

## **Publication**

Benthic fluxes of dissolved organic nitrogen in the Lower St. Lawrence Estuary and implications for selective organic matter degradation

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The distribution of dissolved organic nitrogen (DON) and carbon (DOC) in sediment porewaters was determined at nine locations along the St. Lawrence estuary and in the gulf of St. Lawrence. In a previous manuscript (Alkhatib et al., 2012a), we have shown that this study area is characterized by gradients in the sedimentary particulate organic matter (POM) reactivity, bottom water oxygen concentrations, and benthic respiration rates. Based on the porewater profiles, we estimated the benthic diffusive fluxes of DON and DOC in the same area. Our results show that DON fluxed out of the sediments at significant rates (110 to 430 mu mol m(-2) d(-1)). DON fluxes were positively correlated with sedimentary POM reactivity and varied inversely with sediment oxygen exposure time (OET), suggesting direct links between POM quality, aerobic remineralization and the release of DON to the water column. DON fluxes were on the order of 30 to 64% of the total benthic inorganic fixed N loss due to denitrification, and often exceeded the diffusive nitrate fluxes into the sediments. Hence they represented a large fraction of the total benthic N exchange, a result that is particularly important in light of the fact that DON fluxes are usually not accounted for in estuarine and coastal zone nutrient budgets. In contrast to DON, DOC fluxes out of the sediments did not show any significant spatial variation along the Laurentian Channel (LC) between the estuary and the gulf (2100 +/- 100 mu mol m(-2) d(-1)). The molar C/N ratio of dissolved organic matter (DOM) in porewater and the overlying bottom water varied significantly along the transect, with lowest C/N in the lower estuary (5-6) and highest C/N (> 10) in the gulf. Large differences between the C/N ratios of porewater DOM and POM are mainly attributed to a combination of selective POM hydrolysis and elemental fractionation during subsequent DOM mineralization, but selective adsorption of DOM to mineral phases could not be excluded as a potential C/N fractionating process. The extent of this C-versus N- element partitioning seems to be linked to POM reactivity and redox conditions in the sediment porewaters. Our results thus highlight the variable effects selective organic matter (OM) preservation can have on bulk sedimentary C/N ratios, decoupling the primary source C/N signatures from those in sedimentary paleoenvironmental archives. Our study further underscores that the role of estuarine sediments as efficient sinks of bioavailable nitrogen is strongly influenced by the release of DON during early diagenetic reactions, and that DON fluxes from continental margin sediments represent an important internal source of N to the ocean.

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