The riverine source of CH_4 and N_2O from the Republic of Congo, Western Congo Basin

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

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

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

Abstract. We report concentrations of dissolved CH_4, N_2O, O_2, NO_3^- and NH_4^+, and corresponding CH_4 and N_2O 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 (ROC), during November 2010 (41 samples; "wet season") and August 2011 (25 samples; "dry season"; CH_4 and N_2O only). Dissolved inorganic nitrogen (DIN: wet season; $NH_4^+ + NO_3^-$) was dominated by NO_3^- (63 ± 19% of DIN), total DIN concentrations (1.5-45.3 µmol L^{-1}) being consistent with negligible agricultural, domestic and industrial sources. 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%). Dissolved CH_4 and N_2O were within previously reported ranges for sub-Saharan African rivers. While CH_4 was always super-saturated (11.2 - 9553 nmol L^{-1}; 440-354400%), N_2O 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 CH_4 but can be small sources or sinks for N_2O. Dry season concentration means and ranges of CH_4 and N_2O were indistinguishable for all three land types and seasonal differences in means and ranges were not significant for N_2O for any land type or for CH_4 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 CH_4 was significantly higher in the wet season, possibly reflecting CH_4 derived from floating macrophytes during flooding and/or enhanced methanogenesis in adjacent flooded soils. Swamp rivers exhibited both low (47%) and high (205%) N_2O 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 N_2O were not significantly different. In swamp and forest rivers % O_2 co-varied negatively with log % CH_4 and positively with % N_2O. The strong positive N_2O - O_2 correlation in swamp rivers was coincident with strong N_2O and O_2 under-saturation, indicating N_2O consumption by sediment denitrification. In savannah rivers persistent N_2O super-saturation and a negative N_2O - O_2 correlation may indicate N_2O production mainly by nitrification, consistent with a stronger correlation between N_2O and NH_4^+ than between N_2O and NO_3^-. Our range in CH_4 and N_2O emissions fluxes (33-48705 µmol CH_4 m^{-2} d^{-1}; 1-67 µmol N_2O m^{-2} d^{-1}), is within the range previously estimated for sub-Saharan African rivers but it includes uncertainties deriving from our use of "basin-wide" values for CH_4 and N_2O gas transfer velocities. Even so, because we did not account for any contribution from ebullition, which for CH_4 is likely to be at least 20%, our emissions estimates for CH_4 are probably conservative.

1 Introduction

Methane (CH_4) and nitrous oxide (N_2O) accounted for 17% and 6% respectively, of the total atmospheric radiative forcing by well-mixed greenhouse gases in 2011 (Myhre et al., 2013). CH_4 also impacts tropospheric oxidising

capacity, O_3 and OH radical and is a source of stratospheric O_3 (Myhre et al., 2013) while N_2O is the largest cause of stratospheric O_3 loss, via NO production (Ravishankara et al., 2009). Since the onset of the industrial revolution, tropospheric CH_4 and N_2O have substantially increased but their growth rates have varied. The early 1980s to the mid-2000s saw an overall decline in tropospheric CH_4 growth (Dlugokencky et al., 2009; 2011), which 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) implies this to be a consequence of increased biogenic emissions, particularly in the tropics, where these increased emissions have been linked to an expansion of tropical wetlands in response to positive rainfall anomalies (Nisbet et al., 2016), and/or growing emissions from agricultural sources (Schaefer et al., 2016). The mean CH_4 tropospheric dry mole fraction in 2011, 1803 ± 2 ppbv, was 150% above the pre-industrial value (Hartmann et al., 2013). Of particular note in regard to N_2O, the availability of sufficiently reliable data on the anthropogenic components of river, estuary and coastal zone sources resulted in a change in their classification in the IPCC AR4 synthesis, from "natural" to "anthropogenic" (Denman et al., 2007). A small but significant seasonal to inter-annual variability in N_2O growth rate may reflect climate-driven changes in soil N_2O (Thompson et al., 2013). The current rate of N_2O 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 sources of tropospheric CH_4 and N_2O is small but increasing. The global freshwater CH_4 source could be ~10^{13}-10^{14} g yr^{-1} (Bastviken et al., 2011; Kirschke et al., 2013; Stanley et al., 2016). This order of magnitude range largely reflects a discrepancy between "top-down" approaches based on atmospheric inversions (e.g. Kirschke et al., 2013) and "bottom-up" estimates that necessitate the 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 CH_4 source can be evaluated in the light of natural and total global CH_4 source estimates of 179-484 x 10^{12} g yr^{-1} and 526-852 x 10^{12} g yr^{-1} respectively (Kirschke et al., 2013). Quantifying the global freshwater contribution thus has high inherent uncertainty but based on these estimates it could be ~ 2-56 % of natural CH_4 emissions and ~1-19% of total CH_4 emissions. Converting these to CO_2 equivalents based on a 100 year Global Warming Potential gives ~0.65 x 10^{15} g C (CO_2 equivalent) y^{-1} (Bastviken et al., 2011), a significant offset to the combined terrestrial and oceanic carbon sink ~ 5.5 x 10^{15} g C yr^{-1} (Le Quéré et al., 2015). A global estimate of river N_2O emissions based on microbial production from agriculturally-derived nitrogen is ~ 6.8 x 10^{11} g yr^{-1}, around 10% of the total global anthropogenic N_2O 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 10^{12} g CH_4 and ~10^{10} g N_2O for twelve large river systems in sub-Saharan Africa, including the three largest by catchment area (Congo, Niger, Zambezi). Notably, their CH_4 estimate is 5 times higher than was previously attributed to all tropical rivers (Bastviken et al., 2011) and both estimates are significant at the continental scale given that reported total African emissions are ~ 66 ± 35 x 10^{12} g CH_4 yr^{-1} and 3.3 ± 1.3 x 10^{12} g N_2O yr^{-1} (Valentini et al., 2014).

