Groundwater Sampling Method Comparison: Low-Flow and Passive Diffusion Bag Sampling Results for Volatile Organic Compounds in Fractured Metamorphic Bedrock

Thomas R. Eschner and David Dinsmore, Woodard & Curran.

Abstract

Woodard & Curran recently completed a pilot study at a Superfund Site in central Maine to evaluate passive diffusion bag (PDB) groundwater sampling by comparing analytical results from PDB sampling with results from low-flow groundwater sampling. Although low-flow sampling continues to be a standard groundwater sampling method that is highly recommended by the regulatory community, PDB sampling has been gaining acceptance, particularly in unconsolidated formations or relatively homogeneous sedimentary formations. The method is less widely used in metamorphic and igneous formations in which fractures comprise the majority of the porosity. The samples used in the method comparison were collected from fifteen monitoring wells installed in shallow and deep zones of fractured bedrock. The purpose of the pilot study was to determine whether similar concentrations of volatile organic compounds (VOCs) can be obtained using these two groundwater sampling techniques.

Several techniques were used to assess the sampling results. The results from the study were evaluated by calculating the relative percent difference (RPD) to determine if there were significant differences between the concentrations measured in the samples collected with the PDBs and those collected using the low-flow method in the same well. The RPDs from the study were compared to the EPA field duplicate criterion of 30% to determine how closely the results matched. Almost 90% of the sample pair comparisons in the pilot study had RPDs below 30%, indicating that the results from the two methods compared well. The results of a regression analysis indicated a high degree of correlation between the results for several of the target VOCs. Comparison of results from the two methods to federal maximum contaminant levels (MCLs) indicated 97% agreement between the results that exceed MCLs. In addition, 96% of the PDB sample results matched the low-flow results in terms of presence or absence of a particular compound, which indicated little likelihood of false negative or positive results using the PDB method.

Of particular interest for this fractured bedrock site was whether or not a single PDB sampler would be representative of concentrations over the entire screened interval in the well, or whether multiple PDB samplers would be required. To address this concern, an analysis was performed to evaluate differences between concentrations measured in samples collected from multiple PDB samplers installed within the same well. Multiple PDBs were installed at different depths in groundwater monitoring wells to correspond to the depths at which fractures in the bedrock were encountered during well installation. The results from this comparison were used to evaluate if there had been vertical stratification of VOCs within the monitoring well. Although RPDs greater than 30% were obtained for some of the target VOCs, stratification within monitoring well locations was not conclusively identified.

The pilot study demonstrated that samples collected from PDB samplers provided comparable results to the low-flow sampling method in the fractured metamorphic bedrock at this site. Because PDB sampling is less time consuming than low-flow sampling and does not require as much field instrumentation, substantial cost savings can be realized using this groundwater sampling technique.
Groundwater Sampling Method Comparison: Low Flow and Passive Diffusion Bag Sampling Results for Volatile Organic Compounds in Fractured Metamorphic Bedrock

Introduction

In January 2002, Woodard & Curran completed a pilot study at a Superfund Site in Maine to compare two different groundwater sample collection methods: low flow collection and passive diffusion bag (PDB) collection. Low flow sampling is a conventional, EPA approved collection method that involves active removal of groundwater by pumping from the monitoring well prior to sample collection. During PDB groundwater sampling, there is no groundwater removal prior to sampling. A predetermined number of PDBs are placed into each monitoring well at different depths within the screened interval and retrieved at least two weeks later.

During previous sampling episodes at the site, groundwater samples were collected using the low flow sampling method. Analytical results from these samples have been used to monitor the migration of Site contaminants in the shallow and deep fractured bedrock beneath the Site and surrounding areas. The Site contaminants consist primarily of four volatile organic compounds (VOCs): cis-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene. These compounds have shown good correlation between PDB water and test-vessel water in laboratory tests (Vroblesky, 2001).

The remaining sections of the paper describe the evaluation completed to compare the results obtained using the two sampling methods. This evaluation included a regression analysis and determination of relative percent difference between concentrations. A comparison of detected analytes reported for each set of samples was completed to identify potential bias or selectivity for each particular method. In addition, the results of PDBs positioned at different depths within a single monitoring well were compared to determine if there was stratification within the screened interval.

Site Description

The site is located in a rural section of east-central Maine in the Kearsarge Synclinorium. Bedrock in the vicinity of the site is the Silurian-Ordovician Vassalboro Formation (Osberg et al., 1985), a metasedimentary rock consisting of calcareous sandstone and pelitic layers. The regional strike of bedding in the area is approximately N48°E and dips are nearly vertical, varying from about 80°NW to 90°. The bedrock is fractured with near-vertical fractures.

