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

PROGRESS REPORT
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Klaus Stetzenbach
Irene Farnham

Harry Reid Center For Environmental Studies
University of Nevada - Las Vegas

The work performed during this quarter consists of the continuation of the batch and column studies for several fluorinated organic acids. Preliminary studies were made on the use of solid phase extraction as a concentrating technique and on the development of analytical methods to be used for the multi-tracer field test. A similar project with the Nevada Test Site is also in progress. Due to the combined efforts of these two projects, substantial progress has been made.

BATCH TESTS

The batch tests are used to determine the stability of the potential tracers in an environment similar to that near Yucca Mountain. The stability of the tracer is determined when exposed to J13 water and three types of ground tuff (light, medium, and dark). The tuff material has been identified by DOE geologists as Bullfrog Tuff, a crystal rich, pumiceous, rhyolitic (silica rich) tuff which underlies the Topopah Spring tuff in Yucca Mountain. The samples referred to as light, medium, and dark have been classified as follows: Un-welded "light" tuff, which is lightweight, porous, and easily broken; Moderately-welded "medium" tuff, which is semi-porous and contains some dense areas of collapsed pumice fragments; and the Densely-welded "dark" tuff which is hard, very dense and vitrophyric in nature, and can be classified as an obsidian. To be considered as a viable tracer for this project, the compound must be stable in all three tuffs for a period of sixty days. The fate of these compounds once introduced into the wells is also of relevance to this study; therefore, these analyses are continued passed the 60 day requirement. Listed below are the compounds tested and a summary of the results.

Cinnamic Acids

The cinnamic acids listed below were tested over a 60-day period. These compounds were found to be quite unstable in the batch tests. Large decreases in the concentration of these compounds were observed after only one day. This instability is most probably due to bacterial degradation.

α-Fluorocinnamic acid
4-Fluorocinnamic acid
trans-2,5-Difluorocinnamic acid
2-Fluorocinnamic acid
3,5-Difluorocinnamic acid

Toluic Acids

The toluic acids listed below were found to be stable over a 60-day period. Less than 7% decreases in concentration were observed.

α,α,α-Trifluoro-o-toluic acid
α,α,α-Trifluoro-p-toluic acid
α,α,α-Trifluoro-m-toluic acid

Benzoic Acids

Batch tests for the benzoic acids have been performed for periods from 60 days to one year. These compounds have remained stable in J13 water with less then 15% decreases in concentration observed in the time periods measured.

2,3-Difluorobenzoic acid
3,4-Difluorobenzoic acid
2,4,6-Trifluorobenzoic acid
2,4-Difluorobenzoic acid
3,5-Difluorobenzoic acid
2,4,6-Trifluorobenzoic acid
2,5-Difluorobenzoic acid
2,3,4-Trifluorobenzoic acid
2,3,4,5-Tetrafluorobenzoic acid
2,6-Difluorobenzoic acid
2,4,5-Trifluorobenzoic acid
Pentafluorobenzoic acid

Three batch tests are currently in progress. These tests have all been analyzed over the required 60-day period (see previous report). Large decreases in concentration were observed for several of the compounds in DI water; however, they were found to be stable in J13 water. Batch tests for these compounds (2,3-Difluorobenzoic acid, 2,6-difluorobenzoic acid, and 3,4-difluorobenzoic acid) were then repeated and found to be stable over sixty days in DI water and all three tuffs in the second test. At 90 days, a decrease in concentration of 20-25% was observed for both 2,3-difluorobenzoic acid and 3,4-difluorobenzoic acid in the light tuff - DI water samples (see Figures 1 and 2). This large decrease did not occur in the light tuff - J13 samples (see Figures 3 & 4).

Many of the compounds have been difficult to evaluate in the light tuff due to a large peak that elutes at the beginning of each chromatogram. 2,6-Difluorobenzoic acid and several other compounds elute at a similar time as this peak, making quantitation impossible. This peak is thought to be due to bacterial growth. Unusual results were observed during a current batch test. Chromatograms for the mixture of fluorinated benzoic acids exposed to the light tuff over a 90-day period are shown in Figure 5. A peak began to form on the third day of the study in the light tuff samples in both J13 and DI water. This peak elutes right after 2,6-difluorobenzoic acid (approx. 4 min) and interferes with its quantitation. Because it was not present in the first samples at T_0 and $T_{1,}$, accurate quantitation was achieved on these days. This peak grew larger as time progressed and therefore 2,6-DFBA could not be evaluated through T_{60}. This peak, however, did decrease significantly by T_{90}, as can be seen in the chromatograms on Figure 5. The concentration of 2,6-difluorobenzoic acid present in the T_{90} is the same as the T_0 sample, indicating excellent stability. This compound was also stable in both the medium and dark tuff (DI water) with changes in concentrations of less than 5% (see Figure 6).

