Catchment tracers reveal discharge, recharge and sources of groundwater-borne pollutants in a novel lake modelling approach

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Abstract.

10   Groundwater borne contaminants such as e.g., nutrients, dissolved organic carbon (DOC), coloured dissolved organic matter (CDOM) and pesticides impact the biological quality of lakes. The sources of pollution can, however, be difficult to identify due to high heterogeneity in groundwater flow patterns. This study presents a novel approach for fast hydrological surveys of small groundwater-fed lakes using multiple groundwater-borne tracers. Water samples were collected from groundwater wells installed every 50 m within 5-45 m from the shore and were analysed for tracer concentrations of CDOM, DOC, total

15   dissolved nitrogen (TDN), total dissolved phosphorus (TDP), δ^{18}O isotopes and fluorescent dissolved organic matter (FDOM) components derived from parallel factor analysis (PARAFAC). Based on tracer concentrations and degradation rates, the maximum WRT was estimated to 2 years. Isolation of groundwater recharge areas were based on δ^{18}O measurements and sites with high a degree of recharge was isolated using PARAFAC component C4. Groundwater discharge sites and the fractions of water delivered from the sites were isolated with the Community Assembly via Trait

20   Selection model (CATS) for WRTs between 0.25 and 2 years. The identified recharge sites corresponded to areas adjacent to drainage channels and a cluster analysis of component C4 further identified five sites which showed a tendency of high groundwater recharge rates. Isolated groundwater discharge sites were located in the eastern part of the lake and a single site in the southern part. Observations from the eastern part of the lake revealed an impermeable clay layer that promotes discharge during short precipitation events, which would be difficult to identify using traditional hydrological methods. High

25   tracer concentrations in the southern part in relation to lake concentrations showed that only a smaller fraction of water could originate from this area, thereby confirming the model results. The methodology used can be applied to smaller lakes yielding results within a short time frame with information related to the WRT of the lake.

Introduction

Most lakes are connected to groundwater, which to some degrees define their chemical and biological characteristics

30   (Lewandowski et al., 2015). Particularly in smaller lakes and ponds the groundwater contributes with nutrients, dissolved

organic carbon (DOC), coloured dissolved organic matter (CDOM) or other contaminants, which have a negative impact on the biological quality of the lakes (for nitrogen and phosphorous, see review by Lewandowski et al. (2015)). These inputs often result in unfavorable light conditions for submerged macrophytes due to either increased phytoplankton biomass (Smith, 2003) or increased light absorption due to high CDOM concentrations. These negative impacts of contaminants

35 make the identification of pollutant sources an important management issue for lakes, which however, is complicated for groundwater due to temporal and spatial changes in discharge and associated pollutant concentrations (e.g., Meinikmann et al. 2013). In addition, the lake hydrology itself may be important, particular in small water bodies where e.g., low or fluctuating water levels can have large influence on the biodiversity (Chow-Fraser et al., 1998). There is therefore a need for novel approaches to quickly identify discharge (i.e. groundwater exfiltrating to lake) and recharge (i.e. lake water infiltrating

40 to groundwater) areas at the lake-scale and thereby provide the necessary tools for an effective management strategy for ponds and small lakes.

Groundwater discharge or recharge are traditionally identified and quantified by measurements of the hydraulic head through the installation of piezometers around the lake and of the hydraulic conductivity of the sediments (Rosenberry et al., 2015). This method is often combined with the use of seepage meters which quantifies the water entering or leaving

45 the lake bottom (Lee and Cherry, 1979). To get representative results, it is often necessary to install numerous seepage meters (Rosenberry et al., 2015). Although, the heterogeneous nature of groundwater seepage challenges this method as groundwater seepage rates often are randomly distributed around the lake depending on the hydraulic conductivity of the lake bed sediments (Cherkauer and Nader, 1989; Kishel and Gerla, 2002; Rosenberry, 2005). These methods are also time-consuming and have to be done several times during the season. The heterogeneity and annual variability in groundwater

50 seepage call for a robust and easier method to determine the groundwater inputs and influences.

Various conservative tracers have been used to achieve estimates of groundwater flow and water retention times (WRT) in lakes. These tracers are divided into three main categories: (1) environmental tracers (derived from the atmosphere and transported to the system), (2) historical tracers (anthropogenic tracers such as ^{3}H or ^{36}CL from nuclear testing) or (3) applied tracers (tracers added to the system such as Br, Cl or fluorescent dyes) (Stets et al., 2010). Precipitation-derived

55 environmental tracers, such as δ^{18}O have been shown to be useful for both lakes with short and long WRTs (Stets et al., 2010). In current hydrological approaches the focus has been on conservative tracers neglecting non-conservative biological tracers such as dissolved carbon and nutrients which are partly transferred to the percolating groundwater of different ages and origins (Kidmose et al., 2011).

