Natural Attenuation of Metals, Radionuclides, and Co-Contaminants at the Oak Ridge IFC

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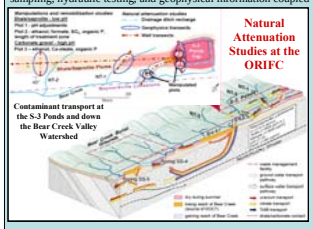
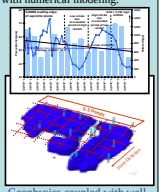
Introduction

Objective: Quantify rates and mechanisms of coupled processes that control natural attenuation of U, Tc, and nitrate along contaminant pathways and transition zones at the Oak Ridge Field Research Center (ORFRC) utilizing a series of novel tracer tests, isotopes, well sampling, hydraulic testing, and geophysical information coupled with numerical modeling.





Geophysics coupled with well data will be used to image transient recharge conditions

Hypotheses: 1) The master variable for U, and possibly Tc, attenuation is pH. Aluminum hydrolysis and the presence of carbonates are the dominant pH buffering reactions impacting U and Tc precipitation and adsorption. 2) Microbial denitrification is the primary mechanism for decreasing NO_3^- flux, where the denitrification rate is governed by pH and electron donor concentration. 3) Recharge during episodic and seasonal precipitation events is the driver of groundwater flux and impacts diffusion, advection, dilution, and delivery of oxygen, dissolved organic carbon (DOC) and higher pH water, which influences coupled geochemical and microbial processes and contaminant migration.

Research Tasks:

Quantify attenuation processes along shale and carbonate pathways:

1) Install well transects at transition zones, conduct watershed sampling, and hydraulic and geophysical testing to define flowpaths.

2) Mass balance analysis of U, Tc, NO_3^- and other natural reactive and nonreactive tracers (e.g., Cl^-, Al, Si, Fe, Mn, Ca, Mg, SO_4^{-2}, CO_3^{-2}) will be used to help understand sorption dynamics and coprecipitation processes along pathways.

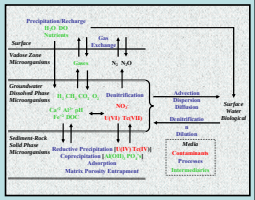
3) Assess N_2/Ar and isotopic composition of nitrate and/or donors ($^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{2}H/^{1}H$, and $^{13}C/^{12}C$) in gas and aqueous phase as bioindicator of denitrification

4) Tracer tests with injected conservative and reactive tracers

5) Spectroscopic and mineralogical studies

7) Microbiological studies

8) Numerical modeling



Assess hydrobiogeochemical impacts of recharge

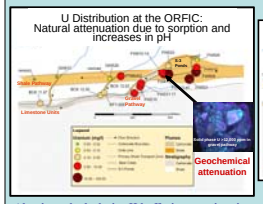
1) Install and monitor well clusters near drainage ditch and areas with wooded natural setting

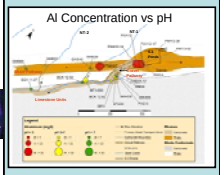
2) Time series geophysics to assess plume dynamics and develop algorithms and new tools for monitoring and assessing natural attenuation

3) Divert flow in drainage ditch and monitor impact on recharge and contaminant migration

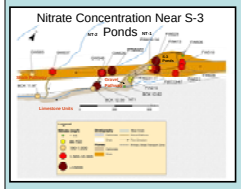
Watershed Investigations

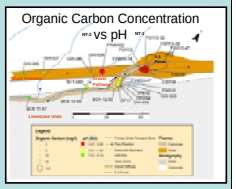
Overview: Extensive sampling is being conducted across the Bear Creek Valley Watershed to assess natural attenuation processes. We are tracking changes in gas concentrations (e.g., N_2/Ar), aqueous phase conservative natural tracers (e.g., Cl from the waste source) and changes in the isotopic composition of water, nitrate and organic carbon electron donors ($^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{2}H/^{1}H$, and $^{13}C/^{12}C$) to help quantify the dominant natural attenuation processes active at the site. As expected pH, contaminant concentration, and recharge/dilution impact these measurements. Contaminant levels appear to have a significant impact on microbial populations and diversity determined from samples taken concurrently with the geochemical and isotope samples.



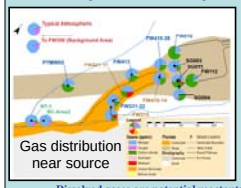


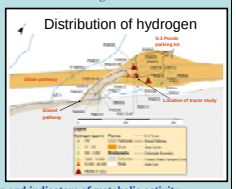
Aluminum hydrolysis pH buffering reactions impact U and Tc precipitation and adsorption





pH and electron donor presence controls nitrate degradation



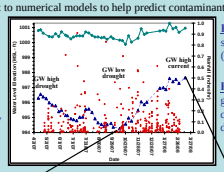


Dissolved gases are potential reactants and indicators of metabolic activity

Watershed Hydrology/Recharge

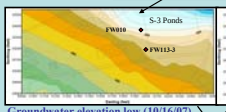
Water level monitoring is being conducted in the watershed to identify changes in groundwater flow patterns and areas of preferential recharge like the drainage ditch and gravel fill. This information is being input to numerical models to help predict contaminant fate and transport.

