

Glycol Biotreatment System

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Background

In the summer of 2001, the Ottawa Macdonald-Cartier International Airport Authority (OMCIAA) began the construction of a new Passenger Terminal Building. The new terminal building was to be located where the Central De-Icing Facility (CDF) had been operating for 5 years, therefore forcing the relocation of the CDF. After looking at numerous options, it was decided to construct the CDF near the north end of the airport lands, close to the threshold of runway 14.

Shortly after the new CDF became operational, elevated levels of ethylene glycol were found in the storm waters originating from the new CDF area and going to the Rideau River outlet. The maximum allowable concentration of Glycol in water, according to the Ministry of Environment of Ontario is 100 mg/L. It was determined that, the new CDF location had changed the aircraft taxi patterns and more aircraft were taking off runway 14 than previously. The storm water catch basins located along the taxiways leading to runway 14 and those along runway 14 discharge directly into the Rideau River outlet where glycol was being observed. The source was determined to be glycol dripping off aircraft that had just been de-iced and finding its way in the storm system.

The elevated levels of glycol in the storm water leaving the airport property needed to be addressed. The obvious solution was the construction of a retention pond where the glycol impacted waters could be treated and then released when the water met the applicable criteria. Given the size of the drainage area and the fact that little or no infiltration would occur during the winter months (frozen ground), it was determined that a very large detention pond would be required. The only available location was several kilometres away from the outlet and the cost of such a system would be enormous.

Another solution was to let the storm water infiltrate under the surface. This system would be very similar to a septic system. The advantage of an underground system is that there would not be a body of standing water near the runways. The fact that the Ottawa airport is built on sand would facilitate the infiltration of the storm water. This type of system was chosen and a suitable area was located near the CDF and close to the threshold for runway 14. Prior to committing to that site, a hydrogeological assessment was completed.

Hydrogeological Assessment

In 2002 and early 2003, two hydrogeological assessments were carried out. These were completed to assess the viability of subsurface infiltration of glycol impacted storm water. More specifically, they were to determine the soil type in the area, groundwater flow velocities and groundwater flow direction. This would then be used to determine if there was sufficient time for glycol to degrade prior to exiting airport premises.

The assessments determined that the soil consisted of fine, medium and coarse grained sand with varying amounts of silt. The groundwater level ranged from approximately 8 m to 10.3 m below ground surface and that the predominant groundwater flow direction in the proposed system area was to the northwest. A hydraulic gradient of 0.007 and a hydraulic conductivity of 1.4×10^{-2} cm/sec were calculated. Using this information, a linear groundwater conductivity of 4.0×10^{-4} cm/sec was calculated. Based on the groundwater flow direction and the distance to the property line, 500 m, it was estimated that groundwater would take about 4 years to exit the property boundary.

At the same time a treatability study was undertaken. These tests were performed to examine the feasibility of an enhanced *in-situ* biodegradation process for the treatment of glycol impacted groundwater.

Treatability Study

The treatability study consisted of bench scale and pilot-scale tests. To conduct the treatability study in conditions that were as close as possible to the actual site conditions, soil samples were collected within the groundwater table during the hydrogeologic assessment to be used during the treatability study. The bench-scale tests used flasks and a bioreactor to determine the suitability of the soil and the ability of indigenous bacteria to breakdown glycol, a pilot-scale test was then performed using a 3 metre column to verify the operational conditions before going into the field.

Flask Test Procedure and Results

The initial testing was conducted on a bench scale using Erlenmeyer flasks. Two sets of samples were run to determine the degradation rates of glycol in native soils, using indigenous bacterial cultures under both aerobic and anaerobic conditions. There was no inoculation or nutrient addition.

Four hundred grams of soil was added and approximately 50 mg/L of ethylene glycol solution to each of the four flasks. Two of the flasks were aerated and the other two were purged with nitrogen. These flasks were left for 28 days. An initial sample was taken from each flask and samples were taken on day 28 (see Table 1).

