



The riverine source of tropospheric CH₄ and N₂O from the Republic of Congo, Western Congo Basin

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Abstract. We report 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, along the Congo main stem and in several of its tributary systems of the Western Congo Basin, Republic of Congo, during November 2010 (41 samples; “wet season”) and August 2011 (25 samples; “dry season”; CH₄ and N₂O only). Dissolved inorganic nitrogen (DIN: wet season; NH₄⁺ + NO₃⁻) was dominated by NO₃⁻ (63 ± 19% of DIN), total DIN concentrations (1.5-45.3 μmol L⁻¹) being consistent with small agricultural, domestic and industrial sources. Dissolved O₂ (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%). Dissolved CH₄ and N₂O were within previously reported ranges for sub-Saharan African rivers. While CH₄ was always super-saturated (11.2 - 9553 nmol L⁻¹; 440-354400%), N₂O ranged from strong under-saturation to strong super-saturation (3.2-20.6 nmol L⁻¹; 47-205%). Evidently, rivers of the ROC are persistent local sources of tropospheric CH₄ but can be small sources or sinks for N₂O. Dry season concentration means and ranges of CH₄ and N₂O were indistinguishable for all three land types and seasonal differences in means and ranges were not significant for N₂O for any land type or for CH₄ in savannah rivers; the latter is consistent with seasonal buffering of river discharge by an underlying sandy-sandstone aquifer. By contrast, swamp and forest river CH₄ was significantly higher in the wet season, possibly reflecting CH₄ derived from floating macrophytes during flooding and/or enhanced methanogenesis in adjacent flooded soils. Swamp rivers exhibited both low (47%) and high (205%) N₂O saturations 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 N₂O were not significantly different. In swamp and forest rivers % O₂ co-varied negatively with log % CH₄ and positively with % N₂O. The strong positive N₂O - O₂ correlation in swamp rivers was coincident with strong N₂O and O₂ under-saturation, indicating N₂O consumption by sediment denitrification. In savannah rivers persistent N₂O super-saturation and a negative N₂O - O₂ correlation may indicate N₂O production mainly by nitrification, consistent with a stronger correlation between N₂O and NH₄⁺ than between N₂O and NO₃⁻. Our range in CH₄ and N₂O emissions fluxes (33-48705 μmol CH₄ m⁻² d⁻¹; 1-67 μmol N₂O m⁻² d⁻¹), is wider than previously estimated for sub-Saharan African rivers but it includes uncertainties deriving from our use of “basin-wide” values for CH₄ and N₂O gas transfer velocities. Even so, because we did not account for any contribution from ebullition, which for CH₄ is likely to be at least 20%, our emissions estimates for CH₄ are probably conservative.

1 Introduction



40 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 (Hartmann 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. Following periods of declining and zero growth from the mid 1980's, tropospheric CH₄ progressively increased from the late 2000's (Rigby et al., 2008; Dlugokencky et al., 2009). Growth ~ 4-5 ppbv yr⁻¹ since 2009 (Sussmann et al., 2012) has been linked to increasing natural tropical emissions (Bousquet et al., 2011). The mean CH₄ tropospheric dry mole fraction in 2011, 1803 ± 2 ppbv, was more than 150% above the pre-industrial value (Ciais et al., 2013). Increasing tropospheric N₂O largely reflects its enhanced emission from soils, freshwaters and coastal waters via the accelerated mobilisation of reactive nitrogen (Syakila and Kroeze, 2011). Consequently the IPCC now classifies river, estuary and coastal zone N₂O sources as anthropogenic (Ciais et al., 2013). 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 (Ciais et al., 2013).

55 The evidence base for freshwater ecosystems (streams, rivers, lakes, and reservoirs) as important sources of tropospheric CH₄ and N₂O is small but increasing. The global freshwater CH₄ source could be ~10¹³-10¹⁴ g yr⁻¹ (Bastviken et al., 2011; Kirschke et al., 2013), the uncertainty reflecting data gaps, notably for major world river basins, and a sampling bias that has necessitated upscaling from exclusively temperate data (Bastviken et al., 2011). Notwithstanding the uncertainty, this freshwater source estimate is ~30-47 % of natural CH₄ emissions and ~12-20% of total CH₄ emissions (Kirschke et al., 2013). Converting it to CO₂ equivalents based on warming potentials and atmospheric lifetimes 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 ~ 3.5 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 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 seasonal emissions ~3-4 x 10¹² g CH₄ yr⁻¹ and ~10¹⁰ g N₂O yr⁻¹ for twelve large river systems in sub-Saharan Africa, including the three largest by catchment area (Congo, Niger, Zambezi). Notably, their CH₄ 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 x 10¹² g CH₄ yr⁻¹ and 3.3 ± 1.3 x 10¹² g N₂O yr⁻¹ (Valentini et al., 2014).

