Field site application of STAR showing ignition/air injection well, thermocouple monitoring network, vapor extraction system, and STAR control trailer. Courtesy Laura Kinsman - SAVRON Solutions.

INTEGRATE RENEW Newsletter

September 2016

In this issue

As we prepare for the INTEGRATE and RENEW annual meetings, we bring you another issue of our newsletter.

This issue has contributions from Fan Yang, Bruce Xu and Laura Kinsman, Fan was in the RENEW program and graduated this past June. He talks about his training experience leading him to become a consultant in numerical modelling. Laura was part of the INTEGRATE project and she graduated in 2015. She is working in an environmental consulting company. And Bruce is on his final steps to graduate from his PhD.

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

Enjoy!

Featured Student

This issue features Bruce Xu, PhD candidate working with Professors Brent Sleep and Barbara Sherwood Lollar.

STAR: From the Lab to the Field

by Laura Kinsman

I started working on research associated with Self-sustaining Treatment for Active Remediation (STAR) as an undergraduate summer student. STAR is an innovative remediation technology based on the principles of smouldering combustion, which has demonstrated success for rapid destruction of source zone contaminants. In smouldering remediation, the contaminant provides the fuel that supports its own destruction. Following a short duration input of heat to support ignition, the process is sustained through a continuous supply of air. The energy released from the smouldering reaction is used to preheat and initiate combustion in adjacent contaminated regions, thereby propagating a self-sustaining combustion front through the contaminated zone. STAR technology development, scale-up, technology transfer and commercialization is one of the major deliverables of the INTEGRATE project.

The expanding applications of STAR technology, both ex-situ and in-situ, have highlighted the importance of laboratory studies for understanding key processes that occur during remediation. During my Master's research at Western, I conducted laboratory column experiments, in combination with numerical and analytical modelling. This work revealed that contaminant migration during smouldering can occur and is dependent on three inter-related conditions: process air flux, viscosity of the contaminant in the preheating zone ahead of the smouldering front and the length of the preheating zone. It was found that contaminant migration can influence smouldering metrics important for large scale design considerations (e.g. highly elevated peak temperatures). My work also demonstrated the robust nature of the smouldering process, with the smouldering front adjusting to accommodate the influx of migrating contaminants and resulting in complete remediation under a range of conditions.

I also used column experiments to investigate the transport and fate of aerosols and condensable compounds in the emissions generated from smouldering of a range of contaminant types under a range of operating conditions (e.g. process air flux, moisture content, etc.). Based on experimental results, the relative proportion of combustion to volatilization is expected to be a function of fuel type and may be controlled to an extent through the manipulation of operational parameters such as moisture content (can be controlled in ex-situ systems) and process air flux. An understanding of the composition and fate of compounds in the emissions stream becomes particularly important for highly volatile contaminants where the relative proportion of volatile compounds in the emissions is likely to increase. While highly volatile contaminants cannot smoulder on their own, they have been shown in the laboratory to be treatable by smouldering when emulsified vegetable oil is added to the soil (Salman et al., 2015). The integration of the work of this previous INTEGRATE student and my own has paved the way for testing EVO injection and smouldering in the field.

In 2015 I graduated and became a remediation engineer with Savron, the technology vendor delivering STAR technology to the marketplace. As one of my first responsibilities, I had a major role in the first in-situ field application of a EVO-supported combustion of Gasoline Range Organic (GRO) and Diesel Range Organic (DRO) compounds at a former refinery in Michigan (Cover picture). Both a "standard" STAR and "EVO-enhanced" STAR test were completed at the site to evaluate the ability of EVO to support combustion of these high volatility compounds.

These two Pre-Design Evaluation (PDE) tests demonstrated that successful injection and combustion of EVO resulted in a more robust smouldering reaction, with a treatment zone radius of influence (ROI) and thickness of 10 ft and 4-6 ft, respectively, as compared to 5 ft and 1-2 ft, respectively, in the "standard" STAR test. Total Petroleum Hydrocarbon (TPH) concentration reductions of greater than 90% were achieved in the target treatment zone, with visual evidence of this treatment shown in the figure below.