SOIL COLUMN STUDY

The column tests are believed to be more rigorous tests for sorption than the batch tests because the tracer is exposed to much more of the ground rock as it flows through the column. Column tests are of much shorter duration and, therefore, degradation is usually of no concern.

The column tests were conducted on the medium and dark tuffs using a 60 cm long by 5 cm ID glass column. Deionized water was pumped through the column at 5 mL/min using an HPLC pump. Detection of the tracers was accomplished using a variable wavelength detector set at 210 nm. Bromide, which is considered to be a conservative tracer, was used as a reference compound for each column (i.e., all times elution times are compared to bromide). The results of the studies are listed in tables 1 and 2.

Table 1. Mean elution values of compounds tested on Medium Tuff

	f	Mean Volumes (ml)	Standard Deviation	RSD (%)	Range
Potassium Bromide	31	211.15	3.72	1.76	205.18-218.01
2,3-difluorobenzoic acid	7	206.19	1.65	0.80	203.29-208.19
3,4-difluorobenzoic acid	8	209.08	5.30	2.53	200.66-215.35
2,3,6-trifluorobenzoic acid	7	206.76	4.10	1.98	201.73-213.26
2,4,5-trifluorobenzoic acid	7	205.15	5.05	2.46	198.45-210.20
3,4,5-trifluorobenzoic acid	7	210.22	1.96	0.93	207.78-213.09
2,3,5,6-tetrafluorobenzoic acid	7	213.74	2.97	1.39	209.46-219.55
pentafluorobenzoic acid	9	207.27	1.18	0.57	204.38-208.36
α,α,α-trifluoro-m-toluic acid	13	210.22	3.16	1.50	204.39-214.76
α,α,α-trifluoro-o-toluic acid	7	206.20	1.78	0.86	204.01-209.02
α,α,α-trifluoro-p-toluic acid	7	212.35	2.13	1.00	210.20-214.78
5-fluorosalicylic acid	8	215.78	1.93	0.90	213.51-218.40
3,5-dichlorosalicylic acid	7	218.32	4.05	1.86	212.40-223.61

Table 2. Mean elution values of compounds tested on Dark Tuff

	f	Mean Volumes (ml)	Standard Deviation	RSD (%)	Range
Potassium Bromide	13	173.20	7.45	4.42	151.58-179.11
2,3-difluorobenzoic acid	7	177.55	6.74	3.79	169.60-184.50
3,4-difluorobenzoic acid	7	159.16	2.35	1.48	156.30-162.13
2,3,6-trifluorobenzoic acid	8	167.54	2.50	1.49	164.00-169.65
2,4,5-trifluorobenzoic acid	7	173.64	3.71	2.14	169.80-175.76
3,4,5-trifluorobenzoic acid	7	169.13	1.43	0.84	167.83-170.65
2,3,4,5-tetrafluorobenzoic acid	8	161.09	3.91	2.43	156.30-166.58
2,3,5,6-tetrafluorobenzoic acid	8	170.96	0.99	0.58	168.49-171.32
α,α,α-trifluoro-p-toluic acid	8	164.21	8.49	5.17	157.08-174.19

If it is assumed that bromide (potassium bromide) does not sorb to the medium tuff (table 1), then all the benzoic and toluic acids also act conservatively. All these acids, except the 2,3,5,6-tetrafluorobenzoic and p-toluic have a mean elution volume that is lower than that of bromide. The elution volume of the p-toluic is only one milliliter or 0.5% higher and the 2,3,5,6-tetrafluorobenzoic is 1.2% higher than bromide. This is well within the instrumental errors associated with these measurements. The two salicylic acids, 5-fluorosalicylic and 3,5-dichlorosalicylic, have elution volumes that are two standard deviations higher than bromide. Even this may not be significant; however, these acids have been shown to degrade under other conditions and would therefore be suspect as tracers for long-term tests.

The tests conducted on the dark tuff column showed very similar results to the medium tuff tests. Again, only two of the acids tested, 2,3-difluorobenzoic and 2,4,5-trifluorobenzoic, showed mean elution times longer than bromide. These times were also well within the error of the measurement.

Measurement Error

The errors associated with these measurements come primarily from the variability of the flow rate of the pump and the ability of the integrator to recognize the peak of the tracer elution curve. The pumping system used for these experiments is reproducible to about 0.1% relative standard deviation (RSD) for replicate analyses and no worse than 1% RSD over a period of days or weeks. The percent RSD values listed in Table 1 are close to the pumping system variability; however, those from Table 2 show more variability than what would be expected from the pumping system. The differences are the ability of the integration system to recognize the center of mass of the elution peak. This is related to the efficiency of the column that is used in the experiment. The medium tuff column was packed more efficiently and therefore produced a sharper peak center which was easier to recognize.