75 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, along the Congo main stem and in several of its tributary systems of 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, with maximal flows in December and May and minimal flows in August and March (Coynel et al., 2005). The Congo Basin (9°N - 14°S; 11° - 31°E) is the largest hydrological system in Central Africa, covering $\sim 3.8 \times 10^6$ km² (~ 12% of the total African land mass; Fig. 1) and incorporating the world's fourth largest wetland area $\sim 3.6 \times 10^5$ 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 $\sim 2.7 \times 10^4$ 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, several of its tributary rivers and some of their sub-tributaries, at sites within the Republic of Congo (ROC: area 3.4×10^5 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 being 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, the central western part of which 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 sandy-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).

3 Sample collection and analytical techniques

We collected 66 surface water samples (~ 0.2 m) from central river channels 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, over filling each by at least one sample volume to avoid bubble entrainment. Samples were inoculated with 25 μ l 0.1 M HgCl₂ to arrest microbial activity, sealed to leave no headspace and 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 $\pm 1\%$.

Temperature, dissolved O₂ and atmospheric pressure were measured *in-situ* using a handheld multi-parameter probe (YSI Pro-Plus, YSI UK Ltd). 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 μ m 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 prior to analysis by segmented flow (Astoria Analyzer; Astoria-Pacific, USA) at Woods Hole, using established methods (U.S. Environmental Protection Agency, 1984). Analytical precisions (1σ) were $\pm 1\%$ 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 Δp 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 $\sim \pm 10\%$ (Raymond et al., 2013). In contrast Aufdenkampe et al. (2011) applied constant k_w values for CO₂ in streams (< 100 m wide: 3.0 m d⁻¹) and in rivers (>100m 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 $k_w \sim 3.9$ 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 $\sim 30\%$ higher based on Raymond et al. (2013). Using both sets of k_w estimates facilitates a 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 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 tropospheric mixing ratios of CH₄ (1797 ppbv) and N₂O (323 ppbv) for the year 2010 (<http://www.eea.europa.eu/data-and-maps/>).

3 Results

While CH₄ and N₂O data are available for all samples, dry season data are not available for dissolved O₂, NO₃⁻ or



NH_4^+ and wet season DIN ($\text{NO}_3^- + \text{NH}_4^+$) is only reported for samples for which both NO_3^- and NH_4^+ are available.

3.1 Dissolved O_2 and DIN

165 In wet season swamp samples dissolved O_2 varied between mildly under-saturated and very strongly under-saturated
 (Fig. 2). The mean ($36 \pm 29\%$) and range (4-91 %) of O_2 saturation were both significantly lower than for forest rivers
 (Mann-Whitney, one-tailed; $P = 0.0001$), the majority of which were mildly to strongly O_2 under-saturated (mean 77
 $\pm 36\%$, range 14-116 %; Fig. 2), and for savannah rivers (Mann-Whitney, one-tailed; $P = 0.002$), which were mildly
 under-saturated to mildly super-saturated (mean $100 \pm 17\%$, range 70-135 %; Fig. 2).

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Low wet season concentrations of dissolved inorganic nitrogen (DIN) components (Fig. 3) are consistent with low
 nitrogen input rates from agricultural, domestic and industrial sources (Clark and Decalo, 2012). The means and
 ranges of total DIN ($\text{NO}_3^- + \text{NH}_4^+$) did not differ significantly between any of the three river “types” (mean savannah
 $6.8 \pm 2.8 \mu\text{mol l}^{-1}$; range 2.5-10.1 $\mu\text{mol l}^{-1}$; $n=10$; mean swamp $5.1 \pm 3.1 \mu\text{mol l}^{-1}$, range 1.5-10.2 $\mu\text{mol l}^{-1}$; $n= 11$;
 175 mean forest $9.4 \pm 11.2 \mu\text{mol l}^{-1}$, range 1.8-45.3 $\mu\text{mol l}^{-1}$; $n=12$), in contrast to the situation for dissolved O_2 .
 Differences in NO_3^- -N were also not significant (mean savannah $4.1 \pm 2.3 \mu\text{mol l}^{-1}$, range 0.8-6.7 $\mu\text{mol l}^{-1}$, $n=11$;
 mean swamp $3.6 \pm 2.1 \mu\text{mol l}^{-1}$, range 1.0-8.8 $\mu\text{mol l}^{-1}$, $n= 16$; mean forest $7.1 \pm 9.2 \mu\text{mol l}^{-1}$, range 1.2-35.1 $\mu\text{mol l}^{-1}$;
 $n=12$) and 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
 180 all samples, the mean NO_3^- contribution to DIN was $63 \pm 19\%$.

