Aquatic methane dynamics in a human-impacted river-floodplain of the Danube

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Abstract

River-floodplain systems are characterized by changing hydrological connectivity and variability of resources delivered to floodplain water bodies. Although the importance of hydrological events has been recognized, the effect of flooding on CH4 concentrations and emissions from European, human-impacted river-floodplains is largely unknown. This study evaluates aquatic concentrations and emissions of CH4 from a highly modified, yet partly restored river-floodplain system of the Danube near Vienna (Austria). We covered a broad range of hydrological conditions, including a 1-yr flood event in 2012 and a 100-yr flood in 2013. Our findings demonstrate that river-floodplain waters were supersaturated with CH4, hence always serving as a source of CH4 to the atmosphere. Hydrologically isolated habitats in general have higher concentrations and produce higher fluxes despite lower physically defined velocities. During surface connection, however, CH4 is exported from the floodplain to the river, suggesting that the main channel serves as an “exhaust pipe” for the floodplain. This mechanism was especially important during the 100-yr flood, when a clear pulse of CH4 was flushed from the floodplain with surface floodwaters. Our results emphasize the importance of floods differing in magnitude for methane evasion from river-floodplain systems; 34% more CH4 was emitted from the entire system during the year with the 100-yr flood compared to a hydrologically “normal” year. Compared to the main river channel, semi-isolated floodplain waters were particularly strong sources of CH4. Our findings also imply that the predicted increased frequency of extreme flooding events will have significant consequences for methane emission from river-floodplain systems.

Recent global estimates on the areal extent of inland waters are greater than previous appraisals (Downing et al. 2012; Verpoorter et al. 2014). This was also linked to higher global estimates of CO2 evasion (Battin et al. 2008; Raymond et al. 2013). Methane (CH4) is recognized as the second most important anthropogenic greenhouse gas (GHG), with a global warming potential 25 times that of CO2, yet much less is known about the emissions of this trace gas from inland waters (Bastviken et al. 2011). Regarding flowing waters, existing research has focused mostly on the emissions from large rivers and is associated with high uncertainty. Downing et al. (2012) emphasized that the contribution of rivers and streams may be ±20 to ±200% greater than previous estimates. The role of fringing floodplains and wetlands and their contribution to global methane emissions have received some attention (Asellmann and Crutzen 1989; Sha et al. 2011). Shallow lakes and wetlands are important for the Earth’s carbon balance, but the majority of existing research covers emissions from large river-floodplain systems such as the Amazon (Mellack et al. 2004; Ringeval et al. 2014) or the Pantanal (Marani and Alvala 2007; Bastviken et al. 2010). More recently, some attention has been given to small wetlands because they possibly contribute more to global methane emissions than previously considered (Yavitt 2010).

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Due to variable hydrology and long-term retention between floods, river-floodplain systems possess ample opportunities to store and process carbon (Battin et al. 2008). Although some studies consider river-floodplains to be carbon neutral (Batson et al. 2015), most identify them as a source of CH₄ to the atmosphere (Denman et al. 2007; Sawakuchi et al. 2014). Saarnio et al. (2009), for example, evaluated total CH₄ emissions from European floodplains and wetlands in a meta-analysis, yet their estimates bear considerable uncertainties due to the small number of studies and high variations in CH₄ emission. One factor that potentially greatly affects CH₄ emissions is hydrological disturbance (Altor and Mitsch 2008; Gatland et al. 2014). Changing hydrology, including seasonal flooding events, results in large temporal changes in methane evasions from floodplains (Otter and Scholes 2000). Nonetheless, the importance of hydrology, especially the occurrence of extreme hydrological events, for CH₄ evasion from European river-floodplains has not received significant attention. An often overlooked, key aspect is the changing area of the inundated floodplain: it must be taken into account when estimating total evasion from such systems (Smith et al. 2000).

Due to river regulation, damming, construction of hydroelectric power stations, agriculture and other anthropogenic activities, the areas of many European floodplains have been reduced significantly (Klimo and Hager 2001), with substantial implications for floodplain functions. There is evidence that human impacts are responsible for increased methane fluxes from wetlands (Petrescu et al. 2015), but the study of Froliking et al. (2011) implies that anthropogenic disturbance may also result in reduced CH₄ emissions. This suggests that anthropogenic degradation of floodplain systems can influence their overall carbon flux. In this light, a potential human impact on CH₄ emissions from modified river-floodplains, including restored sections, remains unclear. Considering that much of Europe's floodplains have been degraded, the significance for CH₄ emissions must be considered.

