoimisesti. Automaattisen vesistöseurannan etu perinteiseen mittaukseen verrattuna on mittausvälin huomattava lyheneminen, jolloin lyhytaikaisten ilmiöiden vaikutukset järvissä voidaan havaita. Lyhytaikaiset ilmiöt järvissä johtuvat usein säätekijöistä. Osatyön III tarkoituksena oli tutkia automaattisten vedenlaadun mittausten sekä meteorologisten mittausten (tuulen nopeus ja ilman lämpötila) avulla sääsyntyisiä sekoittumisilmiöitä ja niiden vaikutuksia suomalaisilla järvillä. Tutkittuja muuttujia järvissä olivat päällys- ja alusveden lämpötilaolosuhteet, päällysveden levämäärä ja -tuotanto sekä alusveden happipitoisuus. Suomalaiset järvet mielletään yleensä kesänaikaisen lämpötilakerrostuneisuutensa suhteen vakaiksi ympäristöiksi, joissa sekoittumisjaksoilla ei ole suurta vaikutusta kerrostuneisuuden vahvuuteen. On kuitenkin mahdollista, että voimakas sekoittuminen pitkän kerrostuneen jakson jälkeen voi aiheuttaa järvessä suuren kemiallisen tai biologisen vasteen.

Voimakkaimmat kesänaikaiset sekoittumisjaksot, jolloin päällysvedessä havaittiin yli 2 °C lämpötilan lasku, toistuivat järvissä 20–92 päivän välein. Sekoittumisjaksot liittyivät tuulijaksoihin (tuulennopeus 2,8–20,7 m s^{-1}) ja ilman lämpötilan laskuun (1,7–15,3 °C). Tutkimusjärvistä heikoimmin vuosittain lämpötilakerrostuvat Pyhäjärvi ja Yli-Kitka sekoittuivat kesä-elokuussa täysin yhdestä kolmeen kertaan. Vaikka järvillä havaittiin vain muutamia voimakkaita sekoittumisjaksoja kesän aikana, myös tuulen ja ilman lämpötilan pienistä muutoksista johtuvilla sekoittumisjaksoilla oli vaikutusta järvien kerrostuneisuuteen. Mittausjaksolla havaittiin yhteensä 50 erisuuruista sekoittumisjaksoa, jolloin päällysveden lämpötilan laski kahden perättäisen päivän ajan. Kylmempään alusveteen siirtyi lämpöä ylemmistä vesikerroksista sekoittumisen seurauksena kaikilla tutkimusjärvillä. Happipitoisuus alusvedessä kasvoi heikosti kerrostuneella Pyhäjärvellä toistuvasti ja kerran myös Yli-Kitkalla, mutta vastaavia äkillisiä muutoksia ei havaittu muilla tutkimusjärvillä.

Levän määrää mitattiin jatkuvatoimisesti Chl-fluorometreillä neljällä tutkimusjärvellä. Suurimmat kesänaikaiset leväpitoisuudet havaittiin tutkimusjaksolla Vanajavedellä ja pienimmät Konnevedellä. Kaikilla tutkimusjärvillä suurimmat leväpitoisuudet mitattiin heinäkuussa, voimakkaimman sekoittumisjakson jälkeen. Vanajavedellä sekoittuminen aiheutti levämäärän pitkäkestoisen lisääntymisen kasvukaudella. Konnevedessä levämäärä pysyi koko jakson pienenä, joskin pitoisuus kasvoi järvessä syksyn täyskiertoon asti. Pyhäjärvessä ja Vesijärvessä havaittiin kaksi muuta levämaksimia, alkukesällä ja kerrostuneen jakson lopulla.

Kesänaikaisten jatkuvatoimisten mittausten avulla pystyttiin osoittamaan, että säällä on merkittävä vaikutus myös vahvasti kerrostuneiden järvien sisäiseen dynamiikkaan. Ravinnemittauksia ei järvillä tehty, joten alusveden ravinteiden kumpuamista ylempiin vesikerroksiin ja sitä seuraavia muutoksia järven tuotannossa ei voitu osoittaa. Ravinteiden pitoisuudet ja monet muut limnologiset muuttujat on yhä mitattava perinteisillä menetelmillä. Perinteisessä vedenlaadun seurannassa ongelmaksi muodostuu usein pitkä mittausväli. Suuret vaihtelut mittaustuloksissa saatetaan tulkita mittausvirheiksi ja jopa poistaa aineistosta.

