"Photoremineralization" of particulate organic carbon

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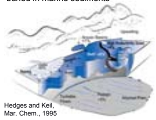
Background

• River delta sediments account for ~44% of organic carbon (OC) buried in marine sediments, globally. (Hedges and Keil 1995). (A, upper right)

• However, deltaic sediments have lower surface-area normalized OC loadings than suspended riverine and non-deltaic shelf sediments (Keil *et al* 1997). (B, middle right)

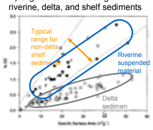
• **"Photodissolution"** of POC from resuspended deltaic sediments is one hypothesis consistent with their lower OC loadings (Mayer *et al* 2006). 15- 25% of POC is typically lost during laboratory irradiations.

A) Distribution of organic matter buried in marine sediments



Hedges and Keil, Mar. Chem., 1995

B) Organic carbon loading of riverine, delta, and shelf sediments

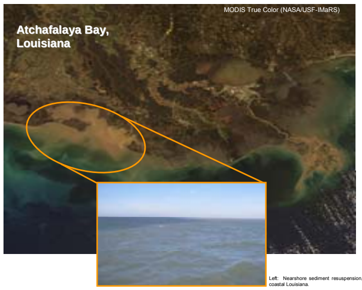


Keil, et al, Geochim. Cosmochim. Acta, 1997

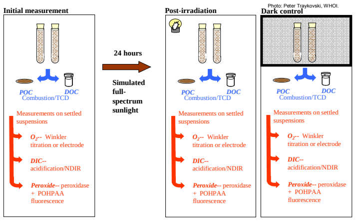
Central question:

Photooxidation may be a significant mechanism for DOC removal from the oceans. Can suspended POC in turbid coastal waters suffer the same fate?

Study Area and Experimental Design



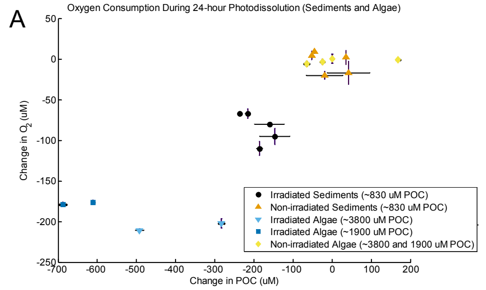
Left: Nearshore sediment resuspension, coastal Louisiana. Photo: Peter Traykovski, WHOI.



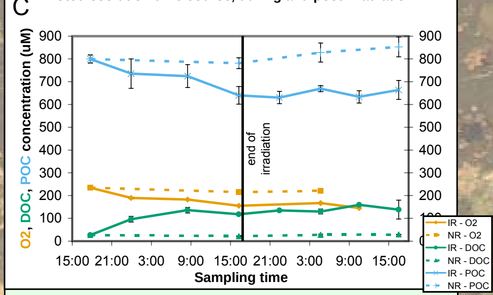
• Suspensions of Atchafalaya bottom sediments and freeze-dried algae (*Tetraselmis* spp., membrane fraction) made up in carbon-free artificial seawater.

• Replicate suspensions were irradiated in a solar simulator or kept in the dark as non-irradiated controls, all at room temperature.

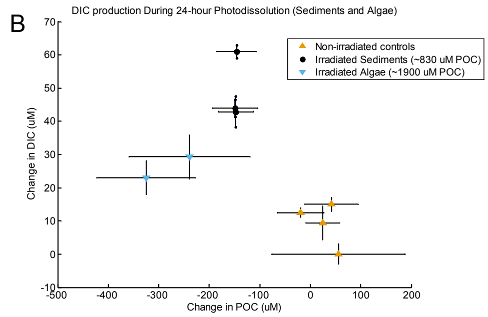
• Suspensions were analyzed for POC, DOC, as well as dissolved O_2, DIC, and/or peroxides before and after irradiation.



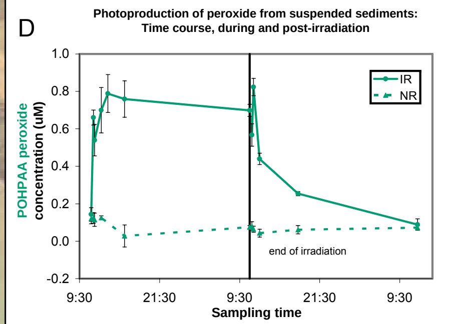
A: Irradiation of sediments depleted dissolved O_2 levels at a molar ratio ($POC:O_2$) of about 3:1 over 24-hour experiments. For suspensions with the highest initial POC concentrations (algae, 3800 uM), O_2 levels after 24 h of irradiation were below detection (after loss of 200uM).



C: POC, DOC, and O_2 monitored for further 24 h after the end of a 24-h irradiation of sediments exhibited no significant additional dissolution, oxygen consumption, or readsorption.

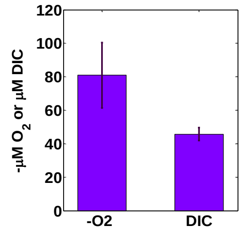


B: Photoproduction of DIC from sediments was equal to 5% of initial POC (molar basis). Photoproduction of DIC from algal membranes was less efficient, equal to 1-2% of initial POC.



D: Peroxide production rapidly reached a steady-state concentration of about 0.8 μM during irradiation of sediments, and decayed slowly post-irradiation, taking an additional 24 hours to return to pre-irradiation levels.

Oxygen consumed and DIC produced during 24 h irradiations of 500 mg/L sediment



Above: O_2 consumed during sediment irradiation experiments exceeded DIC production by about a factor of two. Data above are reported as the difference between irradiated and dark controls.

Discussion Points

• O_2 appears to be consumed in excess relative to DIC production during POC irradiation, implying production of other oxidized photoproducts.

• Steady-state concentrations of peroxides detectable via the POHPAA method are too low for these compounds to account for the remainder of oxygen consumption. Simultaneous destruction of peroxides by a competing process (such as photolysis) or production of large organic peroxides undetectable via the POHPAA method may account for the observed kinetics.

Take-home message:

About 1-5% of suspended POC can be remineralized during irradiation, consistent with observations of marine DOC photooxidation.

References & Acknowledgements

Hedges JI and RG Keil, 1995. *Mar. Chem.* **49**: 81-115.

Keil RG, et al, 1997. *Geochim. Cosmochim. Acta* **61(7)**: 1507-1511.

Mayer LM, et al, 2006. *Limnol. Oceanogr.* **51(2)**: 1064-1071.

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