Science of the Total Environment 648 (2019) 923–934

Contents lists available at ScienceDirect

Science of the Total Environment

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

Dissolved organic matter processing and photoreactivity in a wastewater treatment constructed wetland☆

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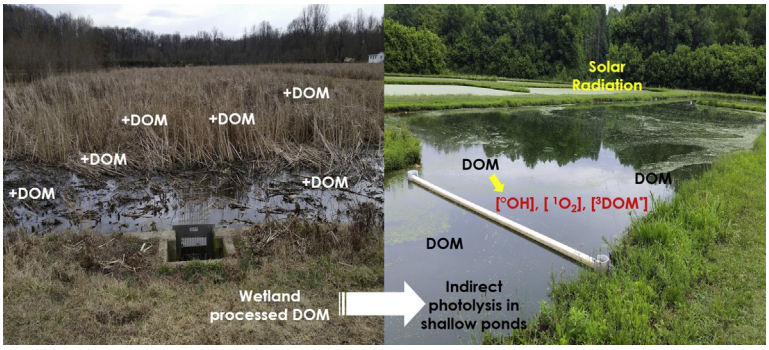
HIGHLIGHTS

- Wastewater treatment constructed wetland processed DOM to a heterogenous terrestrial composition.
- DOM transformation had a corresponding effect on wetland photoreactivity.
- Wetland processed DOM had higher photo-generation of singlet oxygen ($^1O_2$) and triplet excited states of DOM ($^3DOM^*$).
- Microbial assimilation of bio-labile DOM and DOM leaching from plant material influenced DOM transformation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 April 2018
Received in revised form 8 August 2018
Accepted 10 August 2018
Available online 15 August 2018

Keywords:
Constructed wetlands
Dissolved organic matter
Photochemistry

ABSTRACT

Constructed wetlands have the capacity to degrade a host of contaminants of emerging concern through photodegradation via sunlight produced reactive oxygen species. Dissolved organic matter (DOM) is a critical intermediary in photodegradation as it influences the production of reactive oxygen species. In this study, the photochemical behavior of DOM of wastewater treated in constructed wetlands was characterized. Whole water samples and fractionated DOM were characterized using $SUVA_{254}$, spectral slope ratios, excitation emission matrix fluorescence spectroscopy (EEMs), and proton nuclear magnetic resonance (^1H NMR). Photoreactivity was assessed by measuring formation rates and steady state concentrations of hydroxyl radical ($^{\bullet}OH$), singlet oxygen ($^1O_2$), and the triplet excited states of DOM ($^3DOM^*$). The effluent was observed to transition from a microbially sourced protein-like DOM to a terrestrial DOM with higher aromaticity. Size exclusion chromatography revealed an 18% increase in larger molecular weight fractions of vegetated wetland effluent DOM. Additionally, wetland effluent DOM was observed to have a 32% increase in the aromatic region of ^1H NMR spectra as compared to untreated wastewater. ^1H NMR analysis also indicated an increase in the complexity of wetland effluent DOM. Fluorescence intensity fraction of the protein-like Peak T (Ex/Em:278/342 nm) of EEMs decreased by 16% from the untreated wastewater to wetland effluent. A negative correlation between the percent fluorescence of Peak T (Ex/Em:278/342 nm) and Peaks A (Ex/Em:245/460 nm), C (Ex/Em:336/435 nm), and M (Ex/Em:312/400 nm) of the excitation emission spectra confirmed the transition from a spectrum of pure wastewater to a spectrum characteristic of terrestrially derived DOM. Microbial uptake of bio-labile DOM and leaching of humic like substances from vegetated wetland cells were the predominant processes involved in this transition. This transition coincided with an increase in the formation rates of $^1O_2$ and $^3DOM^*$ and in the steady state concentration of $^1O_2$.

☆ The authors declare no competing financial interest.