In the "EVO-enhanced" test, approximately 1500 kg of petroleum hydrocarbons were removed from the treatment zone, with approximately 20% of this mass destroyed via combustion and 80% volatilized and subsequently captured and treated at surface in the vapor extraction system. This ratio of mass destroyed versus volatilized is strongly a function of contaminant type and the ratios and fate of these compounds can be better understood through laboratory experiments, as described previously. This PDE provided demonstrated success at the pilot scale of the use of a surrogate fuel to aid in smouldering of contaminants that would typically be too volatile to achieve a self-sustaining reaction. This expands the range of sites that may be amenable to STAR remediation, increasing its market potential and opportunities. It represents one of a number of successful examples of how INTEGRATE research has helped develop and transfer technology from the bench to the field, supporting the 'technology development pipeline'. It also demonstrates how INTEGRATE's graduate training is leading to environmental engineering jobs based in Ontario that are making a difference. It has been an exciting journey and things are only looking up.

Figure 2 - Pre-STAR soil core from within the target treatment zone (top) and corresponding post-STAR soil core (bottom). Courtesy - Laura Kinsman.

Modelling Isotope Fractionation During Diffusion

by Bruce Xu

Stable isotope fractionation has recently received widespread attention due to its potential to be an indicator of intrinsic bioremediation and to estimate the extent of biodegradation. Many researchers have measured carbon isotopic fractionation (i.e. change in heavy/light isotope ratios) during the biodegradation of petroleum hydrocarbons and chlorinated solvents in samples from both laboratory and field settings. This phenomenon is attributed to the preferential degradation of light isotope bonds versus heavy isotope bonds, which results in isotopic enrichment of heavy isotopes in the residual compounds. Isotope fractionation can be measured through the technology of Compound Specific Isotope Analysis (CSIA) which is recognized as a novel and powerful tool for monitoring intrinsic biodegradation of organic contaminants in the subsurface.

Aqueous phase diffusion is an important natural attenuation process that can dominate contaminant transport under a range of hydrogeological conditions. Molecules containing exclusively light isotopes diffuse slightly faster compared to the same compound molecules containing a heavy isotope, resulting in the potential for heavy isotopes to be

Bruce Xu - PhD Candidate at UofT

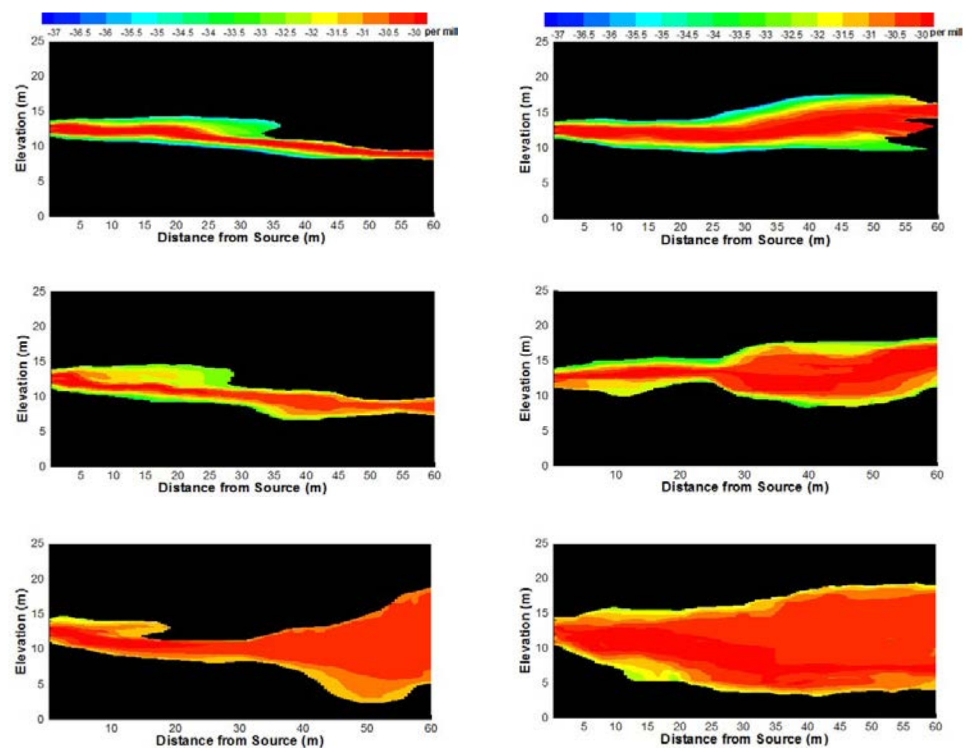
Bruce is a Ph.D. student under the co-supervision of Professor Brent Sleep in the Department of Civil Engineering at University of Toronto and Professor Barbara Sherwood Lollar in Earth Sciences at the University of Toronto. He completed his M.A.Sc. degree under Dr. Sleep's supervision in 2008. His master's study focused on the modeling of volatile organic compounds (VOC) transport and bioremediation in the subsurface. Currently, he is investigating stable carbon isotope fractionation effects induced by aqueous phase diffusion and biodegradation during subsurface transport using modelling approaches. His thesis title is Aqueous Phase Diffusion Related Isotope Fractionation (DRIF) in Groundwater Systems. In this thesis, the factors impacting the observation of DRIF are fully investigated.

