# INTEGRATE RENEW Newsletter

January 2017

# In this issue



Year 5 of the ORF INTEGRATE Project was completed on September 29-30 2016 with our 5th and last annual meeting. The meeting was attended by 67 people, including members of the Science Advisory Board, the Technical Implementation Committee, and representatives of 5 of our private sector partners. Invited keynote addresses were delivered by Professor Lesley Warren (Lassonde Mining Institute, UofT) and Dr. David Reynolds (Geosyntec Consultants). Students and post-doctoral fellows presented their research in 19 oral presentations and over 20 research poster presentations.

In Year 5, 6 Master's students, 11 PhD students, 1 PDF, and 3 undergraduate students we engaged in the project. However, since inception, we have had a total number of 37 post-docs and graduate students. Our former HQP are consultants and scientists in local (6) and international (3) organizations, 7 of them are pursuing academic careers (faculty positions, post-docs, and research associates), and 4 are engaged in PhD research.

INTEGRATE's contribution to science has been outstanding, with 46 journal articles, 3 book chapters, and 142 conference and guest lecture presentations (41 in Year 5, including 8 at Battelle and 8 more at the AGU in December 2016).

The RENEW Program (NSERC CREATE Program), which was awarded to the INTEGRATE PIs, plus Professors Kent Novakowski (Queen's), Clare Robinson (Western), and Neil Thomson (UWaterloo), has offered an excellent transition and continued opportunity to several of the HQP involved in the INTEGRATE project. So far, 12 HQP have transitioned to the RENEW Program.

Throughout these 5 years, we have had great interest and participation from our industrial partners in the research we conduct, particularly in the development of nanoscale zerovalent iron (NZVI) and the synergy with bioremediation, and the self-sustaining treatment for active remediation (STAR). A new field trial at the Dow Chemical Sarnia site is underway as a collaboration among Dow Chemical, CH2M Hill, Geosyntec, and Western University looking at Electrokinetics (EK) combined with nZVI, bioremediation, Thermally Activated Persulfate (TAP), and permanganate. Once again, a suite of monitoring tools are being applied in order to assess technology effectiveness. These involve comprehensive soil coring and groundwater monitoring for microbial and compound specific isotope analyses (CSIA), and contaminant and by-product concentrations with time.

The full-scale application of STAR at the New Jersey field site is ongoing and will finish in 2018. Savron Smouldering Solutions, a commercial vehicle responsible for STAR commercialization, is still growing, with substantial number of clients outside North America. A new STARx proof of concept trial is currently underway at the site of a major oil company in Southeast Asia. This research and field application has been supported partly through additional leveraging investment with Ontario Centres of Excellence, with a grant awarded to Professor Gerhard and Savron Solutions. There are 9 patents for STAR awarded between Years 1 and 5, including in Japan, Australia, and the European Union.

The transition of these technologies from bench scale tests to ex situ reactors, to pilot field tests, and full-scale application brings unprecedented impact for Ontario in terms of scientific advancement, employment, and economic development.

At the end of this issue, you will find a list of our latest publications, and latest updates.

Enjoy!

# Featured Students

In this issue we feature Gavin Overbeeke and Omneya Elsharnouby. They tied for first place in our 3 minute thesis competition that took place during the 5th INTEGRATE Annual Meeting. Gavin is supervised by Professors Gerhard and Edwards, and Omneya is supervised by Professor O'Carroll, Associate Professor at University of New South Wales and Adjunct at Western University. Gavin and Omneya wrote contributions to this issue.

