



Methane dynamics in a large river: a case study of the Elbe River

Anna Matoušů^{1,2} · Martin Rulík³ · Michal Tušer¹ · Adam Bednařík³ · Karel Šimek^{1,2} · Ingeborg Bussmann⁴

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Abstract

We conducted multiple small (2011–2012) and one large sampling campaign (2013) at selected profiles along the Elbe River. With the data we were able to outline spatial and temporal variability of methane concentration, oxidation and emissions in one of the major rivers of Central Europe. The highest methane concentrations were found in human-altered riverine habitats, i.e., in a harbor ($1,888 \text{ nmol L}^{-1}$), in a lock and weirs ($1409 \pm 1545 \text{ nmol L}^{-1}$), and in general in the whole “impounded” river segment ($383 \pm 215 \text{ nmol L}^{-1}$). On the other hand, the lowest methane concentrations were found in the “lowland” river segment ($86 \pm 56 \text{ nmol L}^{-1}$). The methane oxidation rate was more efficient in the “natural” segment ($71 \pm 113 \text{ nmol L}^{-1} \text{ day}^{-1}$, which means a turnover time of $49 \pm 83 \text{ day}^{-1}$) than in the “lowland” segment ($4 \pm 3 \text{ nmol L}^{-1} \text{ day}^{-1}$, which means a turnover time of $39 \pm 45 \text{ day}^{-1}$). Methane emissions from the surface water into the atmosphere ranged from 0.4 to $11.9 \text{ mg m}^{-2} \text{ day}^{-1}$ (mean $2.1 \pm 0.6 \text{ mg m}^{-2} \text{ day}^{-1}$) with the highest CH_4 emissions at the Meissen harbor ($94 \text{ kg CH}_4 \text{ year}^{-1}$). Such human-altered riverine habitats (i.e., harbors and similar) have not been taken into consideration in the CH_4 budget before, despite them being part of the river ecosystems, they may be significant CH_4 hot-spots. The total CH_4 diffusive flux from the whole Elbe was estimated to be approximately $97 \text{ t CH}_4 \text{ year}^{-1}$.

Keywords Diffusive flux · Ebullition · Elbe river · Methane concentration · Methane oxidation rate · Methane turnover time

Introduction

Considering CH_4 as an efficient greenhouse gas, with its 25 times higher global warming potential by mass than carbon dioxide (CO_2) (IPCC 2014), it is important to understand its sources and sinks in the global atmospheric budget. Among natural CH_4 sources, wetlands represent the largest ($175\text{--}220 \text{ Tg CH}_4 \text{ year}^{-1}$; Kirschke et al. 2013), however, there is an increasing awareness of inland waters (i.e., lakes, reservoirs, rivers) being significant contributors to the global budget ($103 \text{ Tg CH}_4 \text{ year}^{-1}$; Bastviken et al. 2011). Despite their small area, these freshwater systems can affect carbon

balances, especially on a regional scale (Cole et al. 2007). While a considerable level of scientific interest has been given to studies of CH_4 emissions in lakes (e.g., Bastviken et al. 2004, 2008; Devlin et al. 2015; Sepulveda-Jauregui et al. 2015) and reservoirs (e.g., StLouis et al. 2000; Delsontro et al. 2011; Beaulieu et al. 2014), relatively few studies have investigated CH_4 dynamics in flowing waters (Bastviken et al. 2011). Nevertheless, high CH_4 production documented in stream beds (Hlaváčová et al. 2005; Wilcock and Sorrell 2008) has been identified as a considerable source of atmospheric CH_4 through ebullition and diffusive flux (i.e., simple CH_4 diffusion; Baulch et al. 2011), especially in impounded rivers (Guérin et al. 2006; Maeck et al. 2013).

The aerobic CH_4 consumption (methanotrophy) by methane-oxidizing bacteria (MOB) is, so far, the best known process providing a natural barrier of CH_4 being released from different ecosystems into the atmosphere. In this process, CH_4 can be either completely oxidized to CO_2 : $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$; or partially oxidized and partially assimilated into the microbial biomass (“x”): $\text{CH}_4 + (2-x)\text{O}_2 \rightarrow (1-x)\text{CO}_2 + \text{CH}_2\text{O} + (2-x)\text{H}_2\text{O}$.

Aerobic MOB inhabit anoxic–oxic interfaces, such as upper sediment layers and surfaces (Auman et al. 2000) or

✉ Anna Matoušů
anna.matousu@gmail.com

¹ Biology Centre CAS, Institute of Hydrobiology,
České Budějovice, Czech Republic

² Faculty of Sciences, University of South Bohemia,
České Budějovice, Czech Republic

³ Department of Ecology and Environmental Sciences, Faculty
of Science, Palacký University, Olomouc, Czech Republic

⁴ Alfred Wegener Institute Helmholtz-Zentrum für Polar-und
Meeresforschung, Helgoland, Germany

suspended particles in the water column (Abril et al. 2007). It has been documented that MOB can oxidize up to 90% of CH_4 diffusing from lake sediments (Utsumi et al. 1998; Kankaala et al. 2006). On the other hand, in the water columns of rivers, microbial CH_4 oxidation is believed to be much less efficient (Zaiss et al. 1982)—for example, the contribution of CH_4 consumption to CH_4 losses via MOB is only about 5% in turbulent rivers (Lilley et al. 1996).

The occurrence of CH_4 in the water and its emissions into the atmosphere may reflect the metabolism and carbon cycling of the aquatic ecosystem. The low solubility of CH_4 in water coupled with its rapid water-atmosphere exchange can cause pronounced heterogeneity in the CH_4 concentrations along a river gradient (Stanley et al. 2016). However, there have been only snap shots of the processes shaping the CH_4 distribution in riverine ecosystems on a local basis. Moreover, this knowledge has been seldom connected to the environmental factors that govern CH_4 -related processes for a whole river continuum. In this study, we focused on processes closely related to the CH_4 cycle: distribution of CH_4 in the water column (i.e., CH_4 concentration), methanotrophic potential in the water column (i.e., CH_4 oxidation rate and turnover time) and CH_4 emissions (i.e., diffusive flux and ebullition) on the longitudinal transect of the Elbe.

The aims of this study were (1) to achieve an understanding of the CH_4 dynamics in a large river, and to determine the hotspots of CH_4 emissions along the river transect, (2) to assess pattern in aerobic methanotrophic activity along a river continuum, and (3) to determine the physical and chemical parameters that influence the activities of methanotrophs.

Materials and methods

Site description

The Elbe rises at an elevation of 1386 m above sea level in the Krkonoše (Giant Mountains) in the northeast of the Czech Republic, flows through the central part of the Czech Republic and through central and northern Germany before discharging into the North Sea at Cuxhaven (Fig. 1). The Elbe basin, comprising the main river and its tributaries, has a catchment area of 148,268 km² and a total length of 1094 km. Prior to 1990, the Elbe was extremely polluted by industrial, communal, and agricultural wastes from the former Eastern bloc (Adams et al. 1996). Despite significant water-quality improvement, the Elbe is still largely affected by ship transportation and other human impact. Considering the different habitats, velocity and anthropological factors, we divided the Elbe into four segments for purposes of this study: The first segment of the river (upstream the city Pardubice) is characterized as a fast flowing natural stream (10–20 m wide; ~1.5 m depth) with meanders and torrential zones (for the purpose of this study called “natural segment”; km 8–116; Fig. 1). The lower Czech reach of the Elbe from the city Hradec Králové to Střekov (for the purpose of this study called “impounded segment”; km 140–326; Fig. 1) has been recognized as one of the most polluted and modified stretches of the Elbe in the Czech Republic (Prange et al. 2000). This section of the river contains 24 locks and represents a channeled river serving mainly for boat navigation (50–60 m wide; 2–5 m depth; Střekov lock 11 m depth). Numerous agricultural, settlement, and industrialized areas