3.2 Dissolved CH_4 and N_2O

Table 2 summarises ranges, means and medians of riverine CH_4 and N_2O concentrations and percent saturations for
 the three land cover types. All samples were highly CH_4 super-saturated, concentrations spanning two orders of
 magnitude ($11.2 - 9553 \text{ nmol L}^{-1}$; 440-354400% saturation). N_2O spanned a much narrower concentration range and
 185 varied from strong under-saturation to strong super-saturation ($3.2\text{-}20.6 \text{ nmol L}^{-1}$; 47-205%). Evidently, while rivers
 of the ROC are strong local sources of tropospheric CH_4 they can act as both small sources and sinks for N_2O .
 Swamp rivers exhibited both the lowest and among the highest N_2O saturations (Table 2) but during the wet season
 had overall significantly lower N_2O than either forest or savannah rivers, which were both always super-saturated
 (103-266%; Table 2) and for which the overall means and ranges of N_2O were not significantly different (Mann-
 190 Whitney, one-tailed: swamp vs forest and swamp vs savannah, $P = 0:004$). For 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 savannah, $P = 0:004$; forest vs savannah,
 $P = 0.03$). In contrast, during the dry season concentration means and ranges of both CH_4 and N_2O were
 indistinguishable for all three land cover types. Seasonal differences in concentration means and ranges were not
 195 significant for N_2O for any of the three land cover types or for CH_4 in savannah rivers, but in both swamp and forest
 rivers 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 CH_4 concentrations in African rivers and even fewer of N_2O . Our CH_4
 200 data for rivers of the ROC (Table 2) are within the ranges compiled for temperate and tropical rivers ($\sim 260\text{-}128000\%$)
 (Upstill-Goddard et al. 2000; Middelburg et al. 2002) and our CH_4 and N_2O data both fall within the ranges recently
 reported for other rivers in sub-Saharan Africa. Studies of CH_4 alone reported $48 - 870 \text{ nmol l}^{-1}$ (2221 - 38719 %
 saturation) in three Ivory Coast rivers (Koné et al., 2010), $25 - 505 \text{ nmol l}^{-1}$ (850 - 21700 % saturation) in the Tana



205 river, Kenya, (Bouillon et al., 2009) and 22-71430 nmol l⁻¹ in the Congo (Borges et al., 2015a). For concurrent measurements of CH₄ and N₂O Bouillon et al. (2012) report 74 - 280 nmol CH₄ l⁻¹ (3450 - 13200% saturation) and 6.2 - 9.6 nmol N₂O l⁻¹ (112-165% saturation) in the Oubangui, a major Congo tributary, Teodoru et al. (2015) found 7-12127 nmol CH₄ l⁻¹ and 2.0-11.4 nmol N₂O l⁻¹ at stations along the Zambezi and Borges et al. (2015b) quote a range of 2-62966 nmol CH₄ l⁻¹ (mean: 2205 nmol l⁻¹) and 0.2-85.4 nmol N₂O l⁻¹ (mean: 9.2 nmol l⁻¹) across 12 sub-Saharan river basins, including those of the Congo, Zambezi and Niger.

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Considering the complete data set, CH₄ was inversely correlated with both N₂O and O₂ (Fig. 2). Highest CH₄ coincident with lowest N₂O and O₂ occurred in swamp rivers and lowest CH₄ coincident with highest N₂O and O₂ was observed in forest rivers, while savannah rivers were intermediate between the two (Fig. 2). Overall, log % CH₄ vs % O₂ showed a weak negative correlation (Fig. 2a; R² = 0.26, n = 41) while % N₂O vs % O₂ showed a weak positive correlation (Fig. 2b; R² = 0.30, n = 41). However, for both swamp and forest rivers individually the negative correlations between log % CH₄ and % O₂ were stronger (swamp R² = 0.38, n = 16; forest R² = 0.45, n = 13) and while there was a stronger positive correlation between % N₂O and % O₂ for swamp rivers than for the complete data set (R² = 0.71, n = 16), the correlation for forest rivers was extremely weak (R² = 0.02, n=13). Conversely, for savannah rivers we found a positive correlation between log % CH₄ and % O₂ (R² = 0.23; n= 12) and a negative correlation between % N₂O and % O₂ (R² = 0.35, n=12). N₂O co-varied positively with both NO₃⁻ and NH₄⁺ (Fig. 3). For the complete data set the correlations were weak (N₂O vs NO₃⁻, R² = 0.28, n = 59; N₂O vs NH₄⁺, R² = 0.23, n = 40) but for all three river types individually, with the exception of N₂O vs NH₄⁺ in savannah rivers, the correlations were stronger and for all NO₃⁻ was a stronger predictor of N₂O (N₂O vs NO₃⁻: R² swamp = 0.50, n = 29; R² forest = 0.75, n = 15; R² savannah = 0.31, n = 15) than was NH₄⁺ (N₂O vs NH₄⁺: R² swamp = 0.29, n = 13; R² forest = 0.47, n = 13; R² savannah = 0.01, n = 14).

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3.3 CH₄ and N₂O emission fluxes

Table 3 summarises ranges, means and medians of CH₄ and N₂O emission fluxes using *k_w* derived from Raymond et al. (2013) and Aufdenkampe et al. (2011). Fluxes broadly followed the distribution of concentrations, for CH₄ being lowest overall in savannah rivers and highest in swamp and forest rivers and for N₂O being 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.