# Nanometal Technology to Remediate 1,2-DCA

***by Omneya Elsharnouby***

Chlorinated Organic Compounds (COCs) were ubiquitously utilized for a number of industrial applications such as: pesticides, detergents, wood preservation, paint removers, dyes, solvents, and as intermediates in the manufacture of other chemicals. Upon release to the environment, these compounds are persistent over relatively long periods of time due to resistance to natural degradation processes. Due to their preservative nature and possible carcinogenic effects, these compounds have been classified as priority pollutants by the U.S. Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry. One of the most toxic and persistent COCs in the environment is 1,2-Dichloroethane (1,2-DCA). Many technologies have been implemented to remove COCs from soil and groundwater. Chemical reduction by monometallic nano zero valent iron (nZVI) or palladized nZVI (Pd-nZVI) has proven to be successful field applicable technology for the removal of COCs. Their tiny size provides a high surface area for the reaction to take place on (surface mediated reaction), and allows them to be injected in the form of a water slurry directly into the area requiring treatment. The technology relies on a redox reaction, where monometallic nZVI or $H_2$ gas in case of Pd-nZVI (produced for water reduction by nZVI), acts as a reductant (electron donor) stripping chlorines from COCs and reducing them to benign hydrocarbons. Nonetheless, nZVI and Pd-nZVI failed to break down 1,2-DCA. On the other hand, dechlorination of 1,2-DCA utilizing only catalysts and $H_2$ has been proven successful for gas phase reactions. Nonetheless, gas-phase reductive dechlorination is carried out at high temperatures (>200ºC) and uses a direct $H_2$ stream which makes it impractical for in-situ applications. Thus, recently research was directed to applying catalyzed dechlorination technology in the liquid phase. However, literature lacks information on 1,2-DCA catalyzed dechlorination in the liquid phase.

Therefore, the overall objective of my study was to develop a nanometal catalyst based field applicable technology capable of reducing 1,2-DCA in the liquid phase. The research work was divided into three studies. For the first and the second studies, the feasibility of catalyzed dechlorination of 1,2-DCA using borohydride as a $H_2$ source over nano Pd (nPd) and nano copper (nCu) in the liquid phase at room temperature was investigated. Complete removal of 1,2-DCA in a matter of days or hours was achieved by either nPd or nCu particles coupled with borohydride. Unlike the nZVI based technologies, the novel dechlorination system produced mainly ethane as the dechlorination by-product, without formation of toxic chlorinated intermediates. This phase also examined how dechlorination kinetics is influenced by different experimental parameters including: metal loading, 1,2-DCA loading, nanoparticles synthesis parameters, and groundwater solutes. It was found that experimental parameters affect nanometals chemical composition as well as oxidation state, which in turn affect dechlorination rates. For the third study, I assessed the efficiency of the developed novel technology (nPd and nCu) in remediating a suite of COCs, including 1,2-DCA, in a groundwater samples from an industrial site. Results were correlated with dechlorination efficiencies using other nZVI based technologies for the same site groundwater. nZVI, Pd-nZVI, and nZVI-dithionite were able to break down COCs with the exception of 1,2-DCA. nZVI-dithionite was able to break down < 20% of 1,2-DCA. nPd or nCu coupled with borohydride were able to break down 55% and

**FAST FACTS ON INTEGRATE**

**49**
number of scientific publications

**142**
number of conference participations

**41**
HQP (+ 22 undergrads + 3 technical staff)

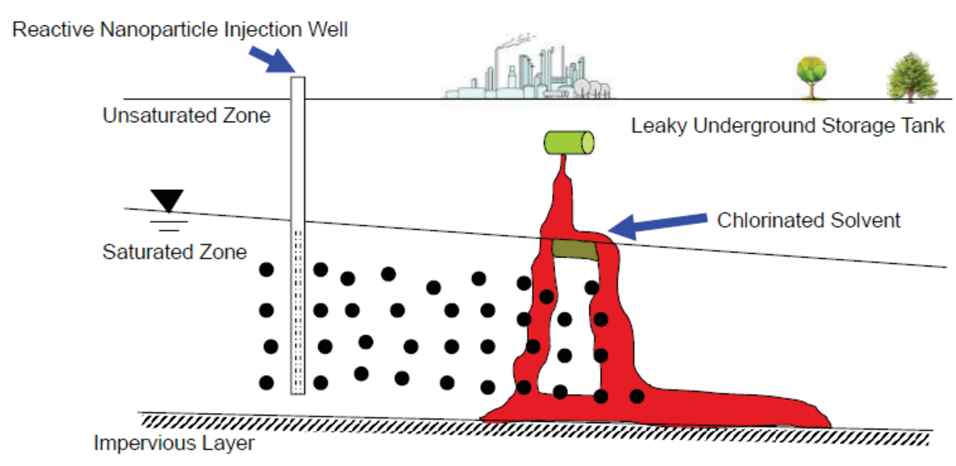



Figure 1: Field injection of nanoparticles, source: Center for Groundwater Research (CGR). 2009, courtesy of Dr. Denis O'Carroll.

