

# Influences of manganese cycling on alkalinity in the redox stratified water column of Chesapeake Bay

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The alkalinity dynamic in coastal environments controls the global burial of carbonate and modulates the ability of the ocean to trap anthropogenic CO<sub>2</sub>. Eleven high vertical resolution profiles from the temperate Chesapeake Bay estuary during two summers allow precise description of carbonate dynamics over the salinity and redox gradient along with the measurement of the speciation of most redox sensitive elements. In the presence of oxygen, carbonate dissolution, primary production and aerobic respiration are able to explain the evolution of total alkalinity (TA) versus dissolved inorganic carbon (DIC), once corrected for fresh and oceanic water mixing. A significant flooding event in 2018 favoured carbonate dissolution. In oxygen depleted waters, an intriguing signature of 2.4 mole of DIC produced per 1 mole of TA was observed for the first time and is consistent over the two years. The stoichiometry of TA and DIC changes suggests this characteristic carbonate signature is produced by MnO<sub>2</sub> reduction followed by Mn carbonate precipitation. Scarcity of reagent in the water column suggests that this original TA/DIC signature was produced in the sediment pore water then transferred in the water column with other by-product of anoxic respiration as the summer begin. Our results underline that Mn is a critical element of the alkalinity dynamic in the river dominated environment, especially because of its ability to limit the H<sub>2</sub>S oxidation to SO<sub>4</sub><sup>2-</sup> and by favouring sulphur burial.