The fate of inflowing carbon and nutrients in lakes are well-known. When groundwater-borne, dissolved

60 phosphorus and nitrate enter the lake, they are taken up by phytoplankton, macrophytes and bacteria, which is either remineralized when dying or buried in the sediments (Kalff, 2002). The removal or retention of phosphorus in lakes is linked to sedimentation rates and WRT, which, in small lakes without a thermocline can be estimated by the Vollenweider model (Vollenweider, 1975). While phosphorus only leaves the system through sedimentation or outflow, nitrate may also be reduced through denitrification processes (Knowles, 1982). The removal of nitrate through denitrification, sedimentation and

65   outflow can also be estimated using models related to the WRT of the lake (Jensen et al., 1995). Dissolved organic matter (DOM), DOC, CDOM and fluorescence DOM (FDOM) are mostly derived from the surrounding terrestrial catchment. The majority of the labile DOM is degraded in the soil before it enters the lake and the residual DOM is mostly composed of structure substances such as lignin (Mantoura and Woodward, 1983). This fraction is mainly refractory to bacterial degradation until exposure to UV-radiation (Madsen-Østerbye et al., 2017). The composition of FDOM can be determined

70   using parallel factor analysis (PARAFAC) which enables tracing of the fractions in aquatic environments (He et al., 2014; Massicotte and Frenette, 2011; Stedmon et al., 2003; Stedmon and Markager, 2005a; Walker et al., 2009). Although the fluorescence of different DOM components provides insight into the fate of DOC (Massicotte and Frenette, 2011), the changes in FDOM concentration between ground and lake-water are still poorly examined.

         In this study, we measured conservative and non-conservative tracers around a small lake with the aim of

75   developing a novel approach to identify groundwater discharge and recharge areas. The specific objectives were to test; 1) if groundwater discharge sites and pollutant sources could be estimated with a maximum entropy model, to identify the minimum number of sites that explains the measured tracer concentration in the lake; 2) if conservative and non-conservative tracers could be used in combination to detect groundwater recharge areas and 3) if catchment-derived tracer concentrations could be used to estimate a range of the water retention times.

Materials and methods

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A small groundwater-fed lake in the sandy north-western part of Denmark was chosen for this study (Tvorup Hul, area: 4 ha, mean depth: 2.4 meters, 56º91 N, 8º46 E, UTM Zone 32). Coniferous forest and heathland dominate the catchment although some agricultural activities are found the eastern part of the catchment (Fig. 1a). Various isoetids including the rare nationally threatened species *Isoetes echinospora* and *Subularia aquatic* inhabited the lake until some decades ago where

85   brownification increased significantly (based on Rebsdorf, 1981 and the present study), probably due to increasing soil pH (Ekström et al., 2011). This has led to a restoration attempt where a drainage channel was established to bypass water from the catchment thus making the lake groundwater fed. CDOM, DOC and the hydrologic conditions in the lake have since been investigated in several projects (Madsen-Østerbye et al., 2017; Solvang, 2016). This has resulted in extensive background data as well as estimations of WRTs between 0.4 and 3.3 years based on water table heights, hydraulic

90   conductivity and seepage meter samplings (Solvang, 2016 and prilimiary work P. Engesgaard personal communications, 2017).

Sampling and laboratory analysis

A total of 30 groundwater samples were taken every 50 meters around the lake, within 5-45 m, in temporary groundwater wells at 1.25 meters of depth in February 2016. The water in the wells was replaced three times before transferring the

95   sample water to an acid rinsed container. The samples were filtered through pre-combusted 0.7 µm nominal pore size

Whatman GF/F filters the same day and kept cool and dark in hermetical closed acid rinsed BOD flasks until examination. Unfiltered samples were also collected.

DOC concentrations were measured using a total organic carbon analyser (TOCV, SHIMADZU, Japan) in accordance to Kragh and Søndergaard (2004). The CDOM absorbance was measured on a spectrophotometer (UV-1800,

100 SHIMADZU, Japan) between 240 and 750 nm in 1 nm intervals in a 1 cm quarts glass cuvette. The samples were analysed for $\delta^{18}O$ concentrations at the Department of Geosciences and Natural Resource Management (University of Copenhagen) by mass spectrometry in accordance to Appelo and Postma (2005). $\delta^{18}O$ results are presented in the standard δ-notation V-SMOW (Vienna Standard Mean Ocean Water) (Turner et al., 1987). Total dissolved phosphorous (TDP) and total dissolved nitrogen (TDN) were determined for groundwater samples while total nitrogen (TN) and total phosphorous (TP) were

105 determined for lake water, as inflowing nutrients become incorporated into aquatic organisms. Nutrients were measured by transferring 5 ml sample water and 5 ml potassium persulfate reagent to acid-rinsed autoclave vials before autoclaving for 45 minutes. Then 2.5 ml borate buffer were added after cooling and analysed in an auto-analyser (AA3HRAutoAnalyzer, SEAL, U.S.A) together with blanks and internal standard row.

