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Supplementary material

Haloform formation in coastal wetlands along a salinity gradient at South Carolina, United States

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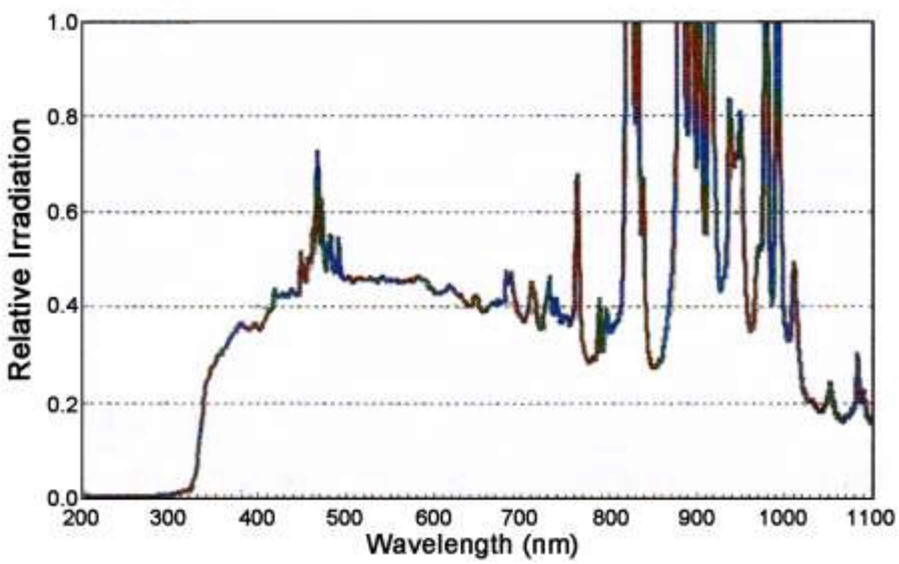

Fig. S1. Spectrum of the simulated sunlight from the xenon lamp.

