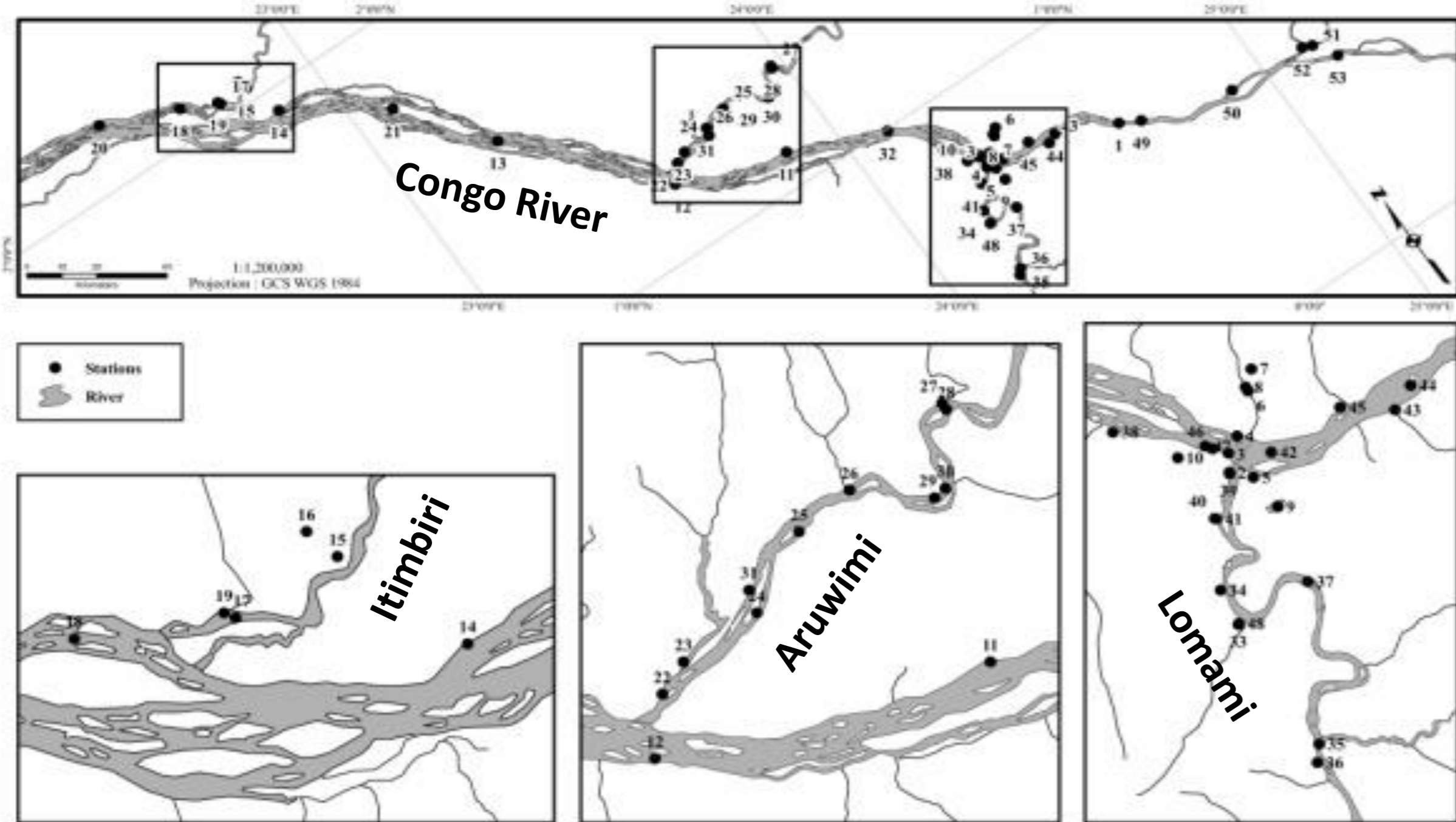
