

**State of Washington Water Research Center
Annual Technical Report
FY 2016**

Introduction

The State of Washington Water Research Center (WRC or the Center) was established 52 years ago as a member of the National Institutes for Water Research (NIWR) under the Water Resources Act (WRRRA) of 1964 (reauthorized in 1984 and several times thereafter), with the charge of (1) arranging for competent research that addresses water problems or expands understanding of water and water-related phenomena, (2) aiding the entry of new research scientists into the water resources fields, (3) helping to train future water scientists and engineers, and (4) disseminating sponsored research results to water managers and the public.

In the spirit of the WRRRA of 1964, the mission of the WRC has three components: 1. To conduct and facilitate applied water-related research. 2. To foster education and training of future water professionals. 3. To serve as a nexus between the academic community, water resource managers and water stakeholders. These three elements of the WRC mission are the fundamental goals supporting the WRC vision, objectives, strategies, and assessment metrics described in this Strategic Plan.

The WRC administration aspires to strengthen the Center's impact through the following activities: 1) Actively engaging water research professionals at other academic institutions to encourage their participation in the administration and activities of the WRC, 2) Developing broader collaborations among water researchers within WSU and between WSU and other water-focused organizations. 3) Increasing programmatic and extramural funding to support the WRC and its activities. 4) Developing more focused and integrated water resource education programs at WSU. 5) Creating a wider network for outreach, and contribute more broadly to information dissemination for water stakeholders and policymakers.

The WRC staff includes a Director (0.5 FTE), and Associate Director (0.25 FTE), a Clinical Assistant Professor (0.5 FTE), a Principal Assistant (0.5 FTE), and a Grant and Contract Coordinator (.375 FTE). The WRC personnel are:

o Jonathan Yoder (Director) o Jennifer Adam (Associate Director) o Julie Padowski (Clinical Assistant Professor) o Nigel Pickering (Research Associate Professor) o Jacqueline McCabe (Principal Assistant) o Katrina Shelton (Grants & Contracts)

the WRC has designated four program coordinators to focus on the critical areas of the WRC mission:

o Research Program Coordinator: Jennifer Adam o Education Program Coordinator: Julie Padowski o Extension Program Coordinator: Robert Simmons o Outreach Program Coordinator: Nigel Pickering The WRC Science Advisory comprises 15 water researchers with a variety of specialists from around the state. This advisory committee provides guidance to the WRC administration in relation to all WRC activities, and acts as reviewers for the annual WRC seed grant program.

Research Program Introduction

WRC's research program is active along several dimensions. First, the WRC manages a seed grant program funded by the Water Resources Research Act (WRRRA) 104(b) funds. Second, it is currently managing several extramural grants to support research. Third, it has submitted and has begun preparing several proposals this past year for additional funding. Finally, it is pursuing a broad strategy for developing and strengthening research funding opportunities and collaborative opportunities within and outside of WSU and the State of Washington.

2106 WRRRA 104(b) Seed Grant program

The WRC funded three small water-related grants (\$27,500/grant) under the WRRRA 104(b) FY2016 grant program.

“Transformation of Graphene Oxide Nanomaterials in the Aquatic Environment.” Chowdhury, Indranil and Rick Watts; Assistant Professor and Professor, Washington State University. Project #2016WA411B.

“Low Energy Precision (/Spray) Applications: Unmanned Aerial System based Rapid Evaluation for Crop and Site Specific System Adaptation in the Pacific Northwest.” Khot, Lav, and Troy Peters, Assistant Professor and Associate Professor, Washington State University. Project #2016WA412B.

“Understanding Links Between Water, Nitrogen, and Greenhouse Gases in “Green” Infrastructure.” Harrison, John, and Kevan Moffett, Associate Professor and Assistant Professor, Washington State University. Project #2016WA420B.

This year, two of the projects (2016WA412B and 2016WA420B) requested extensions due to legitimate research delays or to take advantage of unforeseen opportunities for augmenting data collection. Progress reports with projected completion information are provided in this report. Final reports will be submitted upon completion.

Extramural grant-funded research

2016 Columbia River Basin Long-Term Water Supply and Demand Forecast. Funded by the Washington State Department of Ecology Office of Columbia River. Jennifer Adam (PI), Michael Brady, Michael Barber (U. Utah), Chad Kruger, Mingliang Liu, Dan Haller (Aspect Consulting), Claudio Stockle, and Jonathan Yoder. Three-year project initiated in 2014 and completed this year (\$1.8 million). Skagit Exempt Well Mitigation Study. This study is funded by the Washington State Department of Ecology to identify and assess mitigation options to allow development in the Skagit River Basin. Due to recent court action, there is a moratorium on building in the Skagit without mitigation. This is a short-term study, March-December 2016 (\$72,000).

Publications, presentations, and other materials completed in FY 2016 and supported by these extramural grants are listed in bibliography Appendix A.

Grant development activities

The WRC team continues to pursuing further extramural support in line with the WRC strategic plan. It was a major contributor to a proposal submission to the USDA AFRI CAP Water for Agriculture program, with a request for joint effort between WRC, CEREO, CSANR, and the School of the Environment (\$10 million) submitted through CEREO (this was not awarded). The WRC is taking the lead on another of these grant

Research Program Introduction

proposals this year. In addition, members of the WRC administration are involved in an awarded NSF INFEWS proposals beginning this year (\$3,000,000).

Transformation of Graphene Oxide Nanomaterials in the Aquatic Environment

Basic Information

Title:	Transformation of Graphene Oxide Nanomaterials in the Aquatic Environment
Project Number:	2016WA411B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	Washington-District 5
Research Category:	Water Quality
Focus Category:	Toxic Substances, Surface Water, Water Quality
Descriptors:	None
Principal Investigators:	Indranil Chowdhury, Rick Watts

Publications

1. Chowdhury, I., Guiney, L.M., Hersam, M.C., Influence of Surface Functional Groups on the Degradation of Graphene Nanomaterials in the Aquatic Environment , presented at 252nd American Chemical Society National Meeting, August 21-25, 2016, Philadelphia, PA.
2. In preparation: Shams, M., Mansukhani, N., Henderson, W.M., Zepp, R., Bouchard, D., Hersam, M.C., Chowdhury, I. (2017) Environmental Implications of Two Dimensional Nanomaterials, in preparation (Invited Review to Environmental Science Nano)
3. In preparation: Shams, M., Guiney, L., Hersam, M., and Chowdhury, I. (2017) Influence of Functional Groups on the Degradation of Graphene under Direct Sunlight, in preparation for Environmental Science and Technology.
4. In preparation: Shams, M., Guiney, L., Hersam, M., and Chowdhury, I. (2017) Influence of Functional Groups on the Degradation of Graphene under Indirect Photolysis, in preparation for Water Research.
5. Shams, M., Guiney, L.M., Hersam, M.C., Chowdhury, I., Influence of Functional Groups on the Indirect Photolysis of Graphene t , presented at 254th American Chemical Society National Meeting, August 2017, Washington, DC.

**TRANSFORMATION OF GRAPHENE OXIDE
NANOMATERIALS IN THE AQUATIC
ENVIRONMENT**

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ABSTRACT

Nanomaterials are used in industries for having unique optical, mechanical, electrical, and chemical properties. However, these emerging materials will pose a significant threat to public health and environment, once they are released in the environment. Graphene is a 2D carbon based nanomaterial that has unique properties and whose structure is similar to polycyclic aromatic hydrocarbons (PAH), with carcinogenic properties. Once degraded, the resulting photoproducts are of numerous combination of PAHs that can lead to environmental risk. The objective of this proposed project was to investigate the degradation of graphene-based nanomaterials under sunlight as a function of nitrate, natural organic matter, and minerals. For this, our goal was to focus on GO nanomaterial degradation and factors influencing this degradation process. Our working hypothesis is that degradation process of GO starts from basal planes creating numerous electron holes, where most of the functional groups (especially hydroxyl functional groups that initiate the degradation) are located. Results from this study indicates that sunlight induced photolysis can significantly change the physical and chemical properties of graphene materials. Qualitative results from this study also indicate that functional groups of the samples, mainly the ones that are present on the basal plane, subsequently effects the degradation of graphene materials. In Columbia river water, the rate of indirect photolysis was lower than direct photolysis, which means that there may not be enough photosensitizers present to generate radicals and stimulate indirect photolysis. It also means that most of the degradation of GO will occur due to direct photolysis in Columbia River Water. However, Columbia River Water might contain other minerals or salt that affects the aggregation capability of GO in Columbia River Water. This aggregation and subsequent precipitation occurs even without the presence of sunlight. The result of this research will be useful in understanding the mechanisms of degradation process of carbon-

based materials. These findings on degradation of graphene-based nanomaterials will provide insight into the potential management approaches to mitigate the impacts of these emerging pollutants in the environment.

INTRODUCTION

Nanomaterials are defined as having dimensions of approximately 1 to 100 nanometers and are applied in numerous fields due to their novel characteristics resulting from their small size and other engineered properties. Although nanomaterials are relatively new, they are used in many industries, including electronic, magnetic, biomedical, pharmaceutical, cosmetic, energy, and paint industries, as well as for environmental application such as coating and catalytic applications (Novoselov *et al.*, 2012; Chung *et al.*, 2013; Kemp *et al.*, 2013). Environmental application also includes environmental remediation and membrane applications. Nanomaterials used as sorbents, catalysts, also nano-filtration are found in water and wastewater treatment (Savage and Diallo, 2005). Environmental release, intentional or unintentional, of these nanomaterials is possible throughout the life cycle of nanomaterials during production, use and disposal. This release can be either intentional or unintentional. After exposed to environment, behavior of nanomaterial will be determined by their intrinsic properties as well as specific environmental conditions.

A common class of nanomaterial, graphene family nanomaterials (GFNs), which are used in many environmental applications, is a large sheet that comprises a 2D layer of sp^2 -hybridized carbon atoms, arranged in a hexagonal lattice with unique physical and chemical characteristics. GFN release could occur during environmental applications such as adsorbents for wastewater and drinking water treatment (Zhang *et al.*, 2011; Zhao *et al.*, 2011; Upadhyay *et al.*, 2014), membranes for desalination (Mishra and Ramaprabhu, 2011), catalysts for aqueous organic pollutant oxidation and degradation (Sun *et al.*, 2012), and coating materials for filtration (Gao *et al.*, 2011). Moreover, GFNs could be introduced to the environment during the waste disposal of GFN-containing products. Pristine graphene, graphene oxide (GO), and reduced graphene oxide (rGO) are the most common forms of graphene that are used in different applications. GO is a structural

analog of graphene but differ in properties enormously. The distinction between rGO and pristine graphene is necessitated by the few remaining oxygen-containing functional groups and structural defects, as well as the fact that some properties are never fully recovered.

It is generally accepted that basal plane surfaces of GO contain mainly hydroxyl (-OH) and epoxy (-O-) functional groups while the edges are rich with carboxylate (-COOH) groups (Dreyer *et al.*, 2010). The functional group gives the molecule its properties, regardless of what molecule contains it; they are centers of chemical reactivity, solubility and other physical properties. The atoms of functional groups are linked to each other and to the rest of the molecule by covalent bonds. These groups can enter into reactions in which their covalent bonds break and new one's form.

Photodegradation is a major pathway for the transformation of nanomaterials in the environment (Lowry *et al.*, 2012) and it can happen in both direct or indirect pathways. In direct photolysis, nanomaterial itself acts as a chromophore (light absorbing surface) which means nanomaterial absorbs energy from light, disrupting the chemical bonds and initiating degradation. On the other hand, in indirect photolysis, another compound in the environment acts as the chromophore and then transfers the energy to the nanomaterial resulting degradation. Some common chromophores available in the environment includes nitrate, and dissolved natural organic matter (NOM).

Recent studies have shown that graphene is photoreactive (Matsumoto *et al.*, 2011; Koinuma *et al.*, 2012; Zhou *et al.*, 2012; Gengler *et al.*, 2013). GO can degrade in the exposure of sunlight and form products like rGO and LMW species. These degraded products can either be susceptible to further degradation or be persistent in the environment. However, as graphene is considered to be a large sheet of many fused polycyclic aromatic hydrocarbons, which has carcinogenic properties, it is important to do more research on how this degradation is getting started.

Thus, it is necessary to gather knowledge on how functional groups affect the degradation of graphene nanomaterials and to provide the basis for the design of more sustainable implementation and application of this technology. It may be necessary to create a functional group in the molecule or remove some functional group in order to achieve desired properties or to make it reactive. A broad and detailed insight of the degradation mechanism and its effects on environment and public health is needed to determine their fate, transformation and transport in environment in both qualitative and quantitative terms.

PROBLEMS

Work on the transformation of GO in the environment is barely in existence with just a few studies showing that enzymatic reactions may occur (Kotchey *et al.*, 2011; Gurunathan *et al.*, 2013); which highlights the need for research on the transformation fate of graphene and its derivatives. Recent studies indicated that GO could be suspended and transported in water columns for long time, where phototransformation processes mediated by sunlight would become very important (Chowdhury *et al.*, 2013; Wu *et al.*, 2013; Chowdhury *et al.*, 2014; Lanphere *et al.*, 2014; Qi *et al.*, 2014).

Studies of GO photoreactions are very new in the research field. It has been shown that GO can be photochemically or thermally reduced with exposure to high-energy UV-C and laser light (Matsumoto *et al.*, 2011; Gengler *et al.*, 2013; McDonald *et al.*, 2013). A recent study shows that UV-C irradiation of natural organic matter (NOM) induces the production of highly reactive hydroxyl radical (OH·) at orders of magnitude higher than under solar irradiation (Lester *et al.*,

2013). It indicates that the photoreduction behavior of GO in sunlight is distinct from that under UV-C irradiation in terms of rate and reaction order.

The environmental fate and transport of GO has been investigated and the studies (Chowdhury *et al.*, 2013; Wu *et al.*, 2013) show that GO can be highly stable against aggregation and deposition in the natural aquatic environment, and it is thus likely that GO will remain in the water column where interacting sunlight can result in transformations. Moreover, nitrate and natural organic matter (NOM) in the natural environment can facilitate highly reactive hydroxyl radical formation under sunlight which can further react with graphene nanomaterials.

