28. Project Unit 04-025. Detailed Investigation of Chemical and Microbiological Parameters Over Forest-Ring Edges in Northern Ontario

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INTRODUCTION

Forest rings are large circular features (up to 1.5 km in diameter) commonly observed in the boreal forests of Ontario where soils are carbonate rich and recently developed (<10 Ka). The circular impression reflects a slight topographic depression around the edge of the ring that forms around centres of negative charge in overburden or bedrock. The consumption of oxidizing agents in the overburden results in the propagation of a redox anomaly upward and outward from the reducing source. Thus, a "reduced chimney" is created between the reducing source and the water table, where the propagation stops due to the unlimited source of oxidizing agents above the water table.

In Ontario, forest rings have been reported to form over a dissolved hydrogen sulphide accumulation (Hamilton and Hattori 2008) and are suspected to form over bitumen and coal (Hamilton, Burt et al. 2004). However, field studies using spectral absorbance lasers suggest that over 85% of the several thousand known rings are centred on large accumulations of shallow methane (Hamilton, Burt et al. 2004). The current project takes a microbiological approach in establishing the origin of this natural gas and the role of micro organisms in the formation of the rings themselves. Two methane- and one hydrogen sulphide-centred forest rings, referred to respectively as the "Road ring", the "Bean ring" and "Thorn North", have been sampled in the vicinity of Hearst and Timmins (Figure 28.1). Preliminary work on the 3 selected rings has shown central peaks of dissolved CH_4 and/or H_2S , as well as depletions in O_2 over the rings. At Thorn North, CH_4 occurs only as sharp spikes at the ring edge and these are accompanied by sudden drops in H_2S and O_2 and increases in SO_4^{2-} close to the ring edge. These data suggest elevated biological activity at the ring edge at Thorn North perhaps facilitating some of the redox reactions. Preliminary isotopic evidence for CH_4 collected at methane-sourced rings suggests a young, low-temperature biogenic origin (Hamilton, Hattori and Clark 2005).

Subtle positive spontaneous potential (SP) anomalies in association with negative-inward redox gradients have been noted over forest rings (Hamilton and Hattori 2008). One of the objectives of this project is to test the role of bacteria in the formation of redox and electrical field (SP) anomalies. In general, the understanding of the origin of SP anomalies has benefits for the use of SP in mineral and energy exploration. In addition, methane-sourced forest rings are themselves potential targets for natural gas exploration because of their abundance, large size and visibility on aerial photographs, which allows targeting with minimal exploration expenditures.

Summary of Field Work and Other Activities 2008, Ontario Geological Survey, Open File Report 6226, p.28-1 to 28-8. In addition to these phenomena, numerous other physical and chemical changes occur at the ring edges as evidenced by previous soil sampling, groundwater measurement and other testing. So many processes occur that understanding which are causes and which are effects of other processes is extremely difficult. Particularly enigmatic are clear but apparently inconsistent temperature anomalies that are known to be associated with the rings and related phenomena that occur over known mineral deposits (Hamilton et al. 2004a, 2004b). Since the oxidation reactions occurring at the ring edges are exothermic, investigation of the temperature anomalies are an important component of this study.

METHODOLOGY

Sampling Design

Soil samples were collected and measurements made on high-density, short sampling transects across the ring edges at the 3 sites investigated. The sample media include peat and clay collected using hand augers to the maximum practical sampling depth, which proved to be about 3 m. Samples were split into 3 subsamples, labelled "A", "B" and "C", that are, or will be, subjected to a variety of tests (Figure 28.2). Sample A ("Archive") was preserved and archived for potential future analysis. Sample B ("Bacteria") was collected for microbiological analysis. These samples will be used in an attempt to recreate an *in-vitro* model of the conditions at the edge of a ring in order to determine the distribution and role of bacteria across a forest-ring edge. Methano- and/or sulphotrophic organisms are believed to



Figure 28.1. Location of the tree study areas in Ontario.



