

## TITLE: An initial investigation into the organic matter biogeochemistry of the Congo River

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## ABSTRACT:

The Congo River, which drains pristine tropical forest and savannah and is the second largest exporter of terrestrial carbon to the ocean, was sampled in early 2008 to investigate organic matter (OM) dynamics in this historically understudied river basin. We examined the elemental (%OC, %N, C:N), isotopic ( $\delta^{13}\text{C}$ ,  $\delta^{14}\text{C}$ ,  $\delta^{15}\text{N}$ ) and biochemical composition (lignin phenols) of coarse particulate ( $>63\ \mu\text{m}$ ; CPOM) and fine particulate ( $0.7\text{--}63\ \mu\text{m}$ ; FPOM) OM and DOC,  $\delta^{13}\text{C}$ ,  $\delta^{14}\text{C}$  and lignin phenol composition with respect to dissolved OM ( $<0.7\ \mu\text{m}$ ; DOM) from five sites in the Congo River Basin. At all sample locations the organic carbon load was dominated by the dissolved phase ( $\sim 82\text{--}89\%$  of total organic carbon) and the total suspended sediment load was principally fine particulate material ( $\sim 81\text{--}91\%$  fine suspended sediment). Distinct compositional and isotopic differences were observed between all fractions. Congo CPOM, FPOM and DOM all originated from vegetation and soil inputs as evidenced by elemental, isotopic and lignin phenol data, however FPOM was derived from much older carbon pools (mean  $\delta^{14}\text{C} = -62.2 \pm 13.2\text{‰}$ ,  $n = 5$ ) compared to CPOM and DOM (mean  $\delta^{14}\text{C} = -55.7 \pm 30.6\text{‰}$ ,  $n = 4$  and  $-73.4 \pm 16.1\text{‰}$ ,  $n = 5$  respectively). The modern radiocarbon ages for DOM belie a degraded lignin compositional signature (i.e. elevated acid:aldehyde ratios (Ad:Al) relative to CPOM and FPOM), and indicate that the application of OM degradation patterns derived from particulate phase studies to dissolved samples needs to be reassessed: these elevated ratios are likely attributable to fractionation processes during solubilization of plant material. The relatively low DOM carbon-normalized lignin yields ( $\sim 0.67\text{--}1.12\ \text{mg}(100\ \text{mg OC})^{-1}$ ) could also reflect fractionation processes, however, they have also been interpreted as an indication of significant microbial or algal sources of DOM. CPOM appears to be well preserved higher vascular plant material as evidenced by its modern radiocarbon age, elevated C:N ( $17.2\text{--}27.1$ ) and  $\delta^8$  values ( $4.56\text{--}7.59\ \text{mg}(100\ \text{mg OC})^{-1}$ ). In relation to CPOM, the aged FPOM fraction ( $320\text{--}580\ \text{ybp}$   $^{14}\text{C}$  ages) was comparatively degraded, as demonstrated by its nitrogen enrichment (C:N  $11.4\text{--}14.3$ ), lower  $\delta^8$  ( $2.80\text{--}4.31\ \text{mg}(100\ \text{mg OC})^{-1}$ ) and elevated lignin Ad:Al values similar to soil derived OM. In this study we observed little modification of the OM signature from sample sites near the cities of Brazzaville and Kinshasa to the head of the estuary ( $\sim 350\ \text{km}$ ) highlighting the potential for future studies to assess seasonal and long-term OM dynamics from this logistically feasible location and derive relevant information with respect to OM exported to the Atlantic Ocean. The relative lack of OM data for the Congo River Basin highlights the importance of studies such as this for establishing baselines upon which to gauge future change.

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