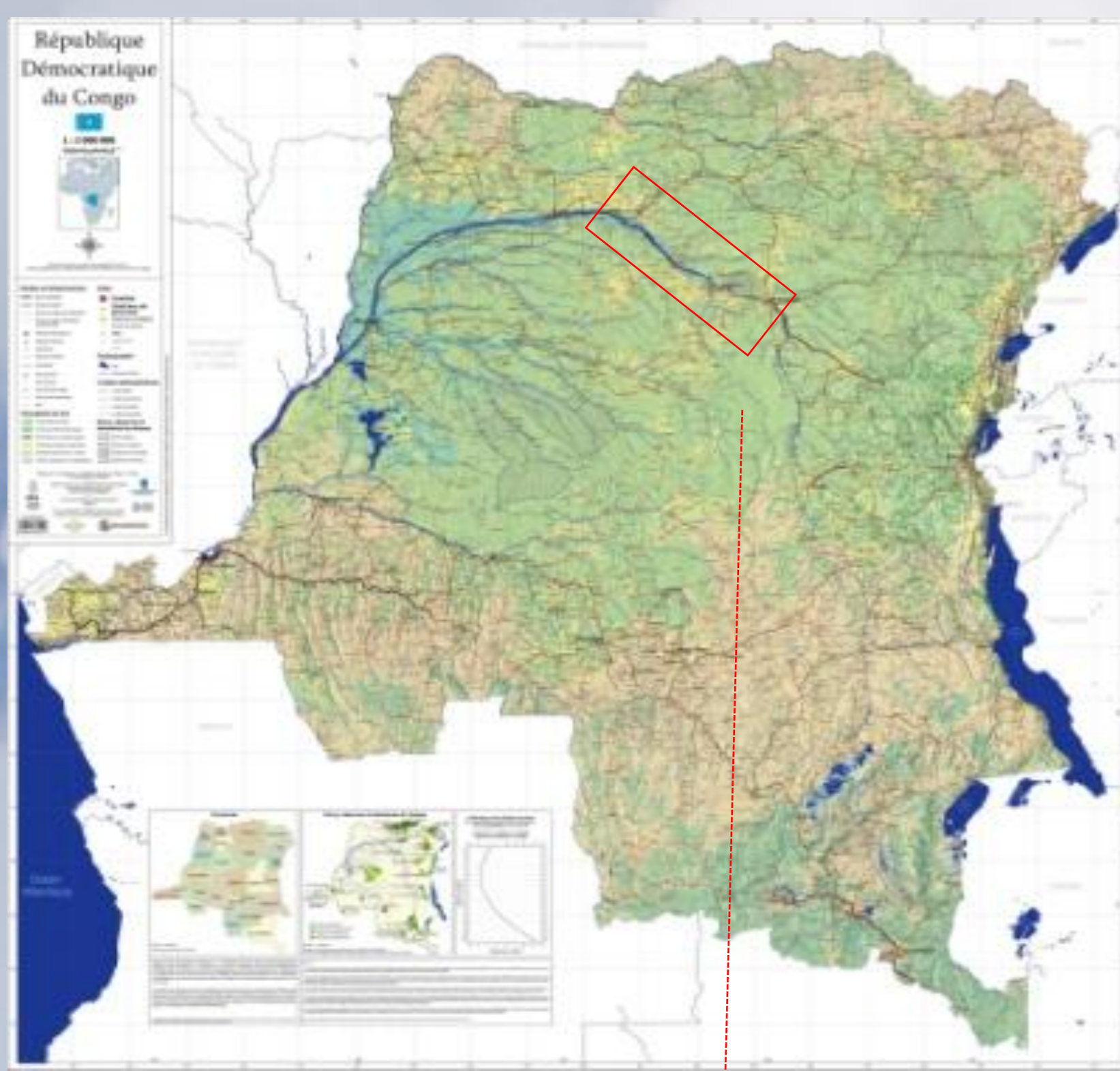


