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Chapter 14

THE INFLUENCE OF GROUNDWATER SAMPLE FLOW RATE ON SUSPENDED SOLIDS, GEOCHEMICAL AND CONTAMINANT CONCENTRATIONS AND ITS EFFECT ON TREND ANALYSIS

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ABSTRACT

Adherence to a standard groundwater sampling method is a fundamental requirement for the accurate assessment of contaminated sites. Confidence in expensive analytical results relied upon to evaluate contaminant fate, transport and risk potential is lost when possible sampling error is suspected. A correlation between suspended solids content and elevated fuel oil hydrocarbon concentrations was observed at sites where aggressive groundwater sampling methods were employed. This relationship was not observed when suspended solids were removed via filtration or at gasoline release sites, independent of filtration. The higher octanol-water coefficient of middle distillate petroleum compounds was attributed to the additive effect imparted by suspended solid-bound contaminants on dissolved phase concentrations. To further explore potential groundwater sampling induced error associated with aggressive purge and sample collection flow rates independent of turbidity, a controlled experiment was conducted over a range of groundwater flow rates at a gasoline impacted site. Volatile petroleum hydrocarbon (VPH) and geochemical parameter levels varied substantially between sampling treatments that ranged from 50 to 1,000 ml/min (including hand bailing) despite achieving stabilization of the geochemical parameters during each treatment. Sample precision was greatest for the 100 ml/min purge and sample flow rate. Possible sources of VPH concentration variability among the various treatments are discussed along with the importance of developing and adhering to site-specific sampling protocols, and the challenge of not doing so to trend analysis.

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1.0 INTRODUCTION

The collection of representative samples and an understanding of site-specific conditions are prerequisites for an accurate characterization of contaminated groundwater at release sites. Inconsistency in the development or adherence to an appropriate groundwater sampling program creates uncertainty in expensive analytical results used to support contaminant trends and direct response actions. Unless the sampler or data analyst take notice of the inherent variability that exists between sample locations and/or events, false assumptions in data interpretation can lead to erroneous conclusions and/or prolonged site closure strategies.

In an effort to standardize the collection of mobile dissolved phase groundwater, the United States Environmental Protection Agency (US EPA) developed a sampling method predicated on the purging and collection of groundwater from monitoring wells at recommended flow rates of 10 to 100 milliliters per minute (ml/min) in an effort to minimize the introduction of suspended solids that can contribute target analytes of interest. Emphasis is placed on limiting groundwater table drawdown to below 0.3 foot with sample collection occurring upon stabilization of monitored geochemical parameters (i.e. temperature, pH, conductivity, dissolved oxygen, redox potential and turbidity). Provided the monitoring well maintains sufficient hydraulic connection with the surrounding formation, the groundwater samples collected are considered to be representative of mobile dissolved phase constituents (US EPA, 1996, 2010).

Unfortunately, site conditions conducive to meeting the US EPA low flow method criteria are not always present. In practice, considerable variability in soil type, zone of contamination and groundwater flow can exist from well to well and between sampling events. Experience also demonstrates that the groundwater purge and sampling flow rates recommended by the US EPA (10-100 ml/min) may not be readily performed due to field technicians being unfamiliar with the method, equipment limitation or perceived inability to achieve well stabilization under low flow rates.

Analytical data obtained from numerous sites impacted with fuel oil or gasoline were compared to the groundwater sampling methods employed to assess the degree to which mobile, dissolved phase contaminant concentrations may be influenced by variations in sampling protocol. As expected, contaminant concentrations were directly related to groundwater purge flow rates and suspended solid content where solid-bound contaminants contributed falsely to

mobile dissolved phase concentrations. This effect was most pronounced at fuel oil-impacted sites with little to no correlation at gasoline impacted sites. In order to evaluate the influence of groundwater purge rates on contaminant concentrations, independent of suspended solids, a field experiment was performed that monitored groundwater conditions at a gasoline-impacted site employing five sampling treatments, inclusive of the use of the hand bailer method.

2. MATERIALS AND METHODS

2.1 Analysis of Site Specific Data

Analytical results were obtained from sites where groundwater was impacted from releases of fuel oil/diesel fuel or gasoline, where groundwater sampling methods evolved from hand bailing to active groundwater purging at relatively high rates (500 to 3,000 ml/min), to the lower rates recommended by the low flow sampling protocol (100 ml/min). The filtering of groundwater samples were performed at gasoline- and fuel-oil impacted sites to evaluate the potential for suspended solid-bound analytes to have an additive effect on dissolved phase concentrations. Field filtered and unfiltered groundwater samples were submitted for laboratory analysis according to the Massachusetts Department of Environmental Protection (MassDEP) volatile petroleum hydrocarbon (VPH) and extractable petroleum hydrocarbon (EPH) Methods (MassDEP, 2002 and 2004 Revision 1.1).

Turbidity was measured as an indicator of the relative amount of suspended solids present in groundwater that could contribute solid-bound analytes to dissolved phase concentrations. While turbidity is readily accepted as a relative measure of the suspended solids content of a water sample, the degree to which suspended solids affect light scatter is dependent upon the type of material suspended. A comparison of suspended solid content in milligram per liter (mg/l) and turbidity measurements (NTUs) demonstrated relatively consistent results at turbidity levels at or below 5 NTUs, whereas results varied substantially at turbidity levels of 10 to 30 NTUs (B. Tease, unpublished data). Groundwater was collected in a clean spectrophotometric cuvette at the discharge end of the flow-through chamber for turbidity screening once stabilization of the geochemical parameters (e.g., temperature, pH, conductivity, dissolved oxygen, and oxidation-reduction (redox) potential) occurred in accordance with US EPA criteria. Continuous monitoring of turbidity was not instituted due to the inherent uncertainty introduced by the frequent fouling of turbidity meter probes. Groundwater samples collected at diesel/fuel oil sites for the analysis of dissolved

phase concentrations were field filtered using in-line Waterra 0.45 micron disposable filters. Turbidity was also measured in the field filtered samples as a means to assess filter failure.

