DOE/NV/10872-T13

IDENTIFICATION AND CHARACTERIZATION OF CONSERVATIVE ORGANIC TRACERS FOR USE AS HYDROLOGIC TRACERS FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION STUDY

DOE/NV/10872--T13

DE92 014671

PROGRESS REPORT

JULY 1, 1991, TO DECEMBER 31, 1991

DOE Cooperative Agreement

No. DE-FC 08-90NV10872

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JULY 1991 TO DECEMBER 1991

The main focus of the work performed during the time period from 07/01/91 to 12/31/91 has been the continuation of (1) LC-MS optimization for tracer identification, (2) batch sorption and degradation studies, (3) neoprene tubing evaluation studies, and (4) soil column evaluation of tracer compounds. All of these areas of research (except perhaps the neoprene tubing evaluation) are ongoing and will continue throughout the coming year.

LC-MS SYSTEM OPTIMIZATION

Several changes have been made in the LC-MS system to improve sensitivity and signal reproducibility. These changes include the replacement of the fused silica capillary tubing in the nebulizer with stainless steel hypodermic tubing, which has improved signal stability drastically. The heater cartridge for the source was replaced with one of higher wattage which improved temperature stability and therefore improved signal reproducibility. The CI ion volume was also replaced with one which has a smaller slit width, which will improve sensitivity. Current work entails the evaluation of several compounds for use as tuning agents in the 150 to 300 mass range. Improvements in the tuning procedures will yield a more accurately resolved mass assignment over the entire mass range, which will lead in turn to a more specific identification of tracers and unknown degradation byproducts.

BATCH SORPTION AND DEGRADATION STUDIES

Potential tracer compounds were studied using dark, medium, and light tuff samples, and both de-ionized water and water from the J-13 well site. Compound concentration versus initial concentration values were monitored on an approximately 0 day (initial values), 1-day, 3-day, 7-day, 15-day, 30-day, and 60-day schedule.

To date, the following compounds have been evaluated for 60 days or longer in batch sorption and degradation studies:

CINNAMIC ACIDS
alpha-Fluorocinnamic acid
4-Fluorocinnamic acid
trans-2,5-Difluorocinnamic acid
2-Fluorocinnamic acid
3,5-Difluorocinnamic acid

SALICYLIC ACIDS
5-Fluorosalicylic acid
3,5-Dichlorosalicylic acid

BENZOIC ACIDS
2,3,4-Trifluorobenzoic acid
Pentafluorobenzoic acid
2,3,4,5-Tetrafluorobenzoic acid
ortho-Trifluoromethylbenzoic acid

Tracer compounds showing positive results in the batch studies are as follows:

60 Day Evaluation:

o-Trifluoromethylbenzoic acid: <7.0% decrease
2,3,4,5-Tetrafluorobenzoic acid: <7.0% decrease
Pentafluorobenzoic acid: <7.0% decrease

2,3,4-Trifluorobenzoic acid: <15.0% decrease
3,5-Dichlorosalicylic acid: <15.0% decrease

5-Fluorosalicylic acid: consistent 50% decrease

30 Day Evaluation:

o-Trifluoromethylbenzoic acid: <7.0% decrease
2,3,4,5-Tetrafluorobenzoic acid: <7.0% decrease
Pentafluorobenzoic acid: <7.0% decrease

2,3,4-Trifluorobenzoic acid: <10.0% decrease
3,5-Dichlorosalicylic acid: <13.0% decrease

5-Fluorosalicylic acid: consistent 50% decrease

Batch sorption studies are nearing the 60-day mark for several of the remaining benzoic acids, including meta-trifluoromethylbenzoic acid, para-trifluoromethylbenzoic acid, and 3,4,5-trifluorobenzoic acid. Preliminary data from these studies show good stability to this point, but the analysis has not yet been fully evaluated at this time. The pentafluorobenzoic acid analysis showed some chromatographic interferences from an unknown compound found primarily in the light tuff samples. Initial (0 day) and final (60 day) concentrations were in close agreement, but several intermediate samples were useless due to this interference. This compound will be re-analyzed using modified solvent conditions (to correct for the interference) in the near future.

