The riverine source of CH$_4$ and N$_2$O from the Republic of Congo, western Congo Basin

Robert C. Upstill-Goddard$^1$, Matthew E. Salter$^2$, Paul J. Mann$^3$, Jonathan Barnes$^1$, John Poulson$^4$, Bienvenu Dinga$^5$, Gregory J. Fiske$^6$, and Robert M. Holmes$^6$

$^1$Oceans and Climate Research Group, School of Marine Science and Technology, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK
$^2$Department of Environmental Science and Analytical Chemistry, Stockholm University, 11418 Stockholm, Sweden
$^3$Department of Geography, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK
$^4$Nicholas School of the Environment, Duke University, P.O. Box 90328, Durham, NC, 27708, USA
$^5$Laboratoire de Physique de L’Atmosphère, Université de Marien Ngouabi, Brazzaville, B.P. 69, Republic of Congo
$^6$Woods Hole Research Center, 149 Woods Hole Road, Falmouth, MA, 02540-1644, USA

Correspondence to: Robert C. Upstill-Goddard (rob.goddard@ncl.ac.uk)

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Abstract. We discuss concentrations of dissolved CH$_4$, N$_2$O, O$_2$, NO$_3^-$ and NH$_4^+$, and emission fluxes of CH$_4$ and N$_2$O for river sites in the western Congo Basin, Republic of Congo (ROC). Savannah, swamp forest and tropical forest samples were collected from the Congo main stem and seven of its tributaries during November 2010 (41 samples; “wet season”) and August 2011 (25 samples; “dry season”; CH$_4$ and N$_2$O only). Dissolved inorganic nitrogen (DIN: NH$_4^+$ + NO$_3^-$; wet season) was dominated by NO$_3^-$ (63 ± 19 % of DIN). Total DIN concentrations (1.5–45.3 µmol L$^{-1}$) were consistent with the near absence of agricultural, domestic and industrial sources for all three land types. Dissolved O$_2$ (wet season) was mostly undersaturated in swamp forest (36 ± 29 %) and tropical forest (77 ± 36 %) rivers but predominantly supersaturated in savannah rivers (100 ± 17 %). The dissolved concentrations of CH$_4$ and N$_2$O were within the range of values reported earlier for sub-Saharan African rivers. Dissolved CH$_4$ was found to be supersaturated (11.2–9533 nmol L$^{-1}$; 440–354 444 %), whereas N$_2$O ranged from strong undersaturation to supersaturation (3.2–20.6 nmol L$^{-1}$; 47–205 %). Evidently, rivers of the ROC are persistent local sources of CH$_4$ and can be minor sources or sinks for N$_2$O. During the dry season the mean and range of CH$_4$ and N$_2$O concentrations were quite similar for the three land types. Wet and dry season mean concentrations and ranges were not significant for N$_2$O for any land type or for CH$_4$ in savannah rivers. The latter observation is consistent with seasonal buffering of river discharge by an underlying sandstone aquifer. Significantly higher wet season CH$_4$ concentrations in swamp and forest rivers suggest that CH$_4$ can be derived from floating macrophytes during flooding and/or enhanced methanogenesis in adjacent flooded soils. Swamp rivers also exhibited both low (47 %) and high (205 %) N$_2$O saturation but wet season values were overall significantly lower than in either tropical forest or savannah rivers, which were always supersaturated (103–266 %) and for which the overall means and ranges of N$_2$O were not significantly different. In swamp and forest rivers O$_2$ saturation co-varied inversely with CH$_4$ saturation (log %) and positively with % N$_2$O. A significant positive correlation between N$_2$O and O$_2$ saturation in swamp rivers was coincident with strong N$_2$O and O$_2$ undersaturation, indicating N$_2$O consumption during denitrification in the sediments. In savannah rivers persistent N$_2$O supersaturation and a negative correlation between N$_2$O and O$_2$ suggest N$_2$O production mainly by nitrification. This is consistent with a stronger correlation between N$_2$O and NH$_4^+$ than between N$_2$O and NO$_3^-$. Our ranges of values for CH$_4$ and N$_2$O emission fluxes (33–48 705 µmol CH$_4$ m$^{-2}$ d$^{-1}$; 1–67 µmol N$_2$O m$^{-2}$ d$^{-1}$) are within the ranges previously estimated for sub-Saharan African rivers but they include uncertainties deriving from our use of “basin-wide” values for CH$_4$ and N$_2$O.
gas transfer velocities. Even so, because we did not account for any contribution from ebullition, which is quite likely for CH$_4$ (at least 20%), we consider our emission fluxes for CH$_4$ to be conservative.

1 Introduction

Methane (CH$_4$) and nitrous oxide (N$_2$O) accounted for 17 and 6%, respectively, of the total atmospheric radiative forcing by well-mixed greenhouse gases in 2011 (Myhre et al., 2013). CH$_4$ also impacts tropospheric oxidising capacity, O$_3$ and OH radical and is a source of stratospheric O$_3$ (Myhre et al., 2013), while N$_2$O is the largest cause of stratospheric O$_3$ loss, via NO production (Ravishankara et al., 2009). Since the onset of the industrial revolution, tropospheric CH$_4$ and N$_2$O have substantially increased but their growth rates have varied. The early 1980s to the mid-2000s saw an overall decline in tropospheric CH$_4$ growth (Dlugokencky et al., 2009, 2011). This has been ascribed to declining fossil fuel emissions and/or variations in the OH radical sink (Rice et al., 2016; Schaefer et al., 2016), punctuated by episodic events such as the 1991–1992 Pinatubo eruption and an intense 1997–1998 El Niño (Nisbet et al., 2016). However, since 2007 increased growth has been sustained. Recent evidence from isotopic studies (Nisbet et al., 2016) and a box model (Schaefer et al., 2016) ascribes this to increased biogenic emissions, particularly in the tropics, where they have been linked to expanding tropical wetlands in response to positive rainfall anomalies (Nisbet et al., 2016), and/or growing emissions from agricultural sources (Schaefer et al., 2016). The mean CH$_4$ tropospheric dry mole fraction in 2011, 1803 ± 2 ppbv, was 150% above the pre-industrial value (Hartmann et al., 2013). Of particular note for N$_2$O, the availability of sufficiently reliable data on the anthropogenic components of river, estuary and coastal zone sources resulted in their classification being changed in the IPCC AR4 synthesis, from “natural” to “anthropogenic” (Denman et al., 2007). A small but significant seasonal to inter-annual variability in N$_2$O growth rate may reflect climate-driven changes in soil N$_2$O (Thompson et al., 2013). The current rate of N$_2$O growth is 0.73 ± 0.03 ppbv yr$^{-1}$ and its tropospheric dry mole fraction in 2011, 324 ± 0.1 ppbv, was ∼20% above its pre-industrial value (Hartmann et al., 2013).

