

# Surfactant Enhanced In-situ Remediation of DNAPL Impacted Soil and Groundwater - Montreal Refinery Case Study

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**Abstract:** A Montreal chemical refinery reduced the dichlorobenzene and other dense non-aqueous phase liquid (DNAPL) impacts on the soil and groundwater where a railway line is adjacent to an above ground storage tank farm. Ivey-sol<sup>®</sup> surfactant mixtures were injected three times during a two week pilot test, into a series of in-situ wells. The soil and groundwater matrix experienced an induced partial vacuum of 75 mm Hg (mercury). Recovery well water samples were analyzed for concentrations of specific DNAPL (Chlorobenzene and Dichlorobenzenes) and BTEX (benzene, ethylbenzene, xylenes, and toluene) solvent “compounds of concern”. Groundwater recovery flow rates were documented and recovered mass estimates were calculated. Compared to projected baseline conditions and efforts, the surfactant enhanced in-situ remediation efforts in this case study, resulted in a significant incremental increase in the recovered mass of the DNAPL and BTEX “compounds of concern”, which had impacted the soil and groundwater. The mass recovery increased by over 500% for the DNAPL compounds, plus an additional 50% of DNAPL mass recovered as free product. Compared to the results of three years of earlier efforts by others, the client was quoted as finding this approach to be a “rapid and cost effective method to achieve site clean up.”

**Key words:** surfactant, in-situ, remediation, DNAPL, refinery

## 1 Introduction

At a Montreal area chemical refinery, commercial activities dating back to the 1950s resulted in multiple reported releases of dichlorobenzenes and other dense non-aqueous phase liquid (DNAPL) and BTEX solvent (benzene, toluene, ethylbenzene, and xylenes) “compounds of concern” associated with the chemical storage, transportation, and handling activities. These compounds impacted the soil and groundwater on the site where a railway line is adjacent to an above ground storage tank farm. Previous efforts to address DNAPL impacts at the refinery had not been satisfactory. Beneath the site, a groundwater aquifer is connected to a municipal potable water supply well.

Surfactants are chemicals that act to reduce the bonding forces between certain “compounds of concern”, and the associated soil particles and water matrix to which these compounds are absorbed. A non-ionic surfactant was selected for the application at the site as it will decrease the surface tension of groundwater water. Organic compounds in contact with a non-ionic surfactant, desorbs from soil particles; become more miscible in groundwater water; hydraulically available for recovery; and biologically and chemically available for bioremediation and chemical oxidation remedial applications.

## 2 Approach

A laboratory bench scale test was performed to identify baseline water quality and surfactant demand and determine appropriate required materials, equipment and support infrastructure for on-site pilot scale demonstration. Consideration was given to the various relationships between the physical, chemical, and sometimes biological characteristics of the site specific soil, water, and “compounds of concern”, as well as to potentially useful surfactant or other treatment compounds that are equivalently or similarly effective. The evaluation included soil particle surface area; applicable chemical bonding mechanisms; water solubility of the compound of concern; and the target concentration of the surfactant or other treatment chemical. The bench scale testing results were a basis for a preferred surfactant recommendation and supply.

The pilot scale demonstration for the controlled injection of the surfactant water mixture into the subsurface soils and groundwater regimes would be conducted to evaluate surfactant dosing estimates determined in bench scale testing and relative performance, evaluate hydraulic control in the area of interest; document the pumping rate from the recovery well, the partial vacuum induced from the air blower, and changes in concentrations of the “compounds of concern” in the recovery water for full scale application design recommendations.

### 3 Site Characterization

In 2007, nine (9) 100 mm diameter polyvinyl chloride (PVC) wells were drilled and installed in the area of interest. Eight (8) of these wells were used for monitoring groundwater conditions. One (1) of these wells was used as a recovery well. Four of the eight monitoring wells were also used for injecting surfactant into the soil groundwater matrix. Located in the center of the injections wells is one (1) groundwater and amendment recovery well. Observations, local regulator environmental goals, and the analytical laboratory results from soil and groundwater samples taken collected for baseline characterization.

