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

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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 under-saturated in swamp forest (36 ± 29%) and tropical forest (77 ± 36%) rivers but predominantly super-saturated 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 super-saturated (11.2 - 9553 nmol L$^{-1}$; 440-354444%), whereas N$_2$O ranged from strong under-saturation 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 super-saturated (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$_2$ under-saturation, indicating N$_2$O consumption during denitrification in the sediments. In savannah rivers persistent N$_2$O super-saturation 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 (33-48705 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 (CH₄) and nitrous oxide (N₂O) accounted for 17% and 6% respectively, of the total atmospheric radiative forcing by well-mixed greenhouse gases in 2011 (Myhre et al., 2013). CH₄ also impacts tropospheric oxidising capacity, O₃ and OH radical and is a source of stratospheric O₃ (Myhre et al., 2013) while N₂O is the largest cause of stratospheric O₃ loss, via NO production (Ravishankara et al., 2009). Since the onset of the industrial revolution, tropospheric CH₄ and N₂O have substantially increased but their growth rates have varied. The early 1980s to the mid-2000s saw an overall decline in tropospheric CH₄ 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 CH₄ tropospheric dry mole fraction in 2011, 1803 ± 2 ppbv, was 150% above the pre-industrial value (Hartmann et al., 2013). Of particular note for N₂O, 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 N₂O growth rate may reflect climate-driven changes in soil N₂O (Thompson et al., 2013). The current rate of N₂O growth is 0.73 ± 0.03 ppb 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 CH₄ and N₂O sources is small but increasing. The global freshwater CH₄ source could be ~10¹³–10¹⁴ g CH₄ 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 upscaling 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 CH₄ source can be evaluated in the light of natural and total global CH₄ source estimates of 179-484 x 10¹² g CH₄ yr⁻¹ and 526-852 x 10¹² g CH₄ 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 CH₄ emissions and ~1-19% of total CH₄ emissions. Converting these to CO₂ equivalents based on a 100 year Global Warming Potential gives ~0.65 x 10¹⁵ g C (CO₂ equivalent) yr⁻¹ (Bastviken et al., 2011), a significant offset to the combined terrestrial and oceanic carbon sink ~ 5.5 x 10¹⁵ g C yr⁻¹ (Le Quéré et al., 2015). A global estimate of river N₂O emissions based on microbial production from agriculturally-derived nitrogen is ~ 6.8 x 10¹¹ g N₂O yr⁻¹, around 10% of the total global anthropogenic N₂O source, but because this involved upscaling 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 x 10¹² g CH₄ and ~10¹⁰ g N₂O for twelve large river systems in sub-Saharan Africa, including the three largest by catchment area (Congo, Niger, Zambezi). Notably, their CH₄ estimate is five 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 x 10¹² g CH₄ yr⁻¹ and 3.3 ± 1.3 x 10¹² g N₂O yr⁻¹ (Valentini et al., 2014).
The potential scale of CH₄ and N₂O emissions from tropical freshwaters and their attendant uncertainties warrant further investigation. In this paper we present and discuss concentrations of dissolved CH₄, N₂O, O₂, NO₃⁻ and NH₄⁺, and corresponding CH₄ and N₂O emissions for river sites in savanna, swamp forest and tropical forest. Samples were collected along the Congo main stem and in seven of its tributary systems 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 x 10⁶ km² (~ 12% of the total African land mass; Fig. 1) and incorporating the world’s fourth largest wetland area ~3.6 x 10⁶ km² (Laporte et al., 1998). The Congo’s annual freshwater discharge is the world’s second largest at ~1300 km³ (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 x 10⁶ km² (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 x 10⁵ km²), in the western Congo Basin (Figure 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 dataset (U.S. 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°W to 25°W and 5°N to 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 600-700m 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 despite the relatively large variation in monthly precipitation (Laraque et al., 2001).
Surface water samples (~0.3 m depth) 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 CH₄, N₂O, O₂, NO₃⁻ and NH₄⁺ analysis, during November 2010 (41 samples) and August 2011 (25 samples; CH₄ and N₂O 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 0.1 M HgCl₂ 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 CH₄ and N₂O were analysed by single phase equilibration gas chromatography (Shimadzu GC 14-B), with flame ionisation detection of CH₄ and electron capture detection of N₂O (Upstill-Goddard et al., 1996). Routine calibration was with a mixed secondary standard (361 ppbv N₂O, 2000 ppbv CH₄) prepared by pressure dilution with ultra-high purity N₂ (Upstill-Goddard et al., 1990). Absolute calibration was against a mixed primary standard (10ppmv N₂O, 5ppmv CH₄) with a certified accuracy of ± 1 % (BOC Special Gases, UK). Overall analytical precisions (1σ) for N₂O and CH₄, established via multiple analysis (n = 15) of the secondary standard, were both ± 1%.