The evidence base for freshwater ecosystems (streams, rivers, lakes, and reservoirs) as important tropospheric CH$_4$ and N$_2$O sources is small but increasing. The global freshwater CH$_4$ source could be ∼10$^{13}$–10$^{14}$ g yr$^{-1}$ (Bastviken et al., 2011; Kirschke et al., 2013; Stanley et al., 2016). This order of magnitude range largely reflects a discrepancy between “top-down” approaches based on atmospheric inversions (e.g. Kirschke et al., 2013) and “bottom-up” estimates that necessitate the upsampling of freshwater observations (e.g. Bastviken et al., 2011). For example, atmospheric constraints on top-down budgets imply that some component emissions of bottom-up approaches may be overestimates (Saunois et al., 2016). Notwithstanding this uncertainty, the global freshwater CH$_4$ source can be evaluated in the light of natural and total global CH$_4$ source estimates of 179–484 × 10$^{12}$ and 526–852 × 10$^{12}$ g yr$^{-1}$ respectively (Kirschke et al., 2013). Quantifying the global freshwater contribution thus has high inherent uncertainty but based on these estimates it could be ∼2–56% of natural CH$_4$ emissions and ∼1–19% of total CH$_4$ emissions. Converting these to CO$_2$ equivalents based on a 100-year global warming potential gives ∼0.65 × 10$^{15}$ g (CO$_2$ equivalent) yr$^{-1}$ (Bastviken et al., 2011), a significant offset to the combined terrestrial and oceanic carbon sink ∼5.5 × 10$^{15}$ g C yr$^{-1}$ (Le Quéré et al., 2015). A global estimate of river N$_2$O emissions based on microbial production from agriculturally-derived nitrogen is ∼6.8 × 10$^{11}$ g yr$^{-1}$, around 10% of the total global anthropogenic N$_2$O source, but this involved upsampling emissions from entirely within the contiguous United States (Beaulieu et al., 2011), it too must be highly uncertain.

Tropical river systems in Africa include some of the world’s largest, together contributing ∼12% of both global freshwater discharge (Valentini et al., 2014) and river surface area (Raymond et al., 2013). Borges et al. (2015b) recently reported annual emissions ∼3–4 × 10$^{12}$ g CH$_4$ and ∼10$^{10}$ g N$_2$O for 12 large river systems in sub-Saharan Africa, including the three largest by catchment area (Congo, Niger, Zambezi). Notably, their CH$_4$ estimate is 5 times higher than was previously attributed to all tropical rivers (Bastviken et al., 2011) and both estimates are significant at the continental scale given that reported total African emissions are ∼66 ± 35 × 10$^{12}$ g CH$_4$ yr$^{-1}$ and 3.3 ± 1.3 × 10$^{12}$ g N$_2$O yr$^{-1}$ (Valentini et al., 2014).

The potential scale of CH$_4$ and N$_2$O emissions from tropical freshwaters and their attendant uncertainties warrant further investigation. In this paper we present and discuss concentrations of dissolved CH$_4$, N$_2$O, O$_2$, NO$_3^-$ and NH$_4^+$, and corresponding CH$_4$ and N$_2$O emissions for river sites in savanna, swamp forest and tropical forest. Samples were collected along the Congo main stem and in seven of its tributaries in the western Congo Basin, Republic of Congo, during November 2010 and August 2011.

2 Study site and sample locations

The ∼4700 km long Congo River (Fig. 1) has an equatorial location that affords it a bimodal hydrological regime. Maximal flows are in December and May and minimal flows are in August and March (Coyne et al., 2005). The Congo Basin (9° N–14° S, 11–31° E) is the largest hydrological system in Central Africa, covering ∼3.8 × 10$^6$ km$^2$ (∼12% of the total African land mass; Fig. 1) and incorporating the world’s fourth largest wetland area ∼3.6 × 10$^5$ km$^2$ (La-
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Figure 1. Locations of river sampling stations in the Republic of Congo.

The Congo’s annual freshwater discharge is the world’s second largest at ∼1300 km$^3$ (Borges et al., 2015b), 50% of all freshwater flow from Africa to the Atlantic Ocean. Rivers and streams in the Congo Basin have a total open water surface area ∼2.7 × 10$^4$ km$^2$ (Raymond et al., 2013). The climate is warm (mean annual temperature 24.8 ± 0.8 °C) and humid with an annual rainfall ∼1800 mm (Laraque et al., 2001).

We sampled the Congo main stem, seven of its tributary rivers and some of their sub-tributaries, at sites within the Republic of Congo (ROC: area 3.4 × 10$^5$ km$^2$), in the western Congo Basin (Fig. 1). Individual catchment areas, freshwater discharge rates and rainfall are listed in Table 1. Around 50% of the ROC land area is classified as tropical forest, with the remainder classified as either swamp or savannah in approximately equal proportion (Clark and Decalo, 2012). Sampling sites were selected to represent each of these three land cover types (Fig. 1), which were georeferenced to the World Geodetic System 1984 (WGS84) and intersected with the highest level sub-watershed polygons defined by the HYDRO1K global hydrological data set (US Geological Survey, 2000). This enabled assigning the fractional cover for each land cover type, and hence the dominant land cover type, to the areas immediately surrounding each sampling location. Swamp includes both temporally and permanently inundated areas of “forest”, with vegetation adapted to poorly drained, anaerobic soils (Mayaux et al., 2002). For all three land cover types the mean annual temperature range (period 1990–2012) is ∼1–3 °C. Temperatures are lowest (∼22–24 °C) in July–August and highest (∼25–26 °C) in March–April (http://sdwebx.worldbank.org/climateportal/). For savannah the average monthly rainfall during July–May (1990–2012) is ∼120–260 mm, typically being maximal in October–November, but < 40 mm falls during June–August (http://sdwebx.worldbank.org/climateportal/). For forest and swamp the annual range in monthly rainfall is less pronounced. Both have two discernable rainfall maxima, during April–May and October–November (∼150–240 mm month$^{-1}$), and a minimum in June–August (∼40–120 mm month$^{-1}$) (http://sdwebx.worldbank.org/climateportal/).