The potential scale of CH_4 and N_2O emissions from tropical freshwaters and their attendant uncertainties warrant

further investigation. In this paper we present and discuss concentrations of dissolved CH_4, N_2O, O_2, NO_3^- and NH_4^+, and corresponding CH_4 and N_2O 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 ~3.8×10^6 km^2 (~ 12% of the total African land mass; Fig. 1) and incorporating the world's fourth largest wetland area ~3.6×10^5 km^2 (Laporte et al., 1998). The Congo's annual freshwater discharge is the world's second largest at ~1300 km^3 (Borges et al., 2015b), 50% of all freshwater flow from Africa to the Atlantic Ocean. Rivers and streams in the Congo Basin have a total open water surface area ~2.7×10^4 km^2 (Raymond et al., 2013). The climate is warm (mean annual temperature 24.8 ± 0.8 °C) and humid with an annual rainfall ~1800 mm (Laraque et al., 2001).

We sampled the Congo main stem, 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 CH_4, N_2O, O_2, NO_3^- and NH_4^+ analysis, during November 2010 (41 samples) and August 2011 (25 samples; CH_4 and N_2O 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 poisoned with 25 µl 0.1 M $HgCl_2$ 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 CH_4 and N_2O were analysed by single phase equilibration gas chromatography (Shimadzu GC 14-B), with flame ionisation detection of CH_4 and electron capture detection of N_2O (Upstill-Goddard et al., 1996). Routine calibration was with a mixed secondary standard (361 ppbv N_2O, 2000 ppbv CH_4) prepared by pressure dilution with ultra-high purity N_2 (Upstill-Goddard et al., 1990). Absolute calibration was against a mixed primary standard (10ppmv N_2O, 5ppmv CH_4) with a certified accuracy of ± 1 % (BOC Special Gases, UK). Overall analytical precisions (1σ) for N_2O and CH_4, established via multiple analysis (n = 15) of the secondary standard, were both ± 1%.

Temperature, dissolved O_2 and atmospheric pressure were measured *in-situ* using a handheld multi-parameter probe (YSI Pro-Plus, YSI UK Ltd). Quoted measurement accuracies are: ± 0.2 °C; ± 2 % dissolved O_2; ± 0.002 bar. Samples for dissolved NH_4^+ and NO_3^- were filtered on collection (Whatman 0.7 µm GF/F; precombusted at 550 °C for 8 h), directly into clean glass vials and stored acidified (pH 2) at 4 °C in the dark for several weeks 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 ± 1% for both. Technical and logistical issues precluded the collection of any dissolved O_2, NH_4^+ or NO_3^- data during August 2011 (dry season) and some NO_3^- and NH_4^+ data during November 2010 (wet season).

