Permeable Reactive Barrier Feasibility Assessment at Goldcorp’s Red Lake Gold Mines: Validation of Seepage Flow Paths through Tracer Testwork

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Abstract
A critical design element in support of a permeable reactive barrier (PRB) feasibility assessment was to maximize the likelihood that the PRB location will intercept seepage pathways that connect a tailings management area (TMA) to downstream surface water receptors. A tracer test was conducted to better define the hydraulic connection between the TMA and downstream receptors through the injection of fluorescent dye tracers into groundwater wells screened in the sand and gravel aquifer, which is interpreted to be the principal conduit for TMA-related seepage. Results confirmed a hydraulic connection between the proposed PRB location and downstream receptors.

Keywords: hydraulic connection, uranine, rhodamine, PTSA, fluorometer

Introduction
The Campbell Complex (Goldcorp’s Red Lake Gold Mines) is located in Balmerton, 7 km northeast of the Town of Red Lake in northwestern Ontario, and has been the site of gold-ore mining and milling operations since 1949. Tailings have been discharged to the current tailings management area (TMA) since 1983. A portion of the water that accumulates in the TMA infiltrates into the subsurface and travels along groundwater flow paths (designated as “Red Lake Flow Path”) that discharge to ditches draining a Golf Course (GC), which in turn feed a downstream wetland and lake. Groundwater along this flow path carries mine-related parameters associated with mill process waters (SO₄, Cl, NH₃, CN, Cd, Co, Cu, Ni and Zn) and re-mobilization from tailings solids (Fe and As).

Goldcorp is assessing the feasibility of using PRBs (Blowes et al., 2000) to intercept and treat TMA-derived seepage to mitigate groundwater degradation and minimize the potential for adverse effects to downstream aquatic receptors. This paper, which describes the results of tracer testwork designed to confirm contaminant pathways, represents the second of a series of three papers relating to PRB feasibility at the Campbell Complex. The other two papers, also presented as part of these proceedings, describe TMA plume distribution and contaminant behaviour (Martin et al., 2018) as well as hydrogeological, geochemical and geotechnical considerations driving PRB design (Crozier et al., 2018).

A key objective of the Phase I PRB (PRB; Crozier et al., 2018) placement is to intercept the seepage pathway that connects the TMA to downstream surface water receptors. To investigate the hydraulic connection between the proposed PRB location and the downstream GC ditch system, tracer testwork was conducted. This involved the injection of fluorescent dyes in key monitoring wells situated within the core of the groundwater plume to be intercepted by the PRB, and monitoring within the downstream ditch network. An improved understanding of the TMA-seepage pathway has relevance to PRB siting, design and performance evaluation.
Methods
Tracer testwork included laboratory and field components: 1) fluorometer configuration and calibration; 2) establishment of fluorometer measurement responses and potential cross-fluorescence effects; 3) tracer injection; and 4) tracer monitoring. Tracer test methods were coordinated by Lorax Environmental, while all on-site lab and field work was conducted by Red Lake Gold Mines.

Fluorescent Dye Tracers
Three fluorescent dye tracers were used in the tracer testwork: 1) Rhodamine WT (rhodamine); 2) Uranine K Liquid (uranine); and 3) 1,3,6,8-Pyrenetetrasulfonic Acid Tetrasodium Salt (PTSA). Tracer selection was based on tracer properties (e.g. availability, affordability and low detection limits), in addition to the sensitivity and availability of fluorometer sensors.

Fluorometer Configuration and Calibration
Fluorescence measurements were collected using a submersible fluorometer (Turner Designs C3) equipped with three optical sensors (rhodamine, uranine, PTSA), rechargeable battery pack and mechanical wiper. All three fluorometer sensors were calibrated prior to field deployment and initiation of the tracer test (i.e. tracer injection).

Fluorometer sensors were calibrated in direct concentration mode with temperature compensation for rhodamine (temperature compensation was not available for uranine or PTSA). A series of tracer standard solutions was prepared by diluting the fluorescent dyes (21.7% rhodamine, 39.5% uranine, and 10% PTSA) with site water collected at GC DITCH (Figure 1). These standard solutions were used to calibrate all three fluorometer sensors and to establish sensor responses throughout their linear measurement range. Tracer standard solution concentrations ranged from approximately 0.05 to 520 ppb (Table 1). The fluorometer was calibrated by conducting a 1-point calibration of each sensor using tracer standards of approximately 50 ppb (53.9 ppb rhodamine, 49.1 ppb uranine, 49.7 ppb PTSA). Once calibrated, the linear response range was established for all three tracers to determine how fluorometer response may be affected by site water chemistry (i.e. GC DITCH water).

