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Phototransformation of sulfamethoxazole (SMX) in open water treatment wetlands

Unit process wetlands and riparian zones

Re-Inventing the Nation’s Urban Water Infrastructure (ReNUWit)

Background
Antibiotics are predominant contaminants which influence human health, livestock, and aquatic life and also resist biological wastewater treatment. Therefore, there is an urgent need to remove them from wastewater. Among these antibiotics is sulfamethoxazole (SMX) which is ubiquitous in wastewater effluents. With increasing populations and with the expansion of water reuse, the amount and concentrations of contaminants such as SMX released to surface waters is of growing concern. The goals of this project are to:
- Provide a fundamental understanding of sulfamethoxazole phototransformation in open water wetlands used to treat wastewater effluent and reverse osmosis concentrate from water reuse.
- Evaluate factors influencing the rate of sulfamethoxazole removal via direct and indirect (photosensitized) pathways.

Approach
Multiple factors affecting SMX removal were evaluated, including: pH, carbonate and bicarbonate concentrations, natural organic matter, and the use of different buffers under experimental conditions.

Experiments were conducted as follows:
- Experiments were conducted in phosphate or borate buffer, in black-painted beakers.
- Experiments were maintained at constant temperature in a water bath (20°C).
- All experiments were constantly stirred.
- Solutions were irradiated with a sunlight simulator.
- Sunlight simulator output was verified at the beginning of each experiment using a spectroradiometer.
- Nitrite and sulfamethoxazole (SMX) were spiked in buffer solutions.
- Sodium perchlorate was added as an ionic strength control.
- Liquid chromatography–mass spectrometry (LC-MS) was used to quantify the decrease in SMX concentration.
- Pseudo-first order rate constants (k) were calculated based on linear regression of the natural log of concentration versus time.

Results
Buffer Effect
No effect of different buffers was observed. Phosphate and borate buffers (both 5 mM) result in the same SMX removal rate.

pH Effect
Experiments were conducted over a range of pH from 6-10.
- pH had no effect on the rate of phototransformation of SMX in the presence of nitrite (5 mM).

Bicarbonate Effect (pH 6)
- The addition of bicarbonate (up to 50 mg/C/L) had no effect on SMX removal rates, indicating a lack of effect of radical scavenging by bicarbonate.

Carbonate Effect (pH 10)
- SMX removal was enhanced by the presence of carbonate (pH 10). This result indicates that carbonate radicals form and react with SMX, increasing removal rates.

Natural Organic Matter (NOM) Effect (pH 7)
- With different amount of Natural Organic Matter (NOM), there is no effect on the SMX removal rates. This result indicates that nitrite-sensitized photolysis occurs via pathways that are not affected (i.e., scavenged) by NOM.

Conclusions
- We notice that the type of buffer used does not impact the rate of elimination of SMX.
- Nitrite contributes to the photolysis of SMX.
- The change in pH over a range of 6-10 has no effect on the rate of removal of SMX in buffer solutions.
- At pH 10, we notice that the concentration of carbonate does impact the rate of removal of SMX. Higher carbonate concentrations result in faster removal.
- Natural organic matter does not affect removal rates of SMX in the presence of nitrite, even at high concentrations (50 mg/L NOM).
- Overall, nitrite-sensitized phototransformation of SMX is not inhibited by common wastewater constituents such as bicarbonate and organic matter.

Next Steps
- Conduct experiments in actual wastewater and reverse osmosis concentrate in order to verify the applicability of our results to a realistic scenario.
- Investigate SMX phototransformation when irradiated by a UV lamp (as used in engineered water treatment).

Acknowledgements
I would like to express my sincere gratitude to my principal investigator, David Sedlak, and my graduate student mentor, Rachel Scholes, at the University of California, Berkeley. I thank my friends who provided me with much emotional support and advice through this journey. In particular, I am grateful to Ives Galley and Jalang Conteh, for advising me and encouraging me to give my best in the work I am doing. Moreover I would like to express an ethos of gratitude to the ReNUWit staff, mostly to Pamela Beth McLeod for her constant help and the video conference workshops she was helping facilitate.

Last but not the least, I would like to thank my family: my parents and my brothers and sisters for supporting me by all means and constituting my true hope. They are the reasons why I have the motivation to do what I am doing.

Supported by the National Science Foundation at:
NSF National Science Foundation