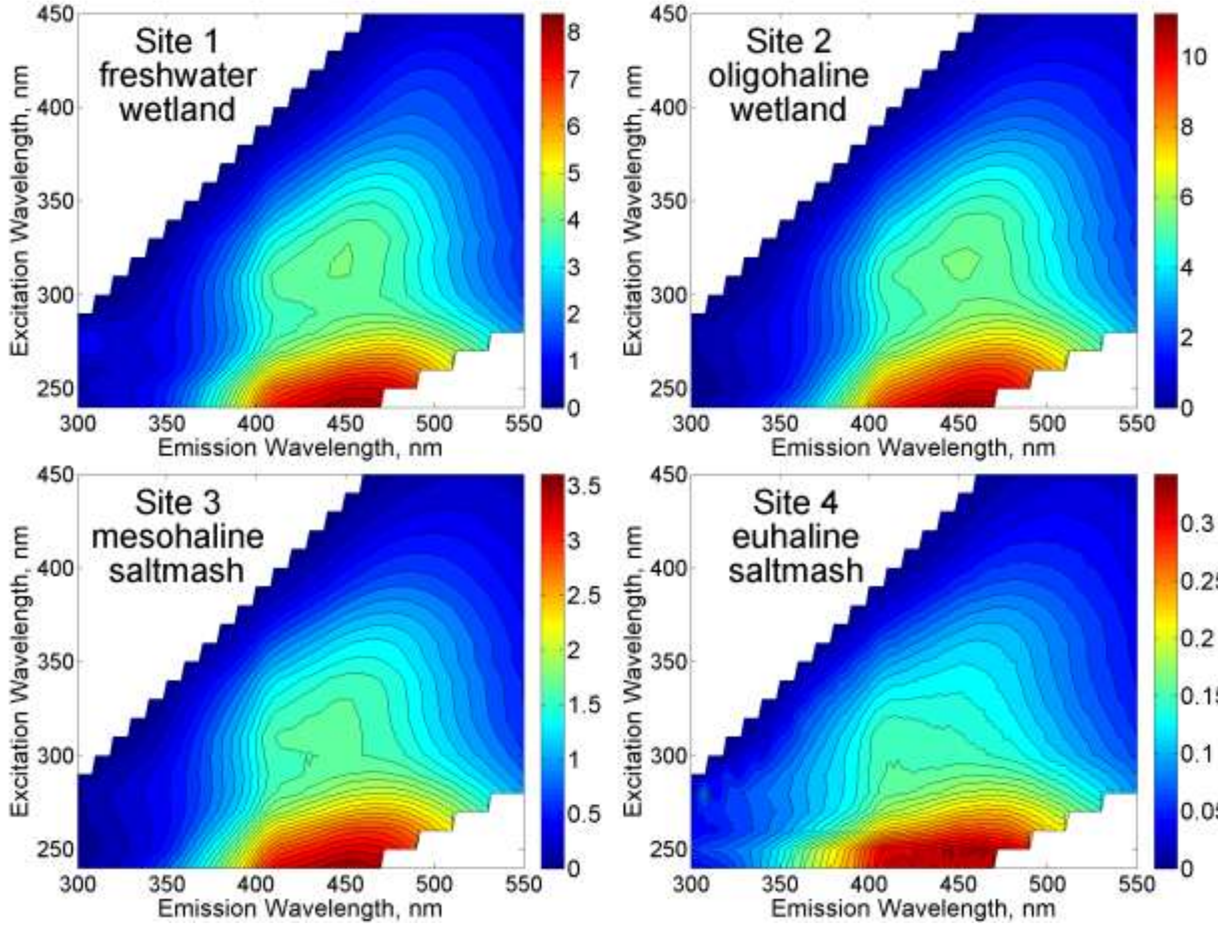

Fig. S2. Fluorescence emission–excitation matrix of water samples of four natural wetlands in North Winhay Bay, SC. Coloured bar shows fluorescence intensity normalised to the integral of the Raman peak at 350-nm excitation and is given in Raman units (RU).