2.2 Design and Evaluation of Field Experiment

An experiment was designed to evaluate the effect of different groundwater purge and sampling flow rates on total VPH fraction concentrations at a gasoline impacted site. Groundwater samples were collected in triplicate from a two-inch diameter, 20-foot deep PVC groundwater monitoring well. The well consisted of 15 feet of PVC schedule 20 well screen, standard well grade sand backfilled to two feet above the top of the well screen, a two-foot bentonite seal, schedule 40 PVC riser pipe to 6 inches below grade backfilled with clean native fill material, and completed with a well head protective box cemented flush to grade. The inlet of the sample tubing was positioned at the midpoint of the water column within the screened portion of the well (i.e. 13.3 feet below ground surface), approximately 3 feet below the contaminant smear zone. The smear zone is demonstrated by the elevated concentrations of total organic vapors (TOVs) detected by photoionization detector field screening of split spoon soil samples collected during well installation, which ranged from 190 parts per million (ppm) to 600 ppm across the 6 to 10 foot depth range. A peristaltic pump capable of achieving a sufficient range in flow rate was used to collect groundwater samples.

The desired flow rate was confirmed by measuring the rate at which groundwater filled a graduated cylinder. An electronic groundwater meter probe was used to measure the groundwater table elevation in feet at the start of each sampling treatment and at five minute intervals to monitor groundwater table drawdown. Geochemical parameters (temperature in degrees Celsius ($^{\circ}\text{C}$), pH, conductivity in microSiemens per centimeter ($\mu\text{S}\cdot\text{cm}^{-1}$), dissolved oxygen in milligrams per liter (mg/l), and redox potential in electron volts (eV) were also recorded in five-minute intervals. Upon stabilization of the geochemical parameters, as determined through observation of repetitive measurements consistent with the US EPA low flow method, groundwater samples were collected for field turbidity screening in Nephelometric Turbidity Units (NTU) and laboratory analysis of VPH fractions in milligrams per liter (mg/l) and target analytes in micrograms per liter ($\mu\text{g}/\text{l}$). All samples were stored on ice at 4 ± 2 $^{\circ}\text{C}$ until delivery occurred to Spectrum Analytical, Inc. of Agawam, MA. Sample collection and parameter measurements began at the 50 ml/min flow rate and proceeded sequentially to 100 ml/min, 500 ml/min, and 1,000 ml/min. At the completion of the low flow sampling series, three well volumes of groundwater were removed from the well using a 1 1/4 inch diameter disposable plastic bailer. The groundwater table elevation was measured before and after well purging via

hand bailer and immediately prior to sample collection for field turbidity measurement and submittal for laboratory analysis. Filtration was not performed to eliminate uncertainty associated with potential volatilization of gasoline related hydrocarbons.

3. RESULTS

3.1 Petroleum Release Sites

Analytical results depicting three representative disposal sites located in Massachusetts are summarized in Tables 1, 2 and 3. Table 1 presents analytical results for groundwater samples collected over a 12 year period where the hand bailing method was used during the 1998 and 2002 sampling events, high volume groundwater purging by peristaltic pump was implemented in 2003, and the low flow sampling method was employed in 2009 and 2010. Filtered and unfiltered samples were submitted in November 2009 for laboratory analysis of dissolved phase and total EPH fractions, respectively.

Total EPH fraction concentrations fluctuated erratically without any clear trend between sampling events, suggesting the potential for inconsistent sample collection. A review of groundwater sampling logs revealed that changes in groundwater table elevation, soil type or smear zone influences were not sufficient enough to account for the variations observed in contaminant concentrations. Variations in sampling methods, however, suggested that elevated levels of suspended solids were introduced into the samples as a result of aggressive well purging, which resulted in the fluctuations observed in EPH fraction concentrations. A decrease in low flow sampling flow rate from 444 ml/min to 100 ml/min resulted in a four-fold decrease in turbidity, and a 10-20 fold decrease in total EPH concentrations. Sample filtration conducted during the November 2009 sampling event resulted in a substantial reduction in turbidity and the absence of EPH fraction concentrations above the minimum laboratory reportable detection limits.

Table 2 summarizes analytical results from a gasoline release site where reductions in groundwater purge rate and turbidity had minimal effects on total VPH fraction and the target analytes ethylbenzene and xylene. Naphthalene concentration appeared to be affected by the reduction in suspended solids where decreased turbidity correlated with decreased concentration, albeit at low levels.

event resulted in the absence of total EPH fraction concentration above the minimum laboratory detection limit.

Table 3. Summary of Total EPH Fraction Concentrations, Turbidity and Groundwater Sampling Flow Rate at a #2 Fuel Oil Release Site

Parameter	Units	Date		
		5/09	11/09	5/10
Flow Rate	ml/min	440	444	100
Turbidity	NTU	89	97	24
Total VPH (filtered)	ug/l	23	13 (<DL)	1.5
Date for unfiltered samples except where noted <DL = less than minimum reportable detection limit				

3.2 Field Experiment

Analytical results depicting VPH fraction concentrations in replicate samples collected and geochemical parameter trends measured during the various groundwater purge treatments are summarized in the figures presented below. The analytical and field measured parameter results are summarized in Tables 4 and 5, respectively. VPH target analytes were not detected above the minimum laboratory reportable detection limit in any of the samples analyzed. The average concentrations of the individual VPH fractions for the various purge treatment sample replicates are depicted in Figure 1, along with turbidity measurements.