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4 Discussion

235 4.1. Sources of CH₄ and N₂O

The concentrations of dissolved CH₄ and N₂O at any specified river location reflect a dynamic and complex balance of 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.

240 Notwithstanding this complexity, the coexistence of CH₄ with dissolved O₂ in rivers of the ROC (Fig. 2a) initially seems enigmatic. While dissolved O₂ 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 CH₄ saturations ranged from ~4000-10000 % (Fig. 2a). These observations seem counterintuitive because the classical view of methanogenesis is that it is exclusively anoxic, carried out by severely O₂-limited archaea (Bridgman et al., 2013). However, recent evidence is for a greater complexity of CH₄ production in river catchments. For example, methanogenesis in “anoxic microsites” within oxic soils is widely acknowledged (e.g. Teh et al., 2005; von Fisher & Hedin, 2007). Methanogens are now considered to be widespread in oxic soils and they are activated during flooding (Bridgman et al., 2013), their activity relating to soil carbon age and composition (Bridgman et al., 1998; Chanton et al., 2008) and likely involving 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 (Hurkuck et al., 2012, have all also been observed. Further, methanogenesis by photoautotroph-attached archaea has been detected in oxic lake water (Grossart et al., 2011), analogous to the “anoxic micro-niches” associated with dead and living particles in oxic sea water (de Angelis and Lee, 1994; Oremland, 1979; Ditchfield et al., 2012). Additional production in oxic seawater may involve biological uptake of organic PO₄³⁻ (Karl et al., 2008) and methylophilic methanogenesis (Damm et al., 2010), both mechanisms being associated with nutrient stress, but neither has yet been identified in freshwaters. 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); 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 between photosynthesis and respiration (Houser et al., 2015) but may also be 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 CH₄ and O₂ in savannah rivers (Fig 2a.) could, at least in part, reflect high macrophyte-related productivity, which can give rise to positive relationships by direct CH₄ production (Stanley et al., 2016) and by indirect production via trapping 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 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 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 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 O₂ was close to or in excess of 100% (Fig. 2a). For the majority of samples that were O₂ under-saturated however, additional mechanisms must be invoked. One possibility is that these distributions largely reflect the mixing of relatively well-oxygenated river waters with



high CH₄, low O₂ groundwater but another possibility is that this relationship is the aggregate of this and several of the other processes previously discussed.

290 A second important aspect of the overall CH₄ distributions is that swamp and forest river CH₄ was highest during the wet season, whereas savannah samples revealed no such inter-seasonal contrast (Table 2). The constancy of CH₄ in savannah rivers might well reflect the buffering of seasonal river discharge by the sandy-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 the flooding of adjacent soils (Bridgman et al., 2013) is also plausible, especially given 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, Tanoé). In these, overall decreases in CH₄ 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 CH₄ seasonality in Ivory Coast rivers to a combination of the dilution of high 300 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 305 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.

310 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 315 acceptor (NO₃⁻ → NO₂⁻ → NO + N₂O → N₂), occurs in soils, sediments and water 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 under-saturations (Nirmal Rajkumar et al., 2008).

320 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), as 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 325 complex balance between the principal sites (groundwater and in-stream) and mechanisms of N₂O cycling, as evidenced by the variable relationships between N₂O, O₂ and DIN we observed. For example, we found both positive and negative relationships between N₂O and O₂ (Fig. 2b). Sediment processes and water concentrations are evidently closely coupled in tropical catchments (Harrison and Matson, 2003) and the strong positive correlation



330 between N_2O and O_2 in swamp rivers coincident with strong under-saturation of both N_2O and O_2 (Fig. 2b) is
consistent with N_2O consumption by sediment denitrification. Although positive relationships between N_2O and
 NO_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), for swamp rivers the stronger correlation between N_2O and NO_3^-
335 than between N_2O and NH_4^+ , which has previously been taken to indicate a sediment N_2O source from denitrification
(Dong et al., 2004), supports our conclusion of a swamp river denitrification sink for N_2O . Similar N_2O vs O_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, S.E. India (Nirmal Rajkumar et al., 2008). In both the Amazon and the Adyar, N_2O was
undetectable in fully anoxic waters (Richey et al., 1998; Nirmal Rajkumar et al., 2008). N_2O and NO_3^- were also
correlated in the Oubangui (Bouillon et al., 2012) and 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
340 leading to high community respiration and low O_2 solubility (Rosamond et al., 2012). Even though denitrification in
rivers may be limited by low levels of NO_3^- (Garcia-Ruiz et al., 1998) a temperate creek nevertheless was a N_2O sink
for combined NO_2^- and NO_3^- concentrations $< 2.7 \mu\text{mol l}^{-1}$ (Baulch et al., 2011), broadly similar to the majority of
 NO_3^- concentrations we observed (Fig. 3a). By contrast, N_2O and NO_3^- were uncorrelated in the Zambezi, for which
there was also no correlation of N_2O with NH_4^+ (Teodoru et al., 2015). For savannah rivers, in which N_2O was
345 always super-saturated (Fig. 2b), a negative correlation between N_2O and O_2 may indicate N_2O production mainly by
nitrification, a conclusion supported by the corresponding stronger correlation between N_2O and NH_4^+ than between
 N_2O and NO_3^- , the opposite to what we found for swamp rivers. Although published measurements of N_2O 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
350 two-fold globally (Mosier et al., 1998). In addition to O_2 and DIN amount and speciation, pH and dissolved organic
carbon are important in controlling net N_2O production via nitrification and denitrification (Baulch et al., 2011) and it
has been suggested that due to variable N_2O yields from these processes, simple diagnostic relationships for N_2O
production in rivers may prove elusive (Beaulieu et al., 2008).