NEOPRENE EVALUATION STUDIES

The delivery of tracer compounds into a ground-water environment represents a critical step in the planned C-well tracer tests. The tubing used to transfer the tracer solutions into the ground water is therefore an essential part of the entire study, and it was considered important that the tubing be tested in a laboratory setting before actual tracer tests were started. Several meters of steel reinforced neoprene tubing were obtained from the USGS, and the following studies were performed in an effort to evaluate the tubing thoroughly. All analyses (unless otherwise specified) were carried out using a Spectra-

Physics HPLC system equipped with a C-18 Reverse-Phase column, a ternary solvent delivery system, variable wavelength UV-Vis detector, and an autosampler.

NEOPRENE SORPTION STUDIES

Several different studies were performed to determine possible neoprene/tracer interactions. In the initial study, a length of tubing was filled with de-ionized water and allowed to sit for one hour. Analysis of the de-ionized water showed a large contaminant peak, with possible molecular weight of 199. Compounds listed as tentative identification of the unknown contaminant were 4-bromo-benzide and 2-bromo-benzide. The amount of contaminant leaching into the de-ionized water was directly proportional to the amount of time spent in the neoprene tubing. This contaminant did not extract significantly into organic solvents. It did extract to a very slight degree into an acidic solution, and to a greater degree into a basic solution, but none of these extractions showed greater than 33% efficiency.

Further analysis was carried out to determine the stability of potential tracers in the neoprene tubing. A mixture of four tracers (2,6-difluorobenzoic; 2,4,5-trifluorobenzoic; 2,3,4,5-tetrafluorobenzoic; and pentafluorobenzoic) was chosen as fairly representative of the potential tracer compounds and was used as a standard mixture for the following analyses. Pentafluorobenzoic acid was evaluated separately at 100 ppm and 1000 ppm concentrations, to determine if the other components in the mixture would effect the behavior of a single compound.

To address the fact that the ground-water temperature could influence the leaching and sorbing characteristics of the tubing, controls were established as follows: standard solutions at 100 and 1000 ppm were kept at both 24°C and 37°C in glass containers to monitor the effect of elevated temperatures on the tracer compounds. A standard solution at both 100 and 1000 ppm was mixed with light tuff (1:1 w/w water:soil ratio), and these samples were kept at both 24°C and 37°C to monitor the behavior of the tracers for sorption or degradation in a tuffaceous environment at elevated temperatures.

100 ppm and 1000 ppm solutions of the standard mixtures were placed in the neoprene tubing at 24°C and 37°C. These solutions were the four-component mixture and the pentafluorobenzoic acid single standard.

All the above samples were allowed to stand for twenty-four hours, with aliquots removed at 2.5, 5.0, and 24 hours for analysis. The 2,4,5-trifluorobenzoic acid and the 2,3,4,5-tetrafluorobenzoic acid in the neoprene tubing showed a very marked decrease in concentration over the time span, the pentafluorobenzoic acid showed a lesser but noticeable decrease (in both the mixture and the single component standard), and the 2,6-difluorobenzoic acid showed the smallest decrease. All compounds in the neoprene tubing showed a much greater decrease in the 37°C samples than the 24°C samples. The standard blanks and soil/solution mixtures did not show these decreases in concentration, and it is felt that this change is due to the neoprene tubing, not the temperature of the solution or the overall stability of the tracer compound (Table #1).

NEOPRENE PRE-CONDITIONING STUDY

The effect of the neoprene tubing on the tracer compounds was disturbing, and it was hoped that some sort of pre-conditioning could be applied which would minimize the loss of the tracer compounds. Four methods of pre-conditioning were proposed and evaluated as outlined below:

1 - In the event that an inorganic compound in the tubing caused the decrease in tracer concentration, a 10% salt solution (NaCl) was placed in the tubing to facilitate ion exchange actions. It was hoped that the organic acids would not be strong enough to displace the salts and would therefore not be sorbed to the tubing.