The site is located on a topographic high and bedrock is shallow or crops out over much of the site. Surficial materials in the vicinity of the site consist primarily of glacial till, outwash, and glaciomarine silt and clay. The thickness of surficial materials ranges to over 100 feet away from the site. In the immediate vicinity of the site the surficial materials are unsaturated and groundwater is found only in bedrock. All wells used in the study are screened in bedrock.

Sample Locations/Sample Identification

Forty-nine groundwater samples were collected using low flow and PDB sampling methods at 15 monitoring wells installed in the shallow and deep metamorphic bedrock that underlies the site and surrounding areas. All samples were identified using the monitoring well location. Sample results with no depth in the identification represent samples that were collected using low flow techniques (e.g., MW-106D). PDB sample results were identified with the monitoring well location followed by a depth in parentheses. This represents the depth in the monitoring well at which the PDB was placed. For example, the PDB sample collected from 77.5’ below ground surface (bgs) in MW-106D is designated as MW-106D (77.5').
Sampling Method Description

The following subsections describe the PDB and low flow sample collection procedures used to collect groundwater samples.

PDB Sample Collection

In late 2001, PDBs were installed into fifteen monitoring wells at the Site. PDBs consist of polyethylene bags that are filled with approximately 220 mL of distilled water. Through diffusion, concentrations of certain chlorinated solvents and breakdown products, including the Site contaminants listed in Section 1, travel with the groundwater, through the polyethylene and into the distilled water. This process continues until equilibrium is reached at which the concentrations of contaminants in the distilled water are the same as the surrounding groundwater in the well.

PDBs were clipped onto a wire harness rig with a stainless steel weight attached to the end. The PDBs were positioned above the weight on the harness rig such that when they were lowered, they would align with known bedrock fractures or designated sampling depths in the screened interval of monitoring well. The number of PDBs that were clipped onto the wire was dependent on the length of the well screen. For monitoring wells with 10-foot screens, three bags were attached. Five bags were attached to rigs lowered into monitoring wells with 20-foot screens. The bags were retrieved from the monitoring wells a minimum of 26 days from installation. Upon retrieval, the bags were unclipped from the harness rig. The end of each bag was cut before gently decanting the contents into vials pre-preserved with hydrochloric acid. Upon retrieval of the PDBs, none were torn or otherwise damaged.

Low Flow Groundwater Sampling

After the PDBs were removed, dedicated tubing was placed into the monitoring wells. A peristaltic pump was used to purge groundwater from each well using the low flow purging techniques consistent with USEPA Region I protocols. Purged groundwater was pumped from the well into a flow cell containing a multi parameter meter. This instrument contains probes that simultaneously measure pH, conductivity, turbidity, dissolved oxygen, oxygen/reduction potential (ORP) and temperature. When these parameters stabilized to consistent readings within the limits specified in the project QAPP, the tubing was disconnected from the flow cell to fill sample containers. For each monitoring well location, groundwater samples were collected using low flow on the same day that samples were obtained from PDBs. This reduced any day-to-day variation in concentrations of Site contaminants that may exist at each sampling location.

Sampling Method Comparison

There are major differences between low flow and PDB sampling techniques. Low flow sampling involves purging groundwater from the well using a pump, during which process physical parameters such as pH, conductivity, turbidity, dissolved oxygen and temperature are monitored until stabilization is reached. Significant time may be required for stabilization of these parameters to occur. The depth to water is also monitored to ensure that, if possible, there is minimum drawdown. Only one sample depth within the screened interval is monitored during low flow sampling, although mixing of groundwater from different depths within the well can occur, particularly if the water level is depressed during purging.

Unlike low flow sampling, there is no purging of groundwater from the monitoring well during PDB sampling. The PDBs are simply clipped to a harness rig or tied to a rope, lowered into the monitoring well, then secured to ensure that the bags remain at a discrete depth. Since there is no purging involved with sample collection as in low flow sampling, parameters such as pH, conductivity, etc. are not monitored. Therefore, instrumentation and pumps are not needed during the collection process with PDB sampling. Multiple PDBs can be attached to the harness to monitor concentrations of site contaminants at several discrete intervals during each sampling event, rather than at just one interval of the monitoring well as with low flow sampling.
Overall, collection of groundwater samples using PDBs is a simpler process than low flow sampling. The need for instrumentation and pumps is eliminated and, since there is no groundwater purged from the monitoring well, there is no contaminated water that must be containerized, tested, and disposed of.