Rhodamine, uranine and PTSA all have unique fluorescing wave lengths that are not expected to interfere with each other under laboratory conditions (when measured with the submersible fluorometer). However, since all three tracers were injected into the same aquifer, lab-based experiments were conducted to assess the potential for cross-fluorescence effects in site waters, over a range of concentrations. Cross-fluorescence testing was conducted by measuring fluorescence of two site water samples containing all three tracers at concentrations of approximately 0.5 ppb and 430 to 470 ppb.

Tracer Injection
Rhodamine, uranine and PTSA were injected into the sand and gravel aquifer (the interpreted principal conduit for seepage of TMA-affected waters) in late August 2016. Tracer injection was conducted at four existing monitoring wells, located up gradient (MW06-1), down gradient (MW15-01B), and within the footprint (MW16-03B, MW16-04B) of the proposed PRB (Figure 1). A single tracer was injected into each well, with uranine injected into two wells (Table 2). A cross-section showing hydrostratigraphy and well locations along the Red Lake Flow Path is provided in Martin et al. (2018), the first of three papers relating to PRB feasibility at the Campbell Complex.

Table 1. Tracer Standard Solutions.

<table>
<thead>
<tr>
<th>Tracer Dye</th>
<th>Undiluted Concentration (Weight %)</th>
<th>Standard Solution Concentrations (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine</td>
<td>21.7</td>
<td>0.054, 0.54, 5.4, 53.9, 516.2</td>
</tr>
<tr>
<td>Uranine</td>
<td>39.5</td>
<td>0.049, 0.49, 4.9, 49.1, 470.2</td>
</tr>
<tr>
<td>PTSA</td>
<td>10</td>
<td>0.50, 5.0, 49.7, 476.1</td>
</tr>
</tbody>
</table>
Tracer dyes were injected with a portable peristaltic pump (Masterflex E/S) equipped with dedicated silicone pump-head tubing (3/8” × 1/4”) connected to HDPE tubing (1/4” × 0.17”) in each well. Undiluted tracer dye was injected into each well by pumping uniformly across the entire screened interval in a single motion, commencing at the bottom and ending at the top of the well screen. Injection volumes were based on tracer dye concentrations, 2-dimensional (2-D) transport calculations, and the detection limits and linear response ranges of the fluorometer sensors. Injection rates ranged from 0.4 to 1.0 L/min.

Hydraulic conductivity measurements at the four injection wells range over slightly more than one order of magnitude (Table 2). Hydraulic conductivity is highest at rhodamine injection well MW06-1 and lowest at PTSA injection well MW15-01B.

Predicted arrival times for the three tracers in the GC ditch network were estimated to range between 87 and 1400 days after injection, based on 2-D transport calculations (results not shown). The predicted arrival times for peak rhodamine, uranine and PTSA concentrations in the GC ditch were 87 days (=2.9 months), 94 and 120 days (=3.1 and 3.9 months), and 1400 days (=3.8 years), respectively, assuming a transport distance of 220 m between the injection wells and monitoring point in GC ditch.

**Tracer Monitoring**

Tracer monitoring was conducted with the fluorometer through a combination of automated, hourly in-situ measurements, and periodic, manual ex-situ measurements (ranging in frequency from three times a week to bi-monthly). Automated monitoring was conducted at GC DITCH (approximately

