

Methane emissions from contrasting urban freshwaters: Rates, drivers, and a whole-city footprint

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Funding information

Deutsche Forschungsgemeinschaft, Grant/Award Number: GRK 2032

Abstract

Global urbanization trends impose major alterations on surface waters. This includes impacts on ecosystem functioning that can involve feedbacks on climate through changes in rates of greenhouse gas emissions. The combination of high nutrient supply and shallow depth typical of urban freshwaters is particularly conducive to high rates of methane (CH₄) production and emission, suggesting a potentially important role in the global CH₄ cycle. However, there is a lack of comprehensive flux data from diverse urban water bodies, of information on the underlying drivers, and of estimates for whole cities. Based on measurements over four seasons in a total of 32 water bodies in the city of Berlin, Germany, we calculate the total CH₄ emission from various types of surface waters of a large city in temperate climate at 2.6 ± 1.7 Gg CH₄/year. The average total emission was 219 ± 490 mg CH₄ m⁻² day⁻¹. Water chemical variables were surprisingly poor predictors of total CH₄ emissions, and proxies of productivity and oxygen conditions had low explanatory power as well, suggesting a complex combination of factors governing CH₄ fluxes from urban surface waters. However, small water bodies (area <1 ha) typically located in urban green spaces were identified as emission hotspots. These results help constrain assessments of CH₄ emissions from freshwaters in the world's growing cities, facilitating extrapolation of urban emissions to large areas, including at the global scale.

KEYWORDS

CH₄ flux, greenhouse gas, land use, urban ecology, urban ponds, urbanization impact

1 | INTRODUCTION

More than half of the world's population currently lives in cities and this fraction is projected to rise to two-thirds by the year 2050 (UN, 2016). This global urbanization trend leads to heavy modifications of freshwaters worldwide, as encapsulated in the "urban stream syndrome" for running waters (Walsh et al., 2005). Symptoms characterizing this syndrome include strong nutrient and pollutant

loading, even when effective sanitation is in place, and disruptive changes in the hydromorphology of urban freshwaters resulting from altered connectivity, surface sealing in the catchment, bank hardening, and channel modification by canalization and a multitude of other engineering measures (Gessner et al., 2014; Grimm et al., 2008; Roy et al., 2016). As a result, strong impacts on urban surface waters have been documented on biological communities and ecosystem properties such as oxygen regimes and organic

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matter dynamics (Birch & McCaskie, 1999; Paul & Meyer, 2001; Waajen, Faassen, & Lürling, 2014).

A particularly important consequence of enhanced oxygen depletion and organic matter loading in freshwaters is the stimulation of methanogenesis in sediments and, thus, increased emission of methane (CH_4) across the water–atmosphere interface (Grinham, Dunbabin, & Albert, 2018). This suggests that urban freshwaters could act as an important source of CH_4 to the atmosphere (Gonzalez-Valencia et al., 2014; Martinez-Cruz et al., 2017; Wang et al., 2018). Empirical data on CH_4 emissions from urban freshwaters are scarce, however, and have not been included in global emission estimates (Bastviken, Tranvik, Downing, Crill, & Enrich-Prast, 2011; IPCC, 2013), nor in systematic assessments of CH_4 evasion from all potential sources in cities (Hopkins et al., 2016; Ware et al., 2019). In fact, most studies on freshwaters assessing urban CH_4 emissions were limited to a single type of water body and a single season (López Bellido, Peltomaa, & Ojala, 2011; Wang et al., 2018; Zhang et al., 2014; Zhang, Huang, Yang, Li, & Dahlgren, 2016), with only one recent investigation in a tropical megacity considering multiple surface waters and temporal patterns (Martinez-Cruz et al., 2017). Equivalent information is lacking from urban freshwaters in temperate climates, where seasonality is more pronounced than in the tropics.

Information available on individual urban water bodies suggests that the drivers behind CH_4 emissions are similar to those in rural, forest, and other natural areas (Martinez-Cruz et al., 2017; Yu et al., 2017). All else being equal, shallow waters, which are typical of urban areas (McEnroe, Williams, Xenopoulos, Porcal, & Frost, 2013), are likely to emit more CH_4 per surface area, because the travel times of CH_4 bubbles generated by ebullition events and rising from the sediment to the water surface are likely to be shorter, limiting CH_4 oxidation by methanotrophy in the oxic water column (Bastviken, Cole, Pace, & Tranvik, 2004; Holgerson, 2015). The small size of most urban water bodies also suggests that land use in the surroundings and associated inputs of organic matter, nutrients, and contaminants can strongly influence water quality and ecosystem properties. Large supplies of labile organic matter, whether from the catchment or through intense primary production boosted by nutrient availability, coupled with subsequent oxygen depletion are both conducive to methanogenesis (Segers, 1998). This points to a high potential of urban freshwaters to produce and emit CH_4 to the atmosphere, unless toxic substances curb biological activity.