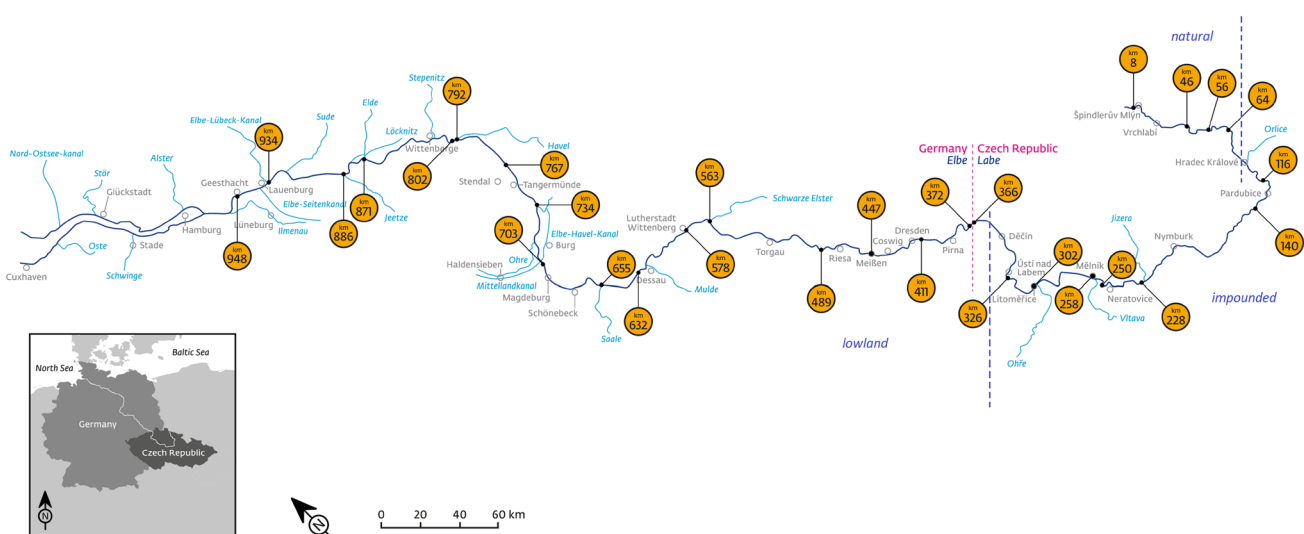


Fig. 1 The sampling sites on the longitudinal profile of the River Elbe. The numbering is determined by the distance from the river source in km (see “River km” in Table 1). Original map: https://commons.wikimedia.org/wiki/File:Lauf_der_Elbe.png; modified

are spread along the river and its tributaries. In the third segment, downstream of the Střekov lock, the Elbe flows freely over a distance of 600 km through low mountains, later becoming a lowland river (for the purpose of this study called “lowland segment”; km 366–948; Fig. 1). In this segment the river is stabilized only by groynes (wing-dams) along most of its flow (120–460 m; 1–4.5 m depth). This segment of the river has a relatively natural morphology and large areas have been preserved close to their natural state (IKSE 2005). The tidal segment of the Elbe is separated from the non-tidal by the Geesthacht lock; this part was the subject of another study (Matoušů et al. 2017).

Sampling

We conducted four small sampling campaigns on the Elbe River in its Czech part (km 8–366) on 24–25 May 2011, 5–6 October 2011, 13–14 March 2012 and 1–2 August 2012. The samples were collected from the river banks or pontoons, from 0.5 m below the surface (“surface” sampling), or in case of higher water levels also from 0.5 m above the bottom (“bottom” sampling). In these small campaigns, selected hydrological parameters (see further) as well as CH₄ concentration, oxidation and turnover time were analyzed.

Additionally, we conducted one large sampling campaign on 8–26 October 2013. During this campaign a longitudinal transect of the Elbe from Špindlerův Mlýn (km 8) to Geesthacht (km 948) and backwards upstream to Děčín (km 356) was sampled over 18 days. In the navigable part (from the km 228), the samples were collected from the main channel using the “Thor Heyerdahl” research vessel, from 0.5 m below the water surface. At km 326 (in the Střekov lock) we took additional samples at 10 m water depth. During this campaign, water samples were taken for hydrological and chemical analyses. In total, we sampled 37 stations (22 during the downstream cruise, 15 upstream). These water samples were treated similarly as in the small sampling campaigns.

Hydrological parameters

Water temperature, conductivity, pH and dissolved oxygen content in the water were measured during sampling using a Universal Pocket Meter (Multi 340i). The water velocities were determined with an electromagnetic water velocity meter (Marsh-McBirney FloMate 2000; Hach USA).

Nutrient composition, suspended particulate matter

Water samples were collected from a vertical Van Dorn sampler (1 m length, 6.4 L volume). During the small sampling campaigns (2011–2012), 200–500 mL (depending on the load) of water were filtered through pre-washed and

pre-weighed Whatman GF/C filters (1.2 µm) for suspended particulate matter (SPM) estimation. Afterwards the filters were dried for 24 h at 60 °C, and reweighed. The filtered water was transferred into 50 mL Falcon tubes and frozen for later analysis in the laboratory.

The filtrates from the previous step were collected (only surface water samples) and frozen prior analyses on nutrient composition in the laboratory. Total dissolved phosphorus (TDP) was determined in the further filtered (0.4 µm) samples with the molybdate method after perchloric acid digestion according to Kopáček and Hejzlar (1993). Water samples (only during the large sampling campaign in 2013) for the estimation of total dissolved nitrogen (TDN) were further filtered through glass-fiber filters of 0.4-µm nominal pore size (GF-5, Macherey–Nagel, Düren, Germany) and analyzed with an Elementar vario TOC cube analyzer (Elementar Analysensysteme GmbH, Germany).

Methane concentration and oxidation

Samples for CH₄ concentration (in triplicates) and CH₄ oxidation rate (in triplicates plus two killed controls) were transferred directly from a water sampler into serum bottles (100 mL Crimp Neck Vials). The bottles were overfilled with approximately two volumes of water, capped with black butyl rubber stoppers (Ochs, Germany), sealed with aluminum crimps, and stored upside down. Care was taken to exclude air bubbles during the procedure.

Samples for CH₄ concentration determination in the water column were preserved immediately after sampling by injecting concentrated sulfuric acid (200 µL per 100 mL of sample) to terminate the microbial activity. The samples were analyzed within 1 month in the laboratory using a headspace technique according to McAuliffe (1971). A 20 mL headspace was created by adding N₂ through a syringe by displacement of an appropriate amount of water through another needle in the stopper. Afterwards, the samples were vigorously shaken and then stored for 24 h at room temperature to allow the equilibration of the gases in the headspace. Subsequently, subsamples (0.2 mL) of the headspace were taken using a 1 mL syringe with needle and analyzed with an Agilent 6890N gas chromatograph (Agilent Technologies, USA) equipped with a flame ionization detector and a 0.53 × 30 m GS Alumina column at 45 °C. Dissolved CH₄ concentrations were calculated with the solubility coefficient of 0.03469 given by Yamamoto et al. (1976).

The CH₄ oxidation rate was determined according to Bussmann et al. (2015). Briefly, immediately after collecting the samples, we injected 100 µL (10 µCi) of ³H-CH₄ (American Radiolabeled Chemicals, Inc.) through the rubber septa into the water samples. Subsequently, the samples were vigorously shaken for 60 s and incubated in the dark at near in situ temperature. The two killed control samples were

preserved by injecting 200 μL of concentrated sulphuric acid before the tracer was added. Activities in “live” samples were stopped in the same way, but after 24 h of incubation. Samples were stored in the dark at 4 $^{\circ}\text{C}$, prior to being analyzed. In the laboratory, the samples were opened, and the total radioactivity of the sample including labeled CH_4 and labeled produced H_2O were measured immediately by mixing a 1 mL aliquot of each sample with 5 mL of scintillation cocktail (Ultima GoldTM LLT) and analyzed with a liquid scintillation counter (Tri-Carb[®] 2900 TR, Packard). Subsequently, the samples were sparged with air for half an hour to expel all remaining CH_4 . Afterwards the microbially-produced radioactive water was analyzed as described above.

