# An Evaluation of Tracers for Use in Vadose Zone Investigations at the Idaho National Engineering and Environmental Laboratory Karen E. Wright Laurence C. Hull 

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#### Abstract

Four naphthalene sulfonate compounds were tested for use as conservative vadose-zone tracers. A well-studied and conservative tracer, 2,4,5 trifluorobenzoic acid, was carried through the experimental procedure for comparison. The experimental design adopted was a four-way classification with three replicates for each treatment. Factors tested were tracer, vadose zone material, tracer concentration, and time. Using a batch method, we exposed aliquots of vadose zone materials to low ( 10 ppb ) or high ( 1 ppm ) concentrations of the tracers. Materials chosen for study consisted of a surface playa sediment, two composite interbed sediments, and a composite crushed basalt sample. The effect of time on sorption was tested by contacting the materials for $1,3,10$, and 14 days. Trifluorobenzoic acid concentrations used were 500 ppb and 10 ppm because of less sensitive detection limits. Naphthalene sulfonates were measured using high-performance liquid chromatography, and trifluorobenzoic acid was measured using ion chromatography. We found 2,4,5 trifluorobenzoic acid and 1,5 naphthalene disulfonate to be conservative with no statistically significant sorption to any of the four materials, for either concentration, for up to 14 days. For the first 10 days of contact, 1,3,6 naphthalene trisulfonate trisodium showed no statistically significant sorption, but showed significant sorption at 14 days. 2 naphthalene sulfonate is removed from the aqueous phase within one day, with nearly $40 \%$ removed for low concentrations after 14 days. Analytical interferences prevented the quantification of 2,7 naphthalene disulfonate disodium. Two tracers tested, 2,4,5 trifluorobenzoic acid, and 1,5 naphthalene disulfonate, were conservative and are useful as vadose zone tracers. For tracer tests of less than 14 days, 1,3,6 naphthalene trisulfonate trisodium could be useful.


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## ACRONYMS

| 2N | 2 Naphthalene sulfonate sodium |
| :--- | :--- |
| 3 F | $2,4,5$ trifluorobenzoic acid |
| 15 N | 1,5 Naphthalene disulfonate disodium |
| 27 N | 2,7 Naphthalene disulfonate disodium |
| 136N | $1,3,6$ Naphthalene trisulfonate trisodium |
| ANOVA | Analysis of Variance |
| ASTM | American Society for Testing and Materials |
| BET | Brunauer, Emmett, \& Teller |
| CEC | Cation Exchange Capacity |
| HPLC | High Performance Liquid Chromatography |
| IC | Ion Chromatography |
| INEEL | Idaho National Engineering and Environmental Laboratory |
| INTEC | Idaho Nuclear Technology and Engineering Center |
| SDA | Subsurface Disposal Area |
| VZRP | Vadose Zone Research Park |

# An Evaluation of Tracers for Use in Vadose Zone Investigations at the Idaho National Engineering and Environmental Laboratory 

## 1. INTRODUCTION

### 1.1 Background

The Idaho National Environmental and Engineering Laboratory (INEEL) (see Figure 1) is a U.S. Department of Energy facility that has historically been devoted to development of nuclear power reactor technology, reprocessing of spent nuclear fuels, and related nuclear research. As a result of these activities, portions of the site have become contaminated with metals, organic compounds, and radionuclides. The INEEL is located over the Snake River Plain Aquifer, a significant water resource for the state of Idaho extending $26,000 \mathrm{~km}^{2}$, and containing approximately $100 \times 10^{9} \mathrm{~m}^{3}$ of water (Smith 2004). Because of the size and importance of this water resource, understanding water and contaminant movement through the subsurface is extremely important to assess risk and evaluate remedial alternatives. Tracer studies are one method that can be used to study water movement through the subsurface.

As early as 1959, scientists had begun to evaluate the impact of the underground disposal of liquid radioactive waste upon groundwater quality in the Snake River Plain Aquifer. To understand the dispersal in the aquifer of contaminants from waste disposed to injection wells, investigators from the U.S. Geological Survey used fluorescein dye injected into a disposal well at the Idaho Nuclear Technology and Engineering Center (INTEC) (see Figure 1) to determine first arrival times to wells 213 to 427 m away from the injection site (Morris 1962). Tracers have more recently been used to help design groundwater remediation. One of the most commonly used tracers, $\mathrm{Br}^{-}$, was directly injected into the aquifer at Test Area North in an effort to characterize flow paths in the aquifer prior to setting up an in-situ bioremediation experiment (Sorenson et al. 2000).

Tracers have also been used in the vadose zone to study perched water and to delineate potential contaminant migration pathways. In 1962, researchers injected fluorescein dye into a monitoring well at the Test Reactor Area to examine the horizontal rate of water movement in a perched water zone. (Morris 1962). During a 1994 experiment, known as the Large-Scale Infiltration Test, researchers used ${ }^{75} \mathrm{Se}$ as a conservative tracer in the vadose zone (Dunnivant et al. 1998). They noted that water flows preferentially through fractures in basalt and laterally along sedimentary interbeds (Dunnivant et al. 1998). In 1999, the U.S. Geological Survey conducted a tracer test at the spreading areas on the INEEL in which they introduced 1,5 naphthalene disulfonate disodium into the vadose zone by adding tracer to water captured in the spreading areas (see Figure 1) during spring runoff. Tracer was detected at multiple locations in the vadose zone and in the aquifer, some 180 m below land surface (Nimmo et al. 2002). Lateral migration of tracers extended over a kilometer and detectable tracer concentrations persisted for up to a year. The tracer 2,4,5 trifluorobenzoic acid was used at the new INTEC percolation ponds by INEEL and Los Alamos National Laboratory scientists to determine the spatial and temporal transport of conservative tracers through the vadose zone (Roback et al. unpublished data).


Figure 1. The location of the INEEL within the state of Idaho, and the location of the study area (green) within the INEEL. Well locations are given by name: UZ98-2, UZ01-01, and VZ-6A. These wells are located between the SDA $(\tan )$ and the spreading areas (dark blue). Well 205 is located at the north end of the Vadose Zone Research Park (brown).

During the summer of 2000, researchers used fluorescent dyes at INTEC in an effort to correlate sources of surface water infiltration to perched water zones beneath the facility. Rhodamine WT and eocine fluorescent dyes were added to waste disposal ponds where they infiltrated into the subsurface. The results of this study were largely inconclusive due to problems with the tracers. While initial concentrations of dye were quite high ( $\sim 24,000 \mathrm{ppb}$ for rhodamine and 100 ppb for eocine), eocine was detected only in wells within about 274 m of the injection site, and rhodamine was detected only in wells within about 457 m of the injection site (Forsythe 2003). Sorption tests conducted at a later date on sediments at INTEC revealed that up to $87.7 \%$ of rhodamine, and up to $58.5 \%$ of eocine sorbed to sediments (Forsythe 2003). Because tracer sorbed to sediments in the vadose zone, it could not be concluded that a lack of detection of the tracer in monitoring wells was proof of a lack of flow connection between an infiltration pond and a perched water zone.

These results suggest that the use of tracers and the interpretation of their results is a complex endeavor. As demonstrated by the use of fluorescent dyes at INTEC, non-conservative behavior of tracers can invalidate the experiment for the conclusions the test was designed to reach. When tracers, assumed to be conservative fail to be so, erroneous conclusions can be drawn from the data obtained from tracer tests, as well as the failure to identify critical flow paths. Prior to using tracers in the vadose zone, researchers need to evaluate how the tracer will interact with the substrate to avoid erroneous or misleading data.

Ideal tracers are not toxic, do not interact with the substrate, do not easily degrade chemically or biologically, flow with the groundwater, are not present in large quantities in the water, and are easily measured in small quantities (Davis 1980). Conducting valid tracer tests in the vadose zone is integral to our understanding of how contaminants migrate from their near-surface geologic repositories in the vadose zone to the underlying aquifer. Unfortunately, the application of tracers to the vadose zone is complicated by the very high surface area to solution ratio in the pore space, which maximizes the potential for sorption of tracers. Thus, tracers that may be conservative in the aquifer may not behave similarly in the vadose zone. To identify suitable tracers for use in vadose zone investigations, we performed a series of batch sorption experiments to identify tracers that can be used, with particular attention to studying a family of tracers that could potentially be used simultaneously to study different flow paths.

### 1.2 Tracers

Numerous tracers have been used to study groundwater movement, including ionized substances (i.e., $\mathrm{Cl}^{-}, \mathrm{Br}^{-}, \mathrm{NO}_{3}^{-}$, and $\mathrm{SO}_{4}{ }^{2-}$ ), radioactive nuclides (i.e., ${ }^{3} \mathrm{H}$ ), organic dyes (i.e., fluorescein), fluorocarbons (i.e., freon), gases, fluorobenzoic acids (Davis et al. 1980; Bowman 1984), and naphthalene sulfonates (Nimmo et al. 2002). However, there are problems with most of these tracers. For example, many groundwaters contain high concentrations of $\mathrm{Cl}^{-}$, making this tracer insensitive at low concentrations. $\mathrm{NO}_{3}{ }^{-}$and $\mathrm{SO}_{4}{ }^{2-}$ can be degraded biologically (Bowman 1984). Federal and state laws often preclude intentionally adding radioactive substances to water. Organic dyes are very useful in karst terrain (Davis et al. 1980) and are used to mimic pesticide movement and sorption in alluvial aquifers (Sabatini and Al Austin 1991); however, because they sorb to sediments they are inappropriate for subsurface travel distances exceeding a few feet (Davis et al. 1980). Fluorocarbons and other gases work well as tracers, but in some cases are toxic (e.g., carbon monoxide), and are difficult to sample and analyze. Naphthalene sulfonates are easy to analyze, but have been studied for use only in geothermal systems (Rose et al. 2001); the low-temperature geochemistry of these compounds has not been studied. The most commonly used tracer is $\mathrm{Br}^{-}$(Bowman 1984; Davis et al. 1980). It is not sorbed by most soils, is inexpensive, and is easily analyzed.