<table>
<thead>
<tr>
<th>Well</th>
<th>Screen Length (m)</th>
<th>Hydraulic Conductivity (m/s)</th>
<th>Injection Date</th>
<th>Tracer</th>
<th>Concentration (Weight %)</th>
<th>Volume (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW15-01B</td>
<td>0.92</td>
<td>9.4x10⁻⁵</td>
<td>24-Aug-16</td>
<td>PTSA</td>
<td>10</td>
<td>6.1</td>
</tr>
<tr>
<td>MW06-1</td>
<td>2.90</td>
<td>1.1x10⁻³</td>
<td>25-Aug-16</td>
<td>Rhodamine</td>
<td>21.7</td>
<td>6.0</td>
</tr>
<tr>
<td>MW16-03B</td>
<td>0.46</td>
<td>8x10⁻⁴</td>
<td>25-Aug-16</td>
<td>Uranine</td>
<td>39.5</td>
<td>1.5</td>
</tr>
<tr>
<td>MW16-04B</td>
<td>0.46</td>
<td>1x10⁻³</td>
<td>29-Aug-16</td>
<td>Uranine</td>
<td>39.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Figure 1** Tracer Test Study Area.
10 m downstream of the junction with the tributary ditch; (Figure 1)) between August 22 and November 11, 2016, at which time the fluorometer was removed from GC DITCH due to freezing temperatures and ice formation. Manual monitoring was conducted thereafter until the end of testing on March 17, 2017. Manual monitoring consisted of the collection of water samples from GC DITCH, GC TRIB and UPPER GC DITCH (Figure 1), and subsequent tracer measurements in the laboratory. Tracer measurements in the lab were collected on a time interval of every second for several minutes. Most manual monitoring at GC DITCH was completed at the primary station (GC DITCH), except for two measurements that were collected at the secondary station GC DITCH 2 on December 12 and 14, 2016 due to snow and ice which prevented sampling at the primary station (Figure 1).

Turbidity was measured in surface water samples collected from UPPER GC DITCH, GC TRIB, GC DITCH and GC DITCH 2 during fluorometer calibration and tracer monitoring, because high turbidity has the potential to interfere with tracer measurements. Turbidity measurements were collected using a portable turbidimeter (Hach 2100Q).

**Results and Discussion**

**Fluorometer Response and Cross-Fluorescence Measurements**

The fluorometer showed linear responses to tracer concentrations in the following ranges: 5 to 520 ppb for rhodamine, 0.05 to 470 ppb for uranine, and 0.5 to 480 ppb for PTSA. Cross-fluorescence was greater at low concentrations. Relative percent difference (RPDs) values between measured and reference standard solutions ranged from 136 to 200% for the low-concentration mixed-tracer solution (0.5 ppb). In contrast, RPD values ranged between 25 and 34% for the high-concentration mixed-tracer solution (430 to 470 ppb).

Rhodamine was not detected in the low-concentration mixed-tracer solution (0.5 ppb), consistent with the rhodamine response measurements. Uranine and PTSA showed strong interference signatures at low concentrations. This is consistent with low uranine levels being detected (0 to 2.8 ppb) while establishing rhodamine and PTSA response measurements, as well as low PTSA levels being detected (0 to 5.5 ppb) while establishing uranine and rhodamine sensor responses.

Based on fluorometer response testing, the lower limits of reliable measurement for the three tracers were estimated to be 5 ppb for rhodamine, 3 ppb for uranine, and 6 ppb for PTSA. Cross-fluorescence effects were expected to result in overestimated uranine and PTSA readings at low concentrations (=0.5 ppb).

**Tracer Monitoring Results**

Automated and manual monitoring results for the GC ditch system for rhodamine and uranine are presented in Figure 2; PTSA results are not shown since it was only detected on three occasions at levels below the limit of reliable measurement. Daily precipitation measured at the Environment Canada Red Lake meteorological station is also shown for reference.

Rhodamine was first detected during manual monitoring at GC DITCH and GC TRIB in early December 2016. However, initial rhodamine levels were low at GC DITCH (0.5 to 0.7 ppb) and GC TRIB (0.5 to 0.7 ppb). Rhodamine levels subsequently decreased rapidly to below detection by mid December 2016 (Figure 2).

Uranine levels at GC DITCH fluctuated within background levels (0 to 3 ppb) during automated monitoring and increased in December 2016 (during manual monitoring), peaking at 6.0 ppb in GC DITCH (December 20) and 6.9 ppb in UPPER GC DITCH (December 29). Uranine levels decreased slowly thereafter, throughout January and February, before levelling off in March 2017 (Figure 2).