The principle of the calculation of the CH_4 turnover time is based on the transformation of added radioactively marked tracer ($^3\text{H}-\text{CH}_4$) into the oxidation products ($^3\text{H}-\text{H}_2\text{O}$) during the incubation (see Eq. 1). In order to calculate the CH_4 oxidation rate, the fraction of CH_4 that was turned over is calculated:

$$F_{\text{CH}_4} = \frac{[\text{H}_2\text{O}]_{\text{produced}}}{[\text{CH}_4]_{\text{injected}}} \quad (1)$$

The fractional turnover rate constant (k) is then determined by dividing by the incubation time (t):

$$k = \frac{F_{\text{CH}_4}}{t} \quad (2)$$

The inverse of the fractional turnover rate (k) is the turnover time (day^{-1}):

$$\tau = \frac{1}{k} \quad (3)$$

The “killed controls” served for estimation of abiotically-formed radioactive H_2O , which could lead to an overestimation and these (on average about 3.5% of total transformation) were subtracted.

Methane emissions

Diffusive flux of CH_4 from the water column into the atmosphere was measured using a set of six floating chambers. The open-bottom floating PE chambers (5 L domes with an area of 0.03 m^2) were maintained on the water surface by a floating body (Styrene) attached to the outside. The chambers were allowed to float on the water surface for 1–3 h (see Rulík et al. 2013; Bednařík et al. 2015). Previous measurements based on the collection of gas samples every 30 min over a 3 h period confirmed a linear dependency between the CH_4 concentration inside the chambers and time. The fluxes were calculated using linear regression based on the

concentration change as a function of time (Duchemin et al. 1999; Silvennoinen et al. 2008).

At each sampling occasion, ambient air samples were also collected for determining initial background concentrations. Samples of headspace gas were collected through the rubber stopper inserted at the top of the chamber and stored in 12 mL Exetainers[®] (Labco Limited, UK). Emissions were calculated as the difference between initial background and final concentration in the chamber headspace, and expressed on the 1 m^2 area of the surface level per day^{-1} according to the formula:

$$F = \frac{\left[\frac{(cI - cR) * 24 * V}{1000 * t} \right]}{p} \quad (4)$$

where F is the gas flux ($\text{mmol m}^{-2} \text{day}^{-1}$), cI is the concentration of CH_4 in the chamber headspace after 1–3 h of collecting ($\mu\text{mol L}^{-1}$), cR is the concentration of CH_4 in background air, V is the volume of the chamber in L, t is time of incubation (h), p is the area of chamber (m^2).

To verify the assumption that the accumulation rate was constant (i.e., floating chamber were not accumulating CH_4 from ebullition) we used F (Eq. 6) to calculate diffusive gas transfer velocity (k) by inverting the equation for Fick’s law of gas diffusion, as follows:

$$k = \frac{F}{(c_w - c_a)} \quad (5)$$

where k is the gas transfer velocity (m day^{-1}), F is taken from Eq. 6 and $c_w - c_a$ is the gas concentration gradient between the river and the atmosphere (mol m^{-3}).

For better comparison of k with different studies, we standardized k of CH_4 to k_{600} (equivalent to k of CO_2 at 20 $^{\circ}\text{C}$) computed according to:

$$k_{600} = k \left(\frac{600}{S_c} \right)^{-0.5} \quad (6)$$

where k is the calculated from Eq. 7, S_c is the Schmidt number for CH_4 *in situ* temperature (Wanninkhof 1992).

In order to estimate the total CH_4 diffusive flux from the whole monitored river stretch, the data were divided into particular sections according to sites of floating chambers measurements. We excluded harbors and groynefields, due to the difficulty of estimating their area. The diffusive fluxes at individual sites along the Elbe continuum were then calculated according to the following equation:

$$E_T = \frac{(\sum P \times E_m \times 365 \times M_{\text{CH}_4})}{1000000} \quad (7)$$

where E_T is total CH_4 diffusive flux from the total river area in t year $^{-1}$; P is the area of a particular river section in

m^2 ; E_m is the mean CH_4 diffusive flux from the particular river section expressed in $\text{mol m}^{-2} \text{day}^{-1}$; M_{CH_4} is the molar weight of CH_4 molecule.

The amount of CH_4 transported by the Elbe out of the Czech Republic and into the estuary was calculated by multiplying the CH_4 concentration and current discharge. Data for the discharge ($\text{m}^3 \text{s}^{-1}$) were obtained from the Elbe data portal (<http://www.elbe-datenportal.de>). We used discharge data measured 18 October 2013 at “Pegel Neu Darchau” (53.2284003N, 10.8858031E) and 26 October 2013 at “Pegel Schöna” (50.8752542N, 14.2350553E).

Ebullition

In case of high production in sediments small gas bubbles (CH_4 , CO_2 , etc.) are formed. Floating subsurface gas collectors were deployed to measure this so called ebullitive gas flux during the 2013 campaign at selected sites of various habitats (weir, lock, groynefield, harbor, free-flowing main stream of the river). Each gas collector consists of an inverted funnel with an opening of 0.3 m^2 attached to the lower end of an 80-cm long gas-storing tube, equipped with a septum-lined cap at the upper end. The collectors were submerged in the surface water, filled with water and enclosed with septum-lined caps. Consequently, they were moored with a loose rope that allowed them to hang at one place. The collectors were balanced so that only a small part of the upper, capped end was visible above the surface, facilitating gas sampling. The funnels were deployed from 2 to 13 h, depending on the possibility to stay on the particular

place. Gas samples were taken by a syringe through the septum-lined cap and transported to Exetainers® for gas composition analysis via gas chromatography.

Statistical analysis

To determine the possible influence of measured hydrological and chemical factors on CH_4 concentration and CH_4 turnover time, Spearman rank order correlation analyses were performed. Calculations and graphical representation were performed using SigmaPlot for Windows Version 11.0 software.

Results

Hydrological and chemical parameters

The obtained chemical and hydrological data from the all sampling campaigns are summarized in Table 1. We did not observe any seasonal pattern for the measured parameters, except the water temperature. The data obtained during the large campaign in 2013 from the Czech section of the river (km 8–366) fit into the range of the previous small campaigns, with the exception of TN which was rather high in contrast to the previous sampling campaigns (2011–2012). The dissolved oxygen obtained during all sampling campaigns indicated sufficient oxygen supply for aerobic methane oxidation (Blees et al. 2014).

Table 1 Overview of obtained data (median) on hydrological and chemical parameters in the water column of the Elbe River from all sampling campaigns (2011–2013): dissolved oxygen (O_2); suspended

particular matter (SPM); water temperature (Water T); pH; dissolved organic nitrogen (TDN; i.e., sum of NO_3^- , NO_2^- and NH_4^+); total dissolved phosphorus (TDP)