However, sometimes it is necessary to use several different tracers simultaneously. In this scenario, it is desirable to have a family of tracers that behave similarly and can be readily analyzed by the same technique. R. S. Bowman demonstrated the use of isomers of fluorobenzoic acid for just such an application (Bowman 1984). Isomers of fluorbenzoic acid in general are conservative (although some are more conservative than others, compare Bowman and Gibbens 1992; Benson and Bowman 1994), and easy to analyze. However, the toxicity of fluorbenzoic acid in humans has not been established.

Our study focuses on the use of four isomers of naphthalene sulfonate and compares them to a well-studied tracer, 2,4,5 trifluorobenzoic acid. The use of naphthalene sulfonates was studied with application to high-temperature geothermal systems (Rose et al. 2001). Their primary interests included determining the thermal stability of the compounds and developing analytical techniques for them. Because naphthalene sulfonates are neither mutagenic nor carcinogenic (Greim et al. 1994), and because they can have detection limits up to 1,000 times lower than that of fluorobenzoic acids, they have potential for wide application as subsurface groundwater tracers.

### 1.3 Geologic Setting

The INEEL is located along the Eastern Snake River Plain, a topographical depression about 400 km long and 100 km wide (Hughes et al. 2002). It is largely underlain by sequences of volcanic rocks (principally basalt flows); the upper 213 m range in age from 500,000 to 100,000 years old (Kuntz et al. 1994). These basalt flows are punctuated by sequences of unconsolidated sediments consisting primarily of fine sand, silt, and clay, which can be up to 9.5 m thick at the SDA (Rightmire and Lewis 1987). Nomenclature for the various basalt flows and interbeds was described by Anderson and Lewis (1989), and is illustrated in Figure 2.

## 2. METHODS

### 2.1 Materials

### 2.1.1 Basalts and Sediments

Tracer sorption is dependent on surface properties of subsurface materials. Rocks and sediments were selected from two locations on the INEEL where future tracer studies are planned. Sediment and basalt core samples were obtained from three wells located near the radioactive waste Subsurface Disposal Area (SDA), and from one well located in the Vadose Zone Research Park (VZRP) (Figure 1). Sediment from wells near the SDA was taken from the B-C interbed, while basalt samples were taken from the overlying B basalt flow (Figure 2). Sediment from two of the three wells located near the SDA consisted of loess, while sediment from the third well (UZ 01-01) was composed primarily of basaltic cinders. These sediments were composited by weight to form one composite interbed sediment sample. We also obtained surface sediment from the SDA. Sediment from the VZRP was taken from the B-C interbed (Figure 2). While we do not have chemical data concerning the specific sediments we used, INEEL sediments in general are well characterized. Interbed sediments are composed of quartz, plagioclase, pyroxene, calcite, and clay minerals (dominantly illite and mixed smectite/illite) (Bartholomay et al. 1989). Cation exchange capacity ranges from 14-44 meq/100 g (Hull et al. 2004).

Sediments were sieved to remove material greater than 2 mm . After sieving, equal weights of sedimentary material from the SDA wells were composited and made as homogeneous as possible by blending the material with a roll cloth.


Figure 2. A cross section of the subsurface southwest to northeast through the Subsurface Disposal Area towards the Vadose Zone Research Park. Geologic nomenclature is from Anderson and Lewis (1989).

Measurement of sorption onto basalt involves compromises. While large blocks of basalt may most realistically represent subsurface conditions, sorption experiments using massive basalt blocks would be complicated by:

- Relatively small surface area resulting in low sensitivity in sorption measurements,
- A significant volume of immobile pore space resulting in matrix diffusion, complicating data analysis and interpretation, and
- Surface coatings of sediments, which make isolation of basalt sorption from sediment sorption difficult.

To address these issues, sorption to basalt was measured on pulverized basalt. Pulverizing basalt also creates complications by:

- Exposing unoxidized basalt surfaces that may have different sorption properties than weathered basalt, and
- Creating much larger surface area than would be encountered by infiltration through fractured basalt.

Creation of additional surface area, making the sorption experiments more sensitive, was considered the better approach to take. Clean basalt samples, with no apparent sediment coverage, were pulverized using a rotary grinder and then sieved to fall in a size range between 0.075 and 2 mm . Basalts from the SDA wells were composited equally by weight to form one basalt sample. In interpreting results from basalt sorption experiments, the high available surface area in the laboratory experiments must be considered when interpreting the applicability of the results to field conditions.

### 2.1.2 Tracers

Five tracers were tested: 2 naphthalene sulfonate sodium $(2 \mathrm{~N}), 1,5$ naphthalene disulfonate disodium ( 15 N ), 2,7 naphthalene disulfonate disodium ( 27 N ), 1,3,6 naphthalene trisulfonate trisodium (136N), and 2,4,5 trifluorobenzoic acid (3F). Naphthalene tracers were supplied by Yick-Vic Chemicals (Hong Kong), whereas the fluorobenzoic acid tracer came from Oakwood Products (West Columbia, South Carolina). We tested the effects of two different concentrations for each tracer. For the naphthalene compounds we used 1 ppm and 10 ppb and for the benzoic acid compound we used 10 ppm and 500 ppb . It is important that the chemical effects and interferences that would be present in the native water be taken into account when investigating tracer behavior. Therefore, tracers were dissolved in simulated river water (see Table 1). The fluorobenzoic acid tracer was adjusted to pH 7.2 prior to diluting it with simulated river water. Naphthalene tracers required no pH adjustment. We prepared tracers for each of the four time periods we tested. We determined the amount of tracer delivered to each sample by computing the amount of residual water remaining after the wash (see Appendix A), and by collecting and analyzing a sample of the tracer used to spike the sediment.

Table 1. The concentration of each compound per liter of deionized water to make one liter of simulated river water; $\mathrm{pH}=7.8$. Data for river water composition was obtained from the U.S. Geological Survey (http://nwis.waterdata.usgs.gov/nwis/qwdata,?site_no=13132520).

| Compound | mmol per Liter |
| :--- | :---: |
| $\mathrm{Na}_{2} \mathrm{SiO}_{3}: 5 \mathrm{H}_{2} \mathrm{O}$ | 0.2 |
| $\mathrm{~K}_{2} \mathrm{SO}_{4}$ | 0.018 |
| $\mathrm{MgCO}_{3}$ | 0.329 |
| $\mathrm{CaSO}_{4}: 2 \mathrm{H}_{2} \mathrm{O}$ | 0.116 |
| $\mathrm{CaF}_{2}$ | 0.005 |
| $\mathrm{CaCO}_{3}$ | 0.751 |
| $\mathrm{H}_{2} \mathrm{SO}_{4}$ | 0.053 |
| $\mathrm{HCl}^{\mathrm{HNO}_{3}}$ | 1.094 |
|  | 0.15 |

### 2.2 Sorption Procedure

We followed procedure ASTM D 4319-93, "Standard Test Method for Distribution Ratios by the Short-Term Batch Method" (Appendix A). This procedure entailed using a riffle splitter to load the desired mass of material into a polypropylene centrifuge tube. This was followed by washing the material three times with simulated river water (see Table 1), and then equilibrating the material overnight with simulated river water. Samples were then centrifuged, decanted, and spiked with simulated river water containing tracer. Samples were equilibrated for a specified period of time ( $1,3,10$, or 14 days), and then were centrifuged, decanted, and analyzed for tracer concentration. All samples were prepared in triplicate. In addition, blanks (tracer, no sediment; and sediment, no tracer) were prepared to check for sorption to centrifuge tubes and interfering analytes. In all, this experiment encompassed data collected from 540 samples, the data from which is shown in Appendix B. Tests to determine tracer sorption to the polypropylene centrifuge tubes showed no detectable loss of any tracer after a three-week contact time.

### 2.3 Analysis Procedure

### 2.3.1 Trifluorobenzoic Acid

All 3F samples were analyzed using a Dionex DX-500 ion chromatograph with a conductivity detector. Separation was achieved using a 4 mm AS-17 column with potassium hydroxide $(\mathrm{KOH})$ as the eluent (see Table 2). Injection volume was $25 \mu \mathrm{~L}$. "High" concentration samples ( $\sim 10 \mathrm{ppm}$ ) were measured once each. Precision is $\pm 2.4 \%$ ( $95 \%$ CI). "Low" concentration samples ( $\sim 500 \mathrm{ppb}$ ) were measured three times each, with their values averaged to achieve a final concentration. In addition, suppression was achieved using an external-water wash, rather than using the recycle mode. Precision for this method is $\pm 8.0 \%$ ( $95 \%$ CI). Detection limit for this method is about 150 ppb . Analysis of blanks showed no interference problems.