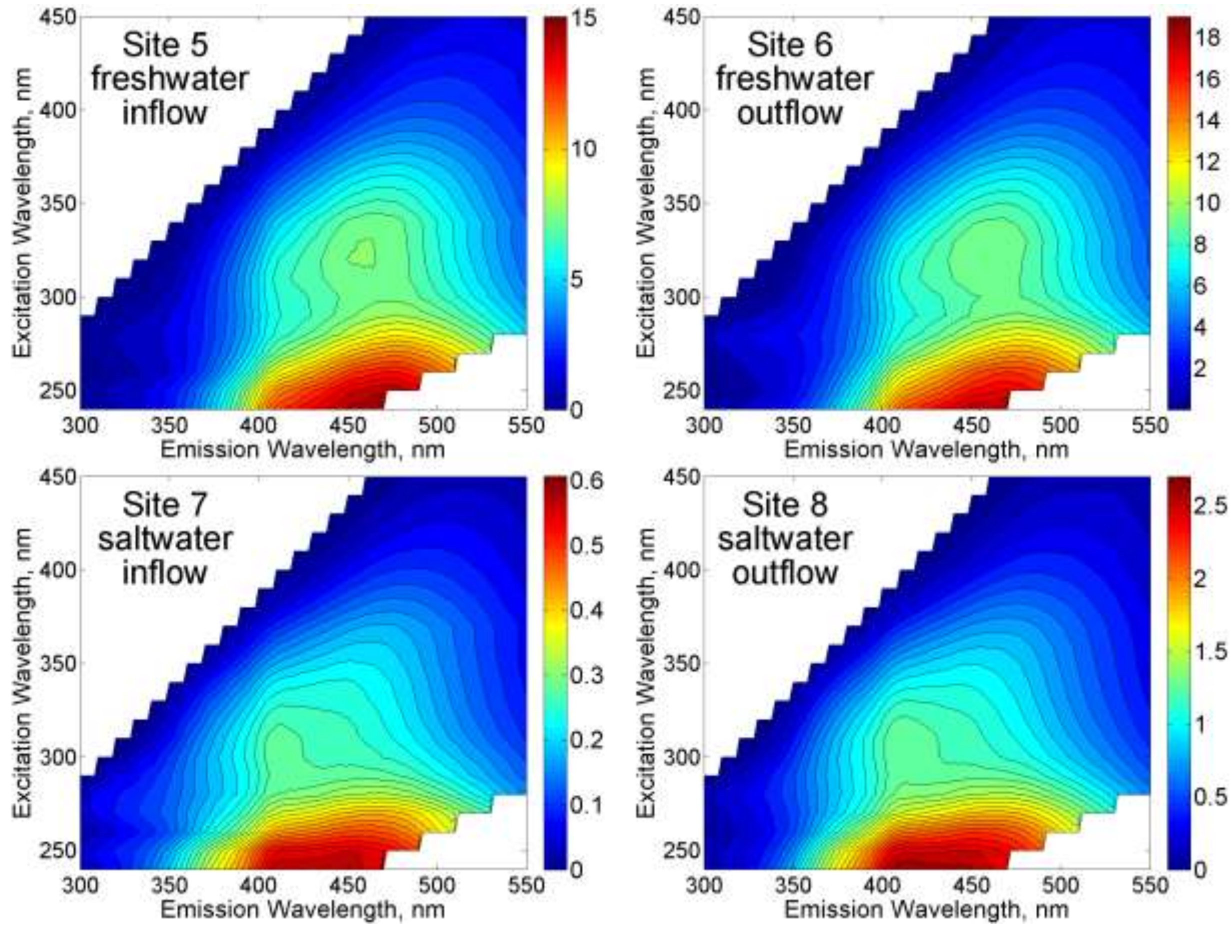

Fig. S3. Fluorescence emission–excitation matrix of water samples of the inlets and outlets of two managed wetlands in South Winyah Bay, SC. Coloured bar shows fluorescence intensity normalised to the integral of the Raman peak at 350-nm excitation and is given in Raman units (RU).

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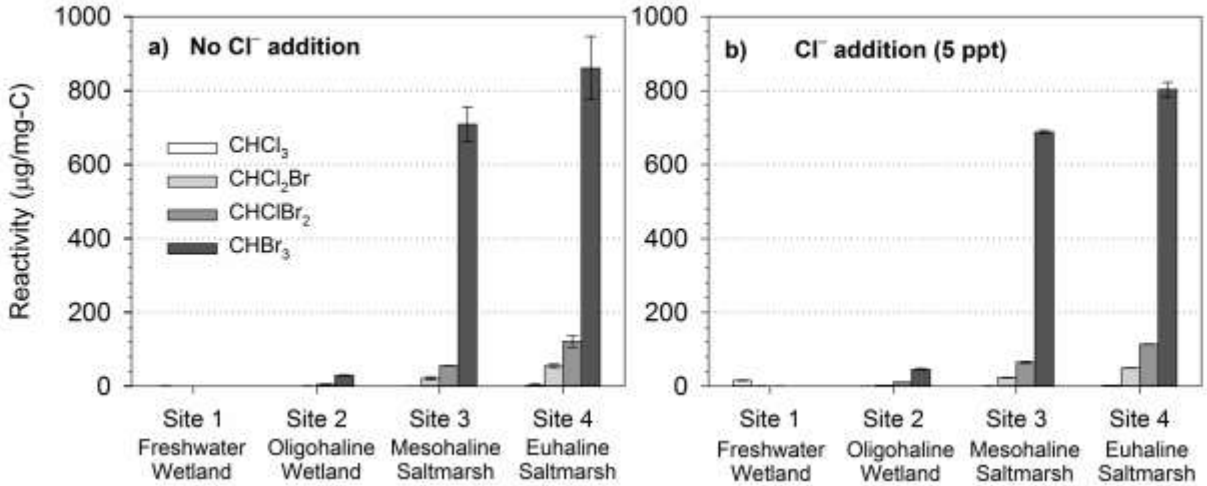

Fig. S4. Effects of chloride on abiotic haloform formation from waters along the salinity gradient for all four sites (Fig. 5 shows only sites 1 and 2)

