INTRODUCTION

Chalk River Field Camp

This field camp, held in and around Deep River and the Chalk River Laboratories (CRL) of Atomic Energy Canada Limited (AECL), will concentrate on the hydrogeology and biogeochemistry of natural waters in the region. The purpose of the camp is to teach students how to measure and interpret a wide range of processes that occur in wetlands, streams, lakes, and near-surface groundwaters. This will involve construction of a regional groundwater flow model, measurement of greenhouse gas (methane, CH_4; carbon dioxide, CO_2) concentrations in wetland sediments, and evaluation of the steady state chemical composition of a small lake. Students will also meet with AECL personnel, learn about their work, and tour the CRL site.

Days will be spent on field exercises. Lectures, laboratory, work and computer exercises will be done in the evenings. Bring clothing to suit a wide possible range of weather conditions - heat, cold, rain; Rain gear, comfortable work or hiking boots, knee-high rubber boots, hat, sunscreen and insect repellent, field notebooks, calculator, and writing materials. Students must bring their own towels.

Organization and Course Requirements

The course is divided into four major units:

1. Tour of Chalk River Laboratories and orientation.

2. Measurement and mapping hydraulic head to assess groundwater flow patterns.

3. Field sampling techniques and gas chromatography to interpret dissolved methane (a potent greenhouse gas) concentrations in wetlands.

4. Analysis of aqueous chemistry and steady state chemical composition of a small lake.

The grading scheme for the course is as follows:

Groundwater flow	25
Methane concentration	25
Lake chemistry	25
Field notes	15
Participation	10

BACKGROUND INFORMATION

Regional Setting

The village of Deep River and the Chalk River Nuclear (CRL) of Atomic Energy Canada Limited are located on the south bank of the Ottawa River, approximately 180 km northwest of Ottawa. The river in this area lies in a graben, or rift valley; the Quebec (northern) bank of the river is one of the major bounding faults of the Ottawa valley, and features up to 300 m of topographical relief. The southern Ontario bank of the river constitutes part of the floor of the rift valley. Relief is much more subdued with topographic highs less than 100 m above the river, which lies at a nominal 112 m above mean sea level (asl). Graben-associated faults and river terraces on the CRL site give a west-northwest to east-southeast trend to the local topography. Within the site, the major features are the Maskinonge-Chalk Lake valley which trends subparallel to the Ottawa River, and the ridge dividing the two.

The climate of the Deep River-Chalk River area is generally classified as humid continental, with warm summers and cold winters. Mean monthly air temperatures range from a low of -12^o C in January to a July high of 19^o C. Precipitation is distrubuted evenly throughout the year; meterological data collected on the CRL site over a 23 year period yields an average annual precipitation of 827 mm. Studies of the water budget in the area have shown that approximately 37 percent of the precipitation contributes to groundwater recharge or runoff. The remainder is returned directly to the atmosphere by evapotranspiration. Almost all of the groundwater recharge occurs during and just after the spring snowmelt. During summer months, evapotranspiration results in soil moisture deficits.

The Ottawa River is the predominant drainage feature in the Deep River-Chalk River area with a mean annual flow of approximately 2.2×10^{10} cubic metres. Only a small region to the north of the Mattawa Road on the CRL property drains directly into the river. Most of the area drains into either the Perch Lake basin on the southern perimeter of the property, or into the Maskinonge Lake basin to the west. Discharge from Perch lake averages 2.0×10^6 cubic metres per year, whereas discharge from Maskinonge Lake is in the order of 4.0×10^6 cubic metres per year.

Surficial Geology

Deep River and the CRL lie within the Grenville Province of the Canadian Shield. Bedrock in the area is Precambrian in age, and consists mostly of faulted and fractured monzonitic granite gneiss. There are three dominant sets of large-scale lineament features in the area. These lineaments are interpreted to be fault zone traces, and have trends of N20^o - 30^o, and N150^o - 160^o. The latter are the most prominent and appear to be associated with the formation of the rift valley. Surface topology in the area is strongly controlled by the relief of bedrock, but it is only exposed over about 10 percent of the region.