Elution Times

It is interesting to note that, with two exceptions on each column, the benzoic and toluic acids had shorter average elution volumes than bromide (although they are considered the same when the measurement standard deviations are considered). Since bromide is presumed not to sorb, one must conclude that there are other mechanisms involved. This could be size exclusion or anion exclusion. Both of these mechanisms are possible as the organic acids are considerable larger than bromide, and the fluorine atoms, attached to the benzene ring, are very electronegative, thus producing a molecule that is repelled from the anionic tuff surfaces

METHOD DEVELOPMENT

The reliability of the results obtained during the field tests is greatly dependent on the analytical methods used to identify and quantitate each tracer compound. High performance liquid chromatography (HPLC) with ultraviolet detection allows for the direct injection of the tracer samples and therefore is considered the method of choice for the analysis of these compounds. The detection limits for the fluorinated benzoic acids are in the upper parts per billion. A tremendous dilution of the tracers occurs following their introduction into the wells, and the amount of sample which can be introduced is limited by its solubility. It is therefore important to use the most sensitive method available. If the tracer exists below the detection limit, concentrating techniques may be used. Solid phase extraction is a promising technique for concentrating these samples. Several solid phase extraction cartridges are presently being evaluated. The cartridge which results in the highest recoveries for the fluorinated benzoic acids will then be used to evaluate its concentrating capabilities.

HPLC conditions must also be found which will provide separation of each compound within a sample before quantitation is possible. Many of the available fluorinated benzoic acids are very similar in structure and are therefore difficult to separate using HPLC. Several HPLC conditions were evaluated in an attempt to separate all of the candidate tracers. At this time, fourteen of the seventeen fluorinated benzoic and toluic acids can be separated. Several of the compounds have identical or very similar retention times and therefore co-elute if analyzed together, making quantitation of either one impossible.

Baseline separation of several of these fourteen compounds was not obtained using any of the tested conditions. The quantitation of these compounds may be possible using the heights of each chromatographic peak rather than the entire peak area, although quantitation using peak areas is generally preferred. A study was performed to test the feasibility of using peak heights to quantitate each of the fourteen compounds. A mixture was prepared containing the compounds listed on the next page. This solution was diluted to obtain standards at three concentrations (1.25 ppm, 2.5 ppm, and 5 ppm). These were then analyzed on the HPLC using 65% .05M KH_2PO_4 in water (pH 2.7) and 35% methanol. These conditions provide the best separation. Although 3,4- and 3,5-difluorobenzoic coelute using any of the LC conditions tested, they were added to this mixture. This was to confirm that these compounds cannot be distinguished from one another and therefore can not be quantified if they are in solution together.

Chlorinated benzoic acids are also being evaluated for a project with Sandia National Laboratories. These compounds have also been shown to be quite stable and therefore good tracer candidates. Several of the chlorinated benzoates were included in this study. The compounds included in this mixture and the average retention times for each are listed below.

1.	*2,6-Difluorobenzoic acid	2.91
2.	2,4,6-Trifluorobenzoic acid	3.70
3.	Pentafluorobenzoic acid	5.08
4.	2,5-Difluorobenzoic acid	7.68
5.	2,3-Difluorobenzoic acid	8.27
6.	2,4-Difluorobenzoic acid	9.96
7.	o-Trifluoromethyl benzoic acid	11.15
8.	2,4,5-Trifluorobenzoic acid	11.79
9.	2,3,4-Trifluorobenzoic acid	13.49
10.	2,3,4,5-Tetrafluorobenzoic acid	15.88
11.	2,5-Dichlorobenzoic acid	18.70
12.	**3,4- and 3,5-Difluorobenzoic acid	20.63
13.	2,4-Dichlorobenzoic acid	30.12
14.	3,4,5-Trifluorobenzoic acid	31.80
15.	m-Trifluoromethyl benzoic acid	52.98
16.	Trifluoromethyl benzoic acid	60.87

* The retention times for 2,6-Difluorobenzoic acid, 2,3,5,6-tetrafluorobenzoic acid and 2,3,6-trifluorobenzoic acid are within 0.2 min. of each other.

** The retention times for 3,4-difluorobenzoic acid and 3,5-difluorobenzoic acid are within 0.2 min. of each other.

Excellent linearity (r^2 = .999 to 1) was observed for the standard curves for each of the above compounds. The retention times were also quite reproducible over all three concentrations with percent relative standard deviations of 0.2% to 1.1%. This indicates that each of these compounds can be identified and accurately quantified.

FUTURE STUDIES

Two compounds (2,3,5,6-tetrafluorobenzoic acid and 2,3,6-trifluorobenzoic acid) remain to be batch tested. These compounds have similar retention times and cannot be analyzed in a mixture. The batch test has, therefore, been delayed while testing the HPLC conditions in hope that separation could be achieved. The batch test for these compounds will be initiated during this quarter to ensure that the stabilities of all available benzoic and toluic acids over sixty days are known at the end of this quarter. The column studies will continue until all the potential tracers have been tested on all three types of tuff. We will also proceed with method development in preparation of the multi-tracer field test.