In view of the importance and large gaps in information on rates and drivers of CH_4 emissions from urban freshwaters, the aims of this study were to (a) determine CH_4 fluxes at different times of the year from a range of contrasting urban freshwaters; (b) identify drivers of CH_4 emissions from the different types of water bodies; and (c) integrate this information to provide an initial flux estimate from a metropolitan area as a potentially important component of global urban CH_4 emissions from freshwaters. Based on the limited information available to date, we predicted rates to be particularly high in small, shallow, and nutrient-rich standing waters with sediments rich in organic matter.

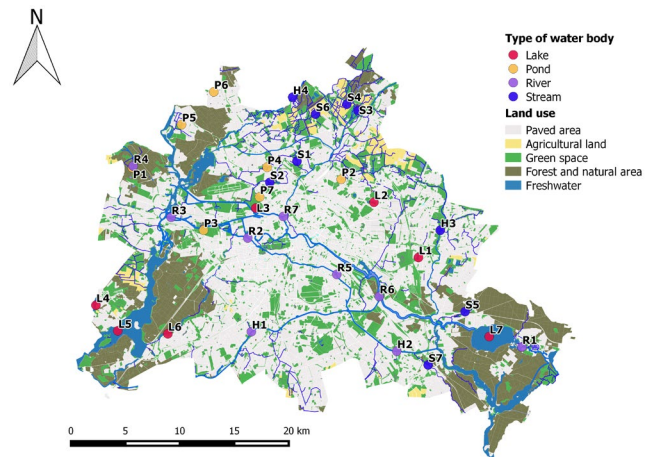


FIGURE 1 Map of the metropolitan area of Berlin, Germany, showing land use and freshwater sampling locations in lakes (L1–7), ponds (P1–7), rivers (R1–7), streams (S1–7), and four additional running water sites characterized by high nutrient concentrations (H1–4)

2 | MATERIALS AND METHODS

2.1 | Study sites

The study was conducted in the city of Berlin, Germany, an urban area with 3.5 million inhabitants on 892 km² (Heberer, 2002), of which 54 km² (6%) are freshwaters (Figure 1). Freshwaters in Berlin include two mid-sized rivers feeding and draining several larger shallow lakes (Knappe, Möller, Dulski, & Pekdeger, 2005), about 60 smaller lakes (>1 ha), and more than 500 ponds (Heberer, 2002). When canals for transportation and ditches for sewage and rainwater collection are added, the surface river network reaches a total length of about 560 km (SenUVK, 2018). River flow is slow because of the low terrain slope (0.01%; Knappe et al., 2005), locks, and weirs. Multiple wastewater treatment plants (WWTP) within the city discharge treated effluents into the urban freshwater network (Heberer, 2002).

Four categories of surface waters were distinguished: lakes, ponds, rivers (including canals), and streams (including ditches). Lakes were classified as water bodies ≥ 1 ha according to a lake inventory for Berlin (SenUVK, 2005). Rivers and streams were differentiated by width (rivers >5 m). Seven locations were randomly selected from each of the four categories. Four additional running water sites were also included because of particularly high nutrient (NO_3^- , NH_4^+ , total phosphorus [TP]) and dissolved organic carbon (DOC) concentrations recorded in a monitoring program over the five previous years (SenUVK 2009–2014). However, CH_4 emissions at these sites were found not to differ significantly from those of the randomly selected sites and were thus treated as rivers (H1–2) or streams (H3–4), depending on size. Thus, a total of 32 sites (Figure 1; Table S1) were each sampled four times, in spring (April–May), summer (July–August), and fall (September–October) 2016, and in winter (February–March) 2017 just after ice out because of unusually cold weather late in the season.

2.2 | CH₄ emissions

Floating chambers were deployed at one selected point in each water body to estimate rates of total, diffusive, and ebullitive CH₄ fluxes to the atmosphere. The chambers were anchored but several meters of rope and tubing allowed for some free movement. The position in lakes was randomly chosen along the contour line of average water depth to avoid potential bias caused by taking measurements at the deepest point (Schilder et al., 2013). Since the bathymetry of ponds was unknown, the central point (not necessarily the deepest) was used in those cases; this was less critical than for lakes because water depth in ponds varied much less. In running waters, chambers were deployed within 2 m from the shore (Grasset, Abril, Guillard, Delolme, & Bornette, 2016).

Cylindrical floating chambers (area: 0.071 m²; headspace volume 5.4 L) were used in lakes and ponds to determine CH₄ emission rates. Slightly wider and shorter but otherwise similar chambers (0.126 m²; headspace volume 16.8 L) were used in streams and rivers. The chamber headspace was connected in a closed loop to an ultra-portable greenhouse gas analyzer (UGGA 24P and 30P; Los Gatos Research) before deploying a single chamber three times at each location to measure CH₄ headspace concentrations every second for 15 min (Pirk et al., 2015). Chambers were opened between series of measurements and equilibrated with the surrounding air. All fluxes were measured between 8 and 12 a.m. to minimize any possible influence of systematic diel variations. Atmospheric pressure and wind speed 1 m above the water surface were simultaneously determined using a portable weather station (Kestrel 4000; Nielsen-Kellerman).