PARAFAC modelling

110 The fluorescent properties of DOM samples were investigated using parallel factor analysis (PARAFAC). PARAFAC analysis is a three-way modelling tool that can separate a mixture of FDOM signals into specific fluorescent components (Stedmon et al., 2003). FDOM samples were initially diluted 2-12 times to account for inner filter effects due to high CDOM absorbance (Kothawala et al., 2013), which were measured spectrophotometric in the range of 240-750 nm (UV-2450, SHIMADZU, Japan). Sample and blank fluorescence were measured using a spectrofluorometer (Cary Eclipse, Agilent

115 Technologies, U.S.A) by excitations between 240 and 450 nm, in 5 nm steps, while scanning the emissions from 300-600 nm in 2 nm increments. Prior to PARAFAC analysis, fluorescence data was processed in R (3.3.1) using the eemR (0.1.3) package. Blank values were subtracted following the documentation provided in the eemR package removing Raman and Rayleigh scattering (Bahram et al., 2006; Lakowicz, 2006; Zepp et al., 2004) the data were then Raman normalized (Lawaetz and Stedmon, 2009) and lastly corrected for inner filter effect (Kothawala et al., 2013) before being exported to Matlab

120 (2015b). In Matlab the fluorescence data was combined with a larger dataset (>1000 fluorescent samples originating from Massicotte and Frenette (2011) from a diversity of aquatic systems) in order to increase the diversity of FDOM components. This allow detection of components insufficient represented in the collected samples (Fellman et al., 2009; Stedmon and Bro, 2008; Stedmon and Markager, 2005b). The drEEM package was used to do the PARAFAC modelling following the same procedure as described in Murphy et al. (2013). A contour map showing the measured FDOM concentration in groundwater

125 were plotted in ArcMap (ArcMap 10.4.1, ESRI, U.S.A) using the inverse distance weighted (IDW) function with barriers fitted around the lake and drainage channels.

Groundwater recharge and areas of high recharge

A hierarchical Euclidean cluster of $\delta^{18}O$ was used to determine groundwater recharge areas, using the Stat package in R. $\delta^{18}O$ was chosen as it is both conservative and biological inert. Changes in $\delta^{18}O$ concentration can occur with precipitation

130 and surface runoff. However, deviations from lake $\delta^{18}O$ concentration was not observed in areas with groundwater recharge due a sampling depth of 1.25 m close to the lake. Groundwater well sites which clustered with the lake were considered as being groundwater recharge sites and were removed for the later estimations of groundwater discharge sites. Hierarchical clustering of fluorescence components from the PARAFAC modelling were done on the basis of the components found. Hence, confirming recharging sites and providing additional information on areas with high groundwater recharge rates.

135 **Groundwater discharge and lake WRT**

Since the concentrations of both conservative and non-conservative tracers in a lake correspond to the mixed concentrations of discharging groundwater, while taking degradation and atmospheric disposition into account, it is possible to utilize the Community Assembly via Trait Selection approach (CATS). The technique models the probabilities that maximize the entropy, or the new knowledge gained, based on a set of constraints that are linear in features (Laliberté and Shipley, 2011).

140 The model has been used to predict the relative abundances of a set of species from measures of community-aggregated trait values (average leaf area, root length etc.) for all species at a site (Shipley, 2010; Shipley et al., 2011, 2006). Further information on the calculations can be found in the supplementary material in the FD package for R (Laliberté and Shipley, 2011). In present study, the concentrations of tracers at groundwater well sites around the lake acted as the individual species at a site and the tracer concentrations in the lake acted as the community-aggregated trait value e.g. the average trait value

145 from all species in the area and was run in the FD package in R (Laliberté and Shipley, 2011). From this, the model predicts the minimum number of groundwater well sites, related to their tracer concentrations, that explains the measured concentrations in the recipient lake. The model outputs maximum entropy probabilities fractions of the groundwater discharge originating from the different groundwater well sites around the lake describing the estimated concentrations in the lake. The model also predicts lambda values from the least squares regression explaining which tracers are most influential

150 on the relative fractions of water originating from the groundwater well sites. The model does a direct comparison of tracer concentrations at the groundwater well sites in relation to the concentrations in the lake. This means that there is a need to estimate how much tracer concentrations have changed, due to sedimentation, bio-photo-degradation etc., since they were discharged from the groundwater. This equilibrium estimation is based on the water retention time of the lake.

WRT of the lake was estimated using traditional hydrological methods in combination with non-conservative tracer

155 concentrations and tracer equilibrium estimates. Previous hydrological models suggested WRTs between 0.4 and 3.3 years. Applying degradation rates of non-conservative tracers enabled an estimate of WRT in the groundwater fed lake based on concentrations found both in the catchment area and in the lake. This was done through an estimation of tracer concentrations if no degradation took place in the lake in relation to increasing WRT. As water retention time increases, the

fraction of degraded or retained tracer increases as well. Thus, with a known tracer concentration in the lake as well as the

160   estimated degraded tracer at known WRTs, in this instance from 0.25 to 3.5 years in 0.25 year increments, it is possible to calculate the mixed inflow concentration to a certain WRT following Eq. (1):

$$MIC = \frac{tr_{lake}}{1 - \frac{ret\,(\%)}{100}},$$ (1)

where MIC is the mixed inflow concentration, tr_{lake} is the tracer concentration found in the lake and $ret\,(\%)$ is the retention percentage of the tracer at a known WRT. Phosphorus equilibrium concentration were found using the Vollenweider model

165   (Vollenweider, 1975) Eq. (2):

$$retP\,(\%) = \frac{1}{1 + \sqrt{WRT}},$$ (2)

where $retP\,(\%)$ is the retention percentage of phosphorus and WRT is the water retention time in the lake. Similarly, nitrate inflow concentrations were estimated using a Danish nitrate removal model derived from Jensen et al. (1995) Eq. (3):

$$retN\,(\%) = 59 \cdot WRT^{0.29},$$ (3)