Sunlight photolysis is one of the primary routes by which carbonaceous nanomaterials react in natural waters. Previous studies (Hou and Jafvert, 2009; Kong *et al.*, 2009; Hou *et al.*, 2010; Kong *et al.*, 2013) have shown that sunlight exposure can photochemically transform fullerene (C₆₀), and its derivative fullerol, into CO₂ and products with significant oxygen containing functionalities. For other nanomaterials such as carbon nanotubes, photo-transformation is strongly dependent on the involvement of reactive oxygen species (ROS) such as hydroxyl radical (Chen and Jafvert, 2010; Hou *et al.*, 2014). Transport properties of nanomaterials have also been found to be affected by exposure to sunlight (Qu *et al.*, 2010; Cheng *et al.*, 2011).

Indirect phototransformation of graphene oxide is another major pathway of degradation of these nanomaterials in surface water. Numerous factors present in surface water (nitrate, minerals, NOM) can also promote this degradation. The light energy absorbed by these chromophores may be transferred to molecular oxygen, thereby forming singlet molecular oxygen (¹O₂), a weak oxidant. Alternatively, the light energy absorbed by the chromophore can be released as a hydrated electron, which then reacts rapidly with molecular oxygen to form superoxide. Superoxide is a weak nucleophile and reductant. Superoxide can also dismutate to hydrogen peroxide, which is

then converted to hydroxyl radical by reaction with transition metals and metal oxide minerals. Hydroxyl radical is a strong, nonspecific oxidant that reacts rapidly with most nanomaterials in water. In some cases, we do need complete degradation of graphene oxide in which the end product, CO₂, is not as harmful as the end product, PAH, formed in the case of partial degradation of graphene oxide.

However, most of the previous studies discuss about the photodegradation processes rather than the actual mechanisms. Whether functional groups have impact on the degradation process or any other property of the nanomaterial is still unknown. Moreover, the rates of these degradation process and which natural water constituents have the greatest effects on the photodegradation rates of graphene oxide nanomaterials have also not been studied yet.

RESEARCH OBJECTIVES

The overall objective of this research is to investigate the degradation of graphene-based nanomaterials under sunlight as a function of nitrate, natural organic matter, and minerals. For this, we have focused on graphene degradation, its mechanism and influence of functional groups on this degradation process.

These set us to undertake the following specific aims:

Specific aim 1 # Determine the reasons of graphene oxide transformation and degradation in aquatic environment under sunlight.

Our working hypothesis is that degradation process of graphene oxide flakes starts from basal planes creating numerous electron holes, where most of the functional groups are located on

graphene oxide (Figure 1). It also includes that sunlight is mainly made up of photons and in sunlight simulated photolysis, functional groups of graphene oxide, specially, hydroxyl functional group (a strong electron donating group) acts as chromophore. It absorbs light and produces many excited electrons which disrupts its chemical bonds. This initiates the breakup of the covalent bonds of hydroxyl functional group and gradually the covalent bonds of GO. If CO and H is removed, a hole is formed (Figure 2).

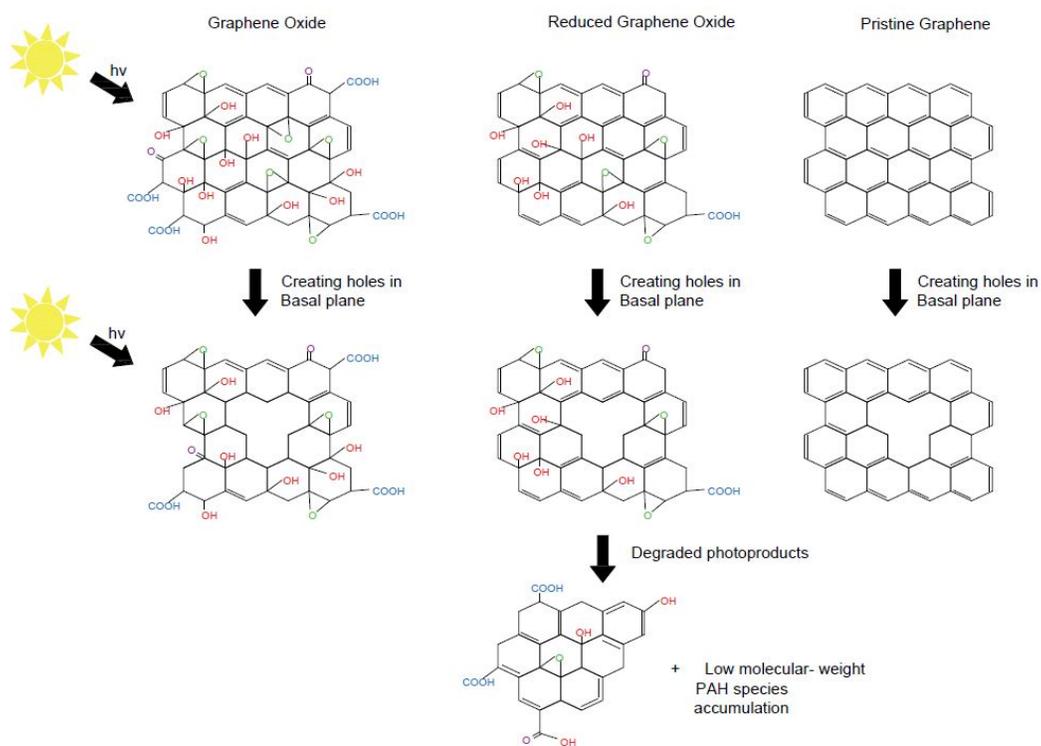


Figure 1. Schematic diagram of direct photolysis and degradation of Graphene nanomaterials

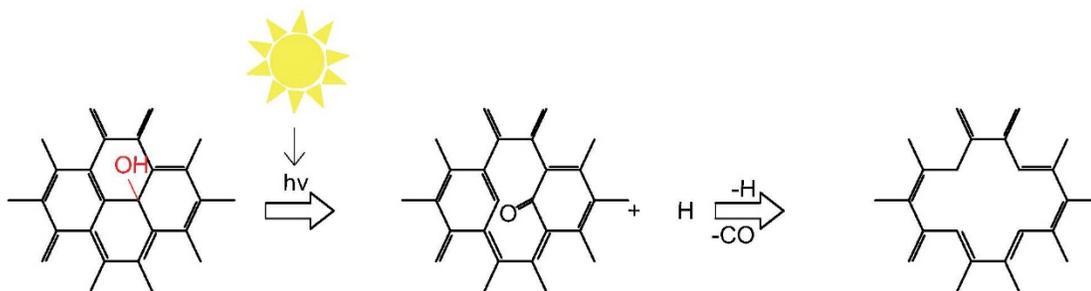


Figure 2. A proposed reaction pathway for hydroxyl functional group reduction by sunlight

Specific aim 2 # Identify the factors present in natural surface water that have the greatest effects on the photodegradation rate.

The most important naturally occurring photosensitizers are humic materials, nitrate, mineral surfaces, and pigments derived from microorganisms (Larson and Weber, 1994). Our hypothesis is that minerals can increase the rate of indirect contaminant photolysis through heterogeneous photocatalysis on their surfaces. Metal oxides can also act as semiconductors by absorbing photons. The absorbed photons might excite a region on the metal oxide surface, leaving a positively charged area on the surface (i.e., an electron hole). The electron hole can potentially oxidize organic contaminants. In addition, the negatively charged region of the surface can reduce contaminants.

In addition to direct electron transfer from the mineral surface to contaminants, we believe that the negatively charged region can release an electron to the molecular oxygen to form superoxide, which can dismutate to hydrogen peroxide (H_2O_2). Transition metal catalysts may then catalyze the decomposition of the hydrogen peroxide to hydroxyl radical which is one of the most reactive

oxidants in the environment that can degrade graphene nanomaterials. Metal oxides also can participate in electron transfer reactions.

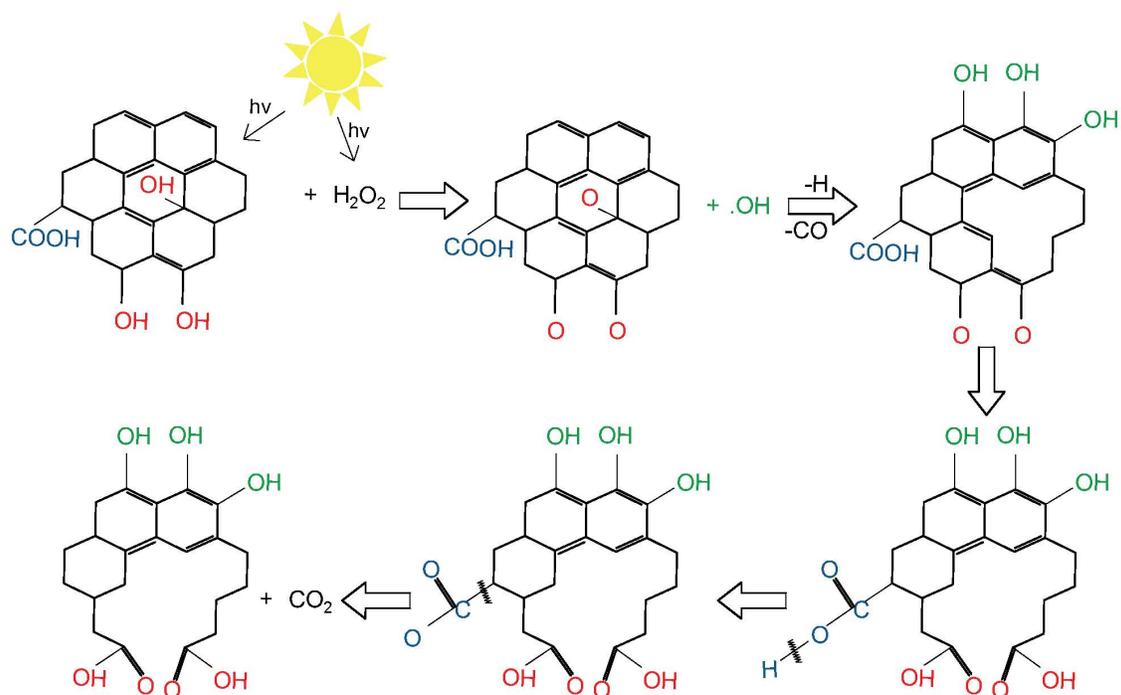
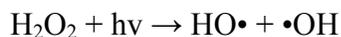


Figure 3. A proposed reaction pathway for degradation of GO in presence of H_2O_2 by sunlight

Initially, here direct photolysis will dominate the degradation process. This process will continue and this will cause hole formation and degradation of GO. Indirect photolysis starts to take effect after some time as it takes time to form hydroxyl radical from different photosensitizer (i.e. nitrate, NOM etc.) through the following reaction.



The hydroxyl radical reactions are extremely fast and they start to attack the GO faster than the direct photolysis induced degradation. This could mean that indirect photolysis starts to take effect

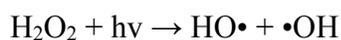
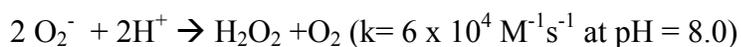
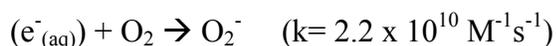
after some time. Three processes, that happens simultaneously, have been hypothesized for the reaction of hydroxyl radical and degradation of GO.

- ✓ **Process 1:** This hydroxyl radical can continuously get attached to GO and forms extra hydroxyl group by hydrogen abstraction and addition. This is because, $\text{OH}\cdot$ behaves like a highly reactive electrophile. This is why the net concentration of hydroxyl group does not show any prominent change.
- ✓ **Process 2:** This hydroxyl radical can further attack the GO specially where existing hydroxyl functional groups starts to break and form carboxyl functional group. This is why, we could assume that carboxyl functional group concentration will increase. This process will also continue to open up the rings and will cause degradation of GO.
- ✓ **Process 3:** This continuous attack of hydroxyl radical can also lead to the complete mineralization of GO to CO_2 . Carboxyl functional group also contains a hydroxyl group. Due to weak acidity of the hydroxyl hydrogen, a cleavage of the hydroxyl oxygen-hydrogen bond occurs. Also, hydroxyl radical has strong affinity towards carboxyl functional group due to the strong H-bonds between $\text{OH}\cdot$ and negatively charged carboxyl oxygen atoms. The carbon atom of a carboxyl group is in a relatively high oxidation state. Because it is already in a high oxidation state, further oxidation with the strong hydroxyl radical oxidant, removes the carboxyl carbon as carbon dioxide. However, there will be a net increase in carboxyl group concentration as formation of carboxyl group in process 2 is at much faster rate than removal in process 3.

As ring opening and degradation is mainly happening via process 2 and direct photolysis, it can also be postulated that indirect photolysis occurs at much faster rate than direct photolysis. All the processes are shown in figure 3.

Specific aim 3 # Detection of Reactive Oxygen Species (ROS) generation and their effect on transformation and degradation of graphene family nanomaterials.

Reactive oxygen species (ROS) are chemically reactive molecules containing oxygen. Examples include peroxides, superoxide, hydroxyl radical, and singlet oxygen. Our hypothesis is that reactive oxygen species in natural waters are produced during the interaction of sunlight with light absorbing substances such as nitrate/nitrite ions, humic substances and minerals. Singlet molecular oxygen ($^1\text{O}_2$), is a short lived, and highly reactive intermediate. It is formed by quenching CDOM (chromophoric dissolved organic matter) excited triplet-states, and is therefore one indicator of the photosensitizing ability of the CDOM. Hydrated electron ($e^-_{(aq)}$) could be produced in water by the action of cosmic rays, by K decay, or through photoionization of endogenous phenolic compounds. Rapid reaction of ($e^-_{(aq)}$) with dioxygen (O_2) would yield superoxide (O_2^-), ultimately leading to the formation of H_2O_2 via O_2^- disproportionation and formation of hydroxyl radical.



METHODOLOGY

Materials

Graphene Oxide sample were obtained from Dr. Mark Hersam (collaborator from Northwestern University). Reduced Graphene Oxide (rGO) 2hr and 5hr were also used for the photodegradation studies for better comparison. To create enough hydroxyl radicals, 100mM of hydrogen peroxide (H_2O_2) was used. All aqueous solutions were prepared using MiliQ water. Each solution was used in the concentration of 50mg/L in MiliQ water.