In this study, we assess CH₄ emissions from a human-modified and from a partly restored river-floodplain section of the Danube near Vienna (Austria). We investigated whether hydrological events differing in magnitude affect the concentration and the evasion of CH₄ and hypothesized that floodplain waters are important sources of CH₄ in comparison to the main river channel. Finally, we discuss possible consequences of variously intense anthropogenic alterations of river-floodplain systems on CH₄ emissions.

**Materials and methods**

**Study area and sampling design**

Our study was conducted in a river-floodplain system located in the Danube Floodplain National Park downstream of Vienna (Austria, river km 1895–1918). Throughout the centuries, this area has been severely impacted by human alterations, considerably decreasing the active flood plain area (Hein et al. 2016). Notably, levees built during the 19th century transformed lotic floodplain water bodies into lentic side-arms (Hohensinner et al. 2013). In recent decades, however, some floodplain sections have been successfully restored with the aim to re-establish conditions typical for “active,” natural floodplain systems. Thereby, near-natural-river-floodplain sections were recreated close to the town Regelsbrunn and in parts close to the area Lobau (Fig. 1) (Schiemer et al. 1999; Schiemer et al. 2006), where frequent surface connection with the main channel (~200 d per year) now occurs. Most parts of Lobau, however, are still heavily protected from direct through-flow (Fig. 1) because only a small downstream opening allows surface connection at higher water flow (Reckendorfer and Hein 2000). Lobau is thus characterized by dampened water level fluctuations (Schiemer et al. 1999) in a number of lentic backwaters, that are only occasionally connected by back-flowing floods (Reckendorfer et al. 2013). There are also completely disconnected parts of Lobau that formerly belonged to the active floodplain but now never experience surface connection to the Danube. Groundwater connection with the Danube, however, does exist (Grieble and Mösslacher 2003). However for this complex processes no detailed data are available so far.

For this study, we selected sites that represent a gradient of connectivity to the main channel. They ranged from isolated (station G, connected 0 d yr⁻¹), through semi-isolated (station F and E, connected 0–20 and 20–180 d yr⁻¹, respectively) to dynamic (station B, C, D, connected > 180 d yr⁻¹) (Fig. 1a). In dynamic water bodies (Fig. 1, stations B, C, D), lotic conditions can be frequently observed, whereas semi-isolated E and F are open-water backwaters mainly characterized by lentic conditions. The completely disconnected, isolated station G is comparably small, lake-like, highly sheltered and shaded. It was once part of the former, active floodplain, but because of the river regulation in the 19th century it is now never connected to the Danube, even during extreme flooding events.

We performed two sampling campaigns, one in 2012 (Apr–Dec) and one in 2013 (Apr-Aug), each covering a spring pre-flood, early summer flood and a post-flood hydrological phase. At the Austrian stretch the Danube receives large amounts of snowmelt and glacial runoff from its southern tributaries and its flow regime is therefore characterized by predictably high water levels in early summer (Heiler et al. 1995). Sampling frequency was adaptive, either bi-weekly or monthly in the pre- and post-flood phase, and increased to 2–3 times per week at the onset of a flood.

**Hydrology and aquatic surface area**

The Danube discharge and water level data were provided by the Hydrological Office of Lower Austria. They were obtained from station A located downstream of the floodplain. Mean water, 1-yr and 100-yr flooding events are defined by discharges of 1930 m³ s⁻¹, 5300 m³ s⁻¹, and 10,500 m³ s⁻¹, respectively (www.noel.gv.at). Flow velocity in the main channel was calculated from the discharge time series and cross section data ("Via Donau"-company, unpublished data).
Stations B and C are located in a hydrologically different area than stations D through F. While the latter stations are subject to backwater flow only—as inflow and outflow take place through a single cross section—the first two are located in a river subsystem generally characterized by through-flow, hence characterized by separate boundary conditions for inflow and outflow. Therefore, different model approaches were selected for these two regions. For stations B and C, flow velocities were obtained from the model by Reckendorfer and Steel (2004), and water levels were computed from gauge readings taken during each sampling campaign. For stations D, E and F, flow velocities were acquired from the hydrological model of Gabriel et al. (2015), and water levels were calculated for the discharges observed at sampling dates with the hydrodynamic model of Tritthart et al. (2011) developed for the Lobau area. The three referenced models are comparable in the quality of their output parameters because all of them were calibrated and validated successfully on measured hydrographs at several gauges located within the study site. As flow velocity follows directly from