Table 1: Natural attenuation of Ethylene Glycol after 28 Days

	Initial (All flasks)	Flask A (Aerobic)	Flask B (Aerobic)	Flask C (Anaerobic)	Flask D (Anaerobic)
Glycol Concentration	52 mg/L	53 mg/L	53 mg/L	53 mg/L	22 mg/L

There did not seem to be any significant reduction in the concentration of glycol in these samples. Although Flask D showed some degradation over the 28 day period, the rate of reduction was considered slow given the controlled laboratory conditions. The reduction in Flask D could be due to the flask being contaminated with non-indigenous bacteria. The slow or non-existent degradation indicated that the soils did not contain enough nutrients, bacteria, or both, for the natural attenuation of glycol contaminated storm water.

Therefore, a source of glycol degrading bacteria needed to be located. The best source of bacteria would be native bacteria that have been exposed to ethylene glycol. A good location for these bacteria was presumed to be in the catch basin sumps which have been previously impacted with glycol. Sediment samples from the catch basin sumps were collected and brought to the laboratory for further experiments. It was also determined that the treatment system could be run more economically in the anaerobic mode. Therefore all subsequent bench and pilot scale testing was performed anaerobically.

Bioreactor Test Procedure and Results

Bioreactor tests were performed to assess the possibility of glycol degradation using bacteria collected from catch basin sumps located along taxiways. The bioreactor test would also help to determine the optimum conditions for the anaerobic biodegradation of glycol in water.

The bioreactor was preconditioned to remove oxygen before it was inoculated with the bacteria colony collected from the Ottawa airport catch basin sumps. A standard mineral salts medium (nutrients) was prepared as per Table 2.

Table 2: Mineral Salts Media Composition (Nutrients)

Nutrient	g/ 3 Litres (oz/0.8 gal)
Ammonium Chloride (NH ₄ Cl)	0.93 (0.03)
Calcium Chloride Dihydrate (CaCl ₂ ·2H ₂ O)	0.06 (0.002)
Potassium Phosphate Dibasic (K ₂ HPO ₄)	4.40 (0.16)
Potassium Phosphate Monobasic (KH ₂ PO ₄)	0.62 (0.02)
Magnesium Chloride Hexahydrate (MgCl ₂ ·6H ₂ O)	0.06 (0.002)

The bioreactor was run twice (the second run a replicate of the first) to determine if the controlled conditions could sustain the degradation of glycol. Table 3 shows the results of this test. There appeared to be a time delay of at least 7 days, after which the concentration of ethylene glycol decreases rapidly to below the detection limit.

Table 3: Results of the First Bioreactor Test

Day	Glycol (mg/L or ppm)
0	39
7	32
14	Below detection limit (<3)

Pilot-Scale Test Procedure and Results

The glycol bioreactor was constructed from a 3 metre section of 200 mm diameter schedule 40 PVC pipe. As the bacteria were required to operate in an anaerobic environment, nitrogen gas was continuously injected throughout the duration of the experiment, such that the system was always under slight positive pressure. The nitrogen gas was allowed to vent through two air locks so that no oxygen could enter. A system schematic is shown in **Figure 1**.