Sample Analysis

Samples obtained using both collection methods were preserved with hydrochloric acid and were stored on ice in coolers. All samples were analyzed for VOCs using USEPA Method 8260.

Analytical Results

The following subsections compare analytical results for the two sampling methods. During the comparisons, the concentrations reported for the EPA approved low flow method were assumed to be the reference results, as this method was used throughout the Remedial Investigation. Methods used to compare the two data sets include calculations of the relative percent difference and regression analysis to determine the correlation of the PDB data to the low flow data. Concentrations of Site contaminants from PDBs at different depths were reviewed to determine the effect of the position of the PDB within the screened interval of the monitoring well. In addition, a comparison of non-detect results obtained from both methods was completed to identify potential false positive or negative results. Finally, concentrations of Site contaminants were compared to federal maximum contaminant levels to determine if there was agreement between results that exceed these values. Quality control data associated with the PDB and low flow results are also discussed in this section.

Relative Percent Difference of VOC Concentrations

The relative percent difference (RPD) was calculated to determine correlation between concentrations of Site contaminants obtained using PDB and low flow collection methods. These results have been tabulated and are presented in Table 1 for the shallow wells and Table 2 for deep wells. The RPD between the low flow and each of the PDB results was calculated as the quotient of the difference between the results and the average of the results using the formula below:

$$\text{RPD} = \frac{[(C_1 - C_2)]}{[(C_1 + C_2)/2]} \times 100$$

Where: $C_1 =$ PDB concentration  
$C_2 =$ low-flow concentration

The RPD was not calculated for positive sample concentrations that were less than five times the detection limit of 1 µg/L because of the high degree of variability indicated by the results for small differences in concentrations at this level. As a result, the RPD between results was not calculated for nine of the 80 results in the deep bedrock monitoring wells. The calculated RPD for the remaining results was compared against the EPA Region I validation limit of 30% for aqueous duplicate samples. Sample results were considered to “compare well” if the RPD between concentrations was less than 30%, or if both sample results were below five times the detection limit.

The RPD between PDB and low flow concentrations of Site contaminants was less than 30% for 100 of 116 (86%) of the shallow bedrock monitoring well results. For the deep bedrock monitoring wells, RPDs were below 30% for 61 of 71 (86%) results. RPDs exceeded 30% for each Site contaminant in at least one sample.

Of the nine shallow bedrock wells, three wells (MW-16IB, MW-106S, and MW-112S) had RPDs of 0% for all four contaminants at each depth. In MW-108S, the only contaminant with an RPD greater than 0% was PCE with RPDs ranging from 10% to 22% depending on depth. In the remaining five shallow bedrock wells that had contaminant concentration RPDs greater than 30%, the RPDs were greater than 30% in 16 of the 60 results (27%).
## Table 1
### Low Flow Versus PDB VOC Results
for Relative Percent Differences (RPD) Shallow Monitoring Wells