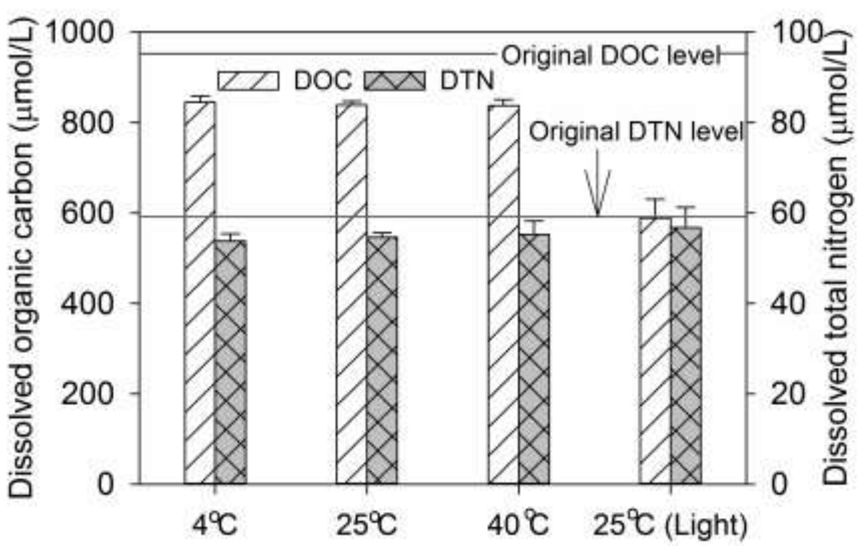

Fig. S5. Dissolved organic carbon and dissolved total nitrogen of wetland water sample after Fenton treatments under different temperature and light conditions.

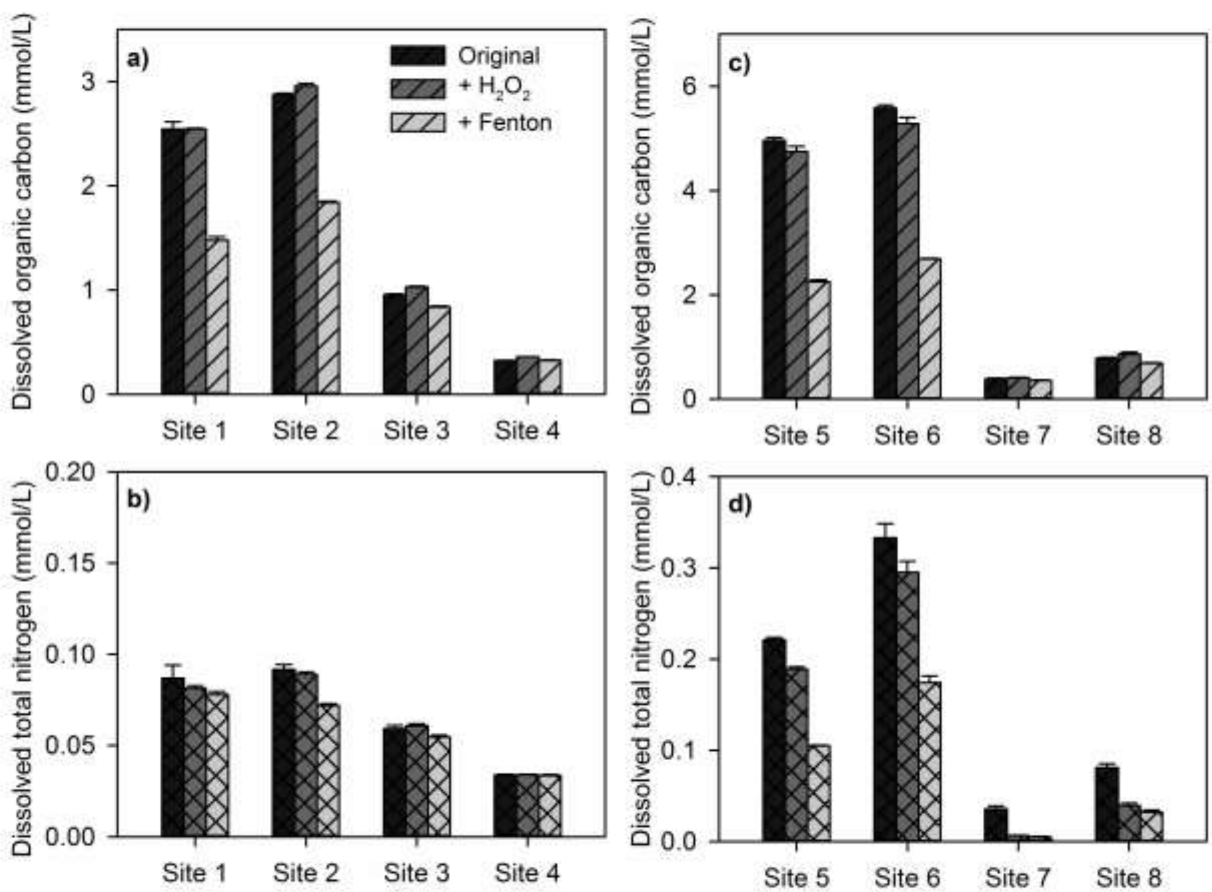

Fig. S6. Dissolved organic carbon and dissolved total nitrogen of wetland water sample after 24-h incubation at room temperature.