FIGURE 1

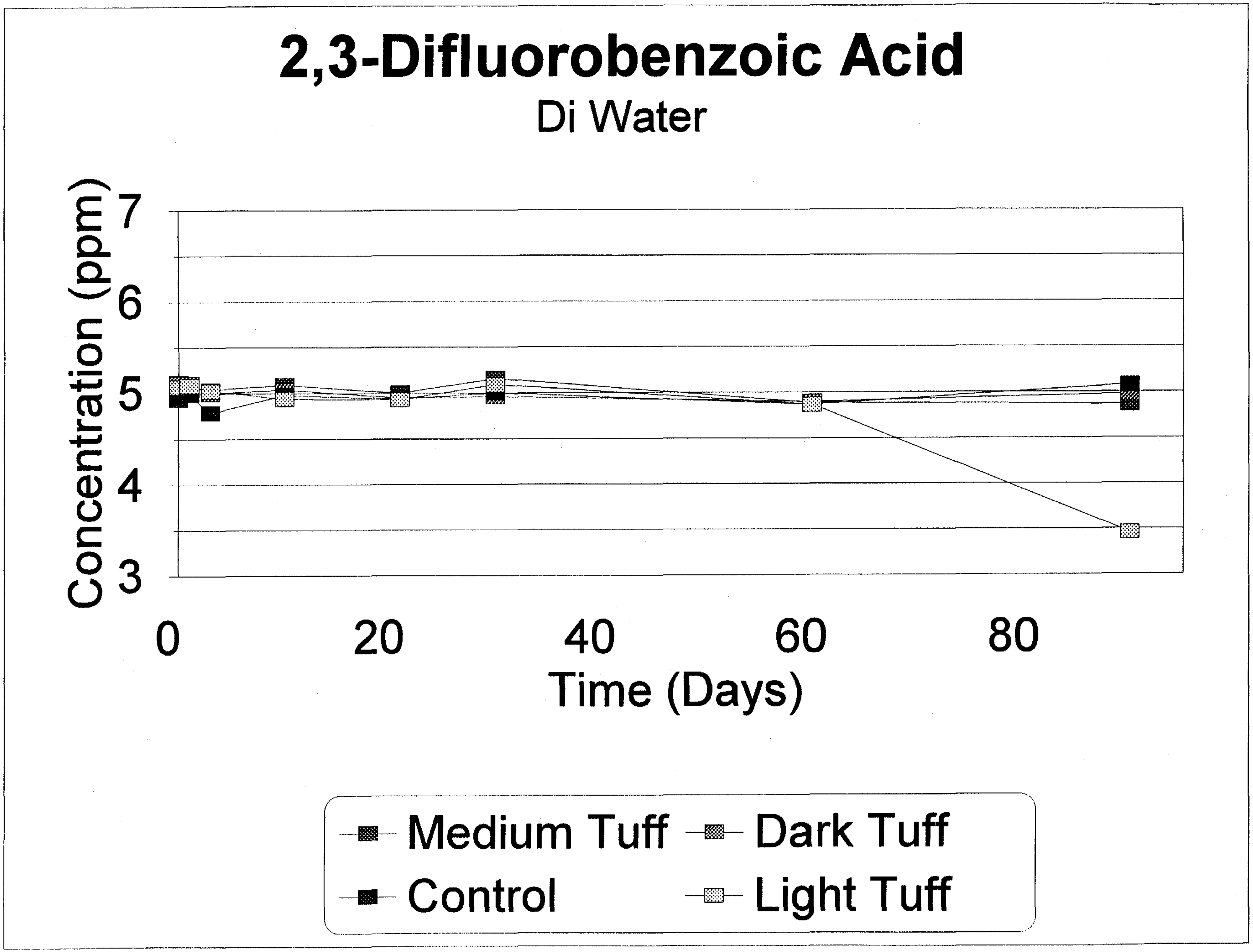

2,3-Difluorobenzoic Acid
Di Water
Concentration (ppm)
7
6
5
4
3
0
20
40
60
80
Time (Days)
Medium Tuff
Dark Tuff
Control
Light Tuff