170   where $retN\,(\%)$ is the retention percentage of nitrate and WRT is the water retention time in the lake. The corresponding retention fractions removed at different WRT were related to the lake concentrations to estimate what the mixed inflow concentration must have been to result in the present lake concentration. The combined summer UV-radiation and bacterial degradation rates of DOC and CDOM in groundwater from the dominating catchment vegetation type of the lake (Madsen-Østerbye et al., 2017) were extrapolated to the rest of the year. This was done by relating the rates to the mean monthly UV-

175   index (DMI, 2015) while assuming a linear relationship between the UV-index and degradation rates. Thus, enabling estimations of the specific removal on a monthly basis related to the concentration measured in the lake at the sampling time following Eq. (4):

$$tr_{lake} = tr_{lakepm} - \left(tr_{lakepm} \cdot \frac{degra\,(\%)}{100}\right) - \left(tr_{lakepm} \cdot mf\right) + tr_{inflow} \cdot mf,$$ (4)

Where tr_{lake} is the lake concentration in the specific month, tr_{lakepm} is the lake tracer concentration in the previous month, mf

180   is the monthly flushing rate (mf = 1/WRT/12), $degra\,(\%)$ is the degradation percentage in present month related to UV-radiation and tr_{inflow} is the inflowing tracer concentration. Eq. 4 was solved in relation to tr_{inflow} and calculated using the same WRTs as the nitrate and phosphorus models.

Results

Groundwater recharge

185   Recharge areas were identified by a Euclidean hierarchical cluster dendrogram of the $\delta^{18}O$ measurements. The cluster revealed two main groups marked with orange and light-blue in figure 2. The first group (orange) shows the groundwater well sites, ranging from site 18 to 29, which clustered together with lake samples. The samples in this orange cluster share a

clear resemblance with lake $\delta^{18}O$ measurements and were therefore considered as groundwater recharge sites. The recharge sites were located in the north and western part of the lake and are marked with orange in figure 1a.

Fluorescent DOM

PARAFAC and split–half analysis modelling identified five distinct fluorescent DOM components (C1-C5, explained variance 96.79 %; Fig. 3). Component C1 was similar to previous found humic-like material (Stedmon et al., 2003). The component absorbs in the UV-C region which has low intensities at the ground surface (Diffey, 2002) and are therefore expected to be photo-resistant (Ishii and Boyer, 2012). Component C2 has been reported to be both marine and terrestrial humic-like (Coble, 1996; Murphy et al., 2006) and seems to be degraded by visible light and produced by microbial degradation in equal amounts (Stedmon and Markager, 2005a). Component C3 was also believed to be of terrestrial humic-like origin and was similar to peak C described by Coble (1996). The component absorbs in the UV-A region and are susceptible to both microbial and photochemical degradation (Stedmon et al., 2007; Stedmon and Markager, 2005b). Component C3 may be an intermediate product since concentration changes even in open oceans (Ishii and Boyer, 2012). Component C4 was found to be similar to one in Stedmon et al. (2003) and are believed to be a combination of peaks N and T produced biological (Coble, 1996). Component C5 is linked to free tryptophan which is a product of microbial activity (Determann et al., 1998). This component has been found to decrease during dark incubations and UV exposure (Stedmon et al., 2007).

The highest fluorescence concentrations were found in the groundwater while the lake water fluorescence concentrations were generally low (Table S1). Component C1 had the highest fluorescence with a value of 7.8 Raman's units (R.U.) in the lake and a maximum fluorescence of 47.1 R.U. at groundwater well site 7. Component C5 had the lowest fluorescence in the lake (0.27 R.U.) and a maximum fluorescence of 2.9 R.U. at groundwater well site number 8. Component C5 also varied much between groundwater samples with a lower value of only 0.1 R.U. or 28 times lower than the maximum concentration. Component C1, C2 and C3 had low lake-like concentrations in recharge areas (orange sites in figure 1a). Concentrations of C4 was generally higher in groundwater around the lake than in the lake (1.1-1.5 versus 1.1 R.U. visualised in figure 1b). Component C4 was chosen as a proxy for groundwater recharge as concentration of the C4 component increase with biological activity and time in the groundwater. The cluster diagram of component C4 showed that especially site 24 grouped with lake samples, but sites 20, 21, 23 and 26 also showed high comparability with the lake figure (Fig. 4) which can also be observed from the IDW map of component C4 around the lake (Fig. 1b).

Groundwater discharge areas and lake WRT

Tracer concentrations narrowed down the possible WRT of the lake. Equilibrium tracer concentrations of DOC, CDOM, TDP and TDN for water retention times between 0.25 and 3.5 years in 0.25 increments revealed that concentrations of TDN in the catchment are not high enough to support WRT-values over 2 years. Thus, catchment tracer data revealed a possible WRT between 0 and 2 years.