Fig. 1. The Danube River and its floodplains downstream of Vienna. The small map shows Austria. (a) The letters indicate the sampling stations. Regelsbrunn and Lobau regions indicate different subsystems of the river-floodplain and the arrows point at the inlet where the flooding water enters these floodplain areas. Floodplain sections used for upscaling are marked with the red line. (b) The aerial extent of mean water (yellow), a 1-yr flood (red) and a 100-hundred-yr flood (blue) in the two studied regions.
an unsteady continuity condition in the river subsystems investigated, it is not expected to be associated with any larger error than the water surface, independent of the model used.

For each sampled water body and sampling time point, the volume and surface area of the flooded region were calculated based on the water level and the digital elevation model (DEM) (Via Donau, unpublished data, resolution: 2.5 \times 2.5 m), using the “3D Analyst Tools” in ArcMap 10.1 (ESRI). The average depth of the water body was obtained by dividing the volume by the surface area of the water body. These values were used to calculate CH4 flux.

**Sampling and gas chromatography**

Temperature, oxygen saturation (%), pH, and conductivity were determined in situ (WTW Oxi 330, WTW pH 330 and WTW Cond 330, respectively). Water and air samples from all stations were collected in triplicate in 50 mL serum bottles to measure CH4 concentrations. Water samples were collected by filling bottles without headspace and closing them with crimp-seal gas-tight rubber stoppers under water. Bottles were prepared with a small amount of precipitated sodium azide (NaN3, final concentration 0.54 mol L\(^{-1}\)) for preservation prior to sampling. Samples were stored at 4°C pending analysis by gas chromatography (Agilent GC 6890N equipped with a flame ionization detector and an automatic gas-injection unit). The GC sampled a headspace that was created by replacing 15–20% of sample water with CH4-free gas-injection unit). The average depth of the water body was computed as

where CH4\(_{\text{eq}}\) is the vertical gas transfer velocity of CH4 (cm h\(^{-1}\)) at the respective water temperature. k\(_{\text{CH4}}\) was computed from:

\[ F = k_{\text{CH4}} \times d\text{CH4} \]  

(2)

where k\(_{\text{CH4}}\) is the vertical gas transfer velocity of CH4 (cm h\(^{-1}\)) at the respective water temperature. k\(_{\text{CH4}}\) was computed from:

\[ k_{\text{CH4}} = k_{600} \times \left( \frac{Sc_{\text{CH4}}}{600} \right)^{-\alpha} \]  

(3)

where k\(_{600}\) is the gas transfer velocity normalized to a Schmidt number of 600 and Sc\(_{\text{CH4}}\) is the Schmidt number of CH4 at the temperature measured in the field (Wanninkhof 2014). We used \( n = 0.67 \) for wind speeds in 10 m height \( u_{10} \leq 3.7 \text{ m s}^{-1} \) and water velocities \( v < 30 \text{ cm s}^{-1} \). Whenever either \( u_{10} \) or \( v \) exceeded the threshold, \( n = 0.5 \) was applied.

We predicted k\(_{600}\) (cm h\(^{-1}\)) based on an additive model developed from CO2 data by (Borges et al. 2004):

\[ k_{600} = 1.0 + 1.719 u_{0.5}^{0.85} h^{-0.5} + 2.58 u_{10} \]  

(4)

from flow velocity \( v \) (cm s\(^{-1}\)), water depth \( h \) (m), and wind speed at 10 m height \( u_{10} \) (m s\(^{-1}\)). The wind speed was obtained from ZAMG measured at nearby meteorological stations. Notably, Eq. 4 takes into account both hydrological conditions and wind as controls on gas transfer velocity, which contrasts classical approaches (Cole and Caraco 1998; Crusius and Wanninkhof 2003; Juutinen et al. 2009), but is considered vital for dynamic floodplain water bodies (Alin et al. 2011). For the completely disconnected station (no flow, sheltered from wind) we used a k\(_{600}\) of 2.13 (cm h\(^{-1}\)) proposed for small, temperate, wind-sheltered lakes by Cole et al. (2010).

