

North Dakota Water Resources Research Institute

North Dakota State University University of North Dakota

ANNUAL REPORT

March 1, 2017 to February 28, 2018

Fiscal Year 2017 Report to the U.S. Geological Survey

June 1, 2018

Annual Report

Fiscal Year 2017 Report to the U.S. Geological Survey

Award No. G17AS00023 U.S. Geological Survey

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June 1, 2018

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INTRODUCTION

This report describes the activities of the North Dakota Water Resources Research Institute (NDWRRI) during the period of March 1, 2017 to February 28, 2018.

The ND WRRI is one of the 54 institutes known collectively as the National Institutes for Water Resources. The NDWRRI was founded in 1965, by authority of Congress (Water Resources Research Acts of 1964, 1972, 1984, and 1990), and is administrated through the United States Geological Survey. Section 104 of the Water Resources Research Act requires the NDWRRI to apply its Federal allotment funds to:

- 1. Plan, conduct or otherwise arrange for competent research that fosters: (a) the entry of new research scientists into the water resources field, (b) training and education of future water resources scientists, engineers, and technicians; (c) the preliminary exploration of new ideas that address water problems or expand understanding of water and water-related phenomena; and (d) the dissemination of research results to water managers and public.
- 2. Cooperate closely with other colleges and universities in the state that have demonstrated the capability for research, information dissemination and graduate training, in order to develop a statewide program designed to resolve State and regional water and related land problems.
- 3. Cooperate closely with other institutes and other organizations in the region to increase the effectiveness of the Institute and for the purpose of promoting regional cooperation.

This year (2017-2018), NDWRRI once again allocated its 104(B) resources to fund Graduate Fellowship research projects. The institute also continued its efforts to enhance communication between the State and Federal agency personnel and university faculty and students. NDWRRI also worked closely with the several departments/programs/schools at North Dakota State University (NDSU) such as Environmental and Conservation Sciences, Civil and Environmental Engineering, Agricultural and Biosystems Engineering, Industrial and Manufacturing Engineering, Chemistry and Biochemistry, Plant Sciences, and Natural Resource Sciences to facilitate water related research proposal collaborations.

The annual base grant amount received by NDWRRI was \$92,335. The amount was used for administration and Fellowship awards. The Fellowship program was supported by the North Dakota State Water Commission with an additional amount of \$18,850.

Program Management

The Institute continued the same administrative mechanism with a director managing the institute program with the help of a State Advisory Committee. Dr. Eakalak Khan, Professor of Civil and Environmental Engineering, served as the Director from March 1, 2015 to January 31, 2018. Dr. Xuefeng (Michael) Chu, Professor of Civil and Environmental Engineering, has served as the Director since February 1, 2018. Linda Charlton-Gunderson, an NDSU employee, has been working part-time for the Institute to assist the director with Institute finances, communications and information transfer. The State Advisory Committee consists of three members representing the three principal water agencies in North Dakota: State Water Commission, State Department of Health, and the U.S. Geological Survey North Dakota District.

In addition, the Institute also seeks advices from the faculty of the two major research universities of the State: NDSU and University of North Dakota (UND).

State Appropriation

The North Dakota State Water Commission (NDSWC) continued its support of 20.4% match (\$18,850) to the 2017-2018 Graduate Research Fellowship program of NDWRRI under federal 104(B) funding. This is the fourteenth year the NDSWC provided support to the Fellowship program.

University Support

North Dakota State University and the University of North Dakota administrations consider the NDWRRI activities important and are supportive of its efforts.

Institute Location

The Institute continues to operate from the Civil and Industrial Engineering building at North Dakota State University in Fargo, North Dakota. The director can be reached at: ND Water Resources Research Institute, North Dakota State University, Department of Civil and Environmental Engineering (Dept. 2470), P.O. Box 6050, Fargo, ND 58108-6050, Phone: (701) 231-9758, Fax: (701) 231-6185, E-mail: xuefeng.chu@ndsu.edu.

State Advisory Committee

The State Advisory Committee provides guidance on water resources research priorities in the State and region, and participates in the review and evaluation of research proposals and projects. The current committee members are:

- 1. Steven Robinson, deputy director for data of the newly-formed U.S. Geological Survey Dakota Water Science Center, Bismarck, North Dakota
- 2. William Schuh, Water Appropriations, North Dakota State Water Commission (NDSWC), Bismarck, North Dakota
- 3. Peter Wax, Water Quality Special Projects, North Dakota Department of Health, Bismarck, North Dakota

The committee members are senior officials in the three major agencies in North Dakota responsible for much of the water resources research done outside of NDSU and UND in North Dakota.

RESEARCH PROGRAM

Annual Base Grant (104-B)

For the last 17 years, NDWRRI has offered competitive fellowships to NDSU and UND graduate students for research on water resources topics under a Graduate Research Fellowship (GRF) program effectively using the modest amount of the 104(B) annual base grant. The program meets the requirements of Section 104 of the Water Resources Research Act of 1984.

The fellowship program encourages entry of young university faculty and new research scientists and engineers into the water resources field; provides training and education to future water resource scientists and engineers; promotes exploration of new ideas that address water problems or expand understanding of water quantity, quality and related phenomena; and engages university faculty in collaborative research programs seeking supports from entities concerned with water problems.

This year, the NDWRRI continued the GRF program and applied bulk of the federal allotment to it. The GRF program is administrated and monitored by the Director. Applications are invited from the graduate students and their advisors of the two research universities of the State, NDSU and UND. A rigorous review by the State Advisory Committee and other water professionals in the State determines the awards. Active participation of the academic advisors of the students in meeting matching requirement and seeking co-funding from local, state and other sources is another positive aspect of the program. Periodical review of the progress of the students in meeting the fellowship expectations is ensured by seeking reports from the students and by encouraging them to make presentations in local, regional, and national technical seminars and conferences.

Guidelines for the 2017-2018 Graduate Research Fellowship were posted at the Institute website in the first week of October 2016, and the request for applications was announced in the faculty news publications of the two university campuses by the second week of October, 2016. The following is the request for application that was published in the UND and NDSU campus newsletters, and distributed by e-mail lists.

2017 ND WRRI graduate research fellowship applications invited

The North Dakota Water Resources Research Institute (NDWRRI) invites applications for its 2017 Graduate Research Fellowship program.

North Dakota State University and University of North Dakota graduate students who are conducting or planning research in water resources may apply for fellowships of varying duration, 3 months to one year. In the past, the typical ranges of fellowship awards have been \$800-\$1,000/month for master's degree students and \$1,000-\$1,400/month for doctoral students. The fellowship funds must be applied between March 1, 2017, and February 28, 2018. A

technical completion report co-authored by the fellow and the adviser is expected of each fellowship research project.

Research proposed for fellowship support should relate to water resources issues in the state or region. Regional, state or local collaborations or co-funding will strengthen an application. Fellowships have a matching requirement of two non-federal dollars to one federal dollar. At the time of applying, applicants should have a plan of study filed and/or should have a thesis research topic selected. Applications need to be prepared in consultation with advisers. Advisers of the applicants should co-sign the applications. Applications from students and advisers who have not met the reporting requirements of their previous fellowship projects will not be considered for funding.

The general criteria used for proposal evaluation include scientific merit, originality, research related to state or region, and extent of regional, state or local collaboration and/or co-funding. The proposals will be reviewed by a panel of state water resources professionals. Announcement of awards will be made by early January subject to the appropriation of funds for the FY 2017 program by the federal government.

Consult the NDWRRI website, <u>www.ndsu.edu/wrri</u>, for background information on the program, and guidelines for preparation of applications. Applications are due by 5:00 PM, Wednesday, November 25, 2016. Submit original and four hard copies of applications to Linda Charlton, Family Life Center (FLC 320), NDSU Department 2030, P.O. Box 6050, Fargo, ND 58108-6050 and an electronic copy in Word format to <u>eakalak.khan@ndsu.edu</u>.

For additional information, contact Eakalak Khan at <u>eakalak.khan@ndsu.edu</u> or Linda Charlton at <u>linda.charlton@ndsu.edu</u>.

The above announcement appeared in NDSU News. An announcement similar in content was also published in the University of North Dakota campus publication University Letter.

NDWRRI Graduate Research Fellowships

In total, nineteen applications were received. Sixteen were from NDSU and three from UND. Out of the nineteen applications, four (3 Ph.D. and 1 M.S.) were for renewal and fifteen (8 Ph.D. and 7 M.S.) are new applications.

An amount of \$69,311 was available for Fellowship projects from the annual base grant. An additional support of \$18,850 came from NDSWC. Fellowships ranging from \$1,800 to \$10,080 were awarded to fifteen graduate students, 10 Ph.D. and 5 M.S., conducting research on water resources topics at NDSU and UND. Selection of student Fellows and the award amounts were based on competitive proposals prepared by the students with the guidance of their advisers. A panel of state water resource professionals and the director reviewed the proposals and selected Fellows. The award amounts were based on the quality of proposals and the priority of the proposed projects for the state and region.

The 2017-18 NDWRRI Fellows, academic programs, university, faculty advisers, and Fellowship research projects are listed as follows:

WRRI funded Projects

- 1. Afshin Shabani, Earth System Science and Policy, UND, Dr. Xiaodong Zhang (Earth Systems Science and Policy Department), "Assessing Devils Lake Water Quality with Remote Sensing and Coupled SWAT and CE-QUAL-W2 Model"
- 2. Ali Rashid Niaghi, Agricultural and Biosystems Engineering, NDSU, Dr. Xinhua Jia (Agricultural and Biosystems Engineering Department), "Crop Evapotranspiration Measurement by Eddy Covariance, Bowen Ratio, and Soil Water Balance for a Control Drained and Subirrigated Field" *Note that this project was co-funded by WRRI and NDSWC*.
- 3. Bosen Jin, Civil Engineering, UND, Dr. Frank Xiao (Civil Engineering Department), "Perfluoroalkyl Substances in Surface Runoff of the Red River Basin"
- 4. Cody Ritt, Environmental Engineering, NDSU, Dr. Achintya Bezbaruah (Civil and Environmental Engineering Department), "Molecularly Imprinted Polymers for Phosphate Removal from Wastewater"
- 5. Hoang Pham, Environmental and Conservation Sciences, NDSU, Dr. Achintya Bezbaruah (Civil and Environmental Engineering Department), "Application of Green Iron Nanoparticles Synthesized Using Barley Polyphenols to Combat Lake Eutrophication Problem"
- 6. Marina Martin, Environmental and Conservation Sciences, NDSU, Dr. Eakalak Khan (Civil and Environmental Engineering Department) and Dr. John McEvoy (Microbiological Sciences Department), "Endoxifen in Wastewater and Surface Water in North Dakota: Detection and Biodegradation"
- 7. Mohsen Tahmasebi Nasab, Civil Engineering, NDSU, Dr. Xuefeng Chu (Civil and Environmental Engineering Department), "Development of a Macro-Scale Physical-Based Gridded Hydrologic Model (GHM) and Applications in North Dakota"
- 8. Swati Sharma, Agricultural and Biosystems Engineering, NDSU, Dr. Halis Simsek (Agricultural and Biosystems Engineering Department), "Nutrient Removal from Domestic and Livestock Wastewaters Using Integrating Electro-coagulation and Biological Processes"
- 9. Nicholas Lindstrom, Civil Engineering, UND, Dr. Frank Xiao (Civil Engineering Department), "Enhanced Natural Wetland Growth Due to Nearby Constructed Wetlands in the Northern Prairie Pothole Region"

- 10. Umesh Acharya, Soil Sciences, NDSU, Dr. Amitava Chatterjee (Natural Resource Science School), "Study On-farm Evaluation of Interactive Effect of Subsurface Tile Drainage, Tillage and Crop Rotation on Nitrate Leaching"
- 11. Umma Salma Rashid, Civil Engineering, NDSU, Dr. Achintya Bezbaruah (Civil and Environmental Engineering Department), "Removal of Trichloroethylene and Fluoride from Water by Nanoscale Zero-valent Iron Supported on Novel Activated Carbon"
- 12. Yavuz Fidantemiz, Agricultural and Biosystems Engineering, NDSU, Dr. Halis Simsek (Agricultural and Biosystems Engineering Department), "Effect of Water Level on Soybean Growth with High Salinity Water"

NDSWC funded Projects

- 13. Kendall Grimm, Civil Engineering, NDSU, Dr. Xuefeng Chu (Civil and Environmental Engineering Department), "Modeling of Runoff Contributing Areas and Hydrologic Connectivity and Applications in North Dakota"
- 14. Zachary Phillips, Environmental and Conservation Sciences, NDSU, Dr. Stephanie Day (Geosciences Department), "Holocene Palaeoflood and Glacial Isostatic Adjustment (GIA) Influence on Fluvial Geomorphology of the Red River Basin"
- 15. Diane Van Hoy, Geology and Geological Engineering, UND, Dr. Taufique Mahmood (Geology and Geological Engineering Department), "Hydrological Responses to Climate Change in a Terminal Lake Basin"

PROJECTS

The details on the fifteen projects funded by WRRI (104-B) and NDSWC are listed below. The information for each project includes: publications, presentations, research description, significance of research, and significant findings.