Note: Groundwater levels observed in 2008 are already significantly higher than the highest levels observed during drought conditions in 2007



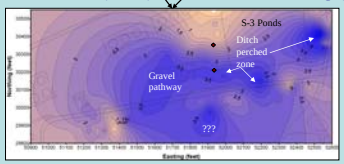
FW010 shows less seasonal change (Area 3 north)

FW113-3 shows greater seasonal change from drainage ditch (Area 3 south)



Groundwater elevation low (10/16/07)

Groundwater elevation high (03/14/08)



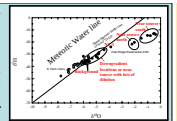
Rise in water level (difference between high and low) indicates areas of greatest recharge?

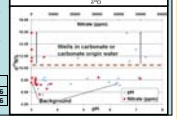
Isotope Studies

The **δ^2H & $\delta^{18}O$ values** of wells near the S-3 Ponds differ significantly from river waters in this region and the meteoric water line. The trend can be **best explained by evaporation from standing water in the S-3 ponds** before capping. Downgradient wells appear to be a mixture of the evaporated water from S-3 ponds and local groundwater. The measured **δ^2H values of H_2 gas** is perhaps the strongest **indication** to date for their **radiolytic origin**. The **$\delta^{13}C$ and δ^2H values of CH_4** and **$\delta^{13}C$ values of CO_2** gases are consistent with **microbial origins**, either acetate fermentation or CO_2 reduction. The elevated **$\delta^{15}N$ values of NO_3 in** wells screened in high pH **carbonate wells suggests microbial degradation** of NO_3 is active in this environment.

Sample	$CO_{2\ ppm}$	$\delta^{13}C\ CO_2$	$CH_{4\ ppm}$	$\delta^{13}C\ CH_4$	$\delta^{2}H\ CH_4$	$H_{2\ ppm}$	$\delta^{2}H\ H_2$
PTMW02	465513	-6.8	1701	-55.3	-184	141	-586
FW106	700844	-21.7	545	-60.0	-312	497	-536

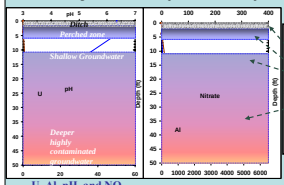
Can isotope data provided by Dr. Sherwood-Lollar of the University of Toronto



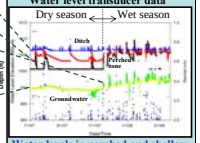


Drainage Ditch Recharge Dynamics

The unlined drainage ditch that surrounds the S-3 Ponds is a source of preferential recharge and provides an excellent opportunity to study the impacts of recharge on contaminant migration. A perched zone exists intermittently beneath the drainage ditch in fill 1–2 m thick. The perched zone has high dissolved oxygen (DO), a pH of 6.5, U (1.0 ppm) and nitrate (<200 ppm). As this high pH and DO perched water migrates down, it mixes and reacts with the lower pH highly contaminated groundwater in deeper zones and a U-pH inverse relationship is observed.

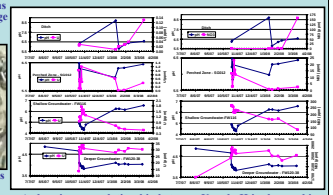


U, Al, pH, and NO_3 groundwater concentrations with depth near the drainage ditch



Water levels in perched and shallow groundwater zones are much more responsive to storms in wet season

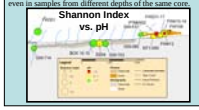
Location of monitoring wells near drainage ditch

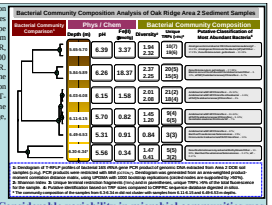


A clear inverse relationship between U and pH is observed in some zones as a result of infiltration and recharge

Microbial Communities

Contaminant levels appear to have a significant impact on microbial populations and diversity determined from samples taken concurrently with the geochemical and isotope watershed samples. Genomic DNAs were isolated from groundwater, purified, amplified with primers 27F and 1492R, and cloned to produce 16S rRNA gene libraries. Over 4000 clones were sequenced, and data was analyzed using DOTUR. GeoChip analysis has also been conducted to determine the impact of nitrate, metal and radionuclide contamination on functional gene diversity. Preliminary results show that T-RFLP fingerprints are highly reproducible in samples from the same core depth, while depth-related variability can be large, even in samples from different depths of the same core.





Considerable variability in microbial communities was observed over a meter core in an Area 2 borehole

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