Table 2. Synopsis of analytical methods.

| Analyte | Instrument | Mobile Phase | Gradient | $\begin{gathered} \text { Excitation } \\ (\mathrm{nm}) \\ \hline \end{gathered}$ | $\begin{gathered} \text { Emission } \\ (\mathrm{nm}) \end{gathered}$ | Detection Limit (ppb) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3F | IC | KOH | $40 \mathrm{mmol} / 0-3 \mathrm{~min}$ $5 \mathrm{mmol} / 3-10 \mathrm{~min}$ | N/A | N/A | 150 |
| 2N | HPLC | $\begin{aligned} & \mathrm{PB}+43.75 \% \\ & \mathrm{MeOH} \end{aligned}$ | N/A | 222 | 334 | 1 |
| 15 N | HPLC | $\begin{aligned} & \mathrm{PB}+29.5 \% \\ & \mathrm{MeOH} \end{aligned}$ | N/A | 222 | 334 | 0.2 |
| 27N | HPLC | $\begin{aligned} & \mathrm{PB}+32.5 \% \\ & \mathrm{MeOH} \end{aligned}$ | N/A | 222 | 334 | ND |
| 136N | HPLC | $\begin{aligned} & \mathrm{PB}+35.5 \% \\ & \mathrm{MeOH} \end{aligned}$ | N/A | 228 | 342 | 1 |
| HPLC = High Performance Liquid Chromatography <br> IC $=$ Ion Chromatography <br> $\mathrm{KOH}=$ potassium hydroxide <br> $\mathrm{MeOH}=$ methanol <br> $\mathrm{N} / \mathrm{A}=$ not applicable <br> $\mathrm{ND}=$ not determined <br> $\mathrm{PB}=$ phosphate buffer $\left(3.17 \mathrm{mM} \mathrm{Na}_{2} \mathrm{HPO}_{4}, 6.21 \mathrm{mM} \mathrm{KH}_{2} \mathrm{PO}_{4}, 5.0 \mathrm{mM}\right.$ tetrabutyl ammonium phosphate) |  |  |  |  |  |  |

### 2.3.2 Naphthalene Compounds

All samples containing naphthalene tracers were analyzed using a Hewlett Packard Series 1050 HPLC with a GTI/Spectrovision FD-300 dual monochromator fluorescence detector. Our analytical methods were based upon those of Rose et al. (2001), with some minor differences. We used a Supelcosil LC $1815 \mathrm{~cm} \times 4.6 \mathrm{~mm}, 5 \mu \mathrm{~m}$ column (Supelco Inc.) with a mobile phase consisting of a solution of $3.17 \mathrm{mM} \mathrm{Na}_{2} \mathrm{HPO}_{4}, 6.21 \mathrm{mM} \mathrm{KH}{ }_{2} \mathrm{PO}_{4}$, and 5.0 mM tetrabutyl ammonium phosphate with varying amounts of methanol (Table 2). Injection volume was $150 \mu \mathrm{~L}$. Detection limit for this method varied with the tracer used (see Table 2). Precision for "low" concentration samples ( $\sim 10 \mathrm{ppb}$ ) was $\pm 8 \%$, while for "high" samples ( $\sim 1 \mathrm{ppm}$ ) was $\pm 2.5 \%(95 \% \mathrm{CI})$. Analysis of blanks showed no interference problems with the exception of tracer 27N, which will be discussed in Section 3.3.1.

### 2.3.3 Surface Area and Porosity Measurements

BET surface area and porosity measurements were made on each of the four materials using a Micromeritics TriStar 3000 surface area and porosimetry analyzer. Prior to analysis, the materials were heated overnight at $125^{\circ} \mathrm{C}$, with a nitrogen purge to remove adsorbed water. The analysis involved putting each sample under vacuum then cooling them cryogenically with liquid nitrogen. Each sample was then exposed to incremental increases in gas pressure to force adsorption onto the surface. During this procedure micropores are filled first, followed by the free surface. Finally, the largest pores are filled. At each pressure increment the equilibrated pressure was compared to the saturation pressure and the ratio of the two pressures was recorded resulting in an adsorption isotherm. When a monolayer of gas has been created on the surface of the material, the process is reversed. Pressure is lowered incrementally resulting in desorption. The adsorption isotherm created provides for surface area determination. On porous samples there is a hysteresis between the adsorption and desorption curves that in combination with the curve shape allows the quantification of porosity.

## 3. RESULTS

For most analyses, the standard deviation of percent sorbed for a treatment group of three replicates was $<5 \%$ sorbed, suggesting good agreement among replicates (Appendix B). The exception was for analyses of samples treated with tracer 2 N . Many of the groups of replicates using tracer 2 N had standard deviations $>50 \%$ sorbed. A possible reason for this is that tracer 2 N appears to degrade, but does so at different rates within replicate treatments. For example, in Figure 3 (a-c), we see chromatograms of replicates of 10 ppb tracer 2 N in contact with basalt for 14 days. These chromatograms show the tracer eluting at 4.05 minutes and an unknown pair of peaks eluting around 1.69 minutes. Both the tracer and the unknown peaks vary considerably in area when replicates are compared to each other. In Figure 3a, the area of the tracer represents 59.2\% removal of tracer from solution. Figures 3b and 3c represent $39.6 \%$ and $9.54 \%$ removal from solution, respectively. The area of the unknown peaks is variable, and does not appear to be related to the area of the tracer peak. This difference in the rate of apparent degradation of tracer 2 N results in replicate analyses that exhibit poor agreement with each other. These variations however, can be accounted for by a statistical examination of the data.

### 3.1 Statistical Analysis

In this experiment, tracer sorption data were obtained for four factors. Each combination of factors was tested in triplicate to provide an estimate of experimental variance. This experimental design permits evaluation of four variation sources (factors), as well as the ability to test interactions among factors based on the variance determined from the replicates. The four factors tested are:

- Tracer - are all the tracers comparable for use in the vadose zone?
- Time - is tracer concentration conservative over a period of two weeks?
- Concentration - does tracer sorption change with concentration?
- Material - do different INEEL subsurface materials sorb tracers differently?

The first factor tested is whether some of the tracers are better than others (i.e., demonstrate significantly less sorption). This will aid in selection of tracers for studies with multiple tracers and help eliminate some tracers for use. Water moving through some of the fractured basalts at the INEEL can move on the order of meters per day (Morris 1962; Nimmo et al. 2002). Total transit time for a tracer test can be on the order of months. Extended tests are needed to fully evaluate the long-term stability of tracers in the subsurface. The scope of this investigation limited the time of experiments to two weeks. During a tracer test, concentrations decrease significantly, often many orders of magnitude, as dilution decreases tracer concentrations. If sorption characteristics change with concentration, this would make interpretation of tracer tests difficult. Finally, we want to determine if different INEEL materials sorb tracers differently. If there are significant differences in materials, then generalizing results from materials at one location on the INEEL to other locations would not be obvious.

A useful approach to simultaneously evaluating whether multiple factors have a significant effect on an experimental result is a statistical technique called analysis of variance (ANOVA) (Wonnacott and Wonnacott 1969). This technique tests whether the average value for a response variable for one factor is significantly different than the average value of the same response variable for the other factors. The response variable selected for the statistical analysis in this study is the percent tracer sorbed. A statistical approach is preferred to a subjective evaluation because it provides a quantitative significance to statements about whether factors show different amounts of sorption.


Figure 3 (a-c). HPLC chromatograms of a set of three replicate treatments of 10 ppb tracer 2 N , exposed to basalt for 14 days. Tracer 2 N elutes at 4.05 minutes. An unknown pair of peaks elutes at 1.69 minutes (the second peak is represented by the small shoulder on the right side of the large, unknown peak). (a) $59.2 \%$ of tracer is removed from solution, (b) $39.6 \%$ of tracer is removed from solution, (c) $9.54 \%$ of tracer is removed from solution.

Histograms and normal probability plots were graphed to evaluate whether the raw data were normally distributed. The percent sorbed data departed from normality by having long tails on both ends of the distribution, but were symmetrical. ANOVA is more sensitive to skewness in the distribution than to kurtosis. Both parametric and nonparametric ANOVA were run on the data, and the results were very similar. Results of the parametric ANOVA are shown in Table 3. To evaluate whether a source of variation is significant, the ratio of the mean square error for an effect is compared to the total mean square error. This ratio of variances is an F ratio, and can be tested for statistical significance using an F test. In Table 3, the F statistic and associated probabilities for testing each source of variation (Effect) against the total variation (Total Error) are shown. Most of the effects and interactions among effects significantly reduce variation below that of the Error term. Ideally, if all the interactions among the
variables are not significant, then the main effects can be tested against the error (Griffiths 1967). In this experiment, however, essentially all of the three-way and two-way interaction terms are significant (see Table 3). This means that no clear conclusions can be drawn about any of the factors (tracer, time, concentration, material) because each factor does not perform the same across all of the values for the other factors. Therefore, the ANOVA does not provide much help in interpreting tracer performance; essentially all of the factors are important, but not uniformly across all effects.