The injection wells were advanced to relative depths of 6.14 – 8.40 metres below the surface soil grade with hollow-stem auger drilling technology. The borehole logs document the physical soil conditions encountered. Geological information was characterized from this activity. From the underside of the hard surface at grade, there is a layer of crushed stone (0.0 – 0.6 metres below grade). Below this is a layer of varying thickness of sand fill material with silt and gravel (0.6 – 1.2 / 1.8 metres below grade). Below this is a layer of varying thickness of native silt material with sand and gravel (1.2 / 1.8 – 5.4 / 7.2 metres below grade). Below this is a relatively stiff native glacial till material (5.4 / 7.2 – at least 8.4 metres below grade). Bedrock was not encountered.

Groundwater was encountered and measured (at relative elevations of 0.83 – 3.83 metres below grade). No free phase product was initially encountered.

Based on the past industrial activities, laboratory analysis was made of soil and water samples for mono-aromatic hydrocarbons, including dichlorobenzene DNAPL and BTEX solvents. During the 2007 characterization activities, twenty (20) soil and thirteen (13) water samples were analyzed. This included two (2) duplicate soil samples. The results were tabulated and compared to the local regulator's applicable environmental goals. Most soil samples had analytical results exceeding some of the regulator environmental goals. This occurred for the BTEX solvents, chlorobenzene, and the dichlorobenzenes, which then became the "compounds of concern" for this case study.

Estimates of groundwater flow rate (2 litres / minute) and hydraulic conductivity ( $3.2 \times 10^{-3}$  cm/s over the initial 110 minutes, and  $1.9 \times 10^{-5}$  cm/s after 110 minutes) were calculated from a short-term pump test. The more rapid hydraulic conductivity was considered to be associated with a more porous sand and gravel portion of the soil matrix. The lower hydraulic conductivity is considered to be representative of the native glacial till material.

The field equipment included a Redi-Flo 2 pump by Grunfos, water level data loggers in the recovery well and injection well IW-4, and an interface probe to measure relative water elevations in other wells under dynamic pumping conditions.

### 4 Surfactant Enhanced Remediation Pilot Test

An in-situ surfactant injection pilot test was conducted to test the feasibility and practicality of a surfactant enhanced remediation of soil and groundwater at this site. The pilot test results regarding both the mass of recovered "compounds of concern", and the equipment, material, and financial resources used, would influence the conclusions and recommendations about applying this approach on a larger scale, and on a more sustained level of effort.

The surfactant-water mixture was gravity fed into each injection well. Groundwater – amendment mixtures were pumped from the recovery well, located in the center of the monitoring and injection wells as shown in Figure 1 below. Observations, relative groundwater elevations, pumping rates, and analytical laboratory results from samples of the recovered fluid were documented.

Figure 1 presents the relative locations of the injection wells with respect to the central recovery well where the groundwater pumping occurred.