355 To conclude, while our data have allowed us to draw some conclusions regarding the production and cycling of CH_4
and N_2O in contrasting rivers of the ROC, we consider these to be more robust for N_2O given that its aquatic sources
are the least diverse. However, for both gases an unequivocal identification of the primary controls of their riverine
distributions would require additional detailed measurements.

4.2 CH_4 and N_2O emissions in the wider context

360 As with the concentration measurements, there are few data for African rivers with which to compare our CH_4 and
 N_2O 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 - 1187 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$, while for the Oubangui Bouillon et al. (2012)
found 38 - 350 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and 0.6 - 5.7 $\mu\text{mol N}_2\text{O} \text{ m}^{-2} \text{ d}^{-1}$. For 12 sub-Saharan African rivers Borges et al.
(2015b) give ranges of 502 - 18019 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and 2 - 16 $\mu\text{mol N}_2\text{O} \text{ m}^{-2} \text{ d}^{-1}$ using k_w from Aufdenkampe et al.
365 (2011), and 583 - 28579 $\mu\text{mol CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ and 2 - 28 $\mu\text{mol N}_2\text{O} \text{ m}^{-2} \text{ d}^{-1}$ using k_w from Raymond et al. (2013). For
comparison, CH_4 emissions estimated for the Amazon River were 4625 - 12562 $\mu\text{mol m}^{-2} \text{ d}^{-1}$ (Bartlett et al. 1990) and
the range for CH_4 in temperate rivers is ~ 0 - 22000 $\mu\text{mol m}^{-2} \text{ d}^{-1}$ (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_2O
emissions ~ 0.25 -6.0 $\mu\text{mol m}^{-2} \text{ d}^{-1}$ for the Amazon River and floodplain while Soued et al. (2016) found N_2O fluxes in
370 Canadian boreal rivers to be highly variable across ecosystem types and seasons, ranging from net uptake $\sim 3.3 \mu\text{mol}$



$\text{m}^2 \text{d}^{-1}$, somewhat lower than the maximum N_2O uptake we observed in swamp rivers (Table 3), to net emissions $\sim 4.8 \mu\text{mol m}^{-2} \text{d}^{-1}$.

375 The overall ranges of CH_4 and N_2O emissions from rivers of the ROC ($33\text{--}48705 \mu\text{mol CH}_4 \text{m}^{-2} \text{d}^{-1}$; $1\text{--}67 \mu\text{mol N}_2\text{O}$
380 $\text{m}^{-2} \text{d}^{-1}$) are somewhat wider than these earlier estimates for African and temperate rivers, the maximum values (Table
3) being around twice as high as previously reported. Nevertheless, 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
385 other available k_w parameterizations show five-fold variability (Barnes and Upstill-Goddard, 2011). Additionally, we
did not measure CH_4 ebullition fluxes. Borges et al (2015b) report an average 20% ebullition contribution to total
 CH_4 emissions from the Congo and Zambezi, although their maximum estimates are considerably higher than this,
and for some other tropical rivers and lakes ebullition is thought to account for 30–98% of total CH_4 emissions
(Melack et al., 2004; Bastkviken et al., 2010; Sawakuchi et al., 2014). The uncertainties related to k_w , notwithstanding,
our emissions estimates for CH_4 at least, are therefore probably conservative.

385 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 CH_4 and N_2O , as they are for CO_2 , although the potential
for significant sinks lends a note of caution for N_2O . Nevertheless, the wide ranges of emissions estimates for CH_4
and N_2O now available for African rivers clearly illustrate the difficulty in deriving representative total emissions
390 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
395 and land use changes are to be predicted and planned for. Lastly, the measurement of CH_4 and N_2O , data calibration
and the emissions estimates deriving would all benefit from agreed, standardized protocols. This is an issue that is yet
to be adequately addressed, not only for freshwaters but for aquatic systems more generally.

