

The Role of Organic Carbon in Absorption Properties of Louisiana Shelf Suspended Particulate Matter

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Motivations

River-derived suspended particulate matter (SPM) in the northern Gulf of Mexico is an important delivery vector to the Louisiana shelf region for particulate organic carbon (POC). Typically these particles contain ca. 1-2% organic carbon (OC) by weight, the balance being made up of fine-grained clay minerals. We have two primary motivations for this study of the relationship between light absorption (300-800nm) by these particles and their OC contents:

- 1) Optical properties of SPM are used as proxy measurements for POC in the study of carbon cycling in spatially- and temporally-variable river-influenced coastal regions.
- 2) Photochemical dissolution of POC has the potential to remove a significant fraction of organic matter from suspended sediments in turbid aquatic and marine systems (references 2, 3, 5). The optical properties of photochemically reactive POC may govern the importance of this type of reaction in the environment.

Approach

The goal of this study was to isolate the light-absorption properties of the organic component of riverine POC by difference, using instrumentation insensitive to scattering to measure mass-specific particle absorption (a_p^*) before and after oxidative removal of organics. A preliminary set of POC augmentation experiments was conducted to establish the extent to which optical absorption by composite mineral-organic particles is a simple sum of the optical properties of each component.

• **Absorbance measurements on particulates** were made using a 15-cm diameter integrating sphere (Labsphere) interfaced to a Cary 300 spectrophotometer. The sphere was equipped with a center-mounted 1-cm cuvette holder allowing nearly-scattering free measurements of particulate suspensions to be made from 300-800nm (1). Subsamples of dry sediments were weighed to the nearest 10 μg (to give SPM concentration accurate to 0.01 g m^{-3}) and resuspended in dilute MilliQ water or CaCl_2 for optical measurements.

• **Mass-specific absorption** was calculated as: $a_p^*(\lambda) [\text{m}^2 \text{g}^{-1}] = 2.303 \cdot A_p(\lambda) / \text{pathlength} [\text{m}] / \text{SPM} [\text{g m}^{-3}]$.

• **Absorbance measurements on humic acid** were made using a Hitachi U1000 dual-beam spectrophotometer, in a 1-cm quartz cuvette. These were corrected to $A(800) = 0$ by subtracting a flat baseline from spectra.

• **POC content** was determined after vapor-phase acidification on a Perkin Elmer 2400 CHN Analyzer. **DOC content** was determined on a Shimadzu TOC-V_{CHN} DOC analyzer.

• **Organic-carbon addition experiments** were conducted by allowing dissolved organic material with known optical properties to physically adsorb to low-organic content clays. a_p^* of particles and OC content were determined before and after organic treatment.

• **Organic-carbon removal experiments** were conducted by oxidatively destroying naturally-present organic material on surface sediments collected from the Atchafalaya River delta and freeze-dried in May 2008. a_p^* and OC content of particles were determined before and after oxidative treatment.

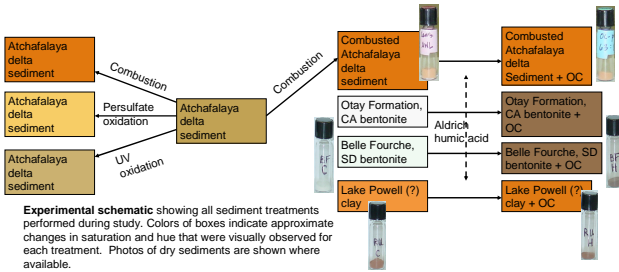
Organic carbon addition/removal methods

• **Combustion** – of dry sediments, at 350 deg. C, for 8 hours.

• **Persulfate oxidation** – 0.36M potassium persulfate (bicarbonate-buffered @ pH 8), stirred at 80 degrees C for varying lengths of time. (4)

• **UV oxidation** – under mercury vapor lamp (1250 $\mu\text{W cm}^{-2}$), cooled to 18 deg. C for varying lengths of time.

• **OC sorption** – Ca^{2+} -saturated, low-OC sediments were stirred in concentrated suspensions of humic acid and CaCl_2 for 24 hours, then alternately rinsed and centrifuged and finally freeze-dried for CHN analysis.



Experimental schematic showing all sediment treatments performed during study. Colors of boxes indicate approximate changes in saturation and hue that were visually observed for each treatment. Photos of dry sediments are shown where available.

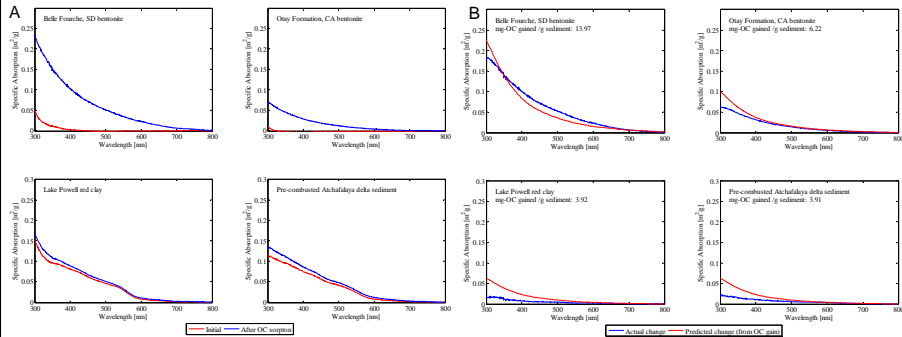
Results – OC sorption experiments

Figure A shows a_p^* of four low-OC sediment types before and after Aldrich humic acid addition.