FIGURE 2

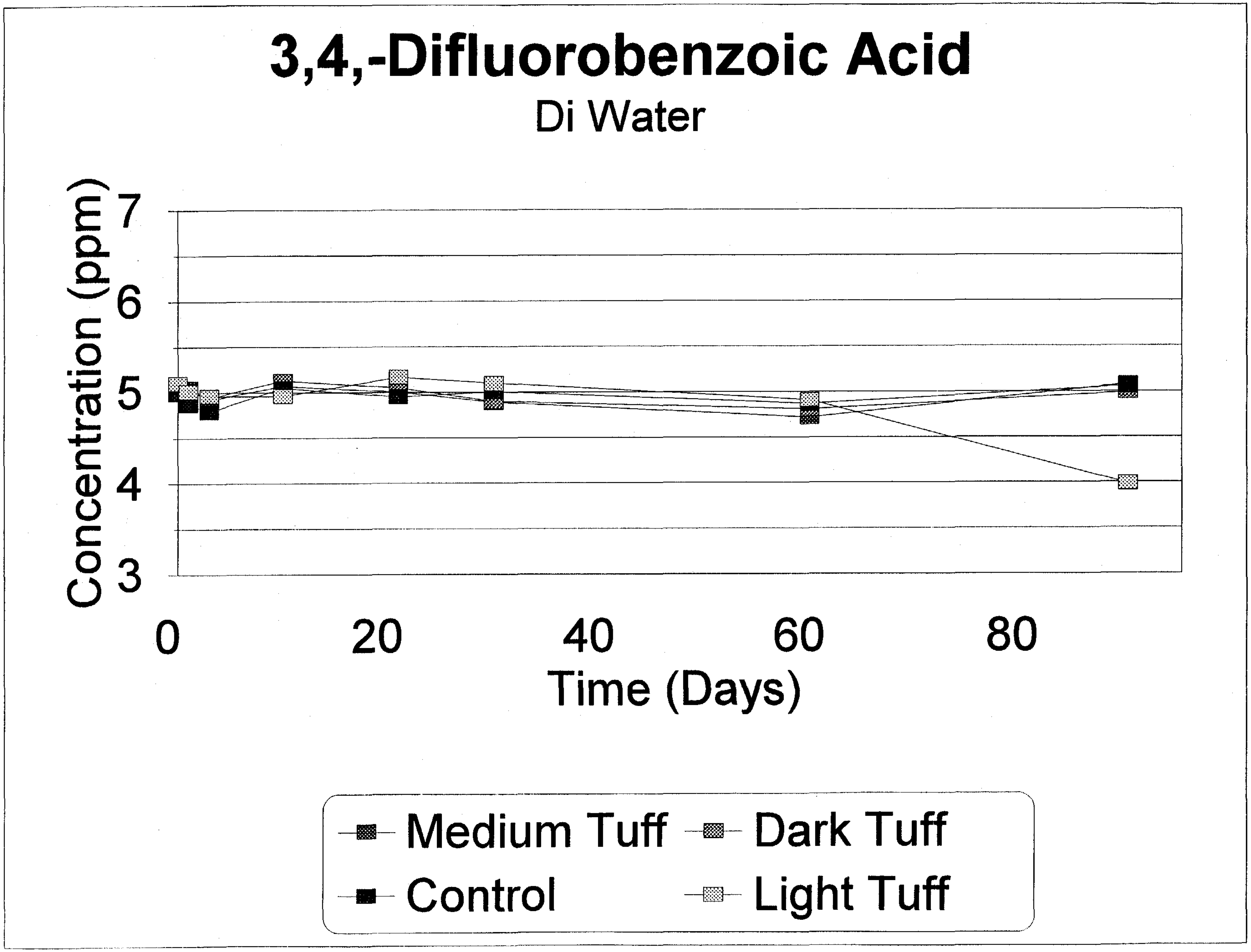

3,4,-Difluorobenzoic Acid
Di Water
Concentration (ppm)
7
6
5
4
3
0
20
40
60
80
Time (Days)
Medium Tuff
Dark Tuff
Control
Light Tuff