To calculate the total CH4 evasion from the whole area (tCH4) (kmol h\(^{-1}\)), the floodplain section belonging to each sampled water body was delineated based on the average connection to the Danube (Reckendorfer and Steel 2004; Tritthart et al. 2011) (Fig. 1a). The total area covered with water during distinct hydrological phases was calculated (Fig. 1b). Then, based on daily mean discharge, the following time periods were established: “mean water,” “1-year flood,” and “100-year flood.” Afterwards, each CH4 flux datapoint was assigned to one of these categories, in each year, respectively. Assuming that our investigation period covered most of the hydrological situations, tCH4 for each section and for the whole river-floodplain was determined by multiplying the average CH4 flux within one time period by the aquatic surface area of the respective section. We then scaled up the CH4 flux to obtain the total, annual evasion of tCH4 (kmol yr\(^{-1}\)) from the whole river-floodplain (Lobau and Regelsbrunn) for each year.

**Statistical analyses**

Statistical analyses were performed with R 3.1.2 (R Core Team 2014), using the package gam (Hastie 2015). Analytical replicates (\( n = 1–3 \)) were averaged for each site and date prior to any statistical analysis to avoid pseudoreplication. To
analyze the effects of the 1-yr and 100-yr floods on concentrations and fluxes, we computed bootstrap-confidence intervals (percentile method, [Manly 2006]) for the differences between pre-flood and flood phases at the various stations. To analyze effects of hydrological isolation on CH4 data, we tested for differences among individual sites and accounted for temporal autocorrelation by a cubic spline smoother in general additive models (Hastie and Tibshirani 1990). To avoid variance heterogeneity, we used log-transformed CH4 concentration or flux as individual responses. In these models, “site” is considered an ordered factor due to differing degrees of hydrological isolation (see above). We also included an interaction between the temporal smoothing term and site to investigate differences in temporal dynamics across sites.

Results

Hydrological conditions in the river-floodplain system

Hydrological conditions in the Danube (and in the floodplain) differed markedly between the two years. In 2012, the main channel discharge ranged from 1061 to 5101 m³ s⁻¹ (Fig. 2), with a typical 1-yr flood in June. According to the gradient of connectivity, the dynamic stations were connected 82% (station C) and 65% (station D) of the sampling events. The semi-isolated stations (E and F) were connected during the flood only, yet without flowing water conditions in 27% and 5% of the sampling events, respectively. In 2013, the Danube discharge ranged between 1338 m³ s⁻¹ and 10,041 m³ s⁻¹ (Fig. 2). The discharge maximum in early June corresponded to a 100-yr flood and resulted in flowing water conditions at the dynamic and semi-isolated stations. Despite the large differences in peak flow, surface connectivity in 2013 was similar to 2012. The surface connection with the Danube in dynamic stations occurred in 90% (B, C) and 65% (D), while in stations E and F it was established in 55% and 18% of the sampling events, respectively. A surface connection between the Danube and station G was never established.

Concentrations of CH4 across the river-floodplain system

At all sampling events, river-floodplain waters were supersaturated with CH4. Atmospheric partial pressures of CH4 were low (1.70–7.46 ppm) and concentrations of CH4 in water were 29–22,281 times higher than expected theoretically for an equilibrium with the atmosphere. Notably, concentrations showed distinct spatial variation, with clear differences among stations depending on connectivity (Fig. 3). Overall, the mean CH4 concentrations in water were lowest in the Danube main channel and increased with decreasing connectivity of floodplain waters (Table 1). The water in the completely isolated station (G, data for 2013 only) was exceptionally oversaturated; reaching extreme values 22,281 times in excess of the atmospheric equilibrium. There was clear temporal autocorrelation as shown by a significant smoothing term for CH4 on time (R²adj = 0.59, deviance explained = 61.7%, p < 0.05, n = 177). Also, we identified a significant interaction between the temporal smoothing term and site, pointing to differences in CH4 dynamics among sites. Notably, excluding the sites measured only in the second year, this interaction can be graphically recognized by converging trends of average CH4 concentration in the second year, that is, less spatial variation across this subset of sites in the year with the 100-yr flood (Fig. 3). The temperature proved to be a driving force for high methane concentrations here, resulting in a significant correlation between CH4 concentrations in station G and temperature (r = 0.62, p < 0.05). Also for dynamic stations, some
dependency on temperature was recorded \( (r = 0.34, p < 0.01) \); at other stations no such correlation was observed.