Uranine was detected at GC TRIB during manual monitoring; however, in contrast to the temporal trends observed at UPPER GC DITCH and GC DITCH (i.e. rise and fall of concentrations), uranine levels largely remained within previously detected levels during automated monitoring at GC DITCH and below the limit of reliable measurement.

Turbidity levels in UPPER GC DITCH, GC DITCH, GC DITCH 2 and GC TRIB water samples were generally below 20 nephelometric turbidity units (NTU). Turbidity lev-
Figure 2 Rhodamine (top) and uranine (bottom) concentrations in the GC Ditch system.

els occasionally spiked up to 140 NTU due to difficulties with sampling through snow and ice and/or low flows. The magnitude of turbidity is not predicted to have had a significant bearing on tracer measurements.

Overall, uranine tracer signatures measured in UPPER GC DITCH and GC DITCH provide evidence of a groundwater connection between the proposed PRB location and GC ditch. This conclusion is based on: 1) uranine concentrations that were at least twice the lower limit of reliable detection; 2) peak concentrations more than twice background levels; and 3) temporal trends characterized by a rise and fall of uranine concentrations typical of dispersion resulting from transport of an instantaneous slug injection through a groundwater flow system. Cross-fluorescence effects are not believed to be significant in the observed uranine concentration ranges. Ura- nine detected at GC TRIB was characterized by relatively stable concentrations that fluctuated within the range of background levels and remained below the limit of reliable measurement. These observations suggest that the groundwater flow path at the proposed PRB location is not strongly connected to the GC tributary ditch or that uranine concentrations had decreased to the extent that they were not measurable above background.

Uranine concentrations measured at GC DITCH peaked on December 20, 2016, approximately 3.7 months after tracer injection at MW16-04B and 3.8 months after injection at MW16-03B. These observed arrival times are close to the predicted arrival times of approximately 3.1 and 3.9 months for injections at MW16-04B and MW16-03B, respectively, lending further confidence to the detection of a tracer signature in the ditch network.

Although rhodamine was detected at GC DITCH and GC TRIB, its tracer signature did not yield conclusive evidence. This relates to detected concentrations that were low and close to lower limits of detection. As such, it is not possible to discern whether rhodamine concentrations measured at GC DITCH and GC TRIB were representative of an actual tracer signature or noise. It should be noted, however, that the period of possible rhodamine detection coincided with the predicted arrival time, lending some confidence to the
possibility of a positive signature in the ditch system, particularly in light of the arrival of uranine.

PTSA was not detected in the GC ditch system. However, this result does not disprove a connection of the groundwater flow path between injection well MW15-01B and the downstream GC PTSA system. Specifically, the lower hydraulic conductivity at MW15-01B ($K = 9.4 \times 10^{-5}$ m/s) would result in significantly longer travel times for PTSA in comparison with the other injection wells. Transport calculations used in the design of the tracer test suggest that tracer monitoring was suspended well before the predicted arrival time of peak PTSA concentrations in the GC ditch system (≈3.8 years).

Conclusions
The salient conclusions of the tracer study can be summarized as follows:

- Tracer calibration and response results for site waters suggest that the use of rhodamine, uranine and PTSA can provide accurate and reproducible results over a wide range of tracer concentrations.
- Uranine tracer signatures measured at UPPER GC DITCH and GC DITCH provided confirmatory evidence of a hydraulic connection between the proposed PRB location and the GC ditch. These data suggest that PRB installation at the proposed location will have a direct influence on water chemistry in the ditch/wetland system.
- The arrival of uranine at UPPER GC DITCH and GC DITCH agreed well with predicted arrival times, illustrating that the understanding of the physical hydrogeology of the site is fairly robust.
- Uranine detected at GC TRIB was characterized by relatively stable concentrations that fluctuated within the range of background levels and remained below the lower limit of reliable measurement. This is indicative of a weak or non-existent connection between the proposed PRB and the GC tributary ditch;
- Rhodamine was detected in GC DITCH and GC TRIB; however, due to the low magnitude of tracer measurements, no definitive conclusions could be drawn.
- The absence of detectable PTSA concentrations in the GC ditch system does not discount the conclusion of a hydraulic connection between the injection well (MW15-01B) and the downstream GC ditch system. Specifically, the lack of a PTSA signature can be linked to the lower hydraulic conductivity at MW15-01B, which would result in significantly longer travel times for the tracer.

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