Comparison of the Wavelength Dependence of Probe Compounds Used for the Quantification of Hydroxyl Radical Production from Sodium Nitrite

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Abstract

The principal objective of this experiment is to determine which probe compound, pCBA, benzene, or methanol, should be used when measuring the production of hydroxyl radical from sodium nitrite at various wavelengths of light. This topic is being investigated as accurate quantification of hydroxyl radical at varying spatial-temporal and climatic conditions, as modeled by the varying wavelengths of light, is important for understanding biogeochemical processes and pollutant dynamics. Three probe compounds (pCBA, benzene, and methanol) were combined with sodium nitrite, a known hydroxyl radical sensitizer, and exposed to LED light at varying wavelengths (255, 275, 295, 308, and 365 nm). The quantum yields of hydroxyl radical were determined by normalizing hydroxyl radical production by light intensity and the light absorption of sodium nitrite at the different wavelengths. The best probe at each wavelength is that which is most selective for the hydroxyl radical, measured by the smallest quantum yield. It was found that methanol is the only probe compound that is suitable for all the wavelengths studied. It was also the most selective probe compound, consistently measuring the lowest quantum yields for hydroxyl radical production.

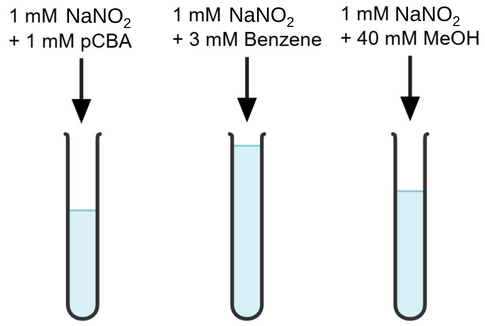
Introduction

Algal and chromophoric dissolved organic matter (CDOM) in natural freshwaters can create photochemically produced reactive intermediates (PPRI) upon the absorption of sunlight; common PPRIs include hydroxyl radical, singlet oxygen, superoxide radical anion, and excited triplet state CDOM.[1] PPRIs impact the biogeochemical processes in freshwater, such as the fate of organic contaminants and the inactivation of biological pathogens.[2] The production of PPRIs is known to be equally impacted by the intensity and wavelength of the light absorbed, but little has been done to explore the wavelength dependence of PPRI formation until recent years.[3] Some past experiments have explored wavelengths over 300 nm, but little has been done in the UV-C range, 200-280 nm.[4]

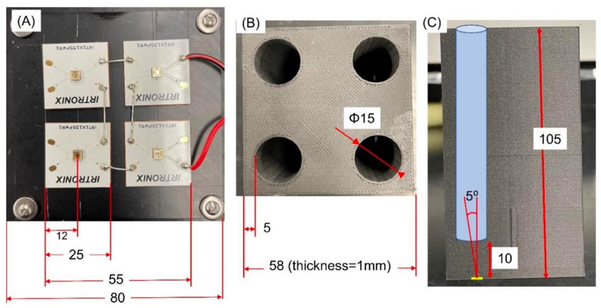
PPRIs are transient in nature and have low steady state concentrations, therefore regular analytical techniques cannot be used for their measurement.[1] Instead, probe compounds are used to detect the presence of PPRIs through the depletion or formation of a specific product, or the modification of the probe itself.[1] In this experiment, the degradation of parachlorobenzoic acid (pCBA), along with the formation of phenol from benzene and formaldehyde from methanol, serve as proxies for hydroxyl radical formation. This experiment focuses on hydroxyl radical, which is especially difficult to measure due to its high reactivity at near diffusion-controlled rates. The ability of each probe compound to quantify hydroxyl radical production from sodium nitrite was compared; sodium nitrite is a known hydroxyl radical sensitizer that generates hydroxyl radicals without producing other low-energy hydroxylating agents.

Methodology

Hydroxyl radical production from sodium nitrite was measured using pCBA, benzene, and methanol.



Solutions of each probe compound, and a blank without sodium nitrite, were exposed to varying wavelengths of UV light using LED reactors.



