Endogenic methylmercury in a eutrophic lake during the formation and decay of seston

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Abstract. Anoxic microniches in sinking particles in lakes have been identified as important water phase production zones of monomethylmercury (MeHg) (endogenic MeHg). However, the production and decay of MeHg during organic matter (OM) decomposition in the water column and its relation to the total Hg concentration in seston are poorly understood. We investigated total Hg and MeHg ~~speciation and~~ in relation to chemical changes in sinking seston and hydrochemical settings in a small and shallow (12-m-deep) eutrophic lake during phytoplankton blooms from April to November 2019. The results show that MeHg proportions reach up to 22 % ~~are high~~ in seston in oxygen super-saturation ~~at the water surface~~ ~~(up to 22 %)~~ and highest values (up to 26 %) at the oxic-suboxic redox boundary ~~(up to 26 %).~~. MeHg concentrations were highest in May and November when algal biomass production was low and the seston dominated by zooplankton. Biodilution of MeHg concentrations could not be observed in the months of highest algal biomass production instead MeHg and THg concentrations in seston were comparatively high. During suboxic OM decomposition, and with decreasing redox-potential (Mn and nitrate reduction), the concentration and proportion of MeHg in seston strongly decreased (< 0.5 %) whereas total Hg concentrations show a 3.8 to 26-fold increase with ~~as the~~ water depth ~~increases~~. Here, it remains unclear to which extent biodilution on the one hand and OM decomposition on the other alter the MeHg and THg concentration in seston. ~~Under these conditions, total Hg concentrations show a 3.8 to 26-fold increase.~~ Changes in OM quality were most intense within or slightly below the redox transition zone (RTZ). The concentrations of MeHg and THg in seston from the RTZ were comparable to those found in the sediment trap material which integrated the changes in seston composition during the entire sampling period suggesting that changes in the MeHg and THg content in the hypolimnion below the RTZ are comparatively small. Our study suggests that in shallow eutrophic lakes, the water phase formation and decomposition of MeHg is intense and controlled by the decomposition of algal biomass and assumingly largely disconnected from Hg methylation in sediments similar to what has been observed in deep oligotrophic lakes.

~~In the hypolimnion environment, changes in MeHg proportions were minimal in sinking seston, and samples collected by sediment traps had MeHg values similar to those measured at the sediment water interface, though higher MeHg~~

concentrations were found deeper in the sediment. Our results indicate that cycling of MeHg and total Hg (THg) in seston within small productive lakes is largely controlled by the decomposition processes of settling seston and that the endogenic MeHg pool appears to be largely disconnected from the sedimentary MeHg pool.

1 Introduction

Lakes are dynamic systems where methylmercury (MeHg) is produced and can become bioaccumulated in the food chain (Ravichandran, 2004). The methylation of inorganic divalent forms of mercury (Hg(Hg(II))) to toxic MeHg is carried out by a variety of obligate anaerobic microorganisms (Peterson et al., 2020; Gilmour et al., 1992; Fleming et al., 2006; Gilmour et al., 2013) that decompose the organic matter (OM) produced mainly by the primary productivity occurring in the upper water column. Thus, lacustrine Hg methylation is, presumably, closely connected to the biological pump and related temporal and spatial changes in redox conditions and related Hg methylating bacteria, as well as being influenced by temporal and spatial variabilities. Aquatic MeHg production has been previously investigated in sediments (Jensen and Jernelöv, 1969; Gilmour et al., 1992; Robinson and Tuovinen, 1984; Hammerschmidt et al., 2004; Hollweg et al., 2009; Sunderland et al., 2004; Bouchet et al., 2013) and more recently in the oxic and anoxic water column (hereafter defined as endogenic source produced MeHg (Gallorini and Loizeau, 2021)) of marine (Topping and Davies, 1981; Soerensen et al., 2018; Cossa et al., 2011; Heimbürger et al., 2015; Ortiz et al., 2015; Wang et al., 2018) and freshwater systems (Eckley et al., 2005; Peterson et al., 2020; Gascón Díez et al., 2018; Watras and Bloom, 1994; Gallorini and Loizeau, 2022). ++Gallorini and Loizeau 2022 Research conducted in the 1980s in marine systems (Topping and Davies, 1981) and in lake systems in the 1990s (Watras and Bloom, 1994) suggested that the endogenous MeHg sources are similar to, or may even exceed, sedimentary MeHg production. Endogenously produced MeHg may increase MeHg exposure at the base of the aquatic food chain which may explain the high MeHg levels observed at higher trophic levels (Heimbürger et al., 2015; Gallorini and Loizeau, 2021). Several studies indicate that maximum MeHg concentrations occur at the middle of the water column. The observed changes in water column MeHg concentrations were related to OM mineralization (Sunderland et al., 2009; Cossa et al., 2011; Cossa et al., 1997; Heimbürger et al., 2010; Heimbürger et al., 2015) below the oxic/anoxic boundary(Mauro et al., 2002) or along redox gradients in the water column (Peterson et al., 2020; Watras et al., 1995). Based on observations of water column MeHg formation under differing states of oxygen (O_2) saturation, anoxic microniches have been proposed as important MeHg production sites in and around settling particles in both lacustrine and the marine water columns (Gascón Díez et al., 2016; Schartup et al., 2015a). However, MeHg formation in anoxic microniches has only been observed directly in marine particles (Ortiz et al., 2015; Gallorini and Loizeau, 2021). Regarding the abundance, chemical composition and microbial colonization, aggregates of settling particles formed in lakes ("lake snow") do not differ significantly from those in marine waters ("marine snow") (Grossart and Simon,

1993). This implies that anoxic microniches ~~can~~should also be formed in lakes~~,~~. A recent study by Gallorini and Loizeau (2022)~~Gallorini and Loizeau (2022)~~ shows MeHg formation in lake snow under oligotrophic and oxic conditions and increasing THg and MeHg concentration in lake snow with depth. Most available studies on water column Hg methylation

65 were carried out on oligotrophic or mesotrophic lakes. As water column MeHg formation is connected to redox conditions and the amount of decaying biomass we hypothesize that it is particularly intensive in eutrophic lakes w~~ith high~~here high OM turnover and formation of redox gradients is pronounced. Although it has shown that high plankton densities in lakes reduce ~~mercury~~Hg biomagnification (Chen and Folt, 2005), ~~P~~previous studies on Hg cycling in mesotrophic and eutrophic lakes have shown that high primary productivity enhances lacustrine Hg sedimentation due to algae scavenging water column Hg (Schütze et al.,

70 2021; Biester et al., 2018). Liang et al. (2022) has recently shown that Hg scavenged or taken up by algae can experience species transformation such as reduction or β-HgS formation under sunlit or dark conditions.~~by aquatic microorganisms and particles may undergo a process of species transformation concurrent with the OM degradation processes that occur during particle settling~~ (Meyers and Eadie, 1993)~~.~~

Degradation is most pronounced in recently produced OM (Higginson, 2009), which is primarily altered in the upper water

75 column (Meyers and Eadie, 1993). Meyers and Eadie ~~(Meyers and Eadie, 1993)~~ showed that OM at different water column depths is decomposed by different biogeochemical processes. Degradation rates decrease with depth, resulting in increasing amounts of refractory OM (Higginson, 2009). The temporal and spatial occurrences of lacustrine MeHg in settling particles and how it changes during OM decomposition throughout the water column are still poorly understood. Most studies are either based on laboratory analysis (Pickhardt and Fisher, 2007), studies using sediment traps (Gascón Díez et al., 2016) or analysis

80 of bottom sediment~~s~~ (Zaferani et al., 2018). Moreover, ~~nearly all~~most of these studies are based on singular sampling from ~~only a~~ few locations in the water column. These low resolution sampling schemes limit our ability to decipher the temporal and depth dependent processes of MeHg formation or degradation in sinking seston~~s. In addition, most existing studies were carried out in oligotrophic boreal lakes. This is important as many lakes outside the boreal zone have high nutrient levels or suffer from eutrophication and often contain comparatively high Hg concentration levels in the sediment~~ (Schütze et al., 2021)~~.~~

85 In this study, we developed water column and seston (particles >25 µm) depth profiles (at 1 m intervals) in a productive lake over seven sampling days between April and November (2019). We ~~This was done to~~ investigate~~d~~ the formation and fate of MeHg during algal blooms and during the degradation of settling seston throughout the seasonal lake cycle. We hypothesize that the high algal biomass production ~~primary productivity~~ in eutrophic lakes and related changes in water column redox conditions provide suitable condition for MeHg scavenging or MeHg formation by or in seston. Moreover, we expect that the

90 ~~Me~~Hg speciation, concentrations and proportions in seston are altered through OM degradation in the water column and that even in shallow eutrophic lakes the endogenic MeHg pool is ~~likely~~ at least partly independent from sedimentary MeHg formation~~.~~ similar to what has been shown for deep oligotrophic lakes.

