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Nutrient Removal & Recovery Group Newsletter

Nutrient Research Periodical

NEWS

Welcome to the first issue of Nutrient Research Periodical! This biannual newsletter has been developed to inform academic, government and industrial stakeholders about activities of the Nutrient Removal and Recovery Group (NRRG). Including recent events, status of projects, presentations and publications related to nitrogen and phosphorus treatment. The current core of NRRG includes the research labs of **Dr. Wayne Parker** (Waterloo), **Dr. Scott Smith** (Wilfrid Laurier) and **Dr. Hyung-Sool Lee** (Waterloo).

Divided into a number of sections, the newsletter will focus on any funding, upcoming conferences or meetings, past oral or poster papers or book chapters contributed to nutrient presentations and published peer reviewed removal and recovery research by members of our research team. The final section will highlight research being conducted toward the advancement of nutrient removal and recovery by one of our student members. Being the inaugural issue of this newsletter, the content will focus profiling the academic members who founded the Nutrient Removal and Recovery Group and on past contributions to developing nitrogen and phosphorus treatment.

Any inquires as to the features or subscription to the Nutrient Research Periodical can be directed to the editor Holly Gray (contact information can be found on the last page of the newsletter). .

FUNDING

In early 2013 **Wayne Parker** (PI), **Scott Smith** and **Hung Sool Lee** (Co-PIs) received a grant from the Canadian Water Network Canadian Municipal Water Consortium (CWN CMWP) for the project titled *"Integrated Sorption Technologies for Recovery of Nitrogen and Phosphorous from Anaerobic Membrane Bioreactor Permeates*." As suggested by the title, this grant will fund a project using sorbents to remove phosphorus and nitrogen from waste water. The nutrients will then be desorbed to produce a feed stock that is optimized for nutrient recycling.

We would like to acknowledge several industrial partners involved with the above mentioned grant. Our partners include: York Region, Halton Region, Region of Waterloo, Water Environment Research Foundation, GE, Ostara and Conestoga Rovers and Associates.

Updates on this project (to date): The first phase of the project investigates sorbents that are currently commercially available. Samples have been gifted from a number of companies (listed below). Preliminary experiments to screen these sorbents will commence in fall 2013.

Past Funding: Members of NRRG have been involved with nutrient research in wastewater for the past several years and have received past research funding from the following sources:

HIGHLY QUALIFIED PERSONNEL (HQP)

The NRRG includes a large group of students (past and present) with very diverse research projects and goals:

Past members of **Smith's** lab (since 2004) include many undergraduate and graduate research students: **Kelly Fischer, Jim Mathers, Lisa Rabson, Sarah Goertzen, Monique Robichaud, Farah Ateeq, Rebecca Gilmore** and **Mehrnoosh Samini**, These past personnel have gone onto success as scientific writers, entrepreneurs, laboratory technicians and teacher's college. Most recently **Petrease Patton** completed her MSc in spring 2013 on a phosphorus project funded by Conestoga-Rovers & Associates. Petrease is starting medical school in fall 2013.

Current HQP in **Smith's** lab include doctoral student **Holly Gray** (co-supervised with **Wayne Parker**) and BSc student **Scott Robinson**. The focus of Holly's Ph.D. research is to use sorbents for nutrient removal and recovery. During her M.Sc. research in **Smith's** lab Holly also looked at the influence on organic matter and treatment technology on a wide range of samples from actual treatment plants (see research article at the end of this newsletter).

Qiaosi Deng is a master student from University of Waterloo supervised by **Hyung-Sool Lee**. Her most recent research topic is ammonium nitrogen removal and recovery using natural zeolite from permeates of anaerobic membrane bioreactors. Ammonium is one of the most important contaminants impairing the quality of water resource. Biological nitrogen removal systems should spend chemicals for electron donor, while the end product is N_2 gas. To transform nitrogen removal technologies, we have developed a nitrogen-recovering technology using zeolite and air stripping.