Total CH₄ flux (F) to the atmosphere was calculated as:

$$F = \frac{\Delta C}{\Delta t} \times \frac{V \times P}{A \times RT} \times 10^{-6} \times 8,640 \times 10^3 \times 16 \left(\text{mg day}^{-1} \text{m}^{-2} \right),$$

where ΔC is the concentration change in the headspace of the static chamber (ppm_v), Δt is the chamber deployment time (s), V is the volume (m³) of the chamber headspace, A is the area of the static chamber (m²), R is the universal gas constant (8.3143 m³ Pa mol⁻¹ K⁻¹), P is atmospheric pressure (Pa), and T is air temperature (K) during the measurement. All concentration data were plotted to visually identify whether any sampling errors or ebullition events occurred. When initial values deviated from the atmospheric concentration measured before deploying a chamber, the first data points were removed and the fluxes calculated based only on the time span where the concentration increased linearly.

Total fluxes were calculated as the difference between initial and final concentrations during the considered deployment time. Diffusion fluxes were computed for the first period of linear concentration increases after the deployments. This was usually during the first 30 s when ebullition was observed. If no ebullition occurred, the period was extended to up to 15 min. When no ebullition event was observed, we calculated diffusive fluxes based on the entire exposure period of 15 min (Gerardo-Nieto, Astorga-España, Mansilla, & Thalasso, 2017). Ebullition events were recognized by sudden steep concentration

increases, which were occasionally followed by a decline. Only concentration increases with an $r^2 > .7$ were taken into account to compute diffusive fluxes (Martinez-Cruz et al., 2017; Sepulveda-Jauregui, Martinez-Cruz, Lau, & Casper, 2018). Ebullition flux was calculated as the difference between the total and diffusive flux.

To assess the reliability of the calculated fluxes from the chamber technique, other commonly adopted methodologies were used in tandem with the flux measurements by the chamber technique. Specifically, CH₄ concentrations of surface waters were used to calculate diffusive fluxes following the thin boundary layer (TBL) methodology (see Supporting information), and inverted funnels deployed above the sediment for a week were used to calculate ebullition fluxes (see Supporting information).

2.3 | Extrapolation of CH₄ emissions

Total CH₄ fluxes measured with the chamber technique were first averaged for each type of water body and season and then extrapolated to the duration of each season (mg CH₄/m²; Panneer Selvam, Natchimuthu, Arunachalam, & Bastviken, 2014). Seasons were defined following the solar calendar: spring (March 20, 2016–June 21, 2016), summer (June 21, 2016–September 21, 2016), autumn (September 22, 2017–December 21, 2017), and winter (December 22, 2017–March 19, 2018). Fifty-five days of ice cover were excluded for the winter estimate, with the period of ice cover being established based on regular visits of a reference lake in Berlin (L7). To standardize the ice-cover period among the different water bodies, we defined the start as the date where the minimum daily temperature dropped below 0°C for 3 days in a row and the end as the date when mean daily temperature rose above the freezing point for at least 1 week. Total annual emissions from each type of water body were estimated by multiplying the seasonal total emission from each type of water body (mg CH₄/m²) by the respective surface area of all water bodies in the city of Berlin assigned to that water body type. The total CH₄ emission footprint of Berlin's surface waters was then calculated as the sum of the annual emissions by each of the four types of water bodies. Estimates of variation (i.e., uncertainties) were obtained by applying error propagation rules at each step.

2.4 | Water chemistry

Dissolved oxygen (DO), pH, electrical conductivity, and temperature were measured at 0.5 m depth with an in situ multiprobe (smarTROLL) or a WTW Multiprobe 3320 (pH320, OxiCal-SL, Cond340i). Integrative water samples were collected from the upper 0.5 m water layer. Alkalinity was measured by titrating (888 Titrand, Metrohm) unfiltered water in the laboratory. To determine particulate organic carbon (POC), known volumes (0.2–2 L) were filtered through precombusted (5 hr, 450°C) and preweighed GF75 glass fiber filters (average pore size 0.3 μm; Advantec). The filters were dried and weighed, and a weighed portion was subsequently used for elemental analysis (Vario EL; Elementar

Analysensysteme GmbH) to determine POC. The filtrate was stored in acid-washed and precombusted glass vials with a polytetrafluoroethylene-lined screw cap for later measurements of DOC and dissolved inorganic carbon (DIC) on a TOC analyzer (TOC-V; Shimadzu). A second GF75 filter produced in the same way was used for spectrophotometric analysis of chlorophyll *a* (chl *a*) after hot ethanol extraction (Jespersen & Christoffersen, 1987). Soluble reactive phosphorus, NO_3^- , NO_2^- , and NH_4^+ in the filtrate were analyzed spectrophotometrically on a flow injection analyzer (FIA compact; MLE GmbH), and TP was determined in the same way after digesting unfiltered water samples with $\text{K}_2\text{S}_2\text{O}_8$ (30 min at 134°C). The concentrations of SO_4^{2-} and Cl^- were measured by ion chromatography (Dionex ICS 1000; Thermo Scientific).