Emission fluxes, F (mol m^{-2} d^{-1}), of CH_4 and N_2O were estimated using $F = k_w L \Delta p$, where k_w is the transfer velocity of CH_4 or N_2O (cm hr^{-1}), L is the solubility of CH_4 or N_2O (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 CO_2 in the Congo. Raymond et al. (2013) estimated a basin-wide k_w of 5.2 m d^{-1} for CO_2, using hydraulic equations involving basin slope and flow velocity. The uncertainty in this estimate is ~ ± 10% (Raymond et al., 2013). In contrast Aufdenkampe et al. (2011) applied constant k_w values for CO_2 in streams (< 100 m wide: 3.0 m d^{-1}) and in rivers (>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 ~3.9 m d^{-1} for CO_2. We converted these estimates to k_w for CH_4 and N_2O by multiplying by $(Sc/470.7)^{-0.5}$, where 470.7 is the Schmidt number of CO_2 in freshwater, and Sc is the Schmidt number of CH_4 or N_2O (Sc_{CH4}=486.8; Sc_{N2O}=476.9), assuming an ambient temperature of 25°C (Wanninkhof, 1992). The resulting k_w estimates are 5.1 and 3.9 m d^{-1} for CH_4 and 5.2 and 4.0 m d^{-1} for N_2O. Resulting emissions estimates are consequently ~30% higher based on Raymond et al. (2013). Using both sets of k_w estimates facilitates a direct comparison with the largest study of CH_4 and N_2O 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 mixing ratios of CH_4 (1797 ppbv) and N_2O (323 ppbv) for the year 2010 (http://cdiac.esd.ornl.gov/tracegases.html).

3 Results

While CH_4 and N_2O data are available for all samples, dry season data are not available for dissolved O_2, NO_3^- or

NH_4^+ and wet season DIN (NO_3^- + NH_4^+) is only reported for samples for which both NO_3^- and NH_4^+ are available. Source data for this paper are available as supplementary material (Table S1).

3.1 Dissolved O_2 and DIN

In wet season swamp samples dissolved O_2 varied between mildly under-saturated and very strongly under-saturated (Fig. 2). The mean (36 ± 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 ± 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 ± 17%, range 70-135 %; Fig. 2).

Low wet season concentrations of dissolved inorganic nitrogen (DIN) components (Fig. 3) are consistent with agricultural, domestic and industrial DIN sources all being negligible (Clark and Decalo, 2012). The means and ranges of total DIN (NO_3^- + NH_4^+) did not differ significantly between any of the three river "types" (mean savannah 6.8 ± 2.8 μmol l^{-1}; range 2.5-10.1 μmol l^{-1}; n=10; mean swamp 5.1 ± 3.1 μmol l^{-1}, range 1.5-10.2 μmol l^{-1}; n= 11; mean forest 9.4 ± 11.2.μmol l^{-1}, range 1.8-45.3 μmol l^{-1}; n=12), in contrast to the situation for dissolved O_2. Differences in NO_3^--N were also not significant (mean savannah 4.1 ± 2.3 μmol l^{-1}, range 0.8-6.7 μmol l^{-1}, n=11; mean swamp 3.6 ± 2.1 μmol l^{-1}, range 1.0-8.8 μmol l^{-1}, n= 16; mean forest 7.1 ± 9.2 μmol l^{-1}, range 1.2-35.1 μmol l^{-1}; n=12) 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 samples, the mean NO_3^- contribution to DIN was 63 ± 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 nmol L^{-1}; 440-354400% saturation). N_2O 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 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-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 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 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) 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 nmol l^{-1} (2221 - 38719 % saturation) in three Ivory Coast rivers (Koné et al., 2010), 25 - 505 nmol l^{-1} (850 - 21700 % saturation) in the Tana river, Kenya, (Bouillon et al., 2009) and 22-71430 nmol l^{-1} in the Congo (Borges et al., 2015a). For concurrent

measurements of CH_4 and N_2O Bouillon et al. (2012) report 74 - 280 nmol CH_4 l^{-1} (3450 – 13200% saturation) and 6.2 - 9.6 nmol N_2O l^{-1} (112-165% saturation) in the Oubangui, a major Congo tributary, Teodoru et al. (2015) found 7-12127 nmol CH_4 l^{-1} and 2.0-11.4 nmol N_2O l^{-1} at stations along the Zambezi and Borges et al. (2015b) quote a range of 2-62966 nmol CH_4 l^{-1} (mean: 2205 nmol l^{-1}) and 0.2-85.4 nmol N_2O l^{-1} (mean: 9.2 nmol l^{-1}) across 12 sub-Saharan river basins, including those of the Congo, Zambezi and Niger.