ROC swamp and forest (Fig. 1) broadly correspond to the westernmost part of the “Cuvette Centrale” (Central Basin). This is a large shallow depression composed mainly of dense, humid forest and extending from approximately 15–25° W and 5° N–4° S. Its central western part remains flooded throughout the rainy seasons. Rivers sampled in this region (Sangha, Likouala-aux-Herbes, Likouala, Lengoue, Mambili: Fig. 1, Table 1) drain predominantly sandy or clayey quaternary deposits. The Kouyou Basin (Fig. 1) borders the “Batéké Plateaux”, a 600–700 m relief sandstone formation to the south, intersected by dry valleys and covering much of the southern ROC. Here, bushy savannah is intersected by the Alima, Nkéni and Léfini rivers. Due to water storage in an underlying sandstone aquifer the hydrological regimes of these three rivers are largely independent of rainfall; they all show only weak seasonality in discharge de-
Table 1. Relevant physical characteristics of rivers studied in this work. All rainfall data are from Laraque et al. (2001), Djoue catchment area and discharge data are from Laraque et al. (1994) and all other data are from Laraque et al. (2009).

<table>
<thead>
<tr>
<th>River/tributary</th>
<th>Catchment area $\text{km}^2$</th>
<th>Discharge $\text{m}^3\text{s}^{-1}$</th>
<th>Rainfall $\text{mm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Congo</td>
<td>3 500 000</td>
<td>40 600</td>
<td>1528</td>
</tr>
<tr>
<td>Alima</td>
<td>21 030</td>
<td>1941</td>
<td>1709</td>
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<tr>
<td>NkÈni</td>
<td>8000</td>
<td>261</td>
<td>1662</td>
</tr>
<tr>
<td>Léfini</td>
<td>14 000</td>
<td>400</td>
<td>1615</td>
</tr>
<tr>
<td>Djoue</td>
<td>5740</td>
<td>140</td>
<td>1547</td>
</tr>
<tr>
<td>Likouala-aux-Herbes</td>
<td>25 000</td>
<td>267</td>
<td>1622</td>
</tr>
<tr>
<td>Sangha</td>
<td>211 120</td>
<td>1941</td>
<td>1511</td>
</tr>
<tr>
<td>Likouala Mossaka</td>
<td>69 800</td>
<td>928</td>
<td>1689</td>
</tr>
<tr>
<td>Kouyou</td>
<td>16 000</td>
<td>191</td>
<td>1566</td>
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<tr>
<td>Lengou</td>
<td>12 125</td>
<td>155</td>
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</tr>
<tr>
<td>Mambili</td>
<td>13 700</td>
<td>161</td>
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<tr>
<td>Motaba</td>
<td>772 800</td>
<td>4000</td>
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</tbody>
</table>

Despite the relatively large variation in monthly precipitation (Laraque et al., 2001).

3 Sample collection and analytical techniques

Surface water samples (~0.3 m) were collected from central river channels using a standard “niskin”-type water sampler (http://www.tresanton.co.uk/standard.html). We obtained 66 samples for dissolved CH$_4$, N$_2$O, O$_2$, NO$_3^-$ and NH$_4^+$ analysis, during November 2010 (41 samples) and August 2011 (25 samples; CH$_4$ and N$_2$O only). Based on the monthly rainfall distribution, for convenience we hereinafter refer to these as “wet season” and “dry season” respectively. Samples were slowly decanted into a series of 125 mL glass screw-top septum bottles (Sigma-Aldrich, UK) via a silicon rubber tube. Each was over filled by at least one sample volume to avoid bubble entrainment. Samples were poisoned with 25 µL of 0.1 M HgCl$_2$ to arrest microbial activity and sealed to leave no headspace. They were subsequently returned to Newcastle for dissolved gas analysis within several weeks of collection. Dissolved gas samples treated in this way can be successfully stored for several months (Elkins, 1980).

Dissolved CH$_4$ and N$_2$O were analysed by single-phase equilibration gas chromatography (Shimadzu GC 14-B), with flame ionisation detection of CH$_4$ and electron capture detection of N$_2$O (Upstill-Goddard et al., 1996). Routine calibration was with a mixed secondary standard (361 ppbv N$_2$O, 2000 ppbv CH$_4$) prepared by pressure dilution with ultra-high purity N$_2$ (Upstill-Goddard et al., 1990). Absolute calibration was against a mixed primary standard (10 ppbv N$_2$O, 5 ppmv CH$_4$) with a certified accuracy of ±1 % (BOC Special Gases, UK). Overall analytical precisions (1σ) for N$_2$O and CH$_4$, established via multiple analysis ($n = 15$) of the secondary standard, were both ±1 %.

Temperature, dissolved O$_2$ and atmospheric pressure were measured in situ using a handheld multi-parameter probe (YSI Pro-Plus: https://www.ysi.com/). Quoted measurement accuracies are ±0.2°C, ±2 % dissolved O$_2$, and ±0.002 bar. Samples for dissolved NH$_4^+$ and NO$_3^-$ were filtered on collection (Whatman 0.7 µm GF/F; precombusted at 550°C for 8 h), directly into clean glass vials and stored acidified (pH 2) at 4°C in the dark for several weeks. Subsequent analysis, at Woods Hole, was by segmented flow (Astoria Analyzer; Astoria-Pacific, USA) using established methods (US Environmental Protection Agency, 1984). Analytical precisions (1σ) were ±1 % for both. Technical and logistical issues precluded the collection of any dissolved O$_2$, NH$_4^+$ or NO$_3^-$ data during August 2011 (dry season) and some NO$_3^-$ and NH$_4^+$ data during November 2010 (wet season).

Emission fluxes, $F$ (mol m$^{-2}$ d$^{-1}$), of CH$_4$ and N$_2$O were estimated using $F = k_w L \Delta p$, where $k_w$ is the transfer velocity of CH$_4$ or N$_2$O (cm hr$^{-1}$), $L$ is the solubility of CH$_4$ or N$_2$O (mol cm$^{-3}$ atm$^{-1}$) (Wiesenburg and Guinasso, 1979; Weiss and Price, 1980) and $\Delta p$ is the corresponding water-to-air partial pressure difference. $k_w$ values were derived from two corresponding estimates for CO$_2$ in the Congo. Raymond et al. (2013) estimated a basin-wide $k_w$ of 5.2 m d$^{-1}$ for CO$_2$, using hydraulic equations involving basin slope and flow velocity. The uncertainty in this estimate is ±10 % (Raymond et al., 2013). Aufdenkampe et al. (2011) applied constant $k_w$ values for CO$_2$ in streams (<100 m wide: 3.0 m d$^{-1}$) and in rivers (>100 m wide: 4.2 m d$^{-1}$). Adjusting for the relative areas of these in the Congo Basin (Borges et al., 2015b) gives a basin-wide mean $k_w$ of 3.9 m d$^{-1}$ for CO$_2$. We converted these estimates to $k_w$ for CH$_4$ and N$_2$O by multiplying by $(Sc/470.7)^{-0.5}$, where 470.7 is the Schmidt number of CO$_2$ in freshwater, and $Sc$ is the Schmidt number of CH$_4$ or N$_2$O ($Sc_{CH_4} = 486.8$; $Sc_{N_2O} = 476.9$), assuming an ambient temperature of 25°C (Wanninkhof, 1992). The resulting $k_w$ estimates are 5.1 and 3.9 m d$^{-1}$ for CH$_4$ and 5.2 and 4.0 m d$^{-1}$ for N$_2$O. Resulting emissions estimates are consequently ~30 % higher based on Raymond et al. (2013). Using both sets of $k_w$ estimates enables direct comparison with the largest study of CH$_4$ and N$_2$O fluxes for African rivers that also used this approach (Borges et al., 2015b). While other relevant work used wind-speed-based $k_w$ estimates (Koné et al., 2010; Bouillon et al., 2012) the unavailability of wind speeds precludes their use here. We applied the global mean mixing ratios of CH$_4$ (1797 ppbv) and N$_2$O (323 ppbv) for the year 2010 (http://cdiac.esd.orl.gov/tracegases.html).