220   Groundwater discharge areas were found using the CATS model combined with nutrient concentrations and dissolved organic matter fractions estimated in relation to WRTs between 0.25 and 2 years. The estimated phosphorus concentrations ranged from 46 to 80 µg P l^{-1} while nitrate concentrations ranged from 1113 to 2417 µg N l^{-1}. CDOM and DOC degradation rates were estimated using the UV-index and varied between 0.64 % in December and 28 % per months in June for DOC and between 0.46 % and 20 % for A$_{CDOM}$(340) in the same months and were significantly different from each

225   other (P < 0.001). The lowest degradation rates were found in December and highest in June as expected from the seasonal variation in irradiance. Thus, estimated mixed inflow concentrations of CDOM ranged from A$_{CDOM}$(340) = 0.43 to 1.04 cm^{-1} while DOC ranged from 1205 µmol l^{-1} to 3160 µmol l^{-1} for WRT between 0.25 and 2 years. The CATS model isolated the minimum number of sites that explained the measured lake concentrations. The model identified the sites 1, 9, 11, 13 and 14 as the possible groundwater discharge sites for all WRTs (Fig. 5). Changes in site distribution and fractions of discharging

230   water were observed between the different WRTs, but in general groundwater from 3-4 sites explain the estimated concentrations in the lake (Fig. 5). Site number 14 delivers more water with higher WRT (to a maximum of 54 % of the total discharge), site 1 peaks at a WRT of 1.25 providing 27 % of the water to the lake, site number 9 delivers less water with increasing WRT, but 49 % at the lowest WRT of 0.25 years. Site number 11 delivers 26 to 34 % of the water to the lake until a WRT above 1.5 years is reached where site 13 explains the concentration in the lake better and provide 29 and 19 % of the

235   water to the lake. Overall 73 to 96 % of water is estimated to arrive from the eastern part of the lake while site number 1 (in the southern part) is estimated to deliver 4 to 27 % of the water. Lambda values, explaining which tracers are the most important when predicting the fractions of water origination from groundwater well sites, showed that CDOM was the most important tracer. Average ranges for lambda values for all WRTs and tracers ranged between -6 and 10, with values around zero indicating equal importance and high values indicating higher importance. The lowest average values were found for a

240   WRT of 0.75 years with a mean of -3.7, meaning that tracers were of about equal importance.

Discussion

The combination of biological and hydrological methods in a novel approach provided better estimates of WRT, identification of groundwater recharge and discharge areas, and the fractions of water coming from each site. Based on the model results and earlier hydrological studies the following questions will be addressed in the discussion below; 1) can

245   recharge and discharge areas be identified and confirmed based on tracer concentrations and their location? 2), which of the tracers works and which could possibly work with refined methods? and 3) how do these findings benefit lake restoration programs?

Determination of groundwater recharge areas

250 Groundwater recharge sites were identified along the northern and western part of Tvorup Hul with a hierarchical cluster analysis of the conservative δ^{18}O tracer. The exact same areas are also the ones with adjacent drainage channels (Fig. 1a), thus facilitating the areas as recharge sites. While δ^{18}O worked well as a general groundwater recharge estimator, it does not indicate which sites deliver more water. An indication of this can be found when examining the non-conservative tracers.

Sites resembling the fluorescence found in the lake will indicate flowing water, while a difference in components 255 between lake and sites will indicate a lower flow rate where there is sufficient time for a significant modification of the components representing the DOM pool. The fluorescent component C4 has previously been found to increase with biological activity (Coble, 1996) which can be used as a proxy to estimate groundwater recharge sites. The hierarchical Euclidean cluster dendrogram of component C4 showed that sites in the northern part of the lake formed a group (sites 24, 20, 21, 23 and 26) (Fig. 4 and visually in Fig. 1b). This information can be of importance related to placement of seepage 260 meters which will result in better estimations of the groundwater discharge and recharge and thereby the modelled WRT. In other words, it might be advantageous to first carry out groundwater sampling to estimate high discharge sites, then estimate WRT utilizing the known discharge sites and finally model groundwater discharge areas by using the improved and narrowed WRT range.

CDOM generally showed much lower absorbance at groundwater recharge sites than in the lake making it less 265 suitable for estimating recharge areas. The decrease in absorption is possibly due to low soil pH causing flocculation of CDOM in the soil matrix (Ekström et al., 2011). The same was observed with fluorescence of component C1, which had lower intensities in recharge areas, indicating that component C1 is linked to CDOM. While component C1 was not particular useful for estimating groundwater recharge, it could potential be useful to estimate discharge. The component should be photo-resistant, as it does not absorb in the UV-A radiation areas and are largely resistant to microbial degradation 270 processes (Ishii and Boyer, 2012). Some degradation of the component C1 must take place though as only sites number 9 and number 11 hold concentrations lower than the lake (Table S1) indicating that most groundwater discharge would originate from these sites. Assessment of the degradation rate for component C1 could be integrated in the model as a tracer for groundwater discharge areas.

Determination of groundwater discharge areas

275 Neither δ^{18}O nor previous seepage meter samplings have achieved a similar understanding of groundwater recharge areas in Tvorup Hul as compared to the present approach. While δ^{18}O provides a way of separating groundwater and surface water, using it to determine groundwater discharge sites is simply not possible due to the homological distribution seen in groundwater (Krabbenhoft et al., 1990). Previous seepage meter samplings provided scattered and momentary estimations of discharge sites, indicating that groundwater entered the lake from the southern bank (Solvang, 2016). This does not 280 correspond to tracer concentrations found in the southern area which show very high CDOM absorbance ($A_{CDOM}(340)$ = 1.3-

3.1 cm^{-1}) and DOC concentrations (3114-10467 µmol l^{-1}) in relation to the lake (A$_{CDOM}$(340) = 0.4 cm^{-1}/DOC 1058 µmol l^{-1}) hinting that the lake is influenced by other water sources. The lowest DOC concentrations in the southern area were several times higher than those from the equilibrium estimation suggesting a WRT above 6 years which is well beyond previous estimates of WRT. Samples from the eastern part had lower concentrations all around suggesting that water from this area

285 influence the lake water. Thus, if the water actually originated from the southern area, the lake would need to have a prolonged WRT resulting in increased removal of tracers from the lake. This requirement conflicts with the remaining tracers, where especially TDN sets an upper limit to the WRT of 2 years.