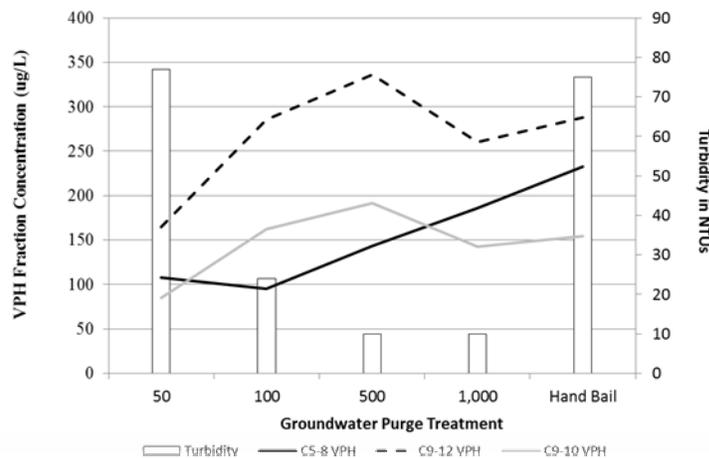


Figure 1. Average VPH Fraction Concentrations and Turbidity per Purge Treatment

In general, the lowest VPH fraction concentrations were detected in the 50 ml/min and 100 ml/min treatment samples. The highest VPH fraction concentrations were detected in the 500 ml/min sample set. Sample turbidity was greatest for the 50ml/min and hand bailer treatments, and least for the 500 ml/min and 1,000 ml/min treatments. No correlation was observed between VPH concentrations and turbidity. The variability in VPH concentrations among the sample replicates is presented in Figure 2 along with Total VPH fraction concentration trends.

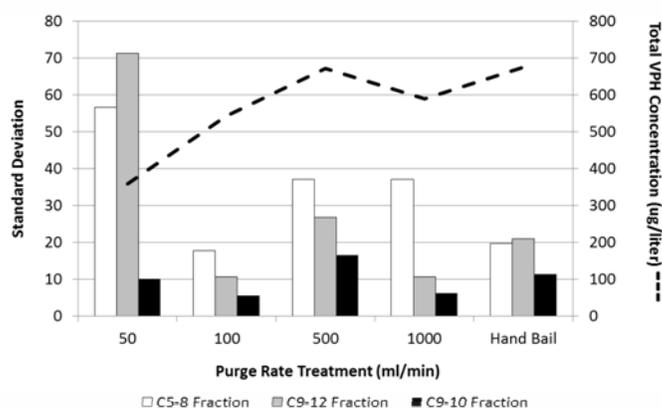


Figure 2. Standard Deviation of Individual and Total VPH Fraction Concentrations per Groundwater Purge Treatment

The VPH fraction concentrations for the 100 ml/min purge treatment replicates exhibited the greatest precision of all treatments, while the samples collected at the 50 ml/min purge rate varied the most, particularly for the C5-8 VPH and C9-12 VPH fractions. The C9-10 VPH fraction concentrations were the most reproducible across all five purge treatments. Figures 3, 4, and 5 depict stabilization trends for the geochemical parameters, dissolved oxygen, redox potential, and conductivity, respectively.