Figure 28.2. Flow chart showing the steps in primary sample preparation for the 3 main sample types (see text for additional details).

occupy the space at the edge of the ring where electron donors and electron acceptors are both present and may facilitate the redox reactions that are known to occur there. The microbiological experiments will test whether and how micro-organisms are involved in the creation of the redox gradient and subtle electrical field characteristics of forest rings. Sample C ("Chemistry") was analyzed directly in the field for pH and oxidation–reduction potential (ORP) as an aid in choosing locations and spacing, but was also prepared for chemical analysis and moisture content in the laboratory.

Care was taken to design a sampling methodology that was particularly suited for the final use of each sample type. All samples were kept as much as possible in their original chemical state by minimizing exposure to oxygen during handling and storage. The B samples were always first to be collected to avoid contamination. Where minimal sampling material was available, priority was given to the C samples, which are subject to the most analyses.

Site Selection and Characteristics

Samples were collected over 3 forest rings in the peat-rich boreal forests of Hearst and Timmins, Ontario. The forest rings were selected based on their road accessibility and the intensity of the redox gradient at their edges as measured in 2004 and 2005 (Hamilton, Burt et al. 2004, and unpublished OGS data). Thorn North, a H_2S centred ring, is located 45 km northwest of Timmins, Ontario. The Road ring and the Bean ring are centred on methane accumulations. They are located, respectively, 60 km northwest and 20 km southwest of Hearst, Ontario. Thorn North and the Road ring have recently been logged, which has affected the vegetative cover and the visibility of the ring from the air and on satellite images.

Sample Collection

Sampling was carried out in August 2008. Sample stations were installed on a line cut perpendicular to the ring edges of each forest ring. Forest-ring edges are typically 10 to 20 m in width. To allow comparison with background signals, the sampling line was extended 20 to 30 m inward and outward of the ring edge. Sampling stations were initially every 5 m. Following the field analysis of the C samples for pH and ORP, the density of sampling stations was increased to 2.5 m where ORP and pH gradients were highest. At each sample station, wooden stakes were hammered into the peat to provide a specific point from which to measure the location and elevation of the sampling stations and ground surface. The positioning of the stakes was done with respect to previously geo-referenced monitoring wells of known elevation and position. Ground surface and standing water levels at each sampling station were determined with centimetre accuracy relative to the stakes to establish the exact topography along the sampling line.

Peat samples were collected using a Dutch auger, as were clay samples when sampling to less than 1 m. Beyond 1 m, a soil spoon was used when sampling from 1 to 3 m. An exception was at Thorn North where the clay was sampled length by length using a soil spoon and this was followed by the reaming-out of the hole to the next sample interval with a Dutch auger. In order to plot the exact stratigraphy, sampling was done at continuous intervals on a spoon-after-spoon basis. Prior to sampling, all tools were cleaned in 3 steps, namely 1) an initial wipe with local moist peat; 2) immersion and scrubbing of the auger and spoon in a pail filled with local lake or peat water; and 3) sterilization using a bottle brush soaked in 95% ethanol.

Each sample was split into the 3 units (A, B and C) using a spatula and steel-knife. Sample B, intended for bacteriological analysis, was collected first to avoid microbial contamination. Using a clean spatula, disinfected with ethanol, approximately 5 g of material were inserted into each of 2 sterile centrifuge vials. One of the "B" test vials ('N') was purged in nitrogen (N₂) to limit changes in the

microbiological community, whereas the material in the second test vial ('X') was sealed with an air headspace that obviously contained O_2 . The remaining material from the auger or soil spoon was split into sample A and sample C. From the moment of sampling, all A and C samples were purged in N_2 to minimize oxidation and maintain their original chemical state. The A samples were triple purged with N_2 , vacuum sealed and immediately frozen on dry ice, whereas B samples were kept cool on ice packs. The C samples were analyzed for pH and ORP directly in the field, within 15 minutes of sampling. Following the analysis, the remainder of the sample was purged with N_2 and frozen.