We further characterized dissolved organic matter (DOM) by absorbance and fluorescence spectrophotometry (Aqualog). Fluorescence spectra were recorded in a 1 cm quartz cuvette at excitation wavelengths ranging from 250 to 600 nm at 5 nm increments and emission wavelengths of 250–650 nm measured at 1.77 nm increments. These optical measurements were performed within 48 hr after sampling. The resulting data yielded the following indicators of DOM quality (Table S2): humification index (HIX), fluorescence index (FIX), biological activity index ($\beta:\alpha$), specific UV absorbance (SUVA), spectral slope between 275 and 295 nm ($S_{275-295}$), spectral slope between 350 and 400 ($S_{350-400}$), and the spectral slope ratio (S_R).

2.5 | Land use

The total area of each type of water body and of four categories of land use (forest and natural areas, green space, agricultural land, paved areas) within a 50 m wide strip along the shores of each site were calculated using Quantum GIS (Development Team), based on land-use data freely available from the Senate Department for the Environment, Transport and Climate Protection of Berlin. Historical reviews and personal communication with citizens and authorities complemented the database to determine whether a given water body was natural or man-made and whether it had any other distinct anthropogenic features.

2.6 | Data analysis

All statistical analyses were performed with R version 3.2.2 (R Development Core Team, 2010). Linear mixed models were used on log-transformed data to test for differences in total CH_4 emissions among seasons, types of water bodies, and the interaction of both, taking into account the repeated-measures nature of the data. Tukey post hoc tests were used for pairwise comparisons. Wilcoxon signed rank test was used to compare estimates of diffusive flux by the TBL and chamber method, as well as to compare ebullitive flux assessed with the funnel traps and the chamber method.

To explore possible controls of total CH_4 emissions, the large number of variables recorded to characterize the water bodies was first condensed by a principal component analysis (PCA). The analysis

was based on water temperature, a range of water chemical variables (conductivity, pH, alkalinity, DO, TP, NH_4^+ , NO_3^- , Cl^- , DOC, DIC, chl *a*), including DOM properties (SUVA, $S_{275-295}$, $S_{350-400}$, S_R , $\beta:\alpha$, FIX, and HIX), and land use (relative coverage by forest, agriculture, paved areas, and green space). All variables were z-standardized prior to the PCA. Subsequently, all principal components with eigenvalues >1 were used as predictors in a multiple linear regression (MLR) model with total CH_4 emission as the response variable. MLR models were built stepwise in both directions and compared by means of Akaike's information criterion to identify the most parsimonious model.

Last, CH_4 emission was individually regressed against all variables contributing most to the PCA axes included as responses in the final MLR.

3 | RESULTS

Total CH_4 emissions determined with the chamber technique from surface waters in the city of Berlin averaged 219 ± 490 (SD) $\text{mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$ across all 32 locations and seasons. These fluxes averaged across all sites were higher in summer ($p < .05$) than in all other seasons, coinciding with the highest water temperatures (Figure 2; Table S4). No significant differences were found among the other seasons. Ponds showed the highest emission ($503 \pm 699 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) in all seasons (Figure 2), with fluxes significantly exceeding ($p < .05$) those from rivers ($123 \pm 285 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) and streams ($118 \pm 348 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$) but not from lakes ($159 \pm 473 \text{ mg CH}_4 \text{ m}^{-2} \text{ day}^{-1}$). Within each of the four types of water bodies, seasonal differences were only significant between summer

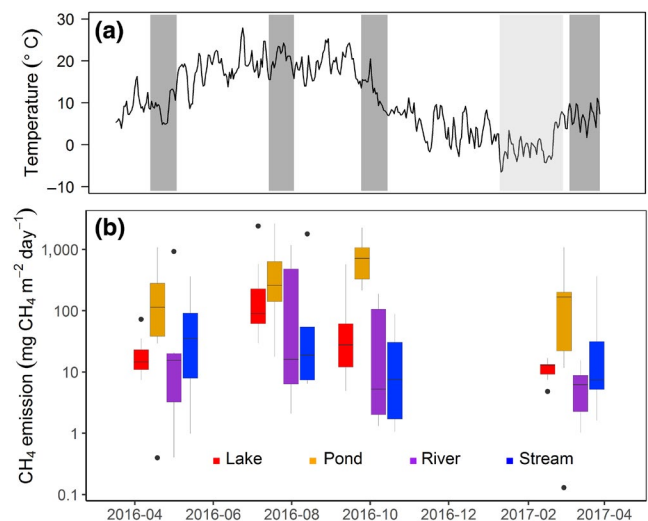


FIGURE 2 Seasonal changes in (a) daily mean air temperature in Berlin Tempelhof recorded by the German Meteorological Office, with the light gray area representing a period of ice cover on the larger lakes and the dark gray areas representing the sampling periods, and (b) Total methane (CH_4) emissions from four types of urban water bodies. Box plots show the median (horizontal line), interquartile range (box limits), highest and lowest values within 1.5 times the box size from the median (whiskers) and outliers (points)

and winter in lakes, ponds, and rivers ($p < .05$), whereas streams never showed any significant difference among seasons.