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Figure 3. (a) Dissolved nitrate vs dissolved ammonium and (b) percent nitrous oxide saturation vs DIN (NO₃⁻ + NH₄⁺) 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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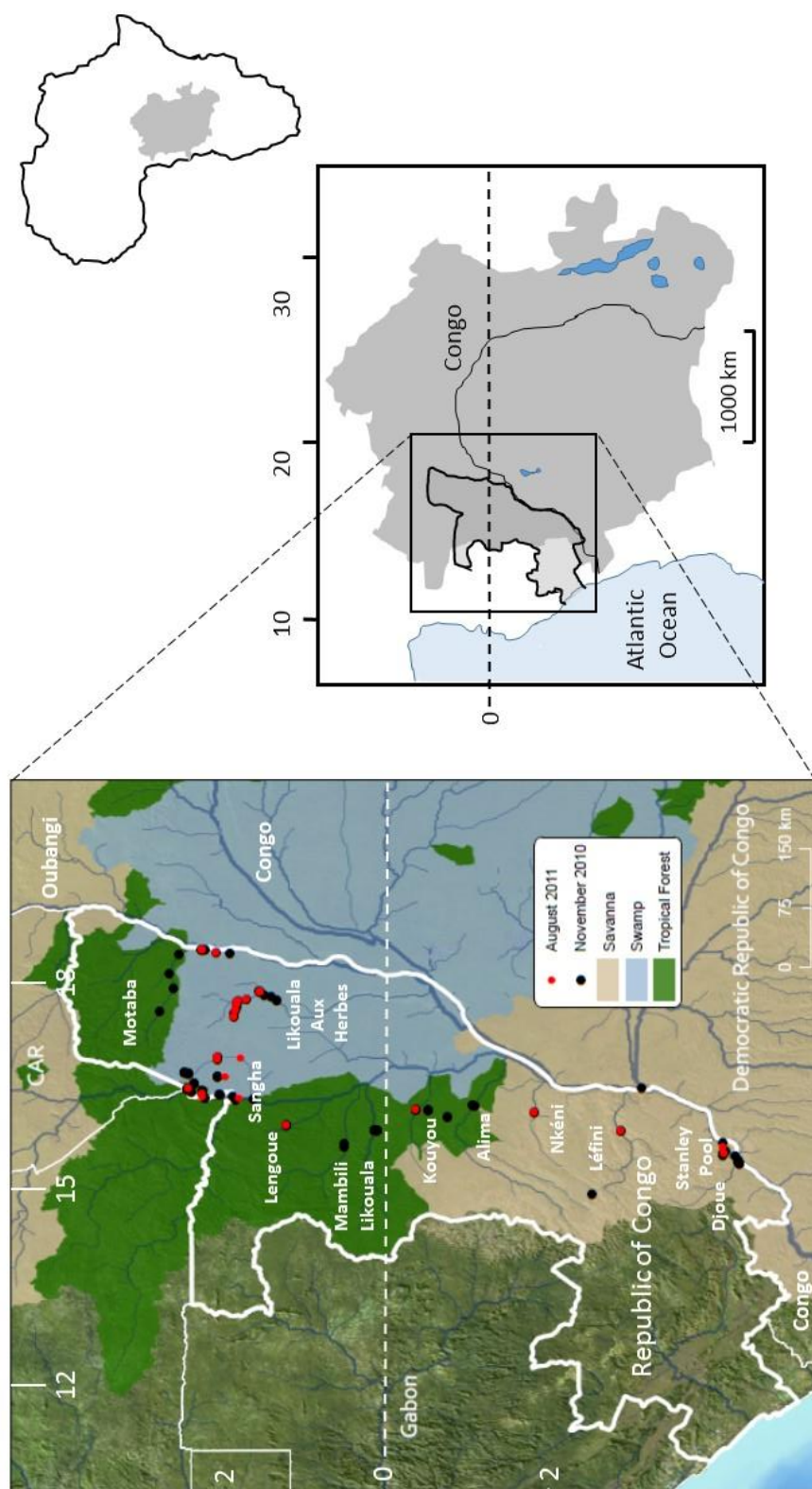


Figure 1.