2 Materials and Methods

2.1 Study site and sampling

95 Lake Ölper (105 m a.s.l., 52°28′80″ N, 10°51′20″ E) is an artificial dimictic lake located in the city of Braunschweig, Germany. We used this lake as a natural laboratory, as it has no direct inflow and receives relatively low surface run-off, which minimizes the external input of MeHg. Moreover, the lake is known to show negligible lateral currents, which may cause frequent mixing. The lake has an area of 0.158 km² and is 10–13 m deep. It is mainly fed by rain and groundwater and receives input from the nearby Oker River during rare flood events only via a small trench (Galggraben). There were no flood events in 2019 and

100 surface run-off was minimal due to very arid conditions. The lake is surrounded by a park, and its catchment is flat and is smaller in area than the lake itself. The vegetation is dominated by willows. Ground elder and reeds are distributed heterogeneously around the lake (mostly present on the south bank). Water and seston samples were taken on seven days between April and November 2019 using a clean stainless steel immersion pump (Comet Combi 12–4T). The water column was sampled over the deepest (~12 m) portion of the lake. Samples were collected from the surface down to the sediment-

105 water interface at 1 m intervals. Samples for chlorophyll a (Chla) determination, following DIN 38409 - H 60 (Deutsches Institut für Normung, 2015), were stored in 0.5 L and 2 L PE flasks that had been pre-rinsed and cleaned with acid. Samples intended for chemical analyses (i.e., THg, DOC, Mn, Fe, major ions) were vacuum filtered using <0.45 µm nylon filters and stored in 50 ml PE Falcon tubes for.

Seston samples were collected by means of a plankton net with a 25-µm mesh and placed into 100-ml acid-cleaned and pre-

110 rinsed flasks. Surface seston samples were collected at 0.2 m depth by drawing the net behind the boat. Seston samples from deeper water layers (up to 4–12 m) were collected by pumping between 60 L and 120 L through the plankton net (tubing was acid washed before sampling). Depending on the plankton abundance and distribution in the water column, sampled depths varied by day between 4 and 12 m, but in most cases covered the upper 4-5 m (except in November where only the upper 2 m were sampled). Additionally, the change in redox conditions between well oxygenated and poorly oxygenated water also

115 impacted the sampling depth. All seston samples were frozen immediately after sampling and subsequently freeze-dried and homogenized with a glass pestle for further analyses (THg, MeHg, CNS). Water temperature, electrical conductivity (EC), pH and O_2 concentrations and saturation were measured in situ using handheld single-parameter probes.

Bulk settling seston was collected over 141 days from early May to late September (06.05–24.09) by means of a sediment trap positioned at the deepest part of the lake approximately 1 m above the sediment-water interface (~ 11 m depth) to obtain a

120 sample which integrates the decomposition changes of seston over the entire sampling period. This material is assumed to largely reflect the composition of the uppermost sediment layer. The sediment trap consisted of two individual particle interceptor traps (PIT). Each trap had a collection area of 0.45 cm² and was kept vertical in the water column by two buoys.

Prior to deployment, each PIT was acid-cleaned and prerinsed with lake water. In addition, a short sediment core (6 cm) was taken using a UWITEC gravity corer at the sediment trap position. Sampling material was frozen immediately after collection, freeze-dried and ground for further analyses (THg, MeHg, CNS).

2.2 Analyses of water samples

2.2.1 Total dissolved Hg

For total dissolved Hg analyses, filtered water samples were stabilized using a 0.5 % (v/v) ultrapure BrCl–HCl solution in order to convert all organic Hg compounds to inorganic Hg^{2+}. THg was determined by means of cold vapour atomic fluorescence spectrometry (CV-AFS, Mercur Analytic Jena AG, Germany) after Hg^{2+} was reduced with stannous chloride according to EPA method 1631. The quality of the measurements was controlled by the certified reference Material ORMS 5 "elevated mercury in river water" (NRC CNRC) with a Hg concentration of 26.2 ± 1.3 ng L^{-1}. The mean recovery was 102.5 % (n= 20) with a mean blank concentration of 0.9 ng L^{-1}.

2.2.2 Iron and manganese

Dissolved iron (Fe) and manganese (Mn) concentrations were analysed in the acidified water samples (1 % (v/v) bidistilled nitric acid ($HNO_{3;}$)) by means of inductively coupled plasma–optical emission spectrometry (ICP–OES, Varian 715 ES, Agilent Technologies Inc., USA).
The quality of the measurements was controlled by CRM SLRS-6 (river water) with an Fe concentration of 84.3 ± 3.6 µg L^{-1} and a Mn concentration of 2.12 ± 0.1 µg L^{-1}. The mean recovery of the CRM (n= 6) was 94.4 % for Fe and 112.1 % for Mn.

2.2.3 Dissolved organic carbon

DOC concentrations were determined after water samples were acidified with HCl to a pH value of two to remove carbonic acid and after thermocatalytic oxidation of the sample by means of a TOC-Analyser (multi N/C 2100, Analytic Jena AG, Germany). Measurements of DOC were validated using CRMs (ION-96.4, TOC20 and NW-Ontario-12), with mean recoveries of 107.7 % (n= 11), 95.3 % (n= 17) and 97 % (n= 9).

2.2.4 Nitrate and sulphate

Nitrate (NO_3^-) and sulphate (SO_4^{2-}) were determined by means of ion exchange chromatography (761 Compact IC, Metrohm AG, Switzerland). The quality of the measurements was controlled by the CRM, Roth Multi-Element Standard solution ($NO_3^- = 24.997\pm0.064$ mg L^{-1}; $SO_4^{2-} = 30.049\pm0.070$ mg L^{-1}) and the IC Multi-Standard solution 02179 (Bernd Kraft)

(NO$_3^-$= 1000 mg L^{-1}; SO$_4^{2-}$= 1000 mg L^{-1}). Mean recoveries for the CRM Roth (n =20) were 97 % for NO$_3^-$ and 96.7 % for SO$_4^{2-}$ and for the CRM IC Multi-Standard solution 02179 (Bernd Kraft) (n=3) 86 % for NO$_3^-$ and 91.1 % for SO$_4^{2-}$.

2.2.5 Chlorophyll a.

~~Chlorophyll~~ Chla was determined according to the German standard procedure DIN 38409 – H 60 (Deutsches Institut für Normung, 2015). Between 1 and 2 litres of lake water were vacuum filtered using Whatman GF/F filters (Carl Roth GmbH + Co. KG, Germany). The filters were folded and homogenized, and the pigments were extracted immediately with 15 ml 90% ethanol (78 °C) in a opaque 50-ml Falcon tubes and stored for 12-24 h in the dark at room temperature. These extracted pigments were clarified by filtration using membrane filters, and their concentration was measured by means of a UV–VIS spectrometer Lambda 25 (Perkin Elmer) at 750 nm and 665 nm against 90% ethanol. The concentration was corrected for phaeopigment by acidification of the sample with 0.3 Vol% 2 M HCl (Deutsches Institut für Normung, 2015).

2.3 Analyses of seston, sediment trap material and bottom sediments

Seston samples, sediment traps and core materials were freeze dried (LYOVAC GT 2- E). The dried seston samples were homogenized using a glass stick. Sediment trap and core samples were ground in a cleaned agate ball mill. All the solid samples were subjected to the same methods for the following analyses.

2.3.1 Total Hg

The THg content in all solid samples was analysed by thermal decomposition followed by preconcentration of Hg on a gold trap and atomic absorption spectrometry using a DMA-80 direct mercury analyser (Milestone, Italy). For quality control, three standard reference materials with different matrices (apple leaves NIST-1515 (THg= 44 ng g^{-1}), Chinese sediment NCS DC 73312 (THg= 40 ng g^{-1}) and plankton material BCR-414 (THg= 276 µg g^{-1}) were measured.
The mean recovery of the CRMs was 111.9 % for apple leaves (n= 20), 93.6 % for Chinese sediment (n= 24) and 107.7 % for plankton material (n= 9).

2.3.2 Methylmercury

The extraction of MeHg from the seston samples was performed using a slightly altered procedure for biota samples suggested by the U.S. Geological Survey's Mercury Research Laboratory (USGS Method 5 A-7) (USGS-Mercury Research Laboratory, 2016). Samples were digested in 5 M nitric acid (instead of 4.5 M) for ~15 h (instead of 8 h) until no visual residues could be observed to ensure complete digestion. Digested samples were buffered with sodium acetate at pH ~4.9 and ethylated using

175 sodium tetraethylborate (NaTEB). MeHg was analysed using a purge and trap CV-AFS (Tekran 2700) methylmercury analyser.

The quality of the measurements was controlled by three CRMs, TORT-2 lobster hepatopancreas (MeHg=163.4 ng g^{-1}), DOLT-5 dogfish liver (MeHg=127.9 ng g^{-1}) and SRM® 15566b oyster tissue (MeHg=14.2 ng g^{-1}). The mean recoveries for the CRMs were 83.11 % for TORT-2 (n= 7), 108.33 % for DOLT-5 (n=6), and 103.6 % for SRM® 15566b-2 (n= 7).