Aineiston tulkintaa tukemaan voidaan käyttää yksinkertaisia ja kustannustehokkaita automaattisia vedenlaadun mittauksia. Osajulkaisussa IV veden laadun automaattista mittausta käytettiin yhdessä perinteisen seurannan kanssa tutkittaessa hapetuskierrätyksen vaikutuksia pitkäaikaiskunnostettuun Jyväsjärveen Keski-Suomessa. Hapetuskierrätyksen tarkoituksena on lisätä alusveden happipitoisuutta ja turvata järven pohjan sedimentin läheiseen vesikerroksen hapekkaat olosuhteet, jolloin fosforin vapautuminen sedimentistä hidastuu. Jyväsjärvessä käytetyssä hapetusmenetelmässä hapekasta päällysvettä johdettiin alusveteen pumppaamalla. Osajulkaisussa hapetuksen vaikutuksia tutkittiin vertailemalla järven lämpötila- ja happiolosuhteita sekä ravinteita ja levien määrää hapetuskierrätyksen aikana ja sen pysäyttämisen jälkeen.

Hapetuskierrätys lyhensi kerrostuneen jakson pituutta alusveden lämmetessä huomattavasti hapetuskierrätyksen vaikutuksesta. Ravinteiden, kokonaisfosforin ja -typen, sekä Chl-a:n pitkäaikaissarjoissa ainoastaan kokonaistypen pitoisuudessa havaittiin merkittävä nousu hapetuskierrätyksen pysäyttämisen jälkeen. Tutkimustulosten perusteella voitiin osoittaa, että Jyväsjärvi on toipunut järveen kohdistuneesta kuormituksesta hyvin ja sama kehityssuunta jatkuu hapetuskierrätyksen lopettamisesta huolimatta.

Tässä väitöskirjassa jatkuvatoimista vesistöseurantaa käytettiin sekä itsenäisenä tutkimusmenetelmänä, että yhdistettynä perinteiseen vesinäytteenottoon ja veden laadun laboratoriomittauksiin. Jatkuvatoimisella seurannalla voitiin tutkia sään aiheuttamia lyhytaikaisia sekoittumisjaksoja, jotka usein jäävät perinteisessä seurannassa huomaamatta. Jatkuvatoiminen mittaus myös auttoi perinteistä tutkimusta paljastamalla hapetuskierrätyksen vaikutukset järven luontaiseen kerrostuneisuuteen ja kiertoon. Tutkimuksissa osoitettiin, että pitkälti optiseen mittaukseen perustuvien jatkuvatoimisten mittauslaitteiden käyttö humuspitoisissa vesissä on mahdollista. Fluoresenssiin perustuvassa mittauksessa on kuitenkin huomioitava humuksen aiheuttama taustavaikutus.

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ORIGINAL PAPERS

I

HOW DOES THE CHANGING COMPOSITION OF DISSOLVED ORGANIC MATTER (DOM) IMPACT ON THE USE OF *IN SITU* SINGLE-WAVELENGTH FOM SENSORS?

by

Jonna Kuha, Elizabeth Ryder, Elvira de Eyto, Eleanor Jennings, Mika Nieminen, Toni Roiha & Juha Karjalainen 2016

Manuscript

II

USE OF SINGLE-WAVELENGTH FLUOROMETERS FOR *IN SITU* CHLOROPHYLL MONITORING OF HUMIC LAKES

by

Jonna Kuha, Marko Järvinen & Juha Karjalainen 2016

Manuscript

III

RESPONSE OF BOREAL LAKES TO EPISODIC WEATHER-INDUCED EVENTS

by

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IV

NEGLIGIBLE EFFECT OF HYPOLIMNETIC OXYGENATION ON THE TROPHIC STATE OF LAKE JYVÄSJÄRVI, FINLAND

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Negligible effect of hypolimnetic oxygenation on the trophic state of Lake Jyväsjärvi, Finland

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ABSTRACT

Hypolimnetic oxygenation by pumping oxygen-rich surface water to the hypolimnion (HLO) is a commonly used tool for the restoration of nutrient-loaded dimictic lakes. However, in recent years its effectiveness has been questioned. In this case study we evaluated monitoring data covering a period of 23-years to show that, although experimental cessation of HLO drastically changed the lake's temperature and dissolved oxygen regimes, it did not significantly affect its trophic status. Thus, we recommend that the limited financial resources available are better directed towards further lowering the lake's external phosphorus load than continuing HLO.