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth (ft.)</th>
<th>c-1,2-DCE</th>
<th>RPD</th>
<th>1,1,1-TCA</th>
<th>RPD</th>
<th>TCE</th>
<th>RPD</th>
<th>PCE</th>
<th>*RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-1B</td>
<td>65</td>
<td>38</td>
<td>3%</td>
<td>210</td>
<td>15%</td>
<td>550</td>
<td>32%</td>
<td>5300</td>
<td>33%</td>
</tr>
<tr>
<td></td>
<td>68.2</td>
<td>37</td>
<td>5%</td>
<td>180</td>
<td>0%</td>
<td>570</td>
<td>35%</td>
<td>4700</td>
<td>21%</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>38</td>
<td>3%</td>
<td>180</td>
<td>0%</td>
<td>420</td>
<td>5%</td>
<td>4800</td>
<td>23%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>39</td>
<td></td>
<td></td>
<td>180</td>
<td></td>
<td>400</td>
<td></td>
<td></td>
<td>3800</td>
</tr>
<tr>
<td>MW-2IB</td>
<td>20</td>
<td>150</td>
<td>60%</td>
<td>120</td>
<td>45%</td>
<td>4200</td>
<td>0%</td>
<td>9400</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>100</td>
<td>21%</td>
<td>160</td>
<td>17%</td>
<td>4200</td>
<td>0%</td>
<td>10000</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>96</td>
<td>17%</td>
<td>160</td>
<td>17%</td>
<td>4500</td>
<td>7%</td>
<td>9600</td>
<td>1%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>81</td>
<td></td>
<td></td>
<td>190</td>
<td></td>
<td>4200</td>
<td></td>
<td></td>
<td>9700</td>
</tr>
<tr>
<td>MW-3B</td>
<td>61</td>
<td>4</td>
<td>93%</td>
<td>8</td>
<td>7%</td>
<td>1&lt;1</td>
<td>0%</td>
<td>25</td>
<td>70%</td>
</tr>
<tr>
<td></td>
<td>64.5</td>
<td>71</td>
<td>146%</td>
<td>10</td>
<td>22%</td>
<td>15</td>
<td>200%</td>
<td>54</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>67</td>
<td>100</td>
<td>160%</td>
<td>6</td>
<td>29%</td>
<td>15</td>
<td>200%</td>
<td>8</td>
<td>167%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>11</td>
<td></td>
<td></td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>MW-13DB</td>
<td>14</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>MW-106S</td>
<td>30</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>34.5</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>MW-108S</td>
<td>32</td>
<td>&lt;1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>11</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>35.5</td>
<td>&lt;1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>11</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>&lt;1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>12</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>44.5</td>
<td>&lt;1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>11</td>
<td>10%</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>&lt;1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>8</td>
<td>22%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MW-112S</td>
<td>42</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
<td>&lt;1</td>
<td>0%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt;1</td>
<td></td>
<td></td>
<td>&lt;1</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>MW-114S</td>
<td>47.5</td>
<td>6</td>
<td>15%</td>
<td>99</td>
<td>11%</td>
<td>77</td>
<td>1%</td>
<td>2300</td>
<td>14%</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>6</td>
<td>15%</td>
<td>100</td>
<td>10%</td>
<td>75</td>
<td>1%</td>
<td>2400</td>
<td>18%</td>
</tr>
<tr>
<td></td>
<td>52.5</td>
<td>5</td>
<td>33%</td>
<td>86</td>
<td>24%</td>
<td>68</td>
<td>11%</td>
<td>2000</td>
<td>0%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>7</td>
<td></td>
<td></td>
<td>110</td>
<td></td>
<td>76</td>
<td></td>
<td>2000</td>
<td></td>
</tr>
</tbody>
</table>

Values that exceed USEPA 30% RPD criteria in bold.
NC = Not calculated. (For values less than 5 times the reporting limit.)
Depths are in feet below ground surface.
c-1,2-DCE = cis-1,2-Dichloroethene
1,1,1-TCA = 1,1,1-Trichloroethane
TCE = Trichloroethane
PCE = Tetrachloroethene
Table 2
Low Flow Versus PDB VOC Results for Relative Percent Differences (RPD) Deep Monitoring Wells

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Depth (ft.)</th>
<th>c-1,2-DCE</th>
<th>RPD</th>
<th>1,1,1-TCA</th>
<th>RPD</th>
<th>TCE</th>
<th>RPD</th>
<th>PCE</th>
<th>*RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-16DB</td>
<td>63</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>12</td>
<td>29%</td>
</tr>
<tr>
<td></td>
<td>66</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>11</td>
<td>20%</td>
</tr>
<tr>
<td></td>
<td>69</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>10</td>
<td>11%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt; 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-106D</td>
<td>77.5</td>
<td>9</td>
<td>40%</td>
<td>73</td>
<td>50%</td>
<td>80</td>
<td>46%</td>
<td>2400</td>
<td>67%</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>7</td>
<td>15%</td>
<td>53</td>
<td>19%</td>
<td>58</td>
<td>15%</td>
<td>1800</td>
<td>40%</td>
</tr>
<tr>
<td></td>
<td>82.5</td>
<td>6</td>
<td>0%</td>
<td>44</td>
<td>0%</td>
<td>51</td>
<td>2%</td>
<td>1400</td>
<td>15%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>6</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-108D</td>
<td>172</td>
<td>&lt; 1</td>
<td>0%</td>
<td>0.5</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>NC</td>
</tr>
<tr>
<td></td>
<td>175</td>
<td>&lt; 1</td>
<td>0%</td>
<td>0.5</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>NC</td>
</tr>
<tr>
<td></td>
<td>178</td>
<td>&lt; 1</td>
<td>0%</td>
<td>0.8</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>NC</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt; 1</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-112D</td>
<td>136</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>139</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>142</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-114D</td>
<td>125</td>
<td>14</td>
<td>13%</td>
<td>210</td>
<td>5%</td>
<td>130</td>
<td>0%</td>
<td>5300</td>
<td>38%</td>
</tr>
<tr>
<td></td>
<td>130</td>
<td>17</td>
<td>6%</td>
<td>230</td>
<td>14%</td>
<td>160</td>
<td>21%</td>
<td>5600</td>
<td>43%</td>
</tr>
<tr>
<td></td>
<td>135</td>
<td>18</td>
<td>12%</td>
<td>250</td>
<td>22%</td>
<td>160</td>
<td>21%</td>
<td>6000</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>18</td>
<td>12%</td>
<td>240</td>
<td>18%</td>
<td>160</td>
<td>21%</td>
<td>5900</td>
<td>48%</td>
</tr>
<tr>
<td></td>
<td>142.5</td>
<td>17</td>
<td>6%</td>
<td>240</td>
<td>18%</td>
<td>160</td>
<td>21%</td>
<td>5800</td>
<td>47%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>16</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td>130</td>
<td>3600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-115D</td>
<td>142</td>
<td>1</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>2</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 2</td>
<td>0%</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>2</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 2</td>
<td>0%</td>
</tr>
<tr>
<td>Low Flow</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values that exceed USEPA 30% RPD criteria in bold.
NC = Not calculated. (For values less than 5 times the reporting limit.)
Depths are in feet below ground surface.
c-1,2-DCE = cis-1,2-Dichloroethene
1,1,1-TCA = 1,1,1-Trichloroethane
TCE - Trichloroethane
PCE = Tetrachloroethene