Considering the complete data set, CH_4 was inversely correlated with both N_2O and O_2 (Fig. 2). Highest CH_4 coincident with lowest N_2O and O_2 occurred in swamp rivers and lowest CH_4 coincident with highest N_2O and O_2 was observed in forest rivers, while 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_2O 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) and while there was a stronger positive correlation between % N_2O 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). Conversely, for savannah rivers we found a positive correlation between log % CH_4 and % O_2 (R^2 = 0.23; n= 12) and a negative correlation between % N_2O and % O_2 (R^2 =0.35, n=12). N_2O co-varied positively with both NO_3^- and NH_4^+ (Fig. 3). For the complete data set the correlations were weak (N_2O vs NO_3^-, R^2 = 0.28, n = 59; N_2O vs NH_4^+, R^2 = 0.23, n = 40) but for all three river types individually, with the exception of N_2O vs NH_4^+ in savannah rivers, the correlations were stronger and for all NO_3^- was a stronger predictor of N_2O (N_2O 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_2O 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_2O emission fluxes

Table 3 summarises ranges, means and medians of CH_4 and N_2O emission fluxes using k_w derived from Raymond et al. (2013) and Aufdenkampe et al. (2011). Fluxes broadly followed the distribution of concentrations, for CH_4 being lowest overall in savannah rivers and highest in swamp and forest rivers and for N_2O being 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_2O. However, swamp rivers were predominantly a N_2O sink during the wet season (11 of 16 individual flux estimates) and predominantly a N_2O source during the dry season (10 of 16 individual flux estimates). As far as we are aware the wet season sink for N_2O in swamp rivers is the first such reported for African rivers.

4 Discussion

4.1. Sources of CH_4 and N_2O

The concentrations of dissolved CH_4 and N_2O 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.

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 CH_4 produced in underlying river sediments, in adjacent floodplain soils and in adjacent wetlands, into aerated river water. Previous

work showed that the CH_4 supply from groundwater to African rivers is generally comparatively low (Balagizi et al., 2015; Borges et al., 2015b) and that the spatial distribution of dissolved CH_4 is more closely related to the wetland distribution within the catchment, wetland water deriving principally from upland runoff (Borges et al., 2015a). In the Congo basin floating macrophytes, both in the centre of river channels and fringing their edges, are important additional sources of CH_4 (Borges et al., 2015a). These sources promote a unidirectional CH_4 flow, towards small and large river channels (Borges et al., 2015a). Where these river channels are shallow and have low levels of surface turbulence, as in the examples studied here, the CH_4 diffusion term evidently exceeds combined CH_4 losses via oxidation and water-to-air exchange, thereby further promoting the accumulation of high river CH_4 concentrations.

In addition to methanogenesis in fully anoxic sediment and soils, CH_4 production can also occur in "anoxic microsites" within oxic soils (e.g. Teh et al., 2005; von Fisher & 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 relating to soil carbon age and composition (Bridgham 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. 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, CH_4 is subject to variable and rapid aerobic and anaerobic microbial oxidation (Megonigal et al., 2004); CH_4 loss rates have been variously estimated at between a few percent and >100% of the rate of methanogenesis (Bussmann, 2013; Shelley et al., 2015). Despite such potentially high losses, water to air exchange by ebullition and by turbulent diffusion driven by wind stress, water depth and flow velocity (Raymond and Cole, 2001) is usually considered the major CH_4 loss term, with ebullition frequently considered the dominant of these two mechanisms (Stanley et al., 2016). Despite this complexity of dissolved CH_4 cycling in rivers, it is nevertheless informative to speculate on our principal observations in the context of potential CH_4 sources and sinks.

The first notable feature of our results is the contrasting relationship between CH_4 and O_2 in swamp and forest rivers (negative) and in savannah rivers (positive) (Fig. 2a). Dissolved O_2 in rivers is primarily driven by the balance 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 super-saturations as high as 150% (Li et al., 2010). The overall positive relationship between CH_4 and O_2 in savannah rivers (Fig 2a.) could, at least in part, reflect high macrophyte-related productivity, which can give rise to positive relationships by direct CH_4 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 O_2 (Caraco et al., 2006). Further inspection of the data shows that the highest dissolved O_2 saturation found in savannah rivers (134%) deviates from the general CH_4 vs O_2 trend (Fig. 2a). This sample was collected close to an area of rapids in the Congo main stem, in the vicinity of Pool Malebo (Formerly known as Stanley Pool) (Fig. 1) where other samples were also O_2 super-saturated. Intense water-air exchange in this region via increased turbulence would tend to enhance dissolved O_2 (Li et al., 2010) while depleting dissolved CH_4. To summarise, notwithstanding possible additional CH_4 losses via oxidation, the CH_4 vs O_2 relationship in savannah rivers (Fig. 2a) could be explained by net macrophyte production imprinted by water-air gas exchange. The inverse of this relationship for swamp and forest rivers (Fig. 2a) was similarly reported for the Zambezi and Amazon Basins, for the latter in fast flowing waters (Teodoru et al., 2015; Richey et al., 1988; Devol et al., 1990). Again, high gas exchange rates are plausible, especially for the small number of tropical forest samples for which O_2

was close to or in excess of 100% (Fig. 2a). For the majority of samples that were O_2 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 CH_4, low O_2 groundwater but another possibility is that this relationship is the aggregate of this and several of the other processes previously discussed.

