

# Using Humalite-Derived Humic Products to Mobilize Soil-Adsorbed Hydrocarbons and Enhance Natural Attenuation

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## ABSTRACT

Residual hydrocarbons adsorbed to the soil present challenges for remediation due to the difficulty in physically removing the residual product and the associated time and cost requirements to do so. When the material is found to be fully sorbed to the soil, and virtually absent in the groundwater, traditional methods of treatment, such as pump-and-treat, are of limited utility.

During historical groundwater monitoring events at an abandoned oil battery site, F2 and F3 hydrocarbons and PAHs have been found in the groundwater in the immediate area of what has been potentially identified as a former flare pit. The presence of deep earth metals, including lead, cadmium and selenium, indicates that impacted groundwater extends some distance downgradient of the flare pit area. While these deep earth metals are found in the downgradient groundwater, hydrocarbons are not observed, indicating that natural attenuation of the hydrocarbons is likely occurring. The remaining hydrocarbons (TEH, C<sub>8</sub> to C<sub>40</sub>) are likely sorbed to the soil within the impacted area.

Research is ongoing on the effectiveness of humic product injection into groundwater in an effort to increase the solubility of hydrophobic organic contaminants. The humic acid products are used as flushing agents to increase the concentration of some hydrophobic organic contaminants in the aqueous phase, in order to mobilize (desorb) the organic compounds from the soil and make them more available for biodegradation.

Early results seem to indicate that the introduction of humic products into the groundwater of our site have been successful in mobilizing sorbed hydrocarbons into the groundwater where they will be more amenable to treatment through either traditional *ex-situ* methods or monitored natural attenuation and biodegradation.

## INTRODUCTION

Aqueous humic substances (HSs) play a key role in controlling the aqueous concentrations, mobility, bioavailability and toxicity of hydrophobic contaminants in the environment. Because of their ability to bind hydrophobic compounds, commercial humic acids in water may be useful agents for flushing organic contaminants sorbed to soils in the subsurface.<sup>1</sup> Studies suggest that the use of high aqueous concentrations (>1 g/L) of commercial HSs would maximize the efficiency of the flushing process. This

could be advantageous in the remediation of older oilfield sites at which weathered hydrocarbons are sorbed to subsurface soils.

## **BACKGROUND**

Devon Canada Corporation's (Devon's) Foothills #9 Battery (site) is an abandoned battery site located near Millarville, Alberta. The well associated with the site was drilled in 1944.