Sampling campaign	River segment	O_2 (mg L^{-1})	SPM (mg L^{-1})	Water T ($^{\circ}\text{C}$)	pH	Conductivity ($\mu\text{S/cm}$)	TDN (mg L^{-1})	TDP ($\mu\text{g L}^{-1}$)
May 2011	Natural ($n=2$)	10.2	3.0	14.5	n.a	n.a	0.3	30.9
	Impounded ($n=8$)	8.9	10.7	21.1	n.a	n.a	0.9	66.3
	Lowland ($n=2$)	9.7	23.0	16.2	n.a	n.a	0.7	35.9
October 2011	Natural ($n=2$)	10.5	2.9	11.3	7.4	n.a	0.2	26.8
	Impounded ($n=9$)	9.3	7.0	18.7	7.9	n.a	0.8	88.5
	Lowland ($n=2$)	9.6	9.0	19.1	8.7	n.a	0.9	84.0
March 2012	Natural ($n=2$)	12.2	25.6	5.6	7.0	163.7	1.2	28.0
	Impounded ($n=6$)	13.5	32.4	8.4	7.2	396.0	3.5	45.0
	Lowland ($n=3$)	18.1	132.0	13.1	7.0	393.0	3.7	50.7
August 2012	Natural ($n=4$)	8.1	10.3	16.5	7.9	204.5	1.4	71.9
	Impounded ($n=5$)	12.9	21.6	24.5	6.1	411.0	2.7	94.1
	Lowland ($n=0$)	n.a	n.a	n.a	n.a	n.a	n.a	n.a
October 2013	Natural ($n=2$)	11.4	n.a	7.0	6.8	136.5	n.a	n.a
	Impounded ($n=9$)	10.7	n.a	12.0	7.6	484.5	n.a	n.a
	Lowland ($n=23$)	10.2	17.2	11.4	7.6	487.0	3.6	68.7

n.a. Data not available

Methane concentration in the water column

The data on CH_4 concentrations obtained during the large sampling campaign in 2013 from the km 8 to 366 (i.e., the Czech section of the river) are consistent with the data-trend from the small sampling campaigns in 2011 and 2012 (Fig. 2). Therefore, we describe the CH_4 dynamics in the Elbe integrative, i.e., including data from all the sampling campaigns together, divided into the above-mentioned classified segments: “natural”, “impounded” and “lowland”. The data were pooled as we observed no difference between “surface” and “bottom” samples.

We observed the following trend for the CH_4 concentration: The spatial variation of CH_4 repeatedly showed very low concentrations at the pristine site at km 8 with a median 11 nmol L^{-1} (0.1–31 nmol L^{-1}). Further downstream CH_4 concentrations usually rapidly increased from

the “natural” sampling site km 56 with median 259 nmol L^{-1} (164–387 nmol L^{-1}) towards the “impounded” sampling site at km 140 with a median 439 nmol L^{-1} (133–825 nmol L^{-1}). The values for additional sites at km 228 and km 302 points (sampled during the 2013 campaign) did not differ from the data pattern obtained during the previous four sampling campaigns. Neither did we observe any unusually high CH_4 concentration after confluences with other Czech main rivers—Vltava (km 258) and Ohře (km 302) in the “impounded” river segment.

Further downstream, at km 326 (the Střekov lock) in the “impounded” segment, very high values were found, ranging from 232 nmol L^{-1} up to 3991 nmol L^{-1} (median 700 nmol L^{-1}), with the highest CH_4 concentration obtained in October 2011 (Fig. 2). At this sampling site, the lowest values were obtained during the large sampling campaign (2013) and in March 2012. Some kilometers downstream at km 366 (“lowland” segment) the CH_4 concentration in the water column decreased again and ranged between 39 and 229 nmol L^{-1} (median 186 nmol L^{-1}). During the large sampling campaign in 2013 (Fig. 3), we obtained a CH_4 concentration of 104 nmol L^{-1} at this site and further downstream the concentration stayed at a comparable level ranging between 30 and 186 nmol L^{-1} till km 886 (the Geesthacht lock), where we observed an elevated CH_4 concentration of 331 nmol L^{-1} (Fig. 3). The CH_4 concentrations in the three sampled groynefields were similar to the values measured in the main stream of the river; only at km 871 did the samples show a slightly elevated CH_4 value. The confluences with some large rivers—Schwarze Elster (km 563), Saale (km 655), and Havel (km 792 and km 802) in the “lowland” segment did not result in elevated CH_4 concentrations. Very high CH_4 concentration were observed at sites which have been considerably human-altered in the water column in the “lowland” river segment, e.g., the Meissen harbor and the harbor on the Elde Canal at Dömitz. Overall, the highest CH_4 concentration (3991 nmol L^{-1}) of the whole monitored river section (i.e., 2011–2013) was found at km 326 (the Střekov lock) in the “impounded” river segment.

On the way upstream (12 Oct 2013) the CH_4 concentrations were significantly different at some of the replicate sites (i.e., km 886, km 734, km 632, km 578, km 447 and km 411) than on the way downstream (18 Oct 2013): at km 886 ($t=18,594$, $P<0,001$), at km 632 ($t=5,98$, $P=0,002$), and at km 578 ($t=4,475$, $P=0,007$). The differences between upstream and downstream measurements ranged from 55 to 170 nmol L^{-1} (Fig. 3).

Among the measured hydrological and chemical parameters we found common significant correlation for all three river segments only with water temperature (Table 2). Correlation with CH_4 and other parameters vary between segments, while the most correlations were found in the

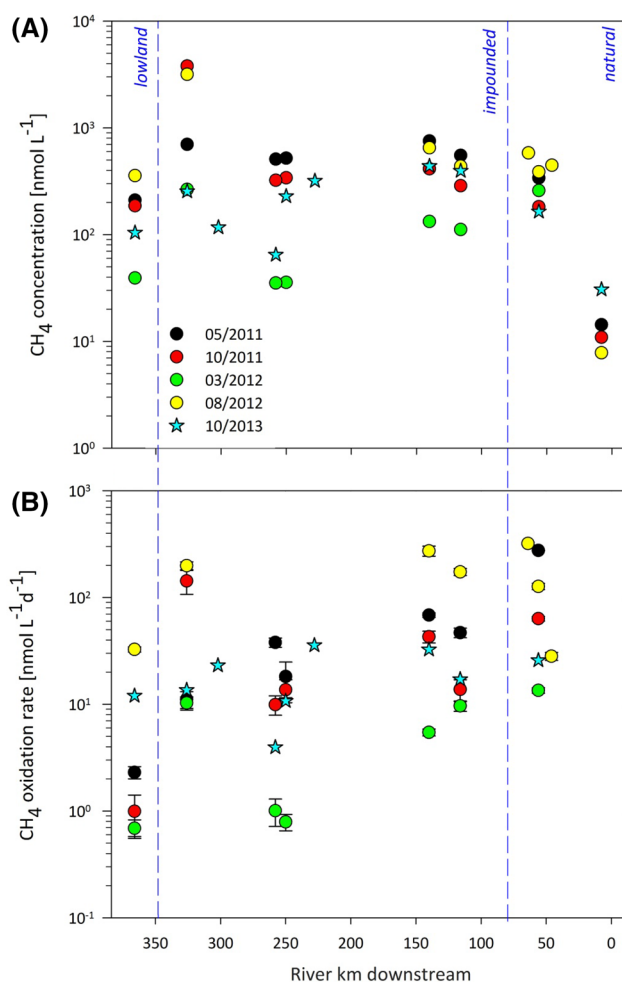


Fig. 2 Methane distribution (a) and related oxidation rate (b) in the water column obtained during 2011–2013 in the Czech part of the River Elbe (mean values \pm SD; in case of overlapping within the symbol size error bars are not shown); note: CH_4 oxidation rate for the first sampling site (km 8) is not shown for its low values (see Results)