Assessing Devils Lake Water Quality with Remote Sensing and Coupled SWAT and CE-QUAL-W2 Model

Fellow: Afshin Shabani Adviser: Xiaodong Zhang Project Number: 2017ND324B Project Period: 03/01/2017 – 02/28/2018

Publications

- 1. Shabani, A., X. Zhang, M. Ell. 2017. Modeling Water Quantity and Sulfate Concentration in the Devils Lake Watershed Using Coupled SWAT and CE-QUAL-W2. Journal of American Water Resources Assessment. 53 (4), 748-760.
- 2. Shabani, A. X. Zhang, X. Chu, T. P. Dodd. 2018. Examining the impact of Devils Lake outlets on flood risk of the Sheyenne River. Under review.

Presentations

- 1. Shabani, A, Zhang, X., Mike Ell. And Timothy P. Dodd. 2018. Examining the impact of Devils Lake outlets on flood risk of the Sheyenne River. Bismarck, North Dakota, March 6-8.
- 2. Shabani, A., Zhang, X. 2017. Examining the impact of Devils Lake outlet on the flood risk of the Sheyenne River. American Geophysical Union conference, New Orleans, Louisiana, 11-15 December.
- 3. Shabani, A., Zhang, X. 2017. Estimated water surface temperature using Landsat 8 TIR bands using split window algorithm. Great Plains / Rocky Mountains American Association of Geographers conference. Grand Forks, North Dakota, 13-14 October.
- 4. Shabani, A., Zhang, X. 2017. Estimated water surface temperature using Landsat 8 TIR bands using split window algorithm. NDGIS user Conference, Bismarck, North Dakota, 19-20 September.

Research Description

Devils Lake is an endorheic lake in the Red River of the North basin in northeastern North Dakota. Since its formation about 11,000 years ago, Devil Lake has experienced significant fluctuation in water levels several times from completely dry to overflowing. Historical accumulation of salts through evaporation has elevated the concentration of salts particularly that of the sulfates, which are much greater than the surrounding water bodies. Devils Lake began its most recent rise in 1993 and in June 2011 reached 443.3 m, the highest record since the 1830s. The rising of the lake water level has caused extensive flooding in the surrounding area and greatly increased the chance of natural spillage to the Sheyenne River. To mitigate the Devils Lake flooding and to avoid its natural spillage, two emergency outlets were constructed at the west and east sides of the lake to drain the lake water to the Sheyenne River in a controlled fashion.

In a recent study, we found that operating the two outlets has lowered the Devils Lake water levels by ~1.0 m for the time period from 2005 to 2016. We also found that the sulfate concentration generally increases from the west end of the lake, where relatively fresh water from the basin flows in, to the east end of the lake, where the natural spillage would occur. Because of this west-east increasing gradient of the sulfate concentration in Devils Lake, we estimated that pumping water from the west outlet alone would raise the average sulfate concentration of the Sheyenne River to 404 mg 1^{-1} , from the east outlet alone to 536 mg 1^{-1} , and from both to 585 mg 1^{-1} . However, it is still unknown how operating the outlets would potentially affect the flood risk of the Sheyenne River. In this study, we coupled SWAT and HEC-RAS models to investigate the impact of operating the outlets on the Sheyenne River discharge and its floodplain. The outcome of this study will aid water management and decision making to mitigate Devils Lake flooding and its impact on downstream rivers by accounting for both quantity and quality of waters.

Significance of Research

The rising water level in Devils Lake has raised concerns regarding both water quantity and quality; however, most of the previous studies on the Devils Lake flooding have been focused on its water balance. The goal of this study is to better understand how the water quality of the lake, particularly its sulfate concentration, changes with a rising water level by simulating both water quantity and quality. We further analyzed the impact of artificial pumping on the water quality and flood risk of the Sheyenne River. The SWAT, CE-QUAL-W2, and HEC-RAS models were selected for this simulation because of their proven capacity in simulating hydrology, water quality, and floodplain. To the best of our knowledge, the impact of Devils Lake outlets on the flood risk of the Sheyenne River has not been studied. The outcome of this study will aid water management and decision making to mitigate Devils Lake flooding and its impact on downstream rivers by accounting for both quantity and quality of waters.

Significant Findings

The SWAT-CEQUAL-W2 coupled model results showed that the operation of the two outlets since August 2005 has lowered the lake water level by ~1 m, while raised sulfate concentration in the Sheyenne River from ~100 to >500 mg l⁻¹. Our coupled SWAT- HEC-RAS model also showed that the maximum impact of the current operating schedule is within the historical confines of the two-year flood in either the increased streamflow, increased river depth or the expanded floodplain, with an average overbank flood depth of 0.2 m. However, the maximum impacts have occurred only 4% of times when the outlets operated with their total capacity during the 5-years of combined outlet operation (2012-2016) and 0.4% of the time of their entire operation period (2005-2016). Currently, the outlets are operating under a revised sulfate standard of 750 mg l⁻¹. Imposing the state-wide sulfate standard of 450 mg l⁻¹ would dramatically reduce the efficiency of the outlets and increase Devils Lake water levels at least by 0.54 m.

Crop Evapotranspiration Measurement by Eddy Covariance, Bowen Ratio, and Soil Water Balance for a Control Drained and Subirrigated Field

Fellow: Ali Rashid Niaghi Adviser: Xinhua Jia Project Number: 2017ND325B Project Period: 03/01/2017 – 02/28/2018

Publications

- 1. Niaghi, A. R., X. Jia., and T. F. Scherer. 2017. Impact of accurate evapotranspiration estimates on DRAINMOD simulation in North Dakota. Proceedings of the ASABE Annual International Meeting, July 16-19, 2017. Spokane, WA. Paper No. 1701500.
- Niaghi, A. R., and X. Jia. 2017. Determination of grass evapotranspiration rates and crop coefficients using eddy covariance method in eastern North Dakota. Proceedings of the ASCE World Environmental & Water Resources Congress (EWRI), May 21-25, 2017, Sacramento, CA.

Presentations

- 1. Niaghi, A. R., Bazrkar, M.H. (2018). Assessing the effect of tile drainage on streamflow and nitrate load using SWAT model. Bismarck Water Quality Conference, March 2018, Bismarck, ND.
- Niaghi, A. R., Jia, X., Scherer, T. F., Steele, D. D. (2018). Assessment of Cool Season Grass Water Use. NDSU poster session, February 2018, North Dakota State University, ND.
- 3. Niaghi, A. R., Jia, X., and Scherer, T. F. 2017. Impact of accurate evapotranspiration estimates on DRAINMOD simulation in North Dakota. ASABE Annual International Meeting, July 16-19, 2017. Spokane, WA. doi:10.13031/aim.201701500.
- Niaghi, A. R., and Jia, X. 2017. Determination of grass evapotranspiration rates and crop coefficients using eddy covariance method in eastern North Dakota. ASCE World Environmental & Water Resources Congress (EWRI) Annual Meeting, May 21-25, 2017, Sacramento, CA. <u>doi.org/10.1061/9780784480601.040</u>.

Research Description

Estimation of crop evapotranspiration (ET_c) , which is a combination of evaporation and transpiration, is very important in crop water management and irrigation scheduling. ET is an essential variable for agricultural productivity and has a direct effect on crop water use efficiency and optimization of water use. Many factors, such as soil moisture, soil temperature, water table depth, weather condition, available energy and soil and crop characteristics affect the ET_c rate. The ET_c measurement includes a variety of direct and indirect methods. Direct methods include weighing lysimeter, Eddy Covariance (EC), Bowen Ratio Energy Balance (BREB), soil water balance (SWB), and mass balance. Indirect methods are used to estimate ET through the reference ET (ET_{ref}), which is based on

temperature, radiation, weather parameters and a crop coefficient. Even though ET_c can be measured using both water mass balance or energy balance methods, the energy balance method is superior to other approaches, especially for fields with shallow water tables.

The research project will focus on ET_c measurement and crop coefficients (K_c) development using the energy balance approaches, including the EC and BREB methods, and SWB approach. In particular, the research will be conducted on a field with controlled drainage and subirrigated (CDS). The specific objectives of the study are to:

- 1) Determine the crop evapotranspiration (ET_c) of the CDS field using the EC, BREB and SWB methods
- 2) Compare the EC, BREB and SWB methods to obtain the accurate ET_c estimation
- Develop crop coefficient (K_c) for soybean using the ET_c estimated by the EC, BREB, SWB and the ET_{ref} estimated by the standardized ASCE-EWRI method

The current project has one complete EC system and one complete BREB, which were installed after soybean planting. Both systems have soil moisture sensors, soil heat plates, temperature sensors to quantify soil heat flux and net radiometer to measure net radiation. Sensible heat flux and latent heat flux were measured by sonic anemometer and KH20 hygrometer for the EC system. For BREB system, sensible heat was calculated by measuring the air temperature at two heights with chromel-constantant thermocouples and water vapor was measured by using a single cooled mirror dew point hygrometer. The water table data were collected at the EC and BREB location using paired pressure transducers, which were located between and on the tile drains. The pair of Hydra Probe II soil moisture sensors were utilized to record the soil moisture changes in various depths (5, 15, 30, 45, 60, 75 and 90 cm) at the EC site. The weather data, such as temperature, rainfall amount, relative humidity, solar radiation, wind speed and wind direction were obtained from a nearby NDAWN weather station at Wahpeton for ET_{ref} calculation.

Significance of Research

In ND, the SWB is a widely used method to directly estimate ET_c , and neutron probes were used to measure the soil moisture changes. Most of the previous research on ET_c was conducted at the NDSU Oakes and Carrington Research stations and used to develop crop coefficient curves for irrigation. The Jensen-Haise equation was used to calculate the ET_{ref} for most of these studies. The combination of the EC and BREB methods provide an accurate on-site ET_c measurements comparing to the EC method itself or traditional ground based method in areas with shallow ground water tables. Proper ET_c estimate in a subsurface drained and subirrigated field can be used to manage crop water use and prevent damage from either crop water stress or over irrigation.

Significant Findings

The energy balance closure of the EC and BREB systems varied in early, mid and late seasons, primarily related to the latent heat flux. In the total available energy (net radiation minus soil heat flux, $R_n - G$), higher latent heat flux (LE) partitions were measured by the EC method than that by the BREB method. However, the regression coefficient between the sum of day time sensible heat flux (H) + LE for the EC and BREB methods showed a good

agreement with a R^2 of 0.86. The results indicated that the average ET_c obtained from the EC method is 25.9% higher than that from the BREB method after closing the energy budget using the residue method, but it is only 6.9% if the Bowen ratio (H/LE) by the BREB is used to close the energy budget on that day. In conclusion, the error for the ET_c measurement by the EC method can be significantly reduced when an independent measured Bowen ratio be applied. Furthermore, the Bowen ratio method provides easy setup and maintenance for data collection which will be suitable for long term field study.

Poly- and Perfluoroalkyl Substances (PFASs) in Surface Runoff and Soil and Their Fate and Effects

Fellow: Bosen Jin Adviser: Feng Xiao Project Number: 2017ND326B Project Period: 03/01/2017 – 02/28/2018

Publications

1. Xiao, F., B. Jin. 2018. Surface and subsurface transport of perfluoroalkyl substances in North Dakota, USA. Water Research, in preparation.

Presentations

- 1. Ryan, H., Bosen, J., and Xiao, F. "Removal and transport of poly-fluoroalkyl substances". Poster presentation at the symposium for the AEESP Distinguished Lecture by Dr. Menachem Elimelech, 4/2017, Minneapolis, MN.
- Xiao, F., Bosen, J. "Surface and subsurface transport of perfluoroalkyl substances in urban runoff of a typical North Dakota city". Society of Environmental Toxicology and Chemistry (SETAC) North America Annual Meeting, November 12-16, Minneapolis, MN.
- 3. Xiao, F., Bosen, J., Bedane, A. "Bioconversion of poly-fluoroalkyl substances in earthworms". Society of Environmental Toxicology and Chemistry (SETAC) North America Annual Meeting, November 12-16, Minneapolis, MN.

