Dark Production of Hydroxyl Radicals by Aeration of Anoxic Prairie Pothole Lake Water

Zi-Yao Ngai

Faculty mentor: Professor William Arnold

Department of Civil, Environmental and Geo-Engineering

Introduction

Hydroxyl radicals (•OH) are molecules produced throughout diverse aquatic and atmospheric environments that have important implications for pollutant processing, carbon cycling in air and water, and oxidative processing of natural organic matter. •OH is produced through solar driven reactions between common water constituents. However, recent research has shown that •OH can also be produced through non-photochemical pathways in water.

The Cottonwood Lakes Study Area contains prairie pothole lakes (depression wetlands) that are high in dissolved organic matter (DOM) and varying concentration of hydrogen sulfide (HS^-). The anoxic water in the sediments with high DOM content are a place to study the production of •OH in the absence of oxygen and processing of natural organic matter and pollutants. Furthermore, the varying sulfide concentrations in the wetlands is also important for understand pollutant processing. In this project, the dark production of •OH was evaluated by the reaction of oxygen with anoxic water samples from four wetlands (P1, P8, P7, and T9).

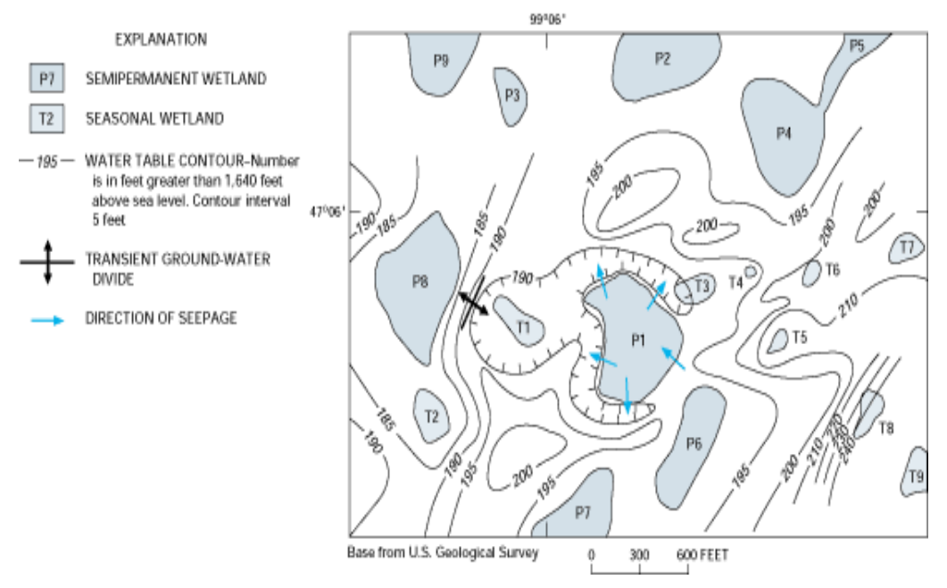


Fig 1. *The Cottonwood Lake Study Area, Stutsman County, North Dakota.*

Methods

The samples from P1, P8, P7, and T9 were previously collected using a dredge and the porewater was collected by centrifugation. The production of •OH was determined by the transformation of terephthalic acid (TA) into hydroxyterephthalic acid (TAOH). The TAOH production is multipled by 5 to get the •OH formation.

Water samples (30 mL) were spiked with concentrated terephthalic acid (TA) in a reactor to make a final concentration of 1 mM. The samples were placed in a reactor (with an anaerobic glovebag) and wrapped in aluminum foil to prevent phototransformation. The samples were then air-equilibrated in the dark by using magnetic stirring. Approximately 1mL of water samples was analyzed over time by high pressure liquid chromatography (HPLC) for monitoring of TA and TAOH concentrations. The total hydrogen sulfide ($[H_2S]_T$) concentration was determined by using methylene blue method. A 1-mL 1:4 (v/v) diluted water sample was mixed with 80 µL of diamine reagent. The methylene blue solution was diluted with ultrapure water in a ratio of 1:50 (v/v) and the absorbance of the solution was measured at 670 nm by a Shimadzu UV-1601 PC spectrometer. Another set of samples P1 and P8 were used for eliminating the hydrogen sulfide in the samples. It was done by reducing the pH to 5, sparging in nitrogen and then raising the pH back to the original value. The samples were then run with TPA and sulfide was spiked into the reactor at the 4th hour to make a final concentration of 2mM as a way to determine the sulfide contribution in •OH production.