Table 3. Variance table for statistical tests.

| Effect | Univariate Tests of Significance for \% Sorbed |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | Sum of Squares | $\begin{gathered} \text { Degrees } \\ \text { of } \\ \text { Freedom } \end{gathered}$ | Mean Square Error | F Ratio | Probability ${ }^{\text {a }}$ |
| Tracer | 12,578.19 | 3 | 4,192.729 | 42.50522 | $<0.001$ |
| Material | 8,366.65 | 3 | 2,788.882 | 28.27324 | $<0.001$ |
| Concentration | 1,302.84 | 1 | 1,302.838 | 13.20797 | $<0.001$ |
| Days | 8,683.14 | 3 | 2,894.379 | 29.34275 | $<0.001$ |
| Tracer by material | 9,550.95 | 9 | 1,061.217 | 10.75845 | $<0.001$ |
| Tracer by concentration | 5,390.14 | 3 | 1,796.714 | 18.21479 | $<0.001$ |
| Material by concentration | 806.33 | 3 | 268.776 | 2.72481 | 0.045 |
| Tracer by time | 13,667.36 | 9 | 1,518.596 | 15.39528 | $<0.001$ |
| Material by time | 6,249.60 | 9 | 694.400 | 7.03972 | $<0.001$ |
| Concentration by time | 673.10 | 3 | 224.368 | 2.27461 | 0.080 |
| Tracer by material by concentration | 2,478.31 | 9 | 275.367 | 2.79163 | 0.004 |
| Tracer by material by time | 14,972.05 | 27 | 554.520 | 5.62164 | $<0.001$ |
| Tracer by concentration by time | 3,011.7 | 9 | 334.641 | 3.39254 | 0.001 |
| Material by concentration by time | 1,063.13 | 9 | 118.126 | 1.19754 | 0.297 |
| Tracer by material by concentration by time | 3,682.06 | 27 | 136.373 | 1.38252 | 0.104 |
| Total error | 25,251.93 | 256 | 98.640 |  |  |

### 3.2 Two-Way Interactions

Trends in the main factors are not consistent across the other factors, making it impossible to draw any general conclusions from the ANOVA. All four of the main factors contribute to variation, but not in a consistent manner. The best way to interpret the data in this case is to graph the interactions to evaluate the effects (Griffiths 1967). Graphs were prepared illustrating the two-way interactions for each tracer. For each graph, a mean value was calculated for each tracer for each value of one of the other factors across the other two factors. For example, in Figure 4, an average percent sorbed was calculated for tracer 3 F on material IB by averaging the experimental percent sorbed data for two concentrations and four times.


Figure 4. Percent sorbed versus tracer by material (least-square means). Tracer 27 N not shown due to analytical problems (see Section 3.3.1). Error bars represent $95 \%$ confidence intervals. Materials are as follows: SDA interbed sediment (IB); SDA basalt (B); SDA surface alluvium (SA); VZRP interbed sediment (VIB).

The tracer and material interaction is shown in Figure 4. For three of the tracers, 3F, 15N, and 136 N , there is little difference among sedimentary materials, with basalt showing slightly higher sorption than the sediments. The higher basalt sorption may be related to the creation of fresh surface area by pulverizing. Even with the elevated surface area, sorption on the pulverized basalt is only a few percent. For the fourth tracer, tracer 2N, there are significant differences among the materials, with SDA surficial sediment having significantly more sorption than the other materials, and VZRP interbed material having significantly less sorption. The statistical significance of the tracer by material interaction term (Table 3), therefore, can mainly be attributed to tracer 2 N . The small differences in sorption for the different materials tested indicate that the results from this investigation can probably be extrapolated to INEEL vadose zone materials in general.

The effect of the concentration interaction by tracer is illustrated in Figure 5. A significant difference in sorption characteristics at different concentrations implies a non-linear sorption isotherm. While no sorption is desired, linear sorption characteristics would be easier to deal with than non-linear characteristics. Three of the tracers, $3 \mathrm{~F}, 15 \mathrm{~N}$, and 136 N , show no significant difference in sorption with a difference in concentration. Tracer 2N, however, shows significantly greater percent sorption at low concentrations, consistent with a concave downward, non-linear sorption isotherm.

The effect of time on sorption of tracers is shown in Figure 6. The effect of time evaluates kinetic effects on sorption. For two of the tracers, 3 F and 15 N , sorption is independent of time. For tracer 136N, there is an increase in sorption after 10 days. Sorption at two weeks is significantly greater at the $95 \%$ level than sorption in the first 10 days. For tracer 2 N , sorption also increases significantly at 14 days.


Figure 5. Percent sorbed versus tracer by concentration (least-square means). Error bars represent 95\% confidence intervals.


Figure 6. Percent sorbed versus tracer by material (least-square means). Error bars represent 95\% confidence intervals.

The graphs illustrate why the two-way interaction terms are significant in this analysis. Each of the three sources of variation tested for each tracer (material, concentration, and time) showed different results for each tracer. Tracer 2N, in particular, does not perform consistently with the other three tracers showing more sorption and greater variation in sorption. Sedimentary materials generally show similar sorption characteristics, with basalt demonstrating slightly higher sorption. Basalt was pulverized to increase sensitivity in these experiments, and may overestimate sorption that would be expected for massive basalt in the subsurface.

### 3.3 Individual Tracer Results

### 3.3.1 2,7 Naphthalene Disulfonate Disodium

Results from tracer 27 N are not shown due to analytical problems. A compound that is leached from the soil (or is a degradation product of the tracer) is chromatographically inseparable (using our HPLC method) from the analyte of interest, making accurate analysis of low concentrations ( $\sim 10 \mathrm{ppb}$ ) problematic. It is possible that the use of a longer column with a smaller diameter matrix might mitigate this issue, but time limitations precluded pursuing this option.

At high concentrations (i.e., 1 ppm ) any sorption that occurs with tracer 27 N is within experimental error, and is therefore not detectable (data not shown). Rose and others (2001) noted an apparently similar interference with tracer 27 N when used as a tracer in a geothermal system, which suggests that the use of tracer 27 N may be problematic in many different types of groundwater systems.

### 3.3.2 2,4,5 Trifluorobenzoic Acid

Figure 4 shows the least-square means distribution for each tracer versus percent sorbed with regard to individual solid materials. For tracer 3F, there is no statistical difference with respect to the various materials tested, nor is the measured sorption statistically different from zero. Tracer 3F is also insensitive to the different concentrations and different times evaluated in this test. For all variables tested, 3F sorption is not statistically different from zero.

### 3.3.3 1,5 Naphthalene Disulfonate Disodium

As shown in Figures 5 and $6,15 \mathrm{~N}$ is insensitive to time and concentration, but sensitive to material type (Figure 4). As shown in Figure 4, 15N sorbs to material B (basalt); however this may be due to the increased surface area caused by pulverization of the basalt. Sorption to the other materials is not statistically different from zero.

### 3.3.4 1,3,6 Naphthalene Trisulfonate Trisodium

Figure 4 illustrates that for 136 N , sorption is no different between materials IB (SDA interbed material), SA (SDA surface alluvium), and VIB (VZRP interbed material), or between materials IB, SA, and B; however, sorption is significantly higher on material B than on VIB (similar to that illustrated by tracer 15 N in Figure 4), but again, this may be due to the pulverization of the basalt. Figure 5 shows that sorption is about the same for both high and low concentrations of 136 N . Figure 6 illustrates that whereas there is no difference between days one and 10 for tracer 136 N , there is an average of $10 \%$ sorption of tracer by day 14 .

### 3.3.5 2 Naphthalene Sulfonate

Sorption of 2N is highly variable between materials (Figure 4). Average sorption of 2N on SA is $30 \%$, compared to about $10-15 \%$ for IB and B, and $0 \%$ for VIB. There are also significant differences between the effects of concentration as illustrated on Figure 5. The percentage of low concentration tracer sorbed is considerably more ( $22 \%$ ) than that of high concentration (5\%). Finally, when we consider the effect of time (Figure 6), we can see that in general, sorption increases with time, up to nearly $40 \%$ at 14 days.

It is important to note that while we use the term "sorption" to refer to the removal of tracer 2 N from solution, we noted in Section 3 that this tracer is probably degrading, and will discus the possibility of diffusion in Section 4.1.

## 4. DISCUSSION

As expected from previous work using tracer 3F (Benson and Bowman 1994), we did not observe any measurable sorption. Nor did we observe any measurable sorption with 15 N . However, we did observe a measurable decrease in aqueous concentrations of tracer 136 N , and a substantial decrease in concentration with 2 N .

### 4.1 Diffusion versus Sorption

Our goal for this study is to determine whether the tracers we are testing are conservative or not. One of the issues that must be addressed is the possibility of these tracers diffusing into the pore spaces in the solid materials and thus are removed from solution, versus the chemical binding of the tracer to the surface of the solid as occurs with sorption. This is an important distinction. In a field-scale tracer study, a tracer that does not chemically bind to the surface of the substrate but rather diffuses into pores can be effectively used. The flow of "clean" water following the introduction of tracer will remove the tracer from pore spaces by mass action. However, if a tracer is chemically bound to the surface, it is not always possible to remove it, or it may require inordinately large volumes of water to do so (Forsythe, 2003)

To test whether diffusion is a possibility it is necessary to know the porosity of the solid materials and to know the diffusion coefficients of the tracers. This information appears in Tables 4 and 5.

