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

Andrew J. McCabe and William A. Arnold*

University of Minnesota, Department of Civil, Environmental, and Geo- Engineering,
Minneapolis MN, 55455

*Corresponding author: phone: 612-625-8582, fax: 612-626-7750 email: arnol032@umn.edu

Word count: 5563, Text: 3463, Figures (5) and Tables (2): 2100

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.

Keywords

Prairie pothole wetlands, Dissolved organic matter, Apparent quantum yield, Photochemically-produced reactive intermediates

1. Introduction

Prairie pothole wetlands are unique, internally drained wetland 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:

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

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 ($\cdot OH$), carbonate radical ($CO_3^{\cdot -}$), singlet oxygen (1O_2), and triplet

excited states of dissolved natural organic matter ($^3\text{DOM}^*$) (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 PPRI. DOM is also a scavenger and quencher of PPRI 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:

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

Where k_a ($\text{Es mol}^{-1} \text{s}^{-1}$) is the specific rate of light absorption, Φ_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 ($\sum k_{PPRI,P} [PPRI]_{ss}$) correspond to a suite of reactions between PPRI and P . The notation, $[PPRI]_{ss}$, represents the steady-state concentration of the PPRI. Finally, $\sum k'$ (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 $^3\text{DOM}^*$ 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).

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

Here, the reactions between PPRI and P have been explicitly defined as second order rate terms, where $k_{T,P}$, $k_{S,P}$, $k_{\bullet OH,P}$, and $k_{CO_3\bullet,P}$ ($M^{-1} s^{-1}$) are the second order rate constants for the reaction with $^3DOM^*$, 1O_2 , $\bullet OH$, and $CO_3^{\bullet-}$, respectively. Further, the steady-state concentrations of the PPRI can be written in terms of quantum yields (Φ_{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 , $\bullet OH$, and $CO_3^{\bullet-}$. The goal of this study was to define the steady-state concentrations and (apparent) quantum yields of $^3DOM^*$, 1O_2 , $\bullet OH$, and $CO_3^{\bullet-}$ 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 Figure S1 for descriptions and locations of sampling sites. Wetlands were classified as either semi-permanent or temporary to indicate if surface water was usually present throughout the

entire growing season or if surface water was absent for some portion of the growing season, respectively. The four native wetlands are located in the Cottonwood Lakes study area (U.S. Geological Survey) near Jamestown, ND, USA. The wetlands included in this study were P1, a semi-permanent, groundwater discharge wetland, P7 and P8, two semi-permanent, groundwater flow-through wetlands, and T9, a temporary, groundwater recharge wetland. P7 is immediately adjacent to cropland and half of T9 is enclosed in cattle pastureland. The two restored wetlands are located in Glacial Ridge National Wildlife Refuge (U.S. Fish and Wildlife Service) near Crookston, MN, USA. These wetlands have been restored since 2007 and local groundwater hydrology has not been well-characterized following prairie and wetland restoration. The wetlands included in this study were R1, a seasonally flooded wetland, and R2, a saturated soil wetland that is immediately adjacent to cropland. The drain tile intake site, D1, is located on a farm near Tracy, MN, USA. R1, R2, and D1 were classified as temporary wetlands.

Samples were collected seasonally (spring, summer, and fall) from the P1, P7, P8, and T9 between July 2012 and November 2014. Samples were collected seasonally from the R1 and R2 between May 2013 and November 2014. Three samples, following snowmelt in March 2013 and two storm events in June 2014, were collected from site D1.

All samples were collected in combusted (550 °C for ≥ 5 hours) glass bottles from the top 50 cm of the water column. Samples were immediately stored on ice. Samples were prefiltered with combusted glass-fiber filters (Millipore, 0.7 μm pore size) and filter-sterilized with nitrocellulose membrane filters (Millipore, 0.22 μm pore size). Nitrocellulose membranes were used from the manufacturer without pretreatment. Samples collected in 2012 were stored frozen and all others were stored at 4 °C until analysis or experimentation. The pH of the samples

changed typically by < 5% over the storage period. The Supplementary Material includes the treatment of frozen samples prior to experimentation.