180 To extract MeHg from the sediment samples, between ~0.5 – 1 g of material was weighed into new 50 mL Falcon tubes and between 20 – 100 µL of an internal standard, an isotopically enriched Me^{200}Hg standard with concentration 1.1 ng g^{-1}, was added and then left to equilibrate for an hour. After equilibration, 10 mL KBr (1.4 M), 2 mL CuSO$_4$ (2 M) and 10 mL dichloromethane, DCM (CH2Cl2) were added to each tube, which was then capped and left for 45 min. To extract MeHg, the samples were rotated at 85 RPM on a sample rotor for 45 min and then centrifuged for 5 min at 3000 RPM. MeHg was analysed

185 using a Tekran® Model 2700 Automated Methylmercury Analysis System connected to an Inductively Coupled Plasma Mass Spectrometer, Thermo–Fisher X- series 2 (ICPMS). Prior to analysis, half the extracted sample was ethylated using sodium tetraethylborate (NaTEB) at pH 4.9 (using 225 µl of a 2 M acetate buffer). The certified reference material (ERM-CC580, estuarine sediment) analysed was on average 110 % of the certified value (75 ± 4 ng g^{-1}) (for a detailed description, please see the method section in the supplementary material).

190 **2.3.3 Carbon, Nitrogen, Sulphur**

Total organic carbon (C)C, nitrogen (N) and sulphur (S) in all solid samples were measured by means of an elemental analyser (EuroEA 3000, Hekatech GmbH, Germany) that combusted 10–20 mg aliquots of each sample in a tin capsule calibrated with a sulphanilamide standard (C= 41.75 ± 0.17 %; N= 16.26 ± 0.22 %; S= 18.64 ± 0.18 %) and BBOT (2.5-Bis (5-tert-butyl-benzoxazol-2-yl)thiophene); C= 72.52 %; N= 6.51 %; S= 7.44 %). All samples were decarbonated using 0.1 M HCL prior to

195 analyses. The quality of the measurements was controlled by three CRM, NIST 1515 apple leaves (N = 2.25 ± 0.19 %), NCG DC 73030 Chinese soil (C= 0.617 ± 0.044 %; S= 0.2 ± 0.03 %), MOC soil standard (C= 3.19 ± 0.07 %; N= 0.27 ± 0.02 %; S= 0.043 ± 0.005 %) and sulfanilamide (1 for every 10 analyses).

Mean recoveries for the CRMs in sulfanilamide (n= 14) were 99.7 % for C, 98.8 % for N and 106.4 % for S; NIST 1515 apple leaves (n= 4), 95.4 % for N; NCG DC 73030 Chinese soil (n= 2), 97.9 % for C and 108.3 % for S; MOC soil standard (n= 4),

200 80 % for N; 99.9 % for C and 106.4 % for S. Average results for the CRMs were sulphanilamide (n = 14) C = 41.6 ± 2.6%, N = 16.1 ± 1.2% and S = 18.5 ± 1.5%; NIST 1515 apple leaves (n= 4) N = 2.1 ± 7.3%; NCG DC 73030 Chinese soil (n= 2) C = 0.6 ± 0.8% and S = 0.22 ± 1.15% and MOC soil standard (n= 4) C = 3.19 ± 0.89%.

3 Results and Discussion

3.1 Changes in algal biomass production ~~phytoplankton productivity~~ and redox conditions

205 Based on the ~~chlorophyll a~~ (Chla~~) concentration~~, pH and O_2 concentrations and saturation (Fig. 1 and S2) ~~results, we found two productive periods. T~~ the month of April and ~~the months~~ those from June to September were defined as periods of high production of algal biomass~~phytoplankton productivity~~, with ~~chlorophyll~~ Chla concentrations between 29 µg L^{-1} in June and 95 µg L^{-1} in September (Fig. S2; August 12 Chl. n.d.), supersaturation of O_2 with values between 115 % and 151 % (except at the 2 m depth in June where the value was 66 %) and high pH values between 8.7 and 9.3 (except at the 2 m depth in June

210 which was 7.8). The highest pH values occurred in the upper two metres of the water column (0-2 m) on August 12 and 19 and were 9 and 9.3 respectively (Fig. 1). May and November are defined as periods ~~the~~of low production of algal biomass.~~phytoplankton productivity period.~~ In May, the surface pH dropped from 9 to approximately 7.7, while O_2 saturation dropped to between 80 and 86.6 %. Chla ~~Chlorophyll a~~ concentrations were 2.5 to 2.8 ~~8~~ µg L^{-1}, indicative of low production of algal biomass.~~phytoplankton productivity.~~ The surface water pH dropped to 7.3 after mixing in November, when production

215 of algal biomass~~productivity~~ was very low (Fig. 1) (Chla n.d.), with correspondingly low O_2 saturation ~~values~~ throughout the entire water column (mean: 28.8 %).

The decrease in pH and O_2 saturation with depth indicates the zone where OM respiration and other oxidative processes began to exceed primary production and where the onset of related changes in redox conditions occur. Bacteria use a fixed sequence of alternative electron acceptors for OM mineralization (O_2 > nitrate (NO_3^-) ~ Mn_{ox} > Fe_{ox} > sulphate (SO_4^{2-})) (Froelich et al.,

220 1979). Thus, the progressive decay of sinking OM is indicated by the concentration profiles of O_2, dissolved NO_3^-, dissolved Mn and Fe. Lake Ölper shows a clinograde seasonal depth profile of dissolved O_2 from April to September, with a sharp oxycline that started to develop in May at a depth of approximately 4 m (Fig. 1). The oxycline occurs at variable depths within the first 4 metres until September when there is a decrease in O_2 saturation to less than 10 % within 1–3 m. There is an increase in Mn concentrations in the zone where the sharp drop in O_2 saturation occurs. This section of changing electron acceptors is

225 hereafter defined as the redox transition zone (RTZ) from oxic to suboxic conditions. The position (1 - 4.5 m) and thickness (1 – 3 m) of the RTZ changed throughout the sampling period and were controlled by the intensity of algal biomass production ~~productivity~~ in the surface layer and its progressive decay during sinking. Mn reduction was first detected in April and then increased and ascended in the water column from May to September, whereas Fe reduction was only detectable below ~ 8 m in May and below 9 m in August and September. After mixing in November, the Mn and Fe concentrations were ~~uniformly~~

230 generally low (Fig. 1). This indicates that during the period of high algal biomass production~~phytoplankton productivity period~~, the amount of algal biomass ~~primary production~~ and OM decay facilitated Mn and, to a lesser extent, Fe reduction (Fig. 1), whereas SO_4^{2-} reduction was not observed during the entire sampling period (Fig. S3).

3.2 ~~Microbial d~~Decomposition of OM in the water column as indicated by C/N ratios

Carbon to nitrogen ratios (C/N) in lake sediments or seston are commonly used to distinguish between autochthonous and allochthonous-derived OM. Seston C/N ratio in Lake Ölper showed a median of 6.4 (n= 42; 4–8.3; excluding two outliers with values of 12.6 and 16.3 in bulk sampled seston in August) (Fig. 2), indicating plankton as the dominant OM source (Müller, 1977).

However, for water column seston samples at individual days, relative changes in C/N ratios in seston can be used as an indicator for OM degradation (Meyers and Lallier-Vergés, 1999). In the photic zone, C/N ratios decreased slightly with depth, which may indicat~~ing~~ selective C mineralization under oxic conditions and relative enrichment of N. Under suboxic conditions, C/N ratios were lowest within the RTZ before they strongly increased again within or below the RTZ (Fig. 2), which may be induced by ~~due to~~ preferential decomposition of nitrogen-rich proteins resulting in a relative enrichment in C~~Ccarbon~~ (Meyers and Lallier-Vergés, 1999) (though this was not observed in September). The decomposition of seston during vertical transport in the water column must be divided into zones of aerobic and anaerobic decay, as suggested by Oguz et al. (2000), with the transition zone (RTZ) in between. ~~Here~~The sharp increase in the C/N ratio within or just below the RTZ visible in June, August and to a lesser extent in May, mark~~, the C/N ratio showed~~ the greatest change in the C/N ratio along the water column, ~~so we~~ suggesting that microbial decomposition and the alteration of OM were more intense within and just below the RTZ compared to the layers above. It is generally accepted that the C/N ratio of planktonic OM increases steadily while decomposing and sinking down to the sediment (Gordon, 1971; Müller, 1977). ~~Here, t~~ ~~The decomposition of seston during vertical transport in the water column must be divided into zones of aerobic and anaerobic decay, as suggested by Oguz et al. (2000), with the transition zone (RTZ) in between.~~ Despite the relatively higher loss of N, both C and N strongly decreased within and below the RTZ in June, August 12 and 19, and September, while S increased (Fig. 2). ~~It was noted that s~~Samples collected ~~closer to the sediment water interface~~ below the RTZ in June, August 12 and 19, and September, had C and N concentrations and C/N ratios that were similar to those observed in the sediment trap material (Fig. 1) and the upper sedimentary layer (0-2 cm: C: 8.8%; N: 0.7 %; S: 0.8 %; C/N: 12.76). Thus, we assume that decomposition appeared to decrease further below the RTZ as OM became more refractory with ~~during~~ decomposition. Similar to Lake Ölper, a maximum of OM decomposition beneath the bottom of the euphotic zone was reported by Saino and Hattori (1987). Such a thin layer with enhanced microbial activity is likely caused by changing redox acceptors and the aggregation of labile OM enriched by nutrients accumulating in areas with neutral buoyancy, which was likely induced by water column stratification during phytoplankton blooms (Schartup et al., 2015a). In April, the increase in decomposition-related C/N ratios occurred continuously below 4 m when O_2 saturation was still relatively high (see also the change in colour of the seston from a light green to darker green–brownish colour at ~6 m (Fig. S~~6~~8)). Here, no decomposition maximum, as indicated by a sharp change in the C/N ratio, could be observed because the neutral buoyancy induced by water column stratification was not sufficiently

developed. The C/N ratios in seston indicate that degradation of OM generally occurs quickly ~~in the upper aerobic water layers,~~

265 ~~including~~within and just below the RTZ, and probably slower below the RTZ. This may indicate that the influence of OM decomposition on MeHg and THg concentrations is strongest ~~in the oxygenated upper waters, especially in stratified water columns.~~within and just below the RTZ.