Research Description

Perfluoroalkyl substances (PFASs) are industrially produced compounds that contain a perfluorinated alkyl moiety of varying chain length and polar functional groups attached to that moiety. PFASs have been massively produced and used for decades in various products including

stain-resistant carpeting, water-proof clothing, non-stick cookware, fastfood containers, aqueous firefighting foams, painting materials, and certain insecticides^{1,2}. They have recently become the target of investigation by water quality/resources researchers and managers due to their environmental persistence, toxicity, and tendency to bioaccumulate



in fish and terrestrial organisms. Because of the strong carbon–fluorine bonds, relatively high solubility, moderate adsorption potentials, and negligible volatility, PFASs are not readily removed by conventional drinking/waste water treatment processes and degraded by physical and chemical mechanisms once in the environment. PFASs such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been measured in fish, birds, mammals, drinking water, municipal wastewater, and surface runoff at numerous sites in the United States^{1,2}. Both PFOS and PFOA have also been observed in >95% of the blood samples collected during U.S. national surveys at health-relevant³⁻⁹ concentrations¹⁰. The associations

of blood PFOS and/or PFOA levels with a series of health problems have been documented, including the decreased sperm count in young men³, hyperuricemia⁵, disruption of thyroid function^{4,6,7}, and children attention deficit/hyperactivity disorder⁸ and lowered immune response to vaccinations⁹. PFOS and PFOA have been measured in surface and drinking water at numerous sites in the United States and other parts of the world¹³⁻²⁰, and drinking water is an important source of exposure for the general population^{1,13,15,18,21-24}. In May 2016, the U.S. EPA released updated drinking-water guidelines for PFOS and PFOA; the lifetime health advisory suggests a maximum combined level of 70 ng/L²⁵.

Although the studies on PFASs are quickly evolved, nothing is currently known on PFASs concentrations in the North Dakota aquatic environment. Because PFOS and PFOA are ubiquitously present in the environment, we believe that they might have already contaminated North Dakota waters. The thesis project of the applicant (Bosen Jin) investigates, for the first time, the distribution and concentrations of PFASs in the North Dakota aquatic environment (drinking water, surface water, runoff, municipal wastewater). Under the support of this fellowship, we have studied urban runoff collected from Grand Forks and Fargo, and estimate the contributions of runoff to the PFAS contamination of the Red River of the North that is the primary drinking-water sources of Grand Forks (population: 52,838) and Fargo (population: 105,549).

Significance of Research

The control of organic contaminants like PFASs is a high priority in water resources management of the Red River of the North that is the drinking-water source for Grand Forks, Fargo, and many other cities in North Dakota and Minnesota. The results of this study 1) contribute to previously very limited knowledge of the level and fate of a major group of emerging contaminants in the Red River Basin; and 2) provide insights for strengthening stormwater BMPs to remove PFASs from runoff and enhancing drinking-water treatment processes against PFASs. Furthermore, this study may enable water resources managers to assess this as part of the TMDL (total maximum daily load) work required by characterizing a water as impaired. Beyond the simple loading calculation required for TMDL this proposal expects to provide managers with specific loadings information with regard to sources within the watershed, storm flow dependence of loadings and water-solid distribution effects on loadings. These additional findings will allow managers in areas outside the Grand Forks and Fargo metropolitan areas to determine the potential for PFASs contamination to their surface waters. Because the stormwater being studied do not have any connections to the manufacture or disposal of PFAS materials, the information determined by this proposal will be relevant to most urban watersheds that receive stormwater.

Significant Findings

Surface runoff samples were collected from different locations of Grand Forks, Fargo, and suburban areas of the two cities. The samples were extracted by a solid-phase extraction (SPE) method with XAD-7 resin, eluted with Optima methanol, concentrated to ~0.5 mL, and filtered using a 0.2 μ m nylon filter to HPLC vials. Concentrations of PFASs in the samples were determined by a Waters Aquity UPLC system coupled with a Waters time-of-

flight mass spectrometer (UPLC–ToF-MS). Monitoring results and statistical analysis show that PFASs in stormwater runoff from residential areas mainly came from rainfall. On the other hand, non-atmospheric sources at both industrial and commercial areas contributed PFASs in surface runoff. The mass flux of PFASs from stormwater runoff in the Grand Forks and Fargo metropolitan area is estimated to be ~2.6 kg/year. Interestingly, we detected high-level PFASs in particles in surface runoff, which cannot simply be explained by the solid–water distribution. We believe some of the PFASs in particles should be originated from PFAS-based industrial/commercial products, entering the waste stream as PFOS containing particles. Supported by the advisor's another grant, the fellow is currently studying the ecological effects of PFASs in surface runoff by exposing earthworms to PFOS, PFOA, and their potential precursor compounds.

Molecularly Imprinted Polymers for Phosphate Removal from Eutrophic Surface Water

Fellow: Cody Ritt Adviser: Achintya Bezbaruah Project Number: 2017ND327B Project Period: 03/01/2017 – 02/28/2018

Presentation

Ritt, C. Molecularly Imprinted Polymers (MIPs) as Sustainable Phosphate Sorbents, Presented to North Dakota State University's Department of Civil & Environmental Engineering, April, 2017 (oral presentation)

Research Description

An unsustainable cycle of phosphorus (P) use has developed in modern society. Excessive amounts of phosphate rock are mined to meet growing agricultural demands with a rising global population. The vast majority of P finds itself permanently residing in surface waters at the end of this cycle, consequently devastating aquatic ecosystems through eutrophication.

The current research aims to develop a sorbent that can engender a more sustainable P reuse cycle by utilizing eutrophic surface waters as viable P resources. The goal was to develop a sorbent which can selectively recover P at low concentrations to mitigate eutrophication while also assessing its potential for reuse in soil amendments.

This research has identified molecularly imprinted polymers (MIPs) as possible sorbents to accomplish the aforementioned goal. Three MIPs were screened for viability by assessing their sorption capacities. After the initial screening, one MIP was selected for further study. The resulting MIP particles were characterized using scanning electron microscopy, electron dispersive spectroscopy, Fourier transform infrared spectroscopy, swelling analysis, and thermogravimetric analysis. The possible mechanisms of P removal were identified, thus providing foresight into the potential for future applications of MIPs as sorbents for P remediation.

Significance of Research

The P cycle in today's society is unsustainable. To develop a more sustainable cycle, P needs to be reclaimed from non-conventional sources and reused for agricultural and industrial applications. There are other factors associated with the P cycle which need to be improved to develop a sustainable system, but recovery and reuse from surface waters has been identified as one of the methods to reduce human dependence on phosphate rock. In order to reach this goal, a technology must be developed that can successfully recover P from natural water bodies that will make P bioavailable for plants as fertilizer. Selective removal of P is necessary in order to make these water bodies usable sources of P recovery.

Without selective removal, P recovered from these sources runs the risk of having associations with constituents which are potentially toxic to crops in high concentrations. Therefore, a technology with selective removal of P is ideal for producing a usable recovery product. Many of the technologies available (i.e. bioremediation, chemical precipitation, etc.) cannot remove P below levels which are commonly found in eutrophic lakes (100 μ g/L). The lack of this capability not only makes it extremely difficult to restore the health of important surface waters, but it also eliminates another major source of recoverable P for reuse in fertilizer applications. In addition to these two innately important criteria for successful P recovery and reuse, the technology must have sorption capacities that are competitive enough to be considered economically justifiable for use. A sorption capacity of approximately 10 – 26 mg P/g can be considered as competitive with many of the technologies currently available.

MIPs showed potential to provide selective removal of P at environmentally significant concentrations.

Significant Findings

- MIP synthesized with the use of the [2-(Methacryloyloxy)ethyl]trimethylammonium chloride monomer showed to have competitive sorption capacities. Increasing the template:monomer ratio was found to increase the sorption capacity. Polymer MM12 had the greatest sorption capacity found (~28 mg P/g) due to having the highest template:monomer ratio of (12:4).
- MIPs studied did not possess full-selectivity toward phosphate removal as interference from coexisting anions was found. This is likely attributed to the nature of the positively charged polymer surface to attract all anions at the pH of interest.
- MM12 exhibited partial-selectivity toward phosphate. MM12 selectively sorbed phosphate after positively charged sorption sites had been saturated with other anions.
- Chemical binding of phosphate in polymer matrix was observed, confirming that electrostatic attraction is not the only mode of P removal. This chemical binding is likely located within the imprinted cavities.
- Sorption capacity of MM12 severely limited by the concentration of P present. Lower concentrations of P witnessed immediate removal until a pseudo-equilibrium was reached. No further P was removed after reaching pseudo-equilibrium, regardless of increased contact time or stirring. This phenomenon is likely attributed to the development of an electric double layer on the surface of the charged polymer.
- Electrostatic attraction was deemed as the predominant phosphate removal mechanism.

Application of Green Iron Nanoparticles Synthesized Using Barley Polyphenols to Combat

Fellow: Hoang Nu Kim Pham Adviser: Achintya Bezbaruah Project Number: 2017ND328B Project Period: 03/01/2017 – 02/28/2018

Publication

1. Pham, H., A. N. Bezbaruah. Biosynthesis of iron nanoparticles using green tea extract for the removal of phosphate from aqueous solution. Journal of Nanoparticle Research, in preparation.

Presentations

1. Poster Presentation: "Biosynthesis of Iron Nanoparticles Using Green Tea Extract for the Removal of Phosphorus from Aqueous Solution" – 2018 ND Water Quality Monitoring Conference.

Research Description

Nutrient problem that is caused by the excess of nutrients such as phosphorous and nitrogen in the aquatic environment is a widespread national problem. In North Dakota, two rivers, including the Red River of the North flowing to Lake Winnipeg and the Missouri River joining to the Mississippi River, are also affected by the nutrient pollution. A report of the North Dakota Department of Health indicated that some of 51 river and stream segments, which were listed for biological impairments, and 42 lakes and reservoirs have been assessed as threatened because of nutrients in North Dakota currently (North Dakota Department of Health, 2016).

Besides the natural factors, many other different human activities also cause an increase in loading rates of the two primary nitrogen and phosphorus compounds affecting to North Dakota's lakes, reservoirs, rivers, and streams (North Dakota Department of Health, 2016).

Phosphorus is one of the key elements necessary for the growth of plants and animals. In the environment, phosphorus exists under the form of phosphates PO₄. Phosphates enter waterways from human and animal waste, phosphorus rich bedrock, laundry, cleaning, industrial effluents, and fertilizer runoff. These phosphates become harmful when they over fertilize aquatic plants and cause stepped up eutrophication.

Because the excess of phosphorus in water affects on aquatic life, various techniques have been employed to remove phosphate from water. However, these methods are not much effective in the case of low concentration (several mg/L) of phosphates (Markebs et al., 2016). It is necessary to find a highly efficient and low-cost process to remove phosphorus.

Over the last two decades, the application of nanotechnology to remediate contaminants in water has attracted many studies and continues to develop. Studies have shown that iron nanoparticles (Fe-NPs) are very effective for the degradation of halogenated solvents. Besides, iron nanoparticles are also shown to be effective against some pesticides, heavy metals, and dyes.

However, there is growing concern in the biological and environmental safety of NPs synthesized from physical and chemical synthesis approaches such as high cost of manufacturing, the usage of toxic chemicals, formation of hazardous byproducts, and contamination from precursor chemicals. Therefore, the application an advanced method, which is more stable, degradable, non-toxic, less time consuming and environmental friendly is necessary.

Until now, Fe-NPs have mostly synthesized using different plant extracts. Polyphenols ingredients in plants act as reducing/stabilizing agents that are degradable and low cost. The most common used and intensively studied for the synthesis of Fe-NPs is tea extract. Fe-NPs were synthesized by Hoag et al. by using green tea (*Camellia sinensis*) extract to react with 0.1 M FeCl₃ solution. Other papers use different tea extracts and/or different precursor to synthesize Fe-NPs. The polyphenols of these extracts served as the reducing/capping agents (Herlekar et al., 2014)

Barley (*Hordeum vulgare L.*) is the oldest domesticated grain that has been cultivated for at least 10,000 years. Two grades of barley are produced in North Dakota. The lower grade is used for high quality livestock feed for dairy and beef cattle and pigs. The higher grade malting barley is for human consumption, mainly for brewing beer. The barley is processed into malt, the same ingredient used in malted milk shakes. A 48-pound bushel of barley will produce about 525 12-ounce bottles of beer. Pearled or hulled barley is an increasingly popular ingredient in cereals, soups, salads and desserts. North Dakota leads the nation in barley production corn (ND Department of Agriculture, 2016).

