Diagenetic markers indicate potential for photochemical release of sedimentary algal toxins

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Background: The photochemical release of dissolved organic carbon (DOC) from resuspended sediment has been shown to correlate with the carbon load of the sediments, and with several qualitative source and diagenetic markers. Long chain carbon preference index (CPI_{24-34}) and terrestrial to aquatic fatty acid ratio (TAR_{FA}) correlate positively with DOC photorelease suggesting that fresh terrestrial sediments photorelease DOC more readily than marine sediments or diagenetically altered terrestrial sediments. Short chain carbon preference index (CPI_{14-22}) correlates negatively with DOC photorelease suggesting that diagenetically altered marine sediments are more photoreactive than freshly deposited marine sediments (Fig. 1).

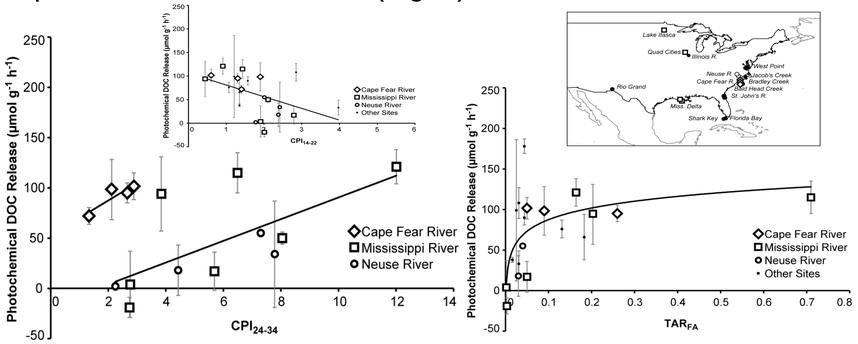

Fig. 1: DOC photorelease is higher in fresh terrestrial and/or diagenetically altered marine sediments.

Harmful algal blooms (HAB) occur frequently in the Gulf of Mexico and have significant impacts on fisheries, tourism and human health. *Karenia brevis* is the organism responsible for HAB's along the Florida Gulf Coast, where "red tides" commonly occur (Fig. 2). The brevetoxin PbTx-2, an algal toxin produced by *Karenia brevis,* has been shown to be released from suspended sediments upon irradiation by simulated sunlight. We hypothesize that there will also be a correlation between photorelease of PbTx-2 and CPI_{24-34}.

Fig. 2: Harmful algae bloom commonly referred to as red tide.

Data: APCI (+) LC/MS is used to determine the concentration of PbTx-2 in natural waters and sediment extracts. The APCI source provides more efficient ionization of brevetoxin analytes which yields greater analytical sensitivity and lower limits of detection than previous analytical methods (Fig. 3). Low detection limits are needed for measuring environmentally relevant concentrations of PbTx-2 and photoproducts.

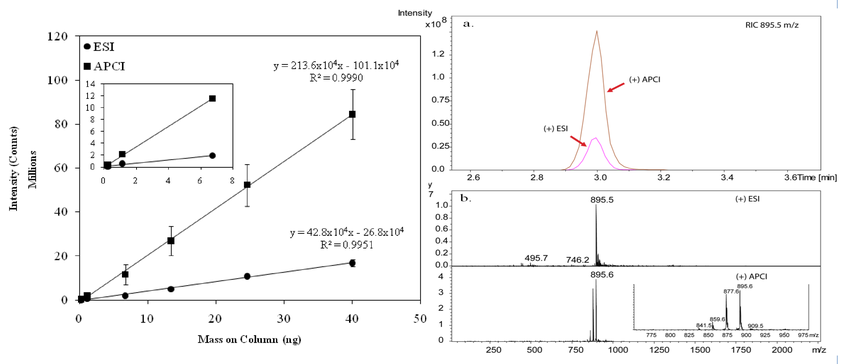

Fig. 3: Recent improvements to LC/MS methodology (APCI+) allow sensitive detection of PbTx-2 extracted from both sediment and aqueous phases.