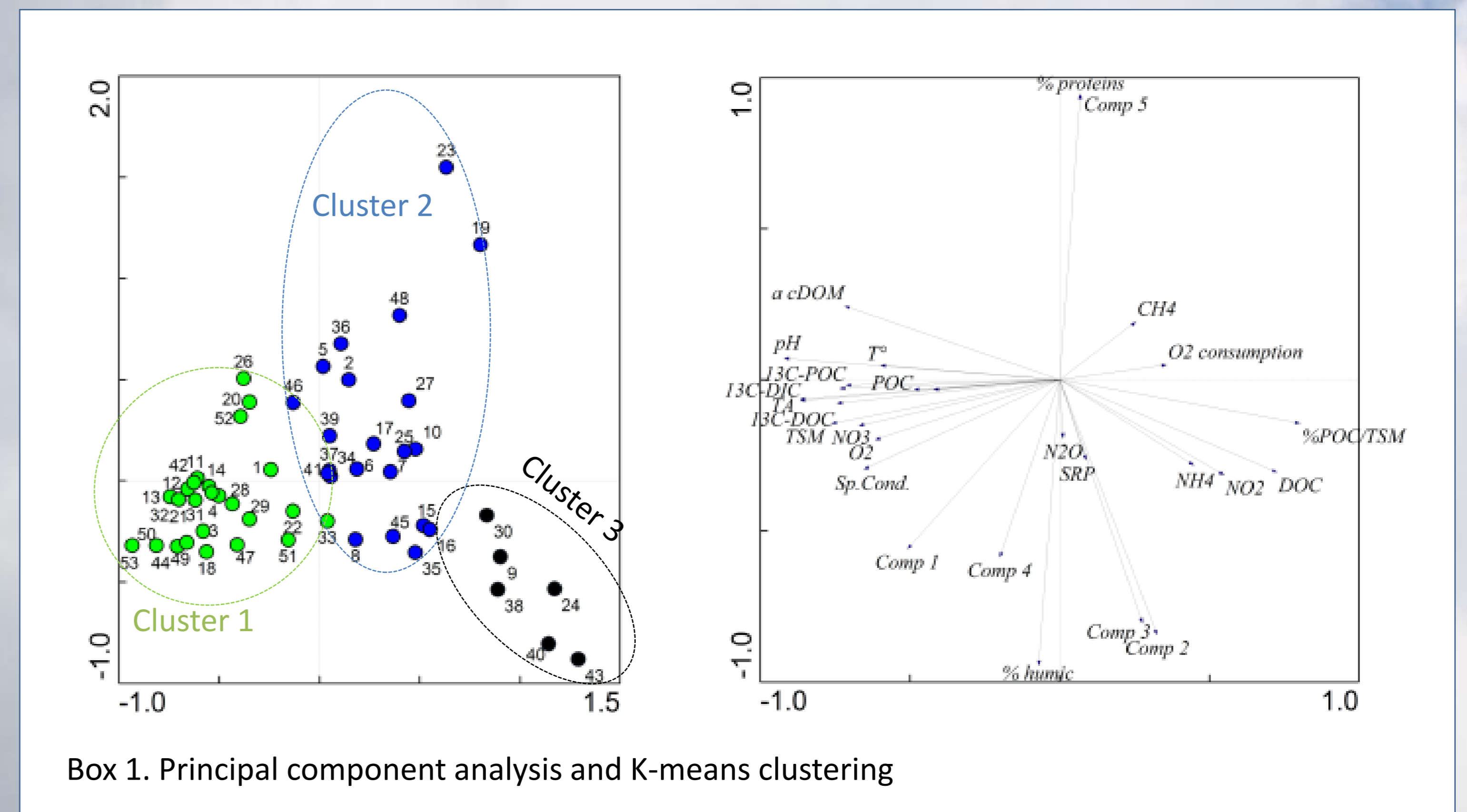
First assessment of the biogeochemistry of the Congo River and tributaries