Significance of Research and Findings

Research Task 1: Barley extract preparation:

Barley seeds (tradition variety) were provided by the Department of Plant Pathology (NDSU). Fifty grams of finely ground barley samples were extracted twice with 500 mL of water and lightly stirred (24 h, room temperature $22\pm2^{\circ}$ C). The supernatants were collected after being centrifuged (3200 rpm, 15 min, room temperature). pH of the extraction ranges in 5.5 to 6.0. The extract is stored at -4^oC for further use (Figure 1).

Research Task 2: Synthesis of iron nanoparticles:

The synthesis was carried out by adding the corresponding extracts to 0.1 M FeCl_3 (pH = 1.60) with the ratio of 1:1 at room temperature, adjusting pH until 6 by the solution NaOH 2M, and constantly stirring for 12 hours. The as-prepared Fe nanoparticles, then, were

centrifuged and washed thoroughly three times with deionized (DI) water, last time with ethanol 70%. They were dried under vacuum for 12 h. Barley extract-based Fe-NPs were ground to powdery form and kept under nitrogen gas for further use (Figure 2).



Figure 1. Barley extraction diagram

Figure 2. Synthesis of Fe NPs from barley

Research Task 3: Characterizations:

The X-ray diffraction (XRD) was used to analyze the crystallinity of the barley extract-based Fe nanoparticles. The samples were placed in stainless steel sample holders and XRD patterns were recorded using Cu Ka radiation (k = 1.5418 Ű) on a Philips X'Pert diffractometer operating at 40 kV and 40 mA between 5 and 90 (2h) at a step size of 0.0167.

Figure 3 shows the XRD pattern of synthesized iron nanoparticles. On the XRD picture, there are five peaks and all together these peaks are characteristic peaks for compound called Strontium Iron Oxide. Meanwhile, there is no peak characterizing for regular crystal as seen in other plant-based Fe NPs.



Figure 3. (a) Barley polyphenol reduced Fe-NPs (b) XRD pattern of Fe NPs. The peaks indicate that the NPs have crystalline structure and contain Fe (complexed with $Sr_2Fe_2O_5$).

Research Task 4: Batch experiments:

Phosphate removal batch study: the sorption capacities of Fe-NPs were evaluated. Fe-NPs (20 mg in 50 mL or 400 mg/L) were added into phosphate solution (50 ml of 5 mg $PO_4^{3^-}$ -P/L) in multiple 50 mL polypropylene plastic vials fitted with plastic caps (reactors). The reactors were rotated end-over-end at 28 rpm in a custom-made shaker to reduce mass transfer resistance. Three of the reactors were withdrawn at specific time interval (0, 10, 20, 30, 60 min) and the content in reactor was centrifuged at 4,000 rpm (Almeelbi & Bezbaruah, 2012).

Similar experiments were carried out with NZVI (Figure 6 and 7) and green tea extract reduced Fe-NPs (Figures 8 and 9). The bulk solution was analyzed for phosphate concentration using a UV-vis Spectrophotometer. Ascorbic acid method was used for phosphate analysis. This method depends on the formation phosphomolybdic acid during the reaction between orthophosphate and molybdate. Ascorbic acid reduces phosphomolybdic to form a blue complex. The color was measured in the UV-Vis Spectrophotometer (HACH, DR 5000) at wavelength of 880 nm. A five-point calibration was done routinely.





Photodegardation of (E)-and (Z)-endoxifen in wastewater treatment plants at North Dakota: Kinetics, By-products Identification and Toxicity Assessment

Fellow: Marina Arino Martin Adviser(s): Eakalak Khan and John McEvoy Project Number: 2017ND329B Project Period: 03/01/2017 – 02/28/2018

Presentations:

- 1. Poster Presentation at North Dakota Water and Pollution Control Conference (First Price on Poster Presentation)
- 2. Oral Presentation at the Institute of Technology-GRDS

Research Description

Cancer cases worldwide are expected to increase by 57% during the next 20 years, and during the last decade the number of people with breast cancer has dramatically increased around the world. North Dakota is no exception to the trend. A statistical study published by the North Dakota Statewide Cancer Registry revealed that breast cancer was a major cancer type in North Dakota from 2008 to 2012. Among different breast cancer types, positive endocrine (ER+) breast cancer accounts for 60-70 % of all cases. Patients with ER+ breast cancer commonly receive selective estrogen receptor modulators (SERMs) as an anti-cancer therapy.

In the United States, for the last 40 years, tamoxifen has been prescribed as a long-term treatment SERM to treat ER+ breast cancer and as a preventive treatment for women with a high-risk of breast cancer. Oncological hospitals in North Dakota, such as Sanford Medical Center in Fargo, also administer tamoxifen as chemotherapy treatment in 99.3% of the cases. The effectiveness of tamoxifen relies on an ability of the liver to actively metabolize the drug to endoxifen. However, endoxifen is not completely metabolized in human body and is actively excreted. As a result, endoxifen is released to the water environment via wastewater treatment plants (WWTPs). The presence of endoxifen in the environment could bring negative effects to aquatic lives. This research investigated the use of ultraviolet radiation (253.7 nm) and natural sunlight to photodegrade endoxifen in water and wastewater, and the generation of photodegradation by-products (PBPs) and their toxicity. The concentration of endoxifen in water was reduced by 99.1% after 35 seconds of UV light radiation generating two highly toxic PBPs. Photodegradation of endoxifen in wastewater at UV light doses used for disinfection resulted in reduction of endoxifen by 30 to 71%. Endoxifen concentration in wastewater was reduced by at least 83% after 150 minutes of solar radiation generating eight PBPs. Seven of these PBPs are potentially more toxic than endoxifen itself. Therefore, highly toxic PBPs are potentially generated at WWTPs if endoxifen is present in the wastewater.

Significance of Research

The research results elucidate the abilities of UV light (253.7 nm) and sunlight to degrade (E)- and (Z)-endoxifen in wastewater collected from Moorhead WWTP. Identification of potential (E)- and (Z)-endoxifen by-products and the estimation of their toxicity in the aquatic environment demonstrate the suitability of UV light (253.7 nm) and sunlight as (E)- and (Z)-endoxifen treatment processes. An effective treatment technique for (E)- and (Z)- endoxifen would be useful in reducing their release to the aquatic environment in North Dakota and in turn potential toxicological effects on aquatic lives or even humans. Identification of the potential environmental effect that endoxifen could cause. In addition, elucidating the fate of (E)- and (Z)-endoxifen in wastewater and receiving surface water lead to a better understanding on potential sources of the compounds and their PBPs in the aquatic environment of North Dakota.

Significant Findings

Photodegradation process based on monochromatic UV light irradiation at 253.7 nm is an efficient process for removing (E)- and (Z)-endoxifen from water. The irradiation resulted in \geq 99.1% elimination of (E)- and (Z)-endoxifen at a light dose of 513 mJ/cm². In addition, the irradiation of (E)-and (Z)-endoxifen with UV light at 244 W cm⁻¹ s⁻¹ for 120 minutes resulted in mineralization of endoxifen in water at 73.4%.

Natural sunlight also photodegraded endoxifen in water. An effective elimination of (E)-and (Z)-endoxifen in water was observed after 180 minutes of solar radiation reducing the concentration by 90 and 93%, respectively.

Although UV and natural sunlight photodegradation is a promising process for degrading (E)- and (Z)-endoxifen in water, seven PBPs, potentially more toxic than (E)- and (Z)-endoxifen, were observed along the photodegradation time course. The presence of these PBPs in the water environment could bring negative effects to aquatic lives

Development of a Macro-Scale Physical-Based Gridded Hydrologic Model (GHM) and Applications in North Dakota

Fellow: Mohsen Tahmasebi Nasab Adviser: Xuefeng Chu Project Number: 2017ND330B Project Period: 03/01/2017 – 02/28/2018

Publications

- 1. Tahmasebi Nasab, M., J. Zhang, X. Chu. 2017. A New Depression -Dominated Delineation (D-cubed) Method for Improved Watershed Modeling. Hydrological Processes, 31(19), 3364–3378.
- Tahmasebi Nasab, M., K. Grimm, N. Wang, X. Chu. 2017. Scale Analysis for Depression-Dominated Areas: How Does Threshold Resolution Represent a Surface? Proceedings of the ASCE World Environmental and Water Resources Congress 2017, American Society of Civil Engineers, Reston, VA, 164–174.

Presentations

- 1. Tahmasebi Nasab, M., Grimm, K., Wang, N., and Chu, X. (2017). "Scale Analysis for Depression-Dominated Areas: How Does Threshold Resolution Represent a Surface?" World Environmental and Water Resources Congress 2017, Sacramento, CA.
- Tahmasebi Nasab, M., Chu, X., Singh, V. (2017). "Depressions as Gatekeepers: How Do Depressions Control Hydrologic Modeling?" World Environmental and Water Resources Congress 2017, Sacramento, CA.
- 3. Tahmasebi Nasab, M., Grimm, K., Wang, N., and Chu, X. (2017). "Hydrologic Monitoring and Modeling for Quantifying Prairie Pothole Dynamics" World Environmental and Water Resources Congress 2017, Sacramento, CA.
- 4. Tahmasebi Nasab, M., and Chu, X. (2017). "A New Physical-Based Gridded Model for Macro-Scale Hydrologic Modeling" ND EPSCoR Annual Conference, Fargo, ND.

Research Description

Models with different scales suggest a trade-off between spatial scales and complexity of the considered processes. Different macro-scale models have been developed to simulate hydrologic processes; but more work is required to tackle important challenges such as scaling and parameter estimation, especially in areas with cold climate. This project was aimed to develop a macro-scale physically-based grid-based hydrologic model (GHM), which takes advantage of downscaled meteorological datasets and can simulate the spatially and temporally varied hydrologic processes across large scales. Particularly, this one-year project focused on: (1) processing the required data for the modeling, (2) incorporating unique algorithms for cold-climate conditions into the GHM, and (3) applying the GHM to macro-scale watersheds in North Dakota. Achieving the project objectives required four tasks to be completed: (1) to complete the computer code; (2) to collect and process the modeling

datasets; and (3) to test the GHM by applying it to different macro-scale watersheds. Required input data such as land use and land cover, soil type distribution, meteorological, and topographic datasets were obtained from different sources. In addition, input data were processed to a compatible format for the GHM. Eventually, different hydrologic processes were simulated by applying the developed GHM to the Red River basin and the state of North Dakota. The output results from the GHM can be linked to other models (e.g., ecological and climatic models) to provide the required information for decision makers, as well as researchers.

Significance of Research

One of the important goals of hydrologic models is to project future changes and trends in water resources and to help decision makers to address hydrologic issues such as seasonal flood and contaminant transport problems. Since different earth systems and hydrologic processes are interdependent, hydrologic models are commonly used to simulate these processes and their interactions. However, inadequate understanding of the macro-scale hydrologic processes in a region may result in unfavorable modeling results. Recurring floods in the Red River basin are an example of the hydrologic issues that necessitate improved macro-scale hydrologic models. According to the National Weather Service Flood Stage, out of past 108 years, the Red River basin has been overtopped 47 times and it has occurred every year from 1993 to 2011. A combination of macro-scale topographical, hydrological, and climatological factors can be responsible for flood events in the Red River basin. Among these factors flat topography, frozen soil, high soil moisture before freezing, lower-than-normal temperatures, simultaneous occurrence of spring thaw with high discharge, and thick snowpack cover across the basin are more tangible than others. Simulating these processes within a proper scale is highly important. Micro- and meso-scale models may be appropriate choices for investigating hydrologic variations at local or slightly larger scales, but they are not efficient tools for macro-scale analyses. Macro-scale models, in contrast, take major hydrologic changes into account and are able to be linked to other models (e.g., meteorological, ecological, land-use change, climate change, and economic models).