1. Introduction

Different methods of hypolimnetic oxygenation (HO*x*) have been suggested for the restoration of eutrophic lakes to prevent deep water anoxia and the consequent accelerated internal loading of phosphorus during stratification (Beutel and Horne, 1999; Gantzer et al., 2009b; Singleton and Little, 2006). Hypolimnetic oxygenation by pumping oxygen-rich surface water to the hypolimnion (HLO) is a form of HO*x* often used in restoration of dimictic lakes in Finland (Lappalainen and Lakso, 2005; Salmi et al., 2014). The aims of HLO are to maintain thermal stratification in summer, oxygenate the hypolimnion and sediment, and allow aerobic decomposition in near-bottom layers (Lappalainen, 1994). However, the method causes increased hypolimnetic temperatures in summer and is expected to promote cooling of the water column under ice (Lappalainen, 1994; Salmi et al., 2014).

HLO is considered a cost-effective restoration method to prevent undesirable effects of progressive anoxia, especially when a lake has a high socio-economical value. This has been the case with Lake Jyväsjärvi, an urban humic lake in the city of Jyväskylä, Central Finland. The lake has been transformed from one of the most heavily polluted lakes in Finland in the 1970s to a scenic part of the townscape of the city with high recreational value (Salonen et al., 2005). Much restoration effort has been put into the lake during its history, including legal obligations for the paper industry. Due to a gradual decrease in the external anthropogenic nutrient loading, the role of HLO in restoration of the lake has recently been questioned, although local environmental authorities have been cautious about stopping the HLO. Results from HO*x* in general and HLO in particular have been variable (Bryant et al., 2011; Horppila et al., 2015; Lappalainen and Lakso, 2005; Liboriussen et al., 2009), and recently even the key role of dissolved oxygen (DO) in regulating internal nutrient load has been questioned (e.g. Gächter and Müller, 2003; Müller et al., 2012; Orihel et al., 2015).

In this case study we investigated seasonal and long-term effects of experimental shutdown of HLO on a dimictic lake with the aid of automated water quality monitoring (AWQM). Effects of HLO on the trophic status of Lake Jyväsjärvi were studied with time series analyses of 23 years of data for nutrients, algal biomass measured as chlorophyll a (Chl a) concentration, DO and water temperature. Our aim was to evaluate whether there is still a need to apply year-round HLO to treat the symptoms of eutrophication in the lake by comparing the last three years without HLO to long-term trends in the lake. We also evaluated seven years of AWQM data to study the seasonal variability in DO and temperature structure of the lake with and without HLO.

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2. Material and methods

2.1. Study site

Lake Jyväsjärvi (3.1 km^2) in Central Finland (62°14.5′N, 25°46.2′E) is surrounded by the city of Jyväskylä and has an urban catchment area of 38 km^2. The lake has a maximum depth of 25 m and a mean depth of 5.8 m. The volume of Lake Jyväsjärvi is 1.8×10^{-2} km^3 with a mean water retention time of 2.7 months. The lake is typically ice-covered from late December to the beginning of May.

Lake Jyväsjärvi suffered from massive eutrophication in the past (Salonen et al., 2005). The lake received a heavy load of untreated paper mill and municipal wastewaters until the establishment of a sewage water treatment plant in the mid-1970s. As frequent DO depletion in the deep water of the lake was observed, HLO was initiated in 1979 and improved in the 1990s when a new HLO system (Mixox-1100, Water Eco Ltd., Kuopio, Finland), pumping 1 m^3 s^{-1} surface water (from 3 m) to the hypolimnion (12 m), was installed at the deepest point of the lake. Since then HLO has been operated year-round with one to three devices, apart from some breaks due to instrument malfunction. The local paper mill, which previously was the most important polluter, was legally obliged to continue HLO until 2010. After this obligation ended, the city of Jyväskylä was advised by the local environment authorities to continue HLO of the lake because a continuing tendency for low DO conditions in the hypolimnion during summer was considered a risk for lake biota and trophic status, and hence for the recreational value of the lake. HLO was stopped on April 10th 2012 for this experiment. However, due to frequent instrument malfunctions during 2011 meaning ineffective HLO, that year was considered the first OFF year in statistical analyses.

