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Using O₂/Ar ratios as a proxy for biological productivity determinations in an Arctic river.

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The biogeochemical cycling of carbon in Arctic rivers is perturbed as more terrestrial organic carbon and nutrients are released upon active layer and permafrost thaw. The majority of the carbon dioxide (CO₂) in rivers is emitted into the atmosphere, but it can also be utilized during photosynthesis, especially with more availability of nutrients, influencing the carbon flow and aquatic ecosystem metabolism. However, the timing and amount of photosynthetic primary production in Arctic rivers are unknown.

Water samples from the Kolyma River in Northeast Siberia were collected in June (late freshet) and August (summer) 2019. For the first time in an Arctic river, we measured biological oxygen supersaturations using the relative oxygen-to-argon ratio above equilibrium, $\Delta(\text{O}_2/\text{Ar})$, which is an indicator of the presence of biologically produced oxygen. This ratio is influenced in approximately equal parts by physical processes, while biological processes unilaterally influence the oxygen content.

In addition, we measured the partial pressure of CO₂, $p(\text{CO}_2)$, dissolved oxygen and inorganic nutrients concentrations. Mass spectrometry was employed to chemically characterize the composition of dissolved organic matter (DOM) and better understand its origin. Microbial communities were elucidated using 16S and metagenomic based sequencing approaches.

In June, the oxygen saturation in turbid and warm waters (average: 14 °C) in the main river channel was on average 10% above atmospheric equilibrium. The $p(\text{CO}_2)$ values were well above equilibrium (2000 μatm). Unlike oxygen saturation, $\Delta(\text{O}_2/\text{Ar})$ was negative (undersaturation); thus, physical processes contributed most to the total oxygen supersaturation (up to 20%), apparently due to contributions of freshet cold gas-rich meltwater, while the net biological oxygen concentration was between -10 and -15%.

In August, the water was colder (3 °C drop), and the total oxygen was mostly undersaturated (up to -10%). However, lower $p(\text{CO}_2)$ and a decrease in the biological oxygen deficit (between 0 and -5%) indicated net biological oxygen input. At the confluence of the main river channel and some tributaries, an algal bloom was observed resulting in up to 6.4% supersaturation in $\Delta(\text{O}_2/\text{Ar})$ and $p(\text{CO}_2)$ near atmospheric equilibrium.

Concentrations of nitrate and silica were higher in August than in June. Dissolved phosphate concentrations were low at both sampling times, but apparently did not limit primary productivity. The microbial community composition varied greatly between sampling times, with differential shifts across the transect. Compared to June, the DOM pattern in August was less diverse in the river due to more stable stream conditions and defined hydrologic connectivity between land and river, promoting also nutrient supply for biological productivity.

Unlike anticipated, the O_2/Ar ratios suggested that net biological oxygen production in the river did not profit during the late freshet, despite unlimited light and CO_2 availability and warm temperatures. Contrastingly, the summer low-flow allowed for photosynthetically-driven oxygen production and CO_2 uptake in some sites. We conclude that the O_2/Ar ratios were essential for quantifying the contribution of biological production, and understand better the fate of CO_2 in an Arctic river influenced by thawing permafrost, as well as the land-aquatic-continuum in the context of climate change.