Omneya Elsharnouby - PhD Candidate at Western

In 2009, Omneya graduated as a Civil and Environmental Engineer from the Alexandria University, Egypt. Her graduation project was on designing wastewater treatment plant and sewer systems for rural areas. From 2009 to 2012, she worked as a research assistant on various projects focusing on water, municipal wastewater, as well as industrial wastewater treatment plants. In 2012, she joined Western University to work on a biohydrogen production, investigating and categorizing types of pure consortia for biohydrogen production from waste. She was awarded the Ontario Trillium Scholarship later in the same year. In April 2013, Omneya joined the Restore group as a direct entry PhD student researching the development of nanometal based technologies for groundwater remediation from chlorinated organic compounds (COCs) with Professor O'Carroll.

Omneya defended her PhD thesis on the 19th of December, 2016. In her own words: "In the past few years, I was very fortunate to be part of the Integrate/Renew graduate training program and to get a chance to attend and learn from the offered seminars, webinars, annual meetings, and workshops. It has been an exciting journey. This also gave me the opportunity to present my research and meet with different students and professors from various universities, and helped me draw a path for my career. Because of the Renew/Integrate program, I am joyfully anticipating the next chapter of my career as a post doctoral fellow with Professor Mumford's research group."

See more on Omneya's research in the article she wrote for this newsletter.

94%, respectively, of 1,2-DCA along with complete removal of all other COCs.

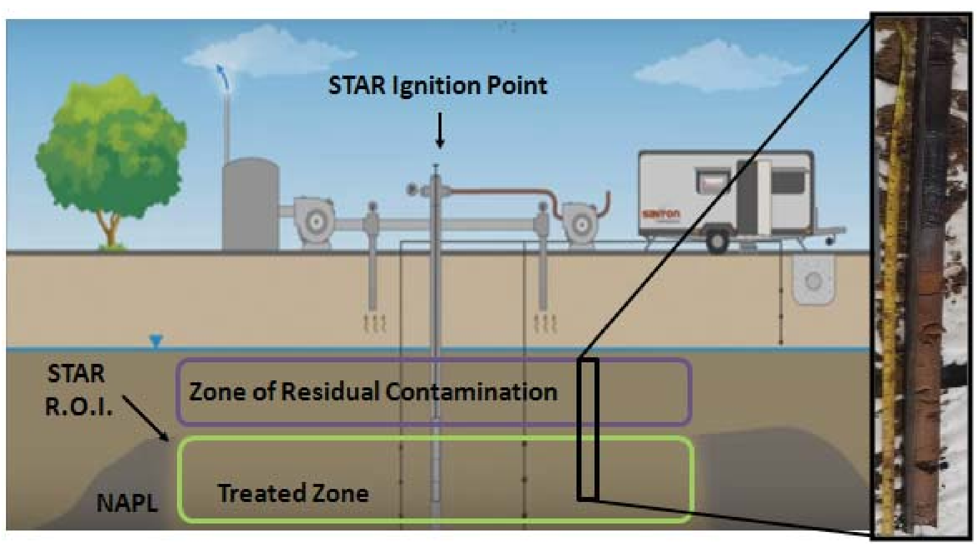
Overall, my research presents a novel nanometal based remediation technology capable of reducing 1,2-DCA. The research results suggest that the developed nanometal based technology can be an effective remediation approach for multi-COCs contaminated groundwater depending upon site conditions.