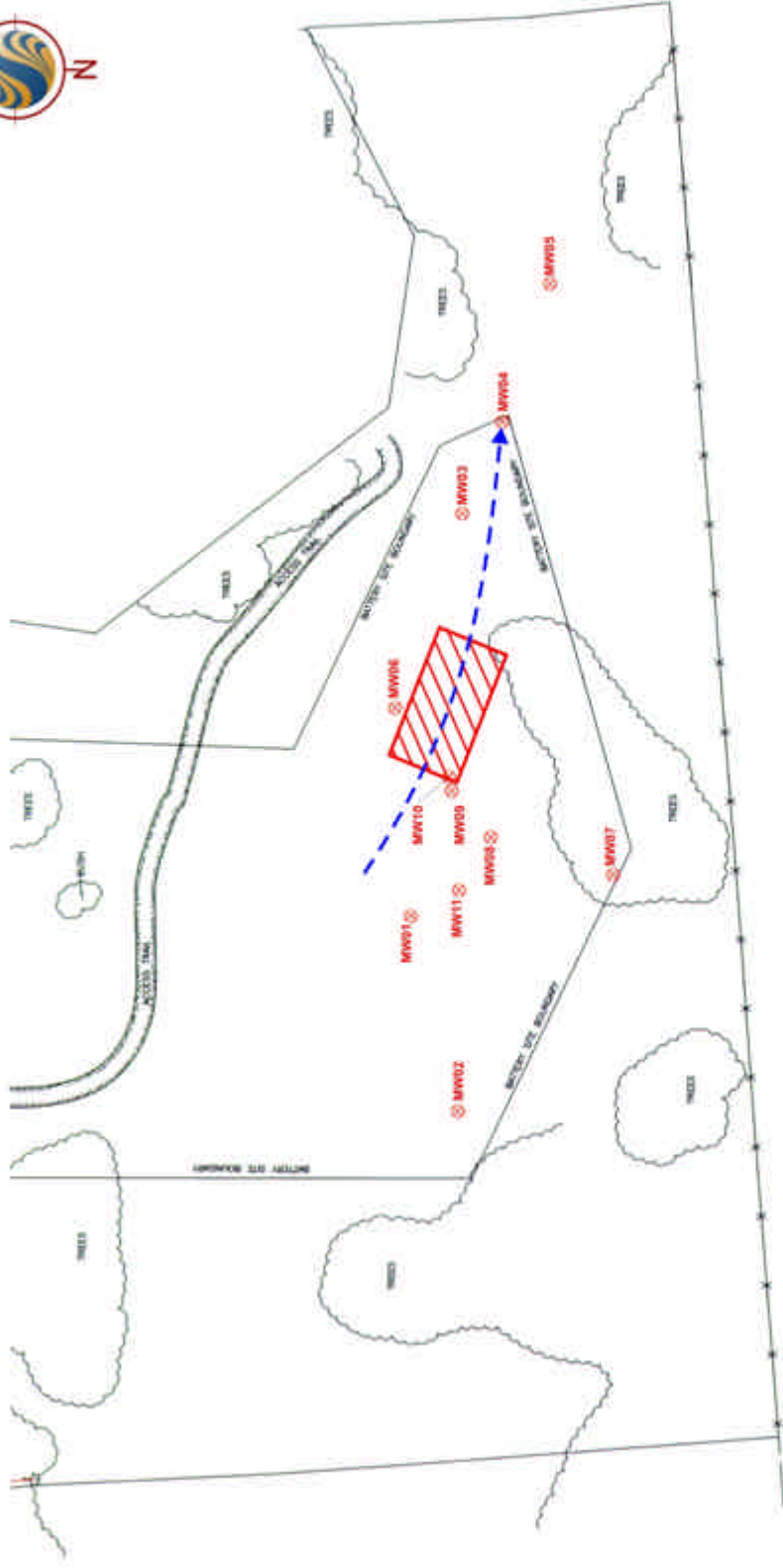
A Phase I investigation and a detailed Phase II investigation of the site in 1996 identified a suspected former flare pit in the southern portion of the site. The site is situated on a terrace of a creek, with the southern portion at the base of the slope of the terrace.

A groundwater investigation performed in 1999 revealed groundwater in near-surface glaciofluvial gravels in the southern portion of the site (study area). The southern portion has not been remediated and soil and groundwater impacts remain in this area. A dual phase vacuum extraction (DPVE) system has been operated on the site in an attempt to remediate the remaining impacts in the southern portion, but the efficacy of this technology is limited since the majority of the contamination is sorbed to the soil, with lesser amounts in the dissolved phase.

Historical groundwater monitoring events, including the most recent in 2003, indicated that relatively low levels of F2 and F3 hydrocarbons and PAHs are present in the groundwater in the immediate area of what has been potentially identified as a former flare pit, near MW09 and MW10 (Figure 1). Based on an analysis of deep earth metals, including lead, cadmium and selenium, impacted groundwater extends to the east of MW03 and to the north of MW06. While deep earth metals are found in the groundwater in these wells, hydrocarbons are not observed, indicating that natural attenuation of the hydrocarbons is likely occurring. The remaining hydrocarbons (TEH, C<sub>8</sub> to C<sub>40</sub>) appear to be sorbed to the soil within the impacted area.

Environment Canada, in partnership with the University of Waterloo and the Petroleum Technology Alliance Canada (PTAC), is currently in the process of conducting testing on the effectiveness of humic product injection in order to increase the solubility of hydrophobic organic contaminants.<sup>2</sup> The humic acid products are used as flushing agents to increase the concentration of some hydrophobic organic contaminants in the aqueous phase, in order to mobilize (desorb) the organic compounds from the soil and make them more available for biodegradation.