We calculated the differences in \( \text{CH}_4 \) concentrations \( (\Delta \text{CH}_4) \) between floodplain sites and the main channel for all sampling dates during times of surface connection with the Danube. Both revealed significant inverse relationships with the Danube discharge (Fig. 4a,b). \( \Delta \text{CH}_4 \) was much larger at low discharge and decreased markedly during times of higher flow (including the 1-yr flood). During the 100-yr flood, the differences between the floodplain and the main channel were either very small or showed negative values, indicating considerable increase in the \( \text{CH}_4 \) concentration in the main channel and concurrent decrease in the floodplain (Fig. 4a,b).

### Table 1.

| Danube main channel | Dynamic stations | Semi-isolated stations | Isolated station |
|---------------------|------------------|------------------------|------------------|
| 0.41 (0.12–3.80)    | 1.51 (0.12–9.70) | 3.58 (0.41–27.85)     | 24.70 (1.08–75.53) |

In parentheses: min–max

### Fig. 3.

\( \text{CH}_4 \) concentrations at the 7 investigated sites differing in hydrological isolation (surface connectivity with the Danube) across the whole study period. The color gradient indicates increasing hydrological isolation (from blue toward red). Lines are cubic spline smoothers of time resulting from a general additive model with an interaction term between (smoothed) time and site. Note converging trends of average \( \text{CH}_4 \) concentration in the second year, that is, less spatial variation across the continuously sampled subset of sites in the year with the 100-yr flood. For stations B and G data was only available for 2013. These two stations showed a strong increase in \( \text{CH}_4 \) concentrations over the short period of sampling in 2013.

### Fig. 4.

Relationships between main channel discharge and river-to-floodplain differences in \( \text{CH}_4 \) concentrations in dynamic (a) and semi-isolated stations (b) during connection with the main channel. Stars indicate samples taken during the onset of the 100-yr flood event.

### CH\(_4\) fluxes across the river-floodplain system—effect of flooding

Overall, methane evasion differed markedly along the connectivity gradient from the main channel, through dynamic, semi-isolated to isolated stations and revealed distinct spatial variation with clear differences among stations (Fig. 5). The lowest average methane fluxes were observed in the Danube main channel (Table 2), and the highest average values always occurred in floodplain waters; the only exception was the 100-yr flood in the main channel of the Danube (Table 2). Furthermore, similar to \( \text{CH}_4 \) concentration
data, differences in the dynamics of CH$_4$ flux among the sites were indicated by a significant interaction between the temporal smoothing term and site ($R^2_{adj} = 0.17$, deviance explained = 22.5%, $p < 0.05$, $n = 181$).

Flooding had variable impact on CH$_4$ evasion from the various river-floodplain stations. The CH$_4$ flux from the Danube main channel and the dynamic stations was higher during the 100-yr flood (Table 2) but due to high variability the difference to pre-flood conditions was not significant (Fig. 6). The 1-yr flood resulted in lower fluxes in dynamic floodplain stations, yet also these could not be identified as significantly different to spring-pre flood conditions (Fig. 6). At semi-isolated stations a significant decrease of CH$_4$ evasion occurred during the 100-yr flood (Fig. 6). At the least connected station (G), the flood had no significant effect on CH$_4$ flux. No significant correlation between CH$_4$ fluxes and temperature was noted except semi-isolated ($r = 0.26$, $p < 0.05$) and isolated station ($r = 0.70$, $p < 0.05$).

**Floodplain waters vs. main channel as important sources of methane**

Based on the evasion rates and the flooded area of the two river-floodplain systems, we evaluated the share of floodplain evasion of CH$_4$ (mol h$^{-1}$) compared to the entire river-floodplain system (Regelsbrunn + Lobau + main

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**Fig. 5.** CH$_4$ fluxes at the 7 investigated sites differing in hydrological isolation (surface connectivity with the Danube) across the whole study period. The color gradient indicates increasing hydrological isolation (from blue toward red). Lines are cubic spline smoothers of time resulting from a general additive model with an interaction term between (smoothed) time and site. Note converging trends of average CH$_4$ concentration in the second year, that is, less spatial variation across the continuously sampled subset of sites in the year with the 100-yr flood. For stations B and G data were only available for 2013. These two stations showed a strong increase in CH$_4$ fluxes over the short period of sampling in 2013.