2.2 Chemicals

Ultrapure water (18.2 MΩ·cm) was supplied by a Milli-Q Academic system (Millipore). All chemicals were used as received from the manufacturers. A list of chemicals and purities is included in the Supplementary Material.

2.3 Water Chemistry Analysis

Conductivity and pH were measured on site and following filtration with a Model 72 Engineered Systems and Design conductivity meter and WTW 340i pH meter with Sensorex S200C probe, respectively. Anions (fluoride, chloride, nitrite, bromide, nitrate, orthophosphate, and sulfate) were measured using a Metrohm 761 Compact ion chromatograph. Alkalinity was measured by HCl titration using bromocresol green indicator (Eaton et al., 1995). Dissolved iron ($[\text{Fe}^{2+}] + [\text{Fe}^{3+}]$) was measured by the ferrozine method (Viollier et al., 2000). Dissolved organic carbon (DOC) concentrations were measured using a Shimadzu TOC-L analyzer operated in non-purgeable organic carbon mode.

Ultraviolet-visible light absorption spectra were measured with a Shimadzu UV-1601PC spectrophotometer using 1-cm quartz cuvettes. CDOM spectroscopic parameters, including the absorption coefficients at 254, 350, and 412 nm (a_{254} , a_{350} , and a_{412} , m^{-1}), specific UV absorbance values (SUVA) at 254 and 350 nm, E2/E3 (a_{250}/a_{365}), spectral slope ($S_{300-500}$, nm^{-1}), and slope ratio (S_R), were determined for all samples (calculations are included in the Supplementary Material). These parameters were used as proxies to assess DOM character. The a_{254} , a_{350} , and a_{412} values were used to assess general trends in UV and visible light absorbance, SUVA values were used to assess DOM aromatic content and DOC specific UV absorbance, and E2/E3, $S_{300-500}$,

and S_R were used to assess DOM photobleaching and molecular weight shifts (Helms et al., 2008).

2.4 Photochemical Experiments

All photochemical experiments were performed in an Atlas Suntest CPS+ solar simulator equipped with a xenon arc lamp and a 290-nm cutoff filter (Figure S2). The light intensity between 300 – 800 nm was set to 350 W m^{-2} . The temperatures of the reaction solutions in the solar simulator were maintained below 30°C by blowing ambient air at $\sim 20^\circ\text{C}$ through the chamber.

The rates of light absorption by the samples in the solar simulator (R_a , $\text{Es L}^{-1} \text{ s}^{-1}$) were calculated following the example of Sharpless et al. (2014). Bimolecular actinometer solutions of p-nitroanisole/pyridine and p-nitroacetophenone/pyridine were used to determine the spectral intensity of the lamp. Calculations of R_a are included in the Supplementary Material.

The (apparent) quantum yields, rates of formation, and steady-state concentrations of $^3\text{DOM}^*$, $^1\text{O}_2$, $\cdot\text{OH}$, and $\text{CO}_3^{\cdot-}$ in the samples were measured with the molecular probes 2,4,6-trimethylphenol (TMP), furfuryl alcohol (FFA), terephthalic acid (TPA), and N,N-dimethylaniline (DMA), respectively. Quantum yield coefficients (f_{TMP} , L Es^{-1}) and pseudo-first order rate constants for TMP loss ($k_{\text{obs,TMP}}$, s^{-1}) were used as surrogates for quantum yields and steady-state concentrations of $^3\text{DOM}^*$, respectively.

All experimental glassware was combusted before use and syringes were rinsed copiously with deionized and ultrapure water. Experimental solutions were prepared by spiking aqueous solutions of probe molecules into 25-mL of filtered surface water. These solutions were split into three quartz test tubes ($13 \times 100 \text{ mm}$). The test tubes were covered with combusted aluminum foil and sealed with rubber septa (Suba Seal). Test tubes were held at a 30° angle from

horizontal and sub-samples were collected for analysis by high-pressure liquid chromatography (HPLC, Agilent 1100) (Table S2). Steady-state concentrations of PPRI were computed assuming photostable conditions in the solar simulator and assuming probe concentrations were low enough such that PPRI steady-state concentrations were negligibly impacted by the probe molecules. Direct photolysis of the probes was assessed in 10 mM borate buffer at pH 8.5. Dark control experiments for each probe were conducted in sample water with foil-wrapped test tubes. Air-saturated conditions were maintained by mixing reaction solutions following sub-sample collection. Complete experimental procedures, analytical protocols, and kinetic models are included in the Supplementary Material.