The CATS model used in this study shows that while a fraction of groundwater enters the lake from the southern bank, most of the water originates from the eastern shore (Fig. 1a). Seepage meter measurements from this area showed both

290 discharging and recharging of groundwater (Solvang, 2016). The same was observed for δ^{18}O samples from the eastern part of the lake, which were lower than the southern groundwater, indicating an influence of newly precipitated water or discharge and recharge of groundwater. Sampling in the north-eastern and eastern part of the lake revealed an area with little groundwater and a clay deposit layer which possibly reduce infiltration to deeper groundwater layers. As a result, precipitations could enter the lake as surface and subsurface runoff water originating from the hills to the east and the plateau

295 in the north-eastern corner (Fig. 1a), resulting in short bursts of discharging water. Under normal circumstances, this would be difficult to observe using seepage meter sampling or δ^{18}O measurements because of the short time span where water enters the lake. The multi-tracer approach enables the determination of discharge areas much more precisely and on a temporal scale related to the WRT of the lake, in this instance the previous 3 to 24 months, and are therefore able to track such uncommon and stochastic events.

300 **Tracer influences**

Most tracers used in this study are less conservative compared to δ^{18}O and can therefore change both in the lake water and the catchment soils. This entails a minimum understanding of processes and rates influencing the concentrations. The temporal variability in nitrate concentrations in groundwater are related to the flow rate rather than seasonal changes (Kennedy et al., 2009). The same was observed for phosphorus, where particularly dry periods followed by heavy rain

305 increases the phosphorus concentration measured in groundwater-fed springs (Kilroy and Coxon, 2005). Thus, in the case of northern Europe, sampling during late winter might be the best solution because soils are generally wet at this time of year (Sand-Jensen and Lindegaard, 2004). Previously polluted areas, for example from wastewater infiltration, with increased concentrations of DOC and nutrients are likely to be in a state of imbalance resulting in a reduction in concentrations over time (Repert et al., 2006). In these areas, it is therefore important to have temporal sampling following decreases in

310 concentrations and to relate them to lake concentrations during sampling. Lake inter-annual DOC and CDOM changes were generally low in our study with an annual CDOM absorbance at A$_{CDOM}$(340) = 0.41 cm^{-1} ± SD 0.05, corresponding to what is observed in larger water bodies where WRT integrates inflowing DOC and CDOM (Winterdahl et al., 2014). Inter-annual DOC and CDOM variations in groundwater from the lake catchment (Fig. S1) showed the same tendency as described for

315 nutrients suggesting that sampling should be done at multiple times or in a period without drought or high rainfall. On a broader scale, the variation in DOC is known to be related to hydrology (Erlandsson et al., 2008), mean air temperature (Winterdahl et al., 2014) and the recovery from acid deposition (Evans et al., 2006; Monteith et al., 2007). Sampling from wet areas with standing surface water resulted in high concentrations of most tracers (Table S1). These areas should therefore be avoided as they provide no information regarding the discharge of groundwater. The removal of CDOM and DOC also changes on an annual basis in lakes and are related to bacterial degradation, photo-degradation, sources and

320 mixing of the water column. A sensitivity analysis of the results was conducted by running the CATS model with a ± 10 % change in tracer concentrations. The results showed that sites generally remained unchanged with only smaller deviations in percent wise distribution in discharge up to a WRT of 1.25 years (Fig. S2). Above this point there are some differences in sites, which changes between sites number 11 and number 13. In conclusion, even when changing multiple parameters in the model, the same five groundwater wells are identified explaining the measured lake concentrations. Future investigations

325 into variation of tracers in groundwater and degradation rates in lakes will likely strengthen this model.

The processes influencing changes in FDOM are still being investigated (Ishii and Boyer, 2012). Tracing FDOM has been done in both rivers and open waters (Baker, 2002, 2001; Stedmon and Markager, 2005b) but only a few studies have been conducted in groundwater. These studies have focused on changes in FDOM from deep groundwater wells (Lapworth et al., 2008) or tracing FDOM using samples that are taken very far apart (Chen et al., 2010). Specific

330 fluorescence intensity of components showed large differences among sites in this study, up to a factor of 28, between groundwater well sites, lowest at site number 11 and highest at site number 8, around the relatively small lake. These findings illustrate the problem when applying FDOM as a tracer over large distances in groundwater. Besides bio- and photo-degradation of fluorescent components, there has also been observed changes in absorption in relation to Fe(III) concentrations (Klapper et al., 2002). This might change the concentrations of FDOM components as they travel from anoxic

335 groundwater with reduced iron into the oxic lake water. Overall, PARAFAC components have the potential to work as groundwater tracers, but there is need for a better understanding of the processes that cause changes in fluorescence characteristics of DOM and hence concentrations of FDOM components both in the lake and in the lake-groundwater interface.