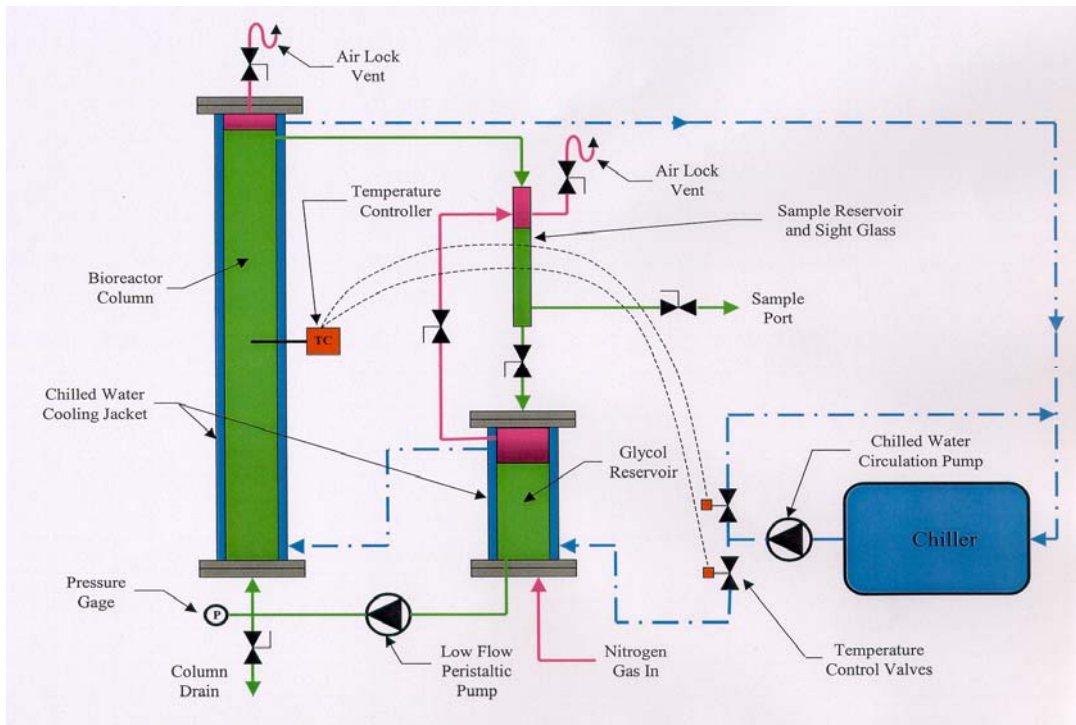


Figure 1: Pilot Scale System Schematic

The column used for the pilot-scale tests contained 100L of sandy soil collected from the Ottawa Airport at the groundwater level. Once the sand slurry was added to the column, the temperature of the system was set to 10^o C. Fifteen litres of water was added to the reservoir and the recirculation pump was set to 20 ml/min. Nitrogen was bubbled through the reservoir at a rate of 50 ml/min. The water in the column was recirculated for two weeks as a conditioning step to purge trapped oxygen. After 4 weeks anaerobic conditions were not achieved. However, due to time constraints, it was then decided to inoculate the column with nutrients and bacteria culture developed from the bioreactor as it was felt that complete anaerobic conditions may not be required for the indigenous bacteria.

After 12 days, glycol was added to the column. Samples were then taken and analysed for glycol as summarised in Table 4.

Table 4: Results of the Pilot Scale Column Test

Day	Glycol (mg/L or ppm)
0	182
1	147
3	157
10	163
21	Below detection limit

As shown in Table 4, after a lag period, the concentration of ethylene glycol diminished to the point where it was no longer detectable within 21 days.

Feasibility Study Conclusion

This investigation demonstrated that it is possible to degrade glycol anaerobically using indigenous bacteria collected from the Ottawa International Airport. There is evidence that would suggest the existing subsurface soil conditions at the Ottawa Airport could not support the biodegradation of glycol as is. An enhanced biotreatment system including amendments and injection of indigenous bacterial culture is required to obtain the objectives. The column test does indicate that once these conditions are met, degradation occurs between 10 and 21 days.

System Design

Following the positive results of the treatability study and approval from the RVCA, design was started on a system that would allow for the infiltration of the impacted storm water into the ground. The system had to accommodate the rain events that occur in Ottawa during the winter and have the capability to redirect the flow to the river when the system was not in use. Flow data collected in previous years was used in the design of the system. Based on storm water flow information and site capacity, it was decided that a 5 year storm event would be the design criteria for the actual system and that an overflow pipe system and a containment berm would be designed to accommodate higher precipitation events.

The infiltration bed was designed to accommodate a flow of 2,700 m³ per day or a volume of 650 m³ at any instant. The system consists of the following components:

- a flow splitter that allows 143L/sec into the Biotreatment System;
- as a pre-treatment of the storm water, an oil/grit separator (Stormceptor™) that has a maximum capacity of 70 L/sec;
- a containment berm;
- an infiltration bed that is 130 m long, 5m wide covered and underlain with 0.6 m and 1.4 m of 50 mm granular fill, respectively; and
- five 150 mm diameter perforated pipes, 130 m in length within the infiltration bed described above.

The granular fill is encased in geotextile fabric to prevent sediment build-up in the system.