4 Results

While CH$_4$ and N$_2$O data are available for all samples, dry season data are not available for dissolved O$_2$, NO$_3^-$ or NH$_4^+$. Wet season DIN (NO$_3^-$ + NH$_4^+$) is only reported for samples.

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Figure 2. (a) Log percent dissolved methane saturation vs. percent dissolved O$_2$ saturation and (b) percent dissolved nitrous oxide saturation vs. percent dissolved O$_2$ saturation for rivers of the Republic of Congo during the wet season: open circles, savannah rivers; filled black circles, swamp forest rivers; filled grey circles, tropical forest rivers.

4.1 Dissolved O$_2$ and DIN

In wet season swamp samples dissolved O$_2$ varied between mildly undersaturated and very strongly undersaturated (Fig. 2). The mean (36 ± 29 %) and range (4–91 %) of O$_2$ saturation were both significantly lower than for both forest rivers (Mann–Whitney, one-tailed; $P = 0.0001$) and savannah rivers (Mann–Whitney, one-tailed; $P = 0.002$). Most forest rivers were mildly to strongly O$_2$ undersaturated (mean 77 ± 36 %, range 14–116 %; Fig. 2) and savannah rivers were predominantly mildly undersaturated to mildly supersaturated (mean 100 ± 17 %, range 70–135 %; Fig. 2).

Low wet season concentrations of dissolved inorganic nitrogen (DIN) components (Fig. 3) are consistent with agricultural, domestic and industrial DIN sources all being negligible (Clark and Decalo, 2012). The means and ranges of total DIN (NO$_3^-$ + NH$_4^+$) did not differ significantly between any of the three river “types” (mean savannah 6.8 ± 2.8 µmol L$^{-1}$; range 2.5–10.1 µmol L$^{-1}$; $n = 10$; mean swamp 5.1 ± 3.1 µmol L$^{-1}$, range 1.5–10.2 µmol L$^{-1}$; $n = 11$; mean forest 9.4 ± 11.2 µmol L$^{-1}$, range 1.8–45.3 µmol L$^{-1}$; $n=12$), in contrast to the situation for dissolved O$_2$. Differences in NO$_3^-$-N were also not significant (mean savannah 4.1 ± 2.3 µmol L$^{-1}$, range 0.8–6.7 µmol L$^{-1}$, $n = 11$; mean swamp 3.6 ± 2.1 µmol L$^{-1}$, range 1.0–8.8 µmol L$^{-1}$, $n = 16$; mean forest 7.1 ± 9.2 µmol L$^{-1}$, range 1.2–35.1 µmol L$^{-1}$; $n = 12$). There was no clear relationship between NO$_3^-$ and NH$_4^+$ for any of the three river types (Fig. 3a). NO$_3^-$ was the dominant DIN component in 24 of the 33 samples for which both NO$_3^-$ and NH$_4^+$ were analysed. Considering all samples, the mean NO$_3^-$ contribution to DIN was 63 ± 19 %.

4.2 Dissolved CH$_4$ and N$_2$O

Table 2 summarises ranges, means and medians of riverine CH$_4$ and N$_2$O concentrations and percent saturations for the three land cover types. All samples were highly CH$_4$ supersaturated, concentrations spanning two orders of magnitude (11.2–9553 nmol L$^{-1}$; 440–354 400 % saturation). N$_2$O spanned a much narrower concentration range and varied from strong undersaturation to strong supersaturation (3.2–20.6 nmol L$^{-1}$; 47–205 %). Evidently, while rivers of the ROC are strong local sources of tropospheric CH$_4$ they can

Figure 3. (a) Dissolved nitrate vs. dissolved ammonium and (b) percent nitrous oxide saturation vs. DIN (NO$_3^-$ + NH$_4^+$) for rivers of the Republic of Congo during the wet season: open circles, savannah rivers; filled black circles, swamp forest rivers; filled grey circles, tropical forest rivers.
act as both small sources and sinks for \( \text{N}_2\text{O} \). Swamp rivers exhibited both the lowest and among the highest \( \text{N}_2\text{O} \) saturations (Table 2) but during the wet season had overall significantly lower \( \text{N}_2\text{O} \) than either forest or savannah rivers. These were always supersaturated (103–266 %; Table 2) and their overall means and ranges of \( \text{N}_2\text{O} \) were not significantly different (Mann–Whitney, one-tailed: swamp vs. forest and swamp vs. savannah, \( P = 0.004 \)). For \( \text{CH}_4 \), concentration means and ranges during the wet season did not differ significantly between swamp and forest rivers but they were significantly higher in both than in savannah rivers (Mann–Whitney, one-tailed: swamp vs. forest, \( P = 0.004 \); forest vs. savannah, \( P = 0.03 \)). In contrast, during the dry season concentration means and ranges of both \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) were indistinguishable for all three land cover types. Seasonal differences in concentration means and ranges were not significant for \( \text{N}_2\text{O} \) for any of the three land cover types or for \( \text{CH}_4 \) in savannah rivers. In both swamp and forest rivers \( \text{CH}_4 \) was significantly higher during the wet season (Mann–Whitney, one-tailed: swamp \( P = 0.01 \); forest \( P = 0.003 \)).