**Table 2.** Average CH$_4$ flux (µmol m$^{-2}$ h$^{-1}$) from the main channel of the Danube, dynamic, semi-isolated and isolated stations during different hydrological phases.

|                  | Danube          | Dynamic stations | Semi-isolated stations | Isolated station |
|------------------|-----------------|------------------|------------------------|------------------|
| Spring pre-flood (both years) | 72.2 (34.7–199.1) | 116.7 (6.9–417.9) | 304.1 (58.8–913.6) | 175.9 (19.1–458.8) |
| 1-yr flood       | 77.4 (36.2–99.7) | 69.5 (18.4–125.8) | 430.9 (90.5–952.5) | no data          |
| 100-yr flood     | 303.2 (44.3–990.2) | 260.1 (26.6–955.6) | 74.1 (40.7–152.8) | 432.8 (198.7–791.1) |
| After flood (both years) | 63.3 (23.5–102.5) | 138.1 (2.6–661.2) | 228.7 (28.8–1203.2) | 871.9 (307.9–1616.2) |

In parentheses: min-max.

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**Fig. 6.** 95% bootstrap confidence intervals (computed from percentiles) for the flood-driven CH$_4$ flux increase (differences flood minus pre-flood) at the various sites ordered along hydrological isolation (surface connectivity) in 2012 (blue) and 2013 (green). Non-overlap of confidence intervals with the zero line indicates a significant difference between hydrological phases. Similarly, non-overlap among pairs of confidence intervals indicates a significant difference between pairs of sites or years. The means of analytical replicates were used for bootstrapping.
channel). Overall, our results revealed that during both years, floodplain waters (dynamic and semi-isolated) accounted for 53% (in 2012 and in 2013) of the CH4 evasion from the investigated river-floodplain system (Fig. 7). The contributions of the isolated station (G) were negligible due to its small surface area.

Most of the CH4 (mol h⁻¹) was lost during the 100-yr flood (Table 3). The highest evasion was estimated from the water surface of the Danube stretch, but high losses were also recorded from the regulated floodplain of Lobau and restored section at Regelsbrunn (Table 3). Our results also revealed that 34% more CH4 (kmol yr⁻¹) were emitted from the entire river-floodplain during the year with the 100-yr flood (Fig. 7).

Discussion

CH4 concentration in river-floodplain sections

High spatial and temporal variability in aquatic CH4 concentrations is characteristic for wetlands (Bloom et al. 2012), rivers (Shelley et al. 2014) as well as for floodplains (Crill et al. 1988). In this study, methane concentrations also covered a broad range (Table 1) (Fig. 3); the main channel had lower values (29–1206 times higher than atmospheric equilibrium), while semi-isolated and isolated floodplain waters were highly supersaturated with CH4 (32–22,281 times higher than atmospheric equilibrium). Hence, floodplain waters, as well as the main channel of the Danube, were always sources of CH4 to the atmosphere. Average aquatic methane concentrations in this study resembled the concentrations reported for the Brazilian Amazon (Belger et al. 2011) rather than the lower concentrations for temperate lowland rivers (Sanders et al. 2007; Trimmer et al. 2009). The elevated aquatic methane concentrations are likely caused by in-situ methanogenesis, which can be considerably high in riverbed sediments (Shelley et al. 2015). The activity of methanogens is affected by temperature (Fu et al. 2015; Tveit et al. 2015), and methane formation is apparently sensitive to temperature increase (Duc et al. 2010). In our study, temperature was the strongest controlling mechanism for CH4 concentration at the completely disconnected station (G). However, the temperature-dependency was less pronounced in other stations, where methane concentrations could also be influenced by other factors such as availability of organic carbon (Christensen et al. 2003; Liu et al. 2011). The quantity and quality of organic substrates delivered to the river-floodplain are highly variable and fluctuate substantially, from mostly allochthonous material during the flood (Sieczko and Peduzzi 2014) to autochthonous material during the post-flood period (Sieczko et al. 2015). The elevated sedimentation of organic matter delivered with a spate could also be responsible for enhanced activity of methanogens during the post-flood period (Van Huissteden et al. 2005; Gatland et al. 2014), especially at semi-isolated stations. Hence, beside fluctuations in methanogen activity, spatio-temporal variation in aquatic CH4 concentration across the river-floodplain system can be purely physically induced by hydrological fluctuations affecting gas exchange (Pulliam and Meyer 1992). This includes flooding events, which may alter CH4 concentrations substantially by flushing otherwise hydrologically isolated habitats. In our study, the highest differences in concentrations between floodplain waters and the Danube were noted when the river flow was lower (Fig.