For Columbia river water work, 10 liter water was collected from a point near Lower Granite Point. Lower Granite Point is part of the Columbia River Basin system of dams. It is located on the lower side of snake river, the largest tributary of Columbia River. This water was gravity filtered with 0.45 μ m filter in lab and stored in 4°C. GO solution, in the concentration of 50mg/L was prepared with this river water.

For atomic force microscope (AFM) imaging, Si wafers were used. Si wafers were cleaned with piranha solution before use and then they were coated with Poly-L-lysine solution.

Photodegradation studies

All sunlight experiments were carried out in an Atlas SunTest CPS+ solar simulator. It is equipped with a 1 kW xenon arc lamp. The sunlight experiments were carried out in glass tubes (outside diameter = 1.3 cm; volume = 24 mL). The tubes were filled up to 10ml with solutions. The sample tubes were sealed with open-top caps lined with gastight polytetrafluoroethylene (PTFE) septa and kept on top of a mesh that helped them being submerged in a thermostatic water bath (25°C) during irradiation. The incident light intensity at the tube surface, summed from 300 nm to 800 nm, was 0.065 W/cm². For kinetic studies, a series of tubes were prepared for irradiation. Photodegradation

tests were continued for 168hr for direct photolysis and for photolysis in Columbia river water and 48hr for indirect photolysis. At specific time periods during irradiation, one tube was removed from the reactor and sacrificed for chemical analysis. After removing, the tubes were wrapped with aluminum foil and kept in refrigerator. Dark control tubes were used in the experiment. These were used (wrapped with aluminum foil) to see whether the degradation is occurring due to sunlight or not.

Characterization of GO, rGO 2hr and rGO 5hr

The degradation processes of the solutions were monitored using the following techniques:

Atomic force microscopy (AFM) was used to monitor the sizes of the graphene oxide flakes. The AFM images were analyzed further to determine the graphene oxide physical dimensions, including flake thickness, perimeter, and surface area, following the procedure described in some earlier studies (Chowdhury *et al.*, 2015; Hou *et al.*, 2015). For AFM imaging, the samples were prepared in the following manner:

Si wafers with a 100 nm thick oxide were immersed in a 2.5 mM Poly-L-lysine (PLL) aqueous solution for 30 min to functionalize them with a self-assembled monolayer. The wafers were then rinsed with water and dried with N₂. GO solutions will be diluted to ~0.01 mg/mL with water, and a 50 µl of this diluted solution were immediately placed on the wafer. After 10 minutes, the samples undergo two cycles of washing with water for ~5 sec and drying with N₂. To avoid issues with residual PLL, the GO sample undergo 30 min of heat treatment at 250 °C. Since this procedure is insufficient to remove excess Pluronic from the surface of the graphene sample, it was instead heat treated for one hour in air at 275 °C. AFM Images were taken at several random locations on the sample.

Ultra violet (UV)-visible spectroscopic images were measured using a Perkin Elmer Lambda 365 UV-visible absorbance spectrophotometer equipped with a 1-cm light path quartz cuvette. Changes in the UV-vis spectra will be used to monitor the decrease of graphene oxide concentration and changes in light adsorption properties.

Zeta potential, hydrodynamic diameter and polydispersity index of the particles were measured using a Zetasizer Nano ZS (Malvern Instruments, Inc.).

FTIR measurements were performed directly on the solutions using attenuated total reflection (ATR) mode on a Nicolet iS50 ATR-IR with Ge crystal. The FTIR analysis method uses infrared light to scan test samples and observe chemical properties. It gives qualitative idea about the formation or destruction of functional groups.

Total organic carbon (TOC) was measured using a Shimadzu TOC analyzer. The obtained information provides the concentration of graphene oxide during the transformation process.

AQ400 analyzer is used for analyzing different chemicals like magnesium, aluminum, calcium, copper, zinc, manganese, iron etc. of Columbia river water.

PRINCIPAL FINDINGS AND SIGNIFICANCE

Figures 4 (a) (b) show the sample of direct photolysis and figures 4 (c) (d) shows the sample of indirect photolysis. Figure 4 (a) shows that as the photodegradation time passes, sunlight exposure darkens the color of GO samples. From figure 4 (b) we can see that after 168hr, the color of the dark control tubes solution did not change. On the contrary, figure 4 (c) shows that as the photodegradation time passes, sunlight exposure lightens the color of GO samples but for dark

samples there was no color change (Figure 4 (d)). From this, we can interpret that the color change of the samples is happening due to sunlight. Color change of the solution in direct photolysis indicates the conversion of GO to rGO (degradation). This color change has previously been suggested as partial restoration of the network within the carbon structure and has been witnessed through chemical reduction of the GO sheets (Kotov *et al.*, 1996; Becerril *et al.*, 2008). For indirect photolysis, color change indicates the conversion of GO to CO₂. Hydrogen Peroxide (H₂O₂) is an oxidizing agent capable of oxidizing organics macromolecules, which have a chromogenic potential. The result of this process is a destruction of the long organic chains into colorless short chains (Seghi and Denry, 1992; Attin *et al.*, 2003; Wiegand *et al.*, 2005; Goldberg *et al.*, 2010). The bleaching mechanism is based on the decomposition of peroxides into free radicals, which react with the organic pigment molecules, transforming them into smaller and less pigmented compounds (Ünlü *et al.*, 2004).

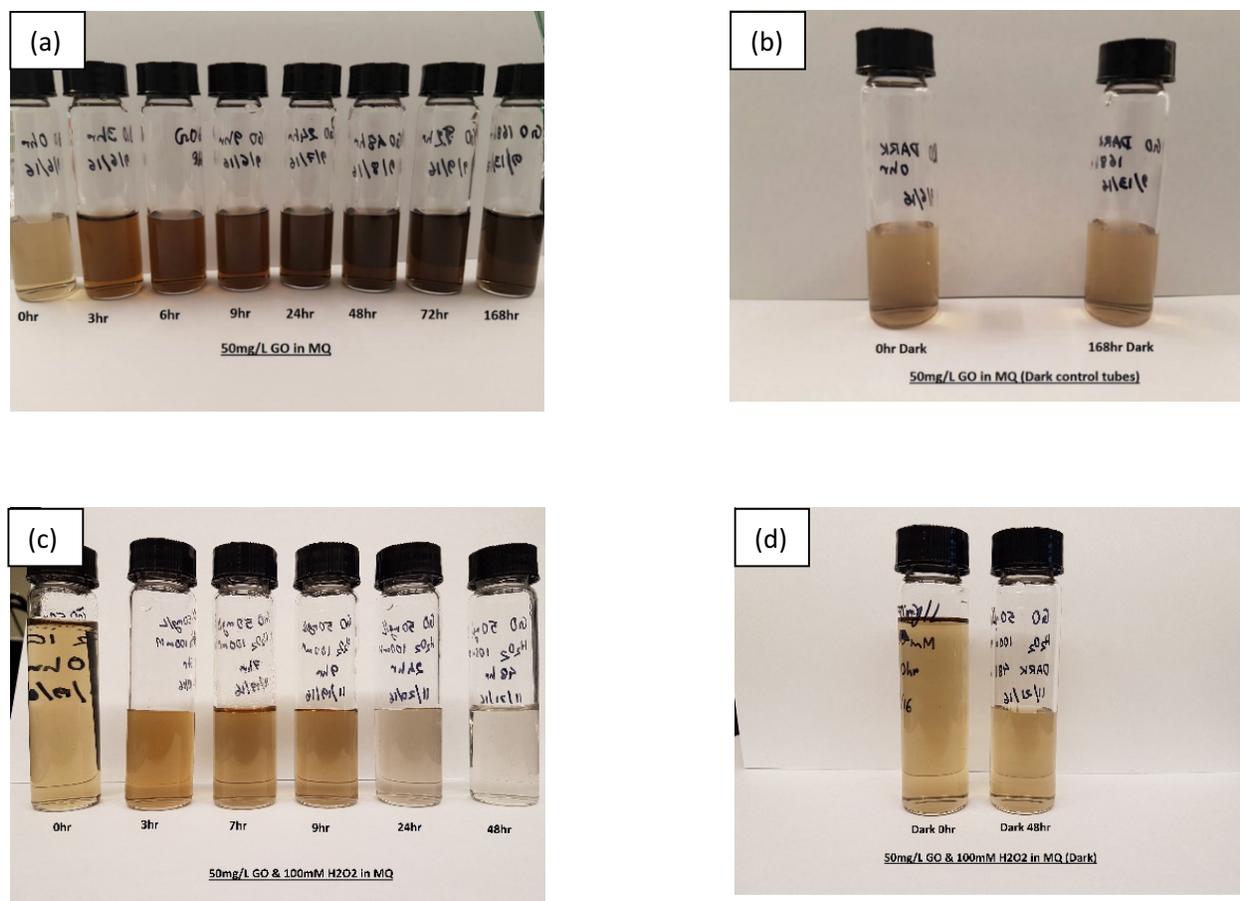


Figure 4. Visual effect of photolysis on (a) 50mg/L GO in MiliQ water, (b) 50mg/L GO in MiliQ water (Dark control tubes), (c) 50mg/L GO and 100mM H₂O₂ in MiliQ water, (d) 50mg/L GO and 100mM H₂O₂ in MiliQ water (Dark control tubes)

Also, visually there is no GO precipitate seen in the figures, which means GO has good dispersion stability. rGO 2hr and 5hr samples showed visible rGO precipitates which indicate poor dispersion stability. The particles got aggregated which might be the reason to not be able to see the color change more clearly. For an initial period of irradiation, the suspension displays little visible change in appearance. However, beyond a certain irradiation time, rGO particles begin to aggregate, first forming visible particulates and then eventually larger, settleable aggregates and finally the supernatant starts to become clear to the naked eye. This aggregation is a serious

problem for rGO particles. However, extent of aggregation could depend on the properties of the material, water quality and light intensity as well. Graphene nanomaterials aggregation and settling characteristics observed in this study are somewhat consistent with some previous studies in which carbon nanotubes (CNTs) were exposed to UV irradiation (Chen and Jafvert, 2010; Bitter *et al.*, 2014).

Figure 5 (a) represents the UV-Vis absorbance spectrum of GO samples. The optical absorption spectra of figure 5 (a) show that the absorption peaks of the GO suspension are around 230 nm related to π - π^* transitions of the aromatic C-C bond, a shoulder at about 300 nm correspond to n - π^* of the C=O bond transition and a long absorption tail down to 1100 nm wavelength for GO in MQ water for 0hr. However as photodegradation time passed, this peak got shifted to around 270nm which means that GO particles might be getting degraded. Also the disappearance of the shoulder at 300nm wavelength suggests the removal of oxygen groups (Zhou *et al.*, 2009; Liu *et al.*, 2011; Han *et al.*, 2013). It also shows that sunlight exposure increases UV-Vis absorbance above 280nm wavelength. It could mean GO degrades rapidly under sunlight exposure.

Figure 5 (b) represents the UV-Vis absorbance spectrum of rGO 2hr samples. Figure 5 (b) shows that the absorption peaks of the rGO 2hr suspension are around 270 nm. However as photodegradation time passed, this peak remained at the same wavelength but the absorbance got decreased up to 24hr. After 24hr, the absorbance values started to increase. It could mean that rGO 2hr samples start to degrade after 24hr and it doesn't start to degraded as quickly as GO sample. From this figure we can also see that although the absorbance is too low even after sonication and dilution, it is higher than GO sample.

Figure 5 (c) represents the UV-Vis absorbance spectrum of rGO 5hr samples. It is almost same as rGO 2hr. Even, the absorbance values also started to increase after 24hr, which again means that

rGO 5hr also starts to degrade after 24hr like rGO 2hr. From these, we can assume that rGO 2hr and 5hr are more resistant to degradation unlike GO but more research is needed to back it up.

Absorption peaks are influenced by functional groups. The functional groups influence the conjugated systems, causing the absorption peaks to change. The color of organic compounds, then, is influenced more strongly by the size of the conjugated system. So, figures 4 and 5 indicate that all the solutions are photochemically altered as darkened photoproducts are being formed and functional groups are absorbing lights after the photodegradation as the absorbance values are increasing.

Figure 6 represents the UV-Vis absorbance spectrum of all indirect photolysis samples. From figure 6 (a) we can see that as photodegradation time is passing, the absorbance value is getting decreased. The initial increase in absorbance in the first 3hr likely can be attributed to direct photolysis of GO. After 3hr, the decrease in absorbance indicates the indirect photolysis.