Two pieces of neoprene tubing were filled with a 10% salt solution (NaCl); one was kept at 24°C, while the other was placed in a 37°C water bath. The solution in both pieces was removed and replaced after 1, 2, and 5 hours respectively. A fresh aliquot of the salt solution was then allowed to stand in the tubing for 24 hours; it was then removed, the tubing was rinsed once with distilled water, and the 1000 ppm standard mixture was added to both pieces and monitored over a 24-hour period, at 37°C.

2 - In the event that an organic compound in the tubing caused the decrease in tracer concentration, methanol was placed in the tubing to leach out the materials that were sorbing the organic part of the acids.

A piece of neoprene tubing at 24°C was filled with HPLC grade methanol. The methanol was removed and replaced after 1, 2, and 5 hours respectively. A fresh aliquot of the methanol was then allowed to stand in the tubing for 24 hours, after which it was removed; the tubing was rinsed once with distilled water, and the 1000 ppm standard mixture was added and monitored over a 24-hour period, at 37°C.

3 - In the event that a water soluble compound in the tubing caused the decrease in tracer concentration, de-ionized water was placed in the tubing to leach out the materials that may possibly sorb the carboxyl portion of the tracer molecules. This was carried out at both 24°C and 37°C.

Two pieces of neoprene tubing were filled with 18.3 megaohm de-ionized water. The water was removed and replaced after 1, 2, and 5 hours respectively. A fresh aliquot of the water was then allowed to stand in the tubing for 24 hours, after which it was removed; the tubing was rinsed once with distilled water, and the 1000 ppm standard mixture was added and monitored over a 24-hour period, at 37°C.

4 - In the event that a volatile compound in the tubing caused the decrease in tracer concentration, a length of neoprene tubing was capped on one end and immersed in a 37°C water bath, so that the open end of the tubing could vent to the air. The tubing was allowed to stand at 37°C for 29 hours, then rinsed once with distilled water, and the 1000 ppm standard mixture was added and monitored over a 24-hour period, at 37°C.

The data from these pre-conditioning steps (Table #2) was carefully compared to the data gathered from the unconditioned tubing studies. It appeared that the preconditioning had no significant reducing effects on tracer losses. The decreases in all four compounds in conditioned tubing were equal to or greater than the decreases in the unconditioned tubing.

NEOPRENE SATURATION STUDY

A saturation study was also performed using the neoprene tubing and both the single pentafluorobenzoic acid standard and the standard mixture containing 2,6-difluorobenzoic, 2,4,5-trifluorobenzoic, 2,3,4,5-tetrafluorobenzoic, and pentafluorobenzoic acids.

100 ppm and 1000 ppm solutions of the above standard mixtures were placed in the neoprene tubing at 37°C. A separate container of each standard solution was kept at room temperature to be used for a calibration standard.

All neoprene samples were allowed to stand at 37°C for twenty-four hours before aliquots were removed for analysis. The tubing was then emptied of the remaining standard solution and refilled with fresh solution. The tubes were capped and replaced in the water bath for another 24 hours. This cycle was repeated four times, so that the results show the concentration values over a four-day period. Amber glass jars containing each standard were placed in the hot bath to monitor any temperature-related changes in the standards. These were sampled at the same times as the neoprene tubing samples but were not replenished after each sampling event.

The 2,4,5-trifluorobenzoic acid and the 2,3,4,5-tetrafluorobenzoic acid in the neoprene tubing still showed a large continuous decrease in concentration over the time span. The pentafluorobenzoic acid showed a continuous decrease as well (in both the mixture and the single component standard), as did the 2,6-difluorobenzoic acid (Table #3). The slight increase in concentration for the standard solutions is most likely due to evaporation over the extended analysis time. The figures given for concentration decreases in the neoprene tubing represent the fourth-day values. All previous data collected for days one through three reflect similar decreases from the original concentration. The repeated replacement of fresh standard solution seemed to have no noticeable effect on the concentration decrease from the tubing. If saturation of the tubing is possible, it is not achievable in four days.

NEOPRENE / LITHIUM BROMIDE STUDY

Lithium bromide, a non-organic compound, was tested in the neoprene tubing to determine if it sorbed or was degraded in the same manner as the previously tested organic tracer compounds.