FIGURE 3

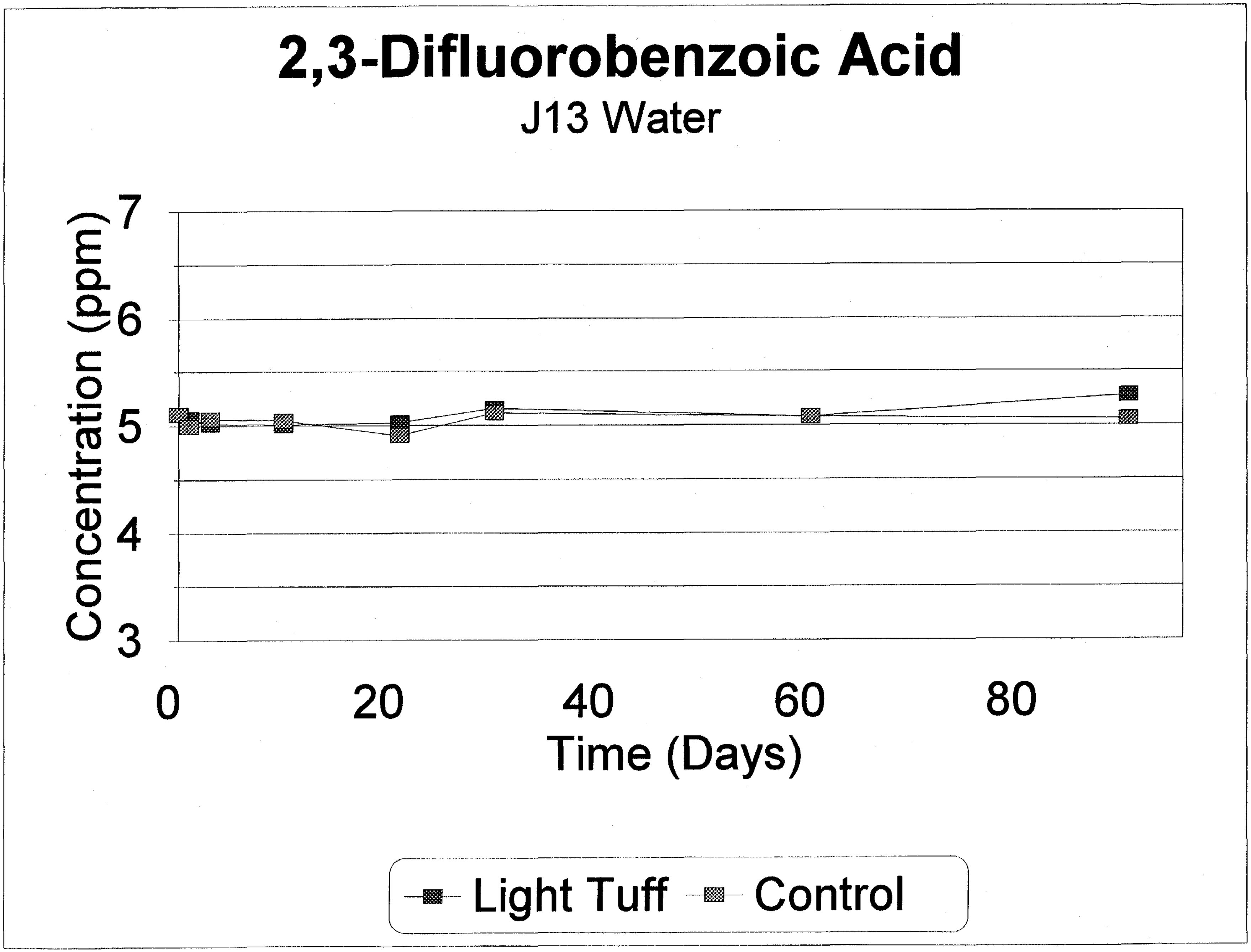

2,3-Difluorobenzoic Acid
J13 Water
Concentration (ppm)
7
6
5
4
3
0
20
40
60
80
Time (Days)
Light Tuff
Control