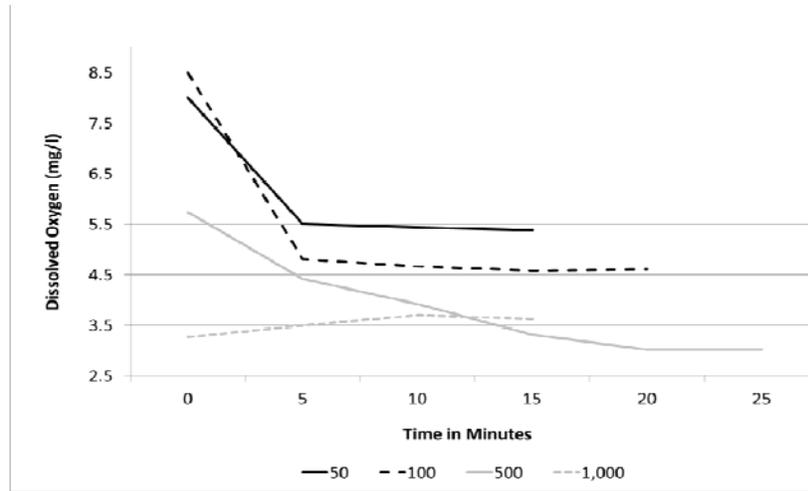


Figure 3. Dissolved Oxygen Concentration Trends per Groundwater Purge Rate

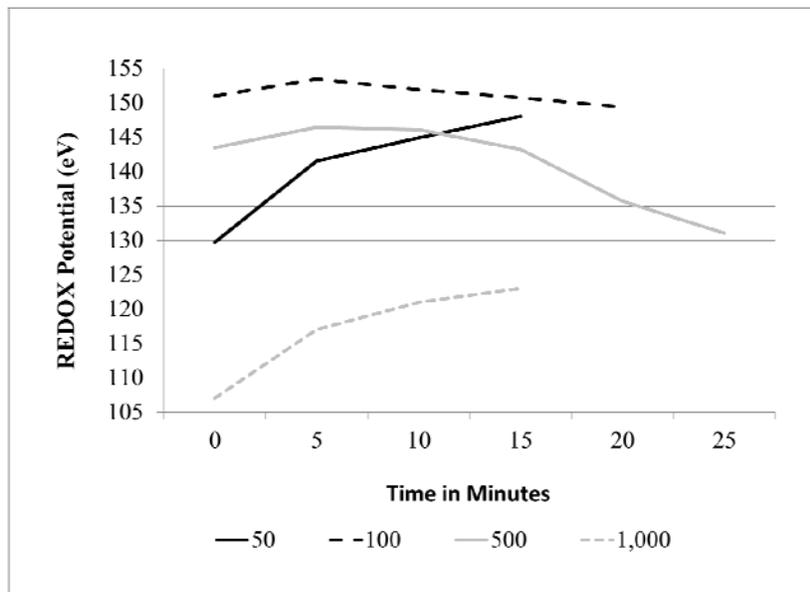


Figure 4. REDOX Potential Trends per Groundwater Purge Rate

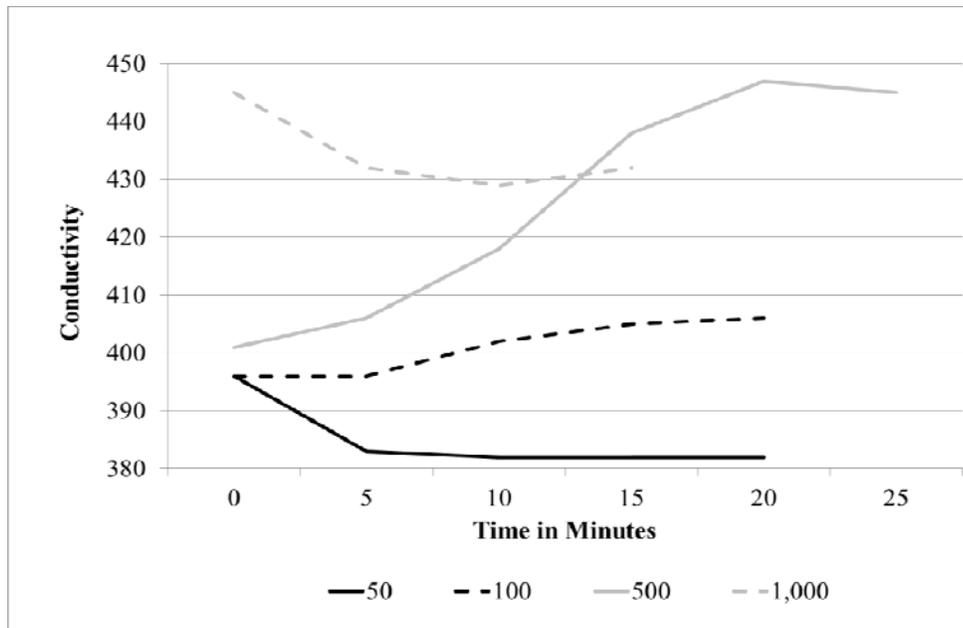


Figure 5. Conductivity Trends per Groundwater Purge Rate

Trends in pH and temperature were similar to the other geochemical parameters as seen in Table 5. Regardless of flow rate, stabilization of the geochemical parameters was achieved within 20 minutes of groundwater purging. Groundwater elevation trends are plotted against purge treatment in Figure 6.

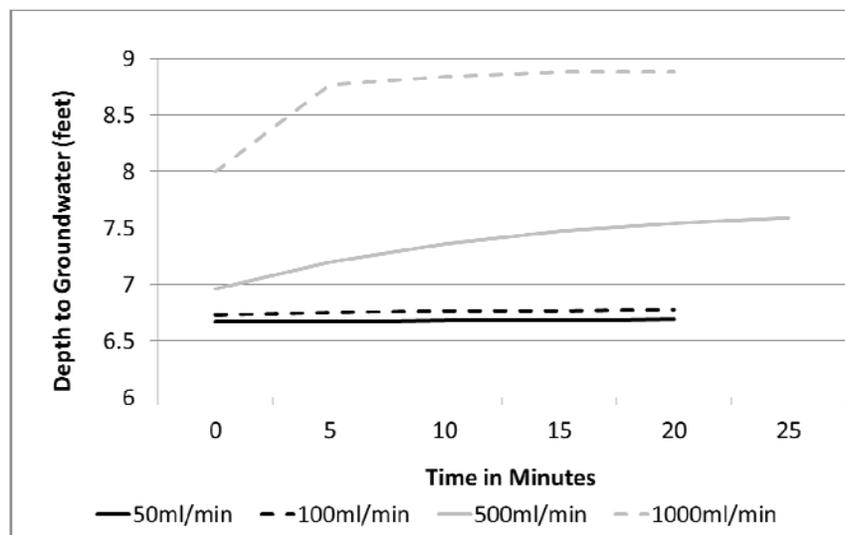


Figure 6. Groundwater Elevation Trends per Groundwater Purge Rate

The groundwater table elevation dropped 0.02 foot and 0.05 foot, respectively, during groundwater purging at the 50 ml/min and 100 ml/min flow rates, whereas the 500 ml/min, 1,000 ml/min, and hand bailer treatments induced a drop in groundwater table elevation of 0.63 foot, 0.88 foot, and 3.54 feet, respectively.