A second important aspect of the overall CH_4 distributions is that swamp and forest river CH_4 was highest during the wet season, whereas savannah samples revealed no such inter-seasonal contrast (Table 2). The constancy of CH_4 in savannah rivers might well reflect the buffering of seasonal river discharge by the 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 (Bridgham 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 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_2O 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_2OH), followed by NO_2^- oxidation to NO_3. Following the first stage, N_2O can be produced through various routes: nitrifier nitrification ($NH_2OH \rightarrow N_2O$), nitrifier denitrification ($NO_2^- \rightarrow NO \rightarrow N_2O$) and nitrification-coupled denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O$) (Kool et al., 2011). Heterotrophic denitrification, in which NO_3^- is the terminal electron acceptor ($NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2$), 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_2O 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_2O 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_2O concentrations for any land cover type, higher N_2O 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 complex balance between the principal sites (groundwater and in-stream) and mechanisms of N_2O cycling, as evidenced by the variable relationships between N_2O, O_2 and DIN we observed. For example, we found both positive and negative relationships between N_2O and O_2 (Fig. 2b). Sediment processes and water concentrations are evidently closely coupled in tropical catchments (Harrison and Matson, 2003) and the strong positive correlation

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^- 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 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 μmol 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 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 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).

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, 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

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 to 1187 μmol CH_4 m^{-2} d^{-1}, while for the Oubangui Bouillon et al. (2012) found 38 to 350 μmol CH_4 m^{-2} d^{-1} and 0.6 to 5.7 μmol N_2O m^{-2} d^{-1}. For 12 sub-Saharan African rivers Borges et al. (2015b) give ranges of 0 to 274,600 mmol CH_4 m^{-2} d^{-1} and -30 to 299 mmol N_2O m^{-2} d^{-1} using k_w from Aufdenkampe et al. (2011), and 0 to 461,967 mmol CH_4 m^{-2} d^{-1} and -37 to 377 mmol N_2O m^{-2} d^{-1} using k_w from Raymond et al. (2013). For comparison, CH_4 emissions estimated for the Amazon River were 4625 to 12562 μmol m^{-2} d^{-1} (Bartlett et al. 1990) and the range for CH_4 in temperate rivers is ~0 to 22000 μmol m^{-2} 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 to 6.0 μmol m^{-2} d^{-1} for the Amazon River and floodplain while Soued et al. (2016) found N_2O fluxes in Canadian boreal rivers to be highly variable across ecosystem types and seasons, ranging from net uptake ~ 3.3 μmol m^{-2} d^{-1}, somewhat lower that the maximum N_2O uptake we observed in swamp rivers (Table 3), to net emissions ~ 4.8 μmol m^{-2} d^{-1}.

The overall ranges of CH_4 and N_2O emissions from rivers of the ROC (33 to 48705 mmol CH_4 m^{-2} d^{-1}; 1 to 67 mmol N_2O 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 k_w is a necessity that takes no account of spatial and temporal k_w variability, that our emissions based on k_w derived from Raymond et al. (2013) are 30% higher than those derived from Aufdenkampe et al. (2011) and that other available k_w 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; Bastviken et al., 2011; Sawakuchi et al., 2014). The uncertainties related to k_w notwithstanding, our emissions estimates for CH_4 at least, are therefore probably conservative.

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 given both the comparatively small size of the available data set and the various approaches that are typically used to derive these emissions. This applies not only to African rivers, but to tropical rivers in general and indeed to freshwaters globally. At least equally important is an insufficiently mature understanding of the processes that link emissions to the environmental controls of process rates and their temporal variability, and to river catchment characteristics that include sources and seasonality of organic inputs and variability in the balance between baseflow and surface runoff. Our understanding of these interactions must improve if the system responses to future climate and land use changes are to be predicted and planned for. Lastly, the measurement of CH_4 and N_2O, 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 CH_4 or N_2O but this is now being addressed via an international SCOR (Scientific Committee on Oceanic Research) Working Group (WG-143: https://portal.geomar.de/web/scor-wg-143/home), which is engaged in inter-laboratory calibration and the dissemination of high quality calibration gases. WG-143 welcomes additional interest from the wider aquatic CH_4 and N_2O research community.