It was anticipated that injecting humic acid products into the groundwater at the site would result in an initial increase of F2 and F3 hydrocarbon fractions in the groundwater, to be followed by a reduction in concentration as these constituents are naturally biodegraded. Field and laboratory monitoring are being used to observe the changes in the natural biodegradation of the hydrocarbons. This portion of the investigation is ongoing and the results will be presented in a later paper.



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Legend

- GROUNDWATER MONITORING WELLS
- FENCES
- DIRECTION OF GROUNDWATER FLOW
- STUDY AREA



FOOTHILLS #9  
 Figure No. 1  
 Title Site Plan

The surficial deposits in the vicinity of the site include coarse stream alluvium, meltwater channel deposits and glaciolacustrine deposits.<sup>3</sup> Bedrock geology in the vicinity of the site consists of Cretaceous Brazeau Formation and Alberta Group. The Brazeau Formation consists of thickly-bedded sandstone and mudstone. The Alberta Group consists of sandstone, shale and siltstone belonging to the Cardium Formation, and shale, siltstone, sandstone and ironstone of the Wapiabi Formation.<sup>4</sup>

The local geology in the study area consists of a sandy loam of glaciofluvial origin that is approximately 3.0 m thick, overlying 1.5 m of brown to grey clay till. The till contains gravel in the range from 5.0 to 8.0 cm with little to no iron staining apparent. Black staining was observed only in the layers that contained soil hydrocarbons.

Groundwater yields in the surficial sediments in the vicinity of the site are stated to be greater than 38.0 L/s, while groundwater yields in bedrock wells adjacent to the site are noted to have yields from 0.1 to 0.4 L/s. Most wells are completed in locally fractured bedrock or alluvial sand and gravels. Numerous springs with flow rates ranging from 1.0 to 2.0 L/s occur near the site.<sup>5</sup>

Groundwater on the site is situated approximately 2.2 to 2.9 m below ground surface within the study area. From previous investigations of the site the groundwater flow was calculated to be 37.87 m/yr, or 10.4 cm/day, based on a hydraulic conductivity of  $3 \times 10^{-5}$  m/s, a hydraulic gradient of 0.010 m/m, and a porosity of 0.25. These values dictated the spacing of the study wells. At the beginning of the current study falling head tests (*i.e.* slug tests) were performed on each of the three injection wells. From these tests the hydraulic conductivities were calculated to be on the order of  $4 \times 10^{-3}$  m/s, two orders of magnitude higher than those previously determined. This hydraulic conductivity indicates a groundwater flow of approximately 13.5 m/day. A rising head test (*i.e.* pump test) was also conducted on 04-MW12, producing a calculated hydraulic conductivity of  $2.3 \times 10^{-5}$  m/s and a groundwater flow of approximately 4.5 cm/day or 16.5 m/yr. Observations made after the second addition of the humic product (*vide infra*) seem to indicate that the slug test results are more truly indicative of actual subsurface groundwater velocities.

## **METHODOLOGY**

A Becker-Hammer Drill Rig was used to advance eight boreholes within the study area to a maximum depth of between 2.5 and 4.0 metres (Figure 2). Each of the boreholes was completed as a groundwater monitoring well. The eight wells were all spaced approximately four metres apart. This spacing, and the total number of monitoring wells installed, were determined based upon the historically calculated groundwater flow velocity and by the amount of time allotted to perform the field study. During installation of the boreholes soil samples were collected and analyzed by Enviro-Test Laboratories of Calgary for benzene, toluene, ethylbenzene and xylenes (BTEX), hydrocarbon fractions F1-F4, PAHs and Tier I metals to determine initial soil conditions.



Monitoring well temperature, pH, specific conductance, electrical conductivity (EC), dissolved oxygen (DO) and oxygen redox potential (ORP) measurements were collected on a weekly basis using a YSI 556 meter. Field measurements were recorded prior to sample collection for monitoring events. When the YSI probe indicated that well conditions were anaerobic groundwater samples were collected and analyzed for speciation of ferrous/ferric iron, nitrate/nitrite nitrogen, and sulfate/sulfite sulfur. Sampling for dissolved metals, BTEX, hydrocarbon fractions F1 & F2 and total extractable hydrocarbons (TEH) was carried out in the injection wells and the first two downgradient monitoring wells. On a monthly basis samples were collected from the three injection wells and the first two downgradient monitoring wells and analyzed for dissolved-metals, BTEX, TEH, and the previously noted speciation parameters. All samples were sent to Enviro-Test Laboratories of Calgary for analysis.