Table 4. Summary of VPH Concentrations (ug/l) and Statistical Parameters per Purge Treatment

Treatment	Replicate	C5-8	C9-12	C9-10	Total VPH
50 ml/min	A	75	158	86	319
	B	75	239	95	409
	C	173	97	75	345
Mean		108	165	85	358
Std Deviation		56.6	71.2	6.4	46.6
t value		3.3	4.0	14.76	13.37
Pr > [t]		0.081	0.057	0.0056	0.0055
Significant Difference		no	no	yes	yes
100 ml/min	A	75	295	168	538
	B	106	287	162	555
	C	105	274	157	536
Mean		95	285	162	543
Std Deviation		0.7	10.6	5.5	10.4
t value		9.4	46.6	51.1	90.08
Pr > [t]		0.011	0.0005	0.0004	0.0001
Significant Difference		yes	yes	yes	yes
500 ml/min	A	138	324	185	647
	B	154	318	179	651
	C	138	367	210	715
Mean		143	336	191	671
Std Deviation		37.1	26.7	16.4	38.2
t value		26.9	21.8	20.2	30.46
Pr > [t]		0.001	0.0021	0.0025	0.0011
Significant Difference		yes	yes	yes	yes

Table 4. Summary of VPH Concentrations (ug/l) and Statistical Parameters per Purge Treatment (continued)

Treatment	Replicate	C5-8	C9-12	C9-10	Total VPH
1,000 ml/min	A	143	250	137	530
	B	204	271	149	624
	C	210	260	141	611
	Mean	186	260	142	588
	Std Deviation	37.1	10.5	6.1	50.9
	t Value	8.7	42.9	40.4	20.01
	Pr > [t]	0.013	0.0005	0.0006	0.0025
	Significant Difference	yes	yes	yes	yes
Hand Bailer	A	249	298	160	707
	B	238	302	161	701
	C	211	264	141	616
	Mean	233	288	154	675
	Std Deviation	19.6	20.9	11.3	50.9
	t Value	20.6	23.9	23.67	22.46
	Pr > [t]	0.002	0.0017	0.0018	0.0019
	Significant Difference	yes	yes	yes	yes

4. DISCUSSION

4.1 Petroleum Release Sites

While the unexpected increases in contaminant concentrations may be indicative of a new release, migrating groundwater plume, or seasonal fluctuations in groundwater table elevation, such increases are not expected at sites where stable concentration trends have been documented over time, or where the above conditions can be ruled out. Spikes in contaminant concentrations can prolong response actions if the unexpected results can not be explained.

The review of the groundwater sampling and analytical data from several fuel oil sites revealed the additive effect contaminant-bound suspended solids have on dissolved phase groundwater concentrations as a result of aggressive well purging methods. The US EPA low flow method recommends limiting purge and sampling flow rates in the range of 10 to 100 ml/min in an effort to minimize the collection of suspended solids, as measured by turbidity levels (ideally less than 5 NTUs), and to maximize the recovery of mobile dissolved-phase groundwater. Since it is mobile groundwater that poses the greatest risk potential to

Table 5. Summary of Geochemical Parameters and Turbidity Levels per Purge Treatment

Treatment	Time	Temp	pH	Cond.	D.O.	Redox	Turbidity
50 ml/min	0	9.15	5.89	396	8.00	130	
	5	8.81	5.82	383	5.51	142	
	10	8.84	5.81	382	5.44	145	
	15	8.86	5.80	382	5.38	148	
	20	-	-	382	-	-	77
100 ml/min	0	8.08	5.89	396	8.50	151	
	5	8.50	5.76	396	4.81	153	
	10	8.04	5.75	402	4.67	152	
	15	8.43	5.74	405	4.59	151	
	20	8.44	5.74	406	4.61	149	24
500 ml/min	0	7.32	5.92	401	5.74	144	
	5	7.11	5.76	406	4.42	146	
	10	7.32	5.75	418	3.92	146	
	15	7.35	5.75	438	3.32	143	
	20	7.40	5.79	447	3.02	136	
	25	7.30	5.81	445	3.02	131	10
1000 ml/min	0	7.15	5.91	445	3.27	107	
	5	7.33	5.83	432	3.50	117	
	10	7.38	5.82	429	3.71	121	
	15	7.40	5.82	432	3.63	123	10
Summary of Geochemical Parameters at Equilibrium per Purge Treatment and Statistical Differences							
Purge Treatment (ml/min)	Temp	pH	COND	DO	redox	NTUs	
50 (a) ¹	8.86	5.80	382	5.38	148	77	
100	8.44	5.74	406	4.61	149	24	
500	7.30	5.81	445	3.02	131	10	
1000 (b) ²	7.40	5.82	432	3.63	123	10	
Standard Deviation	0.77	0.04	28.0	1.04	13.0	31.9	
Mean	8.00	5.79	416	4.16	138	30.3	
US EPA Equilibrium Criteria	+/- 3%	+/- 0.1	+/- 3%	+/- 0.3	+/- 10	+/- 10%	

downgradient receptors, the disturbance and collection of soil-bound contaminants results in the recovery of unrepresentative groundwater samples.

Middle distillate petroleum hydrocarbons (diesel/fuel oil) have a greater affinity for soil as indicated by their higher partitioning coefficients and lower water solubility than lighter gasoline-related fractions (Gschwend and Wu, 1985, MassDEP, 2002 and 2004 Rev 1.1). The two data sets presented in Tables 1 and 3 demonstrate the additive effect of suspended solid-bound petroleum hydrocarbons

on dissolved-phase concentrations particularly at purge rates above 100 ml/min. EPH concentrations were not detected above minimum laboratory reportable detection limits in samples that were field filtered. Critical to demonstrating this additive effect is the monitoring of turbidity levels in filtered samples, given the potential for filter breakthrough. Turbidity levels of 10-50 NTUs are not uncommon in field-filtered samples.