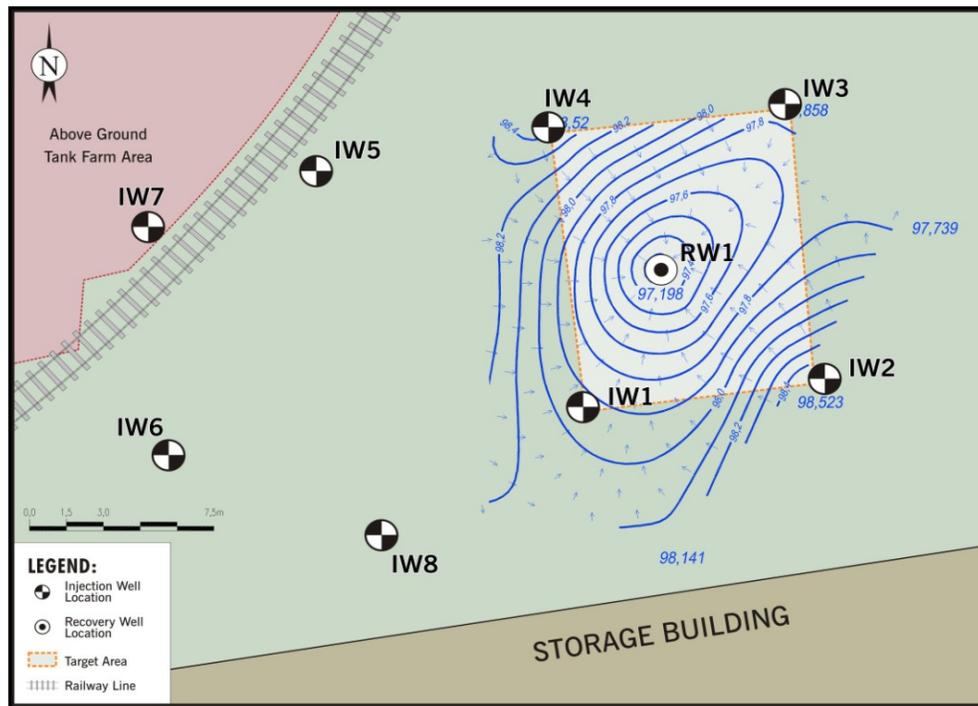


Fig. 1 Relative Recovery and Injection Well Locations Within Pilot Application Area

### Field Demonstration Pilot Test Activities

An on-site field demonstration pilot test consisting of three injection events was conducted to test the anticipated effectiveness of the surfactant enhanced remediation process for mobilization and capture of the “Compound of Concern” mass. Each of the three gravity injections consisted of 40 litres of an Ivey-sol<sup>®</sup> mixture and 100 litres of fresh water. Mixture #1 was used for the first (September 12) and third (September 17) injection events. Mixture #2 was used for the second (September 14) injection event.

Each injection event was performed by gravity feed of surfactant-water mixture in each injection well followed by recovery of groundwater and surfactant-water mixture. The extracted fluid mixture from the recovery well was transferred to a 1,000 litre storage container, and was appropriately treated to meet local and regulatory discharge requirements. Samples were collected for verification prior to being discharged.

The following is a description of the general injection and recovery procedures.

1. The “baseline conditions” reflect the pre-pilot test sampling results prior to surfactant injection. Relative groundwater elevation measurements, and tests for the potential presence of free phase product, were recorded before, during, and after the injection and recovery portions of the pilot test.
2. Temporary extensions were made to each injection well, so that surfactant – water mixtures poured into them would have an increased hydraulic head for gravity injection.
3. Mix ratios of 40 litres Ivey-sol<sup>®</sup> surfactants with 100 litres of fresh water.
4. Gravity feed surfactant-water mixture into the injection wells.
5. Monitor rising head from gravity feed injection until static water level reached.
6. Start groundwater and surfactant-water mixture recovery from the recovery well. Information in the Figure 3 table shows the varying pumping rate. Collect samples of pumped water and evaluate them visually and chemically for the presence of surfactant. Send samples to the laboratory for chemical analysis.
7. Estimate the volumes of fluids pumped from the recovery well.

The samples collected during the test were taken before the injection and at three times during the day of each injection event at approximately 7:30 AM, 12:00 PM, and 5:00 PM.

## Pilot Test Results

Figure 2 presents the changes in the cumulative dichlorobenzene concentrations in recovery well water samples during the pilot test. The Figure 3 table presents a summary of the analytical recovery well sample concentration results for the individual “compounds of concern”.