A suite of unconsolidated sediments of late-glacial and post-glacial origin overlie the bedrock in the Deep River area. Most of the bedrock is covered by a mantle of bouldery silty sand till which, in some areas, occurs as two separate units separated by thin strata of clay. Many portions of the site at elevations below 150 m (asl) are covered by fluvial sands deposited by the Ottawa River between 6,000 and 11,200 years before present (BP) when the precursors of the Great Lakes drained through the Mattawa and Ottawa Rivers. There are some exposures of fluvial sands and gravel that frequently grade into washed till.

In some areas, the fluvial sands have been reworked by wind into sheet deposits of aeolian sand, 1 to 5 m or more in thickness. These large sand dunes provide the terrain with the greatest thickness of unsaturated sediments. The only other type of surfical material that is present in appreciable amounts are actively accumulating organic sediments in wetlands. There are no significant exposures of low permeability clays or silts on the CRL site.

Hydrology and Chemistry of Natural Waters

The world's oceans contain approximately 80 percent of the water comprising the hydrosphere. Of the remainder, 19 percent is in porous geological media underground, 1 percent is trapped in ice, 0.002 percent is in lakes, streams, and wetlands, and 0.0008 percent resides in the atmosphere. Although the amount of water in lakes and streams constitutes only a small portion of the hydrosphere, the rate at which water circulates through these reservoirs is quite rapid. On a yearly basis, the amount of water that is discharged from rivers into the sea approaches the total water content of lakes and streams (ca. 36000 billion tonnes). About three times this amount are returned each year from the atmosphere to land by precipitation (in the form of rainfall or snow). This movement of water through different environments is described by the hydrological cycle.

Natural waters acquire their chemical characteristics through interactions with a variety of solids, liquids, and gases that they come into contact with during the hydrological cycle. As such, water chemistry tends to be highly variable; however, these variations can be interpreted reasonably if the environmental history of the water and corresponding chemical reactions in the water-rock-atmosphere system are considered. A very general mass balance equation showing the sources from which dissolved constituents of water may be derived can be formulated as follows:

$$Rock\ +\ Atmospheric\ Inputs\ =\ Altered\ Rock\ +\ Solution$$

In this scenario, the atmospheric input consists minimally of water, carbon dioxide, oxygen, and various other species in the atmosphere (e.g., nitrogen and sulfur compounds). Hence, the chemical composition of precipitation itself is quite variable. On the other hand, regional geology determines rock mineralogy and erosional regieme. These two factors, in combination with climate, effectively control rates of physical, chemical, and biological weathering (i.e., disintergration and dissolution of minerals in rocks). If the effects of extreme evaporation are ignored, the highest concentrations of dissolved mineral matter generally occurs in water draining evaporite deposits, whereas waters that drain limestone are more concentrated than those draining silicate rocks (e.g., granites, basalts). In any event, the amount of material derived from atmospheric inputs is usually small in comparison to the amount derived from water-rock interactions.

When water is transferred from the atmosphere to the Earth's surface, a number of things can happen to it. Some will remain on vegetation as droplets or pool on the ground and evaporate soon after the precipitation ends. Some of the water will infiltrate into the soil (if there is any) where it may be taken-up by the roots of plants, only to be returned to the atmosphere through leaves in a process called transpiration. Water that is not removed from the soil by plants tends to percolate downwards, and then migrates laterally as groundwater. If the preciptiation event is extremely heavy or too prolonged for infiltration to accommodate all of the water, some will flow on the surface as runoff.

As water comes into contact with the ground, its chemistry undergoes drastic changes. When the water initially migrates through the soil zone, it acquires solutes mainly through the dissolution of minerals. Degradation of plant (and to a lesser degree animal) organic matter by microorganisms provides additional soluble compounds to the water, notably low molecular weight organics as well as nitrogen and phosphorus compounds. Microbial activity can accelerate the breakdown of minerals, particularly through the generation of organic (e.g., acetic acid) and inoranic acids (carbonic acid).