Significant Findings

In this one-year project, a macro-scale Grid-based Hydrologic Model (GHM) was developed and utilized to provide grid-based water balance results for the macro-scale Red River basin and the state of North Dakota. Applying the GHM to these surfaces indicated the capability of the GHM to provide spatially and temporally distributed results for a variety of hydrologic processes (e.g., overland flow generation, infiltration, depression storage, snowpack, snowmelt, soil moisture condition, and subsurface flow). Specifically, results highlighted the significance of flat and depression-dominated topography of North Dakota on the generation of surface runoff. In addition, the GHM simulation results revealed the impacts of the cold climate processes (e.g., snowmelt and frozen soil) on spatio-temporal variations of other hydrologic variables. The gridded simulation results from the macro-scale GHM can be used to better understand the localized (up to a grid) hydrologic processes, and further analyze their variations across space and time, as well as their spatio-temporal trends at a macro scale.

Nutrient Removal from Domestic and Livestock Wastewaters Using Integrating Electro-coagulation and Biological Processes

Fellow: Swati Sharma Adviser: Halis Simsek Project Number: 2017ND331B Project Period: 03/01/2017 – 02/28/2018

Publications

- 1. Sharma, S., H. Simsek. 2018. Mixed cultured algal and bacterial remediation of dissolved organic nitrogen under low solid retention time condition. Journal Desalination and Water Treatment, accepted.
- Sharma, S., O. C. Taner, M. Hammed, D. Nawarathna, H. Simsek. 2017. Organic pollutant removal from edible oil process wastewater using electrocoagulation. Proceedings of ICSAE 2017 4th International Conference on Sustainable Agriculture and Environment, Aug 10-12, Solo City, Indonesia.

Presentations

1. Sharma, S., O. C. Taner, M. Hammed, D. Nawarathna, H. Simsek. 2017. Organic pollutant removal from edible oil process wastewater using electrocoagulation. Proceeding at ICSAE 2017 4th International Conference on Sustainable Agriculture and Environment, Aug 10-12, Solo City, Indonesia.

Research Description

This study focused on the reduction of dissolved inorganic nitrogen, dissolved organic nitrogen (DON), soluble chemical oxygen demand (sCOD) and dissolved organic carbon (DOC) from animal feedlot and domestic wastewaters using pretreatment with electrocoagulation (EC) and following biological treatment with a mixed culture of bacteria and a pure strain of algae *Chlamydomonas reinhardtii*. Wastewater samples were collected from two different sources; (i) the animal feedlot wastewater samples were collected from Animal Nutrition and Physiology Centre (ANPC), North Dakota State University (NDSU), Fargo, North Dakota and (ii) the domestic wastewater samples were collected from the City of Fargo Wastewater Treatment Plant (WWTP).

The wastewater samples were subject to pretreatment with EC at 20V, 0.9A for 25 mins until the water become clear. Aluminum electrodes was used for the process. The samples were then analyzed for the presence of COD, DOC and DON. The EC effluent samples were further inoculated using mixed culture bacteria and pure strain algae. The amount of bacterial and algal inocula introduced to the samples were 2 mL and 3 mL, respectively. All the samples in the bottles were incubated for 21 days and the bottles were aerated once daily. All the samples were agitated at 100 rpm using an orbital shaker. After 21 days of incubation, COD, DOC and DON were measured.

Significance of Research

The livestock wastewaters contain high concentration of organic compounds with high turbidity and color. Hence, direct application of biological treatment methods to raw livestock wastewater is challenging. EC has been efficient as a pretreatment method in the removal of color as well as reduction of organic carbon concentration in various wastewaters including livestock and domestic wastewaters. Degradation of nitrogen compounds through biological treatment has been widely accepted in domestic wastewater. Thus, integrating these two methods for treatment of wastewater derived-nutrients could be successful in improving the quality of receiving waters. An effort to further present a comparative study of batch and continuous operation was proposed to optimize the removal efficiency of both the methods in the degradation of organic nitrogen and carbon. The findings of this research will be presented at national and/or regional conferences and will be submitted for publication in a peer review journal. A final report containing all the information on the project including raw data will be delivered at the end of the project.

Significant Findings

The application of EC using aluminum electrodes into animal feedlot wastewater samples resulted in 50% removal of SCOD at the end of 45 mins of operation time. The initial concentration of SCOD was measured at 539 mg/. The concentration of dissolved NH₃, NO₂ and NO₃ remained unchanged. However, the TN reduced from 135 mg/L to 113 mg/L which can inferred as DON reduction from readily available organic nitrogenous compounds. The EC samples were then introduced to a mixed culture bacteria and pure strain algae for removal or conversion of DON to inorganic nitrogen taken up by algae as growth nutrients. The biological process is still under progress and the complete findings will be reported in the final report.

Capturing the Lost Phosphorus by Enhanced Bioretention Cells Amended with Low-cost Adsorbents

Fellow: Nicholas E. Lindstrom Adviser: Feng Xiao Project Number: 2017ND332B Project Period: 03/01/2017 – 02/28/2018

Publications

1. Xiao, F, N. Lindstrom, D. Soli. 2018. Capturing Phosphorus by Enhanced Bioretention Cells: Batch and Column Studies. Water Research, in preparation.

Presentations

- 1. Feng Xiao, Nicholas Lindstrom. "Removal of Phosphorus by Enhanced Bioretention Cells". Poster presentation at the symposium for the AEESP Distinguished Lecture by Dr. Menachem Elimelech, Minneapolis, MN, 4/2017.
- 2. Feng Xiao, Nicholas Lindstrom. "Removal of Phosphorus by Enhanced Bioretention Cells". Poster Presentation at University of North Dakota Graduate Day Workshops, 11/2017.
- Feng Xiao, Nicholas Lindstrom. "Removal of Phosphorus by Enhanced Bioretention Cells". Oral Presentation at 2018 MN-ND-SD AWWA Surface Water Treatment Workshop, 5/2018.

Research Description

The runoff of phosphorus (P) from agricultural and urban lands is major contributor to the impairment of 24,403 acres of lakes of reservoirs in the North Dakota. Loss of P from agricultural lands applied with conventional fertilizers not only wastes the state billions of dollars every year, but also results in negative agronomic and environmental consequences including decreased crop profitability and water impairment. While P is an essential nutrient for all life forms, application of excessive amounts of P harms soils and crops by reducing populations of earthworms and other beneficial soil organisms and by stimulating weed growth that increases the need to spray herbicides³⁻⁵. The water recourses managers face a continuous challenge to manage P pollution in runoff and to minimize the adverse impacts of P discharge on surface water.

This project proposes to develop and experiment with an innovative bioretention cells amended with low-cost iron-based materials that can strongly retain P and reduce P loadings to surface water. The specific objectives are to 1) study the adsorption of phosphate on the adsorbents in batch adsorption studies; and 2) investigate the removal of PO_4 -P in bioretention cells amended with the adsorbents.

An urban stormwater BMP is believed to be a 'best' way of treating or limiting pollutants especially suspended solids and heavy metals in stormwater runoff⁹. However, as shown in the next section, the removal of P in conventional stormwater BMPs is minimum. <u>This proposed project aims</u> to develop a novel approach for enhancing the P removal by amending biorentention cells with P adsorbents. Such enhanced biorentention cells can be used to reduce P loads to surface water in agricultural, urban and rural settings. The key working hypothesis is that the removal of P especially dissolved P can be greatly improved in biorentention cells by amending with low-cost, iron-based materials. This approach may also be applied to other popular BMPs, including biofilters (swales and strips). The enhanced bioretention cells are expected to effectively capture P runoff of snowmelt and rainfall to surface water, thus protecting the water resources. This fellowship supports one UND graduate student (Nicholas Lindstrom).

Significance of Research

The control of P pollution is a high priority in water resources management in North Dakota and many other states. This project will promote innovation and result in the development of enhanced bioretention cells by amending the bioretention media with PO₄-P adsorbents. This project on the nexus of water resources and agriculture may lead to a mutually beneficial partnership between these two broad areas that results in further innovative technologies to improve the sustainability of both water resources and agriculture. Overall, the anticipated benefits of this project include:

- An innovative approach for capturing P based on the theory of inner-sphere complexation;
- Enhanced understanding of the interactions between PO₄-P with Fe-based materials and minerals;
- An enhanced BMP that can be used in either agricultural, rural, and urban areas to reduce the runoff of P;
- Improved the sustainability and water quality of water resources.

Significant Findings

We have studied the adsorption of P on different types of materials, including iron oxides. Contradictory to the literature reports, we found iron oxides and iron-based materials are not an effective adsorbent of P. We found flocs generated during water treatment processes, however, can effectively remove P to a level below the detection limit. We then performed systematical batch and column studies to evaluate the performance of flocs for P retention. Samples were analyzed for PO₄-P according to *Standard Methods* section 4500-PE (ascorbic acid) with a minimum detection limit of 10 µg PO₄-P/L. Adsorption kinetics, effects of humic and fulvic acids, and effects of pH were determined. Adsorbed concentrations (C_s) were calculated by mass balance. Adsorbent-free controls were run to automatically correct for 'bottle' losses. Adsorption isotherms were fit to the Freundlich model or the Langmuir model. Continuous-flow column experiments have also been conducted to generate PO₄-P breakthrough curve as a function of low-cost adsorbents, media volume fraction, and bed depth.

One undergraduate student (Dana Soli) continues the work by the fellow (Nicholas Lindstrom) who will graduate in May 2018. Dana is supported by another grant of the faculty adviser (Dr. Feng Xiao).

Study On-farm Evaluation of Interactive Effect of Subsurface Tile Drainage, Tillage and Crop Rotation on Nitrate Leaching

Fellow: Umesh Acharya Adviser: Amitava Chatterjee Project Number: 2017ND333B Project Period: 03/01/2017 – 02/28/2018

Publications

1. Acharya, U., A. Chatterjee. 2018. Study on-farm evaluation of interactive effect of subsurface tile drainage, tillage and crop rotation on nitrate leaching, in preparation.

Presentations

1. Acharya U., A. Chatterjee, A.L.M. Daigh (2017) Can we increase yield with adopting tile drainage in Fargo clay soil? 2017 ASA, CSSA, and SSSA International Annual Meetings October 22-25, 2017 Tampa, Florida. (Poster presentation)

Research Description

Subsurface drainage is a common water management practice under Fargo clay soils. Nitrate N can be lost from the soil profile by leaching. Subsequent transport of nitrate N to surface waters occurs through subsurface drainage (tile lines) or base flow. This research was proposed to study interactive effect of drainage, rotation, and tillage on nitrate leaching in Fargo clay. A field experiment was carried out 22 miles west from North Dakota State University near Casselton, Fargo in farmers' field. Subsurface drainage tiles are installed at 1.5 ha experimental area in 2013. Tile lines of 7.6 cm in diameter were installed at 9 m spacing and 0.9 m depth and have drainage coefficient of 0.256 cm day⁻¹. Site is characterized as Fargo clay soil (fine, smectitic, frigid typic epiaquerts) with high organic matter (40-60 %), 0 to 1 percent slopes and is poorly drained. The experiment has controlled subsurface, and no subsurface in the strip as main plot and every drainage has two crop rotation; corn-soybean and continuous corn as sub plot. Under each sub plot, two tillage treatment (chisel and no-till) were laid as sub-sub plot, replicated three times. Chisel plots were plowed using field cultivator to depth of 7.5 cm whereas; no-till plots were undistributed. Individual plot dimension was 9.1 by 3.4 m. Urea was applied as a source of nitrogen at 179.3 kg N ha⁻¹ in the last week of September after harvest. No nitrogen was applied for soybean crop. Roundup Ready Soybean (Mustang 0443) and corn (Dekalb C39-27Ri13) cultivars were planted at 415,000 and 84,000 plants ha⁻¹ respectively, using 55.9 cm wide seed drill every year in the first week of May.

Soil water samples at 60 cm soil depth was collected from the middle of each crop (soybean, corn) plots between rows using suction lysimeter (68cm in length and 2.2 cm diameter: Irrometer Company, Inc., CA, USA). In the laboratory, NO₃⁻ concentrations in the water samples will be analyzed using the ammonia analyzer. Two soil cores were collected from

each plot and combined to create a composite soil sample. The TL-2800 Ammonia Analyzer was used for detection and analysis of inorganic nitrogen at a different depth 0-6 inch and 6-24 inches. At physiological maturity, middle three rows of each plot were harvested using the small plot combine harvester on the last week of September for soybean and third week of October for corn every year. The grain yield (Mg ha⁻¹) for soybean and corn was calculated using 14% moisture content.

Significance of Research

Subsurface tile drainage system has become popular due to repeated wetting cycle. Subsurface tile drainage removes excess water and provides early access for the field operation. However, subsurface tile drainage has potential to increase the nitrate loss through tile drainage. Nitrate lost through tile drain can end up in a drainage ditch or surface water bodies, these can lead to change in food web and environmental pollution.