Other system enhancements were added following the preliminary design:

- The injection port for nutrients was designed to ensure nutrients enter the entire system. This included the installation of a rigid conduit in the center infiltration pipe with perforations located in strategic locations to ensure an equal distribution of nutrients;
- Five stainless steel bacterial retention trays were positioned at predetermined locations. These trays were placed within the system as it was unknown if the

- bacteria would survive when the system became dry and free of nutrients and glycol during the summer months; and
- Two 10 cm bacterial sampling ports were installed within two of the bacterial retention trays.

The sampling ports were designed in order to collect samples to determine if bacterial activity was still present prior to the start of the following season. If the results were negative, additional bacterial inoculation would be required.

Initial Addition of Nutrients Immediately After Construction

In order to prepare the system for inoculation, nutrients were added. The salts mixture (nutrients) outlined in Table 5 were mixed in 600 L of water and injected into the system via the injection port.

Table 5: Inoculation salts injected

Nutrients	Initial load Kg
NH ₄ Cl	47.2
CaCl ₂ ·2H ₂ O	3.2
KH ₂ PO ₄	34.6
MgCl ₂ ·6H ₂ O	3.2

Preparation of the bacteria for inoculation

Twenty litres of sludge from the bottom of selected storm water catch basins were collected and placed in a 205 L drum containing water and nutrients. The drum was then sealed and mixed. Before transport to the area of injection, the contents of the drum were screened through an 800 µm sieve to remove any sediment that could block the infiltration system.

The bacteria containing water (inoculation fluid) was then injected into the system via the injection port. A test was performed to ensure that the bacteria in the above noted inoculation fluid was capable of degrading glycol. This test confirmed that the bacteria in were capable of degrading glycol in less than 21 days. This concluded the inoculation of the Biotreatment System.

Injection of nutrients

During the operations of the Biotreatment System, the nutrient levels must be maintained due to a lack of natural nutrients in the soil. To ensure this, weekly injections of a nutrient solution were performed. Table 6 illustrates the average amounts of chemicals injected per week. The amount of chemicals required was modeled after the macronutrient requirements in laboratory Fermenters. These fermenters were designed for very high metabolic rates, up to 3 orders of magnitude greater than what occurs in nature. The value chosen for this application was one tenth that of the laboratory experiments.

Table 6: Nutrient Injection

Salt	Kg /week
NH ₄ Cl	23.6
CaCl ₂ ·2H ₂ O	1.6
KH ₂ PO ₄	17.3
MgCl ₂ ·6H ₂ O	1.6

The chemicals are weighed off-site, brought to the site, placed in the tote and mixed on site with 600 L of hot water. The container is brought to the site and injected by gravity. The injection time takes approximately 15 minutes.

Shutdown and Restart

No special shut down procedures were required over the summer months; nutrient injections ceased, but monitoring continued. The bacteria were able to weather dry spells and lack of carbon input (e.g. glycol). Inoculation was not required to restart the system as samples collected from the system sampling ports in the fall indicated that the bacteria were well established and were still capable of degrading glycol.

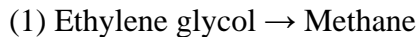
Nutrient injection was restarted after the first use of the CDF to ensure that the bacteria obtained enough nutrients and also to ensure that impacted storm water was treated.

System Monitoring

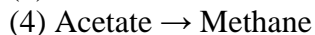
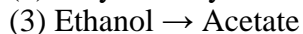
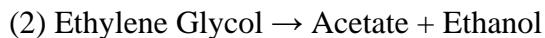
In order to confirm the effectiveness of the Biotreatment System a monitoring program was designed and implemented. The monitoring program included the collection of groundwater samples; assessment of certain parameters; sampling frequency, groundwater flow direction, results of water analyses.

Assessment Parameters

Based on the collected information the following are the relevant reactions that occur when ethylene glycol is degraded under anaerobic conditions (Veltman *et al.*, 1998):



Reaction 1 is the major reaction route. The following equations are the intermediate steps involved in reaction 1.



The organic compounds monitored during the first season were glycols, acetate and ethanol and only acetate during the second year of operation.