At some depth underground, water leaves the soil zone and enters the groundwater system. The water table represents a surface that divides geological media in which the pores are completely filled with water (i.e., phreatic or saturated zone) from those in which the pores are partially filled with air (i.e., vadose or unsaturated zone). Concentrations of organic matter in groundwater are generally lower than those encountered in soil porewater, because of either bacterial degradation or adsorption on mineral surfaces, whereas concentrations of major ions tend to be higher owing to reactions between water and surrounding minerals. Because soil and vadose zone water contents fluctuate rapidly, they typically experience greater variations in water chemistry than groundwater in deeper saturated zones.

The water in lakes and streams may be derived from several sources including runoff, groundwater, and precipitation. In the absence of any input from precipitation, stream and lake waters come directly from regional groundwater systems (i.e., base flow). During and immediately after a precipitation event, the base flow will be augmented to various extents by contributions from runoff and precipitation. Of course, streams, lakes, and wetlands may be a source for groundwater recharge in some areas, particularly in arid regions.

Natural changes that occur in the chemistry of a lake, stream, or wetland are generally small in comparison to changes that take place in the soil zone or groundwater systems. This is because the residence time of water in lakes and streams is short, and because there is relatively little in the way of contact between the water and solid mineral phases. Such changes that do occur are often caused by biological processes and affect primarily nutrient elements (e.g., carbon, nitrogen, phosphorus, and sulfur). The influence of biological activity on stream and lake chemistry is apt to be more highly pronounced in groundwater discharge zones where water escapes from the geological confines of an aquifer to the surface.

The chemistry of many lakes, streams, and wetlands today is strongly influenced by inputs of domestic and industrial wastes. Moreover, it has become recognized increasingly that cultural activities are introducing contaminants into groundwater systems on an enormous scale. The sources include leaching from municipal landfills, hazardous waste burial sites, mine tailings, and spills of various sorts. Even agriculture is a concern for groundwater pollution as intensive use of fertilizers and pesticides is commonplace. In some areas, contaminants in groundwater already threaten supplies of drinking and irrigation water; however, in time these same contaminants are likely to find their way into lakes and streams, thereby adding to the litany of environmental pollution caused by people. Accordingly, a great deal of effort is currently being put into understanding processes that control the chemical compositon of natural waters. This is expected to help in modeling the behavior and fate of contaminants in the subsurface, assist in the development of restoration strategies for existing problems, and facilitate proper design of disposal sites for future use, particularly for radioactive waste.

Redox Reactions and Thermodynamic Conventions

Many of the chemical and biolgocial reactions that proceed in natural waters involve oxidation-reduction (or redox) type reactions. These are reactions in which electrons are transferred from one reactant to another. Recall that when a compound loses electrons, it is said to have been oxidized. Conversely, when a compound gains electrons, it is said to have been reduced. To keep things straight in your mind, just remember the didactic saying, "*LEO the lion roars GER*".to recall the difference between (**L**oss **E**lectrons) **O**xidation and (**G**ain **E**lectrons) **R**eduction reactions.

Just as acids differ in their tendency to dissociate protons, chemical compounds are biased relative to their tendency to lose or gain electrons. The tendency of a compound to accept or donate electrons in a redox reaction is given by its oxidation-reduction potential (Eh). This is the electron motive force, in volts, that can be measured at a platinum electrode when a reductant and oxidant are both present. For example, in a solution containing Fe2+ and dissolved oxygen, the reactions

$$\mathrm{Fe}^{2+} = \mathrm{Fe}^{3+} + e^-$$

and

$$1/4O_2 + e^- + H^+ = 1/2H_2O$$

might be taking place. The combination of these two reactions would fix the potential at some value, but it would have no meaning for the individual redox pair. Consequently, potentials of oxidation-reduction reactions are usually referenced against the redox couple of H_2/H^+ at a hydrogen pressure of 1 atm, 25^o C, and unit proton activity (pH 0). Unfortunately, hydrogen electrodes are difficult to maintain, particularly under field conditions. So investigators commonly use other reference electrodes (e.g., Ag^0/Ag^+) that are calibrated against a hydrogen electrode to measure redox potentials.