![Fig. 7. Total evasion of CH4 (kmol yr⁻¹) from the entire river-floodplain (Regelsbrunn and Lobau) in 2012 and 2013 and relative contribution (%) of different sections: Danube (blue), dynamic (green), semi-isolated (yellow), isolated (red).](image)

Table 3. Average total fluxes of CH4 (mol h⁻¹) from the Danube main channel stretch of the investigated area, Regelsbrunn (restored) and Lobau (regulated) floodplains during different hydrological phases.

|                | Spring pre-flood | 1-yr flood | 100-yr flood | After flood |
|----------------|------------------|------------|--------------|-------------|
|                | Total flux [mol h⁻¹] | Area [km²] | Total flux [mol h⁻¹] | Area [km²] | Total flux [mol h⁻¹] | Area [km²] | Total flux [mol h⁻¹] | Area [km²] |
| Danube main channel | 341.37           | 4.87       | 466.46       | 6.16        | 2196.20       | 7.24       | 296.43          | 4.87       |
| Regelsbrunn    | 63.59            | 0.67       | 229.99       | 2.43        | 1039.91       | 4.35       | 121.36          | 0.67       |
| Lobau          | 284.25           | 1.21       | 545.80       | 2.02        | 1935.67       | 14.96      | 201.74          | 1.21       |
In agreement with Pulliam and Meyer (1992), our results indicate that dissolved CH₄ concentrations in floodplain waters are driven by changes of main channel discharge. This suggests that surface connection between the floodplain and the river may be an important factor controlling CH₄ concentrations in the main channel (Richey et al. 1988). In fact, due to its much higher gas exchange efficiency the river main channel can act as an “exhaust pipe” of the entire river-floodplain system, responsible for evasion of CH₄ produced in floodplain waters. This mechanism has been especially important during the 100-yr flood when floodplain CH₄ concentrations decreased due to dilution, while the main channel CH₄ concentration increased (Fig. 4a,b) at the same time. Hence, a pulse of methane flushed from the slow-flowing floodplain into the river could be responsible for elevated CH₄ in the main channel. This suggests that most of the river CH₄ has originated in the super-saturated waters adjacent to the main channel and suggests that river carbon delivery was driven by surface floodwater supply (Abril et al. 2014; Gatland et al. 2014). Additionally, the high CH₄ peak during the 100-yr flood could also be associated with run-off from upstream forest and agricultural soils (Angelis and Lilley 1987).

**Importance of floods: Implications of increased flooding frequency for methane evasion**

High interannual variations of CH₄ emissions, characteristic for river-floodplains, point to the importance of these systems as methane sources (Marani and Alvala 2007). Rapid hydrological changes, typical for river-floodplains, can substantially affect evasion of greenhouse gases from temporarily inundated systems (Altor and Mitsch 2008), and flooded environments are recognized as sources of methane to the atmosphere (Belger et al. 2011). Our study shows that flooding significantly altered methane evasion. It also emphasizes the importance of spates with different magnitude for CH₄ emission from stations with different connectivity (Fig. 6). During a high-water period, methane evasion can be significantly higher (Devol et al. 1990), with rapid emissions occurring shortly after the onset of the flood (Boon et al. 1997). Similar to a study of Gatland et al. (2014), our findings show that the highest CH₄ loss from the floodplain area occurred during the extreme 100-year flood (Table 3). This suggests that an improved, detailed characterization of hydrological processes is necessary to correctly assess the CH₄ dynamics in river-floodplain systems (Zhu et al. 2013).