3.3 Spatial and temporal distributions of MeHg and THg

The seston MeHg concentration in the upper water layer (upper two metres) was ~~between~~ 1.6 ~~ng g^{-1}~~ to 2~~7~~.8 ng g^{-1} in April

270 and 3~~2~~.48 ng g^{-1} in November (corresponding to 0.5 to 2,0~~1.9~~ % of MeHg of THg in April and ~~12.2~~13 and 18.6 % in November ~~MeHg of THg~~ (MeHg-%)) respectively. (Fig. 3). April, June, August and September, when algal biomass production ~~primary production~~ was high, showed comparatively low MeHg concentrations (1.6–11.4 ng g^{-1}) in the upper two metres. Higher MeHg concentrations were found in May and November (15.6–48 ng g^{-1}) when lower pH (<7.7) indicated low algal biomass production ~~primary productivity~~ (Fig. 1, 3 and 4). Seston samples from the period of low algal biomass

275 production ~~phytoplankton productivity~~ (May and November) ~~might~~ were likely~~be~~ dominated by zooplankton, as the ~~seston samples~~ from the upper water layers showed a ~~comparably~~ significantly higher N content and thus lower C/N ratios (N: 7.5–11 %, C/N: 4.0–4.5) than seston from April, June, August and September (N: 2.5–6.5 %, C/N: 5.2–8.3) (Fig. 4 ~~) (compare~~and Fig. S8~~6~~). This would explain the comparatively ~~elevated~~ higher MeHg in periods of low algal biomass production~~p hytoplankton productivity~~, as biomagnification from phytoplankton to zooplankton is known to increase MeHg concentrations

280 (Wang et al., 2018).

It has been reported mainly based on laboratory experiments that MeHg concentration in algae material are lower when algal biomass is high (biodilution) (Chen and Folt, 2005; Pickhardt et al., 2002). However, biodilution seems to be of minor importance in lake Ölper. In April, when no RTZ was established, MeHg concentrations showed a continuous increase with depth as O$_2$ concentrations decreased and had a comparatively low maximum of 7.6 ng g^{-1} at 9 m depth (Fig. 3). Biodilution

285 might explain the simultaneous increase in MeHg and THg concentrations and the decrease in algal biomass (Chla) with depth here, where redox zonation was not pronounced throughout the entire water column (Fig. S3~~2~~). ~~But w~~However, we ~~suggest~~assume that the observed increase in MeHg and THg concentrations with depth in April are rather caused by mass loss in the sinking seston during decomposition and decreasing redox potential than by biodilution in the epilimnion~~this is caused by mass loss due to decomposition with depth as shown by~~ Gallorini and Loizeau (2022). ~~However~~Furthermore, ~~high MeHg~~

290 ~~concentrations were observed in August and~~ September has the highest algal biomass (indicated by the highest Chla concentration) but does not have the lowest MeHg concentrations. In contrast, September has higher MeHg concentration than April, June and August 12.~~when algal biomass was highest and redox zonation pronounced~~. These high MeHg concentrations could not be explained by abundance of high amounts of zooplankton as relatively high C/N ratios (compared to May and

November) indicate that the seston here is dominated by algal ~~organic matter~~OM. Similar, algal biomass production (Chla) is relatively lower in June and so are MeHg and THg concentrations. This positive relationship between algal biomass and MeHg as well as THg concentrations clearly indicates that biodilution could not explain the observed spatial and temporal variation in MeHg and THg concentrations in our lake.

~~In times of high algal biomass production and redox zonation seston MeHg concentrations are high. In April, when no RTZ was established, MeHg concentrations showed a continuous increase with depth as O₂ concentrations decreased and had a comparatively low maximum of 7.6 ng g⁻¹ at 9 m depth (Fig. 3).~~

During periods in which the RTZ was clearly defined, MeHg concentrations in seston showed a ~~pronounced~~ maximum ~~at~~ within or directly below the RTZ that did not occur in April, and November when no RTZ was observed (Fig. 3). Thus, from May to ~~August~~September, MeHg concentrations showed a continuous increase from the lake's surface to the RTZ or the layer slightly below the RTZ, where the values peaked (Fig. 3). ~~Below the RTZ~~At those days, where we were able to get sufficient material for analyses, MeHg concentrations decreased 1.3 to 4.4-fold even though the water column became progressively anoxic. ~~In September, MeHg concentrations peaked just below the RTZ. However, not enough material for seston analyses could be obtained from deeper layers.~~

The high MeHg concentrations at the RTZ could be explained by settling seston that aggregates within the RTZ (neutral buoyancy induced by water column stratification) (Schartup et al., 2015a). Settling particles such as this may form anoxic microniches, providing a thin vertical layer of high Hg methylation and biological activity, as suggested in other studies (Gascón Díez et al., 2016; Schartup et al., 2015a; Ortiz et al., 2015; Gallorini and Loizeau, 2022)~~; ; Gallorini and Loizeau , 2022.~~ In April, when no RTZ and no stratification-induced neutral buoyancy were observed, the formation of aggregates and ~~thus~~ the development of anoxic MeHg microniches was unlikely. As mentioned above, ~~Mass loss due to progressive organic matter decomposition This would explain~~ the continuous increase in MeHg and THg concentrations with depth, as opposed to the pronounced mid water column-maximum, is attributed to mass loss during decomposition of seston and because redox ~~observed when redox c~~conditions became increasingly anoxic with ~~water~~ depth (compare ~~the~~ dissolved O₂, Fe and Mn concentrations in Fig. 1). ~~similar to what has been observed in Lake Geneva~~~~However, we cannot exclude MeHg release from the sediment here.~~ A similar observation of continuously increasing THg and MeHg concentrations with depth was reported by Gallorini and Loizeau~~Gallorini and Loizeau (2022)~~ (2022) from oligotrophic Lake Geneva where ~~oxygen~~O₂ saturation throughout the entire water column is always above 20 % comparable to the situation in Lake Ölper in April.~~-~~ However, we cannot exclude MeHg release from the sediment here.

There ~~m~~might be other explanations for the MeHg midwater-maximum that we cannot completely exclude, but we assume those to be less ~~critical~~important than the formation of MeHg in anoxic microniches.

~~First~~ For example, MeHg ~~is~~might be transported by diffusion from other sources, such as bottom sediments or the littoral zone, into the RTZ. This ~~is~~appears to be less likely ~~to be negligible~~, as the depth profiles of O_2, Fe, Mn, pH and EC as well as DOC (Fig. ~~XX~~S6) concentrations indicate that mixing is minor during times of high algal biomass production~~productivity~~. MeHg released from bottom sediments is known to be bound to DOM as chloride concentrations in lakes are too low to be competitive. The DOC profiles (Fig. ~~XX~~S6) clearly indicate that DOC release from the sediment occurs in May, August and September as indicated by the ~~highest~~increasing DOC concentrations found in the deepest water samples. ~~But~~However, lowest DOC concentrations were found below the RTZ which indicate that DOC is unlikely transported by diffusion from the sediment into and above the RTZ.

~~and it is likely that~~Even if MeHg is released from decaying ~~organic matter~~OM in the uppermost sediment layers it appears~~is likely is~~ not to be distributed in the water column in times of RTZ formation. It may be released into the water column only during or shortly after the mixing of the lake (~~e.g.~~e.g., in April). However, DOC ~~profiles do not show diffusion gradients during the summer months when the algae blooms occur and~~ concentrations were even higher in the upper water layers compared to the DOC minimum in the hypolimnium indicating DOC release from decomposing algae ~~organic matter~~OM which suggests rather MeHg formation in the water phase (labile algae derived DOM supports microbial MeHg formation in the water phase) than uptake of MeHg released from the sediments.