Figure B shows the **observed** increase (the difference between untreated and OC-augmented particles) relative to the **predicted** increase, which was calculated by scaling the humic acid OC-specific absorption (not shown) to the OC gained on the sediments.

For sediments that **did not** absorb strongly prior to OC augmentation (Otay and Belle Fourche bentonites, top panels), the magnitude of the actual absorption increase is similar to or slightly less than the expected increase. For sediments that **did** strongly absorb light prior to OC augmentation (Fe-containing Lake Powell clay and precombusted Atchafalaya Delta sediments, lower row of panels), the actual a_p^* increase was less than half the expected increase, suggesting that **mineral chromophores may somehow "shade" adsorbed organics**.

Fractionation of carbon and chromophores during sorption of humic acid to particles may explain part of the shortfall in optical absorption, as well as changes in spectral shape in all clay samples.

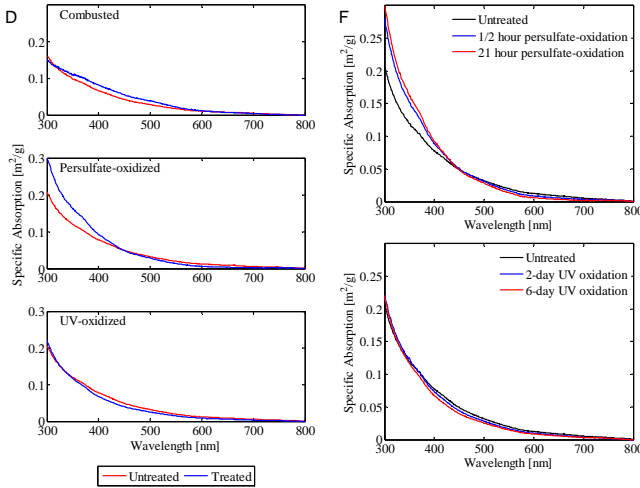


Results – OC oxidative removal experiments

Figure C shows a_p^* of Atchafalaya delta sediment before and after removal of OC by combustion, persulfate, and UV oxidation.

Figure D shows extents of OC removal and absorption changes over varying time periods of persulfate and UV oxidation.

Extent of OC removal for both figures is shown in the table below the figures. Both combustion and persulfate oxidation resulted in an increase in a_p^* by sediments, primarily at wavelengths less than 500 nm. Ultraviolet irradiation resulted in a smaller OC loss (~40% instead of ~80-90) but an increase in absorption was not observed. About twice as much OC (per gram sediment) was removed from the Atchafalaya River delta sediments after 6 days of UV irradiation as was adsorbed to the pre-combusted sediment in the OC-augmentation experiments (Figure B). The differences in magnitude and spectral shape of the resulting changes in a_p^* suggest that the natural organic matter in the Atchafalaya sediments absorbs light much less strongly, and at different wavelengths, than does the humic acid used in the OC-addition experiments.



Treatment	OC [mg-OC g-sed ⁻¹]	OC loss [%]
Untreated	18.8	—
Combusted (8 hours @ 350 deg. C)	3.8	80
K ₂ S ₂ O ₈ oxidized (0.5 hours @ 80 deg. C)	8.0	57
K ₂ S ₂ O ₈ oxidized (21 hours @ 80 deg. C)	2.3	88
UV-oxidized (Hg-vapor lamp, 2 days @ 18 deg. C)	17.9	4.8
UV-oxidized (Hg-vapor lamp, 6 days @ 18 deg. C)	11.0	41

Conclusions

• Adsorptive addition of humic acid to uncolored, low-OC clays suspended in water caused an increase in their mass-specific absorption coefficient, consistent with optical properties of the humic acid. Humic acid adsorption to more strongly colored, low-OC clays resulted in a smaller-than-expected absorption increase, perhaps caused by competitive light absorption by Fe-oxide phases.

• Oxidative removal of 40-90% of the natural organic matter on Atchafalaya River delta sediments by several methods resulted only in small decreases (UV oxidation) or countervailing increases (persulfate and combustion oxidation) in mass-specific absorption by sediments. This could have been due to increased metal-oxide absorption (e.g., iron oxyhydroxide colors vary widely depending on crystallinity and particle size), weakly-absorbing organic matter, or both.

Implications:

- 1) Determination of OC content from marine or aquatic particle optical properties by difference pre-and post-oxidation as conducted here could be most promising when the particles in question do not contain strongly absorbing inorganic materials – e.g. carbonate sediments, sands, and phytoplankton detritus
- 2) Light absorption by suspended clay-associated POC from the Mississippi/Atchafalaya-influenced region of the Northern Gulf of Mexico may be accounted for primarily by the Fe-containing mineral materials, while associated organic material is shaded by strongly-absorbing Fe-oxides, absorbs light only weakly, or both.

References

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