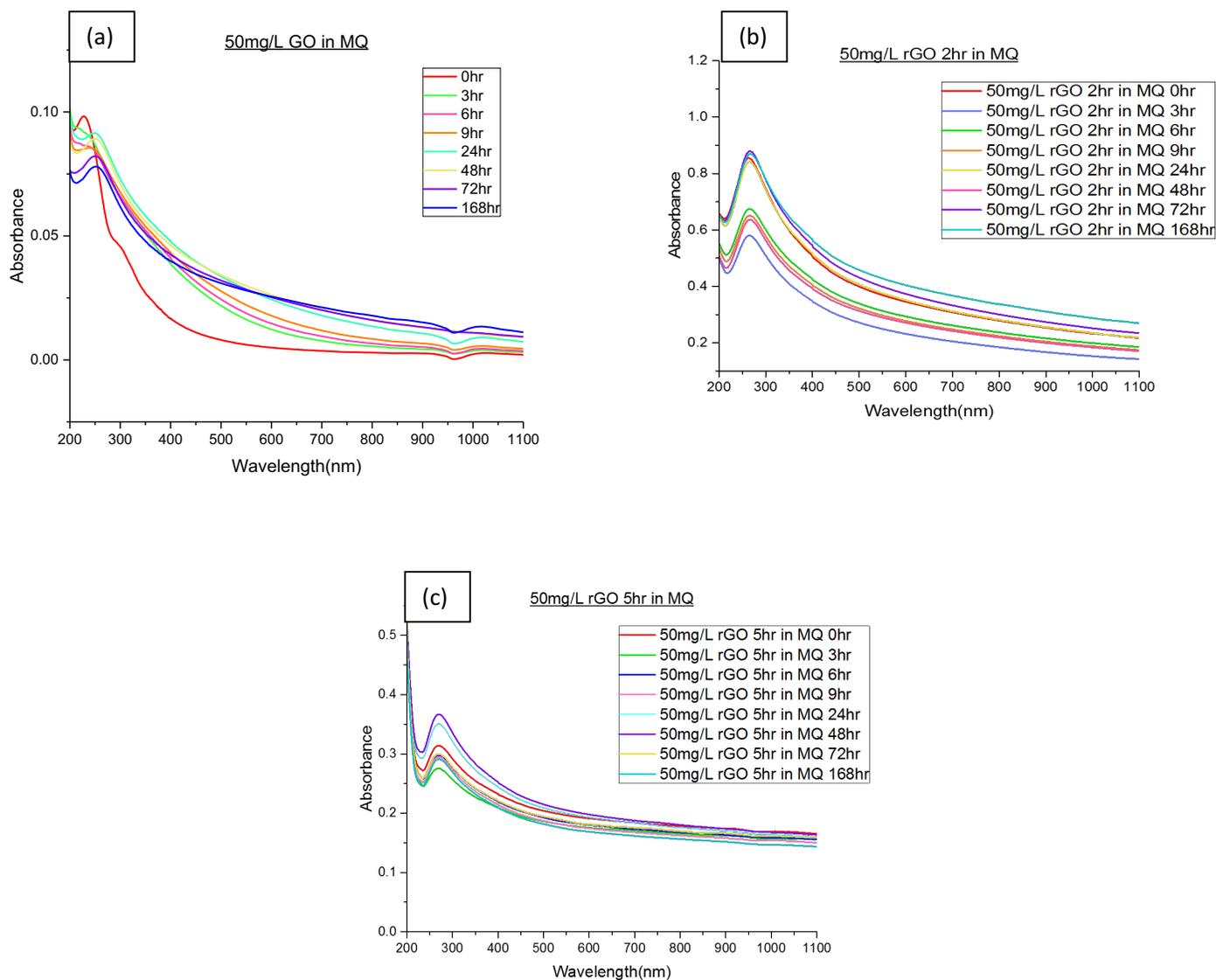


Figure 5. UV-visible absorbance spectra of (a) 50mg/L GO in MiliQ water, (b) 50mg/L rGO 2hr in MiliQ water, (c) 50mg/L rGO 5hr in MiliQ water

In rGO 2hr sample as well, the absorbance value increased in the first 7hr and then started to decrease after that (Figure 6b). In rGO 5hr sample the absorbance value increased in the first 9hr and started to decrease after that (Figure 6c). This initial increase and then decrease in absorbance

suggests that direct and indirect photolysis occurs simultaneously. From this we can say that hydroxyl radical starts to affect quickly in GO samples and takes a bit longer time to effect in rGO 2hr sample and even more longer time in rGO 5hr samples.

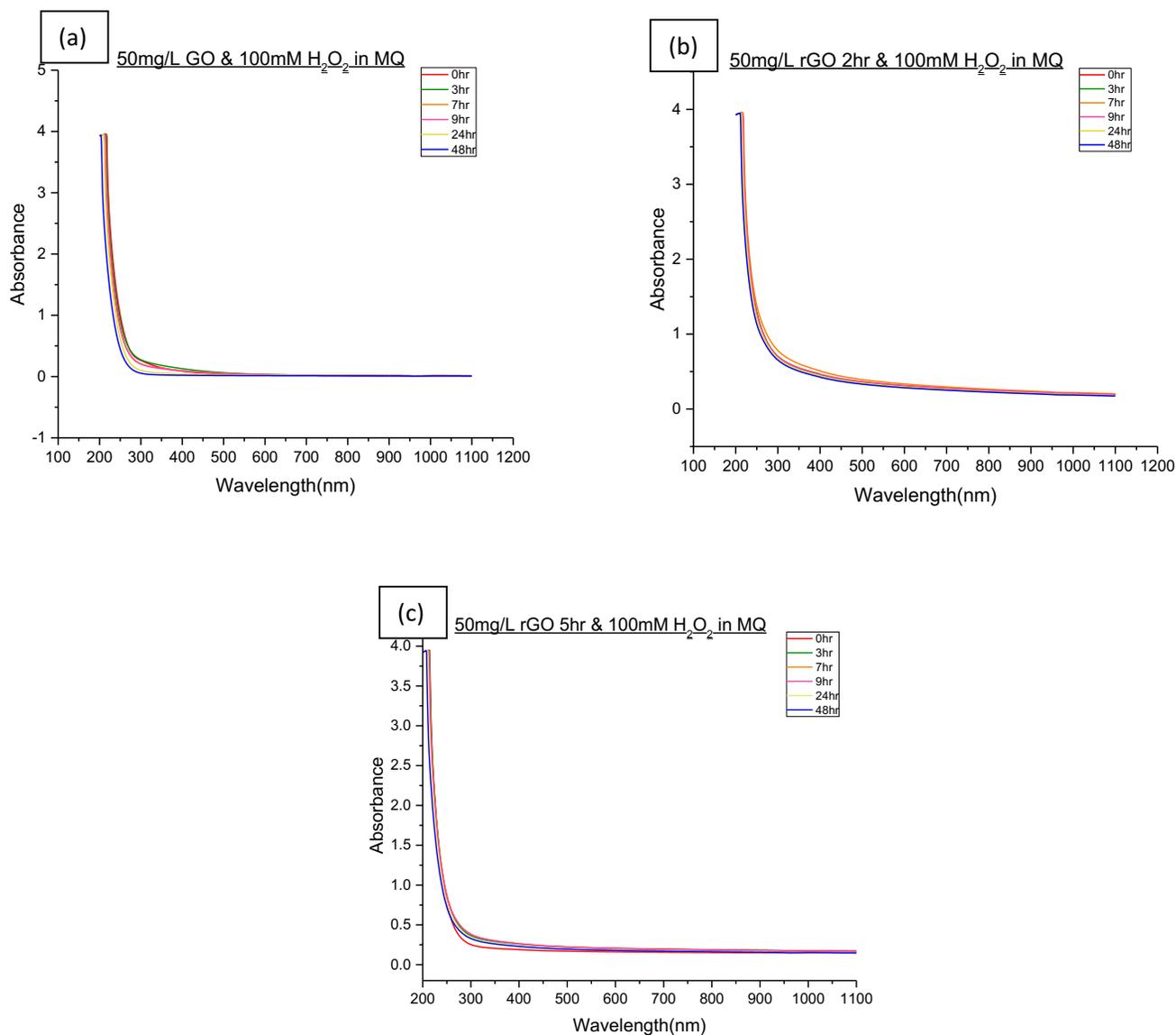


Figure 6. UV-visible absorbance spectra of (a) 50mg/L GO and 100mM H₂O₂ in MiliQ water, (b) 50mg/L rGO 2hr and 100mM H₂O₂ in MiliQ water, (c) 50mg/L rGO 5hr and 100mM H₂O₂ in MiliQ water

Zeta potential is an important indicator of the stability of particles. Its value specifies whether there is an electrostatic repulsion or attraction between particles. Higher zeta potential means the particles are stable and they will resist aggregation. On the other hand, lower zeta potential values mean attraction will take over and particles will coagulate or flocculate. From table 1 and 2, it is clear that for all the samples, ZP value is in the range of -30 to -50mV. In spite of having a negative zeta potential beyond 30mV for all the samples, these suspensions have been shown to be unstable, creating sedimentation upon standing. This indicates that the particle size is may be too large and hence the forces of gravity are becoming extremely dominant and that's why zeta potential might not affect stability. Also, due to functional groups, the hydrophilic GO is becoming hydrophobic. So this might be a reason for the sedimentation as well.

Table 1. Zeta potential values of samples in direct photolysis

GO			rGO 2hr			rGO 5hr	
Time	ZP (mV)		Time	ZP (mV)		Time	ZP (mV)
0hr	-40.1		0hr	-48.87		0hr	-38.9
3hr	-42.62		3hr	-47.23		3hr	-41.27
6hr	-39.14		6hr	-42.43		6hr	-38.7
9hr	-42.58		9hr	-43.37		9hr	-38.8
24hr	-42.5		24hr	-42.4		24hr	-40.03
48hr	-43.46		48hr	-42.5		48hr	-38.53
72hr	-46.42		72hr	-45.7		72hr	-37.93
168hr	-44.76		168hr	-44.97		168hr	-39.43

Table 2. Zeta potential values of samples in indirect photolysis

GO			rGO 2hr			rGO 5hr	
Time	ZP (mV)		Time	ZP (mV)		Time	ZP (mV)
0hr	-46.73		0hr	-41.43		0hr	-39.33
3hr	-43.43		3hr	-41.4		3hr	-39.5
7hr	-49.2		7hr	-45.7		7hr	-41.93
9hr	-46.13		9hr	-40.83		9hr	-38.33
24hr	-45.93		24hr	-41.3		24hr	-41.5
48hr	-43.1		48hr	-40.43		48hr	-37.57

The degradation of graphene oxide is also confirmed by FTIR spectroscopy. Figure 7 (a) shows the typical FTIR spectrum obtained for graphene oxide sample at the range of 500–4000 cm^{-1} . The spectrum of graphene oxide exhibits the presence of O–H (around 3400 cm^{-1}) due to stretching vibration. Carboxyl groups at the edges of GO sheets show stretching vibration and the C=O peak appears at around 1,726 cm^{-1} . The spectra also exhibit several characteristic peaks of GO; C=C at around 1,630 cm^{-1} due to the aromatic C=C bonds, C-O at around 1,246 cm^{-1} due to epoxy C-O stretching vibration (Szabó *et al.*, 2006; Muthoosamy *et al.*, 2015; Rouhollah and Alireza, 2015). From figure 7(a), which is for the photodegraded samples of GO, we can see that as photodegradation time passed, the value of % transmittance got decreased which means that absorbance got increased. It is similar with the increasing absorbance value in UV-vis spectroscopy. We can also see that, O-H, C=O and C-O functional groups are starting to get broadened. It could be expected that as time passed more, they could get more broadened and ultimately get eliminated. It means that when GO will degraded, there will be elimination of these

functional groups. It also suggests that photoreactive site is mainly the basal plane as these reduced oxygen containing functional groups (hydroxyl functional group) are present in the basal plane, consistent with our hypothesis. However, to be completely sure of it, further research is necessary.

Figure 7 (b) shows the FTIR spectrum obtained for rGO 2hr sample at the range of 500–4000 cm^{-1} . From the figure we can see that there is no C=O and C-O functional group present. We also saw that in figure 7(a) that, as GO got reduced, these functional groups will be eliminated. In figure 7(b), % transmittance got decreased and O-H functional group also got broadened. It means that with time O-H functional group in rGO 2hr sample could also get eliminated.

Figure 7 (c) shows the FTIR spectrum obtained for rGO 5hr sample at the range of 500–4000 cm^{-1} . From figure 7(c), which is for the photodegraded samples of rGO 5hr, we can see that as photodegradation time passed the value of % transmittance got decreased which means that absorbance got increased. It is similar to the increasing absorbance value in UV-vis spectroscopy. We can also see that O-H functional groups is starting to get broadened, though not at the same way as rGO 2hr. It is getting broadened at a slower rate but it can be expected that as more time gets passed, this functional group can get eliminated. From here we can also assume that rGO 5hr degrades slowly than rGO 2hr.

From FTIR spectra for Dark controlled tubes for GO and rGO 5hr samples, we can see that as photodegradation time passed, the spectra remained almost same. It could mean that without sunlight, there won't be any change in the functional groups. However, for rGO 2hr we can see that as photodegradation time passed, the spectra did not remain same, rather it changed almost in a similar way like the photodegraded sample of rGO 2hr. It could mean that O-H functional group has an influence in the degradation process even without sunlight.

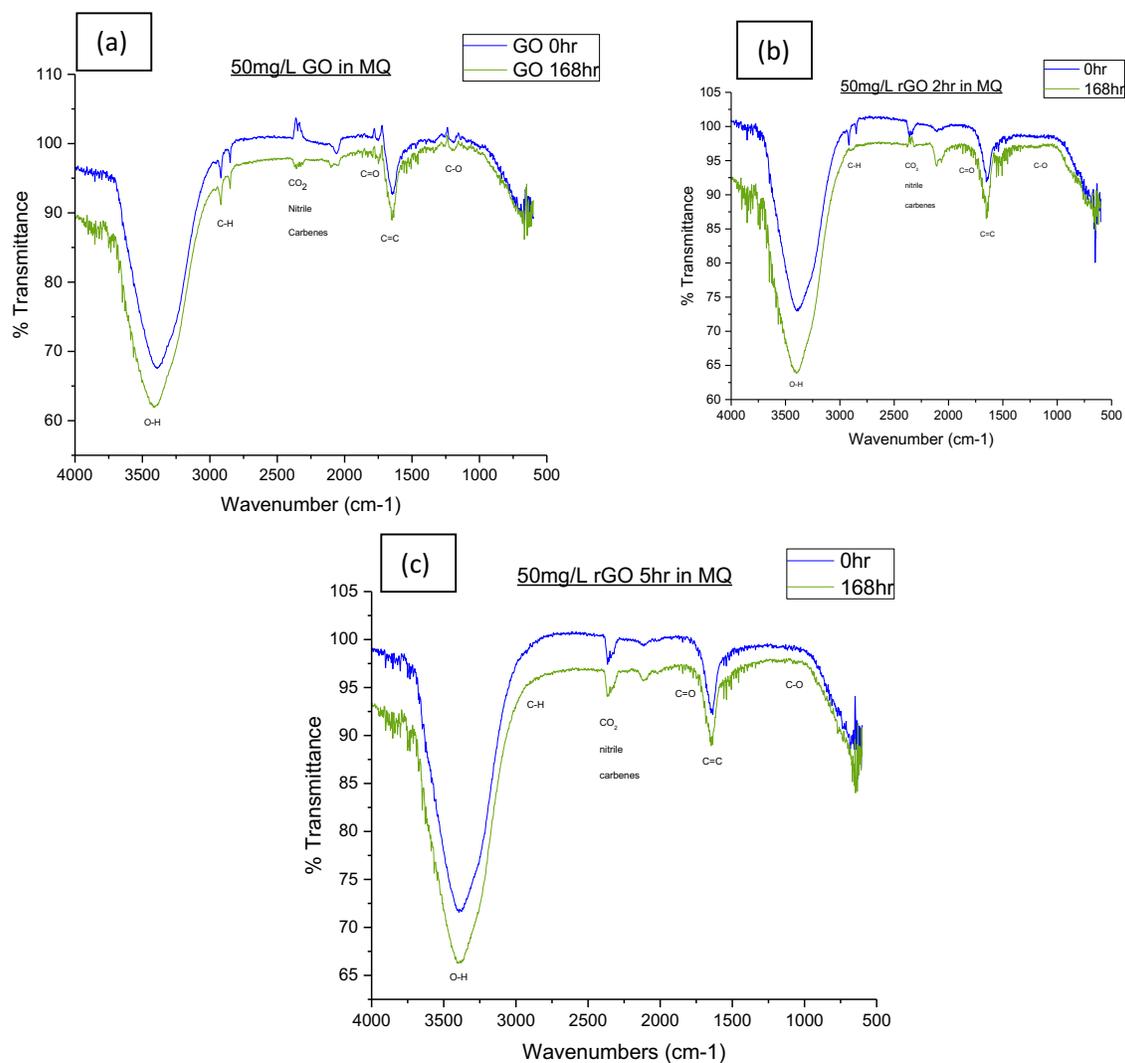


Figure 7. FTIR image of (a) photodegraded GO samples, (b) photodegraded rGO 2hr samples and (c) photodegraded rGO 5hr samples

For all the samples in figure 8 it was expected that there will be a change in hydroxyl functional group as it did for our previous work for direct photolysis but from figure there is no prominent change in hydroxyl functional groups (around 3400 cm^{-1}). However, in all the samples carboxyl functional group (wavenumber 1640 cm^{-1}) is increasing, which is what we had hypothesized. This increase is very much visible in GO (Figure 8a) and rGO 2hr (Figure 8b) samples but not in rGO

5hr (Figure 8c) sample. This could mean that in rGO 5hr, it will take more time for carboxyl functional groups to get formed and this could delay the degradation process.