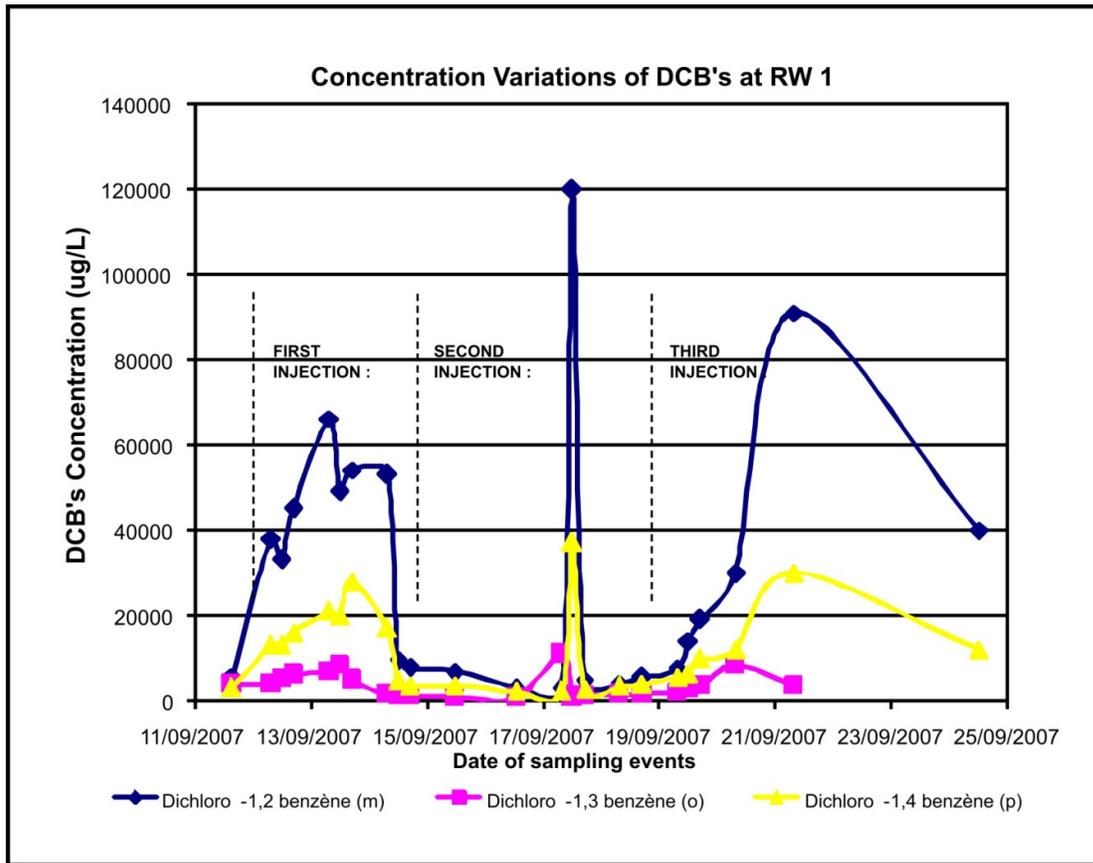


Fig. 2 Cumulative Dichlorobenzene (DCB) Concentrations from Recovery Well

Water samples were collected of the surfactant – water – “compounds of concern” mixture that was pumped from the recovery well. The samples were taken before the injection and at three times during the day of each injection at approximately 7:30 AM, 12:00 PM, and 5:00 PM. Twenty-one (21) water samples were collected from the recovery well and analyzed for contaminants of concern. The laboratory methods, certificates, and results are documented for future reference. A tabulated summary was made of the water fluid sample concentration results of the “compounds of concern,” and of the cumulative total mass being recovered. Excerpts are presented in the Figure 3 table. The same table also presents the varying recovery well pumping rates (L/min).

For comparison purposes below, the “baseline conditions” (i.e. 11/09/2007 15:15 sample results at a flow rate of 2.4 L/min) are those from before the surfactant has been injected (12/09/2007 7:30). “Baseline conditions” were documented for the groundwater conditions encountered, sampled, and analyzed

Calculated estimates were made from the pilot test of the recovered mass of the “compounds of concern.” This was based on multiplying the applicable laboratory sample concentration result ( $\mu\text{g/L}$ ) by the representative recovery well flow rate (L/min) associated with the time interval (minutes) for which the laboratory sample result is considered to be representative.

The recovered cumulative mass of the “compounds of concern” when the surfactant is applied is 2.29 kg. The third surfactant injection contributed the largest portion of mass to this cumulative total.