	UVC	UVC	UVB	UVB	UVA
λ	255	275	295	308	365

The light absorption by sodium nitrite, or Ra, at each wavelength was measured by UV-Vis spectroscopy and actinometry experiments using the following equation. I_{LED} is the irradiance of the LED measured using actinometry experiments, aλ is the decadic absorption coefficient of sodium nitrite found using UV-spectroscopy, and z is the pathlength of light through the solution.

$$Ra = \sum_{Peak\,\lambda\,-5}^{Peak\,\lambda\,+5} I_{LED}(1 - 10^{-a\,\lambda,dec^{*}z})$$

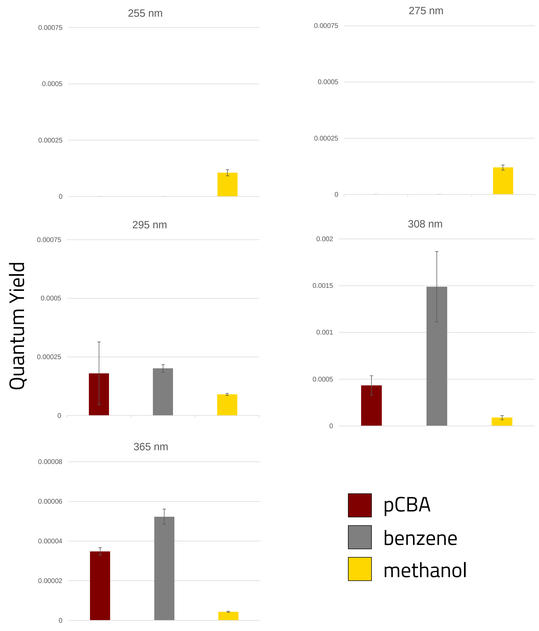
Quantum yields were calculated and compared for each probe compound. R_{OH} is the rate of hydroxyl radical production and Ra is the rate of light absorption.

$$\Phi_{app,\,^{\bullet}OH} = \frac{R_{l,\,^{\bullet}OH}}{R_a}$$

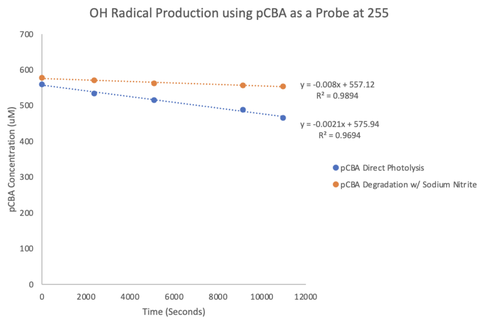
Results

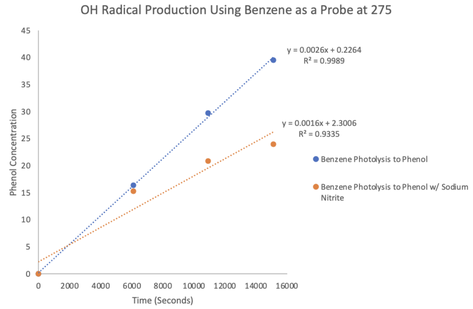
Methanol was the only probe compound that worked at every wavelength studied. Methanol was consistently the most selective, as it resulted in the lowest quantum yield and could detect smaller amounts of hydroxyl radical production than the other probe compounds.

Quantum Yield of Hydroxyl Radical Production from Sodium Nitrite



At lower wavelengths, pCBA and benzene were not suitable probe compounds because the rates of direct photolysis of pCBA and photolysis of benzene to phenol exceeded the rates of their reactions with the hydroxyl radical in the sodium-nitrite containing solutions.





Conclusion

It is concluded that methanol is the best probe compound for use across the studied wavelength range as it is consistently most selective for hydroxyl radical, resulting in the lowest quantum yields. These findings have potential implications for the creation of future environmental models, and for understanding the photochemistry of surface waters. The high quantum yield values using pCBA and benzene may be explained by reactions with the nitric oxide radical, which is formed alongside hydroxyl radical in the reaction of sodium nitrite, water, and light. Similar to hydroxyl radical, nitric oxide radical may open the conjugated hydrocarbon rings in pCBA and benzene via electrophilic addition, resulting in overestimated hydroxyl radical production rates, and therefore higher quantum yields. Methanol, on the other hand, does not contain any ring structures and is unaffected. Future research could include running similar experiments with a different hydroxyl radical sensitizer, such as hydrogen peroxide, which does not create any species besides hydroxyl radical upon sensitization. Organic matter could also be used instead of sodium nitrite to observe the outcomes of the probe compounds in natural systems.

References

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