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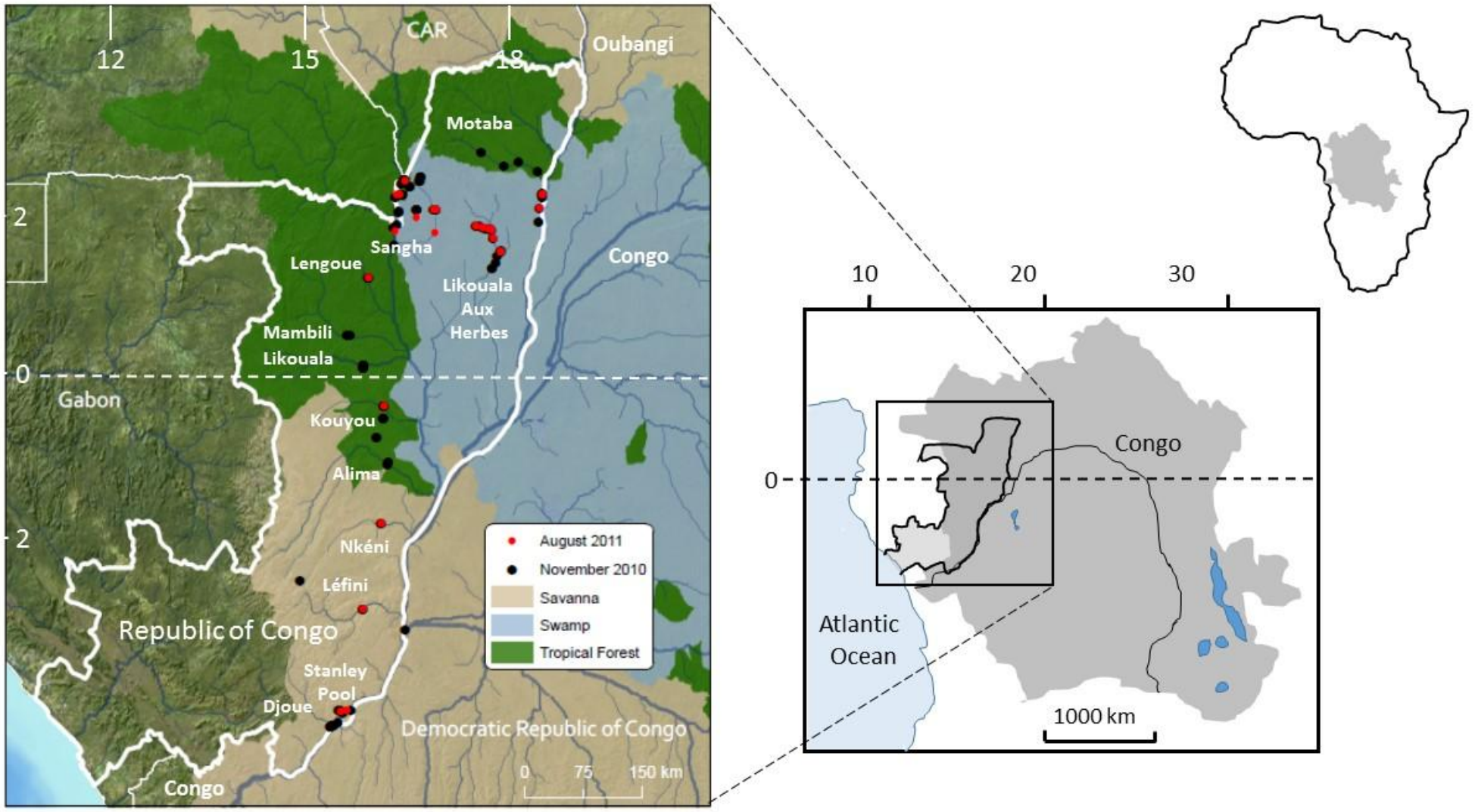
12
15
18
CAR
Oubangi
Motaba
2
Sangha
Lengoue
Congo
Likouala
Aux
Herbes
Mambili
Likouala
0
Gabon
Kouyou
Alima
2
Nkéni
Léfini
August 2011
November 2010
Savanna
Swamp
Tropical Forest
Republic of Congo
Stanley
Pool
Djoue
Democratic Republic of Congo
Congo
0
75
150 km
10
20
30
Congo
0
Atlantic
Ocean
1000 km

Figure 1.