Daniela Conidi is a Ph.D. student under the supervision of **Wayne Parker**. The focus of her research is on phosphate uptake in co-precipitation systems targeting low phosphate concentrations. This research is being conducted in collaboration with EnviroSim Associates Ltd. and Environment Canada. Daniela's work includes modeling and characterization of the kinetics and bioavailability of phosphate at ultra low concentrations. .

CONFERENCES & MEETINGS

WEF/IWA Nutrient Removal and Recovery 2013: Trends in Resource Recovery and Use
Vancouver, British Columbia, Canada (July 28 – 31, 2013)

The 2nd Recovery of Value-Added Products Conference to be held at the University of Waterloo Waterloo, Ontario. (Tentative dates: February 17- 21, 2014).

PUBLICATIONS

The following peer reviewed papers and book chapters were published by the Nutrient Removal/Recovery Group to date:

Haddadi S.; Elsayed E.; Lee H.S. (2013). Implication of Diffusion and Significance of Anodic pH in Nitrogen-Recovering Microbial Electrochemical Cells. Bioresource Technology, 142, 562-569.

Gu, A. Z., Liu, L., Onnis-Hayden, A., Smith, D. S., Gray, H., Houweling, D. and Takács, I. Phosphorus fractionation and removal in wastewater treatment – implications for minimizing effluent phosphorus. WERF White Paper, 2013. IN PRESS.

Smith, D. S., and Gray, H. Surface complexation modeling and aluminum mediated phosphorus removal. WERF White Paper. 2013. IN PRESS.

Liu, H., Jeong, J., Gray, H., Smith, S., and Sedlak, D. L. Algal Uptake of Hydrophobic and Hydrophilic Dissolved Organic Nitrogen in Effluent from Biological Nutrient Removal Municipal Wastewater Treatment Systems. Environmental Science & Technology 46, 2 (2012), 713-721.

Erdal, Z. K., Murthy, S. and Smith, D. S. (2011) Nutrient removal: WEF Manual of Practice No. 34. Water Environment Federation, Alexandria, VA, USA, Ch. 7. Chemical Phosphorus Removal, pp 228-275.

Smith, D. S., I. Takács, S. Murthy, G. Diagger, and A. Szabó (2008). Phosphate complexation model and its implications for chemical phosphorus removal. *Water Environment Research* 80, 428–438.

Szabó, A., Takács, I., Murthy, S., Daigger, G., Licskó, I., and Smith, D. S. The significance of design and operational variables in chemical phosphorous removal. *Water Environment Research 80*, 5 (2008), 407-416.

Takács, I., Murthy, S., Smith, D. S., and McGrath, M. Chemical phosphorous removal to extremely low levels: experience of two plants in the Washington, DC area. *Water Science & Technology 53*, 12 (2006), 21-28.

Smith, D. S., and Ferris, F. G. Specific surface chemical interactions between hydrous ferric oxide and iron reducing bacteria determined using pK_a spectra. *J. Coll. Int. Sci. 266* (2003), 60-67.

Smith, D. S., and Ferris, F. G. Proton binding by hydrous ferric oxide and aluminum oxide surfaces interpreted using fully optimized continuous pK_a spectra. *Environ. Sci. Technol. 35* (2001), 4637-4642.

The following refereed conference publications were published by the Nutrient Removal/Recovery Group to date:

Hauduc, H., Takács, I., Smith, D. S., Szabó, A., Murthy, S., Daigger, G. and Sperandio, M. (2013) A Dynamic physicochemical model for chemical phosphorus removal. In: Nutrient removal and recovery (Vancouver, BC, CAN, July 2013, International Water Association (IWA).

Deng, Q.; Dhar, B.; Lee, H.S.. Ammonium nitrogen removal and recovery by natural zeolite. 48th CENTRAL Canadian Symposium on Water Quality Research, Hamilton, ON, Canada, March 6-8, 2013.

Conidi D., W. Parker, D. Houweling, S. Smith, P. Seto, S. Murthy (2011) Phosphate Uptake in CoPrecipitation Systems Targeting Low Phosphate Concentrations, WEFTEC, Los Angeles, CA.