Table 4. Physical properties of sediments and rocks used in the experiments.

| Material | BET <br> Surface Area ${ }^{\mathrm{a}}$ <br> $\left(\mathrm{m}^{2} / \mathrm{g}\right)$ | Micropore <br> Area <br> $\left(\mathrm{m}^{2} / \mathrm{g}\right)$ | External <br> Surface Area <br> $\left(\mathrm{m}^{2} / \mathrm{g}\right)$ | Surface Area <br> of Pores ${ }^{\mathrm{a}}$ <br> $\left(\mathrm{m}^{2} / \mathrm{g}\right)$ |
| :--- | :---: | :---: | :---: | :---: |
| VIB (VZRP interbed sediment) | 32.3 | 5.77 | 26.5 | 21.4 |
| IB (SDA interbed sediment) | 11.9 | 1.59 | 10.3 | 8.79 |
| SA (SDA surface alluvium) | 27.5 | 5.78 | 21.7 | 16.6 |
| B (SDA interbed basalt) | 0.484 | $*$ | 0.484 | $*$ |

[^0]Table 5. Aqueous diffusion coefficients as estimated by the Hayduk and Laudie method,


| Tracer | Aqueous Diffusion Coefficient <br> $\left(\mathrm{m}^{2} \mathrm{~s}^{-1} \times 10^{-10}\right)$ |
| :--- | :---: |
| $3 \mathrm{~F}(2,4,5$ trifluorobenzoic acid $)$ | 7.82 |
| $2 \mathrm{~N}(2$ naphthalene sulfonate sodium $)$ | 6.64 |
| $15 \mathrm{~N}(1,5$ naphthalene disulfonate disodium $)$ | 5.81 |
| $27 \mathrm{~N}(2,7$ naphthalene disulfonate disodium $)$ | 5.81 |
| $136 \mathrm{~N}(1,3,6$ naphthalene trisulfonate trisodium $)$ | 5.21 |

Since diffusion requires porosity, we would expect that materials most likely to promote diffusion would be those with the greatest porosity. For these study materials that would be VIB $>\mathrm{SA}>\mathrm{IB}>\mathrm{B}$. Porosity of material B is so small as to not be measurable by a nitrogen adsorption/desorption technique. Yet Figure 4 illustrates clearly that for tracer 136 N , material B shows the highest amount of tracer removed from solution. If this tracer was diffusing, it is not likely that diffusion would be greatest on the material with the least amount of porosity.

Table 5 shows aqueous diffusion coefficients for the various tracers tested. Tracer 3 F , which was not removed from solution in this study, has a higher diffusion coefficient than that of tracer 136 N , which began to be removed from solution after 10 days. If diffusion was a major factor in this system, we should expect that tracer 3 F would move quickly into pores, and disappear from solution more rapidly than the slower-moving 136F. In fact the opposite is true. We can see from Figure 6 that over 14 days, there is no change in tracer 3 F concentration, but that 136 N begins to be removed from solution after 10 days. For tracer 136 N , the evidence suggests that diffusion does not have a large effect on the behavior of this tracer. The more likely explanation for the loss of tracer 136 N from solution is sorption.

While there is not strong evidence for diffusion with regards to tracer 2 N , for the same reasons discussed above, tracer 2 N is removed from solution in substantial amounts. As discussed in section 3, 2 N appears to degrade into some other compound or compounds. Kertesz (1999) demonstrated that common soil microorganisms can metabolize aromatic sulfonates under aerobic conditions, while Cook et al. (1998) established the ability of anaerobic bacteria to catabolize sulfonates. While our study was not designed to study microbial degradation, we can see from Figure 3 that the tracer is degrading. Since we did not sterilize the basalts and soils, microbes would be present, thus there is the possibility that the tracer was biologically degraded. In addition, since we did not perform a desorption experiment on the materials, we cannot rule out the possibility of sorption of tracer 2 N (or its apparent degradation products) to the soils or basalt.

### 4.2 Significance of Findings

Certain types of flow paths, such as fast water flow, rapid lateral transport, and extensive vertical transport, are typically dilute. This is due to the rapid dilution and dispersion that occurs to a solute dissolved in water that is transported through such a preferential flow path. Because of the relatively high detection limit of fluorobenzoic acid tracers, this may inhibit the researcher's ability to recognize and detect these flow paths. This is particularly problematic when the issue of concern is contaminant transport, where it is especially important to define such flow paths. Tracer 15 N , which has sorption properties not significantly different from that of tracer 3 F , has a detection limit that is at least 750 times lower, making this tracer a good candidate for tracer studies in the subsurface environment. Tracer 136N
will work as well as tracer 15 N for very short-term studies ( $<2$ weeks) but for longer time periods may not be retained in solution in significant enough quantity to delineate dilute flow paths.

## 5. CONCLUSIONS

2,4,5 trifluorobenzoic acid remains an appropriate conservative tracer for use at the INEEL. We suggest that 1,5 naphthalene disulfonate disodium is as conservative as $2,4,5$ trifluorobenzoic acid (with regard to the materials tested) and has the additional advantage of having a detection limit three orders of magnitude lower. 2,7 naphthalene disulfonate disodium has interference problems that make accurate analysis at low concentrations problematic. Finally, due to its apparent sorption or degradation, 2 naphthalene sulfonate sodium is not useable as a conservative tracer at the INEEL.

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## Appendix A

## Sorption Procedure

## Appendix A

## Sorption Procedure

1. Label centrifuge tubes as to sample designation.
2. Weigh all tubes and record weight on tube and in book to 0.01 g .
3. Using a riffle splitter, add about 10 g sediment to each tube ( 3.5 g to VIB samples).
4. Re-weigh tube and record weight to nearest 0.01 g .
5. Add 30 ml simulated riverwater (SRW) to each tube ( 10.5 ml to VIB samples).
6. Stir for 15 minutes.
7. Centrifuge at 1000 g or more for 5 min . Decant and discard supernatant.
8. Repeat steps $5-7$ two more times (for a total of 3 washes).
9. Add 40 ml SRW to each tube and equilibrate with stirring 24 hours ( 14 ml to VIB samples).
10. Centrifuge and decant as before.
11. Re-weigh tube and record weight to nearest 0.01 g .
12. Using data from step 2 and 4 , compute the amount of sediment in each tube. Multiply this value by 4 . Subtract from this the amount of water remaining in the pore spaces from washing (subtract weight from step 4 from that in step 11). This is how much tracer-spiked SRW will be added in step 13.

Example:

| Empty tube weight: | 11.37 g (step 2) |
| :--- | :--- |
| Full tube weight: | 21.65 g (step 4) |
| Sediment weight | 10.28 g (step 4-step 2) |
| Washed Tube weight: | $24.24 \mathrm{~g}($ (step 11) |
| Water weight: | $2.59 \mathrm{~g}($ step 11-step 4). |
| Spiked solution to add (g) | $38.53(4 \times$ sediment wt. - water weight). |

13. Place tube on balance and tare. Add spiked solution to nearest 0.1 g (i.e., 38.5 g from example above). Re-suspend solids and place tube on a rotator/shaker for at least six hours every day.
14. After one day, measure and record the pH of the solution. Return to shaker if the equilibration time is to be longer than one day; otherwise collect supernatant as in step 15.
15. Supernatant collection: Centrifuge at 1400 g or more for 20 minutes. Decant supernatant and place in clean centrifuge tube or bottle for analysis:

Sediments:
a. SDA B-C interbed sediments composited from 3 wells (IB samples)
b. SDA basalt composited from 3 wells (B samples)
c. SAB Alluvial sediment (SA samples)
d. VZRP interbed sediment (VIB samples).

Tracers:
a. 2 naphthalene sulfonate $(2 \mathrm{~N})$
b. 2,7 naphthalene disulfonate ( 27 N )
c. 1,5 naphthalene disulfonate $(15 \mathrm{~N})$
d. 1,3,6 naphthalene trisulfonate ( 136 N )
e. trifluorobenzoic acid. (3F)

Concentrations of Tracers:
a. 1 ppm for naphthalene compounds; 10 ppm for benzoic acid
b. $\quad 0.01 \mathrm{ppm}(10 \mathrm{ppb})$ for naphthalene compounds; 500 ppb for benzoic acid.

Equilibration Periods:
a. 14 days
b. 1 day
c. 10 days
d. 3 days.

Blanks:
Blanks (sediment plus SRW, No tracer) will be prepared for each sediment and run for 14 day equilibration only.

Replicates:
Each sample will be run in triplicate.

## Appendix B

## Data Collected

## Appendix B

## Data Collected

Sample Naming Scheme
Example: 2N-IB-H-14-1
First number group: indicates tracer used ( $2 \mathrm{~N}, 15 \mathrm{~N}, 27 \mathrm{~N}, 136 \mathrm{~N}$, or 3 F ).
Second number group: indicates substrate (IB, B, SA, or VIB).
Third number group: indicates concentration, high, low or blank (H, L, or B).
Fourth number group: indicates contact time ( $1,3,10$, or 14 days).
Fifth number group: indicates replicate number ( 1,2 or 3 ).