There are comparatively few measurements of \( \text{CH}_4 \) concentrations in African rivers and even fewer of \( \text{N}_2\text{O} \). Our \( \text{CH}_4 \) data for rivers of the ROC (Table 2) are within the ranges compiled for temperate and tropical rivers (\( \sim 260–128 \, 000 \) %) (Upstill-Goddard et al., 2000; Middelburg et al., 2002). Moreover, our \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) data both fall within the ranges recently reported for other rivers in sub-Saharan Africa. Studies of \( \text{CH}_4 \) alone reported 48–870 nmol L\(^{-1} \) (2221–38 719 % saturation) in three Ivory Coast rivers (Koné et al., 2010), 25–505 nmol L\(^{-1} \) (850–21 700 % saturation) in the Tana River, Kenya (Bouillon et al., 2009), and 22–71 430 nmol L\(^{-1} \) in the Congo (Borges et al., 2015a). For concurrent measurements of \( \text{CH}_4 \) and \( \text{N}_2\text{O} \) Bouillon et al. (2012) report 74–280 nmol CH\(_4\) L\(^{-1} \) (3450–13 200 % saturation) and 6.2–9.6 nmol N\(_2\text{O} \) L\(^{-1} \) (112–165 % saturation) in the Oubangui, a major Congo tributary. Teodoru et al. (2015) found 7–12 127 nmol CH\(_4\) L\(^{-1} \) and 2.0–11.4 nmol N\(_2\text{O} \) L\(^{-1} \) at stations along the Zambezi. Borges et al. (2015b) quote a range of 2–62 966 nmol CH\(_4\) L\(^{-1} \) (mean: 2205 nmol L\(^{-1} \)) and 0.2–85.4 nmol N\(_2\text{O} \) L\(^{-1} \) (mean: 9.2 nmol L\(^{-1} \)) across 12 sub-Saharan river basins, including those of the Congo, Zambezi and Niger.

Considering the complete data set, \( \text{CH}_4 \) was inversely correlated with both N\(_2\text{O} \) and O\(_2 \) (Fig. 2). Highest \( \text{CH}_4 \) coincident with lowest N\(_2\text{O} \) and O\(_2 \) occurred in swamp rivers. Lowest \( \text{CH}_4 \) coincident with highest N\(_2\text{O} \) and O\(_2 \) was observed in forest rivers. Savannah rivers were intermediate between the two (Fig. 2). Overall, log % \( \text{CH}_4 \) vs. % O\(_2 \) showed a weak negative correlation (Fig. 2a: \( R^2 = 0.26 \), \( n = 41 \)) while % N\(_2\text{O} \) vs. % O\(_2 \) showed a weak positive correlation (Fig. 2b: \( R^2 = 0.30 \), \( n = 41 \)). However, for both swamp and forest rivers individually the negative correlations between log % \( \text{CH}_4 \) and % O\(_2 \) were stronger (swamp \( R^2 = 0.38 \), \( n = 16 \); forest \( R^2 = 0.45 \), \( n = 13 \)). While there was a stronger positive correlation between % N\(_2\text{O} \) and % O\(_2 \) for swamp
rivers than for the complete data set \((R^2 = 0.71, n = 16)\), the correlation for forest rivers was extremely weak \((R^2 = 0.02, n = 13)\). For savannah rivers we found a positive correlation between \(\log \% CH_4\) and \(\% O_2\) \((R^2 = 0.23; n = 12)\) and a negative correlation between \(\% N_2O\) and \(\% O_2\) \((R^2 = 0.35, n = 12)\). \(N_2O\) co-varied positively with both \(NO_3^-\) and \(NH_4^+\) (Fig. 3). For the complete data set the correlations were weak \((N_2O\ vs. \ NO_3^-, R^2 = 0.28, n = 59; N_2O\ vs. \ NH_4^+, R^2 = 0.23, n = 40)\). For all three river types individually, with the exception of \(N_2O\ vs. \ NH_4^+\) in savannah rivers, the correlations were stronger, and for all rivers \(NO_3^-\) was a stronger predictor of \(N_2O\) \((N_2O\ vs. \ NO_3^-, R^2 = 0.50, n = 29; R^2\ forest = 0.75, n = 15; R^2\ swamp = 0.31, n = 15\) than was \(NH_4^+\) \((N_2O\ vs. \ NH_4^+, R^2 = 0.29, n = 13; R^2\ forest = 0.47, n = 13; R^2\ swamp = 0.01, n = 14)\).

### 4.3 CH4 and N2O emission fluxes

Table 3 summarises ranges, means and medians of CH4 and N2O emission fluxes using \(k_{\text{d}}\) derived from Raymond et al. (2013) and Aufdenkampe et al. (2011). Fluxes broadly followed the distribution of concentrations. CH4 fluxes were lowest overall in savannah rivers and highest in swamp and forest rivers. N2O fluxes were lowest in swamp rivers and highest in savannah and forest rivers. Fluxes were always to air at all sites for CH4 and at all savannah and forest sites for N2O. However, swamp rivers were predominantly a N2O sink during the wet season (11 of 16 individual flux estimates) and predominantly a N2O source during the dry season (10 of 16 individual flux estimates). As far as we are aware the wet season sink for N2O in swamp rivers is the first such reported for African rivers.

### 5 Discussion

#### 5.1 Sources of CH4 and N2O

The concentrations of dissolved CH4 and N2O at any specified river location reflect a dynamic and complex balance. This involves in situ production and consumption impacted by import and export mechanisms that include upstream and downstream advection, groundwater inputs, local surface runoff and water-air exchange.

While dissolved \(O_2\) was undersaturated in the majority of samples, being as low as 4 % in one wet season swamp sample, it was always detectable and indeed was supersaturated in several savannah river samples in which CH4 saturations ranged from \(~4000\ to 10\,000\%\) (Fig. 2a). Notwithstanding that methanogenesis is an exclusively anoxic process carried out by severely \(O_2\)-limited archaea (Bridgham et al., 2013), the existence of high CH4 concentrations in oxygenated rivers is well known (e.g. Richey et al., 1988). It is a consequence of the diffusion of CH4 produced in underlying river sediments, in adjacent floodplain soils and in adjacent...
wetlands, into aerated river water. Previous work showed that the CH$_4$ supply from groundwater to African rivers is generally comparatively low (Balagizi et al., 2015; Borges et al., 2015b). The spatial distribution of dissolved CH$_4$ is more closely related to the wetland distribution within the catchment, wetland water deriving principally from upland runoff (Borges et al., 2015a). In the Congo Basin floating macrophytes, both in the centre of river channels and fringing their edges, are important additional sources of CH$_4$ (Borges et al., 2015a). These sources promote a unidirectional CH$_4$ flow, towards small and large river channels (Borges et al., 2015a). Where these river channels are shallow and have low levels of surface turbulence, as in the examples studied here, the CH$_4$ diffusion term evidently exceeds combined CH$_4$ losses via oxidation and water-to-air exchange. This further promotes the accumulation of high river CH$_4$ concentrations.

