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Report on the Results of Laboratory Tests of Tracer Compounds at Consolidated Unit 16-021(c)-99

Los Alamos
NATIONAL LABORATORY
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1.0 INTRODUCTION

Consolidated Unit 16-021(c)-99 (the 260 Outfall) at Technical Area 16 (TA-16) at Los Alamos National Laboratory (LANL or the Laboratory) is currently subject to corrective action for high explosives– (HE-) contaminated groundwater under the March 2005 Compliance Order on Consent (the Consent Order) (LANL 2007, 098734). Details concerning the site and its groundwater are provided in a series of regulatory documents (LANL 1998, 059891; LANL 2003, 077965; LANL 2007, 098734; LANL 2011, 203711; LANL 2011, 207069; LANL 2012, 213573, and references therein). Both deep perched-intermediate groundwater (700–1200 ft below ground surface [bgs] and regional groundwater [>1200 ft bgs]) are contaminated with HE, particularly RDX (hexahydro-1,3,5-trinitro-1,3,5 triazine), and other related constituents (LANL 2011, 207069). RDX levels are consistently above the risk-based screening level of 6.11 µg/L in deep perched-intermediate groundwater in multiple groundwater wells (R-25, R-25b, CdV-16-1i, CdV-16-2ir, and CdV-16-4ip) (Figure 1.0-1), with the highest values (>200 µg/L) in recently drilled well CdV-16-4ip (screen 1). Currently, regional groundwater wells show RDX at levels below the screening level.

The hydrogeologic framework for the contaminated deep perched-intermediate zone and regional aquifer is complex (LANL 2011, 207069). In a broad sense, the deep perched-intermediate zone is divided into an upper zone and a lower zone, with the upper zone consistently more contaminated than the lower zone; this is expected conceptually because the contaminant source is located at the ground surface. Hydrologic and geochemical data, including water levels, pump-test results, and drilling observations demonstrate the deep perched-intermediate zone is hydrogeologically complex, with localized hydrogeologic regimes (LANL 2011, 207069).

A tracer test will be conducted to support a future assessment of potential remedial alternatives for contaminated groundwater associated with the 260 Outfall (LANL 2012, 213573). A remedial alternatives analysis would likely benefit from an improved understanding of (1) local hydrogeologic gradients and groundwater velocities/fluxes within the deep perched-intermediate zone; (2) lateral contaminant travel times and associated hydrologic parameters within hydrogeologic subunits of the Otowi Formation and Puye Formation; and (3) vertical contaminant travel times, particularly between the upper-perched zone and lower-perched zone and between the lower-perched zone and the regional aquifer. Pathways, groundwater velocities/fluxes, and travel times from near-surface alluvial aquifers to the deep-perched zone are also poorly constrained. All these questions may potentially be addressed through a multiple constituent tracer test.

The tracer work plan (LANL 2012, 210352) proposed passive deployment of multiple nonreactive tracers in wells CdV-16-1(i) and R-25b (Figure 1.0-1), the two deep-perched zone wells located farthest upgradient within the contaminated deep-perched zone and in Peter Seep. The principal tracer types proposed are fluorinated benzoates (FBAs) (Reimus et al. 2003, 209697; Reimus et al. 2003, 210315; Duke et al. 2007, 210313) and naphthalene sulfonates (NSs) (Nimmo et al. 2002, 210314; Wright and Hull 2004, 209698). These tracers are nontoxic, should not interfere with sampling of regulated constituents in the aquifer, are inexpensive, and have been successfully used in other tracer tests in which Laboratory personnel have participated (Reimus et al. 2003, 209697; Reimus et al. 2003, 210315; Duke et al. 2007, 210313). NSs alone were not proposed because they are somewhat experimental and may not be conservative within TA-16 media (Wright and Hull 2004, 209698); however, they offer superior detection limits and thus increase the probability of tracer detection if very low breakthrough concentrations are observed.

This reports presents the results of simple laboratory column tests proposed in the tracer work plan (LANL 2012, 210352) to ensure no analytical interferences between deployed tracer compounds and site constituents, such as the RDX, and to ensure conservative tracer behavior in TA-16 media.

2.0 METHODS

Two sets of column transport experiments were conducted to evaluate the transport of 10 different potential conservative tracers for the TA-16 tracer tests. The tracers evaluated in the experiments are listed in Table 2.0-1. Column experiments were performed instead of batch experiments because the tracers were expected to adsorb little, if at all, to the geologic materials at TA-16, and small amounts of sorption/retardation are easier to quantify (and to distinguish from a lack of sorption) in column experiments than in batch experiments. The experiments were conducted in two separate columns packed with crushed geologic material from TA-16: the first column was packed with material from the Otowi member of the Bandelier Tuff, and the second was packed with material from the Puye Formation. RDX-contaminated water collected from the Otowi Member and the Puye Formation at TA-16 was used in the respective columns.

2.1 Column Methodologies

The Otowi and Puye solids used in the column experiments were derived from R-25 core obtained from the Environmental Programs (EP) Sample Management Facility. The Otowi material was taken from 769.5–770.0 ft below land surface (bls), and the Puye material was taken from two intervals: 846–850.1 ft bls and 1157–1159.2 ft bls. Portions of the core from each interval were crushed and sieved into the 75–500-μm size range. The sieved material from the two Puye intervals was combined in equal weight proportions for column packing. The mineralogy of the materials was not analyzed because it is known from previous work (e.g., Broxton et al. 2002, 072640). The crushing procedure is thought to increase the surface reactivity of rocks by creating new surfaces that have not been weathered by exposure to groundwater. Thus, the use of the crushed materials should have increased the likelihood of tracer interactions with the Otowi and Puye surfaces relative to the surfaces present in the natural flow system, making the column experiments a conservative assessment of tracer reactivity. However, this conservatism may have been somewhat offset by the small sample size of the cores, which likely limited the mineralogical heterogeneity in the column experiments to less than that in the natural system. Also, elimination of the less-than-75-μm size fraction, which is generally considered good practice to avoid column plugging, may have resulted in a slight underrepresentation of any clays in the cores. Clays would be expected to have greater reactivity than most other minerals.

The crushed and sieved Otowi and Puye materials were dry-packed into two glass columns (Kontes Chromflex), 1.5 cm in diameter and 30 cm long (approximately 53-mL total volume). One column was packed with approximately 62 g of the Otowi material and the other with approximately 85 g of the combined Puye material. The columns were then saturated with groundwater collected in July 2012 as part of watershed sampling from CdV-16-1i (Otowi) and CdV-16-2ir (Puye). After the columns were leak tested by pressurizing them with CO_2 gas, the column saturation procedure proceeded as follows: (1) the columns were evacuated using a vacuum pump filled with CO_2 gas and then evacuated again to remove all air and most of the residual CO_2; (2) vacuum-degassed water from either CdV-16-1i or CdV-16-2ir was introduced to the bottom of the evacuated columns and was drawn to the top by a combination of the vacuum and a positive head applied to the water; (3) a positive flow rate of degassed water was then established through the columns to dissolve any residual CO_2 gas bubbles remaining in the columns (although none was observed in either column). The water used to saturate the columns was from the second purge volume from each well, but the water used to establish the positive flow rate in step 3 was from the third purge volume. All subsequent water introduced to the columns was from the third purge volume from the two respective wells (including water containing the tracers). Several pore volumes of this water were eluted through the columns before the tracers were introduced, so the rock surfaces had an opportunity to at least partially equilibrate with the water before it came in contact with tracers.