Date and Time of Recovery Well Sample	"Compounds of Concern": Mono-aromatic Hydrocarbons (ug/L)									Recovery Well Pumping Rate (L/min)
	Benzene	Chlorobenzene (mono)	Dichloro-1,2 benzene (m)	Dichloro-1,3 benzene (o)	Dichloro-1,4 benzene (p)	Ethylbenzene	Toluene	Xylenes (o,m,p)	Cumulative Summation of dichloro-benzene concentrations	
<b>Concentration Goal (ug / Litre) of Regulator</b>	<b>590</b>	<b>130</b>	<b>70</b>	<b>15,000</b>	<b>110</b>	<b>420</b>	<b>580</b>	<b>820</b>		
Laboratory Reporting Limit (ug / Litre)	5	80	200	*	5	2.4	24	300		
Baseline Conditions at Time = 0, prior to Injection Event 1										
11/09/2007 15:15	150	<b>1,900</b>	<b>5,500</b>	1,000	<b>3,000</b>	100	360	310	9,500	2.4
Injection Event 1 (Surfactant Mixture 1)										
12/09/2007 7:30	220	<b>3,000</b>	<b>38,000</b>	3,900	<b>13,000</b>	120	<b>2,600</b>	260	54,900	2.40
12/09/2007 12:00	230	<b>3,200</b>	<b>33,000</b>	4,100	<b>13,000</b>	120	<b>2,600</b>	280	50,100	2.40
12/09/2007 17:00	220	<b>3,100</b>	<b>45,000</b>	5,100	<b>16,000</b>	120	<b>2,700</b>	290	66,100	2.40
13/09/2007 7:30	< 400	<b>3,100</b>	<b>66,000</b>	6,200	<b>21,000</b>	< 200	<b>2,700</b>	< 800	93,200	1.25
13/09/2007 12:00	220	<b>3,000</b>	<b>49,000</b>	6,900	<b>20,000</b>	120	<b>2,400</b>	500	75,900	1.25
13/09/2007 17:00	230	<b>3,300</b>	<b>54,000</b>	8,500	<b>28,000</b>	130	<b>2,600</b>	570	90,500	1.25
Injection Event 2 (Surfactant Mixture 2)										
14/09/2007 7:30	< 80	<b>2,400</b>	<b>53,000</b>	5,000	<b>17,000</b>	< 200	<b>1,700</b>	< 800	75,000	1.25
14/09/2007 12:00	110	<b>1,900</b>	<b>9,600</b>	1,500	<b>4,800</b>	100	520	380	15,900	1.25
14/09/2007 17:00	130	<b>2,300</b>	<b>7,900</b>	1,300	<b>3,600</b>	120	520	280	12,800	1.25
15/09/2007 11:40	84	<b>1,400</b>	<b>6,900</b>	1,200	<b>3,600</b>	58	350	260	11,700	0.80
16/09/2007 13:00	84	<b>1,400</b>	<b>3,300</b>	820	<b>2,300</b>	61	100	230	6,420	2.00
17/09/2007 7:30	110	<b>1,800</b>	<b>3,100</b>	780	<b>2,200</b>	93	79	310	6,080	2.60
17/09/2007 12:00	< 40	<b>4,800</b>	<b>120,000</b>	11,000	<b>37,000</b>	< 20	<b>3,500</b>	< 80	168,000	2.60
17/09/2007 17:00	130	<b>2,100</b>	<b>4,700</b>	960	<b>2,800</b>	140	140	520	8,460	2.60
18/09/2007 7:30	170	<b>2,800</b>	<b>4,100</b>	1,200	<b>3,400</b>	150	190	400	8,700	0.00
18/09/2007 17:00	170	<b>3,100</b>	<b>5,400</b>	1,500	<b>3,900</b>	220	310	570	10,800	0.00
Injection Event 3 (Surfactant Mixture 1)										
19/09/2007 7:30	340	<b>4,600</b>	<b>7,500</b>	1,700	<b>5,600</b>	300	<b>1,100</b>	780	14,800	2.72
19/09/2007 12:00	170	<b>4,100</b>	<b>14,000</b>	2,000	<b>6,500</b>	250	<b>860</b>	500	22,500	2.72
19/09/2007 17:00	360	<b>5,200</b>	<b>19,000</b>	3,000	<b>9,800</b>	320	<b>2,400</b>	<b>1,000</b>	31,800	2.72
20/09/2007 7:30	190	<b>2,800</b>	<b>30,000</b>	3,500	<b>12,000</b>	120	<b>2,100</b>	330	45,500	2.72
21/09/2007 7:30	< 400	<b>3,800</b>	<b>91,000</b>	8,600	<b>30,000</b>	< 200	<b>3,400</b>	< 800	129,600	2.72
24/09/2007 12:00	< 400	<b>2,900</b>	<b>40,000</b>	3,600	<b>12,000</b>	< 200	<b>3,900</b>	< 800	55,600	0.00

Fig. 3 Analytical Recovery Well Sample Concentration Results for the "compounds of concern"

### Injection Event One (September 12, 2007)

Calculated estimates of the mass recovery of the "compounds of concern" are based on a pumping rate from the recovery well of 2.4 L/min from 12/09/2007 7:30 to 13/09/2007 7:30; and 1.25 L/min from 13/09/2007 7:30 to 14/09/2007 7:30.