His interests are also in isotopic effects associated with other non-degradative processes including volatilization, gas-phase diffusion and sorption. Recently, he has also been conducting some field scale simulations to study the non-aqueous phase liquid (NAPL) migration and distribution in the subsurface using real field data collected from Arcadis Canada.

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

depleted at the diffusion front during diffusive transport. This indicates that aqueous phase diffusion also has the potential to cause isotope fractionation, and consequently, may complicate CSIA analysis and lead to misinterpretation of the extent of biodegradation. Therefore, it is important to characterize and quantify aqueous phase diffusion related isotope fractionation (DRIF) during transport of different contaminants under different soil and groundwater conditions. In this way, one can determine whether or not isotopic changes in systems in which intrinsic biodegradation is occurring are significantly affected by aqueous phase diffusion process.

DRIF for stable carbon isotopes was investigated for common groundwater contaminants through modelling to determine under what conditions DRIF effects would be observable. The simulation results propose a critical dispersive enrichment factor of (−0.32‰), above which the isotope fractionation due to different dispersion coefficients of light and heavy isotopologues may be significant. This study also reveals that the key factors constraining the observation of DRIF include the ratio of macrodispersion coefficient to effective diffusion coefficient (λv/Deff), the ratio of initial contaminant concentration to the method detection limit for isotope analysis (C0/MDL), the diffusive fractionation factor, the presence of low-permeability zones, local scale compound specific transverse mechanical dispersion, soil heterogeneity, sampling method and occurrence of biodegradation. This study provides important constraints on the conditions that would merit close investigation of carbon isotope DRIF effects. These conditions include compounds with smaller molar masses (e.g., vinyl chloride or benzene) which can lead to larger diffusive fractionation factors (father from unity) and sites with high C0/MDL ratios (i.e. > 50), low λv/Deff ratios (i.e. < 10), low soil heterogeneity and lack of intrinsic biodegradation. However, in this case the plume thickness is relatively small. Even under these conditions, very closely spaced wells and frequent sampling would be required to detect DRIF due to the small distances at the plume front over which DRIF might be significant. Conventional sampling methods would effectively reduce DRIF effects by mixing the groundwater along the screen during the sampling. If low-permeability zones are present in the subsurface, DRIF is theoretically observable only in thin aquifers with thicknesses on the order of 0.5 m bounded by thick (e.g., meters) aquitards due to the preferential diffusion of light isotopologues into the bounding aquitards. Carbon isotopic fractionation associated with back diffusion from aquitards would not be observable regardless of aquifer thickness. Therefore, this study concludes that where CSIA data are used as a line of evidence for biodegradation, in most cases DRIF effects are unlikely to be a major complicating factor.