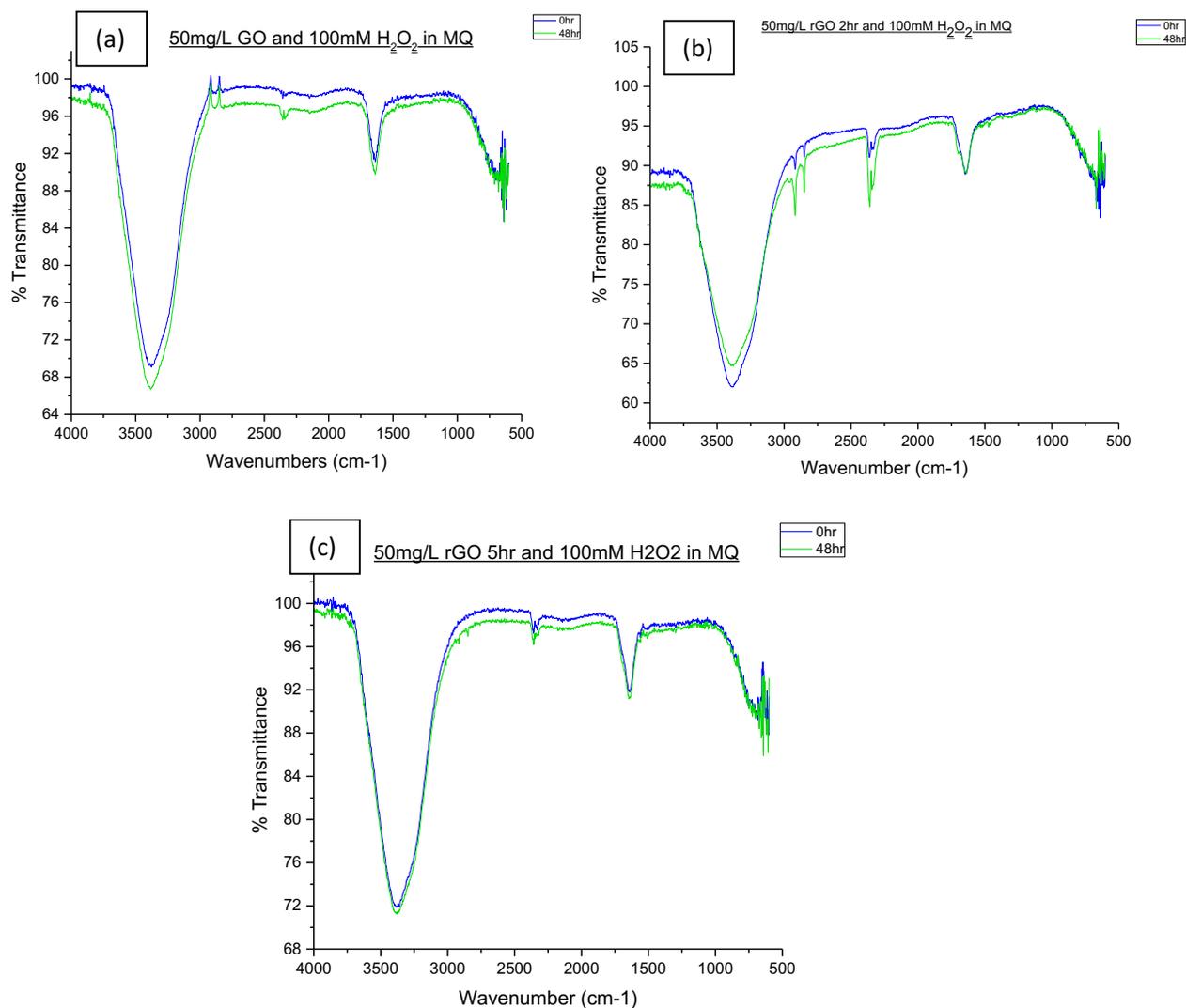


Figure 8. FTIR image of (a) photodegraded GO samples, (b) photodegraded rGO 2hr samples and (c) photodegraded rGO 5hr samples

Also, the partially-reduced graphene oxide possesses oxygen-containing functional groups as well that can form hydrogen bonding with multiple –OH functional groups of organic molecule (i.e. GO) to assist its adsorption. The interaction then allows more rapid oxidation of GO by

photogenerated holes or surface hydroxyl radicals. In indirect photolysis, GO sample completely converts to its mineralized form, CO₂. This can be seen in FTIR spectroscopy as well because the CO₂ functional group (wavenumber 2000-2500 cm⁻¹) is increasing after 48hr.

Total organic carbon (TOC) was measured to get an idea of the concentration of graphene oxide during the transformation process. As expected, the trend showed a decreasing pattern of TOC and this reduction in TOC content as irradiation time increases, indicates that GO is photochemically altered and light absorbing photoproducts are formed. From figure 9a we can see that direct phototransformation of GO is degrading the nanomaterials by almost 32.5% within 2 days and 38.6% within 7days. From figure 9b we can see that indirect phototransformation of GO is degrading the nanomaterials by almost 60.36% within 2days. From this we can interpret that degradation due to indirect photolysis will be at higher rate than direct photolysis which matches our hypothesis and previous characterization results as well.

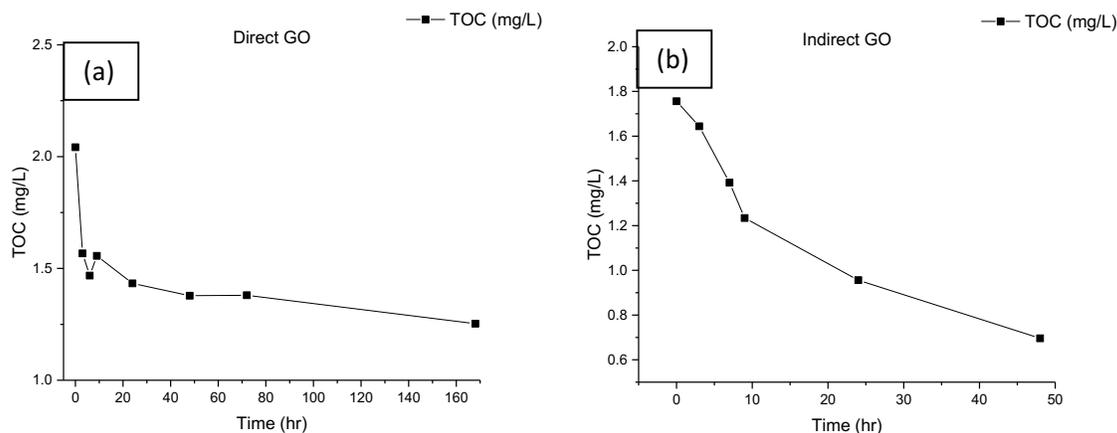


Figure 9. TOC analysis of (a) photodegraded GO samples in direct photolysis, (b) photodegraded GO samples in indirect photolysis

IMPLICATIONS WITH COLUMBIA RIVER WATER

Experiment with GO in Columbia river water was an implication of the project. Columbia river water (CRW) was used to see the effect of GO in practical field condition. Some initial characterization of river water was conducted using AQ400 analyzer. We measured the existing concentration of chloride and alkalinity in the river water (Table 3 and 4). By analyzing, we can see that Columbia river water contains low amount of chloride but significant amount of alkalinity.

Table 3. Concentration of chloride in Columbia river water

Sample ID	Test	Results	Units	Average	Average conc. (mM)
Columbia water 1	Chloride 100	13.24	mg Cl/L	13.19 mg Cl/L	0.37 mM
Columbia water 2	Chloride 100	13.14	mg Cl/L		

Table 4. Concentration of alkalinity in Columbia river water

Sample ID	Test	Results	Units	Average	Average conc. (mM)
Columbia water 1	Alakalin200	86.10	mg/L Ca	82.91mg/L Ca	2.07 mM
Columbia water 2	Alakalin200	79.72	mg/L Ca		

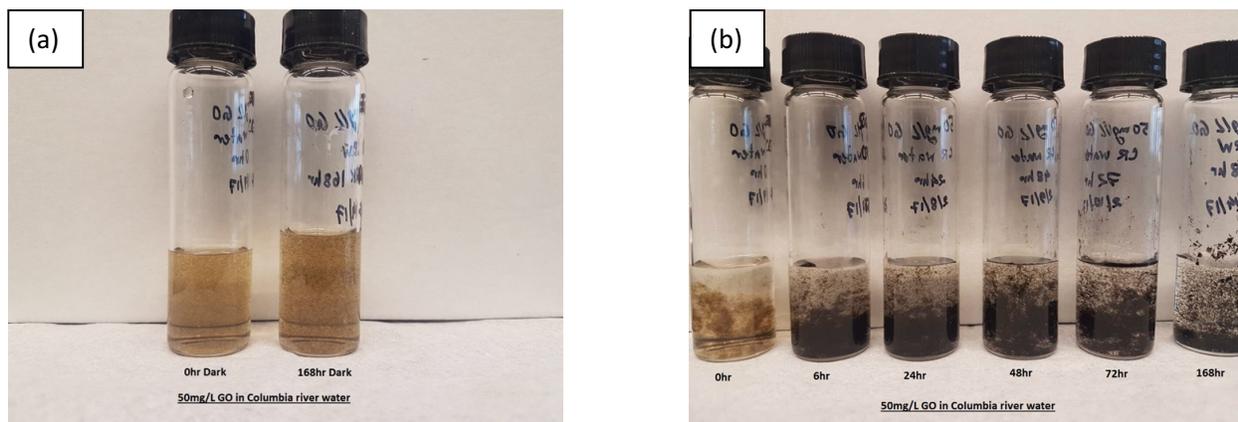


Figure 10. (a) 50mg/L GO in CRW water (Dark control tubes), (b) 50mg/L GO in CRW

Experiments with Columbia river water did show consistency with most of our previous results with a few discrepancies. Even without sunlight, 0hr Dark GO sample started aggregating slowly within 3-6 days (figure 10a). Direct photo-transformation can increase GO aggregation rate in aqueous suspension, suggesting that it will reduce this material's stability in the environment. Aggregation of GO increased with higher irradiation time (figure 10b).

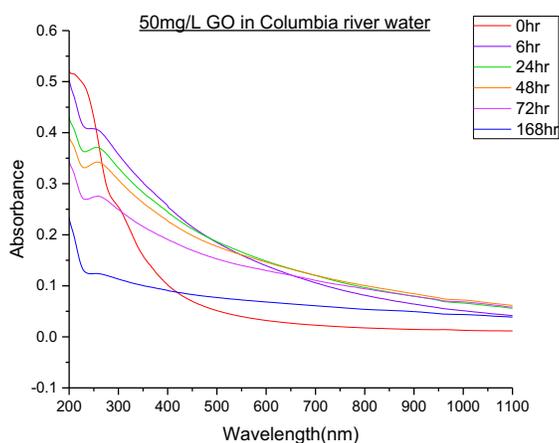


Figure 11. UV-visible absorbance spectra of 50mg/L GO in CRW water

UV-visible absorbance spectra of GO in CRW water (figure 11) showed initial peak at 230nm and shoulder at 300nm, which is consistent with GO. After irradiation, peak got shifted to around 270nm indicating rGO formation. Previously, direct photolysis of GO samples (figure 5a) showed that sunlight exposure increases UV-Vis absorbance above 280nm wavelength. In indirect photolysis, sunlight exposure increased UV-Vis absorbance above 280nm wavelength until 3hr, indicating direct photolysis and after 3hr absorbance started to decrease which indicates indirect photolysis (figure 6a). In Columbia River Water (figure 11a), sunlight exposure increases UV-Vis absorbance above 280nm wavelength until 6hr indicating direct photolysis and after 6hr absorbance started to decrease which indicates indirect photolysis. So, here direct and indirect photolysis is happening simultaneously. Due to similarity in UV-Vis spectrum of direct GO photolysis and GO photolysis in river water, direct photolysis could be dominant in Columbia river water and even though indirect photolysis is occurring, it may not be that dominant. Possible reason for this could be the unavailability of enough NOM to produce hydroxyl radical.

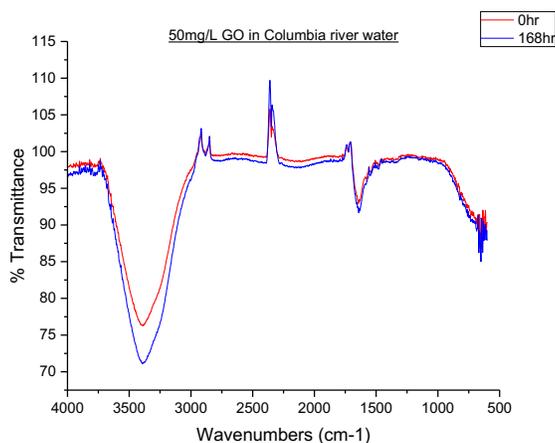


Figure 12. FTIR spectra of photodegraded GO samples in CRW

Just as we had hypothesized, FTIR spectra of GO in Columbia river water (figure 12) showed a decrease in hydroxyl functional group and an increase in carboxyl functional group, similar to figure 8a. So, we can say that, presence of different photosensitizer in Columbia river water (could be NOM or nitrate) is influencing the process and mediating indirect photolysis.