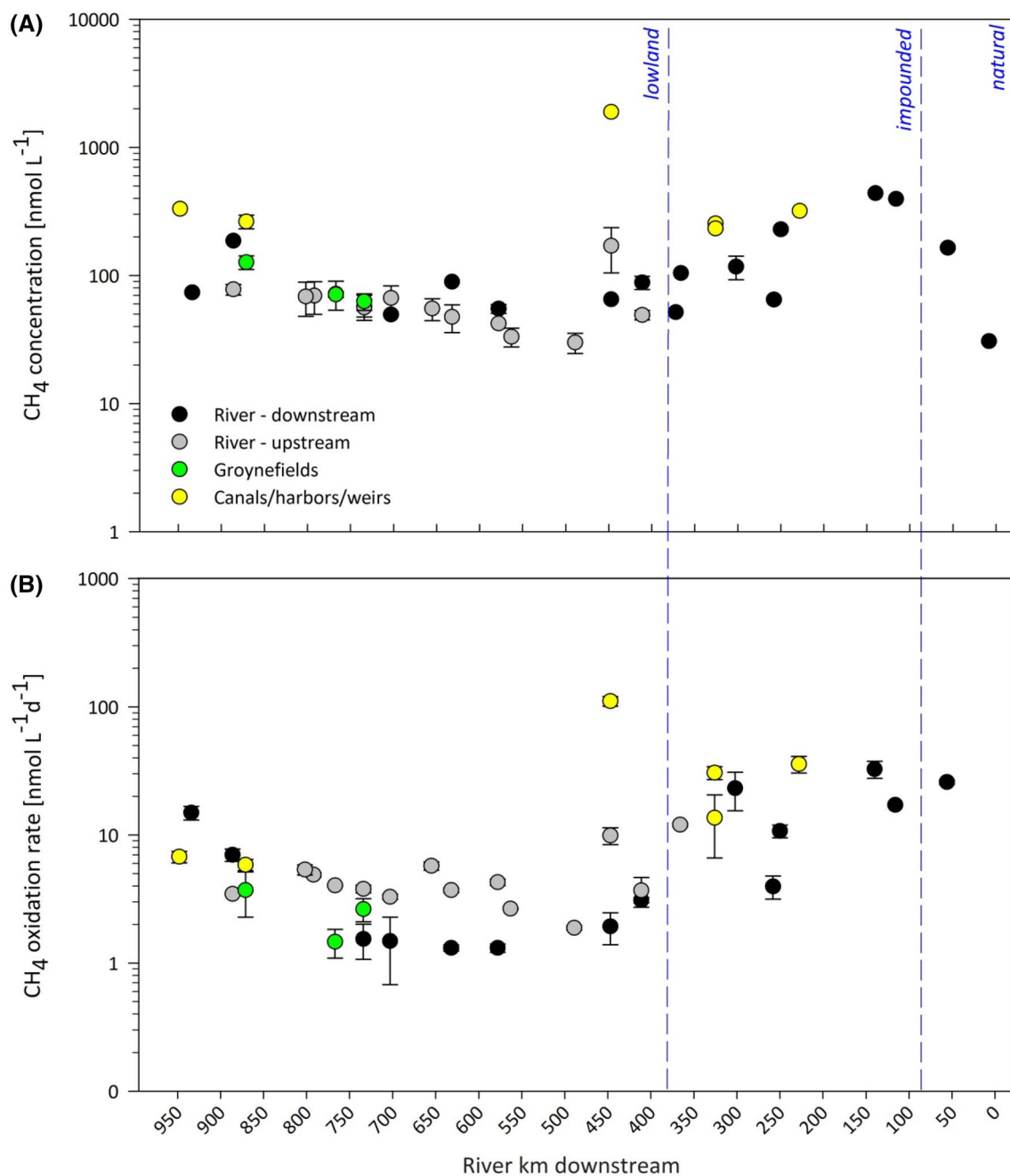


Fig. 3 Methane distribution (a) and related oxidation rate (b) in the water column from the continuous sampling campaign in 2013 along the whole monitored stretch of the River Elbe (mean values \pm SD; in

case of overlapping within the symbol size error bars are not shown); note: CH₄ oxidation rate for the first sampling site (km 8) is not shown for its low values (see Sect. “Results”)

“natural” river segment: positive correlation with SPM, conductivity, dissolved nitrogen and phosphorus (Table 2). In the “impounded” segment only correlation with water temperature was found, while in the “lowland” segment additional positive correlations with pH and a negative correlation with dissolved nitrogen were found.

Aerobic methane oxidation in the water column

The CH₄ oxidation rates obtained during the large sampling campaign in 2013 (km 8–366, Fig. 3) were consistent with the data range from the four previous small sampling campaigns in 2011 and 2012 (Fig. 2). In the following text, the pooled data (“surface” and “bottom”) from the

Table 2 Pearson Product Moment Correlation between CH₄ concentration, CH₄ oxidation rate, turnover time and the chemical and hydrological parameters

	CH ₄			CH ₄ oxidation rate			CH ₄ turnover time		
	Natural	Impounded	Lowland	Natural	Impounded	Lowland	Natural	Impounded	Lowland
CH ₄	–	–	–	0.76**	0.52**	0.10	–0.31	0.29	0.62**
O ₂	0.24	–0.13	–0.29	0.42	–0.13	–0.21	0.08	0.15	–0.10
SPM	0.45	–0.23	–0.16	0.17	–0.01	–0.16	–0.16	–0.09	–0.10
Water T	0.72**	0.36*	0.65**	0.75**	0.52**	–0.22	–0.37	–0.13	0.74**
pH	0.29	–0.05	0.53**	0.18	–0.65**	0.06	–0.55	0.36	0.52*
Conductivity	0.71*	–0.07	0.17	0.38	–0.19	0.46	–0.54	–0.12	–0.53
DN	0.73*	–0.16	–0.82**	0.31	0.12	0.17	–0.28	–0.02	–0.79**
TDP	0.97**	0.22	0.02	0.73	0.59**	0.30	–0.47	–0.50**	0.13

Data from Dömitz canal and Meissen harbor were not included

* $P < 0.05$; ** $P < 0.01$

sampling campaigns 2011–2013 were used, unless otherwise noted.

Methane oxidation rates were higher in the “natural” segment with mean of $71 \pm 113 \text{ nmol L}^{-1} \text{ day}^{-1}$, than in the “impounded” ($43 \pm 60 \text{ nmol L}^{-1}$) or “lowland” segment ($4 \pm 3 \text{ nmol L}^{-1}$). The lowest CH₄ oxidation rates were repeatedly observed at the first sampling site (km 8), ranging from 0.002 to 0.2 $\text{nmol L}^{-1} \text{ day}^{-1}$, which represent a turnover time of 88 to 1800 day^{-1} . Surprisingly, in general the highest CH₄ oxidation rates were observed at km 56 (“natural” segment), ranging from 13 up to 276 $\text{nmol L}^{-1} \text{ day}^{-1}$, which represent a turnover time of 1 to 19 day^{-1} . We found even higher rates at additional sampling point in August 2012 (Fig. 2) and in general, the CH₄ oxidation rates obtained in this river segment were the highest from the whole river stretch. In the “impounded” river segment (km 116–326) the CH₄ oxidation rates fluctuated with slightly increasing tendency between 1 $\text{nmol L}^{-1} \text{ day}^{-1}$ at km 326 in March 2012 up to 273 $\text{nmol L}^{-1} \text{ d}^{-1}$ at km 140 in August 2012. The turnover time ranged between 2 to 65 day^{-1} (median 21 day^{-1} ; 2011–2013) in this particular river segment. In the “lowland” segment the CH₄ oxidation rate was lower than in the previous two segments (i.e., “natural” and “impounded”) with mean value of 5 $\text{nmol L}^{-1} \text{ day}^{-1}$ and turnover time varying between 6 to 68 day^{-1} . On the way upstream the CH₄ oxidation rates were higher than on the way downstream, ranging from 4 to 10 $\text{nmol L}^{-1} \text{ day}^{-1}$ (turnover time ranging from 10 to 20 day^{-1}). No differences were observed between the confluences of the Elbe with some of its important tributaries (Schwarze Elster, Havel, and Saale) or between groynefields with the mainstream.

In the “natural” river segment significantly positive correlations of CH₄ oxidation rate were found with CH₄ concentration and water temperature (Table 2). The same situation was observed also in the “impounded” river segment where we additionally found a negative correlation with pH and

a positive correlation with dissolved phosphorus (Table 2). In the “lowland” river segment no significant correlation between CH₄ oxidation rate and measured parameters was found. On the other hand, we found significantly positive correlation between CH₄ turnover time and CH₄ concentration, and further we also found a significantly positive correlation with water temperature, which implies that higher water temperature, causes lower methanotrophic activity (i.e., longer turnover time) in this segment of the river. A significantly positive relation was found between CH₄ turnover time and pH and negative correlation with dissolved nitrogen in the “lowland” river segment of the Elbe. However, for the total data set no correlations were found.