## The Impact of in situ STAR Treatment on Microbial Populations in the Treatment Zone

***by Gavin Overbeeke***

In situ STAR (Self-sustaining Treatment for Active Remediation) is a novel thermal remediation technology which utilizes smoldering combustion to remove targeted NAPL (Non Aqueous Phase Liquid) pools from the subsurface (Scholes et al. 2015). The STAR smouldering front propagates radially from its ignition well at a rate of 0.5-1 m/day and typically operates at temperatures between 400°C to 1200°C (Pironi et al. 2011; Scholes et al. 2015; Switzer et al. 2009). Thus, it is likely that STAR will sterilize the soil through which it passes. Further, temperatures of these magnitudes are known to remove organic matter, volatilize nutrients and fuse clay, making post-STAR soils harsh environments for microbial life. This has been demonstrated in bench-scale microcosm studies, where inoculated soils which had been previously smouldered exhibited orders of magnitude less recovery than heated (<500°C) and control soils (Pape et al. 2015). However, there are as of yet no studies observing microbial repopulation of STAR treated soil in situ. In situ repopulation has the added advantage of groundwater, which can deliver a relatively constant flux of microbial life to the treated zone, along with organic matter, nutrients and other beneficial compounds. In situ STAR also impacts the soils above the STAR treatment zone. By virtue of their location above the NAPL pool which has been targeted for STAR, these soils are often contaminated with residual blobs of NAPL. Important microbial communities associated with biodegradation of NAPL residuals within these soils may be impacted by STAR indirectly through phenomena such as hot off-gassing, hot contaminant mobilization, boiling groundwater and conductive heat transfer. Considering the effects of STAR on the microorganisms in the treated zone and above it, the objectives of my thesis work are to quantify: (a) in situ microbial repopulation of the STAR-treated zone and (b) the effects of STAR-induced heating on microbial communities above the STAR treatment zone.

To meet these objectives, an 8-month field investigation was carried out in conjunction with a series of column experiments. The field study was performed at a former industrial facility which was heavily contaminated with coal tar. Soil cores were taken from the site 2 months prior to STAR treatment and every 2 months over an 8-month




Cross section showing a typical core section which intersects the treated zone (green outline, red/brown soil in core) and the residually contaminated soil zone above it (purple outline, black soil in core). Samples for this study were taken from both zones and analyzed for total bacteria and microbial community structure both before and at multiple times after STAR. Also shown in this image is the Ignition point from which the STAR reaction propagates radially, consuming the NAPL pool (grey) until it reaches its radius of influence (R.O.I).

Gavin Overbeeke - Master's Student at Western

Gavin Overbeeke is a Masters student in the Department of Civil and Environmental Engineering at Western University, co-supervised by Professors Jason Gerhard and Elizabeth Edwards from UofT. Prior to Western, Gavin finished his undergraduate degree in Earth and Environmental Science at McMaster University, where he wrote his undergraduate thesis as part of a team investigating microbial interactions in a pilot-scale mining waste reclamation project in the Athabasca oil sands. At Western, Gavin now continues to investigate the interactions between microbial life and subsurface remediation. The primary objective of his master's thesis is to quantify the rate of microbial re-population within treated soil zones following in situ STAR. As a secondary objective, his work also seeks to uncover the impacts of STAR on the microorganisms within residually contaminated soil adjacent to the treated soil zone.

See more on Gavin's research in the article he wrote for this newsletter.

period following STAR. In each core, soil samples were taken from both the STAR treated zone and from the residually contaminated soil ~2 ft above the edge of the treated zone. Groundwater samples were also taken from the STAR treatment zone, as well as upgradient and downgradient from it. In all samples, we analyzed for bacterial concentration and microbial community structure, measured respectively via quantitative Polymerase Chain Reaction (qPCR) and Illumina sequencing.

In order to observe the repopulation process in a controlled environment, and to understand the effects of biostimulating amendments on repopulation dynamics, two bench scale column studies were performed. Both experiments consisted of 2 columns, the first packed with untreated and residually contaminated soil from the site (column A) and the other packed with sterile, STAR treated soil, also from the site (Column B). Artificial groundwater (AGW) solution was pumped through column A and into column B, simulating flow of groundwater in typical site conditions. The second column study duplicated the first, but included amendments of sulfate (continuously supplied in the AGW) and lactate (pulsed daily into both columns), evaluating the effects of these amendments on microbial transport and repopulation within STAR treated zones, as well as their effects on the preexisting microbial populations in the residually contaminated soil.