2.2. Data

2.2.1. Water quality monitoring

Lake Jyväsjärvi was monitored for DO, temperature, total phosphorus (P), total nitrogen (N) and Chl a concentrations in summer (June–August 1992–2014) and for DO, temperature, P and N in winter (January–March 1993–2015) at its deepest point (sampling station 510, Finnish Environment Institute database). The sampling occasions represent summer and winter stratification periods after the last substantial change in external loading to the lake. Samples were collected with a Limnos-sampler from depths of 1, 20 and 23 m. DO was analyzed with Winkler titration, P spectrophotometrically (SFS–EN ISO 6878:2004) and N by standard method SFS-EN ISO 11905-1:1998. Epilimnetic samples from the depth of one metre and averages of hypolimnetic samples from depths of 20 and 23 m were used for the time series analysis. Calculation of annual averages of DO, temperature, P and N was based on 3–4, 1–3, 4–6 and 2–4 samples for summer epilimnion, winter epilimnion, summer hypolimnion and winter epilimnion, respectively. Chl a concentration was measured spectrophotometrically after ethanol extraction (SFS 5772:1993) from a 0 to 2 m composite sample taken 3 to 8 times between June and August and the seasonal averages were calculated for the time series analysis.

2.2.2. Automated water quality monitoring

Since 2008 an AWQM station, situated 300 m north from the deepest point of Lake Jyväsjärvi, has measured hourly profiles of temperature and DO (Oxygen Optode 3835, Aanderaa Data Instruments, Bergen, Norway) from 1 to 15 m at intervals of 0.5 m (max depth 16 m at AWQM location). Data were supplemented for temperature (Thermochron 1922L, Express Thermo, San Jose, CA, USA, ±0.5 °C) and DO (YSI6600-V2, YSI Inc., Yellow Springs, Ohio) in cases of instrument malfunction during the 7-year dataset (www.paijanne.org). Winter 2011 data were not used for analysis of the AWQM data.

2.3. Data analysis

The effects of shutdown of HLO (OFF years) on the trophic status of Lake Jyväsjärvi were studied with time series analysis of the 23-year dataset by first fitting linear regressions for the log-transformed annual averages of P, N and Chl a measured from the summer epilimnion in 1992–2010 (ON years), and for P, N, DO and water temperature measured from summer hypolimnion (1992–2010) and winter hypolimnion (1993–2010). The second and third degree polynomials were also fitted but did not explain the data significantly better ($p > 0.05$) than the first degree models. Constant functions (y became a constant value) were used for the P and water temperature data from the winter hypolimnion because the higher degree polynomials did not explain the data significantly better than the constant functions. Secondly, deviation of observed annual values from those estimated by linear regression or by subtracting the constant value (see Table 1 for methods used for each variable) was calculated for all variables and for winters and summers for both ON and OFF years. There was no temporal autocorrelation between the deviations of any variable ($p > 0.05$). Differences in the deviations of P, N, DO, Chl *a* and water temperature between ON and OFF years were tested with *t*-test. Winter ON years were 1993–2010 and 2012, and OFF years were 2011, 2013, 2014 and 2015. Summer ON and OFF years were 1992–2010 and 2011–2014, respectively.

Effects of HLO on winter and summer temperature and DO structure were also analyzed with the 7-year AWQM dataset. A summer

Table 1
Statistical test results (*t*-test) for Chlorophyll a (Chl a), total phosphorus (P), total nitrogen (N) concentrations, water temperature and dissolved oxygen (DO) concentration in winter and summer at different depths between ON and OFF years. The deviations of observed values of each variable from the trend line were compared by *t*-test between ON and OFF years. The *t*-value, degree of freedom (df) and *p*-value of *t*-tests are given separately. The detailed implementation of the *t*-tests is explained in Section 2.3.

Season	Depth	Variable	Type of time series model	*t*-Test between ON and OFF years		
				t	df	*p*
Summer	Epilimnion (1 m)	Chl a	linear regression	0.337	20	0.739
		P	linear regression	0.184	20	0.856
		N	constant function	1.990	21	**0.047**
	Hypolimnion (20 and 23 m)	P	linear regression	0.655	21	0.519
		N	constant function	1.847	20	0.080
		Temperature	linear regression	13.599	21	***p* < 0.001**
		DO	linear regression	2.609	20	**0.017**
Winter	Hypolimnion (20 and 23 m)	P	constant function	0.080	19	0.937
		N	linear regression	3.280	18	**0.011**
		Temperature	constant function	3.341	21	**0.003**
		DO	linear regression	10.645	21	***p* < 0.001**