DRIF effects in the groundwater systems with different soil heterogeneities. Courtesy: Bruce Xu

How an Internship Changed My Career Goals

Interview with Fan Yang

Fan Yang obtained his Master's degree from Queen's University in 2016 and started a career as a numerical modeler at Aquanty Inc. He says: "I was very fortunate to become a member of the Remediation Education Network (RENEW). Based on my personal experience, RENEW is a well-designed program, and offers great opportunities for field training, professional development, and networking with other professionals in subsurface science." Fan is the first RENEW student to start a consulting career right after graduation.

All RENEW students are encouraged to obtain field training exposure, and Fan did this through the course Field Methods in the Hydrogeology of Fractured Rock. At Queen's University. This course is the only one in Canada that is specialized in field methods applied to fractured rock environments. The course was taught jointly by Professor Kent Novakowski, Professor Geoff Hall, and Professor Peter Pehme. During the course, students gain hands on experiences with various geophysics tools, hydraulic testing equipment, and several of drilling methods. The lessons from CIVL 884 had a significant influence on Fan's understanding of fractured rock hydrogeology, and it is certainly one of the most valuable experiences that he had from the RENEW program.

In Sept 2014, Fan presented his research at the SyNRGS conference at University of Toronto. He says: "This was a fantastic opportunity for me to expose to the world of research and meet researchers from the universities across Ontario. It was also my first time presenting in front of a public audience." He was happy with comments received from Professors Brent Sleep and Kevin Mumford, two of his academic role models. "This recognition significantly encouraged me and helped me advancing further. At the conference, I also met Bruce Xu who gave me a significant amount of support during the past two years."

Of his internship, Fan says that he spent "a very pleasant 6 months with the modeling team at Geofirma Engineering. I was quite fortunate to have Dr. Robert Walsh as my internship supervisor. During the internship, Dr. Walsh had always shared his knowledge and tried to bring educational value to my work. During this time, I have developed great interests in numerical modeling. When I look back, the influence from Dr. Walsh might be the main reason behind my modeling career."

Fan says that the success he has experienced so far "would not be possible without the supports from my thesis supervisor Dr. Novakowski and the RENEW program."

Updated Publications

From Years 1 to 4, our contribution to the science and engineering of groundwater remediation has included 47 articles in international refereed journals, 2 book chapters, and 134 conference presentations (28 of these in Year 5).

Our latest journal publication is:
Kocur, C. M. D., Lomheim, L., Molenda, O., Weber, K. P., Austrins, L. M., Sleep, B. E., Boparai, H. K., Edwards, E. A.. O'Carroll, D. M. 2016. Long term field study of microbial community and dechlorinating activity following carboxymethyl cellulose-stabilized nanoscale zero valent iron injection. *Environ. Sci. Technol.*, 2016, 50 (14), pp 7658–7670, DOI: 10.1021/acs.est.6b01745.

Other Updates

Congratulations to Bruce Xu and Ahmed Chowdhury, both completed their PhD thesis and will soon defend them, at UofT and at Western, respectively.

A reminder about our Fifth Integrate and Third Renew Annual meetings that will take place at the Seeley Hall, Trinity College of the University of Toronto, on September 29th and 30th 2016.

We are accepting submissions to the 3 minute thesis (3MT) presentations that will take place during the lunch break on September 30th, We encourage all students in graduate programs in the four participating universities to participate in the competition. Details will be posted on the RENEW and Integrate Websites.

We would like to congratulate Professor Barbara Sherwood-Lollar on being named a Companion of the Order of Canada this past June 2016.

If you would like to write a contribution to our newsletter, please contact us by email (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 Laura Kinsman, Bruce Xu and Fan Yang for their contribution to this issue.

FAST FACTS

47
number of scientific publications

134
number of conference participations

40
HQP (+ 19 undergrads + 3 technical staff)

Integrate RENEW Newsletter

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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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