2.5 Data processing.

Data and statistical analyses were performed using Microsoft Excel 2013 and MATLAB R2014a. Principal component analysis (PCA) was performed using average water chemistry and photochemistry characteristics for each wetland to determine relevant sample groupings. Kruskal-Wallis analysis of variance (ANOVA) was performed to determine if systematic inter-annual variation existed among the data. Further details on statistical processing are provided in the Supplementary Material.

3. Results and Discussion

Wetlands were grouped by class (semi-permanent or temporary) and season (spring, summer, or fall) based on PCA and Kruskal-Wallis ANOVA results to facilitate interpretation of general spatiotemporal trends (Figure S4 and Table S3).

3.1 Water Chemistry

The average observed pH, bicarbonate concentration, DOC, and conductivity was higher in semi-permanent wetlands than in temporary wetlands (Figure 1). Seasonally, the pH remained

207 relatively constant in both wetland classes. Likewise, bicarbonate remained relatively constant

Figure 1. Box-and-whisker plots of seasonal (A) pH, (B) bicarbonate, (C) conductivity, and (D) DOC in semi-permanent (red) and temporary (blue) wetlands. The length of the whiskers (w) are defined as $\pm 1.5 \times$ the inner quartile range. Outliers (x) are defined as values greater than $q_3 + w(q_3 - q_1)$ or less than $q_1 - w(q_3 - q_1)$, where q_1 and q_3 are the quartiles. The dashed gray line indicates a change in the scale of the y-axis. The scale above the gray dashed line is arbitrary and is only used to show outliers within the same scale as the data.

208 from spring to fall in semi-permanent wetlands, but increased by a factor of two in temporary
 209 wetlands. The average DOC increased in semi-permanent and temporary wetlands by 20% and
 210 80% from spring to fall, respectively. Conductivity also increased by 40% and 90% in semi-
 211 permanent and temporary wetlands, respectively.

212 Temporary wetlands had higher average a_{254} values than semi-permanent wetlands which
 213 increased in both wetland classes through the growing season (Figure 2). This suggests either a
 214 concentrating mechanism or input of DOM with high UV absorbance from spring to fall.
 215 Comparison of $SUVA_{254}$ values suggest that temporary wetlands also had DOM with higher
 216 aromatic content than semi-permanent wetlands. Decreasing $SUVA_{254}$ values from spring to fall

217 suggests that aromatic DOM is lost in both wetland classes during the growing season. Semi-
 218 permanent wetlands had higher E2/E3 and S_R values than temporary wetlands indicating that

Figure 2. Box-and-whisker plots of seasonal (A) a_{254} , (B) E2/E3, (C) SUVA₂₅₄, and (D) slope ratio in semi-permanent (red) and temporary (blue) wetlands. The length of the whiskers (w) are defined as $\pm 1.5 \times$ the inner quartile range. Outliers (x) are defined as values greater than $q_3 + w(q_3 - q_1)$ or less than $q_1 - w(q_3 - q_1)$, where q_1 and q_3 are the quartiles. The dashed gray line indicates a change in scale of the y-axis. The scale above the gray dashed line is arbitrary and is only used to show outliers within the same scale as the data.

219 DOM in semi-permanent wetlands was photobleached to a greater degree and that the DOM had
 220 a lower average molecular weight. In both wetland classes, E2/E3 and S_R increased from spring
 221 to fall suggesting that DOM becomes photobleached and with concurrent shifts to lower
 222 molecular weight DOM. Additional water chemistry parameters and discussion are included in
 223 the Supplementary Material.