The three wells situated in a line perpendicular to the groundwater flow (04-MW12 to 04-MW14) were used as injection wells, while the remaining five wells (04-MW15 to 04-MW19), situated in a line running parallel to the groundwater flow, were used as monitoring wells to track the progress of the injected humic product and any resulting changes in the groundwater chemistry. All wells were field screened on a weekly basis for temperature, pH, specific conductance, EC, DO and ORP. The three injection wells and the well immediately downgradient from the injection wells (04-MW15) were sampled on a weekly basis for total extractable hydrocarbons (TEH) to determine if hydrocarbons had become mobilized and were moving in the groundwater.

### **First Round of Humic Product Injection**

The aqueous humic product used in the investigation was “Dry Soluble 80”, which was provided by Black Earth Humates Ltd. (Black Earth) of Edmonton. Dry Soluble 80 is a concentrated “water soluble” powder derived from naturally occurring humic-containing materials from humalite deposits in Alberta. Humalite, which is similar in properties to leonardite, is a naturally-occurring, highly oxidized organic material with high concentrations of humic acids and is found adjacent to sub-bituminous coal.<sup>6</sup> The “water solubility” of the product depends on the definition of “dissolved”. If a distinction is made between dissolved phases and colloidal phases (with particles from approximately one nanometer to one micron in diameter), most aqueous humic products are colloidal in nature, rather than truly dissolved.

An aqueous humic concentration of approximately 33 g/L was the target concentration that we felt would maximize the efficiency of the flushing process. Previous work has showed that HSs sorption on mineral and sediment surfaces are nonlinear; that the concentration of sorbed HSs often reaches a plateau at relatively high aqueous levels apparently because there are only a finite number of surface sites available for HSs sorption. It was also shown that saturation of available surface sorption sites was approached more rapidly at higher HA concentrations, therefore a smaller fraction of dissolved HSs was sorbed over the first few days and a larger fraction of dissolved HA was available for subsequent slow sorption by some other mechanism.<sup>1</sup> The first round of injection was used for initial observations and to investigate site-specific conditions.

Previously reported studies have involved sites with much tighter formations (*i.e.* lower hydraulic conductivities) than this site.<sup>7</sup> See Reference 7 for additional information.

A solution of humic product was mixed in a 205 L polyethylene, open-top drum. Approximately 3.75 kg of Dry Soluble 80 were dissolved in approximately 113.4 L of distilled water to form a solution of approximately 33.1 g/L. The solution was introduced into the three injection wells via pouring with a plastic utility bucket at a rate of approximately 3.33 L/s.

### **Second Round of Humic Product Injection**

For the second round of injection, three 205 L polyethylene, open-top drums were fitted with a ¾-inch brass ball-valve, which was then fitted with a reducer to ½-inch (inside diameter) to accommodate a piece of 5/8-inch (outside diameter) Waterra tubing. A batch of approximately 6.40 kg of Dry Soluble 80 with 189 L of distilled water was mixed to form a solution of approximately 33.9 g/L for injection into 04-MW14. A batch of approximately 6.35 kg of Dry Soluble 80 with 189 L of distilled water was mixed to form a solution of approximately 33.6 g/L for injection into 04-MW13. A batch of approximately 6.30 kg of Dry Soluble 80 with 189 L of distilled water was mixed to form a solution of approximately 33.3 g/L for injection into 04-MW12. Once each batch was prepared, the solution was introduced into the respective wells at a flow rate of approximately 1 L/min.