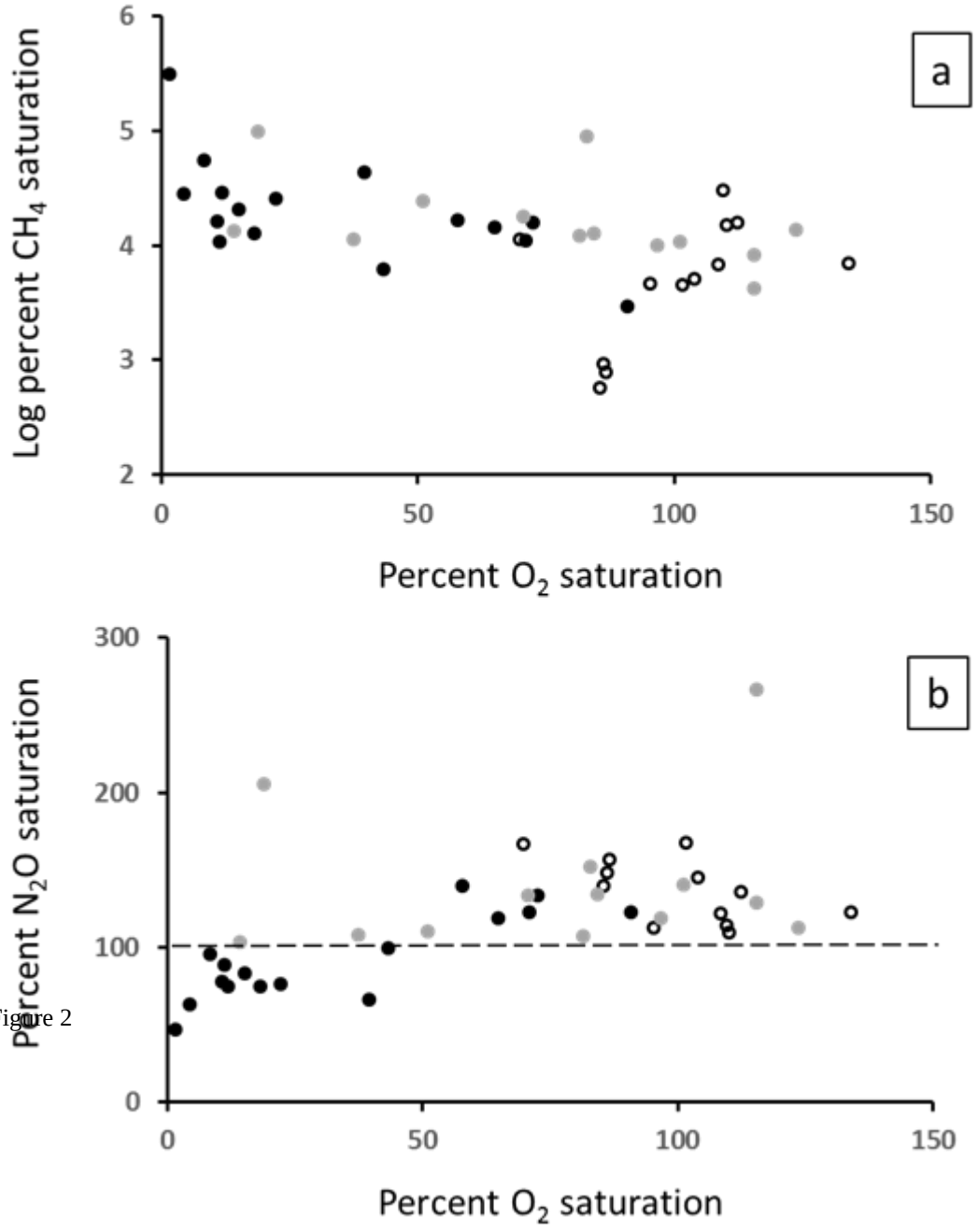
a
Log percent CH_4 saturation
6
5
4
3
2
0
50
100
150
Percent O_2 saturation
b
Percent N_2O saturation
300
200
100
0
0
50
100
150
Percent O_2 saturation