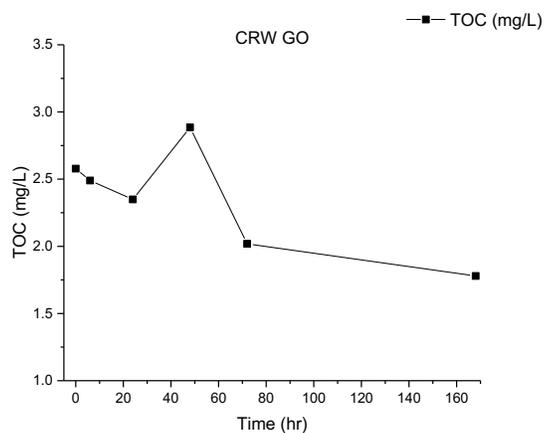


Figure 13. TOC analysis of photodegraded GO samples in CRW

TOC analysis of GO in Columbia river water, also showed the decreasing concentration of GO with increasing irradiation time. From figure 13 we can see that sunlight induced photolysis of GO is degrading the nanomaterials by almost 31% within 7 days, similar to direct photolysis. So we can interpret, that in Columbia river water, the rate of indirect photolysis will be lower than direct photolysis, which means that there may not be enough photosensitizers present to generate radicals and stimulate indirect photolysis. It also means that degradation of GO will occur due to direct photolysis.

CONCLUSIONS

Results from this study indicates that sunlight induced photolysis can significantly change the physical and chemical properties of GO, rGO 2hr and rGO 5hr. These qualitative results also indicate that functional groups of the samples, mainly the ones that are present on the basal plane, subsequently effects the degradation of GO, rGO 2hr and rGO 5hr. Columbia River Basin is a complex ecosystem that contain numerous photosensitizers like NOM, nitrate etc. that can generate hydroxyl radical and initiate photodegradation. However, Columbia River Basin might not contain enough of these photosensitizers to induce indirect photolysis, so the dominant pathway for degradation is the direct photolysis. The result of this research will be useful in understanding the mechanism of functional groups in degradation process which will allow us in future to do functionalization modification of these material. By doing so, we will be able to reuse these material that will have long life and less negative effects on environment. Along with this, we might potentially be able to remove carbon-based nanomaterials from surface waters by increasing photolysis rates.

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APPENDIX

US Geological Survey: 2016WA411B

Project Title: Transformation of Graphene Oxide Nanomaterials in the Aquatic Environment

PI: Indranil Chowdhury

Richard Watts

Student Support		
Degree Level	Number of Students	Number of Dissertations/Theses Resulting from Student Support
Undergraduate	0	0
Masters	1	1
Ph.D.	0	0
Post Doctoral	0	0

Students name, Degree Level

Mehnaz Shams, MS, Civil and Environmental Engineering

Publications	
Publication Type	Publication Citation
Conference	Chowdhury, I. , Guiney, L.M., Hersam, M.C., “Influence of Surface Functional Groups on the Degradation of Graphene Nanomaterials in the Aquatic Environment”, presented at 252 nd American Chemical Society National Meeting, August 21-25, 2016, Philadelphia, PA.
Journal	In preparation: Shams, M., Mansukhani, N., Henderson, W.M., Zepp, R., Bouchard, D., Hersam, M.C., Chowdhury, I. (2017) Environmental Implications of Two Dimensional Nanomaterials, <i>in preparation (Invited Review to Environmental Science Nano)</i>
Journal	In preparation: Shams, M., Guiney, L., Hersam, M., and Chowdhury, I. (2017) Influence of Functional Groups on the Degradation of Graphene under Direct Sunlight, in preparation for <i>Environmental Science and Technology</i> .
Journal	In preparation: Shams, M., Guiney, L., Hersam, M., and Chowdhury, I. (2017) Influence of Functional Groups on the Degradation of Graphene under Indirect Photolysis, in preparation for <i>Water Research</i> .
Conference	Shams, M., Guiney, L.M., Hersam, M.C., Chowdhury, I. , “Influence of Functional Groups on the Indirect Photolysis of Graphene t”, presented at 254 th American Chemical Society National Meeting, August 2017, Washington, DC.

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Follow On	
Source and Amount of Funding,	Funding Period
NSF CBET; \$300,000 (Title: Fundamental Mechanisms of the Environmental Transformation and Degradation of Graphene-Family Nanomaterials)	Applied (in review) (2017-2020)

Awards and Achievements
WSU feature news: https://news.wsu.edu/2016/09/26/wsu-studies-pollution-potential-industrial-nanomaterials/

Low Energy Precision (/Spray) Applications: Unmanned Aerial System based Rapid Evaluation for Crop and Site Specific System Adaptation in the Pacific Northwest

Basic Information

Title:	Low Energy Precision (/Spray) Applications: Unmanned Aerial System based Rapid Evaluation for Crop and Site Specific System Adaptation in the Pacific Northwest
Project Number:	2016WA412B
Start Date:	3/1/2016
End Date:	12/31/2017
Funding Source:	104B
Congressional District:	5
Research Category:	Engineering
Focus Category:	Irrigation, Agriculture, Water Use
Descriptors:	None
Principal Investigators:	Lav R Khot, Troy Peters

Publications

1. Sarwar*, A., L. R. Khot, and R. T. Peters. 2017. Applicability of low altitude multispectral sensing towards crop and site specific adaptation of LESA. Climate Impacts to water conference, Skamania Lodge, Stevenson, WA. January 25-26, 2017 (Paper/Oral Presentation). Link: <http://ext100.wsu.edu/water/wp-content/uploads/sites/53/2017/01/Abid-Sarwar-USE-THIS-ONE-Proceeding-I>
2. (Upcoming) Khot*, L., M. A. Khan, M. Chakraborty, and R. T. Peters. 2017. Low altitude multispectral sensing based evaluation of retrofitted center pivot irrigation systems for site specific adoption in Potato and Mint production. ASABE 2017 Annual International Conference Meeting, Spokane, WA, July 16-19, 2017.
3. (Upcoming) Osroosh*, Y., L. R. Khot, and R. T. Peters. 2017. Web-based crop monitoring system for performance evaluation of center pivot irrigation retrofitted with MESA and LESA. ASABE 2017 Annual International Conference Meeting, Spokane, WA, July 16-19, 2017.

Low Energy Precision (/Spray) Applications: Unmanned Aerial System based Rapid Evaluation for Crop and Site Specific System Adaptation in the Pacific Northwest

L. R. Khot and R. T. Peters, Washington State University, WA; H. W. Neibling, University of Idaho, ID.

Abstract:

Irrigation of agricultural crops is by far the largest use of water in the arid West. Amidst rapidly changing climatic conditions, water has become a valuable resource for use in diverse agricultural cropping systems in Washington State. Thus, growers need to adopt new/improved irrigation technologies, like Low Elevation Spray/Precision Application (LESA/LEPA) for improved and efficient water use. Such techniques have been practiced successfully for years in the Texas Panhandle and Kansas areas; however, have grower adoption concerns in Pacific Northwest. Key criticisms is that the real efficiency differences between LESA and Mid Elevation Spray Application (MESA) are overestimated since the water that is lost to wind drift and evaporation from MESA suppresses crop water use requirements downwind. To help quantify these differences, it is important to measure canopy temperature differences of similar crops. This data would help show where the additional energy is either lost or gained from evaporated water. Therefore, this project focuses on evaluating LESA and compare it with performance of MESA using small unmanned aerial system (UAS) integrated multispectral and thermal imaging. Our 2016 preliminary trials in potato had shown promising results. Small UAS based imagery was acquired during mid-growth stage and developed were the zonal maps. Lower potato crop vigor (Green NDVI of 0.14 ± 0.03) was observed for MESA compared to LESA (0.30 ± 0.03). Similarly, canopies were $\sim 2^{\circ}\text{C}$ cooler when irrigated with LESA compared to MESA. On-going 2017 season experiment campaigns will thus critically assess LSEA and MSEA using small UAS based remote sensing approach and utilize such data in effective extension/outreach of pertinent outcomes.

Brief description of project:

Our project objective is to collect UAS based infrared and multispectral (images) sensing data to effectively quantify the performance of the demonstration fields where we have LESA vs MESA, and LEPA vs MESA systems. Such comparative sites are throughout the state of Washington, Idaho, Nevada, and Oregon. This study will specifically focus on performance evaluation of the demonstration fields in Washington and Idaho.

Project status summary:

In 2016, our team integrated small UAS with the multi-spectral (5-band) and thermal infrared (with capability to have pixelated temperature) sensors for use on this project. Test flights were conducted to optimize the flight parameters and image acquisition protocols. Preliminary trials were conducted in potato crop where the sections of irrigation circle (central pivot) was retrofitted for LESA. Small UAS based imagery was acquired during mid-growth stage. Such imagery was then post-processed using custom developed data processing algorithms to develop the zonal maps. Our team has planned extensive data campaigns for on-going 2017 season where we will evaluate several irrigated crops (mint, alfalfa, beans and wheat). Experiment campaigns

will thus critically assess LSEA and MSEA using small UAS based remote sensing approach and utilize such data in effective extension/outreach of pertinent outcomes.

Results summary (to date and expected results)

Results to date: In 2016, we have integrated small UAS based imaging system. Preliminary trials data revealed lower potato crop vigor (Green NDVI of 0.14 ± 0.03) for MESA compared to LESA (0.30 ± 0.03). Similarly, thermal infrared data suggested that potato canopies were $\sim 2^\circ\text{C}$ cooler when irrigated with LESA compared to MESA.

Expected results: Small UAS based imagery data will aid us in evaluation of how the wetted canopy affects application efficiency, how it may suppress evapotranspiration demand, and it can also be used to see differences in ponding and runoff from the LESA/LEPA and MESA. High resolution images will also supplement physical demonstrations of the LEPA/LESA system and to assuage grower fears of the potential drawbacks of this technology. UAS based high resolution (5-band multi-spectral and thermal infrared sensors) imaging at various crop growth stages (minimum two) will enable our team to quantify the canopy health and water use efficiency for the sites irrigated with LESA/LEPA vs MESA.

Updated timeline of completion:

- Graduate student training (Fall 2016 through Spring 2018)
- Develop/optimize UAS-based remote sensing protocols (Summer, Fall 2016)
- Field data collection (WA & ID field sites) (Summer 2016; Summer & Fall 2017)
- Final Project Report submitted to the WRC (15 December 2017)
- Image analysis algorithms development; data analysis & mapping, peer-reviewed manuscripts (Fall 2016; Spring 2017 through Spring 2018)
- Extension and outreach (Fall 2016; Fall 2017)
- Develop federal grant proposals (Ongoing efforts; extend beyond project period)

Outcomes/Impacts to date:

1) References for any journal articles under review, accepted, or published that this grant supported,

N/A

2) Any presentations or talks relating to this work

Sarwar*, A., L. R. Khot, and R. T. Peters. 2017. Applicability of low altitude multispectral sensing towards crop and site specific adaptation of LESA. Climate Impacts to water conference, Skamania Lodge, Stevenson, WA. January 25-26, 2017 (Paper/Oral Presentation). Link: http://ext100.wsu.edu/water/wp-content/uploads/sites/53/2017/01/Abid-Sarwar-USE-THIS-ONE-Proceeding-Paper-2017_f.pdf

(Upcoming) Khot*, L., M. A. Khan, M. Chakraborty, and R. T. Peters. 2017. Low altitude multispectral sensing based evaluation of retrofitted center pivot irrigation systems for site specific adoption in Potato and Mint production. ASABE 2017 Annual International Meeting, Spokane, WA, July 16-19, 2017.

(Upcoming) Osroosh*, Y., L. R. Khot, and R. T. Peters. 2017. Web-based crop monitoring system for performance evaluation of center pivot irrigation retrofitted with MESA and LESA. ASABE 2017 Annual International Meeting, Spokane, WA, July 16-19, 2017.

3) Provide the number of Ph.D., Masters, and/or undergraduate students supported by this grant

PhD: 1 (Abid Sarwar, Fall 2016); MS: 1 (Momtanu Chakraborty, *partly supported*)

Understanding Links Between Water, Nitrogen, and Greenhouse Gases in Green Infrastructure

Basic Information

Title:	Understanding Links Between Water, Nitrogen, and Greenhouse Gases in Green Infrastructure
Project Number:	2016WA420B
Start Date:	3/1/2016
End Date:	12/31/2017
Funding Source:	104B
Congressional District:	3
Research Category:	Water Quality
Focus Category:	Water Quality, Hydrogeochemistry, Hydrology
Descriptors:	None
Principal Investigators:	John Harrison, Kevan B Moffett

Publications

1. Norton, R. (2016) Effects of Storm Size and Frequency on Nitrogen Retention, Denitrification, and Greenhouse Gas Production in Bioretention Mesocosms, M.S. Thesis, Washington State University.
2. Norton, R., J.A. Harrison, C.K. Keller, and K. B. Moffett (Accepted pending minor revisions) Effects of storm size and frequency on nitrogen retention, denitrification, and N₂O production in bioretention swale mesocosms, Biogeochemistry.
3. Norton R., J. Harrison. Effects of storm size and frequency on N retention, denitrification, and greenhouse gas production in bioretention mesocosms. 2016. Proceedings of the Society of Wetland Scientists.
4. Kintner, S. (In preparation) Quantifying Denitrification in Bioretention Swales under Unsaturated Conditions, M.S. Thesis, Washington State University.
5. 2016 WSU School of the Environment Graduate Research Symposium (Poster): Effects of Heavy Precipitation Events on NO₃⁻ Dynamics in Conventional vs Low Impact Development Stormwater Catchments Reed A. Norton and John A. Harrison.
6. Kintner, Sarah E., Moffett, Kevan B., Harrison, John A. (2017). Understanding Stormwater Nitrogen Pathways in Bioretention Swales. Poster presented at Washington State University Vancouver s Research Showcase, Vancouver, WA.
7. Kintner, Sarah E., Moffett, Kevan B., Harrison, John A. (2017). Understanding Stormwater Nitrogen Pathways in Bioretention Swales. Poster presented at Washington State University Vancouver s Graduate Research Symposium, Vancouver, WA.