LiBr solutions were prepared at 100 and 1000 ppm (in Br) in J-13 well water. 50 ml aliquotes of these solutions were placed in the neoprene tubing in a water bath at 37°C. A separate container of each standard solution was kept at room temperature to be used as a calibration standard. Amber glass jars containing the 100 and the 1000 ppm solutions were placed in the hot bath to monitor any temperature-related changes in the standards. These were sampled at the same times as the neoprene tubing samples.

All the above samples were allowed to stand for twenty-four hours, with aliquots removed at 2.5, 5.0 and 24 hours for analysis. Analysis of the bromide concentration was done using a Dionex Ion Chromatograph with anion capability equipped with an Electrocondutivity detector. The lithium analysis was done with a Plasma 40 ICP/AES.

The bromide showed a decrease in concentration which leveled out between the 5.0 and 24.0 hour samples. The greatest decrease occurred in the 1000 ppm solution (approx 21%), with only a small decrease (approx 10%) in the 100 ppm solution. The lithium concentration remained fairly constant, with the higher concentration once again showing the greatest amount of change over the length of the analysis. The standard solutions remained fairly constant, with no noticeable effect from the elevated temperatures (Table #4).

SOIL COLUMN STUDIES

Data obtained from soil column studies will be used to evaluate the stability of tracer compounds in a dynamic water/tuff environment. All tracers exhibiting positive results in the batch studies will be tested for sorption with the column studies.

For the column test currently underway, ground, dark tuff was packed into a 2 x 12 inch Kontes Chromaflex chromatography column with beaded polymer filters (0.45um pore size) secured to each end of the column. A water jacket was attached to the column and water heated to 35°C was pumped through the jacket at a constant rate.

Water used in this study was obtained from the J-13 well site. The water was filtered through a 0.2 micron millipore filter and stored at 4°C. Water was pumped through the packed column using a Spectra-Physics Iso-Chrom LC pump at flow rate of 2.0 ml per minute, 1.0 ml per minute, and 0.1 ml per minute. Two hundred microliters of 10 ppm tracer solutions were injected into the column.

The detector used in the study was a Spectra-Physics Spectra 200 variable wavelength UV-Vis detector. Two wavelengths were used, 210 nm (to monitor KBr) and 230 nm (to monitor the organic acids). The data was interfaced with a Dionex AL 450 work station.

To date, 5-fluorosalicylic acid, 2,3,4-trifluorobenzoic acid, and 2,3,4,5-tetrafluorobenzoic acid have been evaluated using the dark tuff column. (All three types of tuff will eventually be used to evaluate tracer compounds.) These were compared to potassium bromide, a known conservative tracer compound, to determine if any sorption occurred. Data obtained from the soil column work to date is incomplete, and further work is necessary before any conclusive trends can be identified.

CONTINUING WORK

Several batch studies will continue during the next 6-month period, but the main effort for the sorption studies will be shifted to the column studies. Ames testing will be initiated on all of the fluorinated benzoic acids and the perfluorinated aliphatic acids. Analytical method development with the HPLC-MS will continue, and a comprehensive evaluation of the toxicity of the potential tracers will be initiated.

TABLE #1

NEOPRENE SORPTION STUDY

2,6-DIFLUOROBENZOIC ACID:

1000 ppm standard mix at 24°C: +0.03%
100 ppm standard mix at 24°C: -2.85%

1000 ppm standard mix at 37°C: -2.96%
100 ppm standard mix at 37°C: -1.40%

1000 ppm standard mix in light tuff at 24°C: -1.09%
100 ppm standard mix in light tuff at 24°C: +2.49%

1000 ppm standard mix in light tuff at 37°C: +3.21%
100 ppm standard mix in light tuff at 37°C: +7.84%

1000 ppm standard mix in neoprene at 24°C: +1.78%
100 ppm standard mix in neoprene at 24°C: -1.12%

1000 ppm standard mix in neoprene at 37°C: -12.15%
100 ppm standard mix in neoprene at 37°C: - 4.84%