~~Second~~ Moreover, Hammerschmidt and Bowman (2012) suggested that there might be other methylators not yet identified that are able to methylate Hg even under oxic or suboxic conditions. ~~Third~~Another explanation could be, that~~,~~ the MeHg concentration maxima observed in the RTZ may lie within the habitat of herbivorous and predatory zooplankton that graze the algal biomass. Higher amounts of zooplankton would increase the MeHg concentration in our seston sample due to biomagnification from phytoplankton to zooplankton.

However, the increase in N concentrations with depth was relatively small (between a 1.1 and 1.4-fold increase from the surface to the highest N concentration in the RTZ) compared to changes in N concentration between individual sampling days (up to a 4.4-fold increase at the surface layer) (Fig. 2). Thus, zooplankton occurrence appears to increase MeHg concentrations between individual sampling days, but the effect within individual depth profiles is likely minor and impact the MeHg maxima in the RTZ only marginal. Thus, changes in N and C concentrations with depth are predominantly a result of OM decomposition.

The reasons for the high proportion of MeHg in the seston of the surface layer above the RTZ (up to 22 %) when O_2 saturation was high is unknown. At high O_2 concentrations in the surface layers, the flux of O_2 into settling particles is assumed to be higher than the consumption of O_2 inside the particle. Thus, O_2 concentrations at the surface layer are too high to form anoxic microniches. One possible explanation is that due to vertical mixing above the RTZ, MeHg produced in the RTZ may be

transported to the surface layer where it is taken up or adsorbed by phytoplankton (Kirk et al., 2008). This would explain the elevated MeHg-% even under supersaturated O_2 concentrations in the surface layer.

We suggest that the MeHg midwater maximum in Lake Ölper results from enhanced microbial activity at strong redox gradients related to high biomass production in the surface layers and intense decomposition at layers with neutral buoyancy. The midwater maxima near the surface and the euphotic zone are likely to enhance MeHg exposure to the lacustrine food web.

3.4 Changes in THg/MeHg ratios in seston along redox gradients

The median THg concentrations in the seston were 0.2 µg g^{-1} (0.03–1.2 µg g^{-1}), with 0.13 µg g^{-1} above the RTZ and 0.36 µg g^{-1} within and below the RTZ (Fig. 3). In five out of seven sampling days (excluding May and November), THg concentrations clearly increased from the surface to the deepest sampling point where sufficient material for the analyses could be obtained by factors of 3.8–26.4, with the highest increase occurring within or especially below the RTZ. Gallorini and Loizeau (2022) also observed a continuous increase of THg in sinking seston in a deep oligotrophic lake where no formation of an RTZ occurred. The greatest enrichment was observed in September, when THg concentrations were specifically low in seston from the surface layer. Due to the concentrations of dissolved Hg in the water column of Lake Ölper being relatively constant and low over time and throughout the lake, we conclude that water phase Hg is unlikely to be the major source of Hg enrichment in sinking seston. Concomitant with the THg enrichment, C was depleted 1.2 to 3.9-fold and N 1.2 to 7.7-fold. This loss of mass (loss of N and C) during OM decomposition indicates that THg is somewhat relatively enriched in seston as a result of mass loss.

As discussed in the previous section, the MeHg concentration showed a midwater maximum resulting from enhanced methylation at strong redox gradients (Fig. 3), which is different from the continuous increase in MeHg concentration with depth observed by Gallorini and Loizeau (2022)Gallorini and Loizeau (2022) in lake Geneva where redox zonation was absent . We hypothesize that above the midwater-maximum, MeHg progressively accumulates in sinking seston from the water phase until it reaches the redox boundary, where it accumulates in areas where neutral buoyancy is induced by water column stratification. The decreasing MeHg concentration below the midwater-maximum cannot be explained by decreasing MeHg production alone. Otherwise, we would expect a relative enrichment of MeHg in seston due to carbon loss, as observed for THg.

The varying MeHg concentrations in seston can also not be explained by changing dissolved organic carbon (DOC) concentrations (r= 0.03; p= 0.84). However, recent studies have shown that fresh algae-derived dissolved organic matter (DOM) can enhance MeHg uptake (Schartup et al., 2015b). Due to the absence of continuous inflow, DOM in Lake Ölper is mainly produced in situ by seston decomposition since the catchment influx is low. DOM may play a crucial role in MeHg uptake in oligotrophic lakes or lakes with high catchment runoff but does not appear to play a crucial role in Lake Ölper.

Hence, there must have been a loss of MeHg from the seston within and below the RTZ, which reduces MeHg in the sinking
385 seston. Although we did not determine demethylation rates directly, we conclude that OM decomposition in seston is
accompanied by intense MeHg demethylation during which Hg is released into the water or remains and is reabsorbed by
seston in a different Hg form. The increase in THg concentrations in the seston within and below the RTZ supports the latter
hypothesis.

It is unknown how Hg is bound in degraded OM. Although SO_4^{2-} reduction was not observed in the water phase of lake Ölper
390 during the sampling period, iIt has been shown that microbial SO_4^{2-} reduction, which produces sulphide, occurs in settling
particles within oxygen-deficient zones and in microenvironments within the centre of suspended particles (Raven et al., 2021;
Shanks and Reeder, 1993). The sulphide produced may form insoluble complexes with Hg (Shanks and Reeder, 1993; Bianchi
et al., 2018), such as Hg sulphides (HgS), meaning that Hg becomes less available for methylation (Zhang et al., 2012).
Recently, Liang et al. (2022) Liang et al. (2022) have shown that sunlight facilitates the transformation of Hg in algal cells to
395 less bioavailable species such as β–HgS and Hg-phytochelatins. Thus, Aas S concentrations in the sinking seston of Lake
Ölper strongly increased, within and especially below the RTZ (Fig. 2), the formation of Hg sulphides appears likely.
Suboxic decomposition processes of sinking OM and related redox conditions change THg to MeHg in sestons within a few
metres during summer stratification. Thus, THg and MeHg fluxes to the sediment are largely determined by changes in OM
composition and mass loss during decomposition.

400 **3.5 THg and MeHg in sediment traps and the upper bottom sediment layers**

Seston that settled in the sediment trap contained 1.5 µg g^{-1} THg and 7.8 ng g^{-1} (0.5 %) MeHg. The undecomposed seston from
the upper two metres exceeded the MeHg concentration in the sediment trap material by a factor of 1.2 (median) and by up to
3-fold in the RTZ. The uppermost layer of lake-bottom sediment (0–2 cm) shows THg (2.2 µg g^{-1}) and MeHg (5.86 ng g^{-1})
concentrations comparable to those of the sediment trap material. However, with values of 39 ng g^{-1} (2–4 cm) and 26 ng g^{-1}
405 (4–6 cm), the deeper sediment layers show higher MeHg concentrations at similar THg concentrations (2.06 and 1.96 µg g^{-1})
than the trap material, which indicates that in deeper sediment layers, there might be Hg methylation independent of the
endogenic Hg methylation and/or fluxes to the water that are lower than methylation rates.

On the other hand, THg was up to 41 times higher in the sediment trap material than in seston recovered from the upper two
metres (0.04–0.4 µg g^{-1}) and between 1.3 and 20 times higher than in the seston (0.08–1.2 µg g^{-1}) sampled below the first two
410 metres. The MeHg and THg concentrations and proportions in the deepest seston samples indicate that the closer to the
sediment the seston was collected, the closer the chemical composition (C, N concentrations) and the THg/MeHg ratio were
to that of the surface sediments. In-trap mineralization may further increase the relative enrichment of THg and loss of MeHg
compared to seston at the water surface. Assuming a linear regression of OM fraction loss of -0.001864 per day, as calculated

by Radbourne and Ryves (2020), the initial OM content in our sediment trap material may be reduced by 26.3 % after 141

415 days. This highlights the importance of water column OM decomposition on MeHg cycling in lakes and the need for seston sampling at high spatial and temporal resolutions since sediment traps do not represent all the potential variations in Hg and MeHg cycling in lakes. Hg scavenging and OM decomposition control which Hg species are transported from surface euphotic waters into deeper water and sediments, and the extent to which this occurs. Due to the absence of water mixing during summer stagnation, the decreasing MeHg concentration in seston below the RTZ and the comparable low MeHg concentration in the

420 sediment trap material, MeHg derived from sediments is unlikely to be the major source for the MeHg in seston, specifically during periods of high production of algal mass. ~~This is further supported by the lower MeHg concentrations in the uppermost sedimentary layer compared to those in deeper in the sediment.~~ Thus, in this small eutrophic lake, the epilimnetic pathway is likely of greater importance for MeHg bioaccumulation in the trophic web than the MeHg benthic-hypolimnetic pathway. Additionally, even in this comparatively shallow lake both MeHg pools appear to be largely disconnected, as suggested ~~in a~~

425 ~~recent review~~ by Gallorini and Loizeau~~Gallorini and Loizeau~~ (2021) and Gallorini and Loizeau (2022)~~2022~~ ~~–~~for deep oligotrophic lakes .