224 3.2 Photochemistry

Example kinetic plots of the probe molecules are shown in Figure 3. Because DMA loss in several instances was indistinguishable from its loss in buffered ultrapure water, it was not possible to reliably attribute its loss to reaction with $\text{CO}_3^{\bullet-}$ (Figure 3D). As a result, further analysis of $\text{CO}_3^{\bullet-}$ photoproduction was completed using estimates from $[\cdot\text{OH}]_{\text{ss}}$, alkalinity, and DOC.

The average apparent quantum yield or the quantum yield coefficient for each PPRI was higher in semi-permanent wetlands than temporary wetlands (Table 1). The measured steady-state concentrations of $^1\text{O}_2$, $\cdot\text{OH}$, and $\text{CO}_3^{\bullet-}$ were higher on average in temporary wetlands than semi-permanent wetlands. In contrast, the average steady-state concentration of $^3\text{DOM}^*$ ($k_{\text{obs},\text{TMP}}$) was higher in semi-permanent than temporary wetlands (Table 1).

Figure 3. Example kinetic plots of probe molecules under simulated sunlight: (A) TMP ($[\text{TMP}]_0 = 5 \mu\text{M}$), (B) FFA ($[\text{FFA}]_0 = 20 \mu\text{M}$), (C) hTPA ($[\text{TPA}]_0 = 10 \mu\text{M}$), and (D) DMA ($[\text{DMA}]_0 = 2 \mu\text{M}$). Note changes in y-axis units and scales. Error bars represent 95% confidence intervals derived from calibration curves. Where absent, error bars are smaller than the symbol. The reported p-values correspond to the confidence in the fit coefficients. Points for the P8Aug14 treatments represent averages of triplicate determinations (i.e., the average concentration from three separate test tubes). The average relative standard deviation for triplicate determinations from all experiments was 5.3% for [TMP], 6.3% for [FFA], 16% for [hTPA], and 4.2% for [DMA].

Through the growing season, the average apparent quantum yields or the quantum yield coefficients for all PPRIIs increased by 20% – 80% in both wetland classes (Figure 4). The steady-state concentrations of $^3\text{DOM}^*$, $^1\text{O}_2$, and $\text{CO}_3^{\cdot-}$ increased through the growing season in both wetland classes by 10% – 50%. The steady-state concentration of $^{\cdot}\text{OH}$, however, remained approximately constant in semi-permanent wetlands and decreased by 30% in temporary wetlands (Figure 4).

Table 1. Average photochemical characteristics for semi-permanent and temporary wetlands.

	Semi-Permanent				Temporary				
	P1 (n=8)	P7 (n=8)	P8 (n=8)	Average	T9 (n=7)	R1 (n=6)	R2 [†] (n=5)	D1 (n=3)	Average
$k_{obs,TMP}$ (hr^{-1})	3.8 (± 0.6)	3.5 (± 0.5)	2.3 (± 0.5)	3.2 (± 0.8)	4 (± 2)	2.1 (± 0.4)	1.8 (± 0.6)	3.0 (± 0.6)	3 (± 1)
f_{TMP} ($\times 10^2 \text{ L Es}^{-1}$)	2.9 (± 0.7)	2.3 (± 0.2)	1.3 (± 0.3)	2.2 (± 0.8)	1.1 (± 0.3)	0.6 (± 0.2)	0.4 (± 0.1)	1.2 (± 0.2)	0.8 (± 0.4)
$[^1\text{O}_2]_{ss}$ (pM)	1.3 (± 0.2)	1.2 (± 0.1)	1.0 (± 0.1)	1.2 (± 0.2)	1.6 (± 0.3)	1.2 (± 0.2)	1.4 (± 0.4)	1.5 (± 0.4)	1.4 (± 0.4)
$\Phi_{app,S}$ ($\times 10^{-2} \text{ mol Es}^{-1}$)	8 (± 2)	7 (± 1)	5.2 (± 0.8)	7 (± 2)	4.5 (± 0.9)	3 (± 1)	2.6 (± 0.8)	5.2 (± 0.9)	3.8 (± 1.3)
$[^{\cdot}\text{OH}]_{ss}$ (fM)	0.28 (± 0.07)	0.3 (± 0.1)	0.51 (± 0.09)	0.4 (± 0.2)	0.6 (± 0.2)	0.6 (± 0.2)	0.74 (± 0.07)	1.2 (± 0.4)	0.8 (± 0.3)
$\Phi_{app,S}^{OH}$ ($\times 10^{-5} \text{ mol Es}^{-1}$)	7 (± 2)	5 (± 2)	6 (± 1)	6 (± 2)	5 (± 9)	4 (± 2)	3 (± 8)	4 (± 4)	4 (± 2)
$[\text{CO}_3^{\cdot-}]_{ss}$ (fM)	2.6 (± 0.5)	4 (± 2)	6 (± 1)	4 (± 2)	6 (± 4)	7 (± 3)	6 (± 2)	5 (± 2)	6 (± 3)
$\Phi_{app,CO_3^{\cdot-}}$ ($\times 10^{-6} \text{ mol Es}^{-1}$)	8 (± 2)	8 (± 4)	8 (± 1)	8 (± 3)	5 (± 4)	5 (± 3)	3 (± 1)	2 (± 2)	4 (± 3)