The MassDEP VPH/EPH Final Policy #WSC-02-411 (2002 and Revision 1.1 2004), recommends sample filtration at fuel oil impacted sites where suspended solid content can't be reduced through low flow sample collection methods alone. Conversely, the data set presented in Table 2 demonstrates the limited effect suspended solids have on influencing mobile dissolved-phase gasoline hydrocarbon concentrations; the MassDEP VPH/EPH Policy does not recommend filtration for VPH-related compounds for this reason, and given the potential for volatilization during the filtration process.

4.2 Field Experiment

The absence of a correlation between VPH concentrations and turbidity in the field experiment, and the variable trends observed in VPH fraction concentrations in groundwater samples from the various purge treatments, imply the presence of sampling-induced factors other than suspended solids that can affect contaminant concentrations. The field experiment demonstrated the dissimilarity that can occur in the analytical as well as geochemical results as a consequence of inconsistent groundwater purge rates. Understanding the potential sources of sample variability is critical to the ability to differentiate real concentration trends from those occurring as artifacts of sample collection.

When groundwater is recovered from a monitoring well, the flow rate should be consistent among wells and between sampling events in order to justify an accurate comparison of analytical data collected spatially and temporally. Groundwater within a monitoring well can be viewed as having three source areas: (1) water within the well casing, (2) sand-pack pore water outside the well casing within the bore hole, and (3) formation pore water located outside the bore hole. In theory, if soil conditions permit and the well is constructed properly, a sufficient hydraulic connection is established between formation and well such that the three source areas are in equilibrium with each other. In practice, however, it is not uncommon for the three areas to be distinct due to heterogenic soils, inappropriate well construction and/or age. In this case, the concentration of dissolved phase components of a groundwater sample can vary substantially depending upon where the sample originated from.

Another source of sample uncertainty involves the recovery of mobile versus immobile groundwater. The more water soluble a particular analyte is, the more likely it is to be present in higher concentrations in groundwater that readily flows through the formation (i.e. mobile groundwater). Over time the contaminant concentrations will decrease as this groundwater effectively purges the source area. Conversely, groundwater occupying smaller soil pores retained through capillary forces is considered to be immobile under normal hydraulic gradients. Due to the static nature of this groundwater fraction and its close proximity to more hydrophobic contaminants that have a tendency to associate with soil surfaces due to lower water solubility levels, the concentrations of contaminants in immobile groundwater tend to be higher. During more aggressive well purging actions, the substantial but artificial hydraulic gradients produced are sufficient to overcome the capillary and hydrophobic forces resulting in the recovery of high contaminant concentrations present in immobile groundwater. The observations made during the field experiment are further discussed below as they relate to these sources of groundwater variability.

4.3 Variations Attributed to Multiple Groundwater-Source Areas within a Monitoring Well

The effect groundwater purge rate has on contaminant concentrations can be demonstrated by comparing the volume of groundwater recovered to the volume available within the various source areas of a monitoring well. At lower purge volumes, which tend to be collected at lower flow rates (e.g. 10-50 ml/min) the potential exists for more of the recovered sample to contain groundwater that resided mainly within the well screen than that within the pore spaces of the well sand pack or formation. As recorded during the four low flow purge treatments, the time for geochemical parameter stabilization to occur was between 15-20 minutes for each treatment. Therefore, the volume of groundwater purged was directly related to purge rate.

The volume of groundwater within a typical two-inch diameter PVC monitoring well, constructed of 10-feet of well screen that provides approximately 5 feet of water column, is 0.75 gallons or 3,000 milliliters (ml), with 9 gallons (36,000 ml) available from the pore space of the sand pack.²

² US EPA recommends the placement of a sand pack 3-5 inches beyond the well casing. Assuming a 3-inch sand pack distance surrounding a 2-inch diameter well screen, the groundwater storage capacity within a 5-foot tall sand pack in cubic feet is equal to:

$$(3.14 \times \text{bore radius}^2 \times \text{length} \times 25\% \text{ porosity for standard well grade sand}) - (3.14 \times \text{well radius}^2 \times \text{length})$$

$$(3.14 \times 0.33^2 \times 5 \times 0.25) - (3.14 \times 0.08^2 \times 5) = 1.30 - 0.10 = 1.2 \text{ cubic feet} \times 7.5 \text{ gallons/cubic foot} = 9 \text{ gallons}$$

Under relatively permeable soil conditions, and groundwater drawdown of less than 0.3 foot, the groundwater removed from the well casing is replenished by sand-pack pore water, which in turn gets replenished by a virtually unlimited volume of formation pore water.

One of the founding principles of the US EPA low flow method is that groundwater recharge occurs more laterally than vertically such that the inlet of the sample tubing placed at a specified depth is recovering groundwater from a similar depth. For comparative purposes, an estimate of the vertical zone from which groundwater enters the sample tube inlet will not likely exceed one foot, unless aggressive purge treatments are applied, or under conditions of poor well recharge. In the latter case, the requirements for low flow sampling are voided and such conditions require a different approach to sample collection altogether.

Using the assumed vertical recovery zone estimate of one foot, the known monitoring well and sand-pack diameters, and soil porosity estimate, an approximation of the volume of groundwater available and/or likely recovered from a given source area can be obtained for each of the well purging/sampling treatments (see Table 6). Whether the sand pack pore space is replenished by groundwater from soil pores directly outside the well sand pack will be dependent upon the degree of mixing that occurs between sand pack and native formation pore water, which is directly related to the permeability of soil pores or grain size. For the purpose of this exercise, which also is consistent with the conditions present in the field experiment, the permeability of sand pack material and surrounding soils is considered sufficient to permit unrestricted well recharge.