Smith, D. S., Gray, H. and Neethling, J. B. (2011) Surface complexation modeling and aluminum mediated phosphorus removal. Conference Proceedings of Nutrient Recovery and Management 2011, 1162-1174.

Gray, H., Gu, A., Houweling, D. and Smith, D.S. (2011) Molecular variability in wastewater organic matter and implications for phosphorus removal across a range of treatment technologies. Conference Proceedings of Nutrient Recovery and Management 2011, 129-149.

Takács, I., Johnson, B., Smith, D. S., Szabó, A., and Murthy. Chemical P Removal - From lab tests through Model Understanding to Full-Scale Demonstration. In Proceedings of IWA Conference on Design, Operation and Economics of Large Wastewater Treatment Plants (September 2011). Budapest, Hungary

Gilmore, R. L., Murthy, S., Takács, I., and Smith, D. S. Application of a factorial design to study chemically mediated phosphorus removal. In Nutrient Recovery and Management (Miami, FL, USA, January 2011), Water Environment Federation, WEF, pp. 1175-1191.

Liu, L., Smith, D. S., Houweling, J. D., Takacs, I., Neethling, J. B., Stensel, H. D., Murthy, S., Pramanik, A., and Gu, A. Z. Comparison of Phosphorus fraction in effluents from different wastewater treatment processes. In Conference proceedings, 83rd annual water environmental federation technical exhibit and conference (New Orleans, LA, USA, October 2010), Water Environment Federation, WEF

Gilmore, R. L., Goertzen, S., Murthy, S., Takács, I., and Smith, D. S. Chemically mediated phosphorus removal: optimization of analytical methods. In WEFTEC Conference Proceedings (2008), Water Environment Federation, pp. 3756-3774

Smith, D. S., Gilmore, R. L., Szab, A., Takcs, I., Murthy, S., and Diagger, G. Chemically mediated phosphorus removal to low levels: analysis and interpretation of data. In WEFTEC Conference Proceedings (2008), Water Environment Federation, pp. 3558-3574

Smith, D. S., Szab,ó A., Takács, I., Murthy, S., Licskó, I., and Diagger, G. Significance of chemical phosphorus removal theory for engineering practice. In Nutrient Removal 2007: The State of the Art (2007), Water Environment Federation, pp. 1436-1459

Takcs, I., Murthy, S., Smith, D. S., and McGrath, M. Chemical phosphorus removal to extremely low levels - experience of two plants in the Washington, D.C. area. In IWA Specialized Conference Nutrient Management in Wastewater Treatment Process and Recycle Streams (2005), pp. 43-50

Selected Non-refereed Contributions

Takács, I., Johnson, B., Smith, D. S., Szabó, A., and Murthy. Chemical P Removal -From lab tests through Model Understanding to Full-Scale Demonstration. Influents 6 (2011), 62-66.

Gilmore, R. L., Goertzen, S., Murthy, S., Takács, I., and Smith, D. S. Do you see what I see? Two modications to colorimetry analysis can make phosphorus measurements more reliable. Water Environment Laboratory Solutions 15, 5 (2008)

Smith, D. S. Research driven by regulatory needs: metals and nutrients in aquatic systems. Milton Laurier Lecture Series, January 2013. Milton, ON, Canada [Lecture replayed on Milton local cable TV]

Smith, D. S. Advanced principles of chemically mediated phosphorus removal. WEAO specialty conference: Nutrient removal in Ontario WWTPs: future challenges and options, June 2012. Milton, ON, Canada

Smith, D. S. Advanced Principles of Chemical Phosphorus Removal. WORKSHOP W201 - Sustainable Phosphorus Removal to Low Levels: Phosphorus Characterization, Treatment Technologies, and Operations Considerations, October 2012. New Orleans, LA, USA

Smith, D. S., Gilmore, R. L., Gray, H., Goertzen, S., and Robichaud, M. Colorimetric P speciation analysis: long pathlengths and analysis of model compounds. NEMC, August 2011. Seattle, WA, USA

Smith, D. S. Phosphorus chemistry relevant to chemically mediated nutrient removal during wastewater treatment. WERF Nutrient Challenge: Nutrient Stakeholders Meeting, June 2009. Washington, DC, United States

RESEARCH HIGHLIGHT

The following article highlights the recent research conducted by Holly Gray during her Masters program. The research was presented at the Nutrient Recovery and Management Conference 2011. The full paper of the research can be found in the Nutrient Recovery and Management Conference Proceedings 2011 (for citation see above Gray et al., 2011).