thermocline was considered to exist when a vertical temperature gradient exceeding 1 °C m^{-1} was observed. Water heat content (H, Joules; Wetzel and Likens, 2000) and stability (S, kJ cm^{-2}; Idso, 1973; Schmidt, 1928) were calculated from the temperature data (between May and November for S). Annual maxima for H and S were determined for both ON and OFF years. AWQM data were also used to determine average daily rate of temperature change in the hypolimnion (°C d^{-1}) during both summer and winter (from 15 m). Average daily hypolimnetic DO net-consumption rates (ΔDO, mg l^{-1} d^{-1}) during winter and summer were calculated from the AWQM DO data (observed at 15 m) for the periods between freeze-over and the beginning of stratification and the following DO concentration minimum, respectively.

3. Results

3.1. Effect of HLO on trophic status

The shutdown of the HLO did not significantly delay the rate of recovery of the lake's trophic status (Fig. 1). During summer in the productive epilimnetic layer of the lake, both annual Chl a and P concentrations followed the observed decreasing trend and their deviations from this linear trend did not differ significantly between ON and OFF years (Fig. 1a and b, Table 1). In the epilimnion, the observed annual N concentrations deviated from the linear trend significantly more strongly in ON years than in OFF years (Fig. 1b, Table 1). Deviations from the trend of hypolimnetic P and N concentrations did not differ between ON and OFF years in summer (Fig. 1c), and neither did P in winter (Fig. 1d). However, deviations of N in the winter hypolimnion differed significantly between ON and OFF years (Fig. 1d, Table 1). In the hypolimnion, deviations from the trends of water temperature and DO differed significantly between ON and OFF years in summer and winter (Fig. 2, Table 1); DO concentrations were lower in OFF years in both seasons while the hypolimnetic water temperature in OFF years was lower in winter and higher in summer than in ON years.

3.2. Seasonal changes in thermal structure and DO

During summer, HLO shortened the duration of stratification by an average of 1.8 months (Fig. 3a and b). The summer maximum H varied between 420 and 450 J regardless of the HLO conditions, but an average drop in maximum S of 55 kJ cm^{-2} was observed when HLO was in operation. Temperature increased in the hypolimnion by 0.092 °C d^{-1} and 0.011 °C d^{-1} during ON and OFF summers, respectively. Average ΔDO was 0.093 mg l^{-1} d^{-1} during ON summers and 0.082 mg l^{-1} d^{-1} in OFF summers (Fig. 3c and d).

In winter, HLO mixed the under-ice water column completely, leading to colder near-bottom temperatures (Fig. 4a) and a homogenous DO distribution (Fig. 4c). A gradual increase in both H and hypolimnetic temperature was observed in OFF winters (Fig. 3b). The maximum H under the ice (40–67 J) varied depending on temperature conditions before ice formation. Hypolimnetic DO saturation varied between 46 and 83% in ON winters and between 26 and 93% in OFF winters (Fig. 4c and d). ΔDO was slightly higher (average 0.024 mg l^{-1} d^{-1} higher) in OFF winters than in ON winters.

4. Discussion

Our results show that after the shutdown of HLO the trophic status of Lake Jyväsjärvi did not deviate from the long-term trend of oligotrophication observed in the lake, and therefore we conclude that at the current level of external nutrient loading HLO is no longer necessary for the restoration of the lake. Furthermore, hypolimnetic temperatures in the lake were strongly altered due

