The stoichiometry of oxygen and carbon dioxide in stream water: Implications for stream metabolism and carbon dioxide sources

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Peripheral stream environments, riparian, vadose, and hyporheic areas, are known to be biogeochemically active zones which support organic carbon oxidation as well as anaerobic redox reactions such as denitrification, metal reduction, and methanogenesis. Gaseous end products of anaerobic metabolism such as methane (CH_4) and nitrous oxide are commonly oversaturated in surface waters, suggesting that anaerobic processes are important even in highly oxygenated streams. However, the relative contribution of anaerobic metabolism to overall carbon cycling in streams is unknown.

We approached this question by examining the stoichiometry of oxgyen (O_2) and carbon dioxide (CO_2) in stream surface waters. Aerobic metabolism consumes O_2 and produce CO_2, or vice versa, in approximately equal amounts. Severe deviations from predictable CO_2:O_2 ratios in stream waters suggest CO_2 production is uncoupled from O_2 consumption, which occurs in the presence of anaerobic metabolism.

In three separate datasets covering hundreds of sampling locations throughout the United States, CO_2:O_2 ratio was routinely elevated, suggesting a prevalence of CO_2 production uncoupled from aerobic metabolism. This outcome persisted whether or not samples potentially supersaturated in calcite ($CaCO_3$) were included, suggesting that $CaCO_3$ precipitation was not the main driver of CO_2:O_2 imbalances. Furthermore, methane (CH_4) was oversaturated in nearly every sample collected, indicating recent mixing between oxic and anoxic waters in the streams. In all, > 90 percent of sample locations had elevated CO_2:O_2 ratios. Such sites spanned regions, stream sizes, and seasons. Mass balance calculations of the CO_2:O_2 ratio suggested that > 50 percent of the CO_2 in stream waters arose from anaerobic metabolism.

If correct, our interpretation indicates that a substantial proportion of CO_2 evaded from streams must be produced in anoxic peripheral areas. Likewise, stream connectivity to such peripheral zones may be an important control on stream carbon and nutrient cycling.