Methane emissions and ebullition

Methane diffusive fluxes ranged from 0.4 to 11.9 $\text{mg m}^{-2} \text{ day}^{-1}$ (average of $2.1 \pm 0.6 \text{ mg m}^{-2} \text{ day}^{-1}$), (Fig. 4). The highest values were obtained at km 56 in “natural” river segment (in situ CH₄ concentration 164 nmol L^{-1}) and the lowest values were obtained at the km 326 (the lock at Střekov lock; in situ CH₄ concentration 243 nmol L^{-1}). In the “lowland” river segment, we can see a decreasing trend in the CH₄ diffusive flux along the river flow. The only exception was the Meissen harbor (km 447), with its extraordinarily high CH₄ fluxes - up to 11.9 $\text{mg m}^{-2} \text{ day}^{-1}$. Only at this site we were able to measure ebullition, where CH₄ in the gas bubbles reached 488,436 ppm (data not shown). Although we were able to take gas bubbles into the gas collectors on some sampling sites along the river, the gas content of the bubbles was dominated by carbon dioxide. No correlations with other measured parameters were found.

The total CH₄ diffusive fluxes from the Elbe calculated for the each river reaches along the Elbe are showed in Table 3. The value of the total CH₄ diffusive flux from the whole Elbe was estimated to be approximately 97 t CH₄ year^{-1} .

Fig. 4 The CH_4 diffusive fluxes at selected profiles along the River Elbe from the continuous sampling campaign in October 2013. Replicate sites are differentiated according to the habitat type

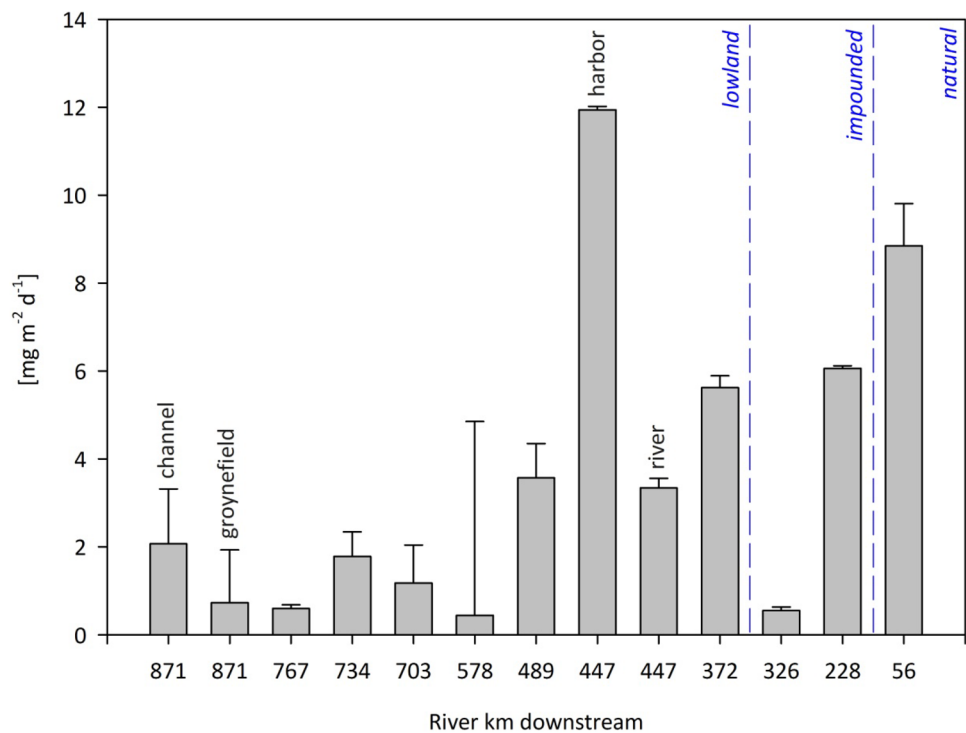


Table 3 The total CH_4 diffusive fluxes for the different river reaches along the Elbe River

River reach (km)	Area (km ²)	Mean CH_4 emissions (mg m ⁻² d ⁻¹)	Total emission (t CH_4 y ⁻¹)
0–142	3.12	8.85	10.1
142–300	11.6	6.06	24.5
300–410	12.65	5.62	25.9
410–468	6.32	3.34	7.7
468–534	6.47	3.57	8.4
534–641	15.9	0.44	2.4
641–787	23.21	1.18	10.0
787–948	31.72	0.73	8.5
0–948	109.6		97.5

Diffusive fluxes from harbors and groynefields were not included

Gas transfer velocities (i_{600}) ranged from 1.6 to 37.2 cm h⁻¹ with mean 14 ± 4.8 cm h⁻¹.

Discussion

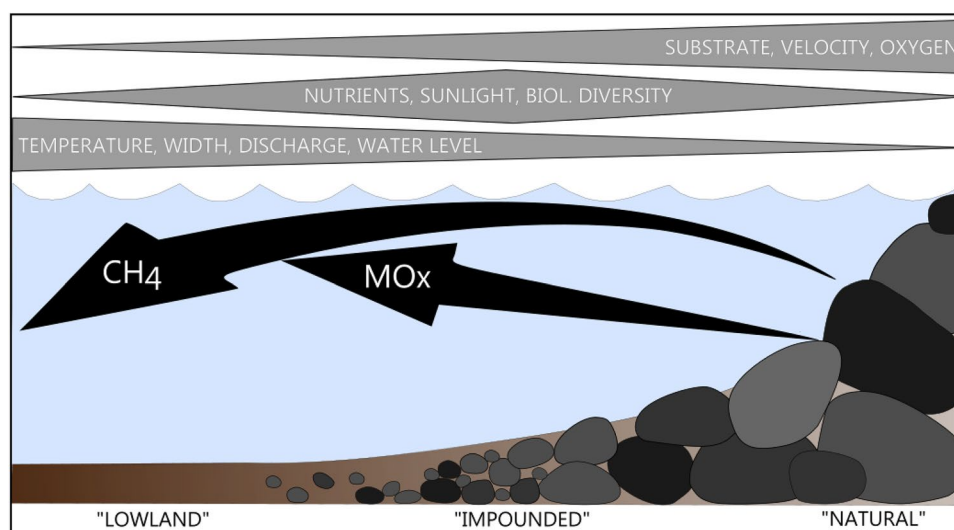
Methane distribution in the water column

Our results on CH_4 concentration show that the water column of the Elbe was supersaturated with respect to atmospheric equilibrium concentrations (i.e., 2.5–4 nmol L⁻¹) along the entire monitored stretch of the river, with the

exception of the most upstream oligotrophic sampling site at km 8. In general, the range of detected CH_4 concentration in the water column of the Elbe (Figs. 2, 3) falls towards the higher end or even exceeds the range of CH_4 concentration reported from other rivers: For instance up to 2000 nmol L⁻¹ at a power plant in the mainstream of the River Saar (Zaiss et al. 1982); between 5 to 1730 nmol L⁻¹ in Oregon rivers (de Angelis and Lilley 1987); between 42 and 97 nmol L⁻¹ in a forest stream (Jones and Mulholland 1998); between 60 and 420 nmol L⁻¹ in the River Willamette (Anthony et al. 2012) or between 20 and 500 nmol L⁻¹ for various Amazonian rivers (Sawakuchi et al. 2014). In the Elbe estuary, the CH_4 concentrations in the area of Hamburg harbour is about 416 nmol L⁻¹, but in the lower segment of the estuary about 40 nmol L⁻¹ (Matoušů et al. 2017). The range of reported CH_4 concentrations in other studies (for an overview see Zhang et al. 2008, and; Middelburg et al. 2002) has a large variation and only some of them (Zaiss et al. 1982; de Angelis and Lilley 1987; Dzyuban 2011) took into account the differences between habitats along the river flow.