Of the six deep bedrock wells, three wells (MW-108D, MW-112D, and MW-115D) had result RPDs of 0% for all four contaminants at each depth. PCE was the only contaminant in two of the wells that had an RPD greater than 0%. The PCE RPD was less than 30% in MW-16DB, but greater than 30% in MW-114D. At MW-106D, contaminant concentration RPDs exceeded 30% in five of the 12 results (42%).

The locations with the greatest number of results with RPDs exceeding 30% include MW-3B, with 7 of 12 results over criteria, and MW-106D, with 5 of 12 results with RPDs greater than 30%. The Site contaminant with the highest number of results over the 30% EPA criterion was tetrachloroethene, with 12 of 46 (26%) RPDs greater than 30%.

Overall, the RPD data indicate that there is acceptable agreement and a good correlation of the results obtained using the two collection methods. Of the fifteen wells sampled, 86% of the results had an RPD between PDB
and low flow concentrations of Site contaminants of less than 30%. Eight of the wells did not have any results with RPDs greater than 30%, and in five of the seven wells that had RPDs greater than 30%, the RPD exceeded this criterion in 25% or less of the results. The results suggest that the PDB sampling method provides results that correlate well with the low flow sampling results, and is an acceptable and effective alternative to the low flow method.

**Regression Analysis**

A regression analysis for each of the four primary Site contaminants was performed to identify potential bias and to determine the extent of correlation between the two sample collection methods. The resulting regression line was compared to the regression line that would have resulted in a perfect correlation. The coefficient of determination (or $r^2$ value) was calculated for comparison against the value obtained with perfect correlation, which is 1. The data for detections of each of the four primary contaminants were plotted along with the results of regression analysis. The regression plots are presented as Figure 1.

The regression plots indicate that the Site contaminant with the best correlation between the two sample collection methods was trichloroethene, with a coefficient of determination of 0.9977. Good correlation was also obtained for tetrachloroethene and 1,1,1-trichloroethane, which had coefficients of determination of 0.9381 and 0.9411, respectively. A less favorable correlation between sample methods was indicated for cis-1,2-dichloroethene, with $r^2 = 0.6186$. The regression analysis provided another indication of the fact that the PDB results are biased high relative to low-flow results. The bias may be due to stratification in wells MW-21B and MW-3B, which may be overcome for low-flow samples by mixing during sample collection.

For the regression plots, the PDB result is plotted as the dependent variable on the y-axis. Since the regression plot line for each Site contaminant is above the perfect correlation line, a high bias is indicated.

**Variability of Concentrations of Site Contaminants with Depth**

In addition to the comparison of PDB results with the low flow sampling method, the concentrations of site constituents obtained for PDBs installed in the same monitoring well were compared. The comparisons were made to determine if there was stratification of constituents within the screened interval of the well. Multiple PDBs were used at six deep and nine shallow bedrock monitoring wells. PDBs were attached onto a harness rig at intervals that would align with depths at which fracture zones were encountered during well installation.