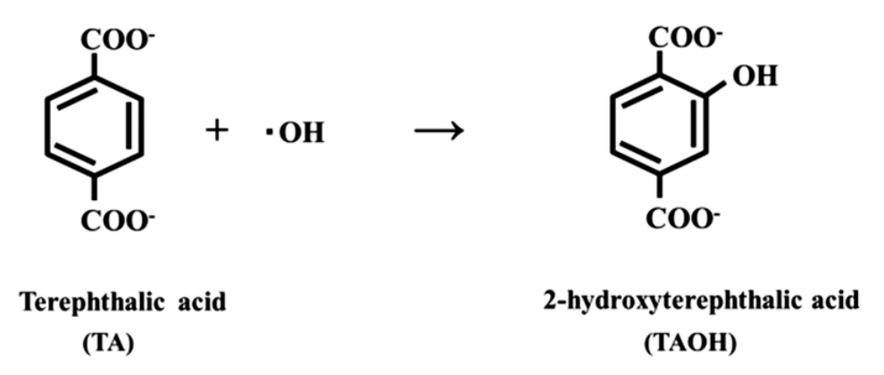


Fig 2. *Terephthalic acid probe reaction*

Fig 3. *Reactor*

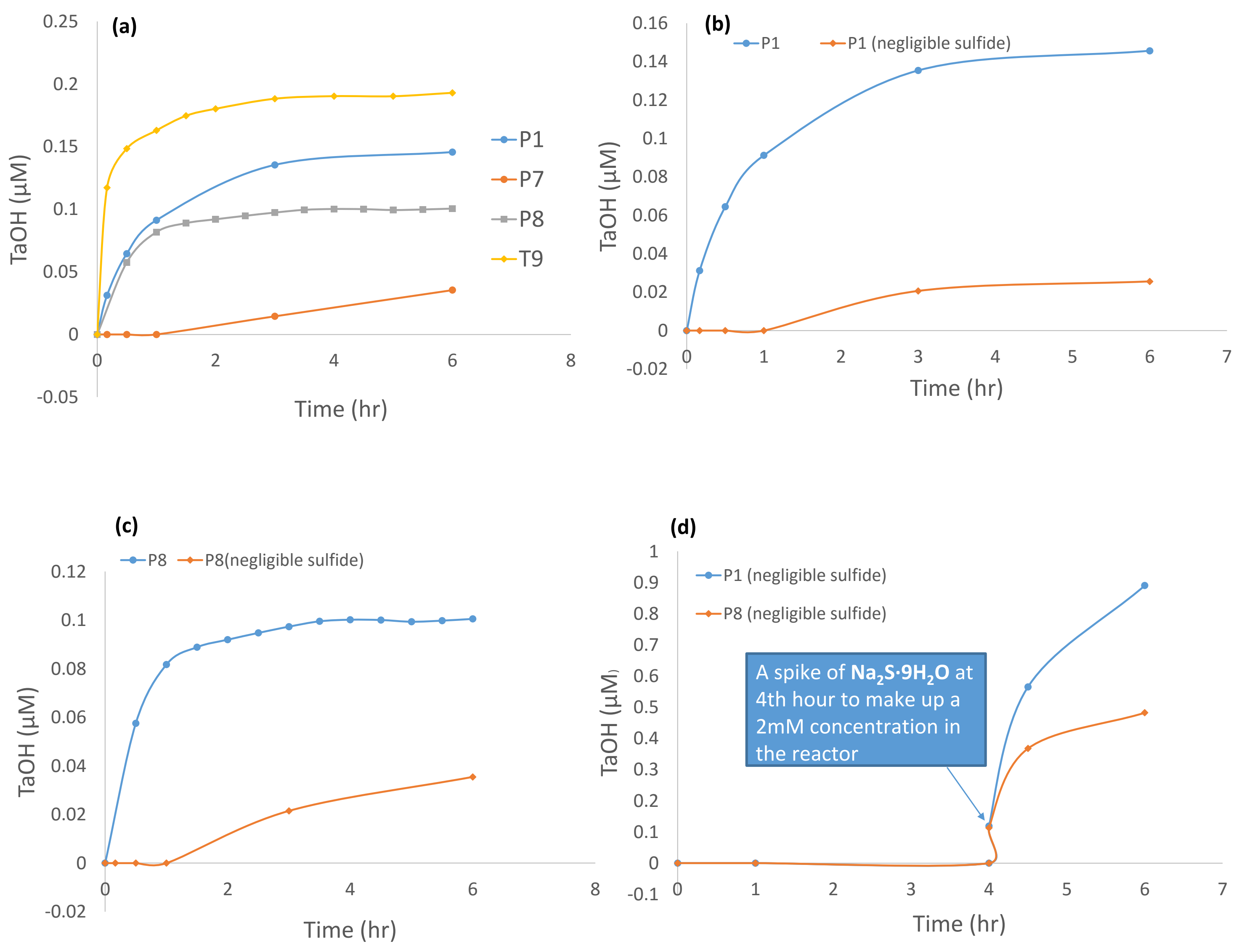
Fig 4. *Methylene blue method used for sulfide measurement*