Values in parentheses represent 1σ to show the dispersion from the mean. *Negative concentrations were set to 0. [†]Excludes R2Nov14 measurements ($k_{obs,TMP}=3.9 \text{ hr}^{-1}$, $f_{TMP}=0.6 \times 10^2 \text{ L mol}^{-1}$, $[^1\text{O}_2]_{ss}=3.6 \text{ pM}$, $\Phi_{app,S}=5.3 \times 10^{-2} \text{ mol Es}^{-1}$, $[^{\cdot}\text{OH}]_{ss}=0.6 \text{ fM}$, $\Phi_{app,OH}=13 \times 10^{-5} \text{ mol Es}^{-1}$, $[\text{CO}_3^{\cdot-}]_{ss}=2.3 \text{ fM}$, $\Phi_{app,CO_3^{\cdot-}}=6.7 \times 10^{-6} \text{ mol Es}^{-1}$).

Apparent quantum yields, quantum yield coefficients, and steady-state concentrations were plotted as functions of water chemistry and DOM spectroscopic parameters to explore trends and to establish predictability of surface water photochemistry from water chemistry (Supplementary Material). These plots show distinctive grouping between semi-permanent and temporary wetlands. The trends suggest that the efficiency of production of all PPRIIs increased with DOC, conductivity, and E2/E3. In contrast, increasing visible light absorption (a_{412}) and

DOM aromaticity (SUVA_{254}) accompanied decreased PPRI photoproduction efficiency. f_{TMP} and $\Phi_{app,S}$ show especially strong direct relationships with E2/E3 (Figure 5), suggesting increasing degrees of DOM photobleaching and decreasing DOM molecular weight result in more efficient $^3\text{DOM}^*$ and $^1\text{O}_2$ production.

The trends between E2/E3 and $\Phi_{app,S}$ and f_{TMP} are consistent with previous reports (Dalrymple et al., 2010; Halladja et al., 2007). Other observed trends, however, are inconsistent with previous laboratory studies. These include the observed impacts of ionic strength on $k_{obs,TMP}$ (Parker et al., 2013) and $\Phi_{app,\bullet OH}$ (Glover and Rosario-Ortiz, 2013) as well as the impacts of photobleaching on f_{TMP} and $\Phi_{app,\bullet OH}$ (Sharpless et al., 2014). Because these wetlands are inherently dynamic, the trends observed here do not equate to causation, requiring further laboratory studies to understand the combined impact of changing multiple water chemistry parameters (i.e. salinity, alkalinity, dissolved oxygen, and DOM character) on the formation of PPRI.

3.3 Impact on pesticide phototransformation rates

The measured PPRI quantum yields were used to predict seasonal trends in PPRI steady-state concentrations in typical semi-permanent and temporary wetlands. These predicted concentrations were used in combination with second order rate constants from Zeng and Arnold (2013) to estimate the seasonal indirect photochemical half-life of the pesticides atrazine, metolachlor, mesotrione, diuron, isoproturon, bentazon, and chlorpyrifos. Seasonal changes in solar light intensity were estimated from Leifer (1988). Temperature and turbidity changes were not considered in the model. Additional details and calculations are presented in the Supplementary Material.