Figure 2

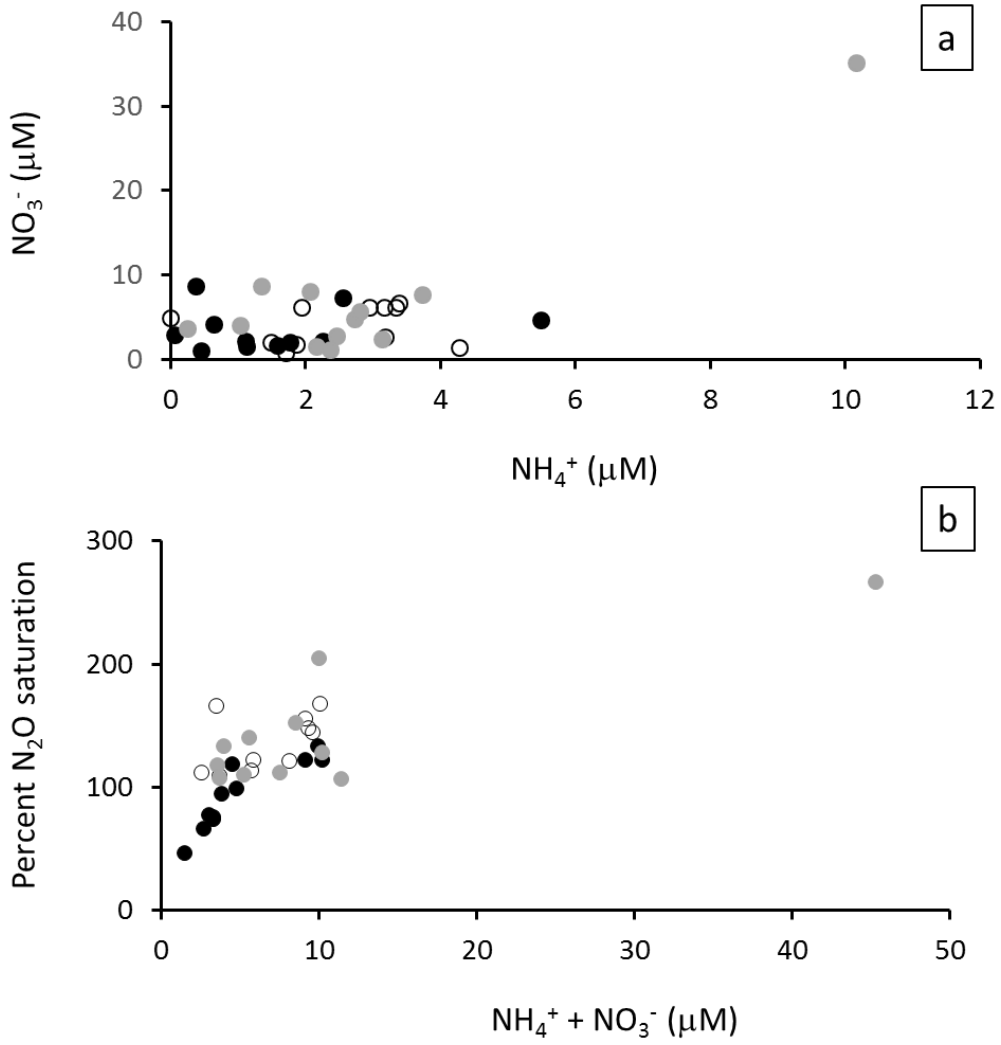
a
40
30
20
10
0
NO_3^- (μM)
0
2
4
6
8
10
12
NH_4^+ (μM)
b
300
200
100
0
Percent N_2O saturation
0
10
20
30
40
50
$NH_4^+ + NO_3^-$ (μM)

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 CH_4 and N_2O in Republic of Congo rivers

Land cover	Date	CH_4 nmol L^{-1}			CH_4 saturation %			N_2O nmol L^{-1}			N_2O 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 CH_4 and N_2O 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_2O emission flux (μmol m^{-2} d^{-1})					
		Raymond et al. (2013)			Aufdenkampe et al. (2011)			Raymond et al. (2013)			Aufdenkampe et al. (2011)		
		Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
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 CH_4 and N_2O 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).

	CH_4 emission flux ($\mu mol\ m^{-2}\ d^{-1}$)		N_2O emission flux ($\mu mol\ m^{-2}\ d^{-1}$)			Reference
River	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		15	(A)	
		18534		19	(R)	Borges et al (2015b)
Ivory Coast		1003			(A)	
		1667			(R)	Borges et al (2015b)
Ogooué		2115		13	(A)	
		4668		28	(R)	Borges et al (2015b)
Niger		502		4	(A)	
		583		5	(R)	Borges et al (2015b)
Zambezi		8348		2	(A)	
		13597		2	(R)	Borges et al (2015b)
Betsiboka		1305		4	(A)	
		3493		9	(R)	Borges et al (2015b)
Rianila		1923		5	(A)	
		4537		12	(R)	Borges et al (2015b)
Tana		568		6	(A)	
		604		6	(R)	Borges et al (2015b)
Athi-Galana-Sabaki		1156		16	(A)	
		1374		19	(R)	Borges et al (2015b)
Nyong		18019			(A)	
		28579			(R)	Borges et al (2015b)