Calculated estimates of mass recovery of the “compounds of concern” are based on a cumulative pumping volume of approximately 5,256 litres (1.825 L/min x 60 minutes / hour x 48 hours).

Dichlorobenzene concentrations increased in the recovery well samples, peaked at 980% over “baseline conditions” (i.e. 93,200 / 9,500 x 100%) in the 13/09/2007 7:30 sample.

The cumulative “compounds of concern” mass concentration recovery rate increased by about 560% over “baseline conditions” (7.65 / 1.37 x 100%). This is based on a 367 g recovery of dichlorobenzene DNAPL over 48 hours of pumping at a weighted average rate of 1.825 L/min.

For 1,2- and 1,4-dichlorobenzene, the 74 – 145 mg/L resulting recovered concentration range also corresponds to between 45%-83% of the compounds water solubility limit. For 1,3-dichlorobenzene, the recovered concentration was in the range to 6 – 7% of the solubility limit. When solubility limits are exceeded, free product may exist, and this influences the choice of surfactant, the remediation infrastructure selection, and the associated operations.

The cumulative mass concentration increased, peaked, and then decreased after the injection.

### **Injection Event Two (September 14, 2007)**

Calculated estimates of the mass recovery of the “compounds of concern” are based on a pumping rate from the recovery well of 1.25 L/min from 14/09/2007 7:30 to 15/09/2007 11:40; 0.8 L/min from 15/09/2007 11:40 to 16/09/2007 13:00; 2.0 L/min from 16/09/2007 13:00 to 17/09/2007 7:30; 2.6 L/min from 17/09/2007 7:30 to 18/09/2007 7:30; and 0 L/min from 18/09/2007 7:30 to 19/09/2007 7:30.

Calculated estimates of mass recovery of the “compounds of concern” are based on a cumulative pumping volume of approximately 9,000 litres (1.57 L/min x 60 minutes / hour x 96 hours).

Dichlorobenzene concentrations in the recovery well samples, peaked at 1,768% over “baseline conditions” (i.e. 168,000 / 9,500 x 100%) in the 17/09/2007 12:00 sample.

The cumulative “compounds of concern” mass concentration recovery rate increased by about 175% over “baseline conditions” (2.40 / 1.37 x 100%). This is based on a 232 g recovery of dichlorobenzene DNAPL over 96 hours of pumping at a weighted average rate of 1.57 L/min.

Starting on September 14, 2007, a second tube leaving the well head of the recovery well, was connected to an air blower that was inducing a partial vacuum on the soil – groundwater matrix. At the recovery well head, the gauge indicated that a partial vacuum existed of approximately 75 mm Hg. After inducing the partial vacuum, there was an increase the groundwater elevation, but also the flow rate of the groundwater and fluid recovered. However, aside from a spiked concentration event, the recovery rate of the mass of the “compounds of concern”, dropped. After the third injection, and highest pumping rate, the mass recovery rate increased again. This is consistent with the information presented in Figure 2 and the Figure 3 table.

The relatively flat, middle portion corresponds with the combined influence of second injection event, the injection surfactant mixture #2, the induced vacuum, and the associated increase in groundwater elevation under dynamic conditions.

An exceptional spike in concentration results is graphically presented in Figure 2, and also presented in the Figure 3 table. A comparison of the combined “spiked” 1,2-dichlorobenzene concentration results (120 mg/L at laboratory temperature), and the solubility in water limit (140 mg/L at 25 °C) suggests that some free product may have existed in the sample that was analyzed.

### **Injection Event Three (September 19, 2007)**

Calculated estimates of the mass recovery of the “compounds of concern” are based on a pumping rate from the recovery well of 2.72 L/min from 19/09/2007 7:30 to 21/09/2007 7:30; and 0 L/min from 21/09/2007 7:30 to 24/09/2007 12:00.

Calculated estimates of mass recovery of the “compounds of concern” are based on a cumulative pumping volume of approximately 20,000 litres (2.7 L/min x 60 minutes / hour x 124.5 hours).

Dichlorobenzene concentrations in the recovery well samples, peaked at 1,360% over “baseline conditions” (i.e. 129,600 / 9,500 x 100%) in the 21/09/2007 7:30 sample.