A photo of a column transport experiment apparatus is shown in Figure 2.1-1. Syringe pumps (Kd Scientific) were used to maintain steady flow through the columns, and fraction collectors (Isco Foxy Jr.) were used to automatically collect water eluting from the columns. All column experiments were conducted at a flow rate of approximately 0.45 mL/h. Tracers were introduced to each column in two separate injections of approximately 35 mL each. The first tracer injection contained sodium iodide and the four FBAs (Table 2.0-1) dissolved in the groundwater(s) at concentrations of approximately 10 mg/L each. The second injection contained the five NSs (Table 2.0-1) dissolved at concentrations of approximately 1 mg/L each. Both injections were accomplished by rapidly switching the syringe on the feed pump from one that contained tracer-free groundwater to another that contained tracer-bearing groundwater. After approximately 35 mL of tracer-bearing groundwater had been injected, the tracer solution was switched to tracer-free groundwater by the same process. Tracer-free groundwater was then injected into the columns until all tracers dropped below detection limits in the column effluents.

The simple anion iodide is known to be a nonsorbing tracer to which the column transport of other tracers can be compared to determine their sorption/retardation characteristics. In a column experiment, tracer sorption is indicated by delayed first and mean arrival times of a tracer relative to a nonsorbing tracer such as iodide. Column experiments are generally better than batch experiments at identifying and quantifying small amounts of sorption because it is easier to observe minor differences between tracer arrival times in columns than it is to observe small differences in tracer concentrations before and after contact with solids in batch reactors. Iodide was not included in the second set of tracer injections into each column, so the arrival times of the NSs had to be compared with the arrival times of the iodide in the preceding tracer injections in each column to evaluate whether the NSs sorbed to the Otowi or Puye material. This process is somewhat more uncertain than comparing the arrival times of coinjected tracers, but it was considered acceptable in this study because the same columns were used for each tracer injection, and the flow rates through the columns were stable over time. Also, the separation of the two ets of tracers allowed for different analytical methods to be used exclusively in each set of experiments.

2.2 Analytical Methods

All tracers were analyzed by high-performance liquid chromatography (HPLC) using a Dionex Summit X2 system running Chromeleon Version 6.70 SP9 software. The iodide and FBAs were separated chromatographically by eluting them through a C18 reverse-phase Dionex Acclaim 120 C18 3 µm 120A 4.6×150-mm column using an eluent consisting of 40% HPLC-grade methanol and 60% 3 mM K_2HPO_4 in deionized water that was buffered to pH ~2.5 using H_3PO_4. The method was adapted from Duke et al. (2007, 210313). The low pH solution caused partial protonation of the FBAs, allowing them to be retained on the reverse-phase column. The iodide was not retained, so it readily separated from the benzoates. The tracers were detected using a Dionex VWD-3400RS variable wavelength detector set to measure ultraviolet absorbance at a wavelength of 222 nm. Typical chromatograms are shown in Figure 2.2-1. Quantification and detection limits were not rigorously evaluated or optimized, but previous work has suggested that they should be on the order of 20–30 µg/L for quantitation limits and 5–10 µg/L for detection limits.

The NSs were separated chromatographically by eluting them through a C18 reverse-phase Waters XBridge C18 3.5µm 4.6×50 column. The eluent in this case was 70% 5 mM tetrabutyl ammonium phosphate (TBAP) in deionized water with a small amount of K_2HPO_4 added to buffer to a near-neutral pH and 30% 5 mM TBAP in HPLC-grade methanol. The TBAP serves as an ion-pairing agent that renders the negatively charged NSs neutral so they are retained in a reverse-phase column. The method was adapted from Rose et al. (2001, 232203). The NSs were detected using a Dionex RF2000 fluorescence detector set to excite at 222 nm and to measure fluorescence emission at 338 nm. Typical chromatograms are shown in Figure 2.2-2. As with the FBAs, quantitation and detection limits were not rigorously evaluated or optimized, but they should both be below about 0.1 µg/L.

The waters from wells CdV-16-1i and CdV-16-2ir used in the Otowi and Puye column experiments contained RDX at representative concentrations for a field tracer test. The ability to analyze the tracers in these waters indirectly confirmed RDX does not pose an analytical interference problem for the tracers. The study did not directly evaluate whether any of the tracers interfere with the RDX HPLC analytical method. However, the RDX method involves reverse-phase liquid chromatography using a different column (Dionex Acclaim Explosive E2 5µm 120A 4.6×250 mm) than the FBAs and NSs, and it also uses a methanol/water eluent that is not pH-adjusted, so it is expected that the FBAs would not be retained at all in the RDX method. Furthermore, it has been our experience that NSs are not retained in reverse-phase columns unless the pH is very low or the TBAP ion-pairing agent is used. In previous work, some retention of the singly sulfonated NSs (1-NS and 2-NS) was observed when running the FBA method, presumably because partial protonation of these anions occurs at a pH of ~2.5 and/or because the singly sulfonated anions are hydrophobic enough that they interact with the C18 column. However, the doubly sulfonated NSs were not retained by the FBA method, so they are not expected to be retained by the RDX method.

3.0 RESULTS

The normalized breakthrough curves of all tracers (normalized concentration = concentration divided by injection pulse concentration, or Co) through the Otowi and Puye columns are shown in Figures 3.0-1 and 3.0-2, respectively. Note that many more samples were analyzed for the iodide and FBA experiments than for the NS experiments. In Figure 3.0-1, it is apparent that all of the tracers transport nearly identically through the Otowi column. Minor differences between the FBAs and the NSs can be attributed to slight differences in the length of the tracer-injection pulse or to small flow-rate variations. Normally, the breakthrough curves from different experiments would be plotted as a function of volume eluted from the column rather than time to compensate for any flow-rate variations, but Figure 3.0-3 shows that when such a plot is generated, the NSs appear to break through the column significantly sooner than the iodide or the FBAs. This result is considered erroneous and misleading because it is highly unlikely that any solute tracer would transport significantly faster than iodide through a porous media column. The result of Figure 3.0-3 most likely reflects sample evaporation during the NS experiment, which occurred when the heating system in the laboratory building malfunctioned, and the temperature in the room rose to the upper 80°F during the experiment.