4 Conclusions

Our data derived from water and seston samples taken) from eutrophic lake Ölper during an eight-month period (April and November) indicates that~~We showed that separation between the sediment- and water-phase MeHg sources occurred not only~~

430 ~~in deep lakes but also in relatively shallow (12–13-m-deep) and productive lakes. Here,~~ ~~internal lake~~algal biomass production ~~productivity~~ and summer stratification strongly control MeHg ~~production~~concentration and proportions in seston within the ~~predominantly~~ oxic and suboxic- water column. Biomagnification of MeHg was observed in Mai and November when algal mass production was low and the seston appears to be dominated by zooplankton. MeHg biodilution during periods of high algal matter production could not be observed. In contrast during periods of high algal matter production Hg concentrations in

435 seston were highest ~~during~~ when algal biomass production was high and C/N ratios indicate minor occurrence of zooplankton. ~~ntensity of phytoplankton productivity, OM decomposition along redox gradients and the formation of summer stratification and anoxic microniches in sestons~~ NO_3^- and Mn reduction occurs around the RTZ, whereas Fe reduction was only detectable in the deepest water layers and sulphate reduction, typical for Hg-methylators, did not occur in the water phase. The intensity of algal biomass production, OM decomposition along redox gradients in the water column and the formation of anoxic

440 microniches in sestons appear to be major controls for MeHg and THg concentrations in seston. ~~are more crucial than depth in terms of MeHg production and Hg scavenging in eutrophic lakes.~~ We further conclude that the decomposition of labile OM and the demethylation or loss of MeHg within the RTZ exert a stronger influence on MeHg ~~fluxes~~ concentration in seston

transported into the sediment than do MeHg formation under anoxic conditions below the RTZ. Water column MeHg formation and degradation in eutrophic lakes appears to be intense and fast.occurs rapidly and at rates similar to what we observed within the bottom sediments Although, dissolved MeHg has not been measured, the distribution of DOC and dissolved Hg in the water column suggests that MeHg fluxes from the sediments are of minor importance in this eutrophic lake specifically during periods of high algal biomass production. Our study suggests that in shallow eutrophic lakes, the water phase formation and decomposition of MeHg is intense and controlled by the decomposition of algal biomass and assumingly largely disconnected from Hg methylation in sediments similar to what has been observed in deep oligotrophic lakes.

The predicted increase in lake water temperatures and nutrient fluxes will enhance phytoplankton productivity and eutrophication in many lakes, which in turn will lead to declining O_2 saturation (Ho et al., 2019; Jane et al., 2021). According to our findings, such changes likely facilitate MeHg bioaccumulation in the trophic web due to increased endogenic MeHg production, especially in small eutrophic lakes.

Data availability:

The authors declare that all data supporting the findings of this study are available within the paper and its supplementary information files.

Author contributions:

L.B. and H.B. designed the study. L.B., C.B.S. and S.J. carried out the laboratory work. L.B. carried out all sampling and data analyses. L.B. and H.B. wrote the manuscript, and all authors edited and revised the manuscript.

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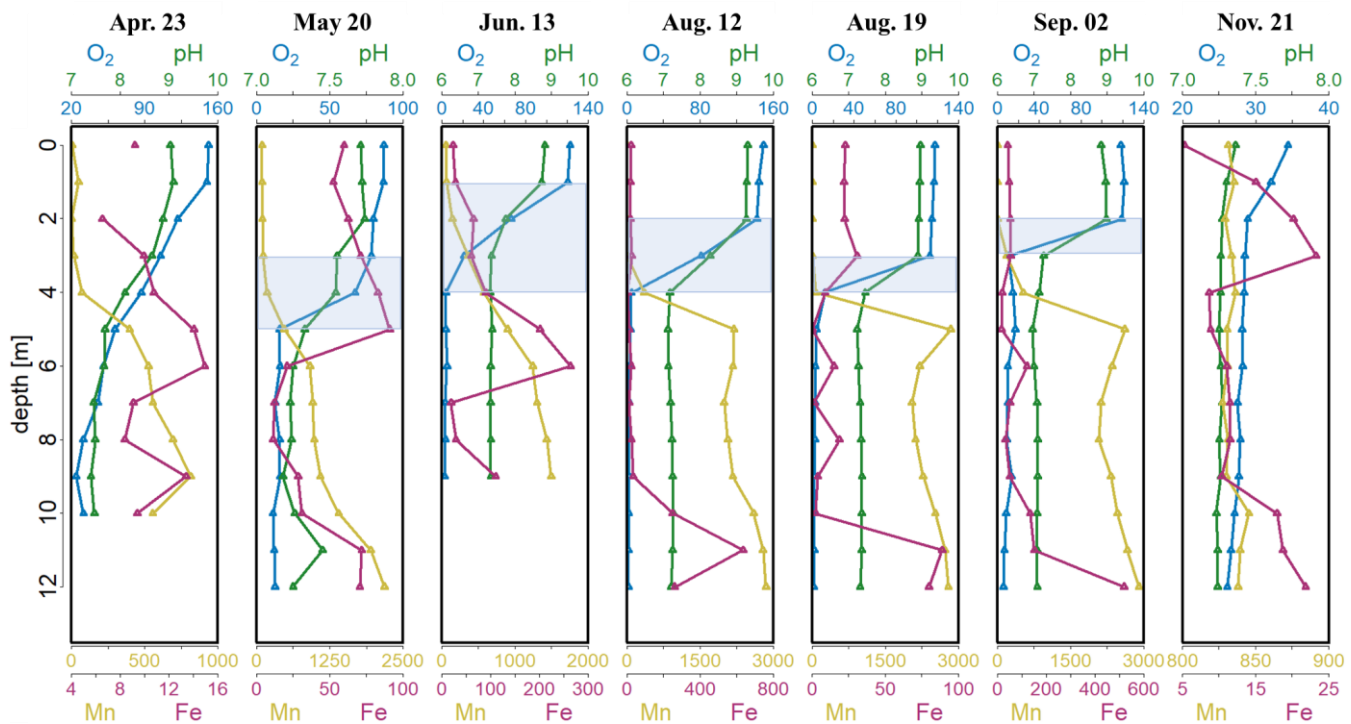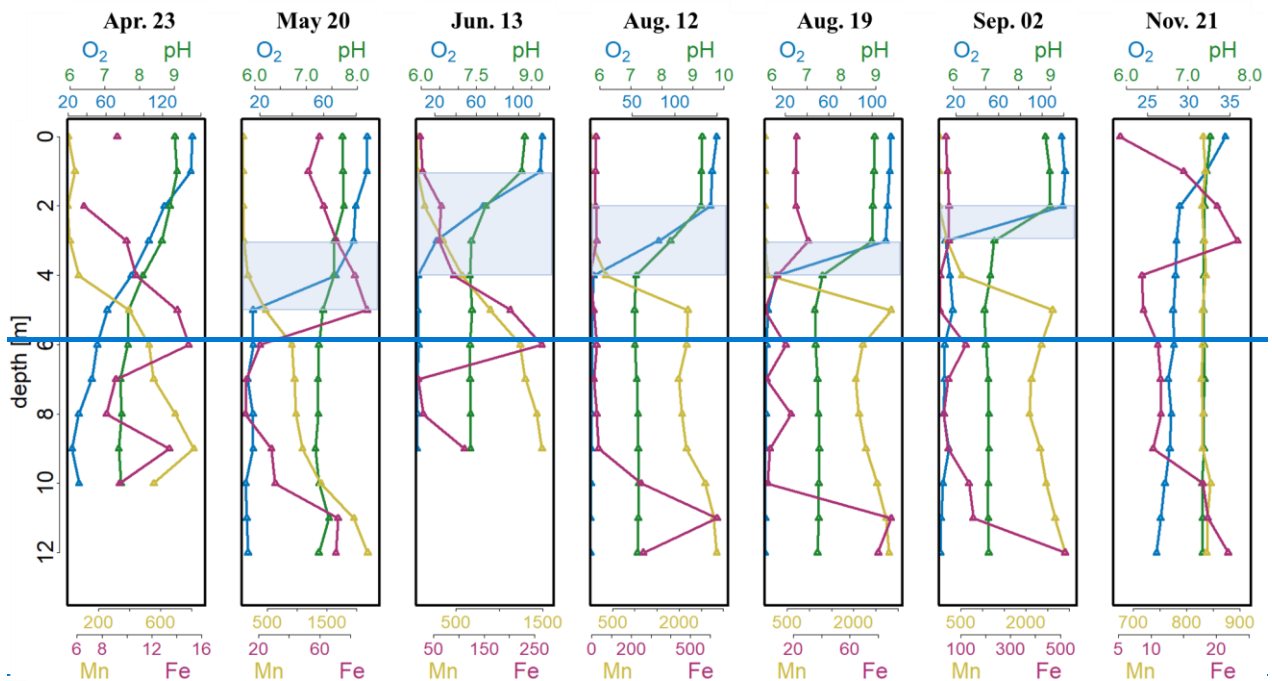
Fig. 1. Depth profiles of O_2 saturation (%), pH and concentrations of dissolved Mn [$\mu g\ L^{-1}$] and Fe [$\mu g\ L^{-1}$] in the Lake Ölper water column from April to November 2019. The depth of the sharp decrease in O_2 concentration and start of Mn reduction (RTZ) are shown in each panel (shaded light blue). Note that each column has an individual scale to better illustrate changes with depth. Depth profiles with the same scale in all columns are shown in the supplements (Fig. S1).