The dependence of redox potential on the concentrations of reacting chemical species is given by the Nernst equation:

$$Eh = E^o - (2.03RT/nF) \log \{ox\}/\{red\}$$

where E^o would be the Eh if all chemical species involved were in their standard states (i.e., unit activity), F is Faraday's constant, R is the gas constant, T is the absolute temperature, and n is the number of electrons involved in the reaction. The parameters {ox} and {red} represent activity products for oxidized and reduced species, respectively. At 25^o C, the equation is:

$$Eh = E^o + (0.059/n) \log \{ox\}/\{red\}$$

This relationship provides a simple way to describe the stability of various compounds where redox reactions are involved.

Natural Redox Potentials and Microbial Activity

Most aerobic environments rarely have redox potentials lower than +400 mV; however, oxygen (a strong oxidant capable of accepting electrons from compounds prone to oxidation) diffusion in saturated soils and sediments is so slow that redox potentials decline rapidly with increasing depth. As a result, a strong gradient of redox potential typically develop in saturated soils and sediments over a depth a short as 2 mm. This may also occur in the water columns of some lakes.

The progressive decrease in redox potential with depth in soils, sediments, and some lakes is achieved primarily through a sequence of microbial reactions. After oxygen is depleted by aerobic respiration, denitrification begins when the redox potential falls to +421 mV. Denitrifying bacteria use nitrate as an electron acceptor in a process called anaerobic respiration. When nitrate is depleted, reduction of Mn^{4+} begins below a redox potential of +396 mV, followed by the reduction of Fe^{3+} at Eh values of less than -182 mV. These reactions are also catalyzed by bacteria that use anaerobic respiration to oxidize organic matter and generate energy. Similarly, many chemotrophic bacteria take advantage of the reverse reactions to genrate energy. For example, *Thiobacillus* *ferroxidans* and *Gallionella ferruginea* oxidize ferrous to ferric iron (rather than organic matter) to satisfy their energy requirements.

In natural environments, there tends to be some overlap between these different zones of microbial activity; e.g., denitrification and manganese reduction may proceed concomitantly in some systems. Below the zone of Fe^{3+} reduction. the redox potential progressively drops to -215 mV where sulfate reduction commences. At an Eh of -244 mV, methanogenesis occurs. Since the concentration of sulfate in most freshwater wetlands is not high, the zone of sulfate reduction tends to be quite small and methanogenic bacteria are therefore extremely active.

Unit 1: Tour of Chalk River Laboratories and Orientation

No assignment. Take good notes and ask questions, as appropriate - remember, you will be handing in your notebooks!

Unit 2: Measurement and Mapping of Hydraulic Head in the Twin Lakes Area and Ogilvie Lake

Working in groups, you will measure water table elevations in wells and multi-level piezometer nests throughout the Twin Lakes area. Start at the tracer site and complete measurements there before expanding to the larger Twin Lakes area. Based on measured data, areal and cross-sectional maps that you will develop, and the attached report (see appendix for unit 2), you will determine the appropriate parameters needed to produce an equipotential (hydraulic contour) map for the Twin Lake area using the FLOWPATH modeling program.

1. Complete all field measurements as instructed. Make the measurements in meters (S.I. units), and make corrections for the elevation of the well standpipe. Hence, all your measurments will be absolute, reported as meters above sea level.

All group data will be compiled and distributed. The rest of the work should be done individually. Note: To maximize use of the computers, some students should start at step 5; however, return to steps 2-4 before going on to 6-8.

2. On the areal map provided in the handout, indicate the elevation of the water table at all measured points and sketch the lines of equal hydraulic head (equipotential lines). **This is to be handed in as a figure with your report.**

3. For the cross-sectional map provided in the handout, indicate the water table elevation at all measurement points and sketch the lines of equal hydraulic head (equipotential lines). Roughly sketch in the main flow lines (direction of groundwater flow). **To be handed in as a figure with your report.**

4. In your report, discuss appropriate boundary conditions for your cross-section and areal maps. Calculate the specific discharge for the Twin Lakes Tracer Site, and estimate average linear velocity (assuming $n_e = n$ for the purposes of the calculation.

5. Review the information provided in Chapter 4 of the FLOWPATH manual, and work your way through the example detailed in Chapter 9 to familiarize yourself with the program.