The calculations presented in Table 6 imply that the 50 ml/min sample originated primarily from the well casing with potentially 12% occurring from the sand pack pore space, whereas the 100 ml/min sample was comprised mostly of groundwater originating from the sand pack (67%); formation pore water (groundwater originating from soil pores outside the well sand pack) was not considered to have contributed to either the 50 ml/min or 100 ml/min sample volumes. Formation groundwater accounted for approximately 85% of the groundwater sample volumes collected during the 500 ml/min and 1,000 ml/min purge treatments. Due to the substantial drawdown incurred during hand bailing (3.5 feet), the groundwater sample collected was considered to be comprised of approximately equal amounts of sand pack and formation water. Given that the drawdown exceeded one foot, the potential vertical recovery zone was over three times greater than the other treatments, such that the proportions of groundwater originating from the well casing and sand pack were greater than those from the formation water for the hand bailer samples compared to the other purge treatment samples.

Table 6. Summary of Groundwater Table Drawdown and Source Estimates for the Well Purging Treatments Applied During the Field Experiment

	Units	50 ml/min	100 ml/min	500 ml/min	1,000 ml/min	Hand Bailer
Total sampling time	minutes	15	20	25	15	NA
Total volume collected	milliliters	750	2,000	12,500	15,000	18,000 ¹
Depth to groundwater at start of purging	feet	6.67	6.73	7.59	8.00	8.88
GW drawdown at end of purging	feet	0.02	0.05	0.63	0.88	3.54
Volume immediately purged within well ²	milliliters	660	660	660	660	2,340 ³
Volume immediately purged outside of well	milliliters	90	1,340	11,840	14,340	15,660
Volume available in 1 foot of sand pack ⁴	milliliters	2,000	2,000	2,000	2,000	7,000 ⁵
Volume of formation water purged or sampled	milliliters	0	0	9,840	12,340	8,000
NA = not applicable GW = groundwater ¹ 18 bailers (1 liter capacity) were used to purge well prior to sample collection ² drawdown in ft x 0.022 sf [surface area of 2 in. well] = cf x 7.5 gall./cf x 4 qrts/gall x 1000 = milliliters in well ³ Volume based on 3.54 foot drawdown of groundwater vs 1-foot estimate ⁴ 1 ft sand pack length x 0.33 ft bore hole radius ² x 3.14 x 0.25 porosity)-(3.14 x 0.08 ² well radius x 1 ft) 0.085-0.020 = 0.065 cubic foot x 7.5 gallons/cf = 0.5 gallons = 2 liters = 2,000 ml ⁵ 3.54 ft sand pack length x 0.33 ft bore hole radius ² x 3.14 x 0.25 porosity)-(3.14 x 0.082 well radius x 1 ft) 0.255-0.020 = 0.235 cf x 7.5 gall/cf = 1.76 gall = 7 liters = 7,000 ml = volume in sand pack based on 3.54 ft of drawdown after hand bailing three well volumes						

The above exercise demonstrates the potential for variability of contaminant concentrations and may explain the lower total VPH concentrations detected and the poorest precision observed in the 50 ml/min purge treatment triplicate samples compared to the other sample sets. The differences observed in the geochemical parameter levels detected may also be explained by variation in potential well source areas. Under non-sampling conditions, groundwater within a properly functioning well should be in equilibrium with the surrounding aquifer provided the hydraulic connection between well and formation is sufficient to sustain the natural flow of groundwater across the well screen. Given the low volumes of groundwater purged during the 50 ml/min treatment (750 ml), the potential exists for groundwater within the well screen to have not been adequately purged

(accounting for the majority of the sample collected), which is not considered to be representative of site groundwater conditions.

4.4 Variations Attributed to the Recovery of Mobile versus Immobile Groundwater

The VPH fraction concentrations detected in samples collected at the 50 ml/min, 100 ml/min, and 500 ml/min purge treatments exhibited increasing trends for all three fractions, as depicted in Figure 1. The concentrations of the C9-12 VPH and C9-10 VPH fractions, however, tailed off in the 1,000 ml/min and hand bailed samples, whereas the C5-8 VPH fraction concentrations did not exhibit this break in concentration. The 100 ml/min purge treatment yielded the sample replicate concentrations with the greatest precision; the C9-10 VPH fraction exhibited the greatest precision among all three fractions and for all purge treatments.

The C9-12 and C5-8 aliphatic VPH fractions have the lowest water solubility (0.07 mg/l and 11 mg/l) and greatest soil partitioning coefficients (150,000 Foc and 2,265 Foc) compared to the C9-10 aromatic VPH fraction, which has the highest water solubility (51 mg/l) and lowest soil partitioning coefficient (1,778 Foc). It may be possible that the C9-10 VPH fraction was least affected by purge rate since it was most likely present in the dissolved phase of the mobile groundwater, whereas the other VPH fractions have a greater potential of being associated with immobile groundwater resulting in greater variability in concentrations as the contaminants present at higher concentrations in the immobile groundwater mixed with the contaminants present at lower concentrations in the mobile groundwater.