Tile drainage is most common in soils with high clay content. Installing subsurface tile drainage can substantially increase the crop productivity. However, the extent of nitrate loss from tile drainage system under Fargo Clay and tile drainage interaction with tile design, tillage and crop rotation is important to minimize the loss.

Significant Findings

Corn-soybean rotation has significant highest corn yield (13.96 Mg ha⁻¹) over continuous corn (12.94 Mg ha⁻¹). Drainage and tillage have no effect on corn yield. However, chisel plow with continuous corn (14.48 Mg ha⁻¹) has significant higher corn yield when compared with other rotation and tillage combinations. Surface drainage with corn-soybean rotation under chisel plow recorded significant highest corn yield (15.03 Mg ha⁻¹) and lowest in the controlled subsurface with continuous corn under no-till. Drainage and tillage have no significant effect on soybean yield. The leachate NO₃⁻ concentration was higher for first week (June 15) for all treatment and decreases with increasing corn growth. The rainfall was higher for first week of leachate sampling (46.74 mm) and decrease in upcoming week (13.46, 7.62, 2.03, 6.86 mm). Surface drainage with continuous corn under no-till recorded highest leachate NO₃⁻ (52.56 mg L⁻¹) followed by CT-CC-CH (49.48 mg L⁻¹) and lowest with CT-CS-CH (14.08 mg L⁻¹). The leachate NO₃⁻ decreases in next week (June 22) for each treatment but no specific trend was observed throughout study period. The total leachate NO_3^- among different treatment was compared and no significant difference was observed with drainage, crop rotation and tillage. Surface drainage (92.01 mg L^{-1}) recorded higher leachate NO3⁻ than controlled subsurface drainage (44.91 mg L⁻¹), continuous corn (82.25 mg L^{-1}) over corn-soybean rotation (54.68 mg L^{-1}) and no till (73.03 mg L^{-1}) over chisel plow (63.9 mg L⁻¹). There was increase in soil residual NO₃ for surface drainage when compared with initial soil NO₃ and soil residual NO₃ was decreased for controlled subsurface drainage except chisel plow with corn-soybean rotation. This shows that surface drainage plots increase N mineralization due to enough moisture for long period when compared with controlled subsurface drainage. There was no significant difference in residual soil NO₃ among the drainage, rotation and tillage in corn plots. Precipitation pattern and residues from

previous growing season affected the leachate NO_3^- concentration but no specific trend was observed in rotation and tillage under different drainage method.

Removal of Trichloroethylene and Fluoride from Water by Nanoscale Zero-Valent Iron Supported on Novel Activated Carbon

Fellow: Umma Salma Rashid Adviser: Achintya Bezbaruah Project Number: 2017ND334B Project Period: 03/01/2017 – 02/28/2018

Publications

1. Rashid, U. S., M. F. Pate, S. Simsek, A. N. Bezbaruah. Coating of NZVI particles with modified starch: Colloidal stability and nitrate reduction studies. Environmental Pollution, in preparation.

Presentations

1. Rashid, U.S., Simsek, S., Bezbaruah, A.N. Tapioca Starch based Polymer for Surface Modification of Iron Nanoparticles, AEESP Distinguished Lecture Series Poster Session, Minneapolis, Minnesota, March 2017.

Research Description

Nanoscale zero-valent iron (NZVI) is an effective reducing agent for removing trichloroethylene (TCE) and an effective adsorptive material for fluoride (F⁻) removal from groundwater. However, bare NZVI agglomerates, settles down very quickly and lose their reactivity in aqueous environment. A wood-based activated carbon (AC) was prepared by chemical activation with metal salt to get higher surface area, pore volume and organized pore structure on the surface of AC. NZVI will be supported on the surface of AC by mixing prepared activating carbon with ferrous sulfate heptahydrate followed by chemical reduction with NaBH₄. Batch studies will be used to evaluate the TCE and fluoride removal efficiency of NZVI-AC. Adsorption isotherm study will be conducted to determine the equilibrium adsorption capacity and adsorption mechanisms. Additionally, commercial activated carbon was modified with citric acid (CA) to increase fluoride removal efficiency. Fluoride removal studies were conducted with different concentrations of F⁻. The effect of pH, temperature, natural organic matter (NOM), and other ions were also investigated. Different equilibrium isotherms were used to model the experimental data and Langmuir isotherm was found to fit the data better. Adsorption mechanisms were also investigated using an intraparticle diffusion model. The physicochemical properties of citric acid modified activated carbon (CAAC), bare NZVI and NZVI-AC will be investigated by FTIR, SEM, XPS, and BET analysis. TCE and fluoride removal capacity of CAAC and NZVI-AC will be compared.

Significance of Research

Trichloroethylene (TCE) was a widely used organic solvent for electronic, metal finishing, machinery, and dry-cleaning application. As a result of improper waste disposal practice in

the past, TCE has become one of the most problematic classes of volatile organic compounds found in groundwater. Numerous studies have reported that the widespread presence of TCE in groundwater is a serious public health concern due to the hazardous nature of this contaminant. The maximum contaminant level (MCL) for TCE in drinking water is 5 ppb (USEPA, 2011).

Fluoride (F^{-}) is an anionic constituent found naturally in surface and groundwater. The most common source of fluoride in groundwater is weathering of fluoride bearing mineral such as fluorospar, cryolite and fluroapatite in rocks. In addition to this, mica, amphiboles, certain clays and villiamites also have great effect on the hydrochemistry of fluoride. Drinking water is the major pathway of fluoride to enter in human body. Intake of fluoride within the permissible limit is beneficial for human health in production and maintenance of healthy teeth and bones. On the other hand, prolonged exposure to high F^{-} levels can lead to dental and skeletal fluorosis. Chronic intake of fluoride may also lead to muscle fiber degeneration, low hemoglobin level, excessive thirst, skin rashes, depression, growth retardation, DNA structural changes. The world health organization (WHO) recommends a threshold of 1.5 mg F/L in drinking water, beyond which fluoride can cause detrimental effect. The USEPA has established a MCL of 4 mg/L to prevent against skeletal fluorosis and a secondary MCL of 2 mg/L to protect against dental fluorosis.

NZVI can treat contaminant plumes and the source significantly because of their high surface area to volume ratio, rapid kinetics, and high reactivity. However, bare NZVI agglomerates and settles quickly in aqueous environment, which reduces the available surface area for reduction to occur. Activated carbons (AC) in both granular and powdered forms are the most widely used adsorbents for removing organic pollutants, heavy metals and industrial dyes. Activated carbons are the amorphous form of carbon characterized by high internal porosity and consequently high adsorptivity which are usually related to their specific surface area, pore volume, and porosity. However, AC doesn't have good fluoride removal capacity. The impregnation of NZVI on AC surface has drawn the attention of researchers in recent years as it can increase the adsorption capacity of AC and at the same time can retain the reactivity of NZVI. Keeping all these in mind, a set of ACs was made by chemical activation with metal salt and metal hydroxides at different ratio to get an organized pore structure, high surface area and high pore volume. Additionally, citric acid can be used to modify the surface of commercial activated carbon by introducing additional carboxyl group onto their surface. Citric acid is biodegradable and widely used in the food and pharmaceutical industries and was selected to modify the surface of commercial activated carbon to increase the fluoride removal efficiency.

Significant Findings

• A set of activated carbon powders (AC) was made by chemical activation with metal salt and metal hydroxides to get an organized pore structure, high surface area and high pore volume. At lower concentration (200 mg/L of methylene blue) all the AC samples showed same amount of removal but at high concentration (500 mg/L of methylene blue) KOH and KCl activated AC showed better removal (99%) than NaOH and NaCl activated AC (66%). The optimum impregnation ratio for KCl to AC is 1:1 and and for NaCl to AC is 1:2.

- Citric acid was used to modify the surface of commercial activated carbon by introducing additional carboxyl group onto their surface.
- Batch studies showed that, with citric acid modified activated carbon (CAAC), F⁻ concentration decreased from 5 ppm to 1 ppm (80% reduction), 10 ppm to 3 ppm (70% reduction) and 20 ppm to 7 ppm (70% reduction) in first 60 min whereas AC removed only 30%, 25% and 23% for the same initial concentrations and the same reaction time.
- Batch equilibrium study was done to find out the point of zero charge (PZC) of CAAC. The PZC of CAAC was found to be 4.09 which means CAAC will adsorb F⁻ more efficiently at pH below 4.09.
- Adsorption isotherm showed that CAAC has fluoride removal capacity of 1.6 mg/g whereas AC has fluoride removal capacity of 0.8 mg/g. Adsorption data were fitted in Freundlich and Langmuir isotherm models and Langmuir isotherm ($R^2 = 0.976$) was found to be fitted better than Freundlich ($R^2 = 0.942$).
- The removal efficiency of F⁻ was maximum (100%) at low pH (= 2) and removal efficiency decreases with the increase of pH till pH = 5 (70%) and after that efficiency is more or less same (70%).
- Desorption study showed that only 10% of adsorbed F⁻ was desorbed in first 24 hours but after that the amount of desorption is insignificant.
- There is no interference by other environmentally significant ions $(SO_4^{2^-}, NO_3^{-}, PO_4^{3^-}, HCO_3^{-}, Cl^-, NOM$ and humic acid) at low concentration of interfering ions (10 ppm).
- F⁻ removal efficiency is not affected by temperature till 30 °C. However, at high temperature (35, 40 and 45 °C) removal efficiency increased by 3%-5%.

Effect of Water Table on Soybean Growth and Yield Parameters

Fellow: Yavuz F Fidantemiz Adviser: Halis Simsek Project Number: 2017ND335B Project Period: 03/01/2017 – 02/28/2018

Research Description

North Dakota (ND) is one of the main states in the United States (US) where soybean is grown extensively. Groundwater contribution is important component affecting substantial growth and yields of soybean. Quantifying how much shallow groundwater can potentially be used for soybean growth can provide knowledge for scheduling irrigation and drainage systems. Climate, irrigation water quality, crop, soil type, and irrigation management are the parameters mostly affect the water table depth on any crop. However, shallow water table depth can cause water logging and oxygen depletions at the root zone. Necessary oxygen for both plants and organisms are depleted under shallow water table conditions. Evaporation is the main component of the water source planning and water management. Close correlation was found between evaporation rates and groundwater depth.

In this study, the effect of different water table depths on soybean growth and yield parameters and groundwater contributions to plants were investigated. The plants were grown in 15 cm diameter and 120 cm height soil columns. Soybean was subject to different water tables varied from 30 to 90 cm from the column surface during the growth period. Water content, temperature, and electrical conductivity were measured at certain depths to evaluate water vapor flux in the columns. As a control treatment, full irrigation was also applied. 30 PVC columns were used and each column was packed using same type of soils. 7.5-liter plastic Mariotte bottles were placed on the adjustable shelves, and each shelf's height has been arranged for the desired water level of the particular water table. This is an ongoing study and has a plan to finalize through December 2018.

Significance of Research

Shallow groundwater can be considered alternative water resource for both dry and irrigated agriculture even though it is overlooked during the water management. A significant amount of water from shallow groundwater can be used by plants when the suitable conditions are met. It will be valuable for the farmers to know the water table effect on soybean plant since there is no irrigation application in North Dakota. A number of parameters such as groundwater depth, groundwater quality, crop growth stage, crop salt tolerance, irrigation frequency and application depth were affected from shallow groundwater level. Due to many parameters affecting groundwater contributions to the plant growth, it is hard to determine its effect in situ conditions. Currently, most of the irrigation programs only use irrigation water to determine the plant water demand and ignore groundwater contribution. Therefore, groundwater contribution should be taking into consideration. Applying column studies in a

greenhouse condition could be a practical method to detect appropriate water demand for plants. Column study in a controlled environment is the best ways to simulate field condition and it has not been commonly studied so far. The results obtained from this study could help to reduce the risk of yield reduction in actual field application. In addition, the results will benefit the farm owner by giving information about soybean tolerance on water levels.

Significant Findings

At the beginning of the experiments, hydraulic properties of soil such as soil moisture release curve (SRC) and hydraulic conductivity were determined by using HYPROP®(Version 10/2011, UMS GmbH Munchen). The values of field capacity, critical point and permanent wilting point were determined. Based on the data from SRC, irrigation time and amount was scheduled.

Results showed that, since the water table has been fixed at the top of the columns to provide moisture for germination before planting, similar moisture percent has been monitored at 30 cm depth for the first month. In addition, similar plant heights and stages have been observed at the 30, 50, and 70 cm water table depths. However, the minimum plant heights were observed at 90 cm water table depth. More results will be available at the end of the experimental study.