Figure 3.0-4 shows the weights of samples collected as a function of sample number during both the FBA and NS experiments in the Otowi column. In the FBA experiment, the samples were weighed and capped frequently, and the temperature in the laboratory was near 70°F. In the NS experiment, the samples were weighed and capped only after the switchover from tracer injection solution to tracer-free water and then again at the end of the experiment. It is apparent that despite draping plastic wrap over the fraction collector to minimize evaporation, a clear linear upward trend is evident in the NS sample weights before each weighing/capping event that is consistent with a steady evaporation rate, causing more weight loss from older samples than younger ones. The difference in cumulative weights between the two experiments before the first arrival of tracers almost exactly matches the difference in eluted volumes before the first arrival of tracers in Figure 3.0-3. The same trends were observed for the Puye column experiments, but they are not presented here.

The NSs in the Puye column (Figure 3.0-2) appear to approach their injection concentrations more slowly than the iodide or FBAs (with the exception of sodium 1,5-naphthalene disulfonate), which more closely follows the FBAs). Although this result might suggest some sorption of the NSs to the Puye material, this possible conclusion should be questioned for several reasons. First, the initial arrivals of the NSs all occur at about the same time as the nonsorbing iodide and the FBAs, which is not generally observed for a sorbing tracer. Second, the elution of the NSs from the column after switching to tracer-free water is nearly identical to that of the iodide and the FBAs, which is also inconsistent with a tracer that is sorbing to the column material. Third, the curve showing the fluorometer measurements of the NSs in Figure 3.0-1 (red squares) does not show any evidence of the slow rise in concentrations of the NSs. This curve represents the combined fluorescence of all five NSs lumped together and cannot distinguish between the different compounds, but if four of the five NSs were truly exhibiting a slow rise in concentration, the composite fluorescence of the NSs almost certainly reflect this slow rise. The fact that the normalized NS concentrations from the bulk fluorescence measurements appear to rise to significantly higher than C/Co = 1, which is technically impossible, cannot be explained. However, it could result if the column serves to filter out small particulates in the injection solution that scatter or reflect light, which might cause a depression of the fluorescence in the injection samples. It is also possible that the NSs adsorbed slightly over time to the plastic bottles used to store the injection solution, and the evaporative losses in the column samples may also have contributed to the elevated NS concentrations in these samples (although the HPLC analyses suggest otherwise). Regardless of the explanation, the fact that C/Co for the combined NSs rises with the iodide and FBAs and ultimately exceeds 1 strongly suggests that none of the NSs sorbed in the Puye column.

The slow rise in individual NS concentrations in the Puye column from the HPLC measurements could be a result of chromatograms with shifting baselines that caused low biases in the integrations of the NS peaks over several consecutive samples. Note that the Puye chromatogram of Figure 2.2-2 has a significantly higher and noisier baseline than the corresponding Otowi chromatogram, which tends to result in more uncertain peak integrations and hence more uncertain concentration measurements for the Puye. Several of the Puye samples were reanalyzed by the HPLC method (some samples not initially analyzed were analyzed for the first time), but despite generally cleaner chromatograms with less noisy baselines, this second set of analyses yielded breakthrough curves that were qualitatively similar to the first set (Figure 3.0-5). Unfortunately, the HPLC pump was slowly failing during the second set of analyses, resulting in shifting tracer peak retention times in the chromatograms, which introduced another source of analytical uncertainty into the measurements. The apparent slow increase in NS concentrations in the Puye column based on the two sets of HPLC measurements is inexplicable, and furthermore, the concentrations are inconsistent with bulk fluorescence measurements that reflect a more rapid increase in NS concentrations. Based on the line of evidence presented above, the NSs most likely transported conservatively through the Puye column, but for inexplicable reasons, a range of samples ran poorly on the HPLC twice, with concentrations that appeared to go up and down with time in a way that is not consistent with any known tracer transport behavior, adsorbing or nonsorbing. A repeat experiment in the Puye column or in a newly packed Puye column would be the preferred way to address this issue further. Reanalysis of samples from the Puye column is also a possibility but cannot be conducted until a new HPLC pump is installed, and the results to date suggest that some of the Puye samples may have been somehow compromised for HPLC analyses.

4.0 CONCLUSIONS AND RECOMMENDATIONS

Despite the inconsistent NS results in the Puye column, it is concluded that none of the FBAs or NSs evaluated in the column transport experiments adsorbed to any measurable degree to either the Puye or Otowi materials used to pack the columns. On this basis, any of the tracers of Table 2.0-1 should be suitable for use as conservative/nonsorbing tracers in the TA-16 field tracer test.

The current TA-16 tracer test work plan (LANL 2012, 210352) calls for the paired injection of NaI and a FBA into R-25b (25 kg each), the injection of another FBA and a NS into CdV-16-1(i) (40 kg and 10 kg , respectively), and the injection of a second NS (100 kg) into Peter Seep/Cañon de Valle alluvial well 2656. The results of this laboratory experimental study support these general recommendations, and they also suggest more specific recommendations as to which tracers would be best to deploy at different injection points.

For the injection into R-25b, it is recommended that either pentafluorobenzoate (PFBA) or 2,5-difluorobenzoate (2,5-DFBA) (specifically, the sodium salts of these two benzoates) be injected along with NaI. These FBAs have the second and third fastest HPLC elution times (after 2,6-difluorobenzoate [2,6-DFBA]), which helps facilitate analyses and sharpens chromatogram peaks. The 2,5-DFBA offers slightly better molar absorbance, increasing its detection limit per unit mass injected slightly over the PFBA. Difluorobenzoate(2,4-) (2,4-DFBA) has a similar molar absorbance to 2,5-DFBA, but its later elution time would tend to make it slightly less detectable per unit mass than the latter FBA. An NS could also be considered for injection into this well, but given the proximity to R-25b of both R-25 and CdV-16-4ip, a low-detection-limit fluorescent NS tracer is probably less important to inject in R-25b than the other injection locations.

For tracer injection into CdV-16-1i, it is recommended that 2,6-DFBA and either 1,5-naphthalene disulfonate (1,5-NDS) or 2,6-naphthalene disulfonate (2,6-NDS) be coinjected. The 2,6-DFBA has the fastest elution time of any of the FBAs, it has a high molar absorbance, and it is comparable in cost with 2,5-DFBA. Both 1,5-NDS and 2,6-NDS can be treated as interchangeable, with availability and cost being the primary considerations in the selection of these tracers. The chromatographic interferences in the Puye/CdV-16-2ir water for these two tracers appeared to be about the same in the laboratory samples. Their rapid retention times relative to the other NSs facilitate analyses. Their superior detection limits to the FBAs (1.5 to 2 orders of magnitude better per unit mass injected, barring significant analytical interferences) make them ideal for early- or low-concentration detection. However, inclusion of 2,6-DFBA as part of the tracer injection mix is recommended because of the more widely accepted nonsorbing transport behavior of the FBAs and the inherent decrease in risk associated with using a second class of nonsorbing tracer. The long-term stability of both the FBAs and the NSs toward biological or other breakdown is not well understood and is not easily evaluated in the laboratory.