Temperature, dissolved O₂ 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 O₂; ±0.002 bar. Samples for dissolved NH₄⁺ and NO₃⁻ 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 (U.S. Environmental Protection Agency, 1984). Analytical precisions (1σ) were ± 1% for both. Technical and logistical issues precluded the collection of any dissolved O₂, NH₄⁺ or NO₃⁻ data during August 2011 (dry season) and some NO₃⁻ and NH₄⁺ data during November 2010 (wet season).

Emission fluxes, F (mol m⁻² d⁻¹), of CH₄ and N₂O were estimated using \( F = k_w L \Delta p \), where \( k_w \) is the transfer velocity of CH₄ or N₂O (cm hr⁻¹), \( L \) is the solubility of CH₄ or N₂O (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 CO₂ in the Congo. Raymond et al. (2013) estimated a basin-wide \( k_w \) of 5.2 m d⁻¹ for CO₂, 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 CO₂ 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 \( k_w \approx 3.9 \) m d⁻¹ for CO₂. We converted these estimates to \( k_w \) for CH₄ and N₂O by multiplying by \( (Sc/470.7)^{0.5} \), where 470.7 is the Schmidt number of CO₂ in freshwater, and Sc is the Schmidt number of CH₄ or N₂O (\( Sc_{CH_4}=486.8; Sc_{N_2O}=476.9 \)), assuming an ambient temperature of 25°C (Wanninkhof, 1992). The resulting \( k_w \) estimates are 5.1 and 3.9 m d⁻¹ for CH₄ and 5.2 and 4.0 m d⁻¹ for N₂O. 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 CH₄ and N₂O 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 CH₄ (1797 ppbv) and N₂O (322 ppbv) for the year 2010 (http://cdiac.esd.ornl.gov/tracegases.html).
3 Results

While CH₄ and N₂O data are available for all samples, dry season data are not available for dissolved O₂, NO₃⁻ or NH₄⁺. Wet season DIN (NO₃⁻ + NH₄⁺) is only reported for samples for which both NO₃⁻ and NH₄⁺ are available. Source data for this paper are available as supplementary material (Table S1).

3.1 Dissolved O₂ and DIN

In wet season swamp samples dissolved O₂ varied between mildly under-saturated and very strongly under-saturated (Fig. 2). The mean (36 ± 29%) and range (4-91 %) of O₂ 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 O₂ under-saturated (mean 77 ± 36%, range 14-116 %; Fig. 2) and savannah rivers were predominantly mildly under-saturated to mildly super-saturated (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 (NO₃⁻ + NH₄⁺) 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 O₂.

Differences in NO₃⁻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 NO₃⁻ and NH₄⁺ for any of the three river types (Fig. 3a). NO₃⁻ was the dominant DIN component in 24 of the 33 samples for which both NO₃⁻ and NH₄⁺ were analysed. Considering all samples, the mean NO₃⁻ contribution to DIN was 63 ± 19%.