Total CH_4 emission derived from all chamber measurements indicated a higher contribution of ebullition (80%). Although the relative contribution of ebullition varied among types of water bodies (Table 1; Figure S2). Estimates of ebullition and diffusive fluxes derived from different methodologies also showed some differences. Ebullition fluxes estimated by 1 week deployments of funnels accounted for an average of 62% of the emissions at those sites where ebullition was observed ($N = 12$), compared to 51% based on measurements at the same sites made with the chamber technique (Table S3). Ebullition fluxes determined with the two techniques were positive correlated (Spearman's $\rho = 0.73$; $p < .01$). There were

TABLE 1 Annual methane (CH_4) emission footprint of the metropolitan area of Berlin, Germany, separated by type of water body (mean \pm SD)

Type of water body	Area (km ²)	Emission footprint (Mg CH_4 /year)	CH_4 emission (mg $\text{CH}_4 \text{ m}^{-2} \text{ day}^{-1}$)	
			Ebullition	Diffusion
Lakes	29.7	1,712 \pm 1,498	100 \pm 342	39 \pm 55
Ponds	2.11	385 \pm 598	300 \pm 564	120 \pm 166
Rivers	21.4	461 \pm 552	109 \pm 275	20 \pm 35
Streams	0.79	37 \pm 218	66 \pm 317	39 \pm 74
Total	54.0	2,594 \pm 1,718		

no significant differences in ebullition fluxes among individual water bodies within each type. In contrast, diffusive fluxes estimated by the two methods were significantly different for lakes ($p < .001$), ponds ($p = .024$), rivers ($p < .01$), and streams ($p < .001$). However, despite these differences, the values obtained with the different methods were in a broadly similar range for most of the observations. Taking into account the calculated areas of the different types of surface waters in the city of Berlin (Table 1), the annual total CH_4 emission estimated by the chamber method was $2.6 \pm 1.7 \text{ Gg } \text{CH}_4$. Lakes alone contributed almost two-thirds to the total emissions, due to the large total lake area, while streams contributed the least (Table 1).

The first four axes of the PCA to characterize the 32 investigated water bodies in terms of water chemistry and land use accounted for 58% of the total variability. PC1 and PC2 clearly separated the four types of water bodies (Figure 3a,c), with PC1 separating running from standing waters mainly based on differences in land use (green space, paved, or agricultural) and the DOM spectral ratio (S_R), and PC2 separating larger from smaller water bodies based on conductivity and solute concentrations (e.g., NH_4^+ , Cl^-), DOM descriptors (SUVA, $\beta:a$), and chl-*a* concentration. PC3 captured smaller scale water chemical differences based on DOM descriptors (e.g., $S_{350-400}$) and proxies of productivity (e.g., NH_4^+ , chl *a*, and DO), and indicates a slight tendency of lakes to differ from other water bodies (Figure 3b,d). Finally, PC4 tended to separate autumn samples from all others, mainly based on high DOC concentrations.

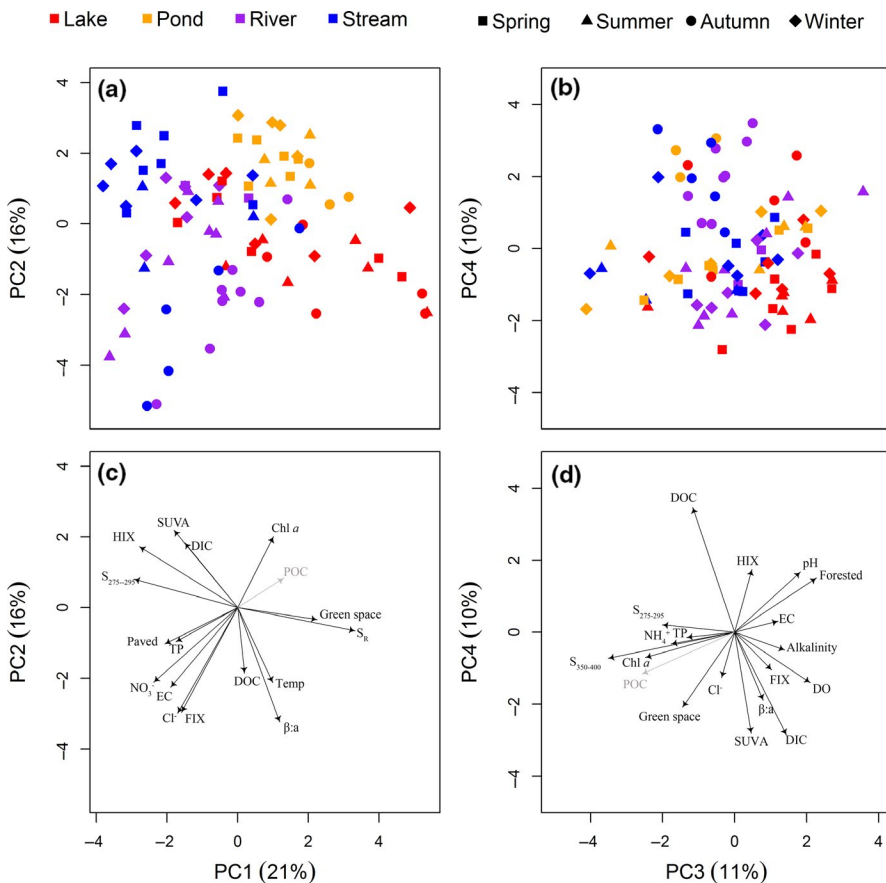


FIGURE 3 Principal component analysis of 32 water bodies sampled over four seasons, based on potential explanatory variables for CH_4 emissions. (a) Water body types differed mainly along the first two principal components, (b) PC3 indicates a slight tendency of lakes to differ from all other water bodies, and PC4 tended to distinguish autumn from all other seasons. (c, d) Dominant variables creating the ordination space relate to land use, water chemistry, and optical properties of dissolved organic matter. Black lines are scaled structure coefficients (scaling factor of 8), that is, correlations with the principal components. Gray lines show analogous correlations with particulate organic carbon, which were added a posteriori because data from only three seasons were available. Only variables with a structure coefficient >0.15 in (c) or (d) were plotted