For tracer injection into Peter Seep/Cañon de Valle alluvial well 2656, it is recommended that a large mass of 2,7-naphthalene disulfonate (2,7-NDS) (~100 kg) be deployed. Although it might seem preferable to inject either 1,5-NDS or 2,6-NDS, whichever tracer is NOT deployed in CdV-16-1i, the HPLC elution times of these two tracers are close enough that deploying both is not recommended. Detecting one in the presence of a large excess of the other could be problematic. Thus, 2,7-NDS is the preferable NS tracer to deploy in Peter Seep/Cañon de Valle alluvial well 16-02656. Although an FBA tracer could be considered for coinjection at this shallow and upgradient location, the lower detection limits of the FBAs, coupled with their higher unit mass costs relative to the NSs, would make deploying FBA quite costly, with little or no potential added benefit over deployment of an NS.

Deploying either 1-NS or 2-NS at any location is not recommended because these tracers probably have the greatest potential to interfere with RDX measurements, although this is still considered an unlikely possibility. These tracers are also considered to have the greatest potential to sorb to geologic or well-completion materials of any of the tracers evaluated. The fact that they did not appear to sorb to either the Otowi or Puye materials in the column experiments is encouraging and adds confidence to the conclusion that all of the recommended tracers should transport conservatively in the field.

5.0 REFERENCES

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Copies of the master reference set are maintained at the New Mexico Environment Department Hazardous Waste Bureau and the Directorate. The set was developed to ensure that the administrative authority has all material needed to review this document, and it is updated with every document submitted to the administrative authority. Documents previously submitted to the administrative authority are not included.

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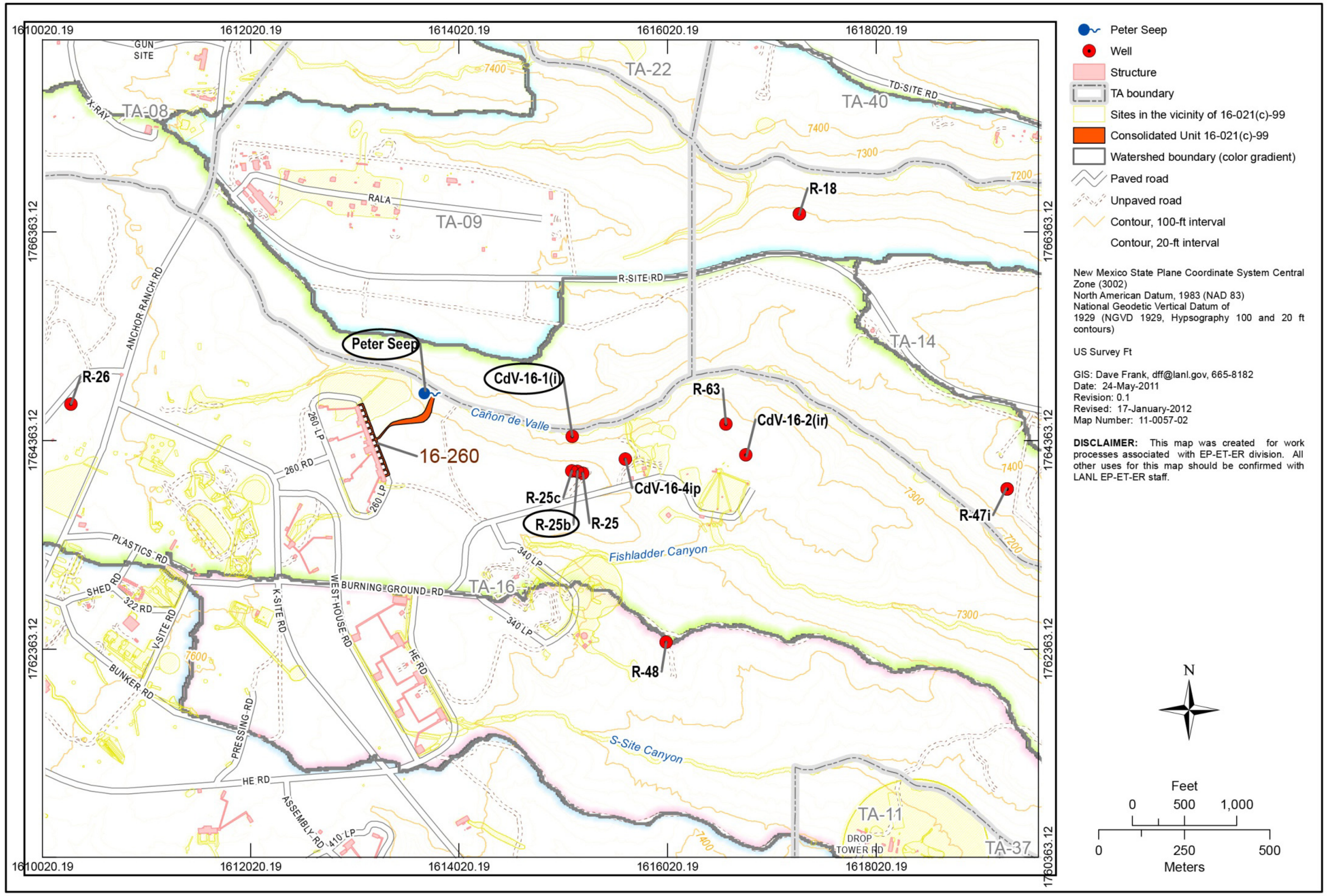


Figure 1.0-1 Wells located at TA-16. Locations where tracers will be deployed are circled.