3.2 Dissolved CH₄ and N₂O

Table 2 summarises ranges, means and medians of riverine CH₄ and N₂O concentrations and percent saturations for the three land cover types. All samples were highly CH₄ super-saturated, concentrations spanning two orders of magnitude (11.2 - 9553 nmol L⁻¹; 440-354400% saturation). N₂O spanned a much narrower concentration range and varied from strong under-saturation to strong super-saturation (3.2-20.6 nmol L⁻¹; 47-205%). Evidently, while rivers of the ROC are strong local sources of tropospheric CH₄ they can act as both small sources and sinks for N₂O. Swamp rivers exhibited both the lowest and among the highest N₂O saturations (Table 2) but during the wet season had overall significantly lower N₂O than either forest or savannah rivers. These were always super-saturated (103-266%; Table 2) and their overall means and ranges of N₂O were not significantly different (Mann-Whitney, one-tailed: swamp vs forest and swamp vs savannah, P = 0.004). For CH₄, 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 savannah, P = 0.004; forest vs savannah, P = 0.03). In contrast, during the dry season concentration means and ranges of both CH₄ and N₂O were indistinguishable for all three land cover types. Seasonal differences in concentration means and ranges were not significant for N₂O for any of the three land cover types or for CH₄ in savannah rivers. In both swamp and forest rivers CH₄ 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 CH₄ concentrations in African rivers and even fewer of N₂O. Our CH₄ data for rivers of the ROC (Table 2) are within the ranges compiled for temperate and tropical rivers (~260-128000%) (Upstill-Goddard et al. 2000; Middelburg et al. 2002). Moreover, our CH₄ and N₂O data both fall within the ranges recently reported for other rivers in sub-Saharan Africa. Studies of CH₄ alone reported 48 - 870 nmol l⁻¹ (2221 -
Considering the complete data set, CH$_4$ was inversely correlated with both N$_2$O and O$_2$ (Fig. 2). Highest CH$_4$ coincident with lowest N$_2$O and O$_2$ occurred in swamp rivers. Lowest CH$_4$ coincident with highest N$_2$O and O$_2$ was observed in forest rivers. Savannah rivers were intermediate between the two (Fig. 2). Overall, log % CH$_4$ vs % O$_2$ showed a weak negative correlation (Fig. 2a; R$^2 = 0.26$, n = 41) while % N$_2$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 % 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 strong positive correlation between % N$_2$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$_2$O and % O$_2$ (R$^2 =0.35$, n=12). N$_2$O co-varied positively with both NO$_3^-$ and NH$_4^+$ (Fig. 3). For the complete data set the correlations were weak (N$_2$O vs NO$_3^-$; R$^2 = 0.28$, n = 59; N$_2$O vs NH$_4^+$, R$^2 = 0.23$, n = 40). For all three river types individually, with the exception of N$_2$O vs NH$_4^+$ in savannah rivers, the correlations were stronger and for all NO$_3^-$ was a stronger predictor of N$_2$O (N$_2$O vs NO$_3^-$: R$^2$ swamp = 0.50, n = 29; R$^2$ forest = 0.75, n = 15; R$^2$ savannah = 0.31, n = 15) than was NH$_4^+$ (N$_2$O vs NH$_4^+$: R$^2$ swamp = 0.29, n = 13; R$^2$ forest = 0.47, n = 13; R$^2$ savannah = 0.01, n = 14).

### 3.3 CH$_4$ and N$_2$O emission fluxes

Table 3 summarises ranges, means and medians of CH$_4$ and N$_2$O emission fluxes using $k_a$ derived from Raymond et al. (2013) and Aufdenkampe et al. (2011). Fluxes broadly followed the distribution of concentrations. CH$_4$ fluxes were lowest overall in savannah rivers and highest in swamp and forest rivers. N$_2$O fluxes were lowest in swamp rivers and highest in savannah and forest rivers. Fluxes were always to air at all sites for CH$_4$ and at all savannah and forest sites for N$_2$O. However, swamp rivers were predominantly a N$_2$O sink during the wet season (11 of 16 individual flux estimates) and predominantly a N$_2$O source during the dry season (10 of 16 individual flux estimates). As far as we are aware the wet season sink for N$_2$O in swamp rivers is the first such reported for African rivers.

### 4 Discussion

#### 4.1. Sources of CH$_4$ and N$_2$O

The concentrations of dissolved CH$_4$ and N$_2$O 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 under-saturated in the majority of samples, being as low as 4% in one wet season swamp sample, it was always detectable and indeed was super-saturated in several savannah river samples in which CH$_4$ saturations ranged from ~4000-10000 % (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 CH$_4$ 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 CH₄ supply from groundwater to African rivers is generally comparatively low (Balagizi et al., 2015; Borges et al., 2015b). The spatial distribution of dissolved CH₄ 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 CH₄ (Borges et al., 2015a). These sources promote a unidirectional CH₄ 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 CH₄ diffusion term evidently exceeds combined CH₄ losses via oxidation and water-to-air exchange. This further promotes the accumulation of high river CH₄ concentrations.