Methane emissions from wetlands have been linked to climate change (Mitsch et al. 2010). Yvon-Durocher et al. (2014) suggested that global warming has a large effect on the relative contributions of CH₄ to total GHG from aquatic ecosystems. Also, impacts of global change, such as increasing frequency of droughts and flooding, summarized by Lehner et al. (2006), are expected to occur in Europe. However, the effect of a shift in hydrological variability—as possibly caused by global climate change—on methane emissions still remains unknown both at tropical latitudes (Mitsch et al. 2010) and in temperate regions. Future scenarios for the Danube River predict an increase in discharge magnitude and in water temperature during spring floods (Zweimüller et al. 2008). In our study, tCH₄ evasion (Fig. 7) was 34% higher during the year of extreme flooding compared to the hydrologically “average” year, suggesting that increased flooding frequency, increase of the flooded area will have marked consequences on overall methane emissions (Sha et al. 2011). Hence, higher emissions from river-floodplains during extensive floods may be expected in the future. Note also that rivers can be important CH₄ sources to the coastal ocean (Scraton and McShane 1991). Pavel et al. (2009), for example, observed a significant input of riverine CH₄ into the Danube Delta during post-flood conditions. Thus, the predicted, intensified spate occurrence in the Danube may also have consequences for the carbon cycle in the Danube Delta and the coastal Black Sea.

**Methane evasion from floodplains with different levels of human impact**

The global emissions of methane from tropical wetlands (Smith et al. 2000) and from temperate regions are most likely underestimated and considerably uncertain (Kirschke et al. 2013). Typically, large tropical floodplains have been considered to be the most important sources of methane due to their extensive area (Bartlett and Harriss 1993). Our data (Table 2), however, show that the average diffusive fluxes from semi-isolated and isolated stations of a temperate floodplain are similar to average methane fluxes measured over flooded tropical Amazon forest (Bartlett and Harriss 1993). Our study also shows that isolated and semi-isolated stations, although exhibiting variability in their relative contribution (Fig. 7), were significantly stronger sources of CH₄ to the atmosphere than the dynamic sites and the respective river stretch (Table 2). Occasionally, the flux per unit water surface area reached 94% higher values than in the main channel (Table 2). Hence, our study points to the importance of semi-isolated and isolated floodplain waters as important sources of methane.

In general, human activities significantly affect the contribution of inland waters to the carbon cycle (Regnier et al. 2013). Due to river regulation, damming or agriculture, most of the European floodplains have been severely impacted. Today, spatially much reduced floodplain areas experience a markedly lowered frequency of connection with the main river (Buijse et al. 2002). The Danube River is regulated along 80% of its length, resulting in 81% reduction of floodplain areas in the entire river basin (Günther-Diringer 2001). Our findings emphasize that most of the CH₄ emissions originated from human-altered, semi-isolated floodplain waters. Approximately 47% of CH₄ emission occurred from the main river stretch (Fig. 7). The investigated isolated station,
due to its small area, did not contribute substantially to the total CH₄ loss from the whole river-floodplain. High CH₄ fluxes from this isolated station (Table 2, Fig. 5), however, suggest that ongoing, complete disconnection of floodplain sections due to river regulation will produce more areas with such water bodies, thus increasing their contribution to the overall CH₄ budget. Our findings indicate that human-induced disconnection of floodplain waters from the river may have significant consequences for the overall methane budget and emphasize the importance of floodplain waters as sources of greenhouse gases. River-floodplains—beside small, dynamic streams and rivers (Benstead and Leigh 2012)—also apparently play an important role in global greenhouse gas fluxes.

Here, we focused only on diffusive fluxes; the ebullition, plant-mediated flux or recently reported microbubble flux (Prairie and Del Giorgio 2013) have not been investigated. Especially ebullition could be an important component of the total methane flux in floodplain waters (Smith et al. 2000; Ringeval et al. 2014). In rivers, diffusive flux is usually the main component of the total CH₄ emission, but ebullition hotspots may contribute substantially (up to 50%) to the total flux (Sawakuchi et al. 2014). The ebullition rates are also temperature-dependent (Wilkinson et al. 2015) and may thus play an increasing role in the total CH₄ flux in the context of global warming. Because ebullition can be the dominant mechanism in floodplains (Devol et al. 1990) and may exceed diffusive fluxes several-fold or even by orders of magnitude in some systems, we consider this study’s estimate as conservative for the contribution of floodplain waters to the overall river-floodplain methane emission. Nevertheless, in line with other studies, our work stresses the importance of CH₄ emissions from temperate river-floodplain systems with different levels of human impact. Temperate river-floodplain systems should be considered in global budgets of CH₄ emission.

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