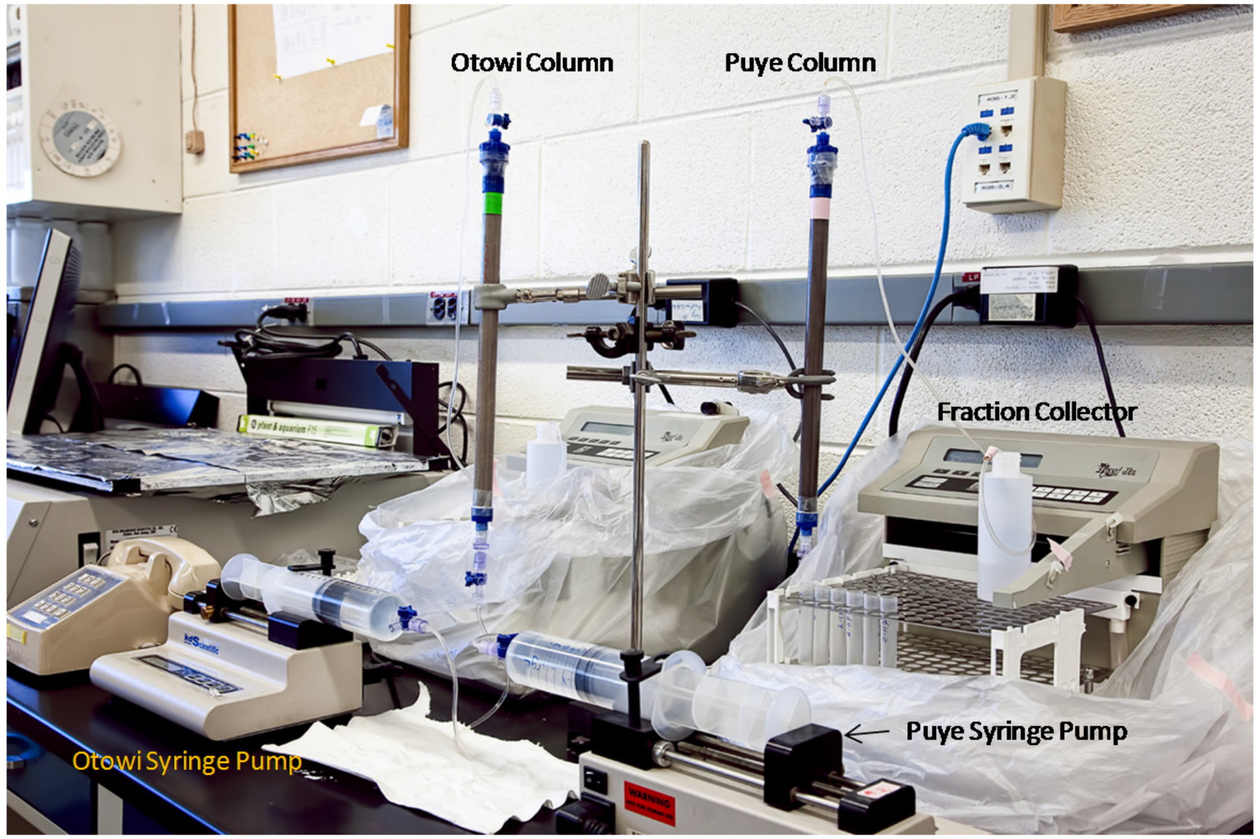


Figure 2.1-1 Photograph showing column experimental apparatus

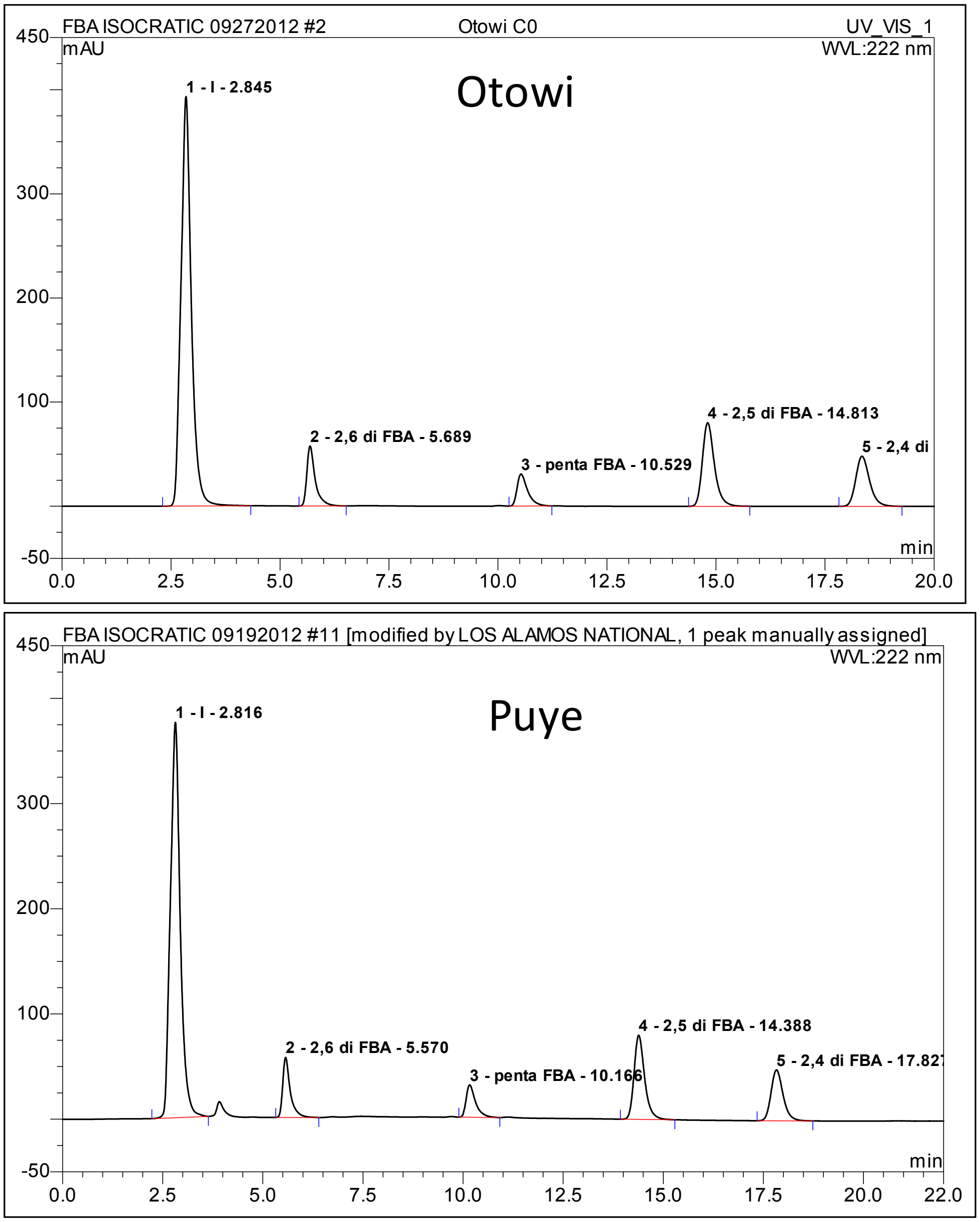


Figure 2.2-1 Typical HPLC chromatograms for iodide and fluorinated benzoates