In general, bacteria will use oxygen as the electron acceptor for respiration. Once the oxygen is depleted, the next best electron acceptor is nitrate, followed by sulphate and ferric iron (Fe (III)). Based on the above, DO, nitrate and sulphate were monitored.

Phosphate was also monitored to determine if an excess amount of nutrients were being added to the system.

Results and Discussion

First Year of Operation

On November 27, 2003, the diversion valve to the Rideau River outlet was closed and the diversion valve to the Biotreatment System was opened. This was deemed the official start-up of operation of the Biotreatment System. Based on calculated groundwater flow velocities and the distance to the closest monitoring well (BH 02-05), located 40 m from the system, it was decided to start sampling this monitoring well on January 20, 2004 (55 days after system start-up). During this sampling event, glycol was not detected.

The following week, both the inlet to the system (CB Inlet) and BH 02-05 were sampled to correlate the glycol concentrations entering the system and the concentrations measured in this down gradient groundwater monitoring well. Sampling of these locations was then carried out on a weekly basis during the months when aircraft anti-icing and de-icing operations were taking place.

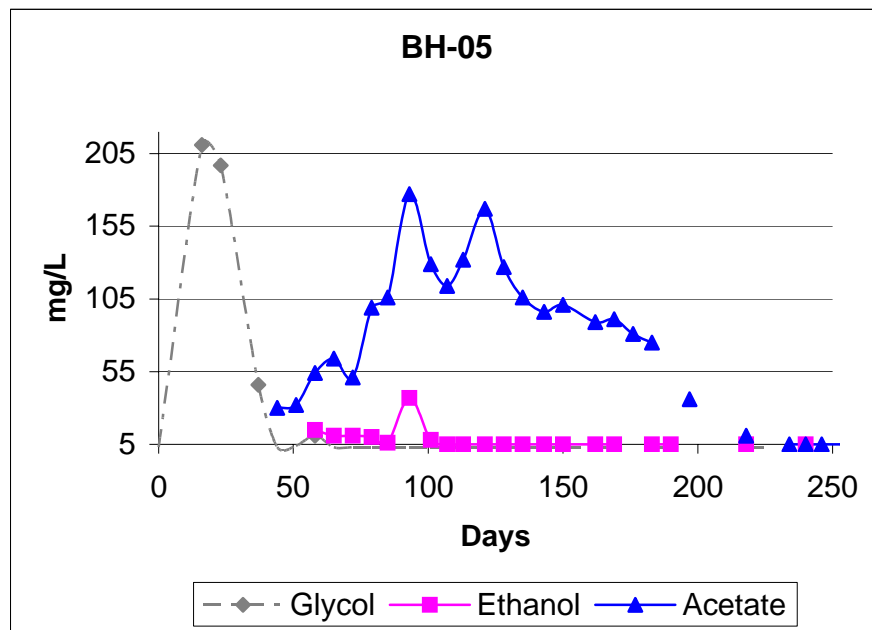


Figure 2: Bore Hole 5 Analysis (First Year)

Glycol was first observed in BH 02-05 on February 5, 2004 at a concentration of 211 mg/L. On February 19, 2004 an odour was detected in the monitoring well BH-02-05 indicating the presence of acetate, which was evaluated the following week. Acetate concentrations were measured at 14 mg/L. Glycols were measured at 46 mg/L during the same sampling event. Figure 2 illustrates the groundwater analytical results for glycols, acetate and ethanol in the samples collected from BH 02-05.

On March 18, 2004, analysis for ethanol began in order to evaluate the glycol degradation process. After less than 60 days the presence of ethanol was non-detectable in BH 02-05 and was never detected in BH 02-06 located 80 meters down gradient from BH 02-05. The analytical results confirmed the degradation by-products as anticipated (to acetate and ethanol). These analytical results also indicated that ethanol rapidly degrades to non-detectable levels.

Groundwater samples were analysed for several other parameters as mentioned above. The groundwater samples collected confirm that the bacterial activity is present in the system. For example, when looking at all graphs, one can see that when glycol was present in the system, the acetate/ethanol concentrations also increase.

Analytical results also indicate that when the acetate/ethanol concentrations increase, the dissolved oxygen decreases, followed by nitrate and sulphate. These are all indicators that the Biotreatment System is functional.