Modeling of Runoff Contributing Areas and Hydrologic Connectivity and Applications in North Dakota

Fellow: Kendall Grimm Adviser: Xuefeng Chu

Publications

- 1. Grimm, K., Tahmasebi Nasab, M., and Chu, X. 2018. TWI Computations and Topographic Analysis of Depression-dominated Surfaces. Water, 10(5), 663:1-12.
- 2. Grimm, K. and Chu, X. 2018. Modeling of Spatio-temporal Variations in Runoff Contribution Areas and Analysis of Hydrologic Connectivity. In review.

Presentations

- 1. Kendall Grimm. "Improved Hydrologic Modeling for Depression-dominated Areas." NDSU Three Minute Thesis Competition 2018, Fargo, North Dakota.
- 2. Kendall Grimm and Xuefeng Chu. "Modeling of Spatio-temporal Variations in Hydrologic Connectivity and Contributing Areas." ND EPSCoR/IDeA 2017 State Conference, Fargo, North Dakota. (Poster)

Research Description

Various watershed delineation methods have been developed, which analyze surface topography differently. Traditional hydrologic modeling and delineation methods do not take into account the spatial arrangement of depressions and lack dynamic contributing area and depression threshold control. In order to model depression-dominated landscapes like those in the Prairie Pothole Region (PPR) in North Dakota, a hydrologic model is needed which simulates the filling-spilling-merging processes of potholes. Therefore, the objective of this 1-year project was to modify HEC-HMS, a widely-used traditional hydrologic model by taking into account the hydrologic effect of depressions and test the new model for some sites in North Dakota. To simulate the hydrologic effect of depressions, a new concept was developed, the depression threshold control proxy. The idea is that this proxy will mimic the filling-spilling processes and dynamic contributing area of depressions within the HEC-HMS model framework. To create the depression threshold control proxy, first, topographic characteristics relating to depressions were obtained using the depression-dominated delineation (D-cubed) method (Tahmasebi Nasab et al., 2017). Second, the topographic characteristics of depressions were processed and divided into puddle-based units (PBUs) and maximum depression storage (MDS) of each PBU. PBUs represent the contributing area to each highest-level puddle on a surface. Third, a storage-discharge function was created by (1) artificially filling each highest-level puddle for each PBU to calculate storage and (2) using the Modified Puls Routing method to calculate discharge. Lastly, the resulting storagedischarge functions for each subbasin were incorporated into the 'reservoir feature' in HEC-HMS. To create the new conceptual framework for HEC-HMS, depressional area (DA) and non-depressional area (NDA) were introduced. Each subbasin is divided into 2 sub-subbasin (i.e., DA and NDA). DA is calculated by summing all PBU areas in a subbasin and NDA is calculated by summing all channel-based units (CBUs) (i.e., contributing area to channels) in a subbasin (Tahmasebi Nasab *et al.*, 2017). To complete the new conceptual framework, NDA is connected to a subbasin outlet, DA is connected to the subbasin 'reservoir feature', and the 'reservoir feature' is connected to the same subbasin outlet as the NDA. The incorporation of these 2 new concepts into the HEC-HMS model significantly improved the hydrologic modeling results compared to the original model. Acceptable values for Nash-Sutcliffe efficiency (NSE), percent bias (PBIAS), and root mean square error standard deviation ratio (RSR) were obtained for both the calibration and validation of streamflow in the improved HEC-HMS model. More specifically, the depression threshold control proxy was able to store water and control the timing and magnitude of outlet discharge. Similarly, the new conceptual framework initially divided the subbasin into contributing area (i.e., NDA) and geographically isolated area (i.e., DA) which controlled the timing and magnitude of outlet discharge.

Significance of Research

Quantifying contributing area to the outlet is imperative when considering water resource availability. 'Where is water going and where is water coming from' are important questions that can be answered by using hydrologic models; however, these models must take into account impacts of the landscape topography. The foundation of this research stems from first understanding the surface topography. Only when there is a clear understanding of spatial and temporal variations in runoff contribution can conclusions be transferred to subbasin-scale models. Many traditional subbasin-scale models employ modify oversimplified methods to handle depressions and runoff initiation. By introducing variables like contributing area to puddles, dynamic contributing area to the outlet, and puddle fillingspilling-merging dynamics, a modified model was developed and used to simulate runoff from subbasin-scale depression-dominated areas. The practicality of my modification techniques, specifically the depression threshold control proxy, is in their ability to be implemented into other subbasin-scale hydrologic models. Specifically, because my methodology to create the depression threshold control proxy utilizes detailed specifics about individual puddle-to-puddle dynamics in a lumped manner, the depression threshold control proxy simulates dynamic contributing area of depression-dominated areas and should be easily implemented into other models which also lump depression storage.

Significant Findings

Significant research progress and findings have been made in topics related to the impact of depressions on hydrologic modeling. Specifically, (1) a depression threshold control proxy was proposed to simulate depression filling and spilling, and (2) a new conceptual framework was introduced to take advantage of dynamic contributing area in depression-dominated areas. These new concepts were implemented into the HEC-HMS model to obtain a more accurate representation of hydrologic processes in depression-dominated watersheds. The modified HEC-HMS model prevented both overestimation and underestimation of total discharge for a storm event due to the storage function and discharge attenuation within the depression threshold control proxy. In addition, peak discharge was more accurately

represented by the modified HEC-HMS model. The division of DA and NDA in the new conceptual framework provided a new tool in which to divide a subbasin into contributing area to the outlet and isolated area/dynamic contributing area to the outlet (i.e., contributing area varies over time).

Holocene Palaeoflood and Glacial Isostatic Adjustment (GIA) Influence on Fluvial Geomorphology of the Red River Basin

Fellow: Zachary R. Phillips Adviser: Stephanie Day

Publications

1. Phillips, Z.R. and Day, S.S. 2018. Exploring and interpreting the distribution of meandercutoffs of the post-glaciolacustrine Red River of the North, (in final stages of development for late-Spring 2018 submission to the) *Journal of Earth Surfaces Processes and Landforms*.

Presentations

- 1. Phillips, Z.R., 2017. Geomorphometry and spatial analyses as assistants in interpreting fluvial geomorphology, invited speaker to NDSU Introduction to GIS "speaker-week", Dec. 2017.
- 2. Phillips, Z.R., 2017. Explaining the possible geomorphic implications of the spatial distribution of meander-cutoffs for the Red River of the North, Geological Society of America Annual Conference, Seattle WA, Oct. 2017.
- 3. Phillips, Z.R., 2017. Is your meandering river stable? Methods for determining controls of historic river meandering, 2017 Upper Midwest Stream Restoration Symposium, La Crosse, WI, Feb. 2017.
- 4. Phillips, Z.R., 2016. Investigation of Post-glacial Fluvial Geomorphology and River Valley Growth: a case study of the Red River basin, ECS Greenbag Seminar Research Proposal Talk

Research Description

My research studies the responses of post-glacial rivers to climate change, post-Glacial Isostatic Adjustments (GIA), changing sediment characteristics, and human impacts using the Red River as a case study. I use interdisciplinary methods of interpreting fluvial systems and deposits as they correlate to the Holocene and late-Pleistocene history. This fellowship year, I explored the Red River's floodplain topography using Geographic Information Systems (GIS) and developed a set of methods to extract areas of meander-cutoff topography from the Digital Elevation Model (DEM). I used the spatial distribution of the meander-cutoffs, as well as their relief and distance from the modern channel (DMC), as interpretive tools to suggest how meandering of the Red River has changed since the draining of Lake Agassiz. Result reporting is currently being conducted for this portion of my PhD project (Phillips and Day, 2018).

Currently, a Landscape Evolution Model (LEM) is being designed and assembled for the Red River Basin, with a focus on the evolution of the meandering path of the Red River. The LEM is being developed using the python-based LandLab modelling package, which will be

used to simulate climate, hydrology, and geomorphology of the Red River Basin. Currently, the climate inputs are being assembled from the current literature and core libraries. Additionally, the DEM is being reconstructed to recreate the late-Pleistocene landscape prior to major elevational change from GIA. This model will depict the erosional history and future of the Red River basin and Red River Valley.

Work will begin this spring performing a series of geomorphic laboratory tests, using laser scanners to monitor fluvial erosion of clays with different water contents. These experiments are designed to simulate the drying and hardening of Sherak and Brenna Formations within the Red River Valley, and test the impacts of drying on erodibility. Lake Agassiz Clays will be used in the Geomorphology lab's stream table, which of will be saturated and then dried for varying periods to differing levels of saturation. Then, the same experiment will be performed on each of the variably dried clays. Results are expected to show that wet clays erode more easily while dryer clays are less erodible.

Significance of Research

This research is significant because it helps people understand the modern effects of climate change and its interactions with rivers and humans. More specifically, regarding the Red River, this research is important because the Red River is a unique, clay-controlled meandering river which is both important and damaging to its floodplain residents. Being geomorphically clay-controlled, the Red River does not meander freely like typical rivers, which makes this an important rare case for which to gain a better understanding. In the southern Red River Valley, Fargo-Moorhead is attempting to harness floods near the F-M Urban area by establishing final plans and building a flood diversion. Building of a successful diversion relies on a thorough understanding of the geomorphology of the river, which has been studied more thoroughly north of the Canadian border. To date, there is no sure answer as to if the northern reaches of the Red River behave geomorphically similar to the southern Red River, but this research has and will continue better detail the Red River's geomorphology and determine the major factors controlling Red River meandering of the past, present, and future.

Significant Findings

The major significant findings of this research are that there are ~158 meander-cutoffs on the Red River, which are skewed toward the south of the river. The widespread nature of low relief cutoffs, with meander-cutoffs being depositional locations, suggests that meandering used to be more active over the entire length of the river, but has slowed relatively recently as signified by the relatively few high-relief meander-cutoffs. High relief meander-cutoffs, that are interpreted as being younger than ~1520 calendar years before present, are present in only in two short, 20-km long reaches centered over top of the Edinburgh and Comstock moraines that were deposited in the Red River Valley by the Des Moines Lobe during the late-Pleistocene (Phillips and Day, 2018). This suggests that these underlying moraines may be influencing the modern morphology of the Red River in these reaches, something that was unknown prior to this research.

Hydrological Responses to Climate Change in a Terminal Lake Basin

Fellow: Diane Van Hoy **Adviser:** Taufique H. Mahmood

Publications

1. Van Hoy, D., Mahmood, TH., Todhunter, P., Jeannotte, T. (2018) Mechanism of Cold Region Hydrologic Changes to Recent Wetting in a Terminal Lake Basin. *Hydrology and Earth System Sciences* (In preparation).

Presentations

- 1. Van Hoy, D., Mahmood, T.H., Jeannotte T. 2017. Hydrological Responses to Climate Change in the Mauvais Coulee Basin. ND EPSCoR 2017 Conference, Fargo, ND. (Poster).
- 2. Van Hoy, D., Mahmood, T.H., Jeannotte T., Todhunter, P. 2017. Impacts of Recent Climatic Wetting on Distributed Snow and Streamflow Responses in a Terminal Lake Basin. In AGU Fall Meeting Abstracts, New Orleans, LA. (Poster).
- 3. Van Hoy, D., Mahmood, T.H., Jeannotte T., Todhunter, P. 2018. Impacts of Recent Climatic Variability on Cold Region Hydrologic Responses in a Terminal Lake Basin. ND EPSCoR 2018 Conference, Grand Forks, ND.