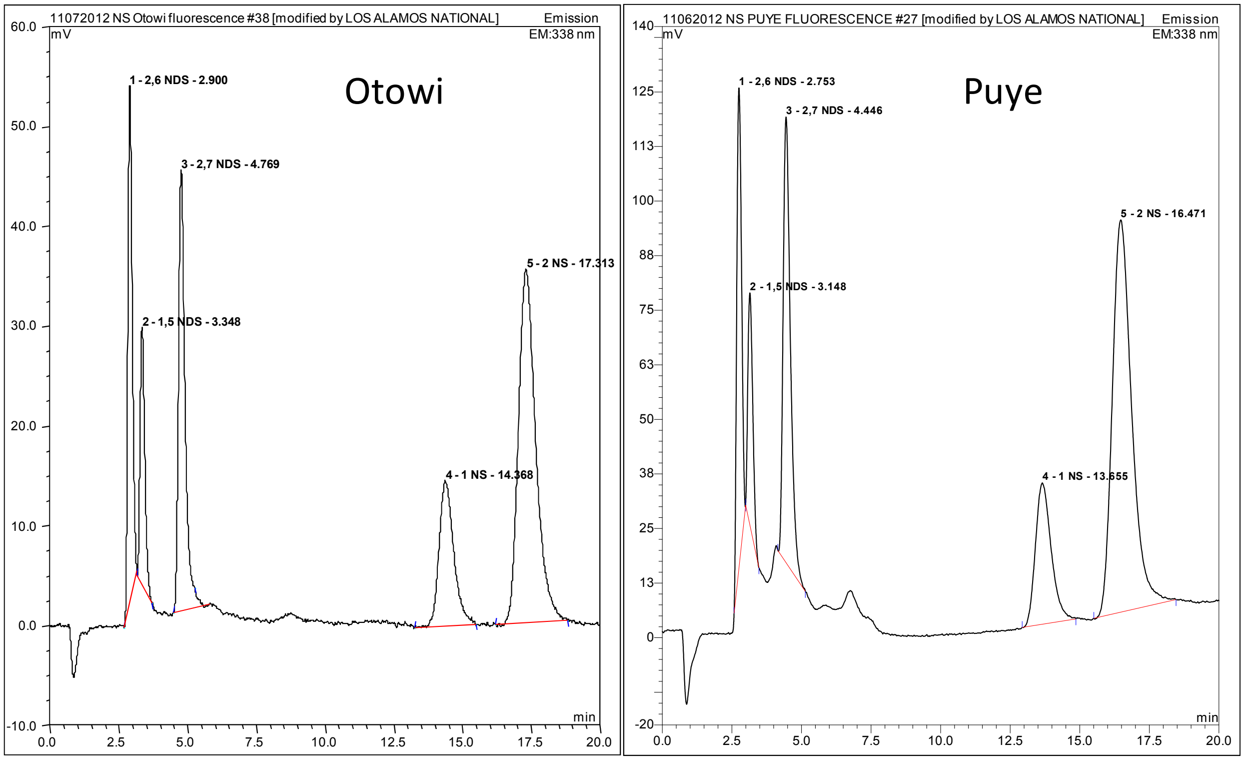


Figure 2.2-2 Typical HPLC chromatograms for NSs

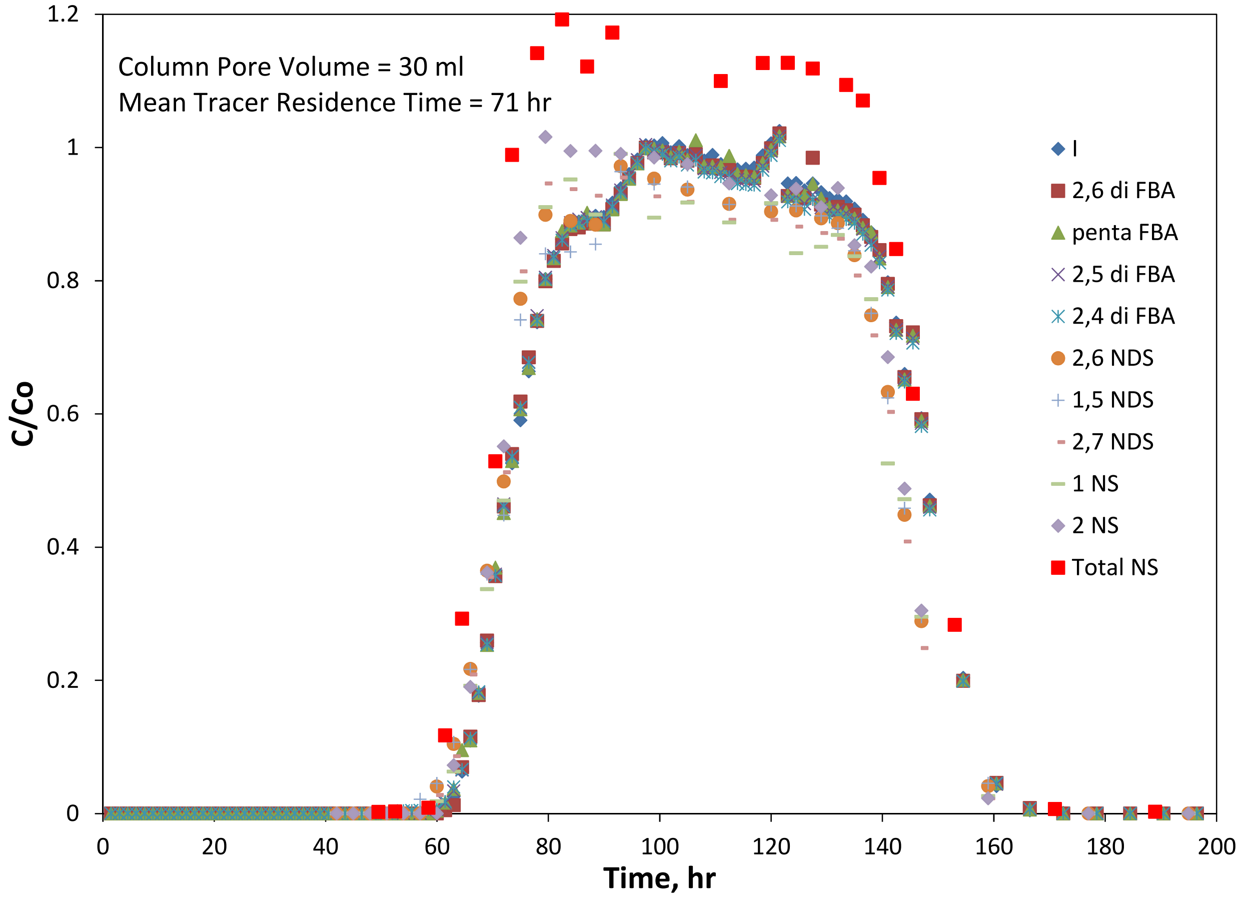


Figure 3.0-1 Tracer breakthrough curves in Otowi column