The CH_4 concentrations obtained during the longitudinal sampling campaign in October 2013 fit into the range of the data from the small sampling campaigns in 2011 and 2012 from the “natural” to the “lowland” river segments (Fig. 2). From this, we can deduce that our data from the large sampling campaign in 2013 show no extraordinary values and might be seen as representative values on CH_4 dynamics of such large river system (generalized in Fig. 5). Moreover, there is an apparent trend in the data showing increasing of

Fig. 5 Commonly observed changes associated with the river continuum concept with the inclusion of CH_4 concentration in the water column (CH_4) and related CH_4 oxidation rate (MOx). Adapted from Ward—A Mountain River, Chap. 23 in River Handbook (Calow and Petts 1992)



the CH_4 concentration together with the stream order. A similar pattern was found in the headwater stream in Tennessee (Jones and Mulholland 1998) where the authors suggested, that the CH_4 increase along the flow is related to catchment geomorphology. On the other hand, there have been few other studies, which reported decreasing CH_4 concentration as a function of the total stream length (Striegl et al. 2012; Crawford et al. 2013; Campeau et al. 2014).

However, the increase of CH_4 concentrations in our study always occurred only until km 140 (“impounded” segment), thereafter the CH_4 concentrations were more or less at the same level or even decreased (see Fig. 2). Km 140 is located in the industrial zone typical for its higher load of pollution (Prange et al. 2000), which is in accordance with the hypothesis that CH_4 concentration increases with the increasing pollution of the river (Swinnerton et al. 1969; Dzyuban 2011). Unfortunately, we were not able to confirm this hypothesis because no correlation of CH_4 with our obtained chemical parameters of the water was found in this river segment (Table 2). However, we found a negative correlation between CH_4 and dissolved oxygen ($r = -0.93$; $P < 0.01$; $n = 7$) and a positive correlation between CH_4 and water temperature ($r = 0.82$; $P = 0.02$; $n = 7$) at this particular site. Both results imply a possible effect of pollution, as warmer water leads to higher mineralization (Gudas et al. 2010), which can lead to anaerobic conditions in the water and especially at the sediment–water boundary and thereby favoring the CH_4 production (Liikanen and Martikainen 2003).

A special setting was found at the Střekov lock (km 326) and Meissen harbor (“Winterhafen”; km 447) both with very high CH_4 concentrations compared to the free-flowing stream in the particular segments. While locks represent characteristic man-made Elbe habitat (hosting 24 weirs with locks along its flow), the Meissen harbor

is similar to dead-arm of the river and like this has been actually never taken into account while sampling rivers, probably due to its negligible size. Nevertheless, both of these man-made river habitats share same feature—high accumulation of organic material and longer water residence time. This implies establishment of anoxic conditions with subsequently high decomposition of the accumulated organic matter, which result in enormous CH_4 production. In this sense, such sites should not be neglected but included in the sampling schemes and CH_4 budget estimations.

The Střekov (km 326) represents currently the last “barrier” for the next free-flowing 600 km of the river till the weir at Geesthach (km 948). Along this “lowland” river segment the CH_4 concentration stayed below the values obtained at the last sampling site in the Czech Republic (km 366). In comparison to the “impounded” segment with its characteristic weirs and locks is the “lowland” segment stabilized with more than 3400 groynes (20–30 m long wing-dams), which support navigation during low water level. Due to the significant decrease of the flow velocity in comparison to the main stream, a counter flowing circulating water between the groynes (in so-called groynefields) leads to high sedimentation of sand and coarse organic material—the amount and location of sedimentation depend on hydraulic processes and type of groynes (Henning and Hentschel 2013). Thus, groynefields represent an artificial transition area between river and floodplain, and so a higher CH_4 concentration in the water there, due to higher CH_4 production in contrast to the main stream, was expected. Nevertheless, we did not detect any higher CH_4 concentration in the groynefields. However, more sampling of different types of groynefields (with different level of sedimentation, size, etc.) through the season are needed before we generalize the statement; that in this way groynefields would represent an counterbalance

to CH₄-producing locks, while all these technologies are designed for navigation.

Neither did we, against our expectations, observe elevated CH₄ concentration after confluences of the Elbe with its main tributaries. This observation can be explained partly by the dilution of the two water masses. This hypothesis is supported by even lower CH₄ concentrations at these sites compared to the values from the previous and following sampling sites (Fig. 3). Another reason could be improper sampling methodology—a better approach would be sampling on horizontal as well as vertical profiles to obtain detailed pattern of mixing of the different water masses.

Our assumption that SPM will be positively correlated with CH₄ concentrations (Upstill-Goddard 2000) were not supported by our data (Table 2). As most of the CH₄ is produced in sediments, their resuspension may result in increased SPM (turbidity) as well as CH₄ concentration in the water column (Bussmann 2005). However, some authors (Abril et al. 2007; Grunwald et al. 2009) showed also a negative correlation, i.e., high CH₄ concentrations in clear-water systems or no correlation (Matoušů et al. 2017; Osudar et al. 2015). This direct relation does not seem to be true in rivers, since in rivers the SPM has its own set of dynamics, i.e., within the river continuum the characteristics of SPM quantity and composition alter in relation to changes in the mobilization of terrestrial versus in-stream sources as well as in-stream autotrophic processes (Dawson et al. 2012). On the other hand, the turbidity may be not always caused by sediment resuspension as we observed that the filters often retained high amounts of algal biomass. Abril et al. (2007) postulated that lower CH₄ concentrations at increased SPM content are due to an increased CH₄ oxidation associated with the particles. However, neither these findings were supported by our data (Table 2).

Aerobic methane oxidation in the water column

Very few quantitative assessments of the role of methanotrophs in a river continuum of temperate zones are currently available. Moreover only few studies investigated both CH₄ concentration and oxidation rates in lotic systems. One such study reports on CH₄ dynamics in a non-tidal estuary (Abril and Iversen 2002), another in diverse small tributaries of a large Russian reservoir (Dzyuban 2011), or on a short stretch of a river in Oregon (Anthony et al. 2012). So far only Zaiss and coworkers (1982) investigated a 240 km long river transect. The uniqueness of our study lies in the repeated seasonal samplings at the given sites. We discovered an interesting spatial pattern of the CH₄ oxidation along the river flow (Fig. 2; generalized in Fig. 5). If there would be drawn a line according to the values along the river flow, this would have always more or less same shape and would shift only up or down on the y-axis according the season. It

appears as the microbes would be adjusted to the particular sites, although we are dealing with highly variable environment of running water. There is still very limited knowledge on the environmental factors shaping these processes in rivers. The wide range of CH₄ oxidation rates obtained in our study might reflect the fact that there are many drivers and their site-specific combinations which controls the microbial CH₄ oxidation (Stanley et al. 2016). With the given hydrological parameters in this study we were able to reveal only some hints of possible effect on the methanotrophic potential (Table 2).

We expected that the availability of CH₄ will be the key factor explaining different methanotrophic activities along the river flow. And indeed, our expectation was supported by the measurements but only in the “natural” and “impounded” river segments (Table 2). In the “lowland” segment, we found an opposite situation—a positive correlation of CH₄ concentration and its turnover time, which actually implies a negative effect of CH₄ concentrations on the methanotrophic activity in the water column. This fact would mean that higher CH₄ concentration does not always support equally higher methanotrophic activity. This can be exemplified on two sites with contrasting characteristics regarding the ambient CH₄ concentrations and related oxidation rates: Verdek (km 56) and Střekov (km 326). At Verdek we found at intermediate CH₄ concentrations (266 ± 2 nmol L⁻¹) a very high CH₄ oxidation rate (101 ± 4 nmol L⁻¹ day⁻¹) and fast turnover time (7 ± 1 day⁻¹). At Střekov lock we found, at very high CH₄ concentrations (1744 ± 110 nmol L⁻¹) an intermediate CH₄ oxidation rate (66 ± 13 nmol L⁻¹ day⁻¹) and long turnover time (34 ± 6 day⁻¹). Many authors propose that river impoundments (weirs, locks, dams, reservoirs) represent the hot-spots CH₄ emissions due to high CH₄ production in these man-made habitats (e.g., Guérin and Abril 2007; Hertwich 2013; Maeck et al. 2013). While others improved these findings by indicating that the methanotrophic oxidation may not always be effective in such habitats (Delsontro et al. 2010). However, the reason for the inhibition of CH₄ oxidation in these habitats still remains unexplained and so needs further research.