Molecular variability in wastewater organic matter and implications for phosphorus removal across a range of treatment technologies.

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Introduction

There is a demand in wastewater treatment for very low levels of phosphorus in wastewater effluents. Eutrophication occurs when large amounts of nutrients are introduced to an aquatic environment and there is an increase algal growth which leads to anoxic conditions. This is detrimental to other organisms in the system (i.e. fish). To prevent eutrophication, total phosphorus concentrations in effluents would need to be on the order of 10s of µg P/L.

There are two types of phosphorus removal in wastewater treatment. (1) Biological removal uses the natural behaviour of microorganisms to remove phosphorus. (2) Chemical removal uses the addition of metal salts to target orthophosphate in wastewater. A possible mechanism of chemical orthophosphate removal was proposed by Smith *et al.* in 2008. Phosphorus removal is species dependent. To achieve low levels of total phosphorus, it is required to remove all chemical forms of phosphorus in wastewater treatment plant effluent. The most refractory phosphorus in terms of removal is so-called "organic phosphorus".

The fluorescence character of wastewater treated through preliminary treatment and primary, secondary and tertiary clarification was the focus of a series of studies (Reynold and Ahmad, 1997; Ahmad and Reynolds, 1999; Reynolds, 2002). These studies found that as wastewaters moved through the treatment process, there was an overall decrease in the intensity of tryptophan-like fluorescence. This decrease was found to be in accordance to the correlating decrease in biological oxygen demand that was also observed. Tryptophan is a dynamic component of DOM in waste water.

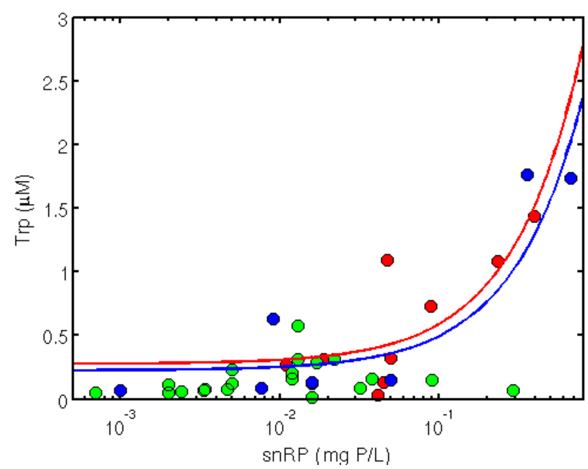
This study represents an effort to probe the relationship between organic phosphorus removal and the molecular nature of dissolved organic matter in wastewater. The results obtained by fluorescence characterization of dissolved organic matter (DOM) in 44 wastewater samples are presented. The samples were collected from 12 wastewater treatment plants and several different technologies, across the United States. Samples within treatment plants at various steps in the treatment process allow the observation of the effects of treatment processes on DOM and phosphorus. PARAllel FACtor analysis (PARAFAC) was used to resolve the fluorescence spectra into three components (humic substances, tyrosine and tryptophan)..

Results and Discussion

Overall, wastewater DOM is highly variable, with variations due to source, as well as within each treatment plant. It was found that proteinaceous fluorophores, tyrosine (Tyr) and tryptophan (Trp), correlate well with nonreactive phosphorus (nRP) removal. The correlation between Trp, or Tyr, and nRP improved with use of biological treatment. In addition to resolving spectral profiles, PARAFAC allows for component concentrations to be determined. This allows for quantitative tracking of fluorescent component concentration variations within and between treatment plants.