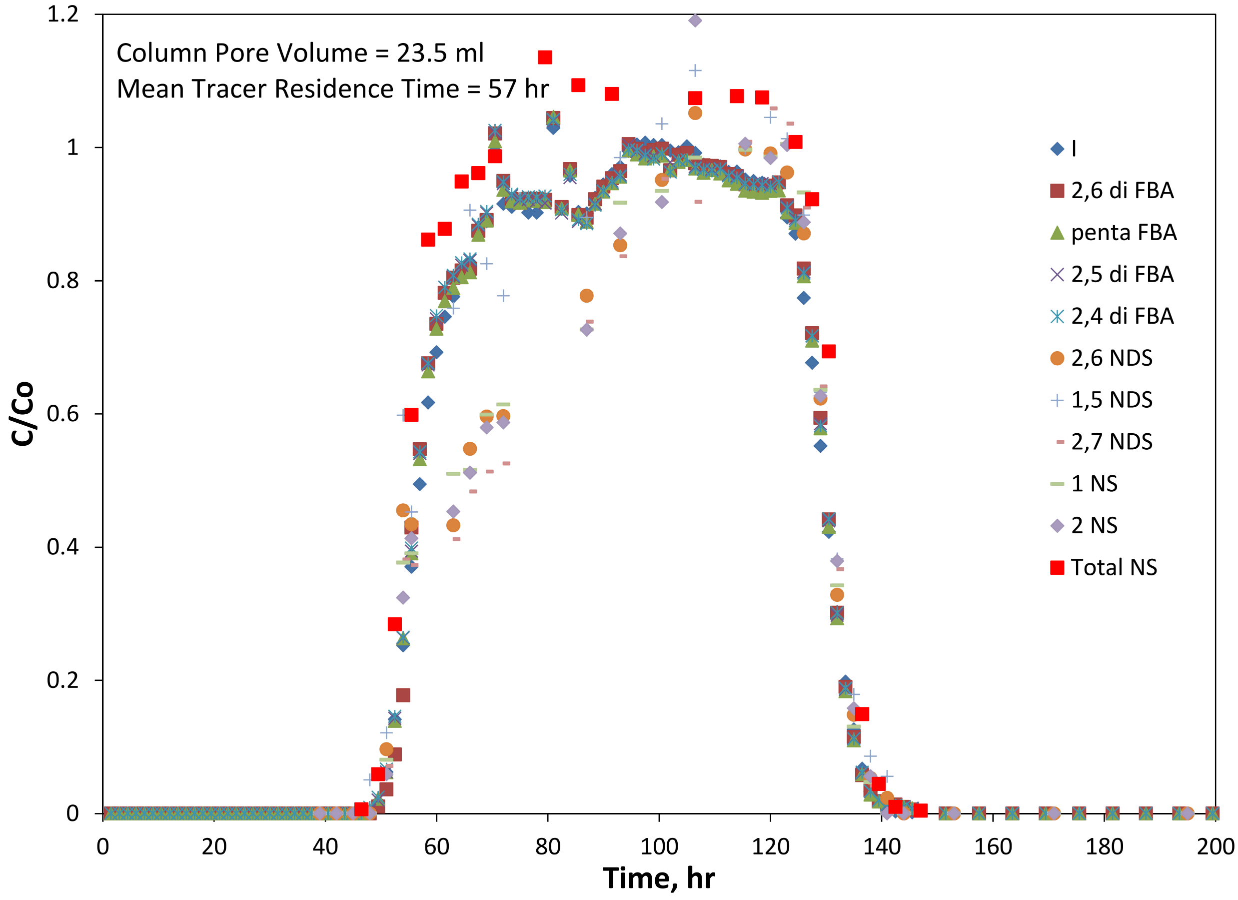


Figure 3.0-2 Tracer breakthrough curves in Puye column

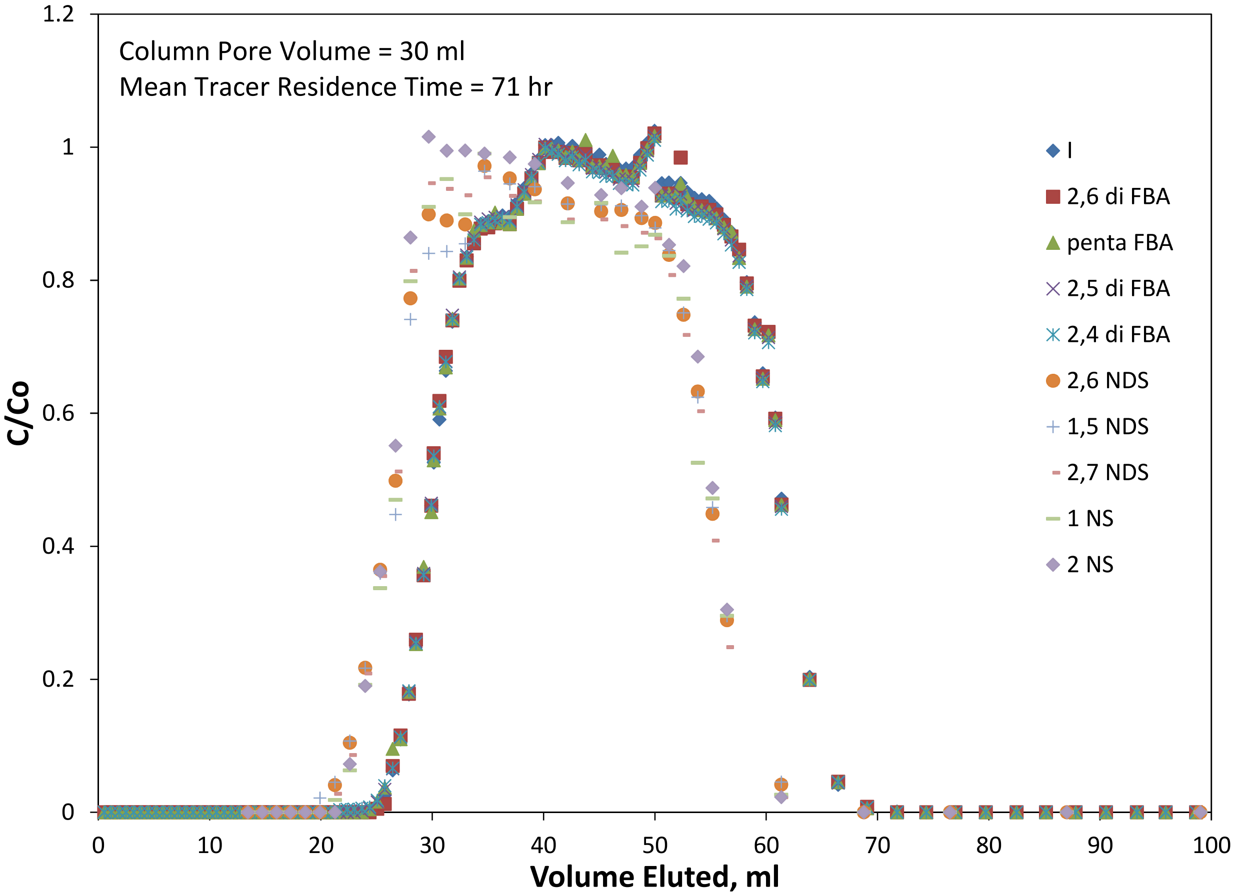
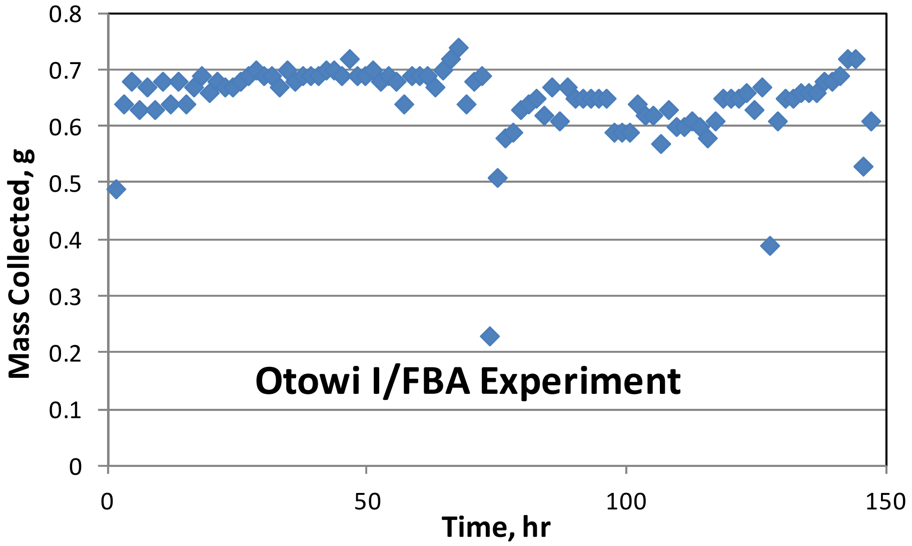


