DOE/NV/10872--T163

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

**PROGRESS REPORT**
**OCTOBER 1, 1994 to DECEMBER 31, 1994**

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MASTER

## DISCLAIMER

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**OCTOBER 1994 to DECEMBER 1994**

The work performed during this quarter consists of the continuation of the batch studies for the fluorinated benzoic acids and column studies for several potential tracer compounds.

**BATCH TESTS**

Batch tests are in progress for several of the fluorinated benzoic acids. In the batch tests, standards containing a mixture of tracers in J13 and DI water are exposed to three types of tuff (light, medium, and dark).The tuffs were collected from an area near Yucca Mountain. One milliliter aliquots are taken from each sample periodically and analyzed to determine whether any changes in concentration have occurred. The compounds within the mixture are selected so that they can be separated using liquid chromatography and accurately quantitated using a ultraviolet detector. A control is also included in the batch test which consists of the tracer mixture in both water types but no tuff.

Three sets of these tests are in progress. One consists of the following compounds: 2,3-difluorobenzoic acid, 2,4-difluorobenzoic acid, 3,4-difluorobenzoic acid, and 2,4,5-trifluorobenzoic acid. These compounds have been analyzed over a 260 day period. The second set consists of: 2,6-difluorobenzoic acid, 2,4,6-trifluorobenzoic acid, 2,5-difluorobenzoic acid, and 3,5-difluorobenzoic acid. This set has been analyzed over a 190 day period. The third set consists of four compounds previously studied. A few compounds gave inconsistent results and therefore these studies were repeated. The results to date are as follows:

BATCH TEST 1

The initial concentration of these compounds was 600ppb. Although this is above the detection limit, the low concentration does result in some experimental variability.

**2,3-Difluorobenzoic acid, 2,4-Difluorobenzoic acid and 3,4-Difluorobenzoic acid**

A less than 10% decrease in concentration, over 260 days, was observed in all J13 samples except one the medium tuffs (Figure 1- 3), in the light tuff in DI water (Figure 4-6), and in both controls. As mentioned in the previous reports, up to a 50% decrease was observed in both the medium and dark tuffs in DI water. This is thought to be due to some type of bacterial contamination introduced into the sample bottles.

The batch test was repeated for 2,3- and 3,4-Difluorobenzoic acid in all tuffs with DI water and in the light tuff with J13 water. An initial concentration of 5ppm was used. Excellent stabilities were observed in all samples, with less then 5% decreases observed over 60 days (see Tables 7 - 10).

**2,4,5-Trifluorobenzoic acid**

A less than 15% decrease in concentration was observed, over 260 days, in all tuffs and both waters (Figures 11 & 12). The large decrease in concentration that occurred for all other compounds in the medium and dark tuff DI water was not observed for this compound.

BATCH TEST 2

**2,5-Difluorobenzoic acid 2,4,6-Trifluorobenzoic acid, and 3,5-Difluorobenzoic acid**

A 10% or less decrease in concentration over 190 days was observed in all except the medium tuff, J13 samples (Figures 13 - 18). Consistently larger decreases (11-22%) were observed for all compounds in the medium tuffs.

**2,6-Difluorobenzoic acid**

Larger fluctuations were observed for this compound over the 190 day period. This compound elutes very rapidly from the LC column and is therefore sensitive to any fluctuations occurring in the mobile phase. A 20% or less decrease is observed in all samples (Figures 19 -20). The large peak consistently observed from the light tuff, interferes with accurate quantitation of this compound.

The batch test for this compound was also repeated using a larger initial concentration (5ppm). Behavior of this compound was tested in the medium and dark tuffs with DI water and the light tuff with both waters. Less than 5% decreases were observed in the medium and dark tuffs (see tables 21 - 22) but analysis of the light tuff samples resulted in the same problems encountered previously. Accurate quantitation of this compound in light tuff was not possible.

## SOIL COLUMN STUDY

The bromide anion has been used extensively as a tracer for mapping the flow of groundwater. It has proven to be both a safe and reliable groundwater tracer. Our goal in this study is to find several tracing compounds with characteristics similar to the bromide anion to be used in multiple well tracing tests.

Four groups of fluorinated organic acids were selected as candidates for groundwater tracers. These groups include fluorinated benzoic acids (FBA) , fluorinated salicylic acids (FSA), fluorinated toluic acids (FTA), and fluorinated cinnamic acids (FCA). These compounds have been shown to move readily with the flow of water and do not adsorb to soil. They are also non-toxic.

In this study, the retention of the fluorinated organic acids on to a soil column is compared to that of the bromide ion.The time required for the elution of each analyte from the soil column is measured using a UV-Vis detector. The soils consist of the light, medium, and dark tuffs used in the batch study.

Procedure

A four liter water reservoir was connected to 1/8 inch tubing leading to a Spectra Physics Iso Chrom liquid chromatography pump. The pump was equipped with an injection port able to accommodate a twenty-five microliter syringe. Tubing from the pump ran to the bottom of the Kontes glass column which had a diameter of 1 3/4 inches and a length of eleven inches. The column was wet-packed with ground-up medium tuff. Wet-packing allowed floating debris to be filtered off to prevent small particles from clogging the detector. A Spectra Physics Spectra 200 UV-VIS was connected to the exit tube of the column and then water was routed to a waste receptacle. A Spectra

Physics chart integrator recorded the chromatogram with its retention time and integrated area.

The potassium bromide and fluorinated tracers were made up to a concentration of ten thousand milligrams per liter or more. Since the area of the tracer's peak was not as critical as the retention time in the study, the concentration of all the tracers varied from acid to acid. The ten thousand milligram per liter level produced a good reproducible peak from run to run. The tracers were dissolved in distilled water by adjusting the pH to a range of 8 to 11. The pH was adjusted with 0.10 N sodium hydroxide (NaOH).

The flow rate of the water was set at five milliliters per minute. The pressure of the system ranged between 75 and 120 psi. Each morning, the top of the column was removed and excess water siphoned off with a twenty-five milliliter syringe to prevent the column from building up excessive back pressure. The excessive back pressure can cause the column to explode one of the end caps from the column. When this was completed the pump was turned on.

The detector was allowed to stabilize for thirty to sixty minutes. The wavelength was set at 210 nanometers and a range of one. The chart integrator was set at 0.1 centimeters per minute.

A twenty-five microliter injection of the tracer was injected into the LC pump and the start button of the integrator was pressed. The flow rate was checked periodically and noted in a lab book. A twenty-five milliliter volumetric flask was filled with the eluting water and timed with a stopwatch. KBr was injected after every three to five injections of a test tracer to determine whether any changes have occurred over time.

Results

During the past quarter, eleven fluorinated organic acids were analyzed on a column containing medium tuff. The fluorinated benzoic acids tested include: 2,3-difluorobenzoic acid (23DFB), 3,4-difluorobenzoic acid (34DFB), 2,3,6-trifluorobenzoic acid (236TFB), 2,4,5-trifluorobenzoic acid (245TFB), 3,4,5-trifluorobenzoic acid (345TFB), and pentafluