Chemosphere 155 (2016) 640–647

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

# Seasonal and spatial variabilities in the water chemistry of prairie pothole wetlands influence the photoproduction of reactive intermediates

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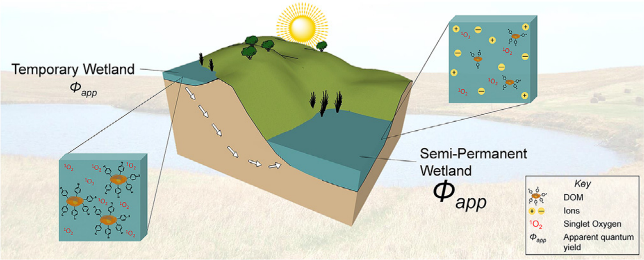
## HIGHLIGHTS

- Variable water chemistry of prairie wetlands influences PPRI formation.
- $\Phi_{app}$ of PPRIs are greater in semi-permanent wetlands than temporary wetlands.
- $[PPRI]_{ss}$ are greater in temporary wetlands than semi-permanent wetlands.
- $\Phi_{app}$ of PPRIs increase through the growing season.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 27 January 2016
Received in revised form
3 April 2016
Accepted 20 April 2016
Available online 9 May 2016

Handling Editor: Frederic Leusch

*Keywords:*
Prairie pothole wetlands
Dissolved organic matter
Apparent quantum yield
Photochemically-produced reactive intermediates

## ABSTRACT

The hydrology and water chemistry of prairie pothole wetlands vary spatially and temporally, on annual and decadal timescales. Pesticide contamination of wetlands arising from agricultural activities is a foremost concern. Photochemical reactions are important in the natural attenuation of pesticides and may be important in limiting ecological and human exposure. Little is known, however, about the variable influence of wetland water chemistry on indirect photochemistry. In this study, seasonal water samples were collected from seven sites throughout the prairie pothole region over three years to understand the spatiotemporal dynamics of reactive intermediate photoproduction. Samples were classified by the season in which they were collected (spring, summer, or fall) and the typical hydroperiod of the wetland surface water (temporary or semi-permanent). Under photostable conditions, steady-state concentrations and apparent quantum yields or quantum yield coefficients were measured for triplet excited states of dissolved organic matter, singlet oxygen, hydroxyl radical, and carbonate radical under simulated sunlight. Steady-state concentrations and quantum yields increased on average by 15% and 40% from spring to fall, respectively. Temporary wetlands had 40% higher steady-state concentrations of reactive intermediates than semi-permanent wetlands, but 50% lower quantum yields. Computed quantum yields for reactive intermediate formation were used to predict the indirect photochemical half-lives of seven pesticides in average temporary and semi-permanent prairie pothole wetlands. As a first approximation, the predictions agree to within two orders of magnitude of previously reported half-lives.

## 1. Introduction

Prairie pothole wetlands are unique, internally drained wetland

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http://dx.doi.org/10.1016/j.chemosphere.2016.04.078
0045-6535/

ecosystems of the Northern Great Plains that are critically important for regional hydrology (Euliss and Mushet, 1996; Hubbard and Linder, 1986; Winter and Rosenberry, 1998), breeding of waterfowl and other birds (Delphey and Dinsmore, 1993), and regional greenhouse gas flux (Tangen et al., 2015). Row crop agriculture throughout the region has resulted in pesticide contamination of many prairie wetlands, posing a risk to human and ecological health (Donald et al., 2007, 2001; Goldsborough and Crumpton, 1998; Grue et al., 1988; Main et al., 2014; Messing et al., 2011). Understanding the spatiotemporal dynamics of pesticide fate in these systems is essential for risk assessment and implementation of control strategies.

Photochemical reactions of pesticides have been well-documented and are important in modeling pesticide fate (Gerecke et al., 2001; Huntscha et al., 2008; Müller et al., 1997; Remucal, 2014). Many pesticides are photochemically transformed in prairie wetland surface waters (Zeng and Arnold, 2013). This study aims to extend this previous work to understand how differing wetland water chemistries, arising from spatial and temporal forcings, influence photoproduction of reactive intermediates and pesticide fate.

The terrain in the prairie pothole region ranges from hummocky glacial till to relatively flat in glacial outwash plains (Sloan, 1972). Depending on the spatial location of wetlands in the landscape and the balance between precipitation and evapotranspiration, prairie wetlands may have long hydroperiods, holding surface water throughout an entire year and only going dry during times of severe drought (lowland permanent and semi-permanent wetlands), or wetlands may have short hydroperiods, regularly going dry at some point throughout a year (upland seasonal, temporary, and saturated soil wetlands) (Dahl, 2014; Sloan, 1972). In addition, depending on the predominant interaction between surface water and groundwater, wetlands are designated as groundwater recharge, discharge, or flow-through (Sloan, 1972). These interactions change as local and regional water balances shift in response to climatic and surrounding land use changes (Euliss and Mushet, 1996; LaBaugh et al., 1998; Winter and Rosenberry, 1995). The varying hydrologic regimes in combination with seasonal changes in temperature, sunlight exposure, and microbial activity cause water chemistry characteristics of the wetlands to vary on temporal and spatial scales (Cook and Hauer, 2007; Detenbeck et al., 2002; LaBaugh, 1989; LaBaugh et al., 1987; Waiser and Robarts, 2004).

Under optically dilute environmental conditions, the aqueous phase phototransformation rate ($R_{l,P}$, M s$^{-1}$) of a pesticide ($P$) follows a pseudo-first order model:

$$R_{l,P} = \frac{d[P]}{dt} = -k_{obs}[P] \tag{1}$$

The pseudo-first order rate constant, $k_{obs}$, includes contributions from direct photochemical reactions (reactions due to direct sunlight absorption by $P$) and indirect photochemical reactions (second order reactions between $P$ and photochemically-produced reactive intermediates (PPRIs)). PPRIs include hydrated electrons, superoxide, hydrogen peroxide, hydroxyl radical (•OH), carbonate radical ($CO_3^{•-}$), singlet oxygen ($^1O_2$), and triplet excited states of dissolved natural organic matter ($^3$DOM*) (Whitehead and De More, 2000; Zafiriou et al., 1984). These reactive species are particularly important in the transformation of contaminants that lack absorption bands >290 nm (Zepp et al., 1981).

Water chemistry characteristics, such as the concentration of dissolved oxygen, ionic strength, and characteristics of dissolved natural organic matter (DOM), are critically important in controlling both direct and indirect photochemical pathways (Parker et al., 2013; Sharpless et al., 2014). Chromophoric DOM (CDOM) absorbs much of the sunlight in the mixed surface layer of water bodies (Schwarzenbach et al., 2003), which consequently impedes the direct phototransformation of $P$. At the same time, when CDOM absorbs sunlight it acts as a photosensitizer undergoing charge-transfer (electron or hydrogen atom) and energy-transfer processes that may react with $P$ or form secondary PPRIs. DOM is also a scavenger and quencher of PPRIs and reaction intermediates, thereby decreasing the net loss of contaminants (Canonica and Laubscher, 2008; Wenk et al., 2011; Young et al., 2013).

Taken together, in natural water systems, $k_{obs}$ is a combination of these processes:

$$k_{obs} = SF \times k_a \Phi_d + \sum k_{PPRI,P}[PPRI]_{ss} - \sum k' \tag{2}$$

where $k_a$ (Es mol$^{-1}$ s$^{-1}$) is the specific rate of light absorption, $\Phi_d$ (mol Es$^{-1}$) is the quantum yield for direct photolysis, and $SF$ is a screening factor that accounts for the fraction of light absorbed by CDOM. The second order terms ($\Sigma k_{PPRI,P}[PPRI]_{ss}$) correspond to a suite of reactions between PPRIs and $P$. The notation, $[PPRI]_{ss}$, represents the steady-state concentration of the PPRI. Finally, $\Sigma k'$ (s$^{-1}$) is a summation of (pseudo-) first and second order processes that accounts for alternative photochemical processes, such as DOM inhibiting reactions between $P$ and $^3$DOM* or reformation of parent contaminants in the dark (Canonica and Laubscher, 2008; Qu et al., 2013; Wenk et al., 2011).

Equation (3) shows the working definition of $k_{obs}$ for this study. The term $\Sigma k'$ is not included in this definition because the contributing processes have only been observed in controlled laboratory experiments and defining these rate constants is beyond the scope of this work. Previous work has demonstrated that this definition accounts for ~90% of the overall observed phototransformation of pesticides in prairie wetland surface waters (Zeng and Arnold, 2013).

$$k_{obs} = SF \times k_a \Phi_d + k_{T,P}\left[^3DOM^*\right]_{ss} + k_{S,P}[^1O_2]_{ss} + k_{^\bullet OH,P}[^\bullet OH]_{ss} + k_{CO3\bullet,P}\left[CO_3^{\bullet -}\right]_{ss} \tag{3}$$

Here, the reactions between PPRIs and $P$ have been explicitly defined as second order rate terms, where $k_{T,P}$, $k_{S,P}$, $k_{•OH,P}$, and $k_{CO3•,P}$ (M$^{-1}$ s$^{-1}$) are the second order rate constants for the reaction with $^3$DOM*, $^1O_2$, •OH, and $CO_3^{•-}$, respectively. Further, the steady-state concentrations of the PPRIs can be written in terms of quantum yields ($\Phi_{PPRI}$) and apparent quantum yields ($\Phi_{app,PPRI}$), defined as the ratio of the rate of production of the PPRI to the rate of light absorption by the water sample. Quantum yields are termed *apparent* when the PPRI is not directly formed from light absorption, as is the case for $^1O_2$, •OH, and $CO_3^{•-}$. The goal of this study was to define the steady-state concentrations and (apparent) quantum yields of $^3$DOM*, $^1O_2$, •OH, and $CO_3^{•-}$ in a variety of prairie wetlands to determine how they vary with season and location. Such an understanding is important to fully understand aquatic dissipation of pesticides.

## 2. Materials and methods

### 2.1. Sample collection

Surface water samples were collected from four native prairie pothole wetlands, two restored wetlands, and one cropland drain tile intake. See Supplementary Material Table S1 and Fig. S1 for descriptions and locations of sampling sites. Wetlands were classified as either semi-permanent or temporary to indicate if surface