2,4,5-TRIFLUOROBENZOIC ACID:

1000 ppm standard mix at 24°C: +0.02%
100 ppm standard mix at 24°C: -2.68%

1000 ppm standard mix at 37°C: -3.06%
100 ppm standard mix at 37°C: -1.35%

1000 ppm standard mix in light tuff at 24°C: -0.78%
100 ppm standard mix in light tuff at 24°C: +2.[illegible]5%

1000 ppm standard mix in light tuff at 37°C: + 4.14%
100 ppm standard mix in light tuff at 37°C: +13.01%

1000 ppm standard mix in neoprene at 24°C: -5.39%
100 ppm standard mix in neoprene at 24°C: -4.13%

1000 ppm standard mix in neoprene at 37°C: -80.15%
100 ppm standard mix in neoprene at 37°C: -68.34%

TABLE #1 CONT.

2,3,4,5-TETRAFLUOROBENZOIC ACID:

1000 ppm standard mix at 24°C: +0.03%
100 ppm standard mix at 24°C: -2.73%

1000 ppm standard mix at 37°C: -3.82%
100 ppm standard mix at 37°C: -2.77%

1000 ppm standard mix in light tuff at 24°C: -1.57%
100 ppm standard mix in light tuff at 24°C: -3.03%

1000 ppm standard mix in light tuff at 37°C: +6.56%
100 ppm standard mix in light tuff at 37°C: +6.31%

1000 ppm standard mix in neoprene at 24°C: -20.55%
100 ppm standard mix in neoprene at 24°C: -22.53%

1000 ppm standard mix in neoprene at 37°C: -88.65%
100 ppm standard mix in neoprene at 37°C: -76.72%

PENTAFLUOROBENZOIC ACID (MIXTURE):

1000 ppm standard mix at 24°C: +0.03%
100 ppm standard mix at 24°C: -3.00%

1000 ppm standard mix at 37°C: -3.00%
100 ppm standard mix at 37°C: -3.00%

1000 ppm standard mix in light tuff at 24°C: -1.00%
100 ppm standard mix in light tuff at 24°C: -3.52%

1000 ppm standard mix in light tuff at 37°C: +7.92%
100 ppm standard mix in light tuff at 37°C: +8.47%

1000 ppm standard mix in neoprene at 24°C: +1.68%
100 ppm standard mix in neoprene at 24°C: -0.83%

1000 ppm standard mix in neoprene at 37°C: -24.10%
100 ppm standard mix in neoprene at 37°C: + 4.84%

PENTAFLUOROBENZOIC ACID (SEPARATE):

1000 ppm pentafluorobenzoic standard at <u>24°C</u>: +0.07%
100 ppm pentafluorobenzoic standard at <u>24°C</u>: -7.41%

1000 ppm pentafluorobenzoic standard at <u>37°C</u>: -7.18%
100 ppm pentafluorobenzoic standard at <u>37°C</u>: -5.42%

1000 ppm pentafluorobenzoic standard in <u>light tuff at 24°C</u>: -5.17%
100 ppm pentafluorobenzoic standard in <u>light tuff at 24°C</u>: -8.69%

1000 ppm pentafluorobenzoic standard in <u>light tuff at 37°C</u>: - 5.06%
100 ppm pentafluorobenzoic standard in <u>light tuff at 37°C</u>: +12.12%

1000 ppm pentafluorobenzoic standard in <u>neoprene at 24°C</u>: -7.70%
100 ppm pentafluorobenzoic standard in <u>neoprene at 24°C</u>: -5.64%

1000 ppm pentafluorobenzoic standard in <u>neoprene at 37°C</u>: -11.61%
100 ppm pentafluorobenzoic standard in <u>neoprene at 37°C</u>: + 5.80%

TABLE #2

NEOPRENE PRE-CONDITIONING STUDY

2,6-DIFLUOROBENZOIC ACID:

