## Pipe or reactor? Carbon dioxide release from river surfaces across an Andes to Amazon floodplain transect

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Globally, river surfaces release  $\sim 1.8 \pm 0.3$  PgC yr<sup>-1</sup> of carbon dioxide (CO<sub>2</sub>). This is larger than the net removal of anthropogenic CO<sub>2</sub> to the land surface of  $1.6 \pm 0.5$  PgC yr<sup>-1</sup>, meaning that river CO<sub>2</sub> could act as a leak of carbon back to the atmosphere over the coming decades. To better understand the impact of this large flux on the carbon cycle, we must seek to connect the geomorphic, hydrological and ecological controls on the export of carbon from the terrestrial biosphere, soils and rocks to river networks. Despite the recognition that the release of CO<sub>2</sub> from river surfaces is substantial, we still lack insight on the source, delivery and/or production of CO<sub>2</sub> along rivers.

Here we assess source and flux of river CO<sub>2</sub> along a ~250 km transect from the Andes to the lowland Amazon floodplain, across the upper Madre de Dios basin in the wet season of March 2019. Using floating chamber methods, we quantify CO<sub>2</sub> release from river surfaces. To explore the competition of CO2 sources from weathering (rock-derived C) and from the biosphere, we use a headspace method to trap CO<sub>2</sub> on zeolite sieves for isotopic analysis (stable carbon isotopes and radiocarbon). The major and trace element dissolved chemistry was assessed to quantify the dominant weathering reactions. We find downstream variability in CO<sub>2</sub> release from river surfaces (ranging from ~650 to 2900 gC m<sup>-2</sup> yr<sup>-1</sup>), with the mainstem of the Madre de Dios at our most downstream location having the highest flux. In contrast, the radiocarbon activity (reported as Fraction Modern, F<sup>14</sup>C) of the CO2 varied much less, with the two major tributaries the Rio Manu and Rio Alto Madre de Dios having F<sup>14</sup>C values of CO<sub>2</sub> of 0.818 and 0.824, respectively, while ~150 km downstream the mainstem F<sup>14</sup>C of CO<sub>2</sub> was 0.809. Together with the stable C isotope composition and dissolved chemistry, these findings suggest a sustained release of old CO2 from carbonate weathering sources across this tropical floodplain transect, but that the overall flux is dominated by CO<sub>2</sub> from the terrestrial biosphere that must be efficiently delivered to the river channel.

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