Results

The sulfide concentration (from high to low) for different hydrologic settings is P8 > P1 > P7 > T9. P1 and P8 samples contain higher sulfide concentration due to sulfate discharge that its receives water from the groundwater system. T9 sample contains lowest sulfide concentration because it is recharge wetland that adds water to the groundwater system. P7 is a flow through wetland between recharge and discharge location. The trend of the •OH production is shown in Figure 5. The •OH production trend (from high to low) for 4 different wetlands is T9 > P1 > P8 > P7 (Fig. 5(a)). To determine the contribution of sulfide to the production of •OH, the hydrogen sulfide in another set of P1 and P8 samples was eliminated to a negligible amount and the experiment is carried out with TPA. The •OH production trend in (Fig. 5(b) and 5(c)) shows negligible •OH production in the absence of sulfide. When the sulfide is spiked into P1 and P8 samples at 4th hour (Fig. 5(d)), the •OH production increases tremendously, which suggests the sulfide is contributing to the •OH production. The reason P1 and T9 samples has higher •OH production than P8 is most probably because of the higher amount of electrons (e-) available in the DOM present in the samples. There are 3 possible reaction mechanisms in this system are shown in (Fig.6)

Table 1. *Table of wetland conditions, TAOH and OH radical formation.*

Water Samples	Date of Sampling	Condition		TAOH Formation at 6th Hour (µM)	Max Hydroxyl radical production at 6th hour (µM)
		Initial sulfide conc (mM)	pH		
P1 March 2015	May 2014	1.57	8.7	0.1457	0.7283
P7 March 2015	May 2014	0.29	~8.5	0.0355	0.1775
P8 March 2015	May 2014	2.11	8.5	0.1005	0.5025
T9 March 2015	May 2014	0.26	~8.5	0.193	0.9649
P1 (negligible sulfide with a spike of sulfide at 4th hour)	Nov 2014	0.15	8.9	0.8903	4.4515
P8 (negligible sulfide with a spike of sulfide at 4th hour)	Nov 2014	0.13	8.7	0.4822	2.411



A spike of **$Na_2S·9H_2O$** at 4th hour to make up a 2mM concentration in the reactor

Fig 5. *Relationship between TAOH formation and the time of reaction. (**a**) Comparison between 4 wetlands (P1, P7, P8, T9). (**b**) Comparison between original P1 and P1 with negligible amount of sulfide. (**c**) Comparison between original P8 and P8 with negligible amount of sulfide. (**d**) Comparison between both P1 and P8 with negligible amount of sulfide with a spike of sulfide at 4th hour.*