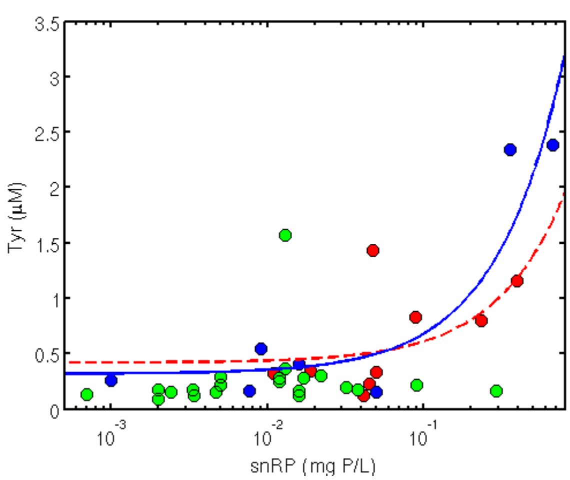
For each sample, using a Pearson Correlation Matrix, the fluorophores were tested for correlations with non-reactive phosphorus. Non-reactive phosphorus is of most interest because this represents the more difficult to remove fraction of total phosphorus. The strongest correlation was found between tryptophan concentration and nRP (Figure 1). Overall, there was a significant relationship between non-reactive phosphorus and tryptophan concentration (r = 0.795, p< 0.01). After organizing the samples into the three different types of wastewater treatment, the relationship between non-reactive phosphorus and tryptophan concentration strengthened for the treatment processes which utilize biological removal. Significant relationships between snRP and Trp concentrations were found for samples obtained from secondary processes (r = 0.801, p< 0.01) and for samples from tertiary biological treatment (r = 0.900, p< 0.01). DOP and Trp correlation coefficients were r=0.790, p = 0.011 for secondary processes, r=0.950, p=0.01 for tertiary treatment with biological removal and r =-0.139, p = 0.516 for tertiary treatment which utilizes physical removal. Observing this correlation, we cannot assume that tryptophan concentrations are directly associated with non-reactive or organic phosphorus. However, it can lead to the reasoning that whichever process in wastewater treatment that is removing tryptophan, may also be removing non-reactive phosphorus.

Figure 1: A plot for the correlation between soluble non-reactive phosphorus (snRP) and tryptophan concentration. with snRP on a logarithmic scale. The red points correspond to secondary treatment, blue points correspond to MBR treatment and the green points correspond to physical removal. Solid lines represent data of statistical significance, while the dashed lines represent data of little statistical significance.



The relationship between non-reactive phosphorus and tyrosine strengthens once the data is organized into the different types of wastewater treatment. Figure 2 depicts the correlation between soluble non-reactive phosphorus (snRP) and Tyrosine (Tyr) fluorophore concentrations. Figure 2 shows Tyr concentration on the y-axis (measured in µmol/L) while snRP concentration is on the x-axis (measured in mg P/L). Again, since the data points are clustered in the bottom left hand corner, Figure 2 shows the same data but with snRP concentration is shown on a log scale. A significant relationship was found between snRP and Tyr concentrations for samples obtained from samples from tertiary biological treatment (*r* = 0.926, *p*< 0.01). Secondary treatment processes with biological removal and physical removal was found to have no correlation between non-reactive phosphorus and tyrosine concentration (*r* = 0.539, *p* = 0.134 and *r* = -0.084, *p* = 0.697, respectively). Dissolved organic phosphorus (DOP) and Tyr correlation coefficients were *r* =0.535, *p* = 0.138 for secondary processes, *r*=0.949, *p*=0.01 for tertiary treatment with biological removal and *r* = 0.026, *p*=0.451 for tertiary treatment which utilizes physical removal. This relationship shows that in wastewater samples from a tertiary biological treatment, when non-reactive phosphorus increases