Combining the two potential sources of groundwater variability, samples collected at sufficient flow rates to permit the recovery of groundwater mainly from the sand-pack should be more representative of mobile groundwater than samples collected at lower or higher purge rate extremes, and have the least variability in contaminant concentration. Groundwater localized in sand pack pores are also protected from adverse conditions within the well screen (i.e. volatilization, aerobic degradation as a result of elevated dissolved oxygen concentrations from the atmosphere) and less likely to be influenced by the recovery of immobile groundwater from formation pore water outside the bore hole.

The groundwater replicates collected during the 100 ml/min purge treatment likely originated mainly from sand pack pore water and had the greatest precision among all replicate samples. Samples from the 500 ml/min and 1,000 ml/min treatments likely originated mainly from formation pore water given the large

volumes purged. The 500 ml/min treatment samples contained the highest total VPH fraction concentrations and poorest precision among all treatment samples, along with the 50 ml/min treatment samples. The 1,000 ml/min and hand bail treatment samples exhibited lower VPH fraction concentrations than the 500 ml/min treatment samples and exhibited similarly poorer sample precision.

The need for precision (i.e. reproducibility of a result) and accuracy (i.e. how close a result comes to the true value) in the collection and analysis of samples is critical to trend analysis, as it is this information that is used to develop and/or support professional opinions concerning risk to sensitive receptors. The emphasis placed on analytical results is magnified at sites that pose a greater risk as indicative of more stringent standards. Conversely, precision and accuracy become lesser commodities when exposure potential is minimized and regulatory standards are less rigorous. For example, the C9-10 VPH fraction concentrations detected in the replicate samples A, B and C for the 500 ml/min purge treatment were 185 ug/l, 179 ug/l, and 210 ug/l, respectively. Given that the applicable GW-1 Method 1 Risk Characterization Standard at this site for this VPH fraction is 200 ug/l, accuracy and precision play a more important role. Conversely, if the level of risk for this fraction is reduced, as is the case at sites where the less stringent Method 1 Risk Characterization Standards GW-2 (7,000 ug/l) or GW-3 (50,000 ug/l) apply, the variation in this data set is irrelevant.

In situations where risk is low, or concentrations are so high that precision and accuracy play a secondary role to general characterization, and likely site closure is far in the future, groundwater sampling at higher flow rates and/or following hand bailer methods may be acceptable. Under certain conditions, the recovery of immobile groundwater may be the desired outcome, as is the case when calculating the total mass of contaminant and remedial additive. Analysis of mobile groundwater conditions alone may underestimate the amount of chemical oxidant or reducing agent.

5. CONCLUSIONS

The concentration of geochemical parameters and petroleum hydrocarbons was shown to be affected by the rate at which groundwater is recovered from monitoring wells. Inconsistency in groundwater purge rate among site specific monitoring wells and between sampling events can complicate the assessment of analytical results by inducing uncertainty in data precision and accuracy.

In addition to the disturbance and collection of suspended solids that results in the contribution of solid bound contaminants to dissolved phase concentrations, aggressive groundwater purge treatments have the potential of extracting what is

typically immobile groundwater, overcoming the hydrophobic and capillary forces that contribute to the retention of groundwater located in tight soil-pore spaces. The US EPA low flow method is intended to minimize the introduction of suspended solids by minimizing groundwater table drawdown and thus maintaining shallow hydraulic gradients during well purging, and thus allowing the recovery of mainly mobile groundwater.

In addition to validating the additive effects that suspended solid-bound contaminants have on dissolved phase concentrations of middle distillate petroleum hydrocarbons, common to fuel oil, the effect of varying purge rates on the source area from which groundwater is recovered was demonstrated during the field experiment. Despite achieving stabilization, the geochemical parameters differed quantitatively among the various purge treatments suggesting the recovery of groundwater from different source areas within the test well. Utilizing the purge volumes collected for each treatment, the well screen, well sand pack pore space, and formation pore space, were considered to represent three separate and distinct sample source areas.

The sample set collected during the 100 ml/min purge rate, which exhibited the greatest precision in analytical results, was considered to have originated from the sand pack pore water and be most representative of mobile groundwater. The C9-10 VPH fraction concentrations exhibited the greatest precision of all fractions regardless of purge treatment. This may be explained at least in part by this fraction being predominant in mobile groundwater due to having the highest water solubility and lowest affinity for soil partitioning of the three fractions. The higher VPH fraction concentrations detected in samples collected during the 500 ml/min purge treatment are considered to be attributed to the recovery of immobile groundwater from primarily formation pore water. The recovery of higher contaminant concentrations associated with immobile groundwater is not representative of mobile groundwater and contributes to the diminished precision and accuracy noted in analytical results obtained.

The need for precision and accuracy in the collection and analysis of groundwater samples is critical to trend analysis, as this information is used to develop and/or support professional opinions concerning risk to sensitive receptors. The emphasis placed on analytical results is magnified at sites that pose a greater risk and, therefore, are regulated by more stringent standards. Conversely, sites where exposure risks are reduced and less restrictive standards exist may not warrant the same demand for analytical precision and accuracy. While hand bailing methods would not be suitable for fuel oil impacted groundwater or at sites where the degree of risk is high (i.e. low standards), the use of hand bailing at gasoline impacted sites where risk is low and standards are

high may be a better use of limited resources than the more costly low flow sampling method.

Trend analysis involves more than the plotting of data over time. Knowledge of the soil conditions associated with a given monitoring well, the presence of contaminant smear zones or preferential migration pathways, decisions behind the selection of groundwater purge rates, the positioning of low flow sample tubing or the selection of hand bailing methods must also be considered before conclusions are drawn from the analytical results. Failure to address these variables can lead to prolonged site closure and unnecessary assessment and/or remedial actions.

6. REFERENCES

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