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Map 1. Sampling sites



Box 1. Principal component analysis and K-means clustering

The Congo River is the second largest river in the World in terms of catchment and discharge after the Amazon River. Yet, there is surprisingly little or no information on carbon (C) cycling in this river. Here, we report a preliminary assessment of the biogeochemistry of the Congo River and tributaries based on >40 variables related to C cycling obtained at 53 stations along a transect of ~400 km in the middle reaches of the river (downstream of Kisangani) obtained from early May to early June 2010 (**Map 1**). Small (width < 2 m) to large tributaries and the Congo River (width > 1000 m) were sampled in order to assess spatial heterogeneity and the respective influence of lateral and longitudinal connectivity on C dynamics.

Principal component analysis and combined **K-means** cluster analysis allow to identify 3 main clusters of sites (**Box 1**).

Cluster 1 corresponded to stations from the main stem of the Congo River and to the largest tributaries (Tshopo, Lindi, Aruwimi). Water was characterized by higher conductivity, neutral pH and O₂ levels near saturation (**Box 2**). Total alkalinity (TA), total suspended matter (TSM) and particulate organic carbon (POC) concentrations were higher in stations from Cluster 1.

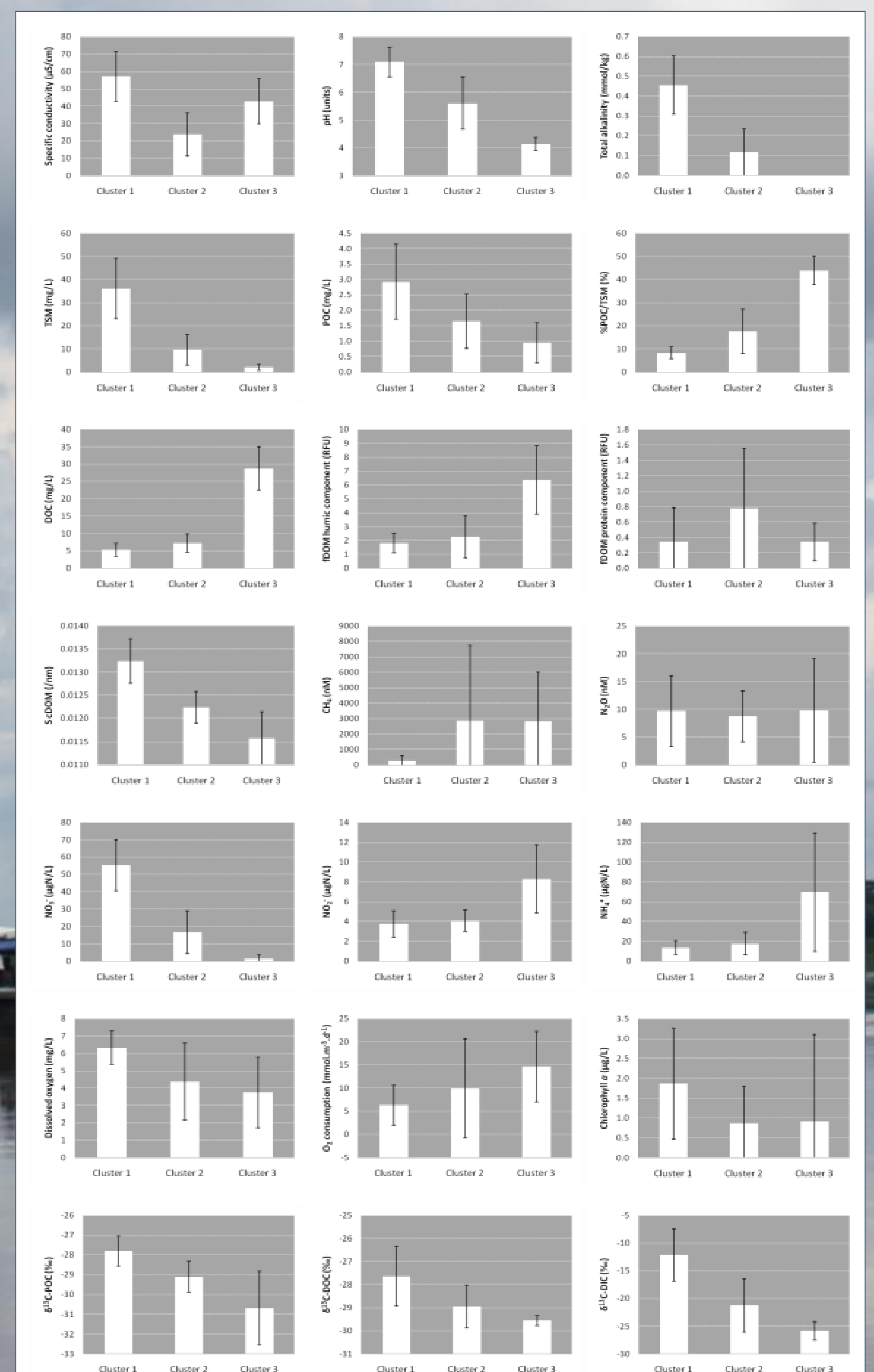
Cluster 2 corresponded to stations from Itimbiri and Lomami and from small to intermediate tributaries. They were characterized by lowest conductivity, slightly acid waters and low TA, TSM and POC concentrations.