In addition to methanogenesis in fully anoxic sediment and soils, CH$_4$ production can also occur in “anoxic microsites” within oxic soils (e.g. Teh et al., 2005; von Fisher and Hedin, 2007). Indeed, methanogens are now considered to be widespread in oxic soils and they are activated during flooding (Bridgham et al., 2013). Their activity relates to soil carbon age and composition (Bridgham et al., 1998; Chanton et al., 2008) and likely involves substrate competition and other interactions. Production by soil macrofauna (Kammann et al., 2009), archeal production related to plant productivity (Updegraff et al., 2001; Dorodnikov et al., 2011) and non-microbial, direct aerobic production, both by living plant tissue (Keppler et al., 2006, 2009) and in soils (Harkuc et al., 2012), have all also been observed. Although methanogenesis by photosynthetic-attached archaea has been detected in oxic lake water (Grossart et al., 2011) this is unlikely in tributaries and wetlands of the Congo, where phytoplankton abundance is low (Descy et al., 2016). Additional to this variability in production mechanisms and rates, CH$_4$ is subject to variable and rapid aerobic and anaerobic microbial oxidation (Megenigal et al., 2004). Oxidative CH$_4$ loss rates have been variously estimated at between a few percent and > 100 % of the rate of methanogenesis (Bussmann, 2013; Shelley et al., 2015). Despite such potentially high losses, water to air exchange by ebullition and by turbulent diffusion driven by wind stress, water depth and flow velocity (Raymond and Cole, 2001) is usually considered the major CH$_4$ loss term, with ebullition frequently considered the dominant of these two mechanisms (Stanley et al., 2016). Despite this complexity of dissolved CH$_4$ cycling in rivers, it is nevertheless informative to speculate on our principal observations in the context of potential CH$_4$ sources and sinks.

The first notable feature of our results is the contrasting relationship between CH$_4$ and O$_2$ in swamp and forest rivers (negative) and in savannah rivers (positive) (Fig. 2a). Dissolved O$_2$ in rivers is primarily driven by the balance of photosynthesis and respiration (Houser et al., 2015). It may be additionally impacted by varying contributions from water-air exchange that under conditions of extreme turbulence may lead to supersaturations as high as 150 % (Li et al., 2010). The overall positive relationship between CH$_4$ and O$_2$ in savannah rivers (Fig. 2a) could, at least in part, reflect high macrophyte-related productivity. This can give rise to positive relationships by direct CH$_4$ production (Stanley et al., 2016) and by indirect production via the trapping of fine-grained organic sediments that support methanogenesis (Sanders et al., 2007). Similar relationships were observed in Amazon floodplain lakes (Devol et al., 1990). Offsetting this, stems and roots respire O$_2$ (Caraco et al., 2006). Further inspection of the data shows that the highest dissolved O$_2$ saturation found in savannah rivers (134 %) deviates from the general CH$_4$ vs. O$_2$ trend (Fig. 2a). This sample was collected close to an area of rapids in the Congo main stem, in the vicinity of Pool Malebo (formerly known as Stanley Pool) (Fig. 1) where other samples were also O$_2$ supersaturated. Intense water–air exchange in this region via increased turbulence would tend to enhance dissolved O$_2$ (Li et al., 2010) while depleting dissolved CH$_4$. To summarise, notwithstanding possible additional CH$_4$ losses via oxidation, the CH$_4$ vs. O$_2$ relationship in savannah rivers (Fig. 2a) could be explained by net macrophyte production imprinted by water–air gas exchange. The inverse of this relationship for swamp and forest rivers (Fig. 2a) was similarly reported for the Zambezi and Amazon basins, for the latter in fast flowing waters (Teodoru et al., 2015; Richey et al., 1988; Devol et al., 1990). Again, high gas exchange rates are plausible, especially for the small number of tropical forest samples for which O$_2$ was close to or in excess of 100 % (Fig. 2a). For the majority of samples that were O$_2$ undersaturated, however, additional mechanisms must be invoked. One possibility is that these distributions largely reflect the mixing of relatively well-oxygenated river waters with high-CH$_4$, low-O$_2$ groundwater but another possibility is that this relationship is the aggregate of this and several of the other processes previously discussed.

A second important aspect of the overall CH$_4$ distributions is that swamp and forest river CH$_4$ was highest during the wet season, whereas savannah samples revealed no such inter-seasonal contrast (Table 2). The constancy of CH$_4$ in savannah rivers might well reflect the buffering of seasonal river discharge by the sandstone aquifer that underlies this region (Laraque et al., 2001). For swamp and forest rivers a number of alternative but not mutually exclusive possibilities might be invoked. In addition to direct and indirect macrophyte production (Stanley et al., 2016; Sanders et al., 2007), as discussed for savannah rivers, methanogenesis following the activation of archaea during flooding of adjacent soils (Bridgham et al., 2013) is also plausible. This is supported by the observation that swamp and forest soils are comparatively poorly drained (Mayaux et al., 2002). In contrast, an opposing behaviour was reported for three rivers of the Ivory Coast (Comoé, Bia, Tanoe). In these, overall decreases in CH$_4$ during the dry to wet season transition (Koné et al., 2010) were similar to trends recorded in some temperate (Eu-
Table 4. Emissions of CH₄ and N₂O published for African rivers: (A) refers to emissions estimated using the relationship of Aufdenkampe et al. (2011) and (R) refers to emissions estimated using the relationship of Raymond et al. (2013).

<table>
<thead>
<tr>
<th>River</th>
<th>CH₄ emission flux (µmol m⁻² d⁻¹)</th>
<th>N₂O emission flux (µmol m⁻² d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>Conoé, Ivory Coast</td>
<td>288 ± 107</td>
<td>15 (A)</td>
</tr>
<tr>
<td>Bia, Ivory Coast</td>
<td>155 ± 38</td>
<td>19 (R)</td>
</tr>
<tr>
<td>Tanoé, Ivory Coast</td>
<td>241 ± 91</td>
<td>0.6–5.7</td>
</tr>
<tr>
<td>Ivory Coast (all)</td>
<td>25–1187</td>
<td></td>
</tr>
<tr>
<td>Oubangui</td>
<td>38–350</td>
<td></td>
</tr>
<tr>
<td>Congo</td>
<td>14 296</td>
<td>15 (A)</td>
</tr>
<tr>
<td></td>
<td>18 534</td>
<td>19 (R)</td>
</tr>
<tr>
<td>Ivory Coast</td>
<td>1003</td>
<td>(A)</td>
</tr>
<tr>
<td></td>
<td>1667</td>
<td>(R)</td>
</tr>
<tr>
<td>Ogooué</td>
<td>2115</td>
<td>13 (A)</td>
</tr>
<tr>
<td>Niger</td>
<td>4668</td>
<td>28 (R)</td>
</tr>
<tr>
<td>Zambezi</td>
<td>502</td>
<td>4 (A)</td>
</tr>
<tr>
<td></td>
<td>583</td>
<td>5 (R)</td>
</tr>
<tr>
<td>Betsiboka</td>
<td>8348</td>
<td>2 (A)</td>
</tr>
<tr>
<td></td>
<td>13 597</td>
<td>2 (R)</td>
</tr>
<tr>
<td>Rianala</td>
<td>1305</td>
<td>4 (A)</td>
</tr>
<tr>
<td></td>
<td>3493</td>
<td>9 (R)</td>
</tr>
<tr>
<td>Tana</td>
<td>1923</td>
<td>5 (A)</td>
</tr>
<tr>
<td></td>
<td>4537</td>
<td>12 (R)</td>
</tr>
<tr>
<td>Athi-Galana-Sabaki</td>
<td>568</td>
<td>6 (A)</td>
</tr>
<tr>
<td></td>
<td>604</td>
<td>6 (R)</td>
</tr>
<tr>
<td>Nyong</td>
<td>1156</td>
<td>16 (A)</td>
</tr>
<tr>
<td></td>
<td>1374</td>
<td>19 (R)</td>
</tr>
<tr>
<td></td>
<td>18019</td>
<td>(A)</td>
</tr>
<tr>
<td></td>
<td>28 579</td>
<td>(R)</td>
</tr>
</tbody>
</table>