Potential management influence for the lake

340 The determination of discharge sites can result in direct management related to specific problematic areas. The model used in this study showed that water entering the lake primarily originated from the catchment to the east of the lake. If water from this part was diverted around the lake, there would be a reduction in CDOM absorbance of 61-89 %, based on calculations relating percent wise discharge, its concentrations and WRT from 0.25 to 2 years in 0.25 increments. On the contrary, diverting water around the lake at site number 1 would result in a lowered inflowing CDOM absorbance of 11-39

345 %. Moreover, in both cases, there would be an increase in photobleaching of present CDOM in the lake caused by the increased WRT. Furthermore, huge reductions would occur for TP and TN, with a decrease of 82-96 % if diverting water

from the eastern shore in contrast to the southern shore with a modelled decrease of 4-18 %. In the future, hydrology is likely to be the main driver of variability in DOM (Erlandsson et al., 2008) with an estimated increase in CDOM by a factor 4 in lakes with a short WRT (Weyhenmeyer et al., 2016). This makes it critical to establish a modelling tool that is capable to

350 pinpoint sites delivering pollutants to lakes and provide us with the ability to take action and reduce the impact on the ecological state of lakes.

Conclusion

The present method and modelling tool can improve estimates of recharge and discharge areas as well as WRT in smaller lakes on a temporal scale. The model provides accurate estimates of discharge fractions, related to field measurements, and

355 can be used for precise management of problematic pollution areas. The hierarchical clustering can be used to estimate groundwater recharge sites which can be incorporated as a guideline for a better estimation of WRT in lakes. Furthermore, the use of multiple tracers strengthens the model and keeps a certain degree of freedom in regard to the choice of tracers related to laboratory capabilities.

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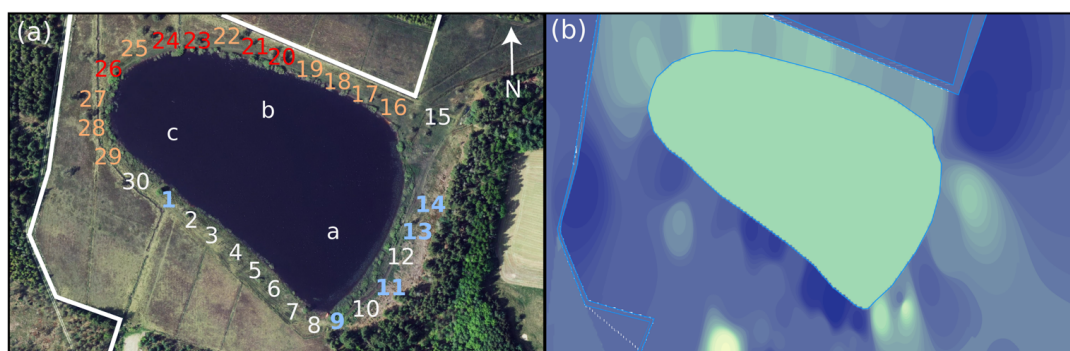
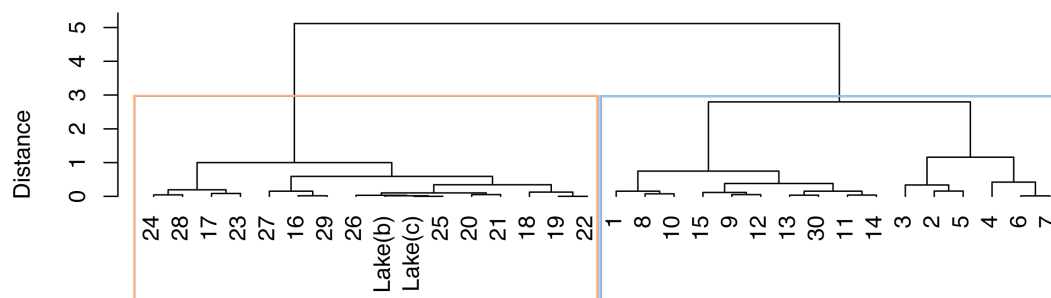
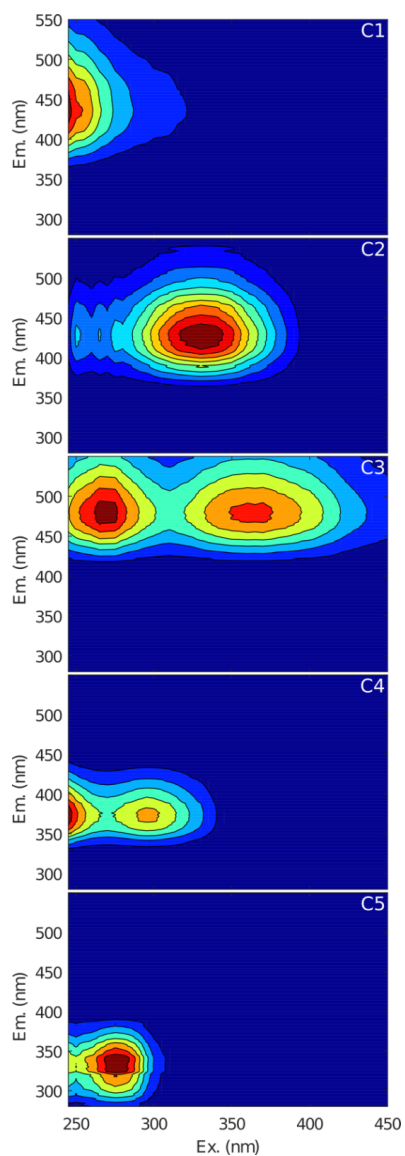