| Sample | Tube wt $(\mathrm{g})$ | $\begin{gathered} \text { Tube + Sed wt } \\ (\mathrm{g}) \\ \hline \end{gathered}$ | Tube wt after Wash (g) | Retained Water wt (g) | Spike Sol'n to Add <br> (g) | Actual Sol'n Added <br> (g) | pH after 24 Hours | Conc of Tracer (calc) | Conc of Tracer (meas) | \% Sorbed |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 27N-IB-B-14-1 | 11.78 | 21.81 | 27.85 | 6.04 | 34.08 | 34.07 | 8.11 |  |  |  |
| 27N-IB-B-14-2 | 11.77 | 21.65 | 26.71 | 5.06 | 34.46 | 34.47 |  |  |  |  |
| 27N-IB-B-14-3 | 11.83 | 21.86 | 27.55 | 5.69 | 34.43 | 34.45 |  |  |  |  |
| 27N-B-B-14-1 | 11.79 | 21.39 | 25.24 | 3.85 | 34.55 | 34.56 | 8.4 |  |  |  |
| 27N-B-B-14-2 | 11.85 | 22.56 | 27.07 | 4.51 | 38.33 | 38.32 |  |  |  |  |
| 27N-B-B-14-3 | 11.82 | 21.39 | 26.73 | 5.34 | 32.94 | 32.93 |  |  |  |  |
| 27N-SA-B-14-1 | 11.83 | 22.27 | 26.95 | 4.68 | 37.08 | 37.07 | 8.71 |  |  |  |
| 27N-SA-B-14-2 | 11.73 | 21.43 | 25.74 | 4.31 | 34.49 | 34.49 |  |  |  |  |
| 27N-SA-B-14-3 | 11.76 | 22.59 | 27.61 | 5.02 | 38.3 | 38.33 |  |  |  |  |
| 27N-VIB-B-14-1 | 11.88 | 15.41 | 17.81 | 2.4 | 11.72 | 11.71 | 8.94 |  |  |  |
| 27N-VIB-B-14-2 | 11.72 | 15 | 17.26 | 2.26 | 10.86 | 10.87 |  |  |  |  |
| 27N-VIB-B-14-3 | 11.77 | 15.09 | 17.38 | 2.29 | 10.99 | 10.96 |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |
| 27N-IB-H-10-1 | 11.87 | 21.92 | 26.55 | 4.63 | 35.57 | 35.57 | 7.9 | 862 | 869 | -0.80 |
| 27N-IB-H-10-2 | 11.88 | 21.95 | 26.2 | 4.25 | 36.03 | 36.01 |  | 871 | 879 | -0.90 |
| 27N-IB-H-10-3 | 11.79 | 21.49 | 25.63 | 4.14 | 34.66 | 34.71 |  | 870 | 881 | -1.25 |
| 27N-B-H-10-1 | 11.81 | 21.4 | 24.97 | 3.57 | 34.79 | 34.78 | 8.2 | 883 | 812 | 8.11 |
| 27N-B-H-10-2 | 11.89 | 22.7 | 30.16 | 7.46 | 35.78 | 35.77 |  | 806 | 845 | -4.81 |
| 27N-B-H-10-3 | 11.81 | 22.18 | 26.07 | 3.89 | 37.59 | 37.63 |  | 883 | 745 | 15.59 |
| 27N-SA-H-10-1 | 11.84 | 22.41 | 26.61 | 4.20 | 38.08 | 38.05 | 8.5 | 877 | 904 | -3.00 |
| 27N-SA-H-10-2 | 11.81 | 22.26 | 26.67 | 4.41 | 37.39 | 37.41 |  | 871 | 908 | -4.18 |
| 27N-SA-H-10-3 | 11.7 | 22.23 | 26.55 | 4.32 | 37.80 | 37.77 |  | 874 | 920 | -5.27 |
| 27N-VIB-H-10-1 | 11.77 | 15.27 | 17.98 | 2.71 | 11.29 | 11.29 | 8.5 | 786 | 845 | -7.51 |
| 27N-VIB-H-10-2 | 11.83 | 15.1 | 17.16 | 2.06 | 11.02 | 10.99 |  | 820 | 877 | -6.92 |
| 27N-VIB-H-10-3 | 11.78 | 15.32 | 17.55 | 2.23 | 11.93 | 11.95 |  | 821 | 878 | -6.94 |
|  |  |  |  |  |  |  |  |  |  |  |
| 27N-IB-L-10-1 | 11.93 | 22.09 | 27.49 | 5.40 | 35.24 | 35.56 | 7.9 |  |  |  |
| 27N-IB-L-10-2 | 11.85 | 21.96 | 28.83 | 6.87 | 33.57 | 36.02 |  |  |  |  |
| 27N-IB-L-10-3 | 11.81 | 21.71 | 26.79 | 5.08 | 34.52 | 34.67 |  |  |  |  |
| 27N-B-L-10-1 | 11.79 | 22.41 | 26.9 | 4.49 | 37.99 | 37.97 | 8.2 |  |  |  |
| 27N-B-L-10-2 | 11.87 | 22.42 | 26.4 | 3.98 | 38.22 | 36.27 |  |  |  |  |
| 27N-B-L-10-3 | 11.94 | 22.7 | 27.2 | 4.50 | 38.54 | 38.52 |  |  |  |  |
| 27N-SA-L-10-1 | 11.87 | 22.28 | 26.57 | 4.29 | 37.35 | 37.35 | 8.4 |  |  |  |
| 27N-SA-L-10-2 | 11.72 | 22.67 | 27.15 | 4.48 | 39.32 | 39.28 |  |  |  |  |
| 27N-SA-L-10-3 | 11.78 | 21.53 | 25.23 | 3.70 | 35.30 | 35.31 |  |  |  |  |
| 27N-VIB-L-10-1 | 11.73 | 14.85 | 16.98 | 2.13 | 10.35 | 10.38 | 8.5 |  |  |  |
| 27N-VIB-L-10-2 | 11.71 | 15.06 | 17.39 | 2.33 | 11.07 | 11.07 |  |  |  |  |
| 27N-VIB-L-10-3 | 11.78 | 15.28 | 17.93 | 2.65 | 11.35 | 11.36 |  |  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |
| 27N-IB-H-3-1 | 11.76 | 21.88 | 26.38 | 4.50 | 35.98 | 35.99 |  | 915 | 923 | -0.85 |
| 27N-IB-H-3-2 | 11.73 | 21.62 | 25.92 | 4.30 | 35.26 | 35.23 |  | 918 | 946 | -3.05 |
| 27N-IB-H-3-3 | 11.8 | 21.87 | 26.65 | 4.78 | 35.50 | 35.77 |  | 908 | 930 | -2.36 |
| 27N-B-H-3-1 | 11.79 | 23.06 | 27.38 | 4.32 | 40.76 | 40.77 |  | 931 | 885 | 4.91 |
| 27N-B-H-3-2 | 11.79 | 23.95 | 29.07 | 5.12 | 43.52 | 43.77 |  | 922 | 875 | 5.12 |



| Sample | Tube wt <br> (g) | Tube + Sed wt <br> (g) | Tube wt after Wash <br> (g) | Retained Water wt (g) | Spike Sol'n to Add <br> (g) | Actual Sol'n Added <br> (g) | pH after 24 Hours | Conc of Tracer (calc) | Conc of Tracer (meas) | \% Sorbed |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 27N-VIB-L-1-2 | 11.78 | 15.26 | 17.28 | 2.02 | 11.90 | 11.91 | 8.49 |  |  |  |
| 27N-VIB-L-1-3 | 11.66 | 15 | 16.94 | 1.94 | 11.42 | 11.41 | 8.49 |  |  |  |
| 136N-IB-H-14-1 | 11.84 | 21.74 | 26.51 | 4.77 | 34.83 | 34.87 | 8.13 | 905 | 718 | 20.64 |
| 136N-IB-H-14-2 | 11.72 | 21.51 | 25.64 | 4.13 | 35.03 | 35.08 |  | 920 | 890 | 3.26 |
| 136N-IB-H-14-3 | 11.83 | 22 | 26.51 | 4.51 | 36.17 | 36.18 |  | 915 | 909 | 0.61 |
| 136N-B-H-14-1 | 11.77 | 21.37 | 25.21 | 3.84 | 34.56 | 34.58 | 8.2 | 926 | 857 | 7.46 |
| 136N-B-H-14-2 | 11.88 | 22.32 | 26.38 | 4.06 | 37.7 | 37.73 |  | 929 | 870 | 6.28 |
| 136N-B-H-14-3 | 11.89 | 22 | 26.48 | 4.48 | 35.96 | 35.96 |  | 915 | 863 | 5.65 |
| 136N-SA-H-14-1 | 11.74 | 21.71 | 26.09 | 4.38 | 35.5 | 35.53 | 8.66 | 916 | 907 | 0.97 |
| 136N-SA-H-14-2 | 11.73 | 21.86 | 26.52 | 4.66 | 35.86 | 35.86 |  | 910 | 552 | 39.36 |
| 136N-SA-H-14-3 | 11.79 | 22.34 | 26.6 | 4.26 | 37.94 | 37.93 |  | 925 | 897 | 2.97 |
| 136N-VIB-H-14-1 | 11.81 | 15.23 | 17.58 | 2.35 | 11.33 | 11.31 | 8.72 | 852 | 859 | -0.84 |
| 136N-VIB-H-14-2 | 11.81 | 14.93 | 17.11 | 2.18 | 10.3 | 10.26 |  | 848 | 865 | -1.99 |
| 136N-VIB-H-14-3 | 11.79 | 15 | 17.23 | 2.23 | 10.61 | 10.6 |  | 850 | 849 | 0.09 |
| 136N-IB-L-14-1 | 11.77 | 22.09 | 27.06 | 4.97 | 36.31 | 36.31 | 8.23 | 9.38 | 8.62 | 8.18 |
| 136N-IB-L-14-2 | 11.72 | 22.08 | 27.02 | 4.94 | 36.5 | 36.51 |  | 9.40 | 9.61 | -2.25 |
| 136N-IB-L-14-3 | 11.88 | 21.47 | 25.76 | 4.29 | 34.07 | 34.07 |  | 9.48 | 7.74 | 18.34 |
| 136N-B-L-14-1 | 11.76 | 22.16 | 26.3 | 4.14 | 37.46 | 37.47 | 8.32 | 9.61 | 7.47 | 22.28 |
| 136N-B-L-14-2 | 11.74 | 21.69 | 25.57 | 3.88 | 35.92 | 35.92 |  | 9.63 | 7.83 | 18.71 |
| 136N-B-L-14-3 | 11.79 | 20.78 | 24.3 | 3.52 | 32.44 | 32.43 |  | 9.62 | 7.60 | 21.01 |
| 136N-SA-L-14-1 | 11.79 | 22.03 | 26.23 | 4.2 | 36.76 | 36.77 | 8.7 | 9.58 | 8.26 | 13.78 |
| 136N-SA-L-14-2 | 11.75 | 21.87 | 25.91 | 4.04 | 36.44 | 36.44 |  | 9.60 | 7.81 | 18.73 |
| 136N-SA-L-14-3 | 11.74 | 22.36 | 27.15 | 4.79 | 37.69 | 37.65 |  | 9.46 | 8.14 | 14.00 |
| 136N-VIB-L-14-1 | 11.81 | 15.14 | 17.43 | 2.29 | 11.03 | 11.04 | 8.62 | 8.84 | 7.29 | 17.54 |
| 136N-VIB-L-14-2 | 11.73 | 15.04 | 17.25 | 2.21 | 11.03 | 11.04 |  | 8.89 | 8.57 | 3.57 |
| 136N-VIB-L-14-3 | 11.79 | 15.71 | 18.38 | 2.67 | 13.01 | 12.95 |  | 8.85 | 7.92 | 10.48 |