## **RESULTS AND DISCUSSION**

Field monitoring of several parameters using the YSI 556 meter was carried out on a weekly basis at each of the eight wells. Measured parameters included pH, temperature, specific conductance, electrical conductivity, total dissolved solids, dissolved oxygen, and oxygen redox potential. It was anticipated that monitoring this information would provide an indication of the movement of the humic product through the subsurface and potentially provide general information on the status of any biodegradation occurring (*i.e.* aerobic or anaerobic). Unfortunately, it appears as though some unidentified component in the subsurface resulted in spurious and/or inconsistent results from the field meter. The use of identical duplicate YSI meters in an attempt to verify the measurements produced wildly different results between the meters even for concurrent measurements from the same well. Consequently, pending further investigation with the use of a flow cell, minimal credence has been placed on the results of the field monitoring program at this time.

The movement of the humic product through the subsurface was monitored visually via the injection and monitoring wells. Following the first injection, and up until the time of the second injection, humic product was visually apparent as a brown coloration in the three injection wells (04-MW12 to 04-MW14). It was anticipated, based on the calculated groundwater flow rate, that the product would become visible in the first downgradient monitoring well (04-MW15) in approximately one to two weeks following injection, and in the subsequent downgradient wells at roughly the same intervals.

Unfortunately, monitoring well 04-MW15 generally had the highest levels of F2 and TEH observed in the groundwater onsite, and was already slightly brown in color. Consequently, there was no definitive visual evidence that the humic product ever migrated to this well. The next downgradient monitoring well, 04-MW16 showed no discoloration in the entire 36 day period that elapsed between the two HS injection events.

Examination of laboratory data from the monthly groundwater analytical events did, however, indicate that certain species could act as indicators as to the presence of the humic material. Notably, potassium, iron, and sulfate concentrations in the groundwater were observed to consistently increase or decrease in all three of the injection wells following the introduction of the humic material (Table 1). The pre-injection samples for which the results are shown in the Table were collected on 30 July 2004, prior to the first humic injection on 3 August 2004. The post-injection results represent samples collected on 31 August 2004.

**Table 1. Pre- and Post-Injection Groundwater Concentrations for Select Parameters.**

		Potassium		Sulfate		Iron		F2		TEH	
		mg/L	Trend	mg/L	Trend	mg/L	Trend	mg/L	Trend	mg/L	Trend
<b>Injection Wells</b>											
04-MW12	Pre-Injection	4.2		53.5	-	4.65	-	6.3	-	22	
	Post-Injection	9.5	-	8.5	-	4.38	-	11	-	37	-
04-MW13	Pre-Injection	4.8		66.8	-	0.633	-	15	-	49	
	Post-Injection	6.0	-	29.0	-	0.368	-	39	-	130	-
04-MW14	Pre-Injection	4.8		74.6	-	1.15	-	5.6	-	21	
	Post-Injection	9.0	-	47.5	-	0.935	-	22	-	79	-
<b>Monitoring Wells</b>											
04-MW15	Pre-Injection	4.7		57.8	-	0.167	-	150	-	490	-
	Post-Injection	5.0	-	13.2	-	0.061	-	34	-	130	-
04-MW16	Pre-Injection	4.9		58	-	1.28	-	3.4	-	14	
	Post-Injection	4.9	Ⓜ	42	-	1.50	-	2.5	-		

Potassium concentrations in the groundwater were observed to consistently increase following addition of the humic product. Conversations with the supplier have indicated that potassium is a major component of the particular humic product used (15.8% by weight), so an increase in potassium levels is not unexpected.

Iron levels in the groundwater decreased following the addition of the humic product. Iron and other metals may form complexes with humic products, resulting in their precipitation and consequent unavailability in the groundwater.<sup>8</sup> Zinc groundwater levels were also observed to follow this trend, albeit at much smaller initial concentrations.

Like iron, sulfate groundwater levels were observed to decrease following introduction of the humic product. Exactly why this should be the case is currently uncertain, however it may be indicative of the presence of anaerobic biodegradation. However, speciation

testing of the groundwater samples was carried out and the presence of sulfite in the groundwater, indicative of sulfate-reduction, was not observed. It is unlikely that the lowered sulfate levels are a result of dilution by the distilled water used as the humic material solute since other ionic species were not observed to also have consistently reduced concentrations.