Being in a peat bog, the auger holes promptly filled with water after soil sampling was complete. Polyvinyl chloride (PVC) pipes with bottom caps were inserted into the holes to a depth of 1.5 m. The bottom 0.5 m of these pipes was slotted and the water that entered at this depth was measured for pH, dissolved oxygen, temperature, conductivity and oxidation–reduction potential using a HANNA instruments[®] HI 9828 multiparameter meter connected to the flow cell. The water was also collected in 1 L jars, filled to 500 mL, and tested after 48 hours for dissolved gases in the headspace using a Linweld[®] Eagle portable multigas detector. Gases measured included CO_2 , CH_4 (high and low range) and O_2 .

Field Measurements: pH and Oxidation–Reduction Potential

The ORP and pH of the C samples were measured on site, at the time of collection, using standard glass-bodied pH combination electrodes and 2 platinum-tipped Ag-AgCl ORP probes connected to a notebook computer via a Consort[®] 6-channel data logger. Prior to measurement, peat and clay samples were mixed into a homogeneous slurry by combining approximately 15 mL of water with an equivalent volume of sample material. Prior to the slurry mixing, the de-ionized water had been stripped of dissolved O₂ by bubbling N₂ through the bottle for a duration of 10 minutes. pH probes were calibrated at the beginning of the day in pH 4, pH 7 and pH 10 solutions. To reduce the effects of polarization, ORP probes were inserted into a reducing pretreatment solution (HANNA instruments[®] HI 7091) of acidic ferrous sulphate for several seconds prior to each measurement. This procedure was repeated twice for the first sample of the day to reduce the effects of polarization due to probe storage. The ORP and pH readings were logged for 5 minutes at 10 second intervals using the data logger. The 5 minute readings for each probe were recorded.

Field Measurements: Temperature

At Thorn North, temperature and water levels were recorded to high degree of precision using 5 stand-alone Solinst[®] Levelogger[®] Gold down-hole data loggers installed in existing monitoring wells at a depth of approximately 6.5 m. The instruments have a temperature precision of 0.003° C and an accuracy of $\pm 0.05^{\circ}$ C. The Leveloggers were installed successively on 2 lines that transect the east and north ring edges, respectively. Data on the east line were continuously gathered at 15 minute intervals from July 2006 to May 2007. On the north line, which is parallel and 10 m west of the 2008 soil sampling line, data were continuously gathered between May 2007 and late August 2007. Additional data are currently being collected on the north line.

Sample Preparation and Analysis

In preparation for laboratory analysis, the C subsample of the peat and clay samples were oven dried at 60°C for approximately 2 weeks. Moisture content was initially determined by measuring the mass of samples before and after drying and will be further characterized by loss-on-ignition analysis. Clay samples were manually disaggregated using a zircon–ceramic mortar and pestle and sieved to -16 (<1.2 mm), -80 (<0.177 mm) and -230 (<0.0625 mm) mesh sizes. Peat samples were mechanically ground in a zircon–ceramic ring-mill and sieved to -80 mesh. Depending on the amount of material

available, the -80 and -230 mesh size-fractions are being analyzed, in order of priority, 3-step loss-onignition (LOI), trace elements (by ICP) and total carbonate by Chittick analysis. An unprocessed portion of each sample was submitted for particle size analysis (PSA). All analyses are being conducted by Geoscience Laboratories, Ontario Geological Survey (OGS) in Sudbury.

PRELIMINARY RESULTS AND DISCUSSION

The limited field and analytical results that were available at the time of writing are being analyzed. As an example of the type of data collected at each site, Figure 28.3A shows a cross section of the area sampled on the north line at Thorn North. Ice was unexpectedly discovered in peat on the inside portion of the visible ring edge and this appears to have contributed to a slight topographic high in the peat. This is despite the sampling being carried out at the hottest time of year and the site being located 200 km south of the southernmost limit of discontinuous permafrost in Ontario. Depressions in the elevation of the mineral soil at the ring edge have been noted at other rings (Giroux, Bergeron and Veillette 2001) and on the east, west, south and northeast edges of the Thorn North ring (Hamilton and Hattori 2008). However, Figure 28.3A shows only a very slight elevation drop in the surface of the sand and almost no depression in the elevation of the underlying clay.