505 **Figure 1: (a) Aerial photo of Lake Tvorup Hul showing groundwater well sampling sites (numbers). Orange numbers denotes groundwater recharge sites, red numbers show sites with a high degree of recharge, white numbers denote possible groundwater discharge sites and light blue show model isolated discharge sites. Position a, b and c shows the three sampling sites in the lake. Missing samples in the north-eastern part are due an absence of groundwater and adjutant drainage channels are marked with white lines. (b) Inverse distance weighted (IDW) contour map of fluorescence component C4. Bluegreen colour corresponds to lake**
510 **concentrations; darker blue indicates increased concentrations and lighter blue denote decreased concentrations throughout the catchment. Areas with low differences between fluorescence in the lake and in the catchment, are seen north of the lake and indicate areas with a fast recharging of groundwater.**

515 **Figure 2: Euclidean hierarchical clustering of δ^{18}O measurements showing two clusters. First cluster, marked with orange, groups with lake samples and therefore are regarded as recharge sites. The other cluster, marked with light-blue, are possible groundwater discharge sites to the lake. The y-axis denotes the linear distance between δ^{18}O measurements fed to the model. The third lake sample was lost during preparation.**

520 **Figure 3: Spectral properties of the five PARAFAC components (C1-C5) found in this study. The x-axis shows the excitation (Ex)
wavelength in nanometre (nm) and the y-axis shows the emission (Em) wavelength in nanometre (nm) with low fluorescence being
blue and high being red.**

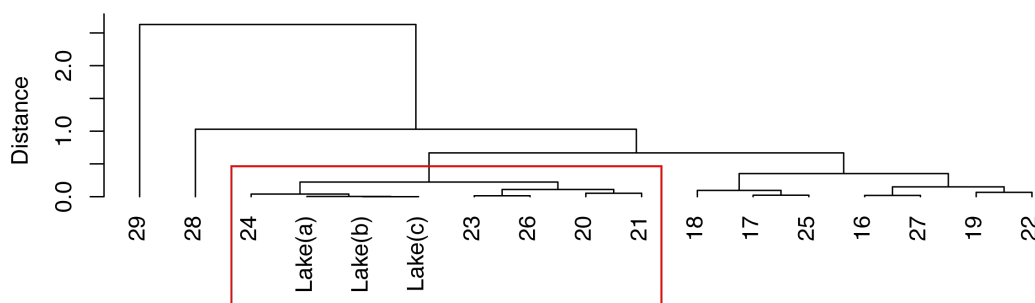



Figure 4: Euclidean hierarchical clustering of fluorescent component C4 from recharging groundwater sites. The fluorescence found at sites 20, 21, 23, 24, and 26 clusters together with lake fluorescence (marked by red). This indicate that these sites have a high degree of groundwater recharge. Groundwater well site number 24 seems to be especially important in this regard.

525

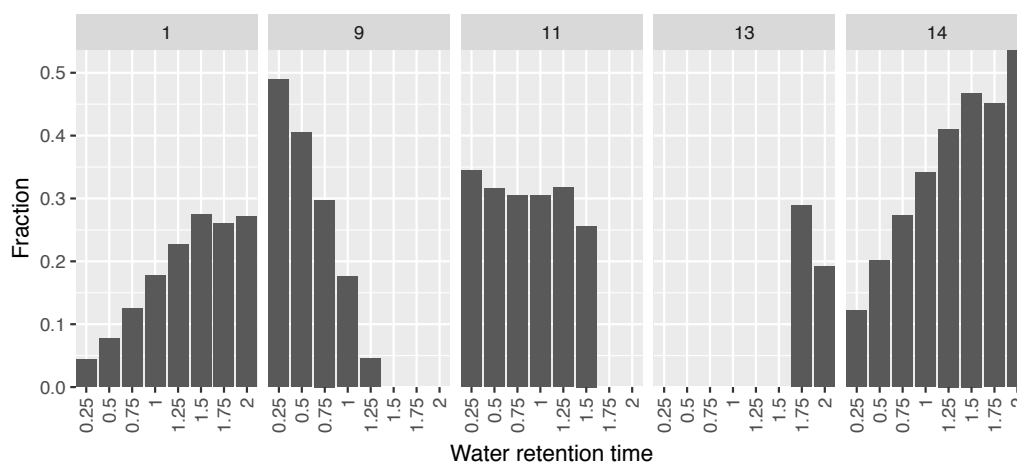



Figure 5: Results derived from the CATS model shown in a bar plot where the groundwater well sites (their numbering) are seen on the top x-axis and the fractions of water estimated to derive from the sites at the y-axis. The bottom x-axis denotes the different water retention times used in this model. Three to four sites generally explain the estimated concentrations in the lake.

530