FIGURE 4

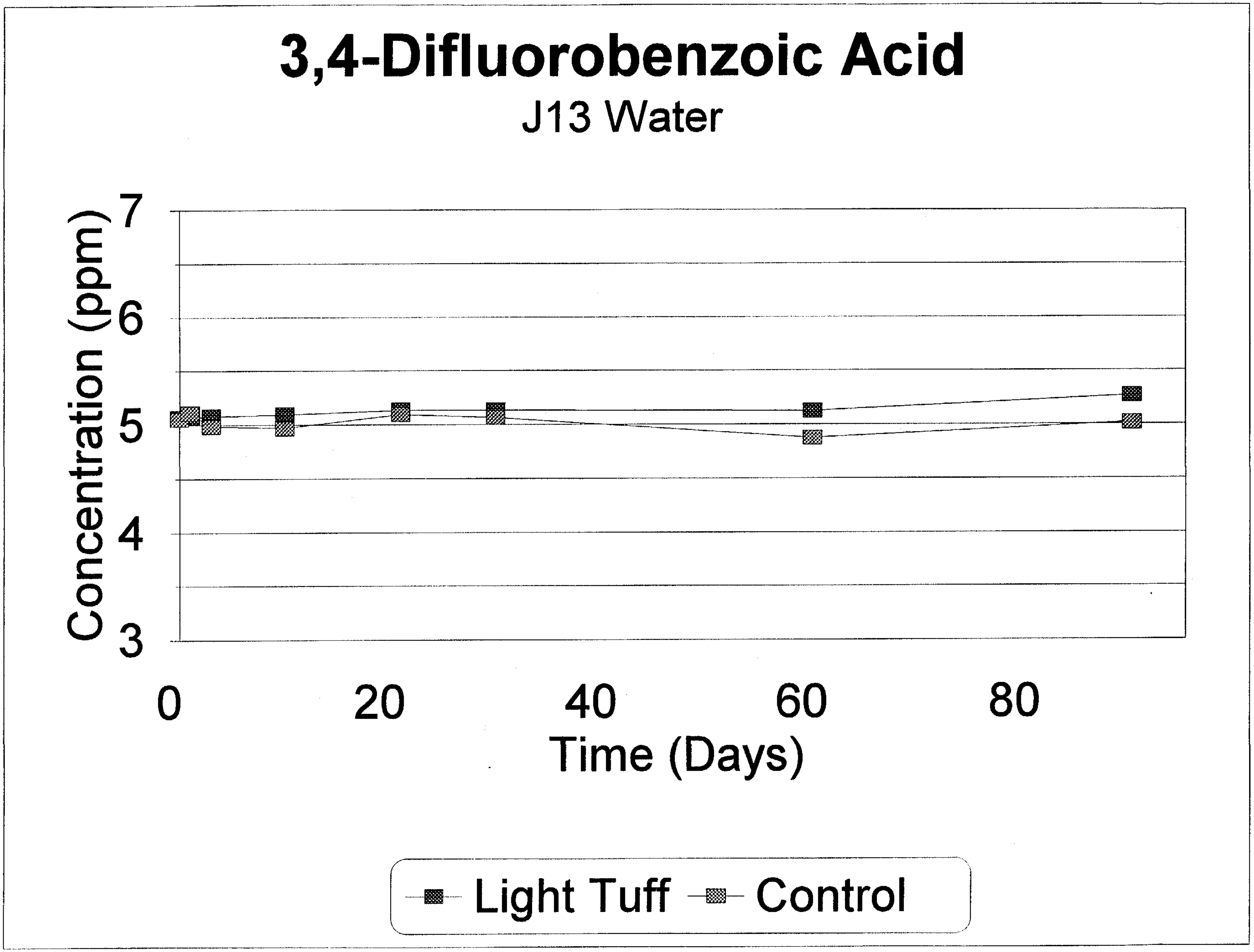

3,4-Difluorobenzoic Acid
J13 Water
Concentration (ppm)
7
6
5
4
3
0
20
40
60
80
Time (Days)
Light Tuff
Control