The first downgradient groundwater monitoring well, 04-MW15, exhibited the same general increasing or decreasing groundwater potassium, iron, and sulfate trends as were observed in the three injection wells. This seems to indicate that the humic material introduced during the first injection event had reached this monitoring well. The next downgradient well, 04-MW16 did not exhibit the same trends, from which one of two conclusions may be drawn. The first is that the humic product had not yet reached this location by the time the post-injection samples were collected. The second is that all of the humic product introduced during the first round of the injection had been “used up”, either as a result of complexing with materials in the groundwater (*e.g.* iron) or sorbing to the soil.

Following introduction of the humic product F2 hydrocarbon fractions and TEH were observed to increase in the groundwater from all injection wells. This seems to indicate that the introduction of the humate was successful in mobilizing sorbed hydrocarbons into the groundwater where they can be further treated. However, the first downgradient monitoring well, 04-MW15 exhibited a significant decrease in groundwater F2 hydrocarbon and TEH levels. This may have resulted if a local contamination “hot spot” was present between the three injection wells and 04-MW15. Such a hot spot would have been a continuing source of the higher hydrocarbon levels observed in the groundwater of 04-MW15. The flushing effect of the humic product may have mobilized much of the source in the time period between the pre- and post-injection sampling events and moved much of the contamination past 04-MW15 prior to it being sampled. The fact that the hydrocarbon levels in 04-MW16 were not elevated may indicate that either the material had not yet had time to reach this well, or that the contaminants (and humic product) had bypassed the well due to subsurface channeling (preferential pathways for groundwater flow).

Following the second injection of humic product on 8 September 2004, visual evidence of the presence of humic product was observed in all eight of the wells in the study area only six days following the injection. The presence of humic product in these wells, most notably 04-MW19 which is approximately 27.5 m downgradient of the injection wells, was unexpected based on the historically calculated hydraulic velocities for the site, however should have been anticipated based on the recent slug testing results. TEH levels in 04-MW19 were measured at 4.5 mg/L pre-injection (first injection), and had increased to 18 mg/L one week after the second injection. This increase seems to also provide additional evidence that the humic product is effective in mobilizing sorbed hydrocarbons.

## **Summary of Results**

Under the conditions observed on Devon's Foothills #9 site, injection of humic product into the subsurface seems to be effective in mobilizing sorbed heavier hydrocarbons into the groundwater where they may be subsequently recovered for treatment, or allowed to naturally attenuate through such processes as biodegradation. The measurement of changing groundwater concentrations of potassium, sulfate, and iron seems to provide an effective means of tracking the movement of the humic product through the subsurface, however colorimetric or spectrometric measurements will likely offer more direct and accurate determination.

## **TOPICS FOR ADDITIONAL INVESTIGATION**

Since the second injection of humic product was carried out on the site concurrent with the preparation of this paper, little information is available to be reported here concerning the results of the slower introductory rate and greater quantity of humics being injected. The results of this investigation will be published at a later date.

Of great interest is the potential for monitored natural attenuation to be used as a method of remediation on this site. Preliminary investigations have been made into the processes of biodegradation that may be occurring once the hydrocarbon contaminants have been mobilized into the groundwater and made bioavailable by the humic product. Speciation sampling of iron, sulfur, and nitrogen compounds has been carried out to investigate anaerobic processes, and dissolved oxygen levels and oxygen redox potentials have been measured in an attempt to determine whether the dominant processes are aerobic or anaerobic in nature.

Attempts will continue to collect reasonable and consistent field screening data using electronic probes. It is anticipated that the use of flow cells and mini- or micro-purging of the groundwater wells will result in stabilized readings and allow the determination of real-time field conditions at each well location. The presence or absence of humic product in monitoring wells will be monitored colorimetrically or spectrometrically, rather than by visual evidence.

At the completion of the 2004 field season boreholes will be installed directly adjacent to the three injection wells for the purpose of collecting subsurface soil samples to evaluate what effect the injection of the humic product has had on the hydrocarbons adsorbed to the soil. It is expected that the amount of adsorbed hydrocarbons will be significantly reduced. Results of this investigation will be published at a later date.

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