The vertical stratification analysis was performed by determining the variability of constituent concentrations at each monitoring well location. The RPD between the highest and lowest concentrations were calculated for each constituent at all of the locations to determine variability. For locations in which the RPD was greater than EPA criteria, significant variation and potential stratification were indicated. The results from these analyses are summarized in Tables 3 and 4.

For the nine shallow bedrock monitoring wells, five of nine (56%) had at least one compound in which the RPD between the lowest and highest concentrations exceeded 30%. The constituent with the highest number of RPDs over 30% was tetrachloroethene at 3 of 9 (33%) locations. Cis-1,2-dichloroethene, 1,1,1-trichloroethane, and trichloroethene had RPDs over 30% at 2 of 9 (22%) locations. The greatest variability was indicated for MW-3B, in which the RPD for all four site constituents exceeded criteria. Interestingly, the highest concentrations for each of the constituents were not obtained from the same PDB, but were obtained from PDBs placed at different depths. For example, the highest concentration of cis-1,2-dichloroethene of the three PDBs placed into MW-3B was 100 µg/L reported for the PDB placed at the 67 foot depth. However, the highest concentration for tetrachloroethene, 110 µg/L, was obtained for the sample collected from the PDB placed at the 61 foot level.
There was generally less variation of the concentrations of site constituents for the deep bedrock monitoring wells. Only one of the six (17%) monitoring wells, MW-106D, had at least one constituent with an RPD that exceeded 30%. Unlike the results for the shallow bedrock wells, the highest concentrations of site constituents were generally obtained from the same depth. At MW-106D, the maximum concentration for each constituent was obtained from the sample collected from the 77.5 foot depth. For MW-114D, the maximum concentrations for each constituent were all obtained for the sample collected from the 135 foot depth.

Although in some instances the concentrations between samples collected at different depths within the screened interval where highly variable, in general, the detected concentrations of constituents within a well were within 30% of one another over the screened interval. The data do not conclusively indicate that stratification in shallow or deep bedrock monitoring wells had occurred.

Analysis of Potential False Positives and Negatives

For each collection method, non-detect results of each of the four primary Site contaminants were reviewed and compared to determine the potential for false positives or negatives. For this evaluation, the low flow results were assumed to be the correct results. A false positive is, therefore, a detection in the PDB sample without a detection in the low flow sample. None of the Site contaminants were detected in samples collected by either method in groundwater samples from MW-16IB, MW-106S, MW-112D and MW-112S.

The results of the evaluation of the potential for false positives or negative results are summarized in Table 5. A favorable comparison between the methods is indicated when either both methods detect the presence of a specific contaminant or both methods do not detect the presence of the contaminant. A less favorable outcome
is when one or the other of the methods detects a contaminant and the other method does not. Of the 196 PDB analyses considered (four compounds for each of 49 PDBs), 188, or 96 percent, matched the low flow result in terms of presence or absence of a particular compound. The remaining eight analyses, or four percent, were all false positives, meaning that the PDB analysis detected the compound whereas the low flow analysis did not. In no instance was a site contaminant detected in a low flow sample and not detected in the corresponding PDB sample. The results of the pilot study indicate that the potential for false negatives using the PDB method is low.

Table 5
Low Flow versus PDB VOC Results
Evaluation of False Positives/False Negatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of Samples</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-Detect Both</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Non-Detect PDB Hit Low Flow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hit PDB Non-Detect Low Flow</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hit Both</td>
<td></td>
</tr>
<tr>
<td>cis 1,2-DCE</td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>TCE</td>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>PCE</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Total:</td>
<td>86</td>
<td>0</td>
</tr>
<tr>
<td>Percent:</td>
<td>44%</td>
<td>0%</td>
</tr>
</tbody>
</table>

Comparison of Sample Concentrations to MCLs

The pilot study concentrations of four primary Site contaminants were also compared to the federal drinking water standards or maximum contaminant levels (MCLs). The MCLs have been tabulated and are presented below.

Federal Maximum Contaminant Levels of Site Contaminants

<table>
<thead>
<tr>
<th>Compound</th>
<th>MCL (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,2-Dichloroethene</td>
<td>70</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>200</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>5</td>
</tr>
<tr>
<td>Tetrachloroethene</td>
<td>5</td>
</tr>
</tbody>
</table>