The exact same pattern as the relation with CH₄ concentration is obvious also between the CH₄ oxidation rate and water temperature (Table 2). Since temperature affects enzymatic processes (Börjesson et al. 2004; Mohanty et al. 2007) it is expectable that higher water temperatures may favor higher methanotrophic activities. This again does not work in the “lowland” segment, where we found a positive correlation with the turnover time which implies a negative effect of higher water temperature on the methanotrophic activity.

As it appears, it is rather impossible to explain the different methanotrophic activities with the given hydrological and chemical parameters. More detailed research at each river segments would be very valuable, especially analyses

of the methanotrophic community compositions as methanotrophs possess different affinity to CH_4 concentrations (Amaral and Knowles 1995; Börjesson et al. 2004): So far it has been found that mainly MOB type I are capable of utilizing CH_4 at lower concentrations, higher oxygen content, and lower temperatures (5–10 °C), while MOB type II are at an advantage at higher CH_4 concentrations, lower oxygen content, and higher temperatures (20 °C).

Methane emissions (diffusive flux and ebullition)

The CH_4 diffusive fluxes measured in this study correspond to the range of those published from other free-flowing rivers in USA (e.g., de Angelis and Scranton 1993; Jones and Mulholland 1998), Amazonian rivers (Sawakuchi et al. 2014) or rivers in Europe (Saarnio et al. 2009), regardless of the methods. Data on the factors controlling CH_4 emissions are commonly restricted to wetlands and lakes (Ortiz-Llorente and Alvarez-Cobelas 2012) and knowledge of these factors in rivers is more elusive. Nevertheless, our data show that both damming of the river as in the “impounded” segment of the Elbe and the occurrence of CH_4 hot-spots (e.g., harbors), may promote CH_4 emissions and contribute to the high variations of CH_4 fluxes at the river scale.

With the exception of the Meissen harbor CH_4 diffusive fluxes showed a decreasing trend along the Elbe’s longitudinal profile, indicating that both low CH_4 production (Bednářik et al. in prep.) coupled with methanotrophy may efficiently control CH_4 release into the atmosphere in the middle part of the Elbe (Fig. 4). In October 18 (2013), the Elbe-discharge at the Neu Darchau measurement stand was $709 \text{ m}^3 \text{ s}^{-1}$, while monthly discharges ranged from 442 to $736 \text{ m}^3 \text{ s}^{-1}$. Assuming that CH_4 concentration in the water column of the Elbe near Lauenburg (km 886; last measured site) was 331 nmol L^{-1} at this time, the river may transport annually 118.7 t of CH_4 to its lower segment above Hamburg, which is consequently the net input of CH_4 to the Elbe estuary. Methane concentration in surface water of the Elbe near the Czech-German border at the km 366 was found to be 104 nmol L^{-1} , while the water discharge was $324 \text{ m}^3 \text{ s}^{-1}$. Based on these values, river water entering Germany may transport annually approximately 17.0 t of CH_4 . Thus, despite the CH_4 removal via emissions to the atmosphere and microbial oxidation in water column, the amount of CH_4 leaving the Elbe near the Lauenburg was seven times higher than the incoming amount of CH_4 from the “impounded” segment into the “lowland”.

Assuming that area of the Elbe River is approximately 109.6 km^2 , the total CH_4 annual flux to the atmosphere might be calculated as $0.9 \text{ t CH}_4 \text{ km}^{-2} \text{ year}^{-1}$. This result is close to other studies estimating the total CH_4 fluxes from lotic ecosystems. For instance, Saarnio et al. (2009) estimated CH_4 efflux from European watercourses to be 2.6 t

$\text{CH}_4 \text{ km}^{-2} \text{ year}^{-1}$. Estimation of CH_4 emissions from rivers based on calculation of Bastviken et al. (2011) is equal to $4.8 \text{ t CH}_4 \text{ km}^{-2} \text{ year}^{-1}$. Mach et al. (2016) estimated total CH_4 efflux to be $3.5 \text{ t CH}_4 \text{ km}^{-2} \text{ year}^{-1}$ for small temperate stream, while $0.9 \text{ t CH}_4 \text{ km}^{-2} \text{ year}^{-1}$ has been estimated for the main stream of Amazon River (Richey et al. 1988). In context of studies mentioned above, an estimation published by Ortiz-Llorente and Alvarez-Cobelas (2012), $465 \text{ t CH}_4 \text{ km}^{-2} \text{ year}^{-1}$, seems to be considerably overestimated.

Obtained gas transfer velocities are in the range of values referred in the literature (Borges et al. 2014), when the k_{600} 12.3 cm h^{-1} is reported for large rivers. Sites with the lowest k_{600} corresponded to sites with the lowest CH_4 concentration. Range of calculated gas transfer velocities (k) showed that gas chambers measurements were not significantly influenced by ebullition in this study.

Undetectable CH_4 content in bubbles captured during ebullition measurement in October 2013 supports our findings of very low CH_4 concentrations found within top sediment layers (Rulík et al. in prep.). This contrasts with general estimates that CH_4 usually accounts for 20–70% of the volume of bubbles released from river sediments (Wilcock and Sorrell 2008; Baulch et al. 2011). We suggest that CH_4 input into the water column is not directly related to the sediment production on the particular site, but likely originates from the upstream parts. One exception to this rule is the Meissen-harbor locality, which represents a “hot-spot” for CH_4 production. In this case, the high CH_4 content in the bubbles (~50%) contributes substantially to the very high emissions of CH_4 into the atmosphere from this site.

Conclusions

Limited assessment of the role of CH_4 concentrations together with its microbial oxidation and environmental factors shaping these processes in a river continuum of temperate zones has been available so far. The conducted sampling campaigns on the Elbe have brought some new insights into the major CH_4 pathways and general CH_4 trends along a large European river (generalized in Fig. 5). Such a longitudinally highly heterogeneous ecosystem consists of more or less natural parts, turning downstream to moderately polluted zones up to highly anthropogenically disturbed regions. Thus, the current situation offers diverse scenarios of various interacting physical as well as chemical environmental drivers (Fig. 5). Our study shows that the CH_4 concentrations in the water column of the Elbe exceed the data from previously reported river systems in the temperate zone. Along the flow of the Elbe CH_4 concentrations increased and culminated in the most polluted and human-altered parts of the river, while later in the free flowing parts they stayed more or less constant (overall varying over two

orders of magnitude; Fig. 3). Regardless the fact that the key factor seemed to be the availability of CH_4 , we found that even in CH_4 -rich environments the CH_4 oxidation was very limited, or practically undetectable. The CH_4 oxidation rates were similarly heterogenic, spanning again over one to two orders of magnitude, with an repeated spatial pattern—the rates were increasing on the longitudinal profile from the “natural segments” towards the “lowland” segments. A special setting was found at the “natural” site Verdek (km 56) with the highest CH_4 oxidation rates, accounting for 5 to 81% CH_4 being oxidized by the MOB. We were not able to convincingly clarify the potential drivers of the methanotrophic activity; it is most probably a specific combination of environmental factors and local circumstances. It seems that near natural habitats with active biofilms and functional interactions with their surrounding (e.g., hyporheal, riparian zones) might function better in terms of self-purification processes. This is in contrast to large-scale human-altered habitats (e.g., an “impounded” river segment with its weirs, locks, harbors, and canals), which may lead to greater eutrophication and greenhouse gas emissions. Ecologically, the free flowing river modified only with groynes, where the CH_4 concentration stayed at a low level with only minor CH_4 emissions, these moderate modifications probably represent a more effective and natural solution for river navigability.

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