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https://doi.org/10.1016/j.scitotenv.2018.08.138
0048-9697/

1. Introduction

Constructed wetlands have been used for decades for the treatment of wastewater (Vymazal, 2011)and have been well documented for their ability to remove wastewater derived organic contaminants. There are several mechanisms available in constructed wetlands for the removal of contaminants of emerging concern (CECs) including microbial processes, physical removal via sorption, plant uptake, and photochemical processes (García et al., 2010; Li et al., 2014b; Lv et al., 2017; Verlicchi and Zambello, 2014; Zhang et al., 2018). One of the least well understood of the aforementioned processes is photodegradation, although it has been shown to play a major role in the attenuation of trace organics in surface flow constructed wetlands (Andreozzi et al., 2003; Matamoros et al., 2008). Specifically, vegetated surface flow and unplanted shallow open-water treatment wetlands can be harnessed for the removal of photolabile trace organics (Jasper and Sedlak, 2013; Prasse et al., 2015). The kinetics of photodegradation are dependent on the dissolved organic matter composition of the effluent, irradiation intensity, and the photochemical properties of the contaminant (Challis et al., 2014; Karpuzcu et al., 2016). Though sunlight exposure in vegetated wetlands cells may be lessened because of shading, research studies have suggested that DOM transformations occurring within wetlands due to plant influence may be favorable in promoting indirect photodegradation of emerging contaminants (Maie et al., 2005; Timko et al., 2014).

Direct photolysis of a contaminant occurs due to absorption of light followed by bond cleavage or molecular rearrangement (Mill, 1999). The rate of direct degradation is compound specific and dependent on molar absorptivity of the compound and reaction quantum yield (Schwarzenbach et al., 2002). Indirect photolysis in natural waters occurs by the formation of reactive oxygen species (ROS) resulting from the interaction of sunlight and the photosensitizer, DOM, present in the water column. Of particular importance in the viability of indirect photodegradation for a compound is the nature of the dissolved organic matter (DOM) within the water. DOM mediates the indirect photodegradation of a compound by forming intermediate species including hydroxyl radical ($^{\bullet}OH$), singlet oxygen ($^1O_2$), the triplet excited states of DOM ($^3DOM^*$), and the carbonate radical ($CO^{\bullet-}$)-formed by scavenging of the hydroxyl radical. The photodegradation rate of a generic emerging contaminant can be modeled as per Fig. 1. This model incorporates the sum of photo-decay contributions from different reactive oxygen species (Bodrato and Vione, 2014; Karpuzcu et al., 2016; Timko, 2015; Xu et al., 2011). The susceptibility of reactive oxygen species to react with organic contaminants relies on the DOM quantity (e.g. dissolved organic content, DOC) and the DOM quality (e.g. structural composition) (Chu et al., 2015; Sharpless et al., 2014; Timko et al., 2014). Microbially derived autochthonous DOM has been observed to increase the indirect photodegradation of select pharmaceutical compounds by increasing the photosensitization of $^3DOM^*$ and $^{\bullet}OH$ (Dong et al., 2015; Guerard et al., 2009; Ryan et al., 2011). Additionally, the presence of wetland plant species *Typha* (cattail) in surface wetlands has been found to favor the photosensitized degradation of some CECs (Lee et al., 2014). In some cases, DOM composition may decrease photoreactivity by scavenging reactive species (Wenk et al., 2011), acting as an antioxidant (Wenk and Canonica, 2012), or by screening UV radiation (Zepp and Cline, 1977). Despite these inhibiting influences, indirect photodegradation is a well-documented and viable contaminant removal pathway in natural waters (Challis et al., 2014; Hong et al., 2013; Lam and Mabury, 2005).