6. Using the areal map provided in the handout, set up a 450 by 600 m grid (with 50 x 50 m spacing) and determine the coordinates of 6 measurement points over the field area. Measured hydraulic heads at these points will be used to *validate* the FLOWPATH model.

7. Use the areal equipotential map constructed from the field data and information from the attached report (see appendix for unit 2) to determine appropriate parameters to input to FLOWPATH to produce a steady-state flow map outlining hydraulic head contours and flow vectors. Some hints for you:

(i) Default parameters for the grid and wells. Select the node spacing and grid parameters as indicated above (50 x 50 m grid).

(ii) Domain boundaries for your system. Make the simplest approximations you can to start.

(iii) Aquifer properties. Look at the schematics you've developed and refer to the report in the appendix for unit 2. Entries must not be zero.

(iv) Thickness/bottom. Are you dealing with a confined or an unconfined aquifer? Make a reasonable estimate of the aquifer thickness based on your field measurements and the report in the appendix for unit 2.

(v) Infiltration/evapotranspiration. Set to zero.

Your report should include a complete list of all the parameters you used, and how you managed to determine them.

8. Produce a steady-state flow map with hydraulic head contours and flow vectors (**a hard copy is to be submitted with your report**). Input measured hydraulic head values for your 6 selected wells, and compare the measurements with computed values in a table (**to be handed in with your report**).

Remember are ***due no later than 22h00 on the second day of the module***.

Unit 3: Measurement of Methane Production in Wetlands

The purpose of this module is to evaluate spatial physical and chemical parameters that are important for the release of methane from wetlands to the atmosphere. This exercise will involve collection of surface water samples and chemical data throughout a wetland area at locations that will be identified precisely using global positioning system (GPS) equipment. Dissolved methane concentrations in the water samples will be subsequently measured by gas chromatography. Data will be mapped using SURFER v 8.0, and multivariate statistics (STATISTICA v 6.0) applied to ascertain correlations between measured physicochemical parameters.

For this exercise, students will work in groups to collect field data and determine dissolved methane concentrations by gas chromatography. All groups will contribute their results to compile a complete data set for mapping and statistical analyses. Reports are to be prepared individually, and are ***due no later than 22h00 on the second day of the module***.

Procedures

Before leaving for the field, each group must perform the following tasks;

(a) Label seven 60 mL syringes to collect water samples – a procedural control (blank), five sampling sites, and one spare.
(b) Equip each syringe with three-way stopcocks, and fill the blank with 30 mL of degassed de-ionized water.
(c) Prepare and similarly label an equal number of DI-caps – these are 60 mL serum vials filled with degassed de-ionized water and crimp sealed with rubber septa.
(d) Calibrate pH/Eh meters using standard buffer solutions.
(e) Become familiar with how to use a GPS unit and record locations in UTM coordinates.
(f) Rubber boots!

In the field, each group of students will be assigned to cover a specific part of a beaver-pond wetland. Some parts of the wetland are particularly rugged, but regardless of where student groups are working, everyone must ***exercise extreme caution in moving about the wetland***. Personal floatation devices must be worn by anyone using a canoe. At each sampling site:

(a) Record the UTM coordinates with the GPS unit.

(b) Collect approximately 30 mL of surface water using a 60 mL syringe. Ensure that the three-way stopcock is closed after sample collection. Take care not to disturb the underlying sediment, which may release gas bubbles.
(c) Measure pH, redox potential (Eh), temperature, and water depth. Record whether the water is standing or flowing, and the nature of the surroundings (e.g., treed or thicket swamp, marsh, sphagnum moss, open water).

After returning from the field, dissolved methane will be extracted from water samples using a helium head-space displacement technique – one group at a time. This will involve use of needles on the sample syringes, so ***care must be taken to avoid injury***. At the same time, other groups can enter their field measurements into an EXCEL spreadsheet to begin compilation of the complete data set. The helium head-space displacement technique involves:

(a) Adding 30 mL of helium to the sample syringes.
(b) Shaking the syringes for 15 minutes – this displaces methane from the water into the gas phase (owing to Henry's Law).
(c) Accurate measurement of water and gas volumes. *It is critical to record these values*
(d) Injection of the gas phase into the previously prepared DI-caps.