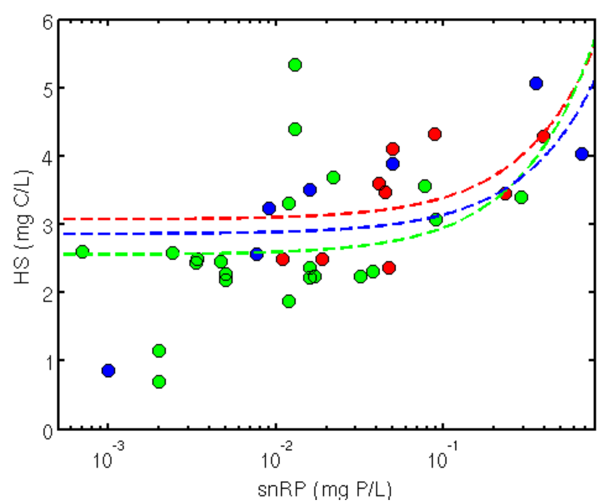
Figure 2: A plot for the correlation between soluble non-reactive phosphorus (snRP) and tyrosine concentration. with snRP on a logarithmic scale. The red points correspond to secondary treatment, blue points correspond to MBR treatment and the green points correspond to physical removal. Solid lines represent data of statistical significance, while the dashed lines represent data of little statistical significance.



there is also an increase in tyrosine. Like the correlations between Trp and snRP, we cannot assume that tyrosine concentrations are directly associated with non-reactive or organic phosphorus.

The correlation between non-reactive phosphorus and humic substances concentration is the last to be presented in Figure 3. Unlike the other two fluorophores, humic substances concentration shows a very weak correlation with an overall R^2 of 0.216 (*r* = 0.464) and *p* < 0.01. As mentioned previously, similar treatment processes have been color coded. Samples from secondary treatment are shown in red, tertiary treatment with biological removal in blue and tertiary treatment using physical removal in green. There were no correlations found between snRP and HS for any of the wastewater treatment plant processes. The correlation coefficients for snRP and HS

Figure 3: A plot for the correlation between soluble non-reactive phosphorus (snRP) and humic substances concentration with snRP on a logarithmic scale. The red points correspond to secondary treatment, blue points correspond to MBR treatment and the green points correspond to physical removal. Dashed lines represent data of little statistical significance.



concentrations were found to be R^2 =0.271with r =0.521, R^2 = 0.304 with r = 0.552 and R^2 = 0.065 with r = 0.256 for secondary treatment, tertiary treatment with biological removal and tertiary treatment with physical removal, respectively (all p values >0.15). The correlation coefficients for DOP and HS concentrations were found to be r =0.486 (p = 0.185), r = 0.607 (p=0.148) and r = 0.344 (p=0.100) for secondary treatment, tertiary treatment with biological removal and tertiary treatment with physical removal, respectively.

Conclusion

Associations between non-reactive phosphorus and the different fluorophores of dissolved organic matter were explored. A correlation was found between snRP and Trp concentrations for secondary treatment (R^2 = .642, r =.801, p<.01) and for tertiary treatment with biological removal (R^2 = .810, r =.900, p<.01). A correlation was also found between snRP and Tyr concentrations for tertiary treatment with biological removal (R^2 = .857, r =.926, p<.01). Wastewater organic matter has variable fluorescent components; water varies in terms of input source as well as within treatment plants. This variability has implications for phosphorus removal. The so-called non-reactive phosphorus (nRP) is defined colorimetrically to include all non-orthophosphate phosphorus. This fraction of total phosphorus tends to be more difficult to remove than orthophosphate. Biological treatment technologies tend to remove nRP to low levels correlated with a decrease in the fluorescent component tryptophan.

Acknowledgements

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Reynolds, D. M. (2002). The differentiation of biodegradable and non-biodegradable dissolved organic matter in wastewaters using fluorescence spectroscopy. *J. Chem. Technol. Biotechnol***. 77**, 965-972.

Reynolds, D. M., Ahmad, R. (1997) Rapid and direct determination of wastewater BOD values using a fluorescence technique. *Wat. Res*. **31**, 2012-2018.

Smith, D. S., I. Takács, S. Murthy, G. Diagger, and A. Szabó (2008). Phosphate complexation model and its implications for chemical phosphorus removal. *Water Environment Research* **80**, 428–438.

Editor's Desk: This newsletter is distributed by the Nutrient Removal & Recovery Group, University of Waterloo and Wilfrid Laurier University. If you know of others who would enjoy this newsletter, or if you no longer wish to receive it yourself, please contact:

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