Linear regression analyses using the PC scores showed that the most parsimonious model explaining total CH₄ emissions involved PC1 and PC3 ($r^2 = .30$; $p < .001$). The most important variables contributing to these two PCA axes were POC, chl *a*, $S_{350-440}$, and DO: Total CH₄ emissions were related to elevated concentrations of POC and chl *a*, lower DOM molecule size, and DO depletion. These patterns appear to be largely driven by differences among lakes (Figure S1), which produced similar relationships with emission data when lakes were analyzed alone. No such patterns emerged for the three other types of water bodies analyzed alone. Ponds were the only exception in that low DO concentrations in surface water were weakly related to CH₄ emission ($r^2 = .19$; $p = .04$).

4 | DISCUSSION

Global estimates of CH₄ emissions from freshwaters and other sources are still plagued by large uncertainties (Bastviken et al., 2011; Deemer et al., 2016; Stanley et al., 2016) with one of the big unknowns being emissions from surface waters of urban areas. Our estimate of the freshwater CH₄ footprint of a large metropolitan area in a western industrialized region is an important step toward reducing these uncertainties. The estimated annual emissions of Berlin's surface waters (2.6 ± 1.7 Gg CH₄, mean \pm SD) are similar to the CH₄ footprint of freshwaters in a tropical megacity, Mexico City (3.7 ± 4.4 Gg CH₄/year; Martinez-Cruz et al., 2017), the only other urban area where a range of surface waters was investigated to obtain an emission estimate for an entire metropolitan area.

The similar annual values for the two cities mask an important difference, however, namely a six times larger total surface area of Berlin's freshwaters compared to Mexico City, although the total land area covered by Berlin is 40% smaller. As a result, the estimated annual CH₄ footprint expressed per surface area of Berlin's freshwaters is eight times lower than in Mexico City (49 vs. 411 Mg CH₄ km⁻² year⁻¹); this number changes only marginally (i.e., by 2%) when potential emissions during the nearly 2 month period of ice cover are added to the annual estimate for Berlin. The discrepancy between the two cities points to several non-mutually exclusive factors driving emissions from urban freshwaters.

Temperature could be one of those factors, as suggested by a trend of increasing emission fluxes toward the tropics identified in a comparison of urban surface waters distributed across the globe (Table 2). However, this relationship with latitude based on data from 17 cities is rather weak (Spearman's $\rho = 0.29$) and not significant ($p = .16$). Furthermore, although the annual mean temperatures in Berlin and Mexico City reflect the location of the two cities in distinct climates, the difference of $<10^\circ\text{C}$ (9.0 and 15.9°C , respectively) cannot account for much more than a twofold, or possibly threefold, difference in microbial metabolic rates (Davidson & Janssens, 2006), even when Berlin's greater temperature variability is taken into account (e.g., Bernhardt, Sunday, Thompson, & O'Connor, 2018).

Ebullition fluxes can show stronger responses to small temperature changes than diffusive fluxes (Aben et al., 2017) but are still unlikely to fully account for the observed difference in CH₄ emissions between Berlin and Mexico City. This suggests that additional features of urban surface may have to be considered. Such features include resource availability related to human population density (10 times higher in Mexico City than in Berlin), pollution control policies (Grimm et al., 2008), and stormwater and sanitary infrastructure (Smith, Kaushal, Beaulieu, Pennino, & Welty, 2017). This conclusion is supported by the hypereutrophic conditions reported for all water bodies analyzed by Martinez-Cruz et al. (2017).

Our budget calculation is based on measurements of total flux including both diffusion and ebullition made with floating chambers. This enabled a first approximation of total annual emissions, for a large metropolitan area encompassing a wide range of different water bodies. Expanding the coverage of these measurements at different scales, both spatial (within and among water bodies) and temporal (diel to interannual), would reduce the uncertainties associated with the estimates available at present. In addition, a comparison with alternative methods can help constrain and validate these estimates. Therefore, we also computed diffusive fluxes by the commonly employed TBL approach and determined ebullitive fluxes at selected sites by deploying funnel traps for 1 week. The TBL approach makes several assumptions, particularly on piston velocities (k) depending on wind speed, which makes this method vulnerable to biases, especially in aerodynamically rough and heterogeneous urban environments. This could be one reason for several discrepancies observed between the two methods used to derive diffusive fluxes in our study (Table S3). The use of anchored rather than freely drifting chambers could also have contributed to the observed differences in running waters, mainly because unnatural water turbulence created by the chambers could unnaturally increase fluxes (Lorke et al., 2015). However, the typically slow flow of the lowland streams and ditches in Berlin makes it unlikely that this error was large. Ebullition fluxes assessed with inverted funnels deployed for 1 week produced remarkably similar results as our short-term measurements of ebullition, despite the documented high stochasticity and spatial heterogeneity of ebullition (Wik, Crill, Varner, & Bastviken, 2013). This suggests that the results of our short-term chamber measurements were broadly realistic across sites.