In addition to methanogenesis in fully anoxic sediment and soils, CH₄ production can also occur in “anoxic microsites” within oxic soils (e.g. Teh et al., 2005; von Fisher & 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), archael 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 (Hurkuck et al., 2012, have all also been observed. Although methanogenesis by photoautotroph-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, CH₄ is subject to variable and rapid aerobic and anaerobic microbial oxidation (Megonigal et al., 2004). Oxidative CH₄ 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 CH₄ loss term, with ebullition frequently considered the dominant of these two mechanisms (Stanley et al., 2016). Despite this complexity of dissolved CH₄ cycling in rivers, it is nevertheless informative to speculate on our principal observations in the context of potential CH₄ sources and sinks.

The first notable feature of our results is the contrasting relationship between CH₄ and O₂ in swamp and forest rivers (negative) and in savannah rivers (positive) (Fig. 2a). Dissolved O₂ 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 super-saturations as high as 150% (Li et al., 2010). The overall positive relationship between CH₄ and O₂ in savannah rivers (Fig 2a.) could, at least in part, reflect high macrophyte-related productivity. This can give rise to positive relationships by direct CH₄ 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). Offset this, stems and roots respire O₂ (Caraco et al., 2006). Further inspection of the data shows that the highest dissolved O₂ saturation found in savannah rivers (134%) deviates from the general CH₄ vs O₂ 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 O₂ super-saturated. Intense water-air exchange in this region via increased turbulence would tend to enhance dissolved O₂ (Li et al., 2010) while depleting dissolved CH₄. To summarise, notwithstanding possible additional CH₄ losses via oxidation, the CH₄ vs O₂ 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...
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 archaean 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 (Comoè, Bia, Tanoè). 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 (European) rivers (Middelburg et al. 2002). Koné et al. (2010) ascribed the CH$_4$ seasonality in Ivory Coast rivers to a combination of the dilution of high CH$_4$ baseflow by low CH$_4$ 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 CH$_4$ 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 CH$_4$ contribution from baseflow often occurs in high elevation headwaters with high soil organic content, while progressive downstream increases in CH$_4$ 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 CH$_4$ trend in a specified river system is evidently complex.

In contrast to CH$_4$, natural sources of aquatic N$_2$O are entirely microbial, and involve several pathways. Nitrification is a two-stage process in which NH$_4^+$ is first oxidised aerobically to NO$_2^-$ via hydroxylamine (NH$_2$OH), followed by NO$_2^-$ oxidation to NO$_3^-$. Following the first stage, N$_2$O can be produced through various routes: nitrifier nitrification (NH$_2$OH $\rightarrow$ N$_2$O), nitrifier denitrification (NO$_2^-$ $\rightarrow$ NO $\rightarrow$ N$_2$O) and nitrification-coupled denitrification (NO$_3^-$ $\rightarrow$ NO$_2^-$ $\rightarrow$ NO $\rightarrow$ N$_2$O) (Kool et al., 2011). Heterotrophic denitrification, in which NO$_3^-$ is the terminal electron acceptor (NO$_3^-$ $\rightarrow$ NO$_2^-$ $\rightarrow$ NO + N$_2$O $\rightarrow$ N$_2$), occurs in soils, sediments and waters that are anoxic, the inhibition of denitrifier activity at very low levels of dissolved O$_2$ being well known (Knowles 1982). Even so, in the complete absence of O$_2$, N$_2$O can be enzymatically reduced to gaseous N$_2$ (Wrage et al. 2001), both in sediments and in the water column, sometimes resulting in extreme N$_2$O under-saturations (Nirmal Rajkumar et al., 2008).

Although we found no statistically significant differences in the means and ranges of wet or dry season N$_2$O concentrations for any land cover type, higher N$_2$O 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 savanna during the rainy season (Castaldi et al., 2006) and throughout much of the year in humid tropical forests (Castaldi et al., 2013). 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$_2$O cycling, as evidenced by the variable relationships between N$_2$O, O$_2$ 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 under-saturation 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}\textsuperscript{−} 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}\textsuperscript{−} than between N\textsubscript{2}O and NH\textsubscript{4}+, 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; Teodoro et al., 2015) and in the Adyar river-estuary, S.E. 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}\textsuperscript{−} 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}\textsuperscript{−} (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}+ (Teodoro et al., 2015). For savannah rivers, in which N\textsubscript{2}O was always super-saturated (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}+ 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 two-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.

