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Dissolved methane in the St. Lawrence estuarine system

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Dissolved methane concentrations ($[CH_4]$s) in the water column of the St. Lawrence estuarine system, i.e. the estuary and Gulf of St. Lawrence (EGSL) and the Saguenay Fjord, were determined during six cruises from 2016 to 2018 covering all four seasons. In the EGSL, $[CH_4]$ in surface water ($[CH_4]_{surf}$) decreased seaward regardless of the season. Mean $[CH_4]_{surf}$ ranged from 20.0 (spring) to 22.9 (autumn) nmol L^{-1} in the upper estuary, 6.1 (summer) to 8.7 (spring) nmol L^{-1}in the lower estuary, and 3.6 (summer) to 4.5 (winter) nmol L^{-1} in the Gulf. $[CH_4]_{surf}$ was supersaturated throughout the sampling area, with the mean degree of saturation varying from 596% (spring) to 665% (autumn) in the upper estuary, 198% (summer) to 255% (autumn) nmol L^{-1}in the lower estuary, and 111% (winter) to 144% (autumn) nmol L^{-1} in the Gulf. Vertical profiles of $[CH_4]$ in the lower estuary and Gulf were mostly characterized by a pronounced peak within or at the base of the intermediate cold layer observed in all seasons except winter. The $[CH_4]$s at the subsurface peak (up to ∼20 nmol L^{-1}) substantially exceeded those expected from solubilities of CH_4, implying in situproduction and/or horizontal input from sources that remain to be elucidated. Elevated $[CH_4]$s were often spotted near the bottom, suggesting release of CH_4 from sediments into the overlying water. $[CH_4]$s of up to 695 nmol L^{-1} in bottom waters over known active pockmarks were measured. CH_4 emitted from the pockmarks was rapidly diluted and consumed by bacteria in the water column before escaping to the atmosphere. In the Saguenay Fjord, $[CH_4]$s were measured along the main longitudinal axis in October 2016. $[CH_4]_{surf}$ ranged from 15.7 nmol L^{-1} to 144 nmol L^{-1} and decreased linearly with increasing salinity. The slope of this linear relation, however, broke at salinity ∼19 and was ∼20 times steeper in the less saline water than in the saltier water. $[CH_4]$s were highly supersaturated in surface water relative to the atmosphere, with the saturation degree ranging from 447% to 4026%. The vertical distribution of $[CH_4]$ was relatively homogeneous in the outer basin of the fjord but became increasingly stratified towards the inner basin and further upstream, conforming to the spatial evolution of the water column density structure. $[CH_4]$ in the deep, inner basin declined with depth, rapidly within the pycnocline and gradually below it. In contrast, $[CH_4]$ in the shallow, upper reach of the fjord increased with depth and reached 389 nmol L^{-1} near the bottom, suggesting a sedimentary input of this gas into the overlying water column. The sources of dissolved CH_4 in the St. Lawrence estuarine system were discussed based on its carbon isotope compositions. This study demonstrates that the St. Lawrence estuarine system is a source of CH_4 to the atmosphere and that the distribution of methane in this area is controlled by the interaction of complex physical and biogeochemical processes.