European) rivers (Middelburg et al., 2002). Koné et al. (2010) ascribed the CH₄ seasonality in Ivory Coast rivers to a combination of the dilution of high-CH₄ baseflow by low-CH₄ surface runoff (e.g. Jones and Mulholland, 1998a, b), higher degassing rates during flooding (Hope et al., 2001) and/or decreased in-stream methanogenesis towards high discharge (De Angelis and Scranton, 1993). Conversely, Bouillon et al. (2012) attributed relatively stable high-discharge CH₄ concentrations (∼100 nmol L⁻¹) in the Oubangui, a major tributary of the Congo, to terrestrial soil production in conjunction with baseflow transport. The largest fractional CH₄ contribution from baseflow often occurs in high elevation headwaters with high soil organic content, while progressive downstream increases in CH₄ in lowland rivers have been linked to increasing in-stream methanogenesis (Jones and Mulholland, 1998a). Assuming such processes are also operative in ROC swamp and tropical forest, interpreting or predicting the direction of any seasonal CH₄ trend in a specified river system is evidently complex.

In contrast to CH₄, natural sources of aquatic N₂O are entirely microbial, and involve several pathways. Nitrification is a two-stage process in which NH₄⁺ is first oxidised aerobically to NO₂⁻ via hydroxylamine (NH₂OH), followed by NO₂⁻ oxidation to NO₃⁻. Following the first stage, N₂O can be produced through various routes: nitrifier nitrification (NH₂OH → N₂O), nitrifier denitrification (NO₂⁻ → NO → N₂O) and nitrification-coupled denitrification (NO₃⁻ → NO₂⁻ → NO → N₂O) (Kool et al., 2011). Heterotrophic denitrification, in which NO₃⁻ is the terminal electron acceptor (NO₃⁻ → NO₂⁻ → NO + N₂O → N₂), occurs in soils, sediments and waters that are anoxic, the inhibition of denitrifier activity at very low levels of dissolved O₂ being well known (Knowles, 1982). Even so, in the complete absence of O₂, N₂O can be enzymatically reduced to gaseous N₂ (Wrage et al., 2001), both in sediments and in the water column, sometimes resulting in extreme N₂O undersaturations (Nirmal Rajkumar et al., 2008).

Although we found no statistically significant differences in the means and ranges of wet or dry season N₂O concentrations for any land cover type, higher N₂O concentrations and emissions are considered likely where soil-water-filled pore spaces exceed 60% due to enhanced microbial production (Davidson, 1993). This has been observed in African savannah during the rainy season (Castaldi et al., 2001) and throughout much of the year in humid tropical forests.
The discrepancy between these and our observations to some extent likely reflects a complex balance between the principal sites (groundwater and in-stream) and mechanisms of N\textsubscript{2}O cycling, as evidenced by the variable relationships between N\textsubscript{2}O, O\textsubscript{2} and DIN we observed. For example, we found both positive and negative relationships between N\textsubscript{2}O and O\textsubscript{2} (Fig. 2b). Sediment processes and water concentrations are evidently closely coupled in tropical catchments (Harrison and Matson, 2003). A strong positive correlation between N\textsubscript{2}O and O\textsubscript{2} in swamp rivers coincident with strong undersaturation of both N\textsubscript{2}O and O\textsubscript{2} (Fig. 2b) is consistent with N\textsubscript{2}O consumption by sediment denitrification. Positive relationships between N\textsubscript{2}O and NO\textsubscript{3} have been variously interpreted to reflect nitrification (Silvennoinen et al., 2008; Beaulieu et al., 2010), or both denitrification and nitrification (Baulch et al., 2011). Even so, for swamp rivers the stronger correlation between N\textsubscript{2}O and NO\textsubscript{3} than between N\textsubscript{2}O and NH\textsubscript{4}\textsuperscript{+}, which is often taken to indicate a sediment denitrification N\textsubscript{2}O source (Dong et al., 2004), supports our conclusion of a swamp river denitrification sink for N\textsubscript{2}O. Similar N\textsubscript{2}O vs. O\textsubscript{2} relationships were identified in the Amazon and Zambezi river basins (Richey et al., 1988; Teodoru et al., 2015) and in the Adyar river estuary, southeastern India (Nirmal Rajkumar et al., 2008). In both the Amazon and the Adyar, N\textsubscript{2}O was undetectable in fully anoxic waters (Richey et al., 1998; Nirmal Rajkumar et al., 2008). N\textsubscript{2}O and NO\textsubscript{3} were also correlated in the Oubangui (Bouillon et al., 2012) and in several other African rivers (Borges et al., 2015b). A similar, persistent correlation in a temperate river was ascribed to denitrification in hypoxic/anoxic sediment, favoured by the ambient low river flow and high temperatures leading to high community respiration and low O\textsubscript{2} solubility (Rosamond et al., 2012). Even though denitrification in rivers may be limited by low levels of NO\textsubscript{3} (Garcia-Ruiz et al., 1998) a temperate creek was a N\textsubscript{2}O sink for combined NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-} concentrations < 2.7 µmol L\textsuperscript{-1} (Baulch et al., 2011), broadly similar to the majority of NO\textsubscript{3}\textsuperscript{-} concentrations we observed (Fig. 3a). By contrast, N\textsubscript{2}O and NO\textsubscript{3}\textsuperscript{-} were uncorrelated in the Zambezi, for which there was also no correlation of N\textsubscript{2}O with NH\textsubscript{4}\textsuperscript{+} (Teodoru et al., 2015). For savannah rivers, in which N\textsubscript{2}O was always supersaturated (Fig. 2b), a negative correlation between N\textsubscript{2}O and O\textsubscript{2} may indicate N\textsubscript{2}O production mainly by nitrification. This is supported by the corresponding stronger correlation between N\textsubscript{2}O and NH\textsubscript{4}\textsuperscript{+} than between N\textsubscript{2}O and NO\textsubscript{3}\textsuperscript{-}, the opposite to what we found for swamp rivers. Although published measurements of N\textsubscript{2}O production via in-stream nitrification are lacking, nitrification rates may frequently exceed denitrification rates in streams and rivers (Richardson et al., 2004; Arango et al., 2008) and nitrification rates are estimated to exceed denitrification rates 2-fold globally (Mosier et al., 1998). In addition to O\textsubscript{2} and DIN amount and speciation, pH and dissolved organic carbon are important in controlling net N\textsubscript{2}O production via nitrification and denitrification (Baulch et al., 2011).