Detections of Site contaminants exceeded the standards listed above for several samples. There were no sample locations for which concentrations exceeded corresponding standards for all Site contaminants. MCL exceedences and non-exceedences were consistent between samples collected using the two collection methods. The results of the evaluation of the comparison of detections in excess of MCLs are summarized in Table 6. A favorable comparison between the methods is indicated when the MCL for a particular compound is exceeded for both methods or is not exceeded for both methods. A less favorable outcome is when an exceedance is noted for one or the other of the methods, but not for the other method. Of the 196 PDB analyses considered (four compounds for each of 49 PDBs), 191, or 97 percent, matched the low flow result in terms of exceedance of the MCL for a particular compound. The remaining five analyses, or three percent, all indicated an MCL exceedance for the PDB analysis but a non-exceedance for the low flow analysis. In no instance was an MCL exceedance indicated for these four site contaminants in the low flow sample but not indicated in the corresponding PDB sample.
Table 6
Low Flow versus PDB VOC Results
Comparison of Maximum Containment Level Exceedances

<table>
<thead>
<tr>
<th>Compound</th>
<th>Below MCL Both</th>
<th>PDB Below MCL Low Flow Above</th>
<th>PDB Above MCL Low Flow Below</th>
<th>Above MCL Both</th>
<th>Totals</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis 1,2-DCE</td>
<td>44</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>49</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>43</td>
<td>0</td>
<td>1</td>
<td>5</td>
<td>49</td>
</tr>
<tr>
<td>TCE</td>
<td>30</td>
<td>0</td>
<td>2</td>
<td>17</td>
<td>49</td>
</tr>
<tr>
<td>PCE</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>31</td>
<td>49</td>
</tr>
<tr>
<td>Total:</td>
<td>135</td>
<td>0</td>
<td>5</td>
<td>56</td>
<td>196</td>
</tr>
<tr>
<td>Percent:</td>
<td>69%</td>
<td>0%</td>
<td>3%</td>
<td>29%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Quality Control Results Summary

Blank and field duplicate results were reviewed to ensure that the data generated from the pilot study were of sufficient quality for their intended end use. In general, these results were satisfactory and indicate that this was achieved.

Two different blanks were collected in the field as part of the pilot study: a bag blank and a tubing blank. The purpose of collecting these blanks was to eliminate positive sample results that may be the result of contamination already within the sample matrix or introduced from sampling or analytical activities. The bag blank was collected from a PDB that was not deployed into a monitoring well. The purpose of this blank was to determine if concentrations of Site contaminants were present in the distilled water matrix of the bags before they were installed into monitoring wells. A tubing blank was collected by pumping distilled water through the same polyethylene and pumphead tubing that was installed into the monitoring wells. Tetrachloroethene was detected in the bag blank and tubing blank at concentrations of 0.6 µg/L and 0.5 µg/L, respectively. There were no other Site contaminants detected in either of the blanks. Several low level concentrations of tetrachloroethene were qualified as non detect using USEPA Region I validation procedures. Samples for which this applied included MW-161B (17.5’), MW-106S, MW-106S (45.5’), MW-108D, MW-115D (142’), MW-115D (145’) and MW-115D (148’).

Duplicate samples of low flow and PDB samples were collected to assess the precision of the concentrations of Site contaminants. A summary of the duplicate results obtained using PDB and low flow sample collection techniques is presented in Table 7. All of the results have RPDs that are less than the USEPA Region I criterion of 30%, indicating that the precision for each of the Site contaminants is satisfactory. The RPDs for PDB samples ranged from 0 to 10%, whereas RPDs for low-flow samples ranged from 0 to 15%. The PDB method yielded duplicate sample results that showed generally lower RPDs than the low-flow method, particularly at higher concentrations.
## Table 7
**Duplicate Low Flow and PDB VOC Results**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>1,1-DCE RPD</th>
<th>1,1-DCE NC</th>
<th>c-1,2-DCE RPD</th>
<th>c-1,2-DCE NC</th>
<th>1,1,1-TCA RPD</th>
<th>1,1,1-TCA NC</th>
<th>TCE RPD</th>
<th>TCE NC</th>
<th>PCE RPD</th>
<th>PCE NC</th>
<th>RPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW-21B(26')</td>
<td>7</td>
<td>13%</td>
<td>96</td>
<td>2%</td>
<td>160</td>
<td>6%</td>
<td>9600</td>
<td>0%</td>
<td>4500</td>
<td>4%</td>
<td></td>
</tr>
<tr>
<td>Duplicate</td>
<td>8</td>
<td>98</td>
<td>170</td>
<td></td>
<td></td>
<td></td>
<td>9600</td>
<td></td>
<td>4700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-16DB(66')</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>11</td>
<td>0%</td>
<td>10%</td>
</tr>
<tr>
<td>Duplicate</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-108D</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>0.5</td>
<td>NC</td>
<td>&lt; 1</td>
<td>0%</td>
<td>4</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>Duplicate</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td></td>
<td></td>
<td>&lt; 1</td>
<td></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-112S</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td>&lt; 1</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>Duplicate</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td>&lt; 1</td>
<td></td>
<td></td>
<td>&lt; 1</td>
<td></td>
<td>&lt; 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW-114D</td>
<td>24</td>
<td>23%</td>
<td>17</td>
<td>0%</td>
<td>230</td>
<td>9%</td>
<td>160</td>
<td>7%</td>
<td>5600</td>
<td>15%</td>
<td></td>
</tr>
<tr>
<td>Duplicate</td>
<td>19</td>
<td>17</td>
<td>210</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Values that exceed USEPA 30% RPD criteria in bold.
NC = Not calculated. (For values less than 5 times the reporting limit.)
Depths are in feet below ground surface.