Cluster 3 included only stations from the smallest tributaries (width < 20 m). pH was acid (< 5) and the TA was null. Waters were characterized by very low TSM but very high dissolved organic carbon (DOC) concentrations. These were black waters with high chromophoric and fluorescent dissolved organic matter (cDOM and fDOM).

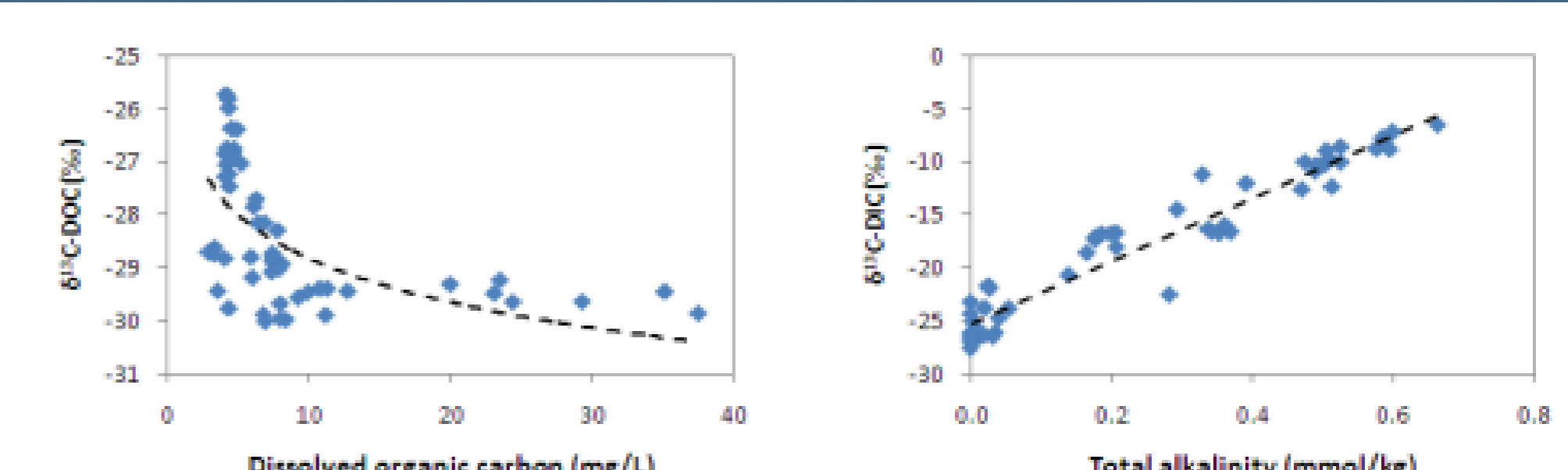
A shift between reduced and oxidized forms of dissolved inorganic nitrogen (i.e., respectively, NH₄⁺ vs NO₂⁻ and NO₃⁻) was observed from Cluster 3 to Cluster 1. O₂ consumption rates were higher in waters from Cluster 3 suggesting that ammonification of organic matter was dominant in black waters (Cluster 3) while nitrification dominated in larger tributaries and in the main stem (Clusters 2 and 1).

There was a clear decreasing trend of δ¹³C-POC, δ¹³C-DOC and δ¹³C-DIC from Cluster 1 to Cluster 3. δ¹³C-DIC values ranged from -28 ‰ (in black waters) to -7 ‰ (in the main stem). As there was a negative relationship between δ¹³C-DIC and TA (**Box 3**), we may hypothesize that DIC in black waters mainly originated from organic matter respiration (leading to extremely negative values of δ¹³C-DIC) while weathering processes mainly explained δ¹³C-DIC values in larger rivers. The decreasing trend between δ¹³C-DOC and DOC indicated an increasing part of C3- instead of C4-derived carbon in black waters (**Box 3**). The fDOM was dominated by humic components, especially in rivers from Cluster 3 (black waters).

This data set highlights very marked dynamics of C and N in the different sub-systems of the Congo River, with strong lateral and horizontal gradients.



Box 2. Mean and standard deviations of the main limnological variables. The stations were grouped following a K-means clustering.



Box 3. Relationships between δ¹³C-DOC and DOC, and between δ¹³C-DIC and TA