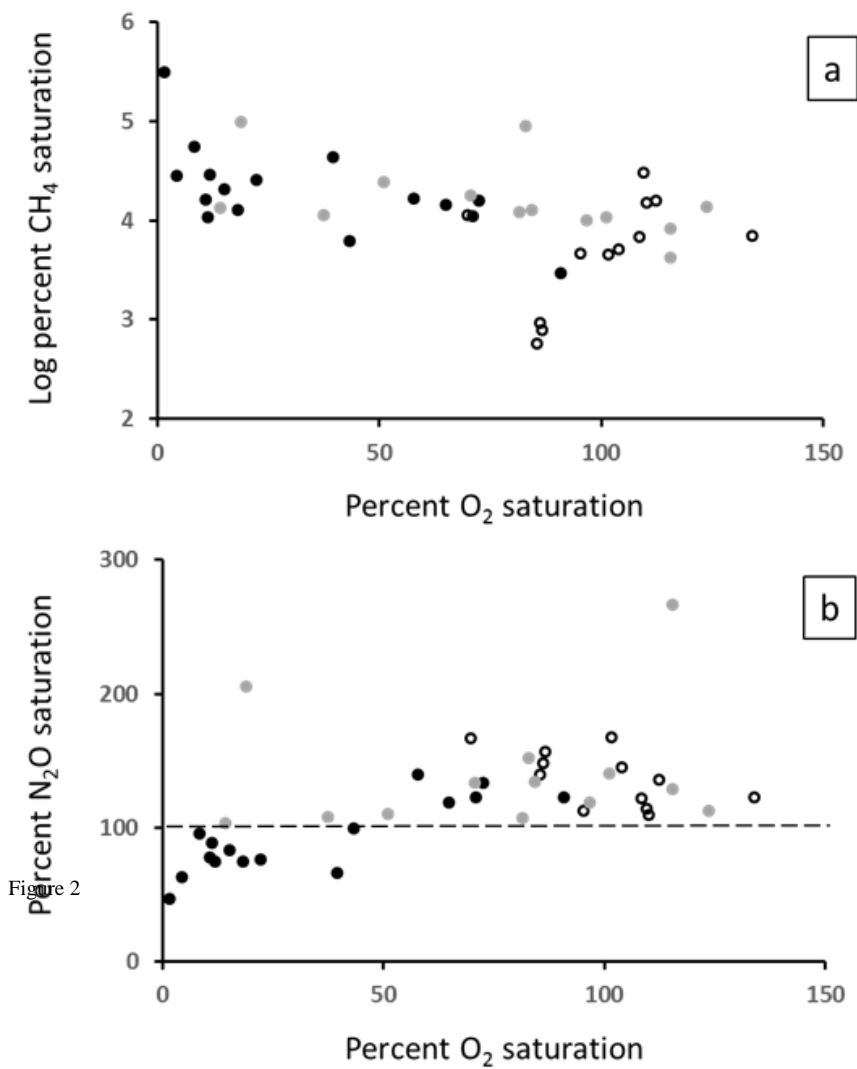


Figure 2

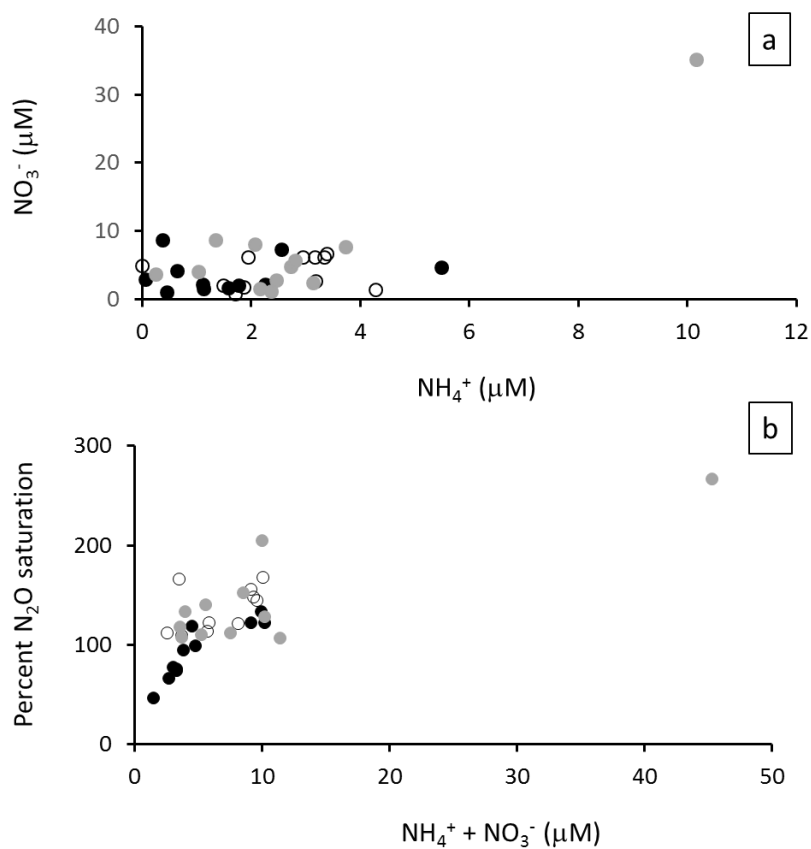


Figure 3



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).