It has been suggested that, due to variable N\textsubscript{2}O yields from these processes, simple diagnostic relationships for N\textsubscript{2}O production in rivers may prove elusive (Beaulieu et al., 2008).

In summary, our data have allowed us to draw some conclusions regarding the production and cycling of CH\textsubscript{4} and N\textsubscript{2}O in contrasting rivers of the ROC. However, for both gases an unequivocal identification of the primary controls of their riverine distributions would require additional detailed measurements.

### 5.2 CH\textsubscript{4} and N\textsubscript{2}O emissions in the wider context

As with the concentration measurements, there are few data for African rivers with which to compare our CH\textsubscript{4} and N\textsubscript{2}O emissions estimates (Table 3). Previously published emissions estimates are listed in Table 4. For three rivers of the Ivory Coast Koné et al. (2010) reported 25 to 1187 µmol CH\textsubscript{4} m\textsuperscript{-2} d\textsuperscript{-1}, while for the Oubangui Bouillon et al. (2012) found 38 to 350 µmol CH\textsubscript{4} m\textsuperscript{-2} d\textsuperscript{-1} and 0.6 to 5.7 µmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1}. For 12 sub-Saharan African rivers Borges et al. (2015b) give ranges of 0 to 274 600 mmol CH\textsubscript{4} m\textsuperscript{-2} d\textsuperscript{-1} and –30 to 299 mmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1} using \( k_w \) from Aufdenkampe et al. (2011), and 0 to 461 967 mmol CH\textsubscript{4} m\textsuperscript{-2} d\textsuperscript{-1} and –37 to 37 mmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1} using \( k_w \) from Raymond et al. (2013). For comparison, CH\textsubscript{4} emissions estimated for the Amazon River were 4625 to 12 562 µmol m\textsuperscript{-2} d\textsuperscript{-1} (Bartlett et al., 1999) and the range for CH\textsubscript{4} in temperate rivers is \( \sim 0 \) to 22 000 µmol m\textsuperscript{-2} d\textsuperscript{-1} (De Angelis and Scranton, 1993; Lilley et al., 1996; Jones and Mulholland, 1998a, b; Hope et al., 2001; Abril and Iversen, 2002). Guérin et al. (2008) reported N\textsubscript{2}O emissions \( \sim 0.25 \) to 6.0 µmol m\textsuperscript{-2} d\textsuperscript{-1} for the Amazon River and floodplain, while Soued et al. (2016) found N\textsubscript{2}O fluxes in Canadian boreal rivers to be highly variable across ecosystem types and seasons. These ranged from net uptake \( \sim 3.3 \) µmol m\textsuperscript{-2} d\textsuperscript{-1}, somewhat lower that the maximum N\textsubscript{2}O uptake we observed in swamp rivers (Table 3), to net emissions \( \sim 4.8 \) µmol m\textsuperscript{-2} d\textsuperscript{-1}.

The overall ranges of CH\textsubscript{4} and N\textsubscript{2}O emissions from rivers of the ROC (33 to 48 705 mmol CH\textsubscript{4} m\textsuperscript{-2} d\textsuperscript{-1}; 1 to 67 mmol N\textsubscript{2}O m\textsuperscript{-2} d\textsuperscript{-1}. Table 3) fall within the ranges encompassed by these earlier estimates for African and temperate rivers. It should be acknowledged that the use of “basin-wide” values for \( k_w \) is a necessity that takes no account of spatial and temporal \( k_w \) variability, that our emissions based on \( k_w \) derived from Raymond et al. (2013) are 30 % higher than those derived from Aufdenkampe et al. (2011) and that other available \( k_w \) parameterisations show 5-fold variability (Barnes and Upstill-Goddard, 2011). Additionally, we did not measure CH\textsubscript{4} ebullition fluxes. Borges et al. (2015b) report an average 20 % ebullition contribution to total CH\textsubscript{4} emissions from the Congo and Zambezi, although their maximum estimates are considerably higher than this. For some other tropical rivers and lakes ebullition is thought to account for 30–98 % of total CH\textsubscript{4} emissions (Melack et al., 2004; Bastviken...
et al., 2011; Sawakuchi et al., 2014). The uncertainties related to \( k_w \) notwithstanding, our emissions estimates for CH\(_4\), at least, are therefore probably conservative.

### 6 Conclusions

Our data from the ROC support the growing consensus that river systems in Africa may be disproportionately large contributors to the global freshwater sources of tropospheric CH\(_4\) and N\(_2\)O, as they are for CO\(_2\). Even so, the potential for significant sinks lends a note of caution for N\(_2\)O. The wide ranges of emissions estimates for CH\(_4\) and N\(_2\)O now available for African rivers clearly illustrate the difficulty in deriving representative total emissions given both the comparatively small size of the available data set and the various approaches that are typically used to derive these emissions. This applies not only to African rivers but to tropical rivers in general and indeed to freshwaters globally. At least equally important is an insufficiently mature understanding of the processes that link emissions to the environmental controls of process rates and their temporal variability, and to river catchment characteristics that include sources and seasonality of organic inputs and variability in the balance between baseflow and surface runoff. Our understanding of these interactions must improve if the system responses to future climate and land use changes are to be predicted and planned for. Lastly, the measurement of CH\(_4\) and N\(_2\)O, data calibration and the emissions estimates for aquatic systems deriving would all benefit from agreed, standardised protocols. There are currently no internationally agreed calibration standards for CH\(_4\) or N\(_2\)O, but this is now being addressed via an international SCOR (Scientific Committee on Oceanic Research) working group (WG-143: https://portal.geomar.de/web/scor-wg-143/home), which is engaged in inter-laboratory calibration and the dissemination of high quality calibration gases. WG-143 welcomes additional interest from the wider aquatic CH\(_4\) and N\(_2\)O research community.

**Data availability.** All available data for this project are in the accompanying on-line supplement.

**The Supplement related to this article is available online at doi:10.5194/bg-14-2267-2017-supplement.**

**Competing interests.** The authors declare that they have no conflict of interest.

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