625

Sediment trap material:
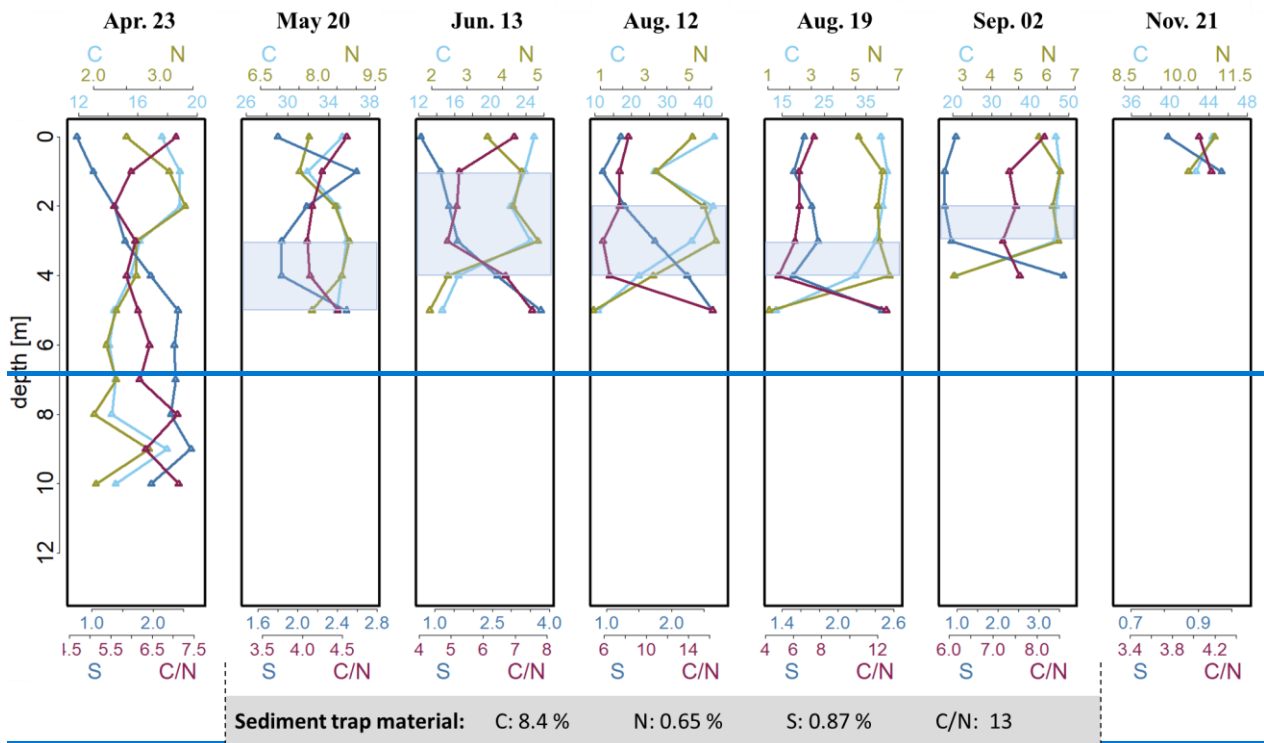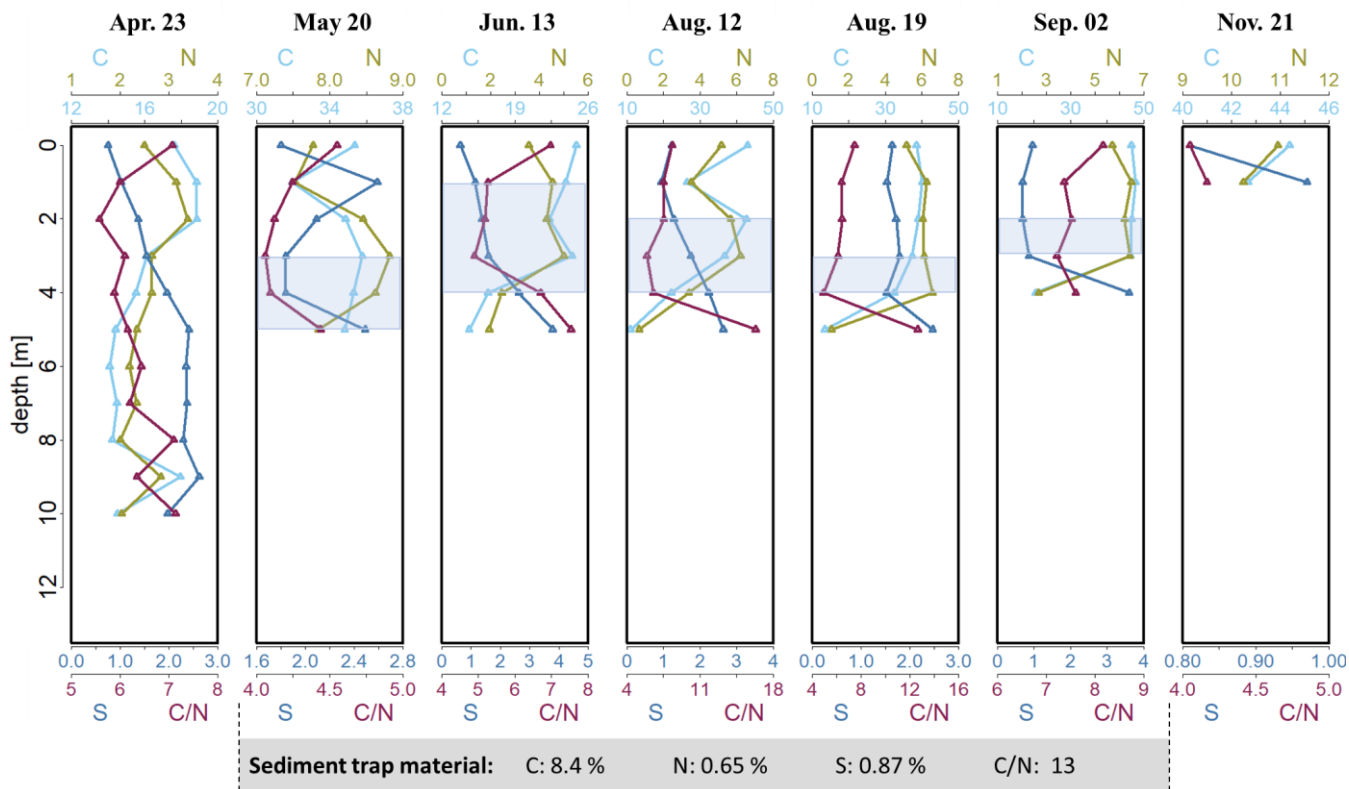
Fig. 2. Depth profiles of C [%], N [%], S [%] concentrations and calculated C/N ratio in the seston in Lake Ölper from April to November 2019. The depth of the sharp decrease in O_2 concentration and start of Mn reduction (RTZ) are shown in each panel (shaded light blue). Concentrations of C [%], N [%], S [%] and the C/N ratio of the sediment trap material collected during the 141 days between May 6th and September 24th are given in the grey box below. Note that each column has an individual scale to better illustrate changes with depth. Depth profiles with the same scale in all columns are shown in the supplements (Fig. S4).