1000 ppm standard mix in neoprene (37°C salt sol.) at 37°C: -18.8%
1000 ppm standard mix in neoprene (37°C salt sol.) at 37°C: -10.5%
1000 ppm standard mix in neoprene (24°C methanol) at 37°C: -16.5%
1000 ppm standard mix in neoprene (37°C dry heat) at 37°C: -15.8%

2,4,5-TRIFLUOROBENZOIC ACID:

1000 ppm standard mix in neoprene (24°C salt sol.) at 37°C: -88.9%
1000 ppm standard mix in neoprene (37°C salt sol.) at 37°C: -78.6%
1000 ppm standard mix in neoprene (24°C methanol) at 37°C: -84.9%
1000 ppm standard mix in neoprene (37°C dry heat) at 37°C: -86.8%

2,3,4,5-TETRAFLUOROBENZOIC ACID:

1000 ppm standard mix in neoprene (24°C salt sol.) at 37°C: -80+%
1000 ppm standard mix in neoprene (37°C salt sol.) at 37°C: -80+%
1000 ppm standard mix in neoprene (24°C methanol) at 37°C: -80+%
1000 ppm standard mix in neoprene (37°C dry heat) at 37°C: -80+%

PENTAFLUOROBENZOIC ACID (MIXTURE):

1000 ppm standard mix in neoprene (24°C salt sol.) at 37°C: -33.5%
1000 ppm standard mix in neoprene (37°C salt sol.) at 37°C: -25.9%
1000 ppm standard mix in neoprene (24°C methanol) at 37°C: -30.6%
1000 ppm standard mix in neoprene (37°C dry heat) at 37°C: -31.1%

TABLE #3

NEOPRENE SATURATION STUDY

2,6-DIFLUOROBENZOIC ACID:

1000 ppm standard mix at 37°C: +5.50%
100 ppm standard mix at 37°C: +4.21%

1000 ppm standard mix in neoprene at 37°C: -21.79%
100 ppm standard mix in neoprene at 37°C: -12.56%

2,4,5-TRIFLUOROBENZOIC ACID:

1000 ppm standard mix at 37°C: +6.22%
100 ppm standard mix at 37°C: +4.39%

1000 ppm standard mix in neoprene at 37°C: -78.88%
100 ppm standard mix in neoprene at 37°C: -73.49%

2,3,4,5-TETRAFLUOROBENZOIC ACID:

1000 ppm standard mix at 37°C: +6.18%
100 ppm standard mix at 37°C: +4.15%

1000 ppm standard mix in neoprene at 37°C: -74.96%
100 ppm standard mix in neoprene at 37°C: -79.48%

TABLE #3 CONT.

PENTAFLUOROBENZOIC ACID (MIXTURE):

1000 ppm standard mix at <u>37°C</u>: +6.52%
100 ppm standard mix at <u>37°C</u>: +4.38%

1000 ppm standard mix in <u>neoprene at 37°C</u>: -16.32%
100 ppm standard mix in <u>neoprene at 37°C</u>: - 3.18%

PENTAFLUOROBENZOIC ACID (ALONE):

1000 ppm pentafluorobenzoic standard at <u>37°C</u>: +4.93%
100 ppm pentafluorobenzoic standard at <u>37°C</u>: +4.48%

1000 ppm pentafluorobenzoic standard in <u>neoprene at 37°C</u>: -37.10%
100 ppm pentafluorobenzoic standard in <u>neoprene at 37°C</u>: - 1.37%

TABLE #4

NEOPRENE - LITHIUM BROMIDE STUDY

LITHIUM CONCENTRATIONS BY ICP:

1000 ppm lithium bromide solution at 37°C: -4.27%
100 ppm lithium bromide solution at 37°C: -6.63%

1000 ppm lithium bromide solution in neoprene at 37°C: -7.11%
100 ppm lithium bromide solution in neoprene at 37°C: +0.21%

BROMIDE CONCENTRATIONS BY ION CHROMATOGRAPH:

1000 ppm lithium bromide solution at 37°C: +0.95%
100 ppm lithium bromide solution at 37°C: +0.95%

1000 ppm lithium bromide solution in neoprene at 37°C: -10.10%
100 ppm lithium bromide solution in neoprene at 37°C: -20.74%

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