Characteristics of DOM

Natural coastal wetlands

DOM characteristics varied along the salinity gradient of natural coastal wetlands in Winyah Bay, SC. Generally, higher levels of DOM were found in the lower-salinity freshwater forested wetlands (salinity <0.5 ppt) and oligohaline wetland (salt-affected forested wetlands, 0.5–5.0 ppt) compared to the higher-salinity mesohaline saltmarsh (5.0–18 ppt) and euhaline saltmarsh (30–40 ppt). The highest DOC concentration was observed in the oligohaline wetland with an average of 2.88 mmol L^{-1} at 5.45 mS cm^{-1} (2.9 ppt), whereas the lowest DOC concentration was observed in euhaline saltmarsh with an average of 323 μmol L^{-1} at 54.3 mS cm^{-1} (35.9 ppt). In addition to the difference in concentration, DOM in freshwater environments had lower nitrogen (as indicated by higher C/N ratios) and higher aromatic contents (as indicated by higher SUVA values) than that from saline environments.

The optical properties of DOM also changed along the salinity gradient, which reflected a variation of reactive oxygen species production under sunlight irradiation.[1,2] The marine humic acid-like peak (M peak: excitation <250 and 290–325 nm, emission 370–430 nm[3]) dominating the fluorescence EEM indicated that euhaline saltmarsh was highly influenced by seawater (Fig. S1). Because high slope ratios (S_R) are indicative of low molecular weight (MW) DOM,[4] and the humification index (HIX) is associated with the hydrogen/carbon ratio and positively linked to the humification degree,[3] the significantly lower HIX and SUVA and higher S_R in euhaline saltmarsh waters compared with other natural wetlands showed that the DOM in the water samples from saline environments was likely (i) smaller in size, with (ii) a lower degree of aromatic content. Also, a higher E2/E3 value suggested DOM in euhaline wetlands could have higher quantum yields in singlet oxygen ($^1O_2$) under sunlight irradiation than those from freshwater, oligohaline and mesohaline environments.[2]

Managed coastal wetlands

Similarly to natural wetlands, the concentrations and characteristics of DOM were related to water salinity in these managed wetlands. The managed freshwater wetland had significantly higher DOC concentrations than the managed saltwater wetland, ranging from 4.96 to 5.58 mmol L^{-1} and 386 to 784 μmol L^{-1} respectively. The highest DOC was observed at the outflow of the managed freshwater wetland with an average of 5.58 mmol L^{-1} and electrical conductivity at temperature 25 °C (EC_{25}) of 0.16 mS cm^{-1}. Similarly, the managed freshwater wetland had a significantly higher C/N ratio than managed saltwater wetlands (C/N = 16.8–22.4), followed by the natural mesohaline saltmarsh (C/N = 16.1). The managed saltwater wetland had the lowest C/N ratio at ~10. In addition, higher SUVA and HIX values but lower S_R and E2/E3 values were also observed in managed freshwater environment, suggesting its DOM had a higher degree of humification and aromatic carbon content.

In terms of their degradability against oxidation, DOM in all water samples (both natural and managed wetlands) was quite resistant to H_2O_2 treatment (no Fe^{3+} addition). DOC concentrations of all waters were insignificantly different or only slightly less than original samples after 24-h reactions with H_2O_2 (Fig. S6). In contrast, significant loss of DOC concentrations after Fenton treatment was observed in freshwater wetland, oligohaline wetland and managed freshwater wetlands. DOC loss was less significant in mesohaline saltmarsh, euhaline saltmarsh or managed saltwater wetlands, suggesting that DOM from the freshwater environments have greater contents of carboxylic and other functional moieties that could bind or complex with Fe in resulting coagulation.[5]

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