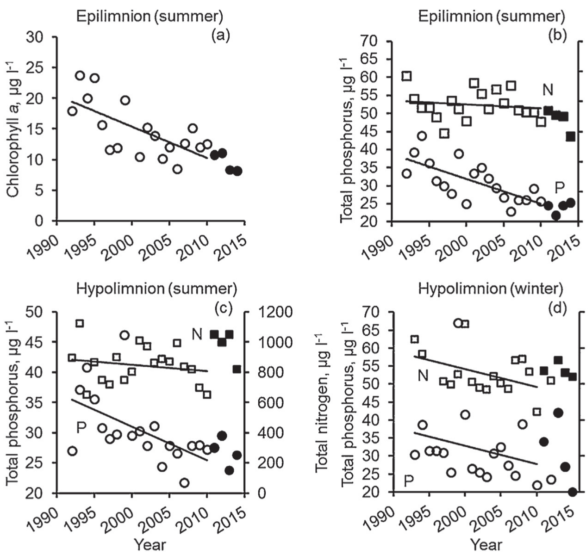

Fig. 1. Annual average concentrations of Chlorophyll a, total phosphorus (P, circles) and total nitrogen (N, squares) in Lake Jyväsjärvi. (a) Epilimnetic (depth of 1 m) Chlorophyll a concentration in summer (June–August 1992–2014); (b) epilimnetic P and N concentrations in summer; (c) hypolimnetic (average from depths of 20 and 23 m) P and N concentrations in summer; and (d) hypolimnetic P and N concentrations in winter (January–March 1993–2015). Solid black symbols represent years when hypolimnetic oxygenation was not in operation (since 2012 and individual winter 2011).

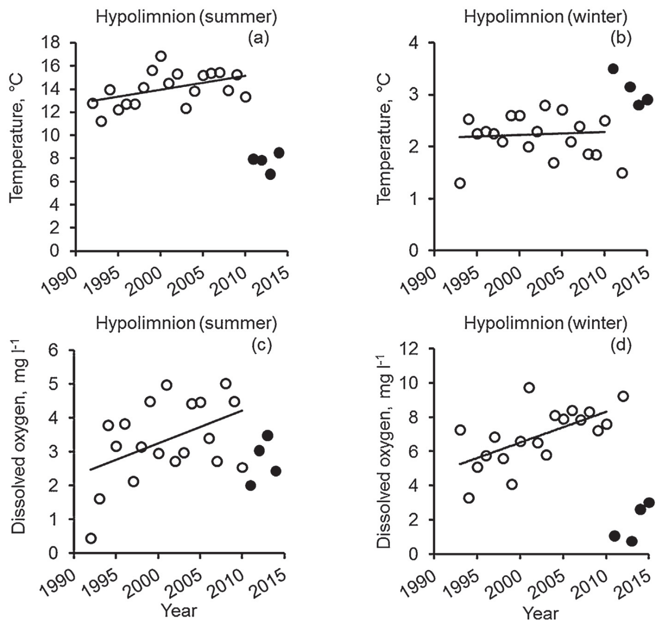

Fig. 2. Annual averages of water temperature and dissolved oxygen (DO) concentration in Lake Jyväsjärvi. (a) Hypolimnetic (average from depths of 20 and 23 m) water temperature in summer (June–August 1992–2014); (b) hypolimnetic water temperature in winter (January–March 1993–2015); (c) hypolimnetic DO in summer; and (d) DO in winter. Solid black symbols represent years when hypolimnetic oxygenation was not in operation (since 2012 and individual winter 2011).

to use of this method. Oxygenation methods based on mechanical agitation are known to have a major impact on hypolimnetic temperature (Grochowska and Gawrońska, 2004; Salmi et al., 2014). In summers without HLO, cold hypolimnetic water remained relatively well-oxygenated, but as stratification continued DO concentrations eventually fell below 2 mg l^{-1}. In winter, HLO slowed down the development of low DO conditions in deep water layers due to the oxygen supply and induced complete mixing of the

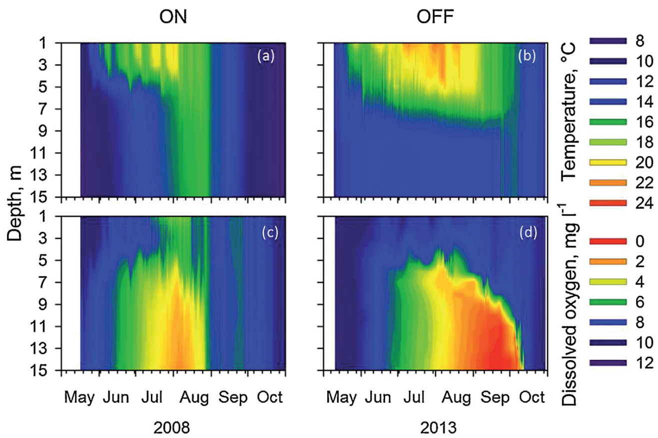

Fig. 3. Examples of development, fluctuation and decay of thermal stratification (a) and (b) and dissolved oxygen (DO) concentration (c) and (d) with and without hypolimnetic oxygenation (HLO) as registered by the automated water quality monitoring (AWQM) station near the main basin of Lake Jyväsjärvi during the first AWQM summers with (in 2008) and without (in 2012) HLO (ON = with HLO and OFF = without HLO).