Progress Report for USGS 104b project: Understanding Links Between Water, Nitrogen, and Greenhouse Gases in “Green” Infrastructure

Low impact development (LID) structures (rain gardens, bioretention swales) are widely regarded as a cost-effective way to reduce flooding and pollution associated with urbanization. Within the past decade, Portland, OR, alone has spent more than \$145 million implementing LID. Plans are proposed to implement green infrastructure across Washington State and in cities nation-wide. The Portland/Vancouver area is a leader in the installation of LID, with over 1,500 individual local LID projects, a nationally recognized “green streets” program, and award-winning installations near the WSU Vancouver campus. These factors ideally place WSU Vancouver, in collaboration with the Washington Stormwater Center of WSU Puyallup and other interested parties, to grow a research hub focused on LID functionality, natural and human costs and benefits, and value within the context of urban resilience to climate change. Cities across the U.S. have already committed to spend billions of dollars on green stormwater infrastructure in coming decades, but scientific understanding of these systems is still quite rudimentary. Little is known about how these systems actually work to retain water and pollutants, and even less about how they will respond to climate change. The scale, accessibility, and diversity of LID systems also make them wonderful laboratories in which to test established theories and develop new basic science linking hydrologic and biogeochemical processes.

Despite their design goals, the efficacy of installed LID systems for reducing flooding and removing pollutants is seldom tested post-construction. These dual services are linked by the control that soil water saturation and residence time exert on oxygen availability, and so on biogeochemistry. One important pollutant thought to be mitigated by LID is reactive nitrogen (N). High levels of N are common in urban runoff, sourced from industrial and vehicular fossil fuel emissions, fertilizer (farms, lawns, gardens), and septic/sewage effluent. When present in excess, N can damage aquatic ecosystems and risk human health via harmful algal blooms, hypoxia, and degraded drinking water quality. The N retention documented in LID systems is highly variable, from 85% N reduction to 650% N enrichment in runoff. This variability is not well understood, nor even whether the key controls are biogeochemical or hydrological; this hinders further advancements in LID design, investment, and management. Furthermore, since microbes in these systems produce potent greenhouse gases (GHGs; e.g., N₂O, CO₂, CH₄), it is unknown to what degree LID systems may trade one environmental problem (water pollution) for another (GHG production).

Better understanding how water and N processing in LID structures respond to storm events of varying size and frequency will become increasingly important in coming decades as Washington State experiences progressive climate change and urbanization. Regional mean annual runoff is projected to increase as much as 34% by the 2080s and the frequency of heavy precipitation events (>5 cm/day) is also expected to increase, as already evident in recent rainfall records. Heavy precipitation on urban impervious areas exacerbates N delivery to aquatic environments and provides a substantial fraction of total annual runoff to LID systems (~20% according to one estimate) and an even greater fraction of the annual N inflow (>40%). An improved understanding of the relationships between storm intensity, LID hydraulics, water retention, aeration, and N cycling are required before we can predict how urban stormwater systems will respond to the co-occurring stresses of N loading, urbanization, and climate change, and so better help planners scale LID investments to meet future water quality goals.

To address these critical gaps in basic understanding of LID function, we have been working to address the following research questions: 1) *How do bulk LID denitrification, N retention, and GHG production respond to different storm intensity and frequency?* and 2) *How is storm rainfall of different intensity and frequency partitioned within an LID into soil moisture storage, deep drainage, and evapotranspiration, and how does this partitioning and patterns of percolation alter the transient biogeochemically-relevant (i.e., moisture, temperature, oxygen) soil conditions?* This research has focused on generating key data from experiments in established LID mesocosms while we have worked toward the process-based numerical models and extensions to the field settings across regional urbanization and climate gradients that are intended to be the foci of subsequent external funding proposals.

To address these research questions, six bioretention column mesocosms at WSUP have been, and will continue to be, used to emulate full-scale LID bioretention facilities in replicate, with experiments in two stages. In Stage 1, experimental focus was on understanding the mesocosms as bulk (“black box”) biogeochemical reactors; in particular, on quantifying the magnitude of overall denitrification (using novel methods) and GHG production under

different storm intensities and frequencies. In Stage 2, focus is on "opening the black box" to understand the spatially and temporally variable internal linking of hydrological and biogeochemical functions of LID bioretention structures under varied storm intensities and frequencies. Stage 1 was carried out largely by project M.S. student Reed Norton and has resulted in a M.S. thesis, several poster presentations, and a manuscript currently accepted pending minor revisions at *Biogeochemistry*. Stage 2 is currently underway and makes up the bulk of M.S. student Sarah Kintner's thesis research. Support from this grant was instrumental in getting Ms. Kintner started on her research, and we anticipate she will finish her M.S. thesis and submit a manuscript for publication in fall of 2018.

A final report will be submitted to the State of Washington Water Research Center by 15 December, 2017.

Information Transfer Program Introduction

The WRC staff has been active in outreach with water research and management professionals through presentations and event participation, development of educational programs, service to various professional associations, conference hosting and sponsorship, and through its website and social media presence. This This information Transfer section includes a summary of WRC activities beyond the 104b-funded seed grant and administrative support, including extramural grants, presentations, service, and education programs.

Information Transfer Plan for the State of Washington Water Research Center

Basic Information

Title:	Information Transfer Plan for the State of Washington Water Research Center
Project Number:	2016WA423B
Start Date:	3/1/2016
End Date:	2/28/2017
Funding Source:	104B
Congressional District:	3
Research Category:	Not Applicable
Focus Category:	None, None, None
Descriptors:	None
Principal Investigators:	Jonathan Yoder, Jennifer Adam

Publications

1. Yoder, Jonathan, Jennifer Adam, Michael Brady, Joseph Cook, Stephen Katz, Shane Johnston, Keyvan Malek, John McMillan, and Qingqing Yang. 2017. Benefit-Cost Analysis of Integrated Water Resource Management: Accounting for interdependence in the Yakima Basin Integrated Plan. *Journal of the American Water Resources Association* 1-22. DOI: 10.1111/1752-1688.12507.
2. Yoder, Jonathan, Michael Brady, & Joseph Cook. 2016. Water markets and storage: Substitutes or complements for drought risk mitigation? *Water Economics and Policy* 2(2):21 pp.
3. Marsh, Thomas, Jonathan Yoder, Tesfaye Deboche, Terry McElwain & Guy Palmer. 2016. Pastoralists' decisions on livestock vaccination translate into increased human capital and increased school attendance by girls. *Science Advances*: 2(12) e1601410, DOI: 10.1126/sciadv.1601410. Winner of the Western Agricultural Economics Association Outstanding Published Research Award for 2017.
4. Quinlan, Robert J., Isaya Rumas, Godfrey Naisikye, Marsha B. Quinlan, & Jonathan Yoder. 2016. Searching for Symbolic Value of Cattle: Tropical Livestock Units, Market Price and Cultural Value of Maasai Livestock. *Ethnobiology Letters* 7(1):76-86.
5. Skolrud, Tristan, Gregmar Galinato, Suzette Galinato, C. Richard Shumway, & Jonathan Yoder. 2016. The Role of Market Structure and Federal Renewable Fuel Standards in the Growth of the Cellulosic Biofuel Sector. *Energy Economics* 58:141-151. <http://dx.doi.org/10.1016/j.eneco.2016.06.024>.
6. D'Angeli, M., J. Baker, D. Call, M. Davis, K. Kauber, U. Malhotra, G. Matsuura, D. Moore, C. Porter, P. Pottinger, V. Stockwell, C. Wagner, R. Wohrle, J. Yoder, L. Yoke, P. Rabinowitz. 2016. Antimicrobial stewardship through a one health lens: observations from Washington State. *International Journal of Health Governance* 21(3):114-130. <http://www.emeraldinsight.com/doi/abs/10.1108/IJHG-02-2016-0009>.
7. George A. Wudiri, J. Osiri, F. Lankester, M. Subbiah, J. Yoder, S. Pepper, T. McElwain and G. Kaufman. 2016. A multidisciplinary Approach to Mitigating Antimicrobial Resistance. *Journal of the International Academy for Case Studies* 22(1):124+.
8. Padowski, J.C. and Gorelick, S.M., 2016. Global analysis of urban surface water supply availability. In *Sustainable Cities: Urban Planning Challenges & Policy*, K. Etingoff, ed., CRC Press.
9. McDonald, R.I., Weber, K., Padowski, J., Boucher, T., Shemie, D., 2016. Quantifying watershed degradation and its impact on water treatment costs for the world's largest cities. *Proc. Nat. Acad.*

Information Transfer Plan for the State of Washington Water Research Center

- Sci. Early Edition. doi: 10.1073/pnas.1605354113
10. Padowski, J.C., Carrera, L. and Jawitz, J.W., 2016. Overcoming urban water insecurity with infrastructure and institutions. *Water Res. Manage.* 30(13), 4913-4926
doi:10.1007/s11269-016-1461-0
 11. Barik, M.G., J.C. Adam, M.E. Barber, and B. Muhunthan, 2016. Improved landslide susceptibility prediction for sustainable forest management in an altered climate. *Engineering Geology* (in revision).
 12. Malek, K., J.C. Adam, C.O. Stockle, and T. Peters, 2017. Climate change reduces water availability for agriculture by decreasing non-evaporative irrigation losses. *Journal of Hydrology* (in review).
 13. Malek, K., C.O. Stöckle, R. Nelson, K.J. Chinnayakanahalli, Liu, M., Rajagopalan, K., Muhammad, B., and J. C. Adam, 2016. VIC-CropSyst: A regional-scale modeling platform to simulate the nexus of climate, hydrology, cropping systems, and human decisions, *Geoscientific Model Development-Discussion*, doi: 10.5194/gmd-2016-294 (in review).
 14. Rajagopalan, K.R., K. Chinnayakanahalli, C.O. Stockle, R. Nelson, A. Hamlet, M. Brady, M. Barber, C. Kruger, K. Malek, G. Yorgey, S. Dinesh, and J.C. Adam, 2017, Impacts of near-term regional climate change on agricultural production in the Columbia River basin. *Water Resources Research* (in review).
 15. Allen, E., J. Stephens, G. Yorgey, C.E. Kruger, S. Aahamed, J. C. Adam, 2017. Climate science information needs among natural resource decision-makers in the Northwest U.S.? *Climate Services*, doi: 10.1016/j.ciser.2017.03.002.
 16. Hall, S., J.C. Adam, M. Barik, J. Yoder, M. Brady, D. Haller, M. Barber, C. Kruger, G. Yorgey, M. Downes, C. Stockle, B. Aryal, T. Carlson, G. Damiano, S. Dhungel, C. Einberger, K. Hamel-Reiken, M. Liu, K. Malek, S. McClure, R. Nelson, M. O'Brien, J. Padowski, K. Rajagopalan, Z. Rakib, B. Rushi, and W. Valdez, 2016. Columbia River Basin Long-Term Water Supply and Demand Forecast, Washington State Legislative Report,
<https://fortress.wa.gov/ecy/publications/SummaryPages/1612001.html>.
 17. Shehata, Mahmoud, John Petrie, 2016, Hydrodynamics in the confluence of the Snake and Clearwater Rivers, in *River Flow 2016*, International Conference on Fluvial Hydraulics, IAHR, St. Louis, MO.

Summary of WRC Staff Activities

The resources that the WRRRA 104b and university support provides is the foundation upon which to pursue extramural grant activities, research supported by it, and outreach. Table IT1 provides a summary of WRC staff activities beyond the WRC seed grant program (about which information is provided in the research section of this report). The WRC staff (1.75 FTE associated directly with the WRC, 3 FTE total) has submitted proposals for over \$10 million grants in each of the last two years. Some of these grants are administered through the WRC, some are administered through other centers. Table IT1 also summarizes student support programs, presentations, journal articles, and other outputs.

Table IT1: Summary of WRC activities and outputs, FY 2016-2017.

Metric	FY17		FY16	
	#	\$ Mil.	#	\$ Mil.
Journal articles published by WRC staff	11	-	10	-
Journal articles in press by WRC staff	4	-	4	-
Presentations by WRC staff	20	-	19	-
Outreach and service activities by WRC staff	26	-	27	-
Grant research reports submitted by WRC staff	2	-	1	-
Grant proposals submitted by WRC staff	8	\$16,132,512	10	\$13,555,108
New grants received by WRC staff	2	\$137,288	3	\$2,088,462
Pending grant proposals by WRC staff	0	\$0	6	\$4,327,724
Ongoing grant projects by WRC Staff	3	\$1,974,535	6	\$2,18,0797
Grant proposal submitted through WRC	6	\$12,271,990	7	\$4,420,059
New grants administered by WRC	1	\$137,288	1	\$86,921
Ongoing grant projects administered by WRC	1	\$1,921,335	2	\$1,843,921
Graduate students funded by WRC staff or grants	27	-	11	-
Undergraduates funded by WRC staff or grants	14	-	8	-
Journal articles from seed grants, past 5 years	10	-	7	-
Theses/dissert'ns from seed grants, past 5 years	3	-	2	-
Present'ns/posters from seed grants, past 5 years	7	-	2	-
Water Club enrollment (max # in year)	20	-	-	-
Water-related internships coordinated by WRC	2	-	0	-

Education programs in addition to student research support

The WRC has worked closely with the School of the Environment (SoE) to finalize and submit an undergraduate certificate program titled "Water Resources Science and Management" for undergraduate students at WSU. This certificate takes advantage of the breadth of existing water-related courses currently available throughout WSU and

requires students to complete coursework spanning for major water themes: 1) Subsurface and Surface Hydrology, 2) Water Chemistry/Ecology/Biology, 3) Water Methods & Analysis and 4) Water Policy and Management along with a set of extracurricular activities. The extracurricular activities are designed to bring together students and faculty interested in water by participating in networking, professional development and other educational events. In addition to an undergraduate certificate, the WRC has also been working closely with SoE to lay a foundation from which a “floating” interdisciplinary graduate program can be established. The first step in this process- designing an interdisciplinary core course- has already been accomplished and is currently under review with the Registrar. Pending course approval, the WRC will work with SoE to finalize an interdisciplinary water certificate program for graduate students.