Figure 28.3. A) Shallow stratigraphy on sampled line. B) Temperature minima measured in water pumped from 1.5 m depth in auger holes. Water levels shown in (A) were measured immediately after sampling and are not necessarily static. The dip in the level at -5 m may be due to a lower permeability in the shallow frozen peat.

Figure 28.3B shows temperature minima of groundwater extracted from the 1.0 to 1.5 m interval in peat in each auger hole and measured on 10 second intervals in a flow cell using the HANNA instruments[®] multi-parameter instrument. The data show a clear decrease in temperature toward the ring edge and the lowest temperature understandably was measured on groundwater extracted from just beneath the ice occurrence. Temperatures measured in auger holes at the Road ring (not shown) show a similar trend with lower temperatures occurring at the ring edge. No temperature data were collected at the Bean ring.

This temperature trend at Thorn North is a major phenomenon that occurs laterally, over tens of metres, and also vertically, deep into the clay. Figure 28.4 shows weekly temperature data logger trends collected throughout the summer of 2007 in the 7 m deep monitoring wells on the north line located 10 m west and parallel to the sample line shown in Figure 28.3. The lowest temperature is located at approximately the same location that the shallower readings indicated, that is, where the ice was present.

Figure 28.4 shows another important phenomenon. The rate at which the ground at 6.5 m depth responds to seasonal changes in air temperature is higher at the ring edge than in the adjacent areas. The data show that the coldest month of year for soils at 6.5 m depth is August, due to the lag in summer warming at that depth. However, the ground in the ring edge reaches its coldest temperature on July 20, whereas, the ground in adjacent areas does not reach its coldest for about a month later. Data for the east line over almost a full year (not shown) demonstrate that this phenomenon also occurs during the warmest months, which on the east line, occurs in November–December. Here, the peak warmest date for wells in the ring edge is November 17, but, in the outermost wells tested, it occurs a month later.

These data taken together suggest yet another unusual physical phenomenon is occurring at the ring edges and that was hitherto unknown. They indicate that soils in the ring edge have a higher thermal conductivity than soils in adjacent areas. Mean annual air temperatures in high latitude areas range from



Figure 28.4. Weekly temperature records from data loggers installed to 6.5 m depth in 7 m deep monitoring wells on the north line of Thorn North between May and August 2007. Distances are from well number TN-13, located near the centre of the ring.

several to about 5°C colder than soil temperatures (Williams and Gold 1976). A vertical zone of elevated thermal conductivity in near-surface soils would serve to lower general ground temperatures during parts of the year and raise them at other times, but, because of the lower average air temperatures, the net effect on soils at the ring edge would be to lower their average temperature relative to adjacent areas. Since the average air temperature in Timmins is very close to zero (1.7°C: Environment Canada, 25 year average), it is not surprising that the conditions at the ring edge have resulted in deep, colder temperatures and even ice in peat throughout much of the summer. This would account for the lingering ground frost in the area, but does not account for the elevated thermal conductivity (~permeability) of the clays at this location. Our further investigation of this phenomenon will start by quantifying the change in thermal conductivity and will then try to understand why it occurs. The role of permeability, texture, and chemical and biological processes on thermal conductivity will be investigated.

Ongoing investigation in the fall of 2008 of biological processes occurring at the ring edge will focus on the creation of *in-vitro* redox gradients in the presence of the micro flora collected from the strongest part of the redox gradient at the 3 ring sites. Small amounts of the native clay will be suspended in agar as an inoculum and to provide a realistic substrate for organisms to colonize. A redox gradient will then be established with oxygen at one end and a source of CH_4 and/or H_2S at the other. Change in pH, redox and electrical field will be monitored over a period of about a month. Other studies may include a detailed laboratory investigation of pH and redox of soils (on the A samples) if the *in-vitro* studies determine that such studies are warranted.

ACKNOWLEDGMENTS

This project is part of a Master's thesis project by the first author. It is supported in part through an Natural Sciences and Engineering Research Council (NSERC) grant to Keiko Hattori at the University of Ottawa, the Ontario Geological Survey and through grants from the Society of Economic Geologists and the American Association of Petroleum Geologists to the first author. We would like to thank Victoria Lee for excellent assistance in both the field and office.

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