Although lower than in Mexico City, the calculated total annual emission per km² from Berlin's freshwaters (49 Mg CH₄ km⁻² year⁻¹) is more than twice that of the global average (22 Mg CH₄ km⁻² year⁻¹) reported by Bastviken et al. (2011) for 4.6 million km² of global freshwater surfaces. The fraction of urban areas contributing to freshwater surfaces globally is unknown, but our rates for Berlin, like those for other urban freshwaters (Table 2), were higher than both the average calculated for lakes and ponds at northern latitudes (Wik, Varner, Anthony, MacIntyre, & Bastviken, 2016) and values for streams and rivers globally (Stanley et al., 2016). This could suggest that urban areas in general contribute disproportionately to CH₄ emissions from freshwaters. Given that there are >500

TABLE 2 Methane (CH₄) emission fluxes from urban freshwaters

Climatic zone and location	Elevation (m asl)	CH ₄ flux (mg CH ₄ m ⁻² day ⁻¹)		Reference
		Total	Diffusive	
Boreal				
Lake Vesijärvi in Enonselkä, Finland	81		3.8	López Bellido et al. (2011)
Pond in Linköping, Sweden	56	128		Natchimuthu, Panneer Selvam, and Bastviken (2014)
Temperate				
Lakes in Berlin, Germany	30	159	35	This study
Lake Rotsee, Lucerne, Switzerland	419		7	Schubert et al. (2010)
Ponds in Berlin, Germany	30	503	117	This study
Open water in a wetland in Florida, USA	31	123		Morin et al. (2017)
Rivers in Berlin, Germany	30	123	20	This study
Streams in Berlin, Germany	30	118	41	This study
Small modified streams in Baltimore, USA	6		11.5	Smith et al. (2017)
Streams receiving WWTP effluents, Germany			13.3	Alshboul et al. (2016)
Modified section of the Jian River in Shunyi, Beijing, China	33	374		He, He, Wang, Li, and Wang (2018)
Dammed section of the Chaobai River in Shunyi, Beijing, China	33	2,134		He et al. (2018)
Ponds in Queensland, Australia	276	129		Grinham, Albert, et al. (2018)
Subtropical				
Nambol Turel stream in Nambol, State of Manipur, India	777	134		Khoiyangbam and Basanta Kumar (2014)
Shanghai River network, Shanghai, China	12		3.1–296	Yu et al. (2017)
Pond in Yichang, Hubei Province, Central China	60	595		Xiao et al. (2014)
Yangtze River network in Chongqing, South-west China	259		22.4	Wang et al. (2018)
Lake Donghu, Wuhan, China	10	23.3		Xing et al. (2005)
Lakes in the urban areas of States of Mexico and Michoacán, Mexico	2,080–2,840	277		Gonzalez-Valencia et al. (2014)
Lakes in Mexico City, Mexico	2,230	500		Martinez-Cruz et al. (2017)
Ponds in Mexico City, Mexico	2,230	20		Martinez-Cruz et al. (2017)
Rivers in Mexico City, Mexico	2,230	2,400		Martinez-Cruz et al. (2017)
Tropical				
Lakes in the urban areas of State of Veracruz, Mexico	464	2,819		Gonzalez-Valencia et al. (2014)

Note: Values are arithmetic means provided in or computed from data in the cited studies. Elevation based on Google Earth if not given in the publication.

urban centers worldwide with >1 million inhabitants each and that urbanization trends continue (UN, 2016), emissions of CH₄ from urban areas may be sufficiently considered in large-scale estimates. An extremely rough estimate assuming 3 Gg of CH₄ emitted annually by each of the 500 most densely populated cities in the world results in a total annual emission of 1.5 Tg CH₄, but emissions from the total urbanized area globally are evidently much larger. A related question is whether surface waters also contribute significantly to the total CH₄ footprint of metropolitan areas. Currently, the answer to this question is speculative, too, because other sources of CH₄ have not been quantified. However, a recent estimate of 20,000 Tg

of CO₂ emitted by the city of Berlin in 2012 (Reusswig, Hirschl, & Lass, 2014) suggests that even the high total CH₄ fluxes from Berlin's surface waters would contribute little to the total greenhouse gas emissions from the city, equivalent to 0.004% in CO₂ equivalents.