Communications and branding development

The WRC Website is accessible at swwrc.wsu.edu. It includes summaries of recent and current 104b seed grant projects, recent and current extramural research projects managed through the WRC, a news page, and information about affiliated agencies, institutes, and researchers. We also maintain a twitter account: @WA_WRC with which we post WRC and Washington State water related news. We are in the process of looking to hire an additional web developer to help us take the next step to a vibrant, information-rich website.

In support of this effort, the WRC staff has been working to organize and archive the research records of the WRC, with the intent of creating a searchable and “browsable” database. We are also using list serves, twitter, and a news page on our website to disseminate news. We are working to contract with another office at WSU or an outside web developer to complete and maintain development.

Collaboration building within WSU and beyond

The WRC continues to expand its collaborative network within WSU and the State of Washington. With the hiring of our water quality and stormwater expert, we are building stronger ties with the WSU Stormwater Center. Because WSU water researchers are scattered across several campuses, we are examining the possibility of adding a WSU Water Program Coordinator to help facilitate collaboration among faculty across campuses.

The WRC currently has two primary connections to State government at the Washington State Department of Ecology, and the State Legislature. The Department of

Ecology has been the source of a substantial share of WRC extramural funding in recent years to support WRC research to provide long-run water supply and demand forecasts for the State of Washington, which the Ecology Office of Columbia River oversees on a five year cycle. The WRC is also currently building stronger ties to the Ecology Water Resource Program, which oversees a broader array of water resource and regulatory issues. The State legislature has over the last several years identified the WRC as a source of independent research on water-related issues.

In addition, we are strengthening our collaborations with Pacific Northwest National Laboratories and the USGS Washington Water Science Center through building a more robust student internship conduit to these organizations. We have also submitted a proposal to the WSU academic administration to begin an undergraduate interdisciplinary water science and management certificate, which would be the first coordinated interdisciplinary water program at WSU.

The WRC administration intends to continue fostering its role as an independent source of quality research to help address the State of Washington's needs. The WRC administration is in communication with the WSU office of State relations to begin to explore ways of securing additional state base funding to support personnel for actively, permanent outreach and research programs.

External organization involvement and service

Adam, Jennifer and Jonathan Yoder. Universities Council on Water Resources (UCOWR) Yoder, Lead Delegate for WSU, Adam, Delegate. Yoder is on the UCOWR Board of Directors.

Padowski, J.C.; Adam, J.C.; Yoder, J., McCabe J. 2015. NSF FEW Workshop White Paper- Addressing the Food-Energy-Water System Trilemma: Balancing Reliance on Technological and Institutional Solutions. Submitted to the National Science Foundation in partial satisfaction of an NSF workshop grant focusing on the Food-Energy-Water Nexus.

Yoder, Jonathan. Yearlong: DNR expert council on Climate and environmental change.

Yoder, Jonathan 2016-2017. Editorial board member, Journal of Water Economics and Policy

Yoder, Jonathan 2015-2017. Universities Council on Water Resources (UCOWR) Board of Directors.

Yoder, Jonathan 2016. WA State Department of Natural Resources Expert Council on Climate and Environmental Change.

Yoder, Jonathan 1/15/2015 and 1/30/2015. WA State House of Representatives meeting on water market development

Padowski, Julie 2016. Scientific Advisor for the 2016 Columbia River Basin Forecast Project.

Padowski, Julie 2015-2016. Ad hoc reviewer for the following peer-reviewed journals: Water Resources Research, Forests, Environmental Research Letters, and Ecological Economics.

Padowski, Julie 2015-2016. Faculty rep on Executive Committee for Sustainability and Environmental Committee at WSU

Adam, Jennifer 2015-2016. Sat on PhD and MS committees outside of Civil and Environmental Engineering (e.g., Keyvan Malek in Biological Systems Engineering who I co-advise with Claudio Stockle, Muhammad Azeem Khan in Biological Systems Engineering, Justin Poinsett and Sarah Anderson in Biology, Cody Miller in the School of the Environment, and Tristan Mullis in computer sciences)

Adam, Jennifer 2015-2016. Participated in water-related meetings and conferences, including the American Geophysical Union (AGU) which is the largest hydrologic science meeting of the year, the annual Pacific Northwest Climate Science Conference, the Washington State Tree Fruit Association (WSTFA) annual meeting, the American Water Resources Association (AWRA) Washington State annual meeting. Dr. Adam had invited talks related to WRC research at most of these meetings.

Adam, Jennifer 2015-2016. Acted as water lead for the moving of water faculty from three colleges (VCEA, CAS, CAHNRS) into the new PACCAR Environmental Technology Building, where the WRC administration is now co-located with CEREO. Dr. Adam continues to act as water lead for all PACCAR-related activities.

Adam, Jennifer 2015-2016. WSU President Search: Advisory Committee Member

Adam, Jennifer provided services for AGU Hydrology Section: Horton Research Student Grant Program Reviewer and Panelist.

Adam, Jennifer provided services for American Meteorological Society (AMS): Hydrology Committee member.

Adam, Jennifer provided services for CUAHSI hydrologic model benchmarking working group member. Dr. Adam was invited to a related workshop in Boulder, CO to share her ideas about the importance of hydrologic connectivity in hydrologic models.

Grant proposals, ongoing grant projects

Washington State Dept of Ecology Office of Columbia River 2016 Water Supply and Demand Forecast. \$1,800,000. Jennifer Adam Principal Investigator, Jonathan Yoder Project Director and Co-PI. Ongoing.

PMU: WSC-Category 3: Watershed Integrated System Dynamics Modeling (WISDM): Feedbacks among biogeochemical simulations, stakeholder perceptions, and behavior.

Kolden, Crystal et al.. July 2015. Advancing Resilience to Compounding Disasters: An Integrated Natural-Human Systems Assessment of Wildfire Vulnerability. National Science Foundation, Interdisciplinary Research in Hazards and Disasters, Science, Engineering and Education for Sustainability NSF-Wide Investment (NSF Hazards SEES). \$2.8 M.

Grant proposals submitted or in preparation

Yoder, Jonathan, Tanyalee Erwin, and John Stark. Proposal to House the U.S. Environmental Protection Agency Pacific NW Environmental Finance Center (PNWEFC). \$4.8Million. Not funded.

Katz, Stephen, et al. 2015. Maximizing the utility and adaptability of agricultural water-use science in supporting management for the Columbia River Basin's next 30 years. Submitted to the USDA Water For Agriculture program. \$9,997,942. Not funded.

Padowski, Julie, Jonathan Yoder, Jennifer Adam, Stephanie Hampton, and Chad Kruger. August 2015. Addressing the Food-Energy-Water System Trilemma: Balancing Reliance on Technological and Institutional Solutions. National Science Foundation SEES workshop proposal: Interactions of Food Systems with Water and Energy Systems. \$44,953. Funded and completed.

Coastal SEES Collaborative Research: Shaping sustainable trajectories for coastal watersheds: The role of model predictions, uncertainty and risk. \$469,594. Pending. In collaboration with University of Washington.

Big Data Spoke for Drought Mitigation led by New Mexico State University. NSF Big Data Regional Innovation Hubs (BD Hubs) program.

<http://www.nsf.gov/pubs/2016/nsf16510/nsf16510.htm>. Not funded.

NSF Innovations at the Nexus of Food, Energy and Water Systems (INFEWS), Track 1: "Increasing regional to global-scale resilience in FEW systems through coordinated management of storage in concert with innovations in technology and institutions." In

preparation. With other WSU faculty in collaboration with PNNL (Ian Kraukunas, PNNL Lead). \$3,000,000 budget limit.

NSF Innovations at the Nexus of Food, Energy and Water Systems (INFEWS), Track 1: "Food-Energy-Water Systems in Mountainous Coastal Watersheds: Examining historical trajectories and the influence of human decisions". In preparation. In collaboration with University of Washington. \$3,000,000 budget limit.

Padowski, Julie. Co-PI on USDA Water CAP proposal: Maximizing the utility and adaptability of agricultural water use science in supporting management for the Columbia River Basin's next 30 years. (Not funded.)

Padowski, Julie. Co-PI on Palouse Basin Aquifer Committee proposal -- Active Management Option for Slowing or Halting the Decline of Grand Ronde Water Levels in the Moscow-Pullman Corridor. (Not funded.)

Publications by staff for WRC activities not included in NIWR.net database categories

Padowski Julie, 2015- "Assessment of human-natural system characteristics influencing global freshwater supply vulnerability: peer reviewed.

Padowski, Julie 2016. "Measuring urban water security through infrastructure and institutions", submitted paper.

Padowski, Julie and McDonald, Weber, 2016. "Quantifying watershed degradation and its impact on water treatment costs for the world's largest cities", submitted paper.

Padowski, Julie 2016

USGS Summer Intern Program

None.

Student Support					
Category	Section 104 Base Grant	Section 104 NCGP Award	NIWR-USGS Internship	Supplemental Awards	Total
Undergraduate	1	0	0	0	1
Masters	5	0	0	0	5
Ph.D.	2	0	0	0	2
Post-Doc.	0	0	0	0	0
Total	8	0	0	0	8

Notable Awards and Achievements

Jennifer Adam, Outstanding Research Faculty Award, Department of Civil & Environmental Engineering, WSU, 2016

Team Award (PI J. Yoder): Bruce Gardner Prize for Applied Policy Analysis, Agricultural and Applied Economics Association, 2016

Team Interdisciplinary Award for our Yakima Basin Integrated Plan Cost-Benefit Analysis (PI J. Yoder) sponsored by CAHNRS, 2016

Publications from Prior Years

1. 2015WA404B ("Bedload dynamics at the confluence of large rivers") - Conference Proceedings - Shehata, Mahmoud, John Petrie, 2016, Hydrodynamics in the confluence of the Snake and Clearwater Rivers, in River Flow 2016, International Conference on Fluvial Hydraulics, IAHR, St. Louis, MO.
2. 2015WA404B ("Bedload dynamics at the confluence of large rivers") - Other Publications - Shehata, Mahmoud, John Petrie, 2016, Mixing zone hydrodynamics in a large confluence: a case study at the confluence of the Snake and Clearwater Rivers, BioEarth Annual Meeting, Washington State University (February 2016).
3. 2015WA404B ("Bedload dynamics at the confluence of large rivers") - Other Publications - Shehata, Mahmoud, John Petrie, 2016, Mixing zone hydrodynamics in a large confluence: a case study at the confluence of the Snake and Clearwater Rivers, Pacific Northwest Water Research Symposium, Oregon State University (April 2016).
4. 2015WA404B ("Bedload dynamics at the confluence of large rivers") - Dissertations - Lara Pracht, PhD student supported by the grant, graduated with her degree in January 2017. Her thesis includes results supported by the grant: Arsenic contaminated groundwater: Exploration of the role of organic carbon in mobilization processes and evaluation of mechanisms of arsenic sequestration by in situ treatment systems
5. 2015WA394B ("Climate Change Effects on Water Supply: Linkages Between Wildfire and Accelerated Snowmelt") - Dissertations - Lara Pracht, PhD student supported by the grant, graduated with her degree in January 2017. Her thesis includes results supported by the grant: Arsenic contaminated groundwater: Exploration of the role of organic carbon in mobilization processes and evaluation of mechanisms of arsenic sequestration by in situ treatment systems
6. 2014WA381B ("Interactive effects of nutrients and grazing on the control of cyanobacteria blooms: a comparison across a eutrophication gradient in freshwater systems in Washington state") - Articles in Refereed Scientific Journals - Rose+ V, Rollwagen-Bollens G, Bollens S. (2017) Interactive effects of phosphorus and zooplankton grazing on harmful algal blooms in a shallow temperate lake. *Hydrobiologia* 788: 345-359.
7. 2009WA264B ("Understanding Controls on Cyanobacteria Blooms: Vancouver Lake as a Model System") - Articles in Refereed Scientific Journals - Lee* T, Bollens S, Rollwagen-Bollens G, Emerson J. (2016) The effects of eutrophication and invasive species on zooplankton community dynamics in a shallow temperate lake. *Fundamental and Applied Limnology* 188: 215-231.
8. 2009WA264B ("Understanding Controls on Cyanobacteria Blooms: Vancouver Lake as a Model System") - Articles in Refereed Scientific Journals - Lee* T, Rollwagen-Bollens G, Bollens S. (2015) →→→The influence of water quality variables on cyanobacteria blooms and phytoplankton community composition in a shallow temperate lake. *Environmental Monitoring and Assessment* 187: 315. doi:10.1007/s10661-015-4550-2
9. 2011WA326B ("Understanding Toxin Production by Harmful Algae: Vancouver Lake as a Model System") - Articles in Refereed Scientific Journals - Lee* T, Rollwagen-Bollens G, Bollens S, Faber-Hammond J. (2015) Environmental influences on cyanobacteria abundance and microcystin toxin production in a shallow temperate lake. *Ecotoxicology and Environmental Safety* 114: 318-325.
10. 2011WA326B ("Understanding Toxin Production by Harmful Algae: Vancouver Lake as a Model System") - Articles in Refereed Scientific Journals - Lee* T, Rollwagen-Bollens G, Bollens S, Faber-Hammond J. (2015) Environmental influences on cyanobacteria abundance and microcystin toxin production in a shallow temperate lake. *Ecotoxicology and Environmental Safety* 114: 318-325.
11. 2009WA264B ("Understanding Controls on Cyanobacteria Blooms: Vancouver Lake as a Model System") - Articles in Refereed Scientific Journals - Rollwagen-Bollens G, Bollens S, Gonzalez A, Zimmerman J, Lee* T, Emerson J. (2013) Feeding dynamics of the copepod *Diacyclops thomasi* before, during and following filamentous cyanobacteria blooms in a large, shallow temperate lake. *Hydrobiologia* 705: 101-118

12. 2009WA264B ("Understanding Controls on Cyanobacteria Blooms: Vancouver Lake as a Model System") - Articles in Refereed Scientific Journals - Boyer* J, Rollwagen-Bollens G, Bollens S. (2011) Microzooplankton grazing before, during and after a cyanobacterial bloom in Vancouver Lake, Washington, USA. *Aquatic Microbial Ecology* 64: 163-174.