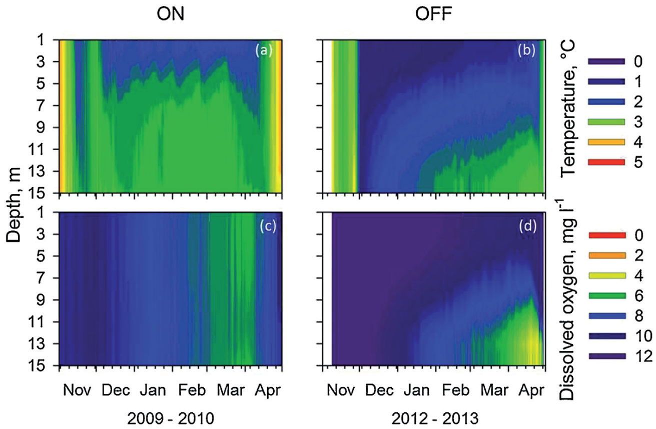

Fig. 4. Examples of development, fluctuation and decay of winter stratification (a) and (b) with dissolved oxygen (DO) concentration (c) and (d) with and without hypolimnetic oxygenation (HLO) as registered by the automated water quality monitoring (AWQM) station near the main basin of Lake Jyväsjärvi during the first AWQM winters with (2009–2010) and without (2012–2013) HLO (ON = with HLO and OFF = without HLO).

water column. Specifically, DO demand under ice is known to be controlled by the amount of organic matter in the water column (Golosov et al., 2007) and no new DO is added to the system by HLO (Lappalainen, 1994). Changes in summer and winter DO conditions due to HLO had no effect on the trophic status of the lake.

Based on the classical study of Mortimer (1941, 1942) lake managers assumed for decades that maintaining aerobic conditions in sediment overlaying water generally minimized benthic phosphorus release and hence contributed to lake water quality restoration. This concept has been repeatedly questioned because the sediment processes are actually more complex, with phosphorus release determined by its amount, quality and transformation in sediment, and varying between lakes (Bryant et al., 2010; Gächter, 1987; Gächter and Müller, 2003; Gächter and Wehrli, 1998; Gantzer et al., 2009a; Hupfer and Lewandowski, 2008; Orihel et al., 2015; Schaller et al., 1997). Some studies on the effects of HO*x* on lake nutrient status have reported that the observed changes in P concentrations have been mainly caused by the decrease in external loading rather than by the oxygenation itself (Horppila et al., 2015; Liboriussen et al., 2009; Matzinger et al., 2010; Schindler, 2006) and that DO consumption in the hypolimnion is caused by current lake productivity (Matzinger et al., 2010) rather than sediment uptake. However, HO*x* has been observed to suppress metal concentrations (e.g. mercury and manganese) by controlling their release from the sediment (Beutel et al., 2014; Gantzer et al., 2009a).

It has been proposed that HO*x* may have positive effects on benthic invertebrates by improving hypolimnetic DO conditions (Doke et al., 1995) but this has not always been the case (Dinsmore and Prepas, 1997). The HLO used in this study may alter the benthic community by favouring eurythermic and warm-water species and reducing habitat for the cold-water species often used as indicator species for oligotrophic conditions (Jyväsjärvi et al., 2013). Despite the HLO, the recent ecological status of the benthic community in Lake Jyväsjärvi has been categorized as poor or moderate (Jyväsjärvi et al., 2013). Thus, HLO does not seem to be an effective restoration method for benthic communities in order to achieve good ecological status of the lake (Jyväsjärvi et al., 2013). HLO may also reduce suitable habitat for cold-water fish such as vendace (Coregonus albula, Hamrin, 1986) and smelt (*Osmerus eperlanus*, Keskinen et al., 2012; Nellbring, 1989) which prefer water temperatures <15 °C.

In conclusion, continuous HLO does not currently seem to be a necessary restoration action for reducing the P load in Lake Jyväsjärvi. Considering the gradual decrease in external nutrient loading due to enhanced land and wastewater management policies, Lake Jyväsjärvi and other lakes may no longer benefit from this type of HLO, and rehabilitation of these lakes may actually be impeded because limited management resources are being directed ineffectually towards controlling internal nutrient loading. The focus should instead be shifted towards management of catchment areas to further lower the external P load.

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