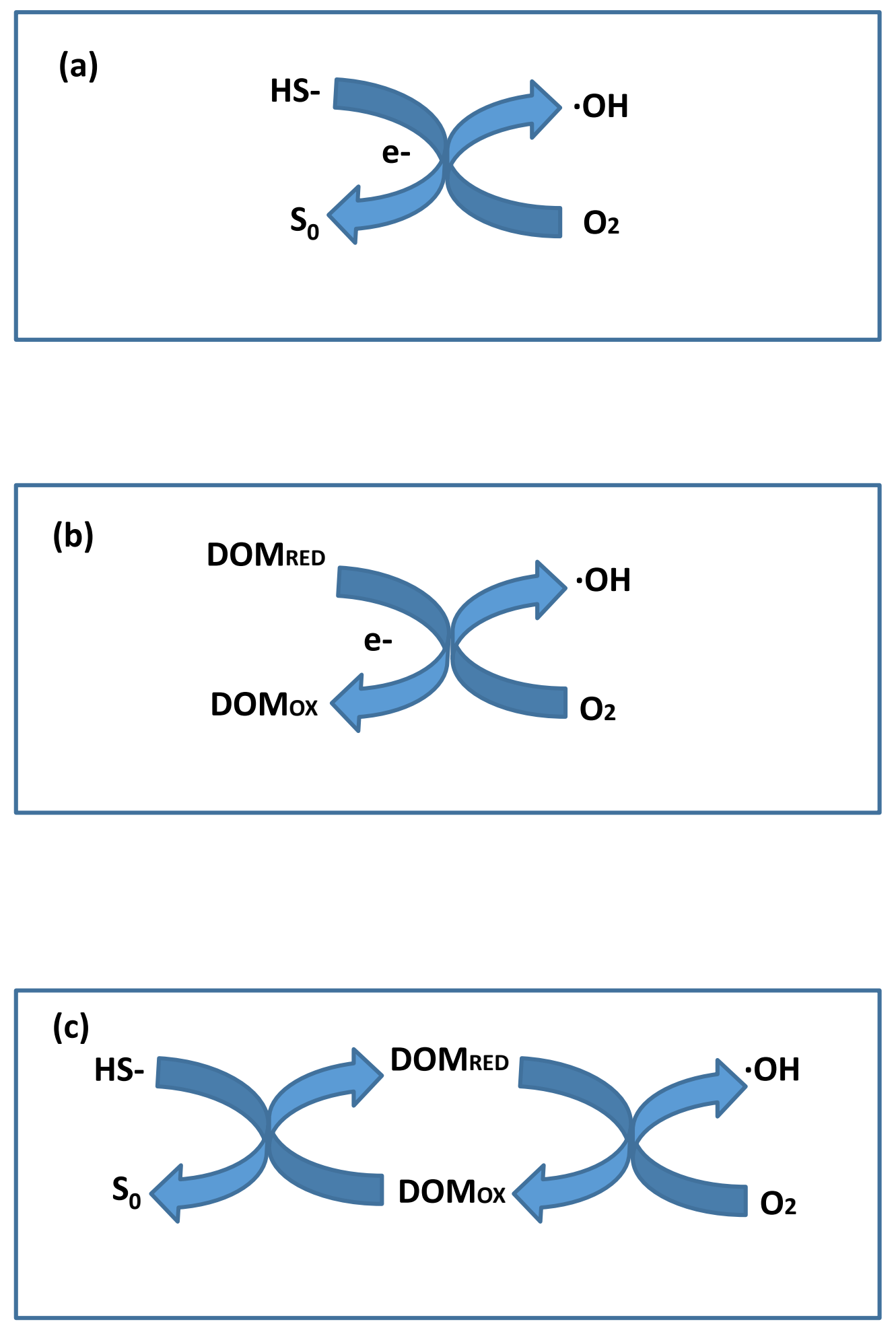


Fig 6. *Possible pathways of ·OH production. (**a**) Hydrogen sulfide reacting with oxygen. (**b**)DOM reacting with oxygen (**c**) Hydrogen sulfide reacting with DOM and oxygen.*

Conclusions

The results highlight the contribution of dissolved organic matter (DOM) and varying concentration of hydrogen sulfide (HS^-) in the prairie pothole lake water sample to the •OH production. Therefore, the different hydrologic setting of wetlands induce a significant effect on •OH production. The high •OH production at the wetlands also shows high potential for pollutant transformation at the prairie pothole lakes. There are 3 possible reaction mechanisms in this system which are hydrogen sulfide reacting with oxygen, DOM reacting with oxygen and hydrogen sulfide reacting with DOM and oxygen. With the project moving forward, it is crucial to investigate which reaction mechanism is governing the system in the prairie pothole lakes.

References

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