In general, it was found that microorganisms were capable of repopulating the initially sterile and nutrient depleted STAR treated soil, although to lower concentrations (i.e., $10^6$-$10^7$ bacteria/g of soil). However, by adding biostimulants during the column studies, we were able to increase the final bacterial concentrations in STAR soil by an order of magnitude, suggesting that repopulation rates depend heavily on groundwater chemistry, which may be altered to enhance the rate of repopulation. Within the residually contaminated soil above the STAR treated zone, microorganisms which were negatively impacted by heat from STAR rapidly recolonized the soil to very high concentrations (i.e., $10^9$ bacteria/g of soil). It was interesting to note that many of the various microbial genera colonizing these soils are commonly associated with biodegradation on hydrocarbon contaminated sites, suggesting possible biodegradation of residual contaminants at this site also. Overall, results from this study suggest that the complete or partial sterilization events caused by STAR on the microbial communities in and above the treatment zone are reversible within a reasonable time-frame.

References: [1] Pape et al. 2015. Geoderma 243, 1-9. [2] Pironi, et al. 2011. ES&T 45, 2980-2986. [3] Scholes, et al. 2015. ES&T 49, 14334-14342. [4] Switzer et al. 2009. ES&T 43, 5871-5877.

# Updated Publications

Our latest publications are:

1. Gerhard, J.I. 2016. Smouldering Remediation. Online Textbook "*Remediapedia*". Environmental Restoration Wiki, A SERDP/ESTCP program initiative.

2. Kinsman, L., J. I. Gerhard, and J. L. Torero. 2016. Smoldering remediation and non-aqueous phase liquid mobility. *Journal of Hazardous Materials*, 325, 101-112. doi: /10.1016/j.jhazmat.2016.11.049

3. Molnar, I.L., P.C. Sanematsu, J.I. Gerhard, C.S. Willson, and D.M. O'Carroll, 2016. Quantified Pore-Scale Nanoparticle Transport in Porous Media and the Implications for Colloid Filtration Theory, *Langmuir*, 32 (31), pp 7841–7853. doi: 10.1021/acs.langmuir.6b01233

4. Koenig, J., H.K. Boparai, M. Lee, D.M. O'Carroll, R.J. Barnes and M. J. Manefield. 2016. Particles and enzymes: Combining nanoscale zero valent iron and organochlorine respiring bacteria for the detoxification of chloroethane mixtures. *J. Hazardous Materials*. Volume 308, 106–112

# Other Updates

On November 24th 2016, 50 students from UofT, UWaterloo and Western attended the second Geosyntec workshop organized by Julie Konzuk of Geosyntec. The event took place at the Delta Hotel and Convention Centre in Guelph, Ontario. We would like to thank Julie and all speakers from Geosyntec that took their time to provide our students with insights into the consulting world, and soil and groundwater remediation. We would also like to thank the whole staff at the Geosyntec office in Guelph for taking the time to network and have lunch with our students that day. After lunch, students went on a tour of the SiREM labs.

Congratulations to Nicole Soucy for her Master's defense at Queen's University and to Omneya Elsharnouby for her PhD defense at Western University.

A reminder about our RENEW Soft Skills workshop that will take place at UofT on February 22nd and 23rd. Participation is by invitation only, and program and agenda will be sent to all in January 2017.

If you would like to write a contribution to our newsletter, please contact us by e-mail (glaucia.lima@utoronto.ca) with your proposed text. We prioritize students and post-docs, but all are welcome to contribute.

## Acknowledgements

We would like to thank Omneya and Gavin for their contributions to this issue.

Integrate

RENEW

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**For questions and inquiries:**
Gláucia Lima
glaucia.lima@utoronto.ca
**Department of Civil Engineering**
**University of Toronto**
35 St. George St. | Tel: 416-978-4396
Toronto | ON | M5S 1A4
www.integrate.utoronto.ca
www.renew.utoronto.ca

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