Contaminant fate studies in field wetlands (Jasper and Sedlak, 2013; Karpuzcu et al., 2016; Lee et al., 2011, 2014; Matamoros et al., 2008) and laboratory microcosms (Sharif et al., 2014; Westerhoff et al., 2014) have reported that factors such as hydraulic rate, plant density, and wetland effluent photochemistry influence the DOM transformations, and consequently, the kinetics of photo-decay of trace organics. Correlating these factors with generation of ROS in natural wetland effluents has been performed by using optical (McKay et al., 2017; Timko et al., 2014) and chromatographic techniques (Maizel and Remucal, 2017a, 2017b; Maizel et al., 2017; Mostafa et al., 2014) for DOM characterization. The spatial and temporal trends in quantum yields, steady state concentrations, and formation rates of ROS species act as indicators of DOM photoreactivity (Bodhipaksha et al., 2017; Ryan et al., 2011). Understanding DOM structure and composition in conjunction with ROS photo-generation in wastewater treatment wetlands is essential to develop predictive tools for estimating indirect photodegradation.

DOM composition of wetland waters from surface flow wastewater treatment wetlands has been observed to have higher aromaticity with a high molecular weight due to humification and leaching of terrestrial plant substances (Chon et al., 2013; Barber et al., 2001; Pinney et al., 2000). Humic substances in aquatic environments are a major contributor to the chromophoric dissolved organic matter (CDOM) concentration (Cooper et al., 1989). Furthermore, multiple irradiation studies have suggested that matrices with abundance of terrestrial humic like DOM have higher photoreactivity (Coelho et al., 2011) and at suitable concentrations these favorable DOM moieties do not inhibit photo-generation efficiencies (Peterson et al., 2012). Hydroxyl radical ($^{\bullet}OH$) photo-generation has been found to be directly correlated to optical indicators of aromaticity ($SUVA_{254}$) and CDOM (Abs_{254}) for natural waters (Batista et al., 2016; Timko et al., 2014) and inversely related to molecular weight in wastewater effluents (Lee et al., 2013). Similarly, singlet oxygen ($^1O_2$), and triplet excited states of DOM ($^3DOM^*$), are correlated to either CDOM indicators or fluorescent DOM components (Bodhipaksha et al., 2015; Sharpless et al., 2014). However, the significance of these correlations varies in different systems (Paul et al., 2004) and specific correlations between DOM properties and photoreactivity are needed for wastewater treatment wetlands.

In this study, a suite of spectroscopic and chromatographic techniques for DOM characterization were applied to provide a quantitative longitudinal profile of DOM processing and photoreactivity in a wastewater treatment wetland. Spectroscopic indices (UV–Vis, EEMs) and chromatograms (SEC, ^1H NMR) were determined and correlated with the generation of reactive oxygen species and photo-lability of wetland DOM.

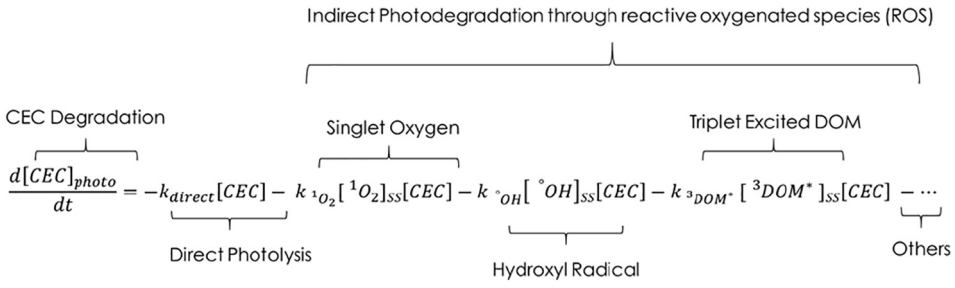

Fig. 1. Photodegradation of a labile emerging contaminant (CEC) modeled as first order direct photolysis and second order indirect photolysis. k_{direct} is the first order photolysis rate constant whereas $k_{^1O_2}$, $k_{^{\bullet}OH}$, and $k_{^3DOM^*}$ represent the second order rate constant for the reaction between CEC and respective reactive oxygen species.