| Sample | Tube wt (g) | $\begin{gathered} \text { Tube }+ \text { Sed wt } \\ (\mathrm{g}) \\ \hline \end{gathered}$ | Tube wt after Wash <br> (g) | Retained Water wt (g) | Spike Sol'n to Add <br> (g) | Actual Sol'n Added (g) | pH after 24 Hours | Conc of Tracer (calc) | Conc of Tracer (meas) | \% Sorbed |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 136N-IB-L-1-1 | 11.73 | 21.7 | 29.04 | 7.34 | 32.54 | 34.65 | 8.35 | 7.63 | 8.31 | -8.85 |
| 136N-IB-L-1-2 | 11.89 | 21.65 | 27.87 | 6.22 | 32.82 | 32.83 | 8.3 | 7.78 | 7.58 | 2.47 |
| 136N-IB-L-1-3 | 11.78 | 22.28 | 28.74 | 6.46 | 35.54 | 35.55 | 8.16 | 7.83 | 7.87 | -0.60 |
| 136N-B-L-1-1 | 11.75 | 22.57 | 26.58 | 4.01 | 39.27 | 39.26 | 8.67 | 8.39 | 7.53 | 10.28 |
| 136N-B-L-1-2 | 11.81 | 22.7 | 26.88 | 4.18 | 39.38 | 39.37 | 8.67 | 8.36 | 7.69 | 8.00 |
| 136N-B-L-1-3 | 11.86 | 22.56 | 26.67 | 4.11 | 38.69 | 36.63 | 8.8 | 8.32 | 8.07 | 2.93 |
| 136N-SA-L-1-1 | 11.8 | 21.96 | 25.63 | 3.67 | 36.97 | 36.99 | 8.67 | 8.41 | 7.95 | 5.57 |
| 136N-SA-L-1-2 | 11.78 | 22.38 | 25.64 | 3.26 | 39.14 | 39.12 | 8.76 | 8.54 | 8.42 | 1.42 |
| 136N-SA-L-1-3 | 11.81 | 22.44 | 25.65 | 3.21 | 39.31 | 39.27 | 8.75 | 8.55 | 8.33 | 2.62 |
| 136N-VIB-L-1-1 | 11.76 | 15.08 | 17.15 | 2.07 | 11.21 | 11.22 | 8.8 | 7.81 | 8.13 | -4.08 |
| 136N-VIB-L-1-2 | 11.82 | 15.22 | 17.44 | 2.22 | 11.38 | 11.38 | 8.84 | 7.74 | 7.84 | -1.27 |
| 136N-VIB-L-1-3 | 11.77 | 14.98 | 16.99 | 2.01 | 10.83 | 10.82 | 8.76 | 7.80 | 9.27 | -18.81 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3F-IB-H-14-1 | 11.78 | 22 | 27.257 | 5.26 | 35.62 | 35.63 | 8.02 | 8.21 | 8.01 | 2.37 |
| 3F-IB-H-14-2 | 11.74 | 21.75 | 28.248 | 6.50 | 33.54 | 33.53 |  | 7.89 | 7.63 | 3.34 |
| 3F-IB-H-14-3 | 11.79 | 21.72 | 28.894 | 7.17 | 32.55 | 32.55 |  | 7.72 | 7.59 | 1.67 |
| 3F-B-H-14-1 | 11.83 | 21.61 | 24.946 | 3.34 | 35.78 | 35.78 | 8.19 | 8.62 | 8.08 | 6.18 |
| 3F-B-H-14-2 | 11.77 | 22.44 | 24.742 | 2.30 | 40.38 | 40.39 |  | 8.91 | 8.18 | 8.18 |
| 3F-B-H-14-3 | 11.81 | 21.85 | 25.6 | 3.75 | 36.41 | 36.41 |  | 8.54 | 7.94 | 7.04 |
| 3F-SA-H-14-1 | 11.87 | 22.1 | 26.08 | 3.98 | 36.94 | 36.96 | 8.53 | 8.50 | 8.44 | 0.77 |
| 3F-SA-H-14-2 | 11.74 | 22.02 | 26.042 | 4.02 | 37.10 | 37.1 |  | 8.50 | 8.28 | 2.53 |
| 3F-SA-H-14-3 | 11.76 | 21.31 | 24.977 | 3.67 | 34.53 | 34.55 |  | 8.52 | 8.30 | 2.58 |
| 3F-VIB-H-14-1 | 11.75 | 15.19 | 17.456 | 2.27 | 11.49 | 11.48 |  | 7.87 | 8.04 | -2.18 |
| 3F-VIB-H-14-2 | 11.7 | 15.09 | 17.179 | 2.09 | 11.47 | 11.48 |  | 7.97 | 8.15 | -2.22 |
| 3F-VIB-H-14-3 | 11.79 | 14.99 | 17.065 | 2.08 | 10.73 | 10.73 |  | 7.89 | 7.97 | -0.93 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3F-IB-L-14-1 | 11.74 | 21.58 | 26.214 | 4.63 | 34.73 | 34.73 | 8.03 | 448 | 466 | -4.02 |
| 3F-IB-L-14-2 | 11.8 | 22.16 | 31.674 | 9.51 | 31.93 | 31.93 |  | 391 | 389 | 0.46 |
| 3F-IB-L-14-3 | 11.73 | 21.98 | 28.343 | 6.36 | 34.64 | 34.65 |  | 429 | 446 | -4.02 |
| 3F-B-L-14-1 | 11.78 | 22.11 | 26.345 | 4.24 | 37.09 | 35.13 | 8.23 | 453 | 465 | -2.66 |
| 3F-B-L-14-2 | 11.77 | 22.18 | 27.692 | 5.51 | 36.13 | 36.13 |  | 440 | 449 | -1.91 |
| 3F-B-L-14-3 | 11.82 | 22.03 | 26.524 | 4.49 | 36.35 | 36.36 |  | 452 | 461 | -1.99 |