Research Description

Devils Lake is a terminal lake basin created by glaciation in the Northern Great Plains (NGP). The NGP has been known to experience a highly variable cold and continental climate. Over the last century there have been a series of wet and dry periods of variable magnitude and intensity impacting cold region hydrologic responses and land surface conditions in many ways resulting in extreme hydrologic responses such as drought and flood. The recent wet period has led to extensive flooding that has caused millions of dollars in infrastructure damage and converted valuable farm land into wetlands. This project utilized a physically based model known as the Cold Region Hydrological Model (CHRM) to investigate the impacts of recent wetting (2004-2017) on distributed snow and streamflow simulations and detect mechanisms of hydrologic changes. The CHRM was chosen because it was specially designed to handle cold region processes and land surface conditions such as frozen soil infiltration, snow accumulation, blowing snow transport, sublimation, snowmelt runoff, and rain on snow events. The study area is a headwater of the Devils Lake Basin (DLB) known as the Mauvais Coulee Basin (MCB). MCB was chosen because it has a variety of land cover types from tall native prairie grass to a wide range of cultivated crops and small patches of both conifer and deciduous forest. It also has the highest relief with an approximately 231-meter change in elevation from Turtle Mountain at the northwest corner of the subbasin to the outlet of MCB. The MCB contributes to a set of lakes that eventually flow into DL. The model was tested simultaneously against snow and streamflow observations. Since, there were no snow observation available in MCB, my group collected

snow depth, density, and snow water equivalent (SWE) for the 2016-17 and 2017-2018 winters at distributed locations in the MCB. I forced the model with the climatic data including temperature, relative humidity, wind speed, incoming short wave radiation, and precipitation. Streamflow data was also collected from the United States Geological Survey's gage located near Cando, ND. The model was spatially discretized using hydrologic response units (HRUs), which were derived based on land use/cover maps, digital elevation model and soil maps. The results suggest that snow simulations agree well with observations at distributed locations for 2017 winter season. Further model assessments indicate a strong model performance while simulating streamflow during 2004-2017 periods. The simulated SWE maps exhibit large spatiotemporal variation during 2016-17 winter due to spatial variability in precipitation, snow redistribution from stubble field to wooded areas, and snow accumulations in small depressions across the subbasins. The main source of snow appears to be the troughs and depression of the eastern and western edges of the basin, while the main sink is the large flat central valleys. The water balance analyses indicate the cold region hydrologic responses transition from a streamflow dominated system to ET dominated system during 2011. Finally, this study has demonstrated the influences of frozen soil condition/basal ice layer and antecedent winter soil moisture on spring snowmelt runoff during 2004-17 periods.

Significance of Research

This study is the first high-resolution physically based modeling study in the Devils Lake Basin. In this study, we also present snow observations at distributed locations since there are no snow observations available. Accurate snow observations are a vital part of model evaluation of snow distribution. The simulated maps on a HRU scale created from model output to examine spatiotemporal variability in peak SWE, number of snow cover days, etc. are unique to this project. These maps of modeled snow distribution can be a useful tool in land management. For example, a farmer could decide where to create a ditch to capture snow or divert runoff, to avert the loss of valuable farmland to flooding during spring snowmelt. The model can be expanded to the rest of the Devils Lake Basin to help city planners decide the best location to place structures that need to be relocated and determine what roads need to be raised. The model created for this project can also be run under various climate change scenarios to find areas that could be vulnerable to extreme hydrologic responses. Finally, our findings provide useful information regarding streamflow generation mechanism during flood years such as 2005, 2009, 2011, 2013 and 2017.

Significant Findings

The findings of this study report that the recent increase in precipitation results in two major hydro-climatic phases: pre-2011 and post-2011. The springs of the pre-2011 phase are dominated by snowmelt induced streamflow while evapotranspiration is only major output flux during the post-2011 period. During wet years during from 2014 to 2017, frozen soil conditions and antecedent soil moisture exert a strong influence on snowmelt –induced streamflow generation. Snowmelt and rain on snow are found as major contributors to annual streamflow in a cold region terminal lake basin setting. Trend analysis of temperature from data collected at Cando, ND has revealed that April, November, and December are all

experiencing a decreasing trend in temperature while the remainder of months are experiencing an increasing trend. The recent increase in temperature in summer and fall in this region maybe a contributing factor behind the increase in the rain contribution to total yearly precipitation. The increase in rain has led to a change in the streamflow from the traditional unimodal spring snowmelt runoff to a multimodal system with one or more summer or fall rainfall related peaks.

INFORMATION DISSEMINATION

Information Transfer Program Introduction

Information dissemination is done through an annual newsletter, and presentations and publications by grant and fellowship recipients. A website also helps disseminating institute research information. The institute's website address is https://www.ndsu.edu/wrri. Past newsletters can be accessed through the institute website. Technical reports of the Fellowship projects authored by the Fellows and advisers are also available at the institute website.

Information Dissemination and Communication

Project Number: 2017ND336B Start Date: 3/1/2017 End Date: 2/28/2018 Principal Investigator: Eakalak Khan

The major activities to disseminate information related to the Institute and research under this project included:

- 1. Maintaining the institute website as an effective way communicating to the public
- 2. Publishing the annual institute newsletter
- 3. Publishing Fellowship and other research done through the Institute
- 4. Hosting the annual "Distinguished Water Seminar"
- 5. Presenting research results by affiliated faculty and Fellows
- 6. Sponsoring or co-sponsoring local or regional conferences

The website of the Institute was updated at least quarterly, and more often when updates on a research project were available or when a Fellow graduated. The website provided additional details on the research. The list of the Institute Affiliate Faculty with their expertise was updated. Research reports published by the institute were uploaded to this website when they became available. The institute website is: <u>https://www.ndsu.edu/wrri</u>.

The Institute continued its annual newsletter, which highlighted the graduate research fellowship program, the research grants associated with it, and general summaries of ongoing research. The newsletter profiled institute research and researchers and published other newsworthy water issues in the State.

The Institute also encouraged its Fellows and affiliated faculty to present their work at seminars and conferences. Here is a list of seminar and conference presentations made by Fellows and affiliated faculty in this funding year:

1. Acharya U., A. Chatterjee, A.L.M. Daigh. 2017. Can we increase yield with adopting tile drainage in Fargo clay soil? 2017 ASA, CSSA, and SSSA International Annual Meetings, October 22-25, 2017 Tampa, Florida.

- Grimm K., Chu, X. 2017. Modeling of spatio-temporal variations in hydrologic connectivity and contributing areas." ND EPSCoR/IDeA 2017 State Conference, Fargo, North Dakota.
- 3. Niaghi, A. R., Bazrkar, M. H. 2018. Assessing the effect of tile drainage on streamflow and nitrate load using SWAT model. Bismarck Water Quality Conference, March 2018, Bismarck, ND.
- 4. Niaghi, A. R., Jia, X., Scherer, T. F., Steele, D. D. 2018. Assessment of cool season grass water use. NDSU poster session, February 2018, North Dakota State University, ND.
- Niaghi, A. R., Jia, X., and Scherer, T. F. 2017. Impact of accurate evapotranspiration estimates on DRAINMOD simulation in North Dakota. ASABE Annual International Meeting, July 16-19, 2017. Spokane, WA. doi:10.13031/aim.201701500.
- Niaghi, A. R., and Jia, X. 2017. Determination of grass evapotranspiration rates and crop coefficients using eddy covariance method in eastern North Dakota. ASCE World Environmental & Water Resources Congress (EWRI) Annual Meeting, May 21-25, 2017, Sacramento, CA.
- Pham, Hoang Nu Kim, Bezbaruah, A. 2018. Biosynthesis of iron nanoparticles using green tea extract for the removal of phosphorus from aqueous solution, 2018 ND Water Quality Monitoring Conference, Bismarck, ND.
- 8. Phillips, Z.R. 2017. Geomorphometry and spatial analyses as assistants in interpreting fluvial geomorphology, invited speaker to NDSU Introduction to GIS "speaker-week", Dec. 2017.
- 9. Phillips, Z.R. 2017. Explaining the possible geomorphic implications of the spatial distribution of meander-cutoffs for the Red River of the North, Geological Society of America Annual Conference, Seattle WA, Oct. 2017.
- Phillips, Z.R. 2017. Is your meandering river stable? Methods for determining controls of historic river meandering, 2017 Upper Midwest Stream Restoration Symposium, La Crosse, WI, Feb. 2017.
- 11. Rashid, U.S., Simsek, S., Bezbaruah, A.N. 2017. Tapioca starch based polymer for surface modification of iron nanoparticles, AEESP Distinguished Lecture Series Poster Session, Minneapolis, Minnesota, March, 2017.
- 12. Ritt, C. 2017. Molecularly imprinted polymers (MIPs) as sustainable phosphate sorbents, North Dakota State University's Department of Civil & Environmental Engineering, April, 2017.
- 13. Ryan, H., Bosen, J., and Xiao, F. 2017. Removal and transport of poly-fluoroalkyl substances. Symposium for the AEESP Distinguished Lecture by Dr. Menachem Elimelech, 4/2017, Minneapolis, MN.
- Shabani, A, Zhang, X., Mike Ell. And Timothy P. Dodd. 2018. Examining the impact of Devils Lake outlets on flood risk of the Sheyenne River. Bismarck, North Dakota, March 6-8.

- 15. Shabani, A., Zhang, X. 2017. Examining the impact of Devils Lake outlet on the flood risk of the Sheyenne River. American Geophysical Union conference, New Orleans, Louisiana, 11-15 December.
- 16. Shabani, A., Zhang, X. 2017. Estimated water surface temperature using Landsat 8 TIR bands using split window algorithm. Great Plains/Rocky Mountains American Association of Geographers conference. Grand Forks, North Dakota, 13-14 October.
- 17. Sharma, S., OT Can, AM Hammed, Nawarathna D., Simsek, H. 2017. Organic pollutant removal from edible oil process wastewater using electrocoagulation. ICSAE 4th International Conference on Sustainable Agriculture and Environment, August 10-12, Solo City, Indonesia.
- Tahmasebi Nasab, M., Grimm, K., Wang, N., and Chu, X. 2017. Scale analysis for depression-dominated areas: How does threshold resolution represent a surface? ASCE World Environmental and Water Resources Congress 2017, Sacramento, CA.
- 19. Tahmasebi Nasab, M., Chu, X., Singh, V. 2017. Depressions as gatekeepers: How do depressions control hydrologic modeling? ASCE World Environmental and Water Resources Congress 2017, Sacramento, CA.
- Tahmasebi Nasab, M., Grimm, K., Wang, N., Chu, X. 2017. Hydrologic monitoring and modeling for quantifying prairie pothole dynamics. ASCE World Environmental and Water Resources Congress 2017, Sacramento, CA.
- 21. Tahmasebi Nasab, M., Chu, X. 2017. A new physical-based gridded model for macroscale hydrologic modeling. ND EPSCoR Annual Conference, Fargo, ND.
- 22. Van Hoy, D., Mahmood, T.H., Jeannotte T. 2017. Hydrological responses to climate change in the Mauvais Coulee Basin. ND EPSCoR 2017 Conference, Fargo, ND.
- 23. Van Hoy, D., Mahmood, T.H., Jeannotte T., Todhunter, P. 2017. Impacts of recent climatic wetting on distributed snow and streamflow responses in a terminal lake basin. AGU Fall Meeting, New Orleans, LA.
- 24. Van Hoy, D., Mahmood, T.H., Jeannotte T., Todhunter, P. 2018. Impacts of recent climatic variability on cold region hydrologic responses in a terminal lake basin. ND EPSCoR 2018 Conference, Grand Forks, ND.
- 25. Xiao, F., Bosen, J. 2017. Surface and subsurface transport of perfluoroalkyl substances in urban runoff of a typical North Dakota city. Society of Environmental Toxicology and Chemistry (SETAC) North America Annual Meeting, November 12-16, Minneapolis, MN.
- 26. Xiao, F., Bosen, J., Bedane, A. 2017. Bioconversion of poly-fluoroalkyl substances in earthworms. Society of Environmental Toxicology and Chemistry (SETAC) North America Annual Meeting, November 12-16, Minneapolis, MN.
- Xiao, F., Lindstrom, N. 2017. Removal of phosphorus by enhanced bioretention cells. Symposium for the AEESP Distinguished Lecture by Dr. Menachem Elimelech, Minneapolis, MN, 4/2017.

Seventh Annual Distinguished Water Seminar

The 7th Annual Distinguished Water Seminar sponsored by the Institute was held on February 28, 2018. The featured speaker was Dr. Doug Chivers, Distinguished Professor in the Department of Biology at the University of Saskatchewan, where he has worked since 1999. He teaches courses in Ichthyology and Animal Behavior and he has supervised numerous graduate students and postdocs. He and his students and collaborators conduct basic and applied research on the behavioral ecology of fishes including how anthropogenic disturbance influences anti-predator behavior of fishes in the wild. He has published over 240 papers in high impact journals, which have been cited over 13,000 times. Early in his career he was awarded a prestigious New Investigator Career Award by the Animal Behaviour Society. In 2016 he was elected as a Fellow of the Animal Behaviour Society.

The title of Dr. Chivers' presentation was "Cognitive Ecology of Fear in a Changing World." His presentation focused on how ocean acidification, rising sea temperatures, and coral degradation alter prey behaviour and ultimately predation dynamics in coral reef systems. It was well attended by affiliated faculty and Fellows, and NDSU faculty and students in general.