### 4.2 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) report 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\textsubscript{w} from Aufdenkampe et al. (2011), and 0 to 461,967 mmol CH\textsubscript{4} m\textsuperscript{−2} d\textsuperscript{−1} and -37 to 377 mmol N\textsubscript{2}O m\textsuperscript{−2} d\textsuperscript{−1} using k\textsubscript{w} from Raymond et al. (2013). For comparison, CH\textsubscript{4} emissions estimated for the Amazon River were 4625 to 12562 μmol m\textsuperscript{−2} d\textsuperscript{−1} (Bartlett et al. 1990) and the range for CH\textsubscript{4} in temperate rivers is ~0 to 22000 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 ~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 ~ 3.3 μmol m⁻² d⁻¹, somewhat lower that the maximum N₂O uptake we observed in swamp rivers (Table 3), to net emissions ~ 4.8 μmol m⁻² d⁻¹.

The overall ranges of CH₄ and N₂O emissions from rivers of the ROC (33 to 48705 nmol CH₄ m⁻² d⁻¹; 1 to 67 nmol N₂O m⁻² d⁻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 kₑ is a necessity that takes no account of spatial and temporal kₑ variability, that our emissions based on kₑ derived from Raymond et al. (2013) are 30% higher than those derived from Aufdenkampe et al. (2011) and that other available kₑ parameterizations show five-fold variability (Barnes and Upstill-Goddard, 2011). Additionally, we did not measure CH₄ ebullition fluxes. Borges et al (2015b) report an average 20% ebullition contribution to total CH₄ 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 CH₄ emissions (Melack et al., 2004; Bastviken et al., 2011; Sawakuchi et al., 2014). The uncertainties related to kₑ notwithstanding, our emissions estimates for CH₄ at least, are therefore probably conservative.

5 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 CH₄ and N₂O, as they are for CO₂. Even so, the potential for significant sinks lends a note of caution for N₂O. The wide ranges of emissions estimates for CH₄ and N₂O 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 CH₄ and N₂O data calibration and the emissions estimates for aquatic systems deriving would all benefit from agreed, standardized protocols. There are currently no internationally agreed calibration standards for CH₄ or N₂O 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 CH₄ and N₂O research community.

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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.

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Figure 1.
Figure 2

(a) Log percent CH₄ saturation vs. Percent O₂ saturation

(b) Percent N₂O saturation vs. Percent O₂ saturation
Figure 3

(a) Relationship between NO$_3^-$ (μM) and NH$_4^+$ (μM).

(b) Relationship between Percent N$_2$O saturation and NH$_4^+$ + NO$_3^-$ (μM).
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>
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<tr>
<th>River/Tributary</th>
<th>Catchment Area km$^2$</th>
<th>Discharge m$^3$ s$^{-1}$</th>
<th>Rainfall mm</th>
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<td>21030</td>
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<td>1709</td>
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<td>Nkèni</td>
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Table 2. Dissolved CH$_4$ and N$_2$O in Republic of Congo rivers

<table>
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<tr>
<th>Land cover</th>
<th>Date</th>
<th>CH$_4$ nmol L$^{-1}$</th>
<th>CH$_4$ saturation %</th>
<th>N$_2$O nmol L$^{-1}$</th>
<th>N$_2$O saturation %</th>
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<td>Median</td>
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<td>15-793</td>
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<td></td>
<td>Dry</td>
<td>66-243</td>
<td>144 $\pm$ 70</td>
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<td>Swamp</td>
<td>All</td>
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Table 3. Emissions of CH₄ and N₂O to air from rivers in the Republic of Congo. Negative values in parentheses indicate uptake from the atmosphere.

<table>
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<tr>
<th>Land cover</th>
<th>CH₄ emission flux (µmol m⁻² d⁻¹)</th>
<th>N₂O emission flux (µmol m⁻² d⁻¹)</th>
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<td>465 ± 526</td>
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Table 4. Emissions of CH\textsubscript{4} and N\textsubscript{2}O published for African rivers: (A) refers to emissions estimated using the relationship of Aufdenkampe et al (2011) and (B) refers to emissions estimated using the relationship of Raymond et al. (2013).

<table>
<thead>
<tr>
<th>River</th>
<th>CH\textsubscript{4} emission flux (µmol m\textsuperscript{-2} d\textsuperscript{-1})</th>
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<td>0.6-5.7</td>
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<td>18534</td>
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