Sediment trap material: THg: 1.5 µg g⁻¹   MeHg: 8 ng g⁻¹   MeHg-%: 0.53 %
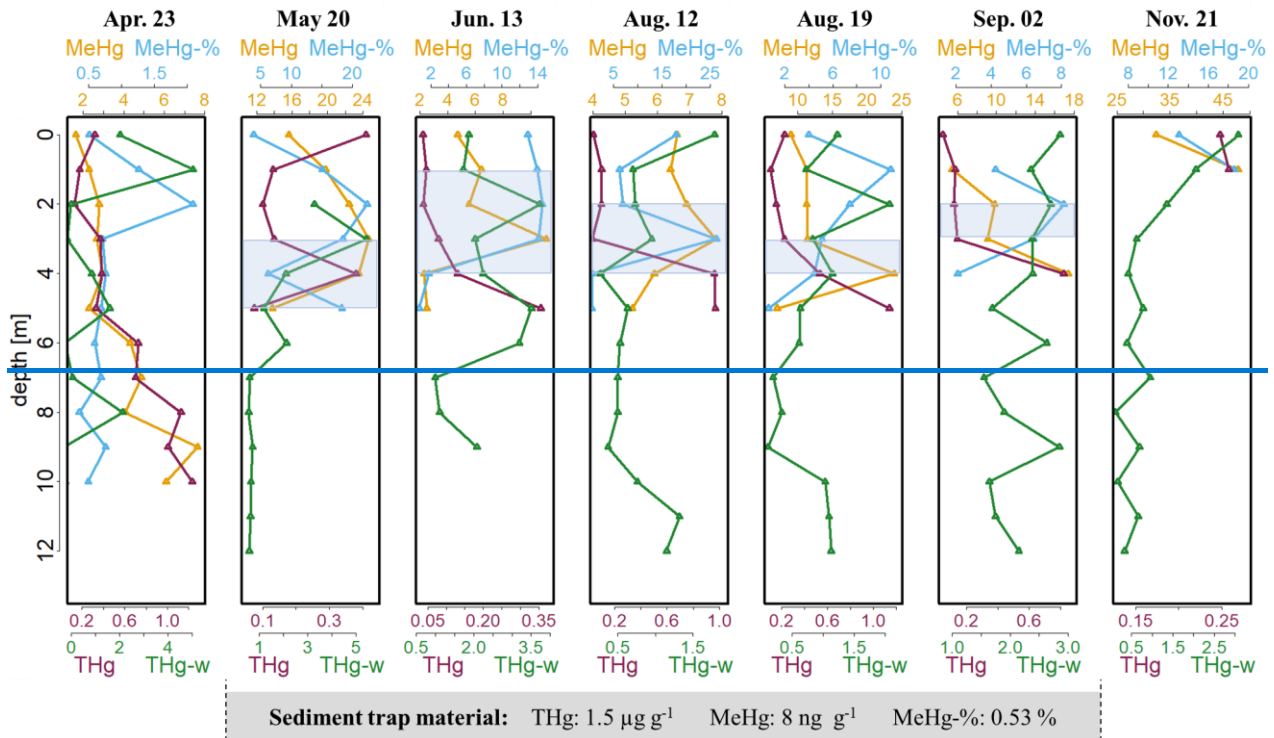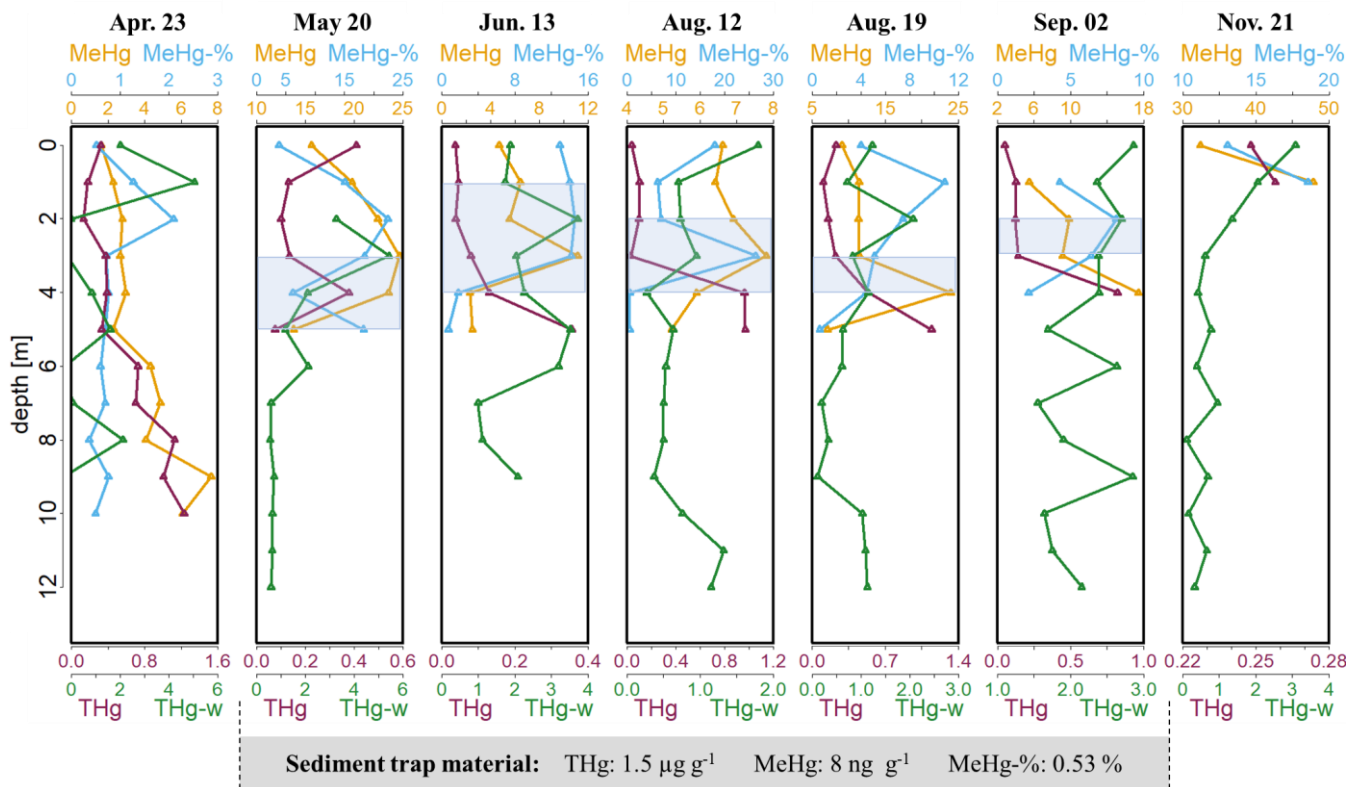
Fig. 3. Depth profiles of MeHg [ng g⁻¹] concentrations, percentage of MeHg [%] of THg (MeHg-%), THg concentrations in seston [µg g⁻¹] and dissolved THg [ng L⁻¹] in the water column (THg-w) of lake Ölper from April to November 2019. The depth of the sharp decrease in O_2 concentration and start of Mn reduction (RTZ) are shown in each panel (shaded light blue). Concentrations of THg [µg g⁻¹], MeHg [ng g⁻¹], MeHg-% [%] of the sediment trap material collected over the 141 days between May 6th and September 24th are given in the grey box below. Note that each column has an individual scale to better illustrate changes with depth. Depth profiles with the same scale in all columns are shown in the supplements (Fig. S5).
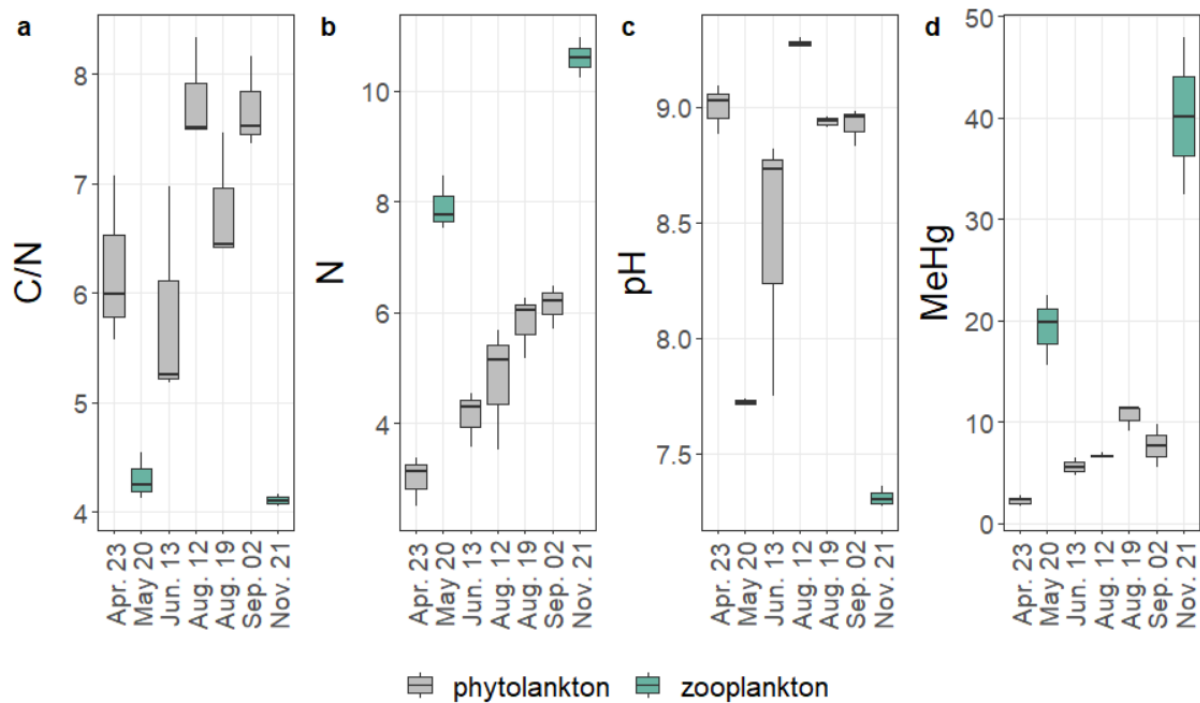
Fig. 4. C/N ratio (a), N concentration [%] (b), pH (c) and MeHg concentration [ng g^{-1}] (d) of the individual sampling days from the upper two oxic metres (0; 1; 2 m). Colours indicate differences in plankton dominance; green symbolizes higher amounts of zooplankton; grey symbolizes higher amounts of phytoplankton. The relative dominance of zooplankton was estimated from visible inspection and from pH only.