River/Tributary	Catchment Area km ²	Discharge m ³ s ⁻¹	Rainfall mm
Congo	3500000	40600	1528
Alima	21030	1941	1709
Nkèni	8000	261	1662
Léfini	14000	400	1615
Djoue	5740	140	1547
Likouala aux-Herbes	25000	267	1622
Sangha	211120	1941	1511
Likouala Mossaka	69800	928	1689
Kouyou	16000	191	1566
Lengoué	12125	155	
Mambili	13700	161	
Motaba	772800	4000	



Table 2. Dissolved CH₄ and N₂O in Republic of Congo rivers

Land cover	Date	CH ₄ nmol L ⁻¹			CH ₄ saturation %			N ₂ O nmol L ⁻¹			N ₂ O saturation %		
		Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Savannah	All	15-793	204 ± 195	150	571-29721	7442 ± 73427	5444	7.6-11.9	8.9 ± 1.1	8.6	6-167	131 ± 19	122
	Wet	15-793	229 ± 141	153	571-29721	8505 ± 4111	5936	7.6-11.9	9.1 ± 2.2	9.0	106-167	136 ± 34	137
	Dry	66-243	144 ± 70	150	1660-8717	4888 ± 2878	5444	8.0-9.2	8.4 ± 0.5	8.2	113-130	119 ± 6	117
Swamp	All	17-9553	955 ± 2150	299	659-354444	35025 ± 79578	10913	3.2-15.3	7.2 ± 2.2	7.2	47-205	101 ± 30	98
	Wet	77-8394	1052 ± 1992	456	2945-309533	38485 ± 73488	16292	3.2-10.3	6.5 ± 2.1	5.7	47-139	92 ± 28	86
	Dry	17-9553	858 ± 2359	196	659-354444	31565 ± 87529	7090	5.3-15.2	7.9 ± 2.2	7.7	78-205	111 ± 29	109
Tropical Forest	All	11-2730	551 ± 784	321	440-98582	16966 ± 22958	11302	7.6-20.6	89.6 ± 3.3	8.4	103-266	135 ± 42	28
	Wet	110-2730	691 ± 852	331	4205-98582	21205 ± 24858	12729	7.6-20.6	10.0 ± 3.7	5.7	103-266	140 ± 47	128
	Dry	11-232	94 ± 103	67	440-82183	3319 ± 3360	2310	8.0-8.5	8.3 ± 0.2	8.3	108-132	120 ± 12	120



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.

Land cover	Date	CH ₄ emission flux (μmol m ⁻² d ⁻¹)			N ₂ O emission flux (μmol m ⁻² d ⁻¹)								
		Raymond et al. (2013)	Aufdenkampe et al. (2011)		Raymond et al. (2013)	Aufdenkampe et al. (2011)							
Savannah	All	61-4030	1027 ± 997	752	47-3081	785 ± 762	575	3-25	11 ± 7	8	3-19	8 ± 5	6
	Wet	61-4030	1159 ± 1157	876	47-3081	887 ± 885	670	3-25	12 ± 7	13	3-19	9 ± 5	10
	Dry	321-855	595 ± 356	602	245-654	455 ± 272	460	5-11	7 ± 2	6	4-8	5 ± 2	5
Swamp	All	74-48705	4856 ± 10964	1512	56-37245	3713 ± 8384	1196	(-19)-41	1 ± 11	(-1)	(-15)-31	1 ± 9	(-1)
	Wet	378-42798	5349 ± 10160	2313	289-32728	4090 ± 7769	1769	(-19)-15	(-3) ± 10	(-5)	(-15)-12	(-2) ± 8	(-4)
	Dry	74-48705	4363 ± 12029	985	56-37245	3336 ± 9198	753	(-8)-41	4 ± 11	3	(-6)-31	3 ± 9	3
Tropical Forest	All	43-13911	2795 ± 4000	1624	33-10638	2318 ± 3059	1242	1-67	13 ± 16	9	1-51	10 ± 13	7
	Wet	549-13911	3512 ± 4387	1677	420-10638	2686 ± 3324	1282	1-67	15 ± 19	10	1-51	11 ± 14	7
	Dry	43-1167	465 ± 526	326	33-892	356 ± 403	249	3-11	7 ± 3	7	3-8	15 ± 3	5



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 (B) refers to emissions estimated using the relationship of Raymond et al. (2013).

River	CH ₄ emission flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)		N ₂ O emission flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)		Reference
	Range	Mean	Range	Mean	
Conoé, Ivory Coast		288 ± 107			Koné et al (2010)
Bia, Ivory Coast		155 ± 38			Koné et al (2010)
Tanoé, Ivory Coast		241 ± 91			Koné et al (2010)
Ivory Coast (all)	25-1187				Koné et al (2010)
Oubangui	38-350		0.6-5.7		Bouillon et al (2012)
Congo		14296 18534		15 (A) 19 (R)	Borges et al (2015b)
Ivory Coast		1003 1667		(A) (R)	Borges et al (2015b)
Ogooué		2115 4668		13 (A) 28 (R)	Borges et al (2015b)
Niger		502 583		4 (A) 5 (R)	Borges et al (2015b)
Zambezi		8348 13597		2 (A) 2 (R)	Borges et al (2015b)
Betsiboka		1305 3493		4 (A) 9 (R)	Borges et al (2015b)
Rianila		1923 4537		5 (A) 12 (R)	Borges et al (2015b)
Tana		568 604		6 (A) 6 (R)	Borges et al (2015b)
Athi-Galana-Sabaki		1156 1374		16 (A) 19 (R)	Borges et al (2015b)
Nyong		18019 28579		(A) (R)	Borges et al (2015b)