The cumulative “compounds of concern” mass concentration recovery rate increased by about 1,100% over “baseline conditions” ( $15.3 / 1.37 \times 100\%$ ). This is based on a 1901 g recovery of dichlorobenzene DNAPL over 124.5 hours of pumping at a weighted average rate of 2.7 L/min.

The cumulative mass concentration increased, peaked, and then decreased after the injection. Injection Event 3 is associated with the highest flow rate (2.7 L/min), sustained over a longer time period (about 5 days). These characteristics, combined with a recovery mass concentration similar to the after the first injection, resulted in a greater area under the Figure 2 curve, and a greater total mass of recovered “compounds of concern”.

### Lessons Learned

Some unintended mixing of near free phase hydrocarbon in the recovered water fluid occurred (i.e. the Injection Event 2 spiked sample results), which may have been associated with the turbulent fluid flow from the impellor action of the pump used, as opposed to the use of another type of pump, which may have better maintained a laminar flow. Alternatively, the combination of a relatively low flow rate and a large temporary holding storage tank retention time would also encourage a low, laminar flow rate.

The Figure 3 table pumping rate values demonstrate that the pump equipment used did not operate all of the time. This experience influences the equipment selection decision making on a larger full-scale application.

### Discussion

The relative groundwater elevation measurements, under pumping conditions, demonstrated the presence of a hydraulic flow gradient and hydraulic zone of influence between the recovery well and the injection wells. The observed surfactant foam in the recovery well demonstrated the presence of a hydraulic capture zone between the recovery well and injection well. The distances from the injection wells to the recovery well ranged from approximately 4 – 5 metres.

On September 14, 2007, a partial vacuum (75 mm Hg at the air blower) was induced in the in-situ soil groundwater conditions as Injection Event 2 began. Under the relatively low flow site conditions, the groundwater elevation under dynamic pumping conditions rose to similar elevations as under static conditions. The recovery well water pumping rate increased from 1.25 to 2.6 – 2.7 L/min.

Injection event 3 had the greatest mass recovery, when the sustained vacuum assisted pump flow rate was the greatest, and surfactant mixture #1 was being applied.

## **5 Conclusions and Recommendations**

“Compounds of Concern” identified in Figure 3 of this case study, exceeded the applicable environmental goals of the local regulator. The values for individual “compounds of concern” were sometimes more and sometimes less than these cumulative average values. Continuing the pilot test would have continued the recovery of “Compound of Concern” mass. Some of the individual compound concentrations at the end of the pilot test were greater than the corresponding ones at the beginning of the pilot test.

Compared to projected baseline conditions and efforts, the surfactant enhanced in-situ remediation efforts in this case study, resulted in a significant incremental increase in the recovered mass of the DNAPL and BTEX “compounds of concern”, which had impacted the soil and groundwater at this Montreal area chemical refinery.

Compared to “baseline conditions” the incremental increase in the recovered mass of the DNAPL “compounds of concern” from the recovery well water, with the surfactant enhanced approach demonstrated in the pilot test, is approximately 550%. This is based on the ratio of the mass recovery flux rates (7.6 g / hour with surfactant versus 1.37 g / hour without surfactant). This does not include or account for the recovered 1.3 kg mass of free phase DNAPL product that was recovered on September 11, 2007.

Compared to “baseline conditions” the incremental increase in the recovered mass of the DNAPL “compounds of concern” from the free phase product and recovery well water, with the surfactant enhanced approach demonstrated in the pilot test is 3 kg (= 2.1 + 1.3 – 0.37).

A full scale design of a surfactant enhance remediation application was prepared. Based on the pilot test results, full-scale design would require an increased surfactant concentration. Specifically, surfactant mixture #1, used during the first and third injection events, was more effective than mixture #2, used during the second injection event.

Alternative recovery well pumping equipment will be identified in order to lessen the potential for emulsification to occur (i.e. the highest concentration between the second (September 14) and third (September 17) injection events, as presented in Figure 2 and the Figure 3 Table).

A quote from the Ivey International Inc. client regarding this case study application - "The in-situ application of the Ivey-sol<sup>®</sup> surfactant technology significantly increased DNAPL and BTEX mass recovery from the impacted soil and groundwater on-site. We were very pleased by these results leading to our recommending a full scale site application as a rapid and cost effective method to achieve site clean up."