High variability of CH₄ emissions rates in space and time is common (Deemer et al., 2016; DelSontro, McGinnis, Sobek, Ostrovsky, & Wehrli, 2010) and also apparent in our dataset on surface waters in Berlin. Despite this high variability both within and across water bodies, PCA could differentiate between standing and flowing waters, and subsequent regression analyses identified water chemistry and the

predominant land use near each site as factors influencing CH₄ emissions (Figure 3). Ponds, in particular, were identified as hotspots of CH₄ emissions in Berlin, with the annual average emissions four times higher than from lakes, streams, and rivers (Table S3). This information is important, not least because anthropogenic ponds are neglected water bodies in terms of CH₄ emissions both in cities and other landscapes (Grinham, Albert, et al., 2018). For example, Berlin has a detailed inventory of all lakes and their water quality is regularly assessed in monitoring programs. In contrast, no systematic information is available on ponds, despite the fact that these small water bodies are increasingly recognized as important urban habitats (Hassal, 2014). Although emissions did not significantly differ when lakes and ponds were statistically treated as categories, a significant negative relationship emerged between log-transformed CH₄ emission flux and lake and pond surface area ($r^2 = .46$; $p = .01$), corroborating a previously observed pattern of increasing CH₄ flux to the atmosphere with decreasing size of water bodies (Bastviken et al., 2004; Grinham, Albert, et al., 2018; Holgerson & Raymond, 2016; Wik et al., 2016).

Nevertheless, even though ponds had high emissions, their contribution to the overall emission budget is low in comparison to lakes, which account for more than 50% of the total emission from freshwaters in Berlin (Table 1), owing to the 14 times larger total water surface area of lakes. In addition to differences in depth and shoreline development, land use adjacent to the ponds and lakes (Figure 3d) could play a role in producing this relationship, since half of the investigated lakes in Berlin are surrounded by forests. In contrast, urban ponds are mostly associated with green spaces throughout the city where they are likely to receive anthropogenic inputs resulting, for example, from feeding of waterfowl, fertilizer application, or pet waste (Hobbie et al., 2017).

The particularly high variability in emissions rates that we observed from running waters was not clearly related to riparian land cover or other characteristics. High emission rates characterized some stream sites experiencing diffuse nutrient inputs from agriculture (S3 and S6) or some highly engineered streams (paved riparian areas, channelization; S7, S2), but this was not universally true for other water bodies showing similar characteristics (S1 and S4). This inconsistency is not readily explained by toxic effects, because concentrations of a range of heavy metals and synthetic chemicals that we analyzed were mostly below detection limits in both water and sediments (S. Herrero Ortega, M.O. Gessner, G.A. Singer, & P. Casper, unpublished data). Likewise, a strong influence of WWTP was not apparent. While emissions at some sites receiving WWTP discharge (H1 and R7) were higher than at other sites, those at S5, which was also influenced by WWTP effluents, were among the lowest. This variability differs from other observations where a contribution of WWTP to CH₄ concentrations was significant (Alshboul, Encinas-Fernández, Hofmann, & Lorke, 2016; Garnier et al., 2013), and may be due to the fact that our study sites were not located directly downstream of WWTP outlets.

The relation between oxygen concentration and total CH₄ emission was also weak ($r^2 \leq .12$), although oxygen concentrations varied widely across sites (Table S4). When interpreting these data, it

must be borne in mind, however, that our measurements in surface water are not necessarily good proxies of conditions conducive to methanogenesis in sediments. Furthermore, differences in chemical characteristics and land use had little explanatory power; only their combination produced a clear relationship while substantial scatter still remained. Clearly, a multitude of factors create complex environmental conditions in urban freshwaters that make it a challenge to tease apart individual drivers of CH₄ emissions from these systems. Overall, however, the variables with the highest explanatory power in our study (i.e., POC, chl *a*, and DO) all point to trophic state as a determinant of CH₄ emissions from urban freshwaters. This is in line with results of Martinez-Cruz et al. (2017) and DelSontro, Beaulieu, and Downing (2018) and is also reflected by the conspicuous peaks in DOC and chl *a* in autumn (Figure 3; Table S4) when the emissions from ponds were highest. This result and our finding that ponds act as hotspots of CH₄ fluxes to the atmosphere are important contributions toward robust assessments of CH₄ emissions from whole cities and extrapolation to large areas, including global estimates.

ACKNOWLEDGEMENTS

We are grateful to the many students and technicians for their invaluable assistance during extensive fieldwork, especially to C.N. Stratmann, L. Meinhold, I. Ajamil, G. Idoate, L.T. Bistarelli, A. Sultan, R. Schulte, E. Tupper, T. Fuß, A. Wieland, and M. Bethke. We also thank M. Sachtleben for help and advice with material preparation and construction, A. Sepúlveda-Jauregui for advice on calculating gas fluxes, K. Pypkins for support with GIS, B. Kleinschmit for advice in sampling strategy and data analyses, A. Köhler at the Senate Administration for Environment, Transport and Climate Protection Berlin (SenUVK) for providing data on water quality, and the numerous administrative bodies and private pond owners for granting sampling permissions. This study was funded by the German Research Foundation (DFG) as part of the Research Training Group on Urban Water Interfaces (GRK 2032).

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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How to cite this article: Herrero Ortega S, Romero González-Quijano C, Casper P, Singer GA, Gessner MO. Methane emissions from contrasting urban freshwaters: Rates, drivers, and a whole-city footprint. *Glob Change Biol*. 2019;25:4234–4243. <https://doi.org/10.1111/gcb.14799>