Figure 4. Biplots of average [PPRIs]_{ss} versus quantum yields for 3DOM* (A and E), 1O2 (B and F), •OH (C and G), and CO3•- (D and H). A – D show seasonal trends by individual wetlands. E – H show seasonal trends by wetland class. Asterisks in A – D indicate sample collected in the spring. Relative standard deviations for data in A – D are ~20% (error bars were omitted for clarity). Error bars in E – H indicate $\pm 1\sigma$. Biplots by individual sample are shown in the Supplementary Material.

Figure 5. Trends between E2/E3 and (A) f_{TMP} and (B) $\Phi_{app,S}$. The equations for the lines of best fit are shown with correlation coefficients and p-values for the significance of the fit slopes. Dotted lines indicate 95% confidence intervals for the line of best fit and the dashed lines are the 95% prediction intervals. The red alternating dotted-dashed line in (B) shows the relationship from Dalrymple et al. (2010). The range of E2/E3 was $\sim 3 - 7$ for the Dalrymple correlation.

276 In semi-permanent wetlands, [PPRIs]_{ss} were predicted to increase by 12 – 42% from
 277 spring to summer and decrease by $\sim 50\%$ from summer to fall. Similar trends are predicted in
 278 temporary wetlands for $^3\text{DOM}^*$, $^1\text{O}_2$, and $\text{CO}_3^{\cdot-}$, but the trend for $\cdot\text{OH}$ was slightly different due
 279 to increases in DOC and alkalinity, causing sequentially lower [$\cdot\text{OH}$]_{ss} through the growing
 280 season. If the observed changes in quantum yields were ignored and springtime quantum yields
 281 for PPRI formation remained constant through the growing season, [PPRI]_{ss} would be 8 – 42%
 282 lower in semi-permanent wetlands and 23 – 47% lower in temporary wetlands (excluding the
 283 decrease in $\Phi_{app,\cdot\text{OH}}$ from spring to summer) in the summer and fall. The pesticides were
 284 predicted to undergo indirect phototransformation 7 – 59% faster in temporary wetlands than
 285 semi-permanent wetlands (Table 2). This is particularly important because in the past 20 years >
 286 90% of wetlands lost in the prairie pothole region have been temporary wetlands and most of the

gains in wetland area have been semi-permanently flooded wetlands. This has resulted in an underrepresentation of temporarily flooded wetlands throughout the region (Dahl, 2014) and may have important implications for regional rates of pesticide dissipation.

Table 2. Modelled indirect photochemical half-lives for pesticides in semi-permanent and temporary prairie pothole wetlands.

Pesticide	Semi-Permanent t_{half} (hr)			Temporary t_{half} (hr)			t_{half} (hr)*
	Spring	Summer	Fall	Spring	Summer	Fall	
Atrazine	16	12	26	7.6	10	15	115
Metolachlor	7.8	6.4	13	3.3	4.8	6.7	124
Mesotrione	6.2	5.1	10	2.6	3.8	5.2	126
Diuron	4.8	3.6	7.5	2.9	3.3	5.4	19
Isoproturon	3.6	2.7	5.7	2.4	2.6	4.2	N/A
Bentazon	0.67	0.51	1.1	0.57	0.45	0.77	21
Chlorpyrifos	6.5	5.2	11	3.5	4.1	6.2	270

N/A: not available *Calculated from Zeng and Arnold (2013) Table S11.

3.4 Conclusions

Prairie pothole wetlands have dynamic water chemistries. Both seasonal changes in sunlight intensity and spatiotemporal changes in PPRI quantum yields influence the photochemical fate of contaminant pesticides in these wetlands. Regional trends in agricultural expansion and wetland losses may also be changing the dominant phototransformation pathways of contaminant pesticides in these wetlands. Additional work must be completed to understand the combined impact of changing water chemistry (ionic strength, dissolved oxygen, [DOC], pH and alkalinity) and DOM quality on PPRI formation.