### Summary and Conclusions

Comparison of the results of analysis of groundwater samples collected using the low flow and PDB sampling techniques indicates that at the fractured bedrock site for which this study was undertaken, the PDB method yields samples that are comparable to low flow samples:

- Relative percent differences between low flow sample results and PDB sample results are less than 30% for 161 of 187 analyses (86%).

- Correlation coefficients obtained from regression analysis of concentrations of the four primary Site contaminants were 0.938 for PCE, 0.998 for TCE, and 0.941 for 1,1,1-TCA, indicating a very strong correlation between the results of the two methods, and 0.619 for cis-1,2-DCE, indicating a less favorable correlation.

- Contaminant concentrations within a well generally varied 20 percent or less. The variability or potential for stratification is not higher in wells with 20-foot screens than it is in wells with 10-foot screens.

- Of the 196 PDB analyses considered (four compounds for each of 49 PDBs), 188, or 96%, matched the low flow result in terms of presence or absence of a particular compound. In no instance was a site contaminant detected in a low flow sample but not detected in the corresponding PDB sample. The results of the pilot study indicate that the potential for false negatives using the PDB method is low.

- Of the 196 PDB analyses considered (four compounds for each of 49 PDBs), 191, or 97%, matched the low flow result in terms of exceedance of the MCL for a particular compound. In no instance was an MCL exceedance indicated for these four site contaminants in the low flow sample but not indicated in the corresponding PDB sample.

In conclusion, the results of the pilot study indicate that water-filled PDB samplers at mid-screen are suitable for long-term monitoring of VOCs in groundwater wells in the fractured bedrock at the site. Based on the results of this study, the following activities are recommended prior to deployment of PDBs for monitoring in...
order to determine if PDB sampling is applicable in a fractured bedrock geological setting and to verify that PDB samples from mid-screen adequately represent concentrations in the screened interval:

- Identify the depths of fracture zones in the bedrock.
- Complete a pilot study to determine if vertical stratification is going to provide significantly different results at different depths.

Acknowledgement

We would like to thank Timothy M. Sivavec, GE Corporate Research & Development, for his comments on an earlier draft of this paper.

References


Biographical Sketches

Thomas R. Eschner is a Senior Project Manager with Woodard & Curran (41 Hutchins Drive, Portland, ME, 04101; Phone: (207) 774-2112; Fax: (207) 774-6635; teschner@woodardcurran.com). He received a B.S. in geology and German from Syracuse University and an M.S. in Earth Resources from Colorado State University. Mr. Eschner has more than 24 years experience in groundwater and surface water investigations, including 17 years involving hazardous waste sites under CERCLA, RCRA, and various state Superfund programs.

David Dinsmore is a Project Scientist with Woodard & Curran (41 Hutchins Drive, Portland, ME, 04101; Phone: (207) 774-2112; Fax: (207) 774-6635; ddinsmore@woodardcurran.com). He received a B.S. in biology from the University of Southern Maine. A Portland area native, Mr. Dinsmore has over 15 years experience implementing and managing investigations at Superfund and RCRA sites around the country. He has particular expertise in groundwater sampling and field analytical methods.
Figure 1
Regression Plots

**Tetrachloroethene**

\[ y = 1.0688x + 377.65 \]
\[ R^2 = 0.9381 \]

**Trichloroethene**

\[ y = 1.0178x + 30.987 \]
\[ R^2 = 0.9977 \]

**1,1,1-Trichloroethane**

\[ y = 1.0286x - 0.552 \]
\[ R^2 = 0.9411 \]

**cis-1,2-Dichloroethene**

\[ y = 1.2713x + 5.3045 \]
\[ R^2 = 0.6186 \]