Post-de-icing Season Monitoring (1st year)

Monitoring was continued after the de-icing season. By April 30, 2004, acetate concentration began to appear in BH 02-06 at concentrations of 22 mg/L. Acetate concentration increase to about 70 mg/L and by October 20, 2005, was no longer measurable in this monitoring well. In the fall of 2004, additional monitoring wells were installed in strategic locations. These monitoring wells were monitored for phosphate, nitrate, sulphate, glycols, acetate and dissolved oxygen.

The results indicate a depletion of nitrate when compared to the background concentrations. This indicates that the groundwater plume that was initially impacted by the presence of glycol has reached this monitoring well. The dissolved oxygen concentrations also indicate that the groundwater plume that was initially impacted by glycol reached the down gradient monitoring wells. When compared to the groundwater flow direction the dissolved oxygen plume follows the general groundwater flow direction.

All of the above indicate that glycol is degraded to acetate and ethanol by bacterial activity. Laboratory analyses and field measurements confirmed that dissolved oxygen levels are first depleted, followed by nitrate, and then sulphate. The by-products of glycol degradation are ethanol and acetate, both of which were measured in the groundwater near the Biotreatment System. When the groundwater from the monitoring wells located further from the treatment system was analysed, the ethanol or acetate concentrations were either non-detectable or lower in concentration. The furthest groundwater monitoring well sampled did not reveal the presence of acetate or ethanol but the depletion in dissolved oxygen and nitrates indicates that the groundwater impacted by glycol had travelled to this monitoring well.

Second Year of operation

Prior to the onset of the second year of operation, additional monitoring wells were installed.

At that time, it was unknown if the bacteria would have survived the summer months. Prior to the start of operation of the Biotreatment System, the bacteria retention trays were sampled to evaluate if the system required an additional inoculation. The analytical results were impressive. One day after the samples collected from the bacteria retention trays were spiked with glycol, the glycol was almost fully degraded. This was indicative of an active bacterial colony. Therefore, re-inoculation of the Biotreatment System was not deemed necessary. However, upon reactivation of the system, nutrient injections resumed as per the previous year.

As mentioned above, several monitoring wells were added to supplement the required data to assess the system performance. These monitoring wells were placed at selected locations for monitoring purposes. One was installed immediately adjacent to the system, one was added 40 m from the system, one was added 140 m from the system and three others were placed between BH 02-06 and BH 02-07 and are labelled BH 04-11A to BH 04-11C.

To date, with the exception of the detection of glycol in BH 04-10, located 5 m from the Biotreatment System), glycol has not been detected in the other down gradient groundwater monitoring wells. However, acetate, a degradation by-product, was detected in BH 02-05 and BH 02-05A that are located down gradient of BH 04-10. This further indicates that glycol is being degraded by the system. This trend held true for the third year of operation.

CONCLUSION

After completion of the bench scale and pilot tests, it was proven that in laboratory conditions ethylene glycol did not readily degrade *in-situ*. However, following the addition of bacteria collected from the on-site catch basins assisted with nutrients, glycols degrade rapidly.

Following 3 years of system analyses, the analytical data confirms the conclusions of the bench and pilot scale studies as follows:

- Ethylene glycol does not readily degrade in indigenous soil conditions;
- Ethylene glycol readily degrades when inoculated with bacteria that has been subjected to long term exposure to glycol;
- Bacteria provided with inorganic nutrients degrade ethylene glycol;
- In anaerobic conditions, degradation by-products of ethylene glycol are acetate and ethanol as previously documented (methane has not been observed yet in the monitoring wells);
- Glycol bio-degradation occurs in less than 30 days, given the right conditions;
- Ethanol degrades *in-situ* within 2-3 months;
- Acetate or acetic acid (vinegar) is not considered a substance that requires remediation and is not considered a hazardous substance as per discussions with the Ontario Ministry of the Environment. However, monitoring for acetate is being completed and to this date has not migrated in an area even close to the property boundary.

The Ottawa Airport, aided by SAIC, has implemented a relatively simple and inexpensive Biotreatment System that takes full advantage of local site conditions and naturally degrades glycol.

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