Figure 3.0-3 **Tracer breakthrough curves as a function of volume eluted through the Otowi column (total NS breakthrough curve not shown)**



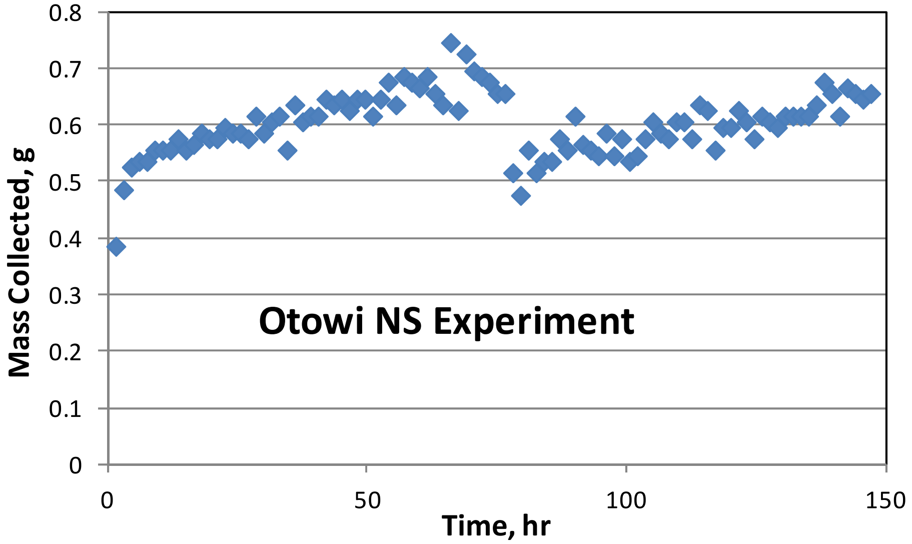


Figure 3.0-4 **Sample masses collected as a function of time in the Iodide/FBA experiment (top) and the NS experiment (bottom) in the Otowi column**

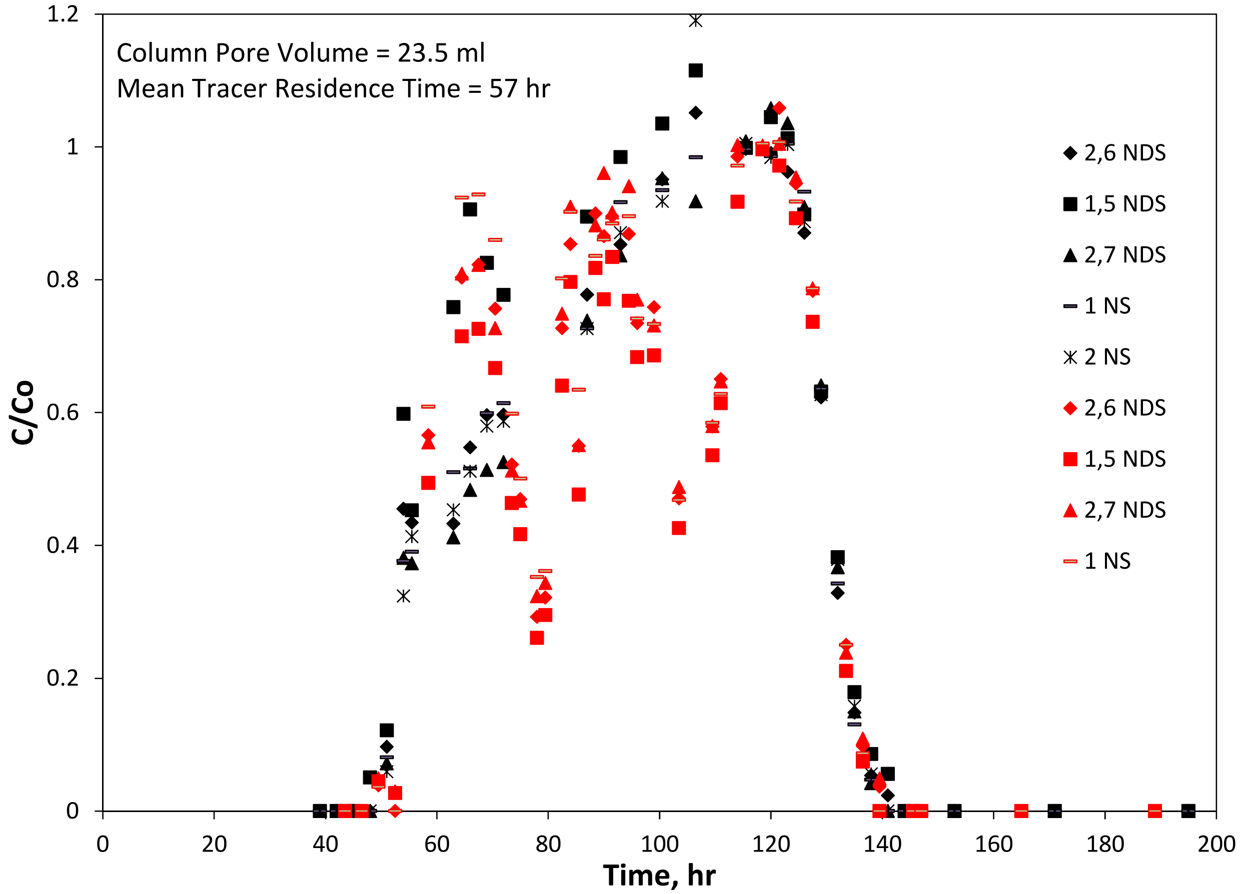


Figure 3.0-5 **NS breakthrough curves in Puye column from two sets of HPLC analyses. The first set (from Figure 3.0-2) is shown as black symbols, and second set is shown as red symbols. 2-NS results are not shown for the second data set because the failing HPLC pump caused the 2-NS to elute too late from the HPLC column to be captured on the chromatograms.**

Table 2.0-1
Tracer Compounds Tested in Column Experiments

First Tracer Injection (Iodide and FBAs at ~10 mg/L)	Second Tracer Injection (NSs at ~1 mg/L)
Sodium Iodide	Sodium 2,6-Naphthalene disulfonate
Sodium 2,6-Difluorobenzoate	Sodium 1,5-Naphthalene disulfonate
Sodium Pentafluorobenzoate	Sodium 2,7-Naphthalene disulfonate
Sodium 2,5-Difluorobenzoate	Sodium 1-Naphthalene sulfonate
Sodium 2,4-Difluorobenzoate	Sodium 2-Naphthalene sulfonate

Note: Coinjected tracers are listed in the same column and in the order of HPLC analytical method elution time.