The fate of PbTx-2 and other brevetoxins in the water column is largely unknown and their cycling is very complex (Fig. 4)

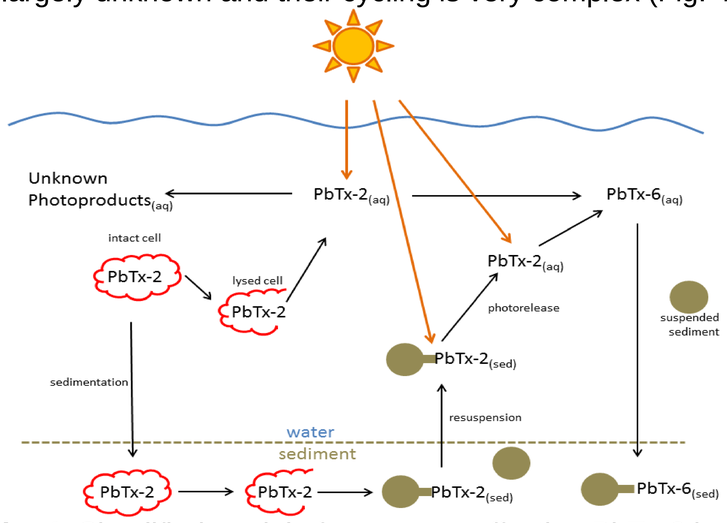

Fig. 4: Simplified model of processes affecting PbTx-2 in natural waters.

PbTx-2 is epoxidized upon solar irradiation in seawater and converted to PbTx-6. Experimental data has shown that PbTx-2 and the resulting PbTx-6 photoproduct can adsorb onto particles. Once sediment containing PbTx-2 is resuspended into the photic zone it may be released into the water column.

Changes in aqueous phase PbTx-2 were measured after suspended sediments were exposed to a full day of simulated solar irradiation (Fig. 5).

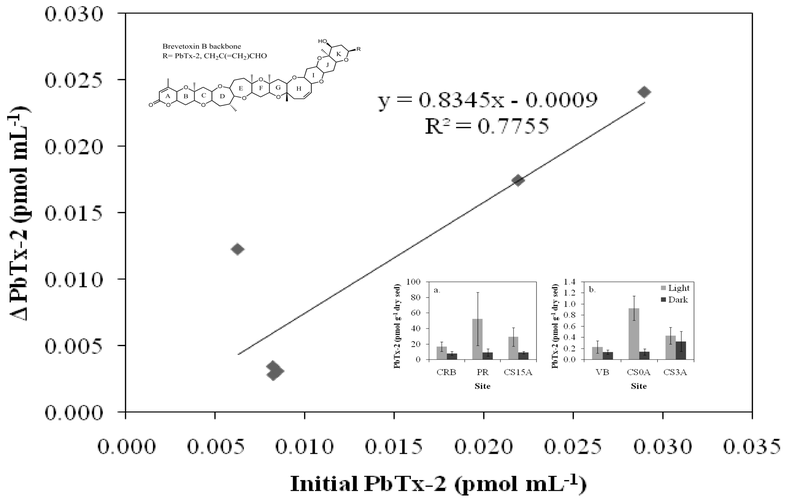

Fig. 5. Aqueous photorelease of sedimentary PbTx-2 (inset) may be driven by its initial concentration.

Discussion: If a correlation is observed between photorelease of PbTx-2 and CPI_{24-34} the state of diagenetic processing could be used to predict possible impacts of resuspension events in areas previously affected by red tide. Tidal creek sediments have a wide range of diagenetic states and are frequently subjected to natural and anthropogenic resuspension events as well as harmful algal blooms.

Future Work: Sediments containing PbTx-2 will be irradiated in a seawater suspension with simulated sunlight to measure PbTx-2 photorelase. Sediments will be characterized by CPI_{24-34} to determine if there is a correlation between photorelase and diagenetic state. Brevetoxin photo-products and metabolites are being investigated for use as possible sedimentary biomarkers.

References:
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Kieber Robert, Pitt Jaclyn, Skrabal Stephen, Wright Jeffrey (2010) Photodegradation of the brevetoxin PbTx-2 in Coastal seawater. Limnology and Oceanography. 55, 6, 2299-2304.

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