FIGURE 5

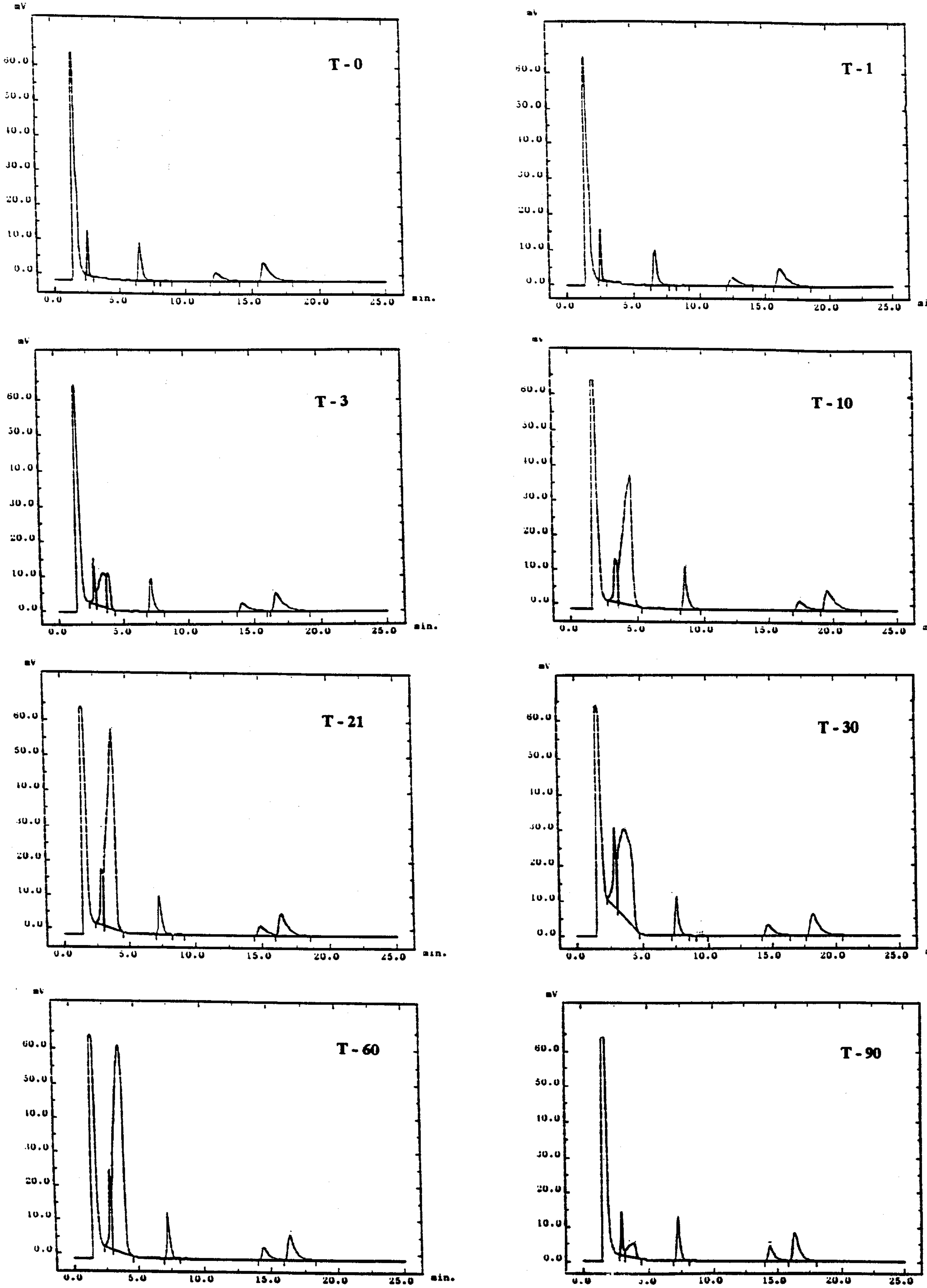
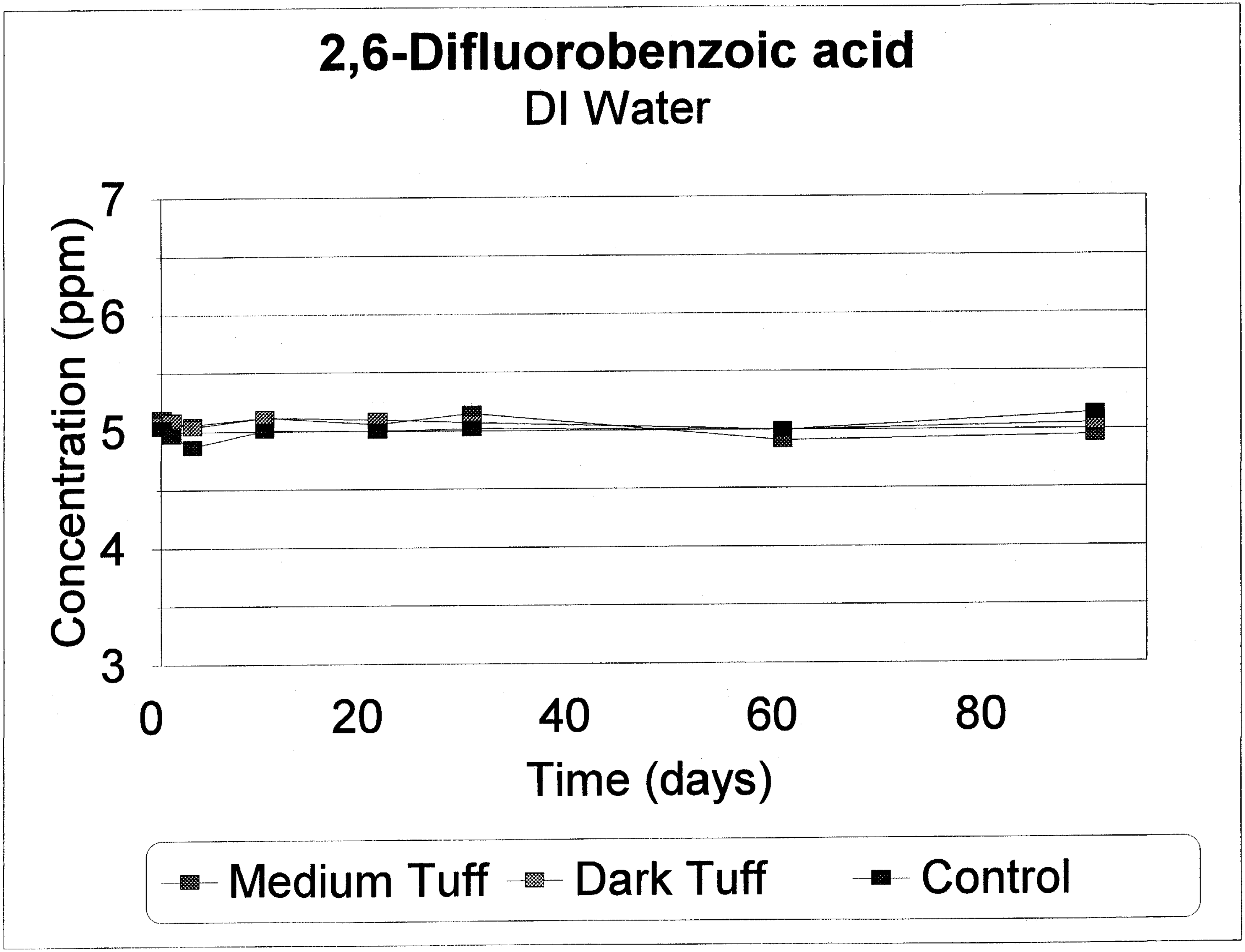

T - 0
T - 1
T - 3
T - 10
T - 21
T - 30
T - 60
T - 90
mV
60.0
50.0
40.0
30.0
20.0
10.0
0.0
0.0
5.0
10.0
15.0
20.0
25.0
min.

FIGURE 6


2,6-Difluorobenzoic acid
DI Water
Concentration (ppm)
7
6
5
4
3
0
20
40
60
80
Time (days)
Medium Tuff
Dark Tuff
Control