| Sample | Tube wt <br> (g) | Tube + Sed wt <br> (g) | Tube wt after Wash <br> (g) | Retained Water wt <br> (g) | Spike Sol'n to Add <br> (g) | Actual Sol'n Added <br> (g) | $\begin{gathered} \hline \mathrm{pH} \text { after } \\ 24 \text { Hours } \end{gathered}$ | $\begin{gathered} \hline \begin{array}{c} \text { Conc of Tracer } \\ \text { (calc) } \end{array} \\ \hline \end{gathered}$ | $\begin{gathered} \hline \begin{array}{c} \text { Conc of Tracer } \\ \text { (meas) } \end{array} \\ \hline \end{gathered}$ | \% Sorbed |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3F-VIB-L-10-2 | 11.71 | 15.11 | 17.25 | 2.14 | 11.46 | 11.45 |  | 428 | 452 | -5.79 |
| 3F-VIB-L-10-3 | 11.77 | 15.13 | 17.13 | 2.00 | 11.44 | 11.43 |  | 432 | 472 | -9.29 |
| 3F-IB-H-3-1 | 11.73 | 21.81 | 26.103 | 4.29 | 36.03 | 36.03 | 8.17 | 8.84 | 8.60 | 2.79 |
| 3F-IB-H-3-2 | 11.89 | 21.74 | 26.305 | 4.57 | 34.84 | 34.84 |  | 8.75 | 8.91 | -1.83 |
| Sample | Tube wt (g) | $\begin{gathered} \hline \text { Tube }+ \text { Sed wt } \\ (\mathrm{g}) \end{gathered}$ | Tube wt after Wash $(\mathrm{g})$ | Retained Water wt (g) | Spike Sol'n to Add (g) | Actual Sol'n Added $(\mathrm{g})$ | $\begin{gathered} \hline \mathrm{pH} \text { after } \\ 24 \text { Hours } \\ \hline \end{gathered}$ | Conc of Tracer (calc) | $\begin{gathered} \text { Conc of Tracer } \\ \text { (meas) } \end{gathered}$ | \% Sorbed |
| 3F-IB-H-3-3 | 11.79 | 21.9 | 26.209 | 4.31 | 36.13 | 36.14 |  | 8.84 | 8.84 | 0.08 |
| 3F-B-H-3-1 | 11.71 | 22.35 | 26.267 | 3.92 | 38.64 | 38.64 | 8.62 | 8.99 | 8.92 | 0.78 |
| 3F-B-H-3-2 | 11.87 | 22.63 | 26.739 | 4.11 | 38.93 | 38.94 |  | 8.95 | 9.09 | -1.58 |
| 3F-B-H-3-3 | 11.83 | 21.09 | 25.758 | 4.67 | 32.37 | 32.37 |  | 8.65 | 8.72 | -0.76 |
| 3F-SA-H-3-1 | 11.76 | 21.88 | 27.392 | 5.51 | 34.97 | 34.96 | 9 | 8.55 | 8.69 | -1.67 |
| 3F-SA-H-3-2 | 11.73 | 22.39 | 28.979 | 6.59 | 36.05 | 36.08 |  | 8.37 | 8.43 | -0.75 |
| 3F-SA-H-3-3 | 11.77 | 22.17 | 27.366 | 5.20 | 36.40 | 36.4 |  | 8.66 | 8.84 | -2.01 |
| 3F-VIB-H-3-1 | 11.77 | 15.55 | 17.948 | 2.40 | 12.72 | 12.71 | 8.95 | 8.33 | 8.66 | -3.96 |
| 3F-VIB-H-3-2 | 11.77 | 15.62 | 18.199 | 2.58 | 12.82 | 12.82 |  | 8.24 | 8.68 | -5.31 |
| 3F-VIB-H-3-3 | 11.76 | 15.33 | 17.599 | 2.27 | 12.01 | 12 |  | 8.32 | 8.57 | -2.98 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3F-IB-L-3-1 | 11.8 | 21.24 | 25.149 | 3.91 | 33.85 | 35.7 | 8.2 | 457 | 430 | 6.11 |
| 3F-IB-L-3-2 | 11.75 | 21.34 | 25.854 | 4.51 | 33.85 | 33.85 |  | 448 | 433 | 3.35 |
| 3F-IB-L-3-3 | 11.8 | 22.19 | 26.744 | 4.55 | 37.01 | 37.01 |  | 452 | 439 | 2.76 |
| 3F-B-L-3-1 | 11.73 | 21.84 | 25.852 | 4.01 | 36.43 | 36.46 | 8.46 | 457 | 450 | 1.60 |
| 3F-B-L-3-2 | 11.77 | 22.49 | 26.415 | 3.93 | 38.96 | 39 |  | 461 | 458 | 0.60 |
| 3F-B-L-3-3 | 11.78 | 22.45 | 27.461 | 5.01 | 37.67 | 37.66 |  | 448 | 451 | -0.63 |
| 3F-SA-L-3-1 | 11.78 | 22.13 | 27.34 | 5.21 | 36.19 | 36.19 | 8.9 | 444 | 491 | -10.65 |
| 3F-SA-L-3-2 | 11.8 | 22.59 | 27.457 | 4.87 | 38.29 | 38.28 |  | 450 | 469 | -4.14 |
| 3F-SA-L-3-3 | 11.74 | 21.74 | 26.625 | 4.89 | 35.12 | 35.11 |  | 446 | 431 | 3.27 |
| 3F-VIB-L-3-1 | 11.86 | 15.58 | 17.886 | 2.31 | 12.57 | 12.63 | 9 | 429 | 440 | -2.52 |
| 3F-VIB-L-3-2 | 11.74 | 15.26 | 17.65 | 2.39 | 11.69 | 11.68 |  | 421 | 402 | 4.59 |
| 3F-VIB-L-3-3 | 11.86 | 15.23 | 17.491 | 2.26 | 11.22 | 11.23 |  | 423 | 411 | 2.72 |
|  |  |  |  |  |  |  |  |  |  |  |
| 3F-IB-H-1-1 | 11.79 | 22.01 | 27.77 | 5.76 | 35.12 | 35.13 | 8.19 | 8.66 | 8.86 | -2.30 |
| 3F-IB-H-1-2 | 11.77 | 21.51 | 27.06 | 5.55 | 33.41 | 33.95 | 8.24 | 8.66 | 8.84 | -2.01 |
| 3F-IB-H-1-3 | 11.78 | 21.92 | 26.67 | 4.75 | 35.81 | 35.79 | 8.33 | 8.90 | 8.36 | 6.10 |
| 3F-B-H-1-1 | 11.86 | 22.67 | 27.14 | 4.47 | 38.77 | 38.77 | 8.63 | 9.04 | 8.91 | 1.40 |
| 3F-B-H-1-2 | 11.78 | 22.21 | 26.58 | 4.37 | 37.35 | 37.3 | 8.68 | 9.02 | 9.04 | -0.16 |
| 3F-B-H-1-3 | 11.77 | 22.21 | 29.51 | 7.30 | 34.46 | 34.4 | 8.7 | 8.32 | 9.04 | -8.69 |
| 3F-SA-H-1-1 | 11.79 | 22.16 | 26.15 | 3.99 | 37.49 | 37.51 | 8.33 | 9.11 | 9.22 | -1.16 |
| 3F-SA-H-1-2 | 11.88 | 22.12 | 26.35 | 4.23 | 36.73 | 36.77 | 8.49 | 9.04 | 9.14 | -1.06 |
| 3F-SA-H-1-3 | 11.81 | 21.78 | 25.67 | 3.89 | 35.99 | 35.98 | 8.46 | 9.10 | 9.16 | -0.69 |
| 3F-VIB-H-1-1 | 11.82 | 14.94 | 16.797 | 1.86 | 10.62 | 10.63 | 8.43 | 8.58 | 8.87 | -3.37 |
| 3F-VIB-H-1-2 | 11.9 | 15.07 | 17 | 1.93 | 10.75 | 10.9 | 8.38 | 8.56 | 8.79 | -2.64 |
| 3F-VIB-H-1-3 | 11.89 | 15.13 | 17.129 | 2.00 | 10.96 | 10.98 | 8.42 | 8.53 | 8.84 | -3.70 |


| Sample | Tube wt (g) | $\begin{gathered} \hline \text { Tube + Sed wt } \\ (\mathrm{g}) \\ \hline \end{gathered}$ | Tube wt after Wash $(\mathrm{g})$ | $\begin{aligned} & \hline \text { Retained Water wt } \\ & (\mathrm{g}) \end{aligned}$ | Spike Sol'n to Add (g) | Actual Sol'n Added $(\mathrm{g})$ | $\begin{gathered} \hline \mathrm{pH} \text { after } \\ 24 \text { Hours } \\ \hline \end{gathered}$ | $\begin{gathered} \hline \begin{array}{c} \text { Conc of Tracer } \\ \text { (calc) } \end{array} \\ \hline \end{gathered}$ | Conc of Tracer (meas) | \% Sorbed |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3F-IB-L-1-1 | 11.77 | 21.6 | 27.34 | 5.74 | 33.58 | 33.56 | 7.93 | 433 | 440 | -1.46 |
| 3F-IB-L-1-2 | 11.69 | 21.58 | 26.41 | 4.83 | 34.73 | 34.76 | 8.08 | 446 | 460 | -3.20 |
| 3F-IB-L-1-3 | 11.83 | 21.79 | 26.26 | 4.47 | 35.37 | 35.37 | 8.21 | 451 | 459 | -1.83 |
| 3F-B-L-1-1 | 11.72 | 22.92 | 27.28 | 4.36 | 40.44 | 40.45 | 8.46 | 458 | 477 | -4.17 |
| 3F-B-L-1-2 | 11.73 | 22.84 | 27.74 | 4.90 | 39.54 | 39.53 | 8.44 | 452 | 471 | -4.38 |
| 3F-B-L-1-3 | 11.78 | 23.33 | 28.75 | 5.42 | 40.78 | 40.79 | 8.51 | 448 | 472 | -5.46 |
| 3F-SA-L-1-1 | 11.74 | 21.98 | 26.48 | 4.50 | 36.46 | 36.46 | 8.47 | 452 | 475 | -5.19 |
| 3F-SA-L-1-2 | 11.83 | 21.98 | 26.24 | 4.26 | 36.34 | 36.34 | 8.7 | 454 | 471 | -3.78 |
| 3F-SA-L-1-3 | 11.77 | 21.91 | 25.89 | 3.98 | 36.58 | 36.6 | 8.61 | 458 | 459 | -0.30 |
| 3F-VIB-L-1-1 | 11.8 | 14.71 | 16.54 | 1.83 | 9.81 | 9.81 | 8.4 | 428 | 439 | -2.71 |
| 3F-VIB-L-1-2 | 11.77 | 15.07 | 17.24 | 2.17 | 11.03 | 11.04 | 8.38 | 424 | 426 | -0.40 |
| 3F-VIB-L-1-3 | 11.89 | 15.01 | 16.98 | 1.97 | 10.51 | 10.5 | 8.36 | 427 | 453 | -6.04 |


[^0]:    ${ }^{(*)}$ indicates quantity is too small to be measured by a nitrogen adsorption/desorption technique.
    a. BET surface area, micropore area, and surface area of pores are determined by the shape and hysteresis of nitrogen adsorption/desorption isotherms.
    b. External surface area is calculated by subtracting micropore area from BET surface area.