Acknowledgements

The authors thank David Mushet, Matthew Solensky, David Richardson, Jessica Dowler, Megan Zopfi, Trina Brennan, and two others who wish to remain anonymous for help coordinating sampling trips and collecting samples. The authors also thank Jennifer Strehlau for help with dissolved iron measurements. Funding for this work was provided by the United States Geological Survey-National Institutes for Water Resources (G12AP20153) and by the Moos Fellowship from the College of Biological Sciences, University of Minnesota (awarded to A.M.).

Ancillary support was provided by the Minnesota Environment and Natural Resources Trust Fund as recommended by the Legislative-Citizen Commission on Minnesota Resources (LCCMR).

Appendix A. Supplementary Material

Additional experimental details, tables, and figures as noted in the text.

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Figure Captions for

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

Andrew J. McCabe and William A. Arnold

Color online-only is acceptable for all figures.

Figure 1. Box-and-whisker plots of seasonal (A) pH, (B) bicarbonate, (C) conductivity, and (D) DOC in semi-permanent (□) and temporary (□) wetlands. The length of the whiskers (w) are defined as $\pm 1.5 \times$ the inner quartile range. Outliers (x) are defined as values greater than $q_3 + w(q_3 - q_1)$ or less than $q_1 - w(q_3 - q_1)$, where q_1 and q_3 are the quartiles. The dashed gray line indicates a change in the scale of the y-axis. The scale above the gray dashed line is arbitrary and is only used to show outliers within the same scale as the data.

Figure 1 is intended to be a single column figure.

Figure 2. Box-and-whisker plots of seasonal (A) a_{254} , (B) E2/E3, (C) SUVA₂₅₄, and (D) slope ratio in semi-permanent (□) and temporary (□) wetlands. The length of the whiskers (w) are defined as $\pm 1.5 \times$ the inner quartile range. Outliers (x) are defined as values greater than $q_3 + w(q_3 - q_1)$ or less than $q_1 - w(q_3 - q_1)$, where q_1 and q_3 are the quartiles. The dashed gray line indicates a change in scale of the y-axis. The scale above the gray dashed line is arbitrary and is only used to show outliers within the same scale as the data.

Figure 2 is intended to be a single column figure.

Figure 3. Example kinetic plots of probe molecules under simulated sunlight: (A) TMP ([TMP]₀=5 μM), (B) FFA ([FFA]₀=20 μM), (C) hTPA ([TPA]₀=10 μM), and (D) DMA ([DMA]₀=2 μM). Note changes in y-axis units and scales. Error bars represent 95% confidence intervals derived from calibration curves. Where absent, error bars are smaller than the symbol. The reported p-values correspond to the confidence in the fit coefficients. Points for the P8Aug14 treatments represent averages of triplicate determinations (i.e., the average concentration from three separate test tubes). The average relative standard deviation for triplicate determinations from all experiments was 5.3% for [TMP], 6.3% for [FFA], 16% for [hTPA], and 4.2% for [DMA].

Figure 3 is intended to be a single column figure.

Figure 4. Biplots of average [PPRIs]_{ss} versus quantum yields for 3DOM* (A and E), 1O₂ (B and F), •OH (C and G), and CO₃•⁻ (D and H). A – D show seasonal trends by individual wetlands. E – H show seasonal trends by wetland class. Asterisks in A – D indicate sample collected in the spring. Relative standard deviations for data in A – D are ~20% (error bars were omitted for clarity). Error bars in E – H indicate $\pm 1\sigma$. Biplots by individual sample are shown in the Supplementary Material.

Figure 4 is intended to be a 1.5-column figure.

Figure 5. Trends between E2/E3 and (A) f_{TMP} and (B) $\Phi_{app,S}$. The equations for the lines of best fit are shown with correlation coefficients and p-values for the significance of the fit slopes. Dotted lines indicate 95% confidence intervals for the line of best fit and the dashed lines are the 95% prediction intervals. The red alternating dotted-dashed line in (B) shows the relationship from Dalrymple et al. (2010). The range of E2/E3 was ~3 – 7 for the Dalrymple correlation.

Figure 5 is intended to be a single column figure.