Measurement of methane concentrations will be done subsequently using a gas chromatograph equipped with a flame ionization detector – one group at a time. As each group completes their measurements, they can add their methane concentrations to the growing EXCEL spreadsheet data set. Once the data set is fully compiled, mapping and statistical analyses will be performed with all groups in attendance. Students will then be able to complete their reports.

Because there are times in this module where only one group will be busy at a time preparing samples, and conducting gas chromatography, other groups are urged to begin working on their reports. For example, the introduction and methods sections can be written, and some data can be tabulated. Reports must include:

(a) An introduction giving study objectives and background information.
(b) Methods outlining how sampling and analytical procedures were accomplished, including equipment that was used. A good methods section is one that another researcher should be able to read and then accurately reproduce your work.
(c) Results, a narrative that describes your findings and emphasizes key observations in reference to tables and figures of data. In your report include: a table of ***YOUR group's*** field data and methane concentrations, as well as maps and statistical plots of the compiled data.
(d) Discussion, a narrative that explains your results in reference to other studies, including a final concluding paragraph.
(e) A list of references – papers provided for reading, books from the "field camp" library (yes, we have a library!).

Remember, reports are to be prepared individually, and are ***due no later than 22h00 on the second day of the module***.

Unit 4: Regulation of the Chemical Composition of Natural Waters

This field and laboratory exercise will evaluate the steady-state chemical composition of a small lake. Recall that much of the chemistry of freshwater lake systems depends on the kinetics of various physical, chemical, and biological processes rather than on equilibrium conditions. Accordingly, the simplest model describing the aqueous chemistry of lakes is the time-invariant one-box steady state model in which chemical inputs are balanced by output (i.e., source fluxes are balanced by sink fluxes). In such cases, the concentration of an element remains relatively constant if it is added to the lake at the same rate that is removed.

Work in groups as follows:

1. Measure the water flow velocity at the spring/stream recharge and discharge points at opposite ends of Ogilvie Lake. You'll need something that floats, a ruler, measuring tape, and watch. Remember to measure stream width and depth at several points to calculate mean values (include mean values only in your report). Water inflow (Q_{in}) and outflow (Q_{out}) are calculates as follows;

$$Q\ (\mathrm{m^3/yr}) = \text{velocity (m/yr)} \times \text{stream depth (m)} \times \text{stream width (m)}$$

To help in your later calculations, convert values for Q to L/yr (there are 1000 L in 1.0 $\mathrm{m^3}$).

2. Determine the mean depth and volume of Ogilvie lake using map provided in the appendix to this unit (lake volume = mean depth x surface area) Make notes on the nature of the surrounding bedrock, overburden, and vegetation as well as water clarity.

3. Collect water samples as instructed in 125 mL plastic bottles. Measure pH, TDS, and Em (to estimate Eh) at each sample site.

4. Filter water samples as instructed, and conduct chemical analyses for iron and sulfate using the HACH spectrophotometer.

5. Consult and review the MINEQL instruction manual and work through the first example problem to gain some familiarity with this geochemical modeling program.

6. Using your field data, input analytical concentrations for the various elements and compounds measured into MINEQL. Run the program to chemically speciate dissolved constituents, and to determine whether the lake water is supersaturated with respect to any minerals.

When the field work, sample analyses, and geochemical modeling are completed, each student will prepare a report. The following information must be included (**use tables** and number them).

1. Introduction and methodology (sampling and analyses)

2. Input and output flux values for water and dissolved constituents.

3. A comparison of dissolved and particulate fractions of analyzed species , their total burden in the lake, and identification of any non-conservative sinks (e.g., incorporation into sediments via sedimentation) with relevant resident times.

4. Verify your Eh/pH and Fe results with diagrams in textbooks. Is the Eh/pH diagram consistent with the aqueous speciation determined using MINEQL.

5. Does the geochemical data provide any insight relevant to understanding input flux, output flux, and residence times of the various chemical constituents of the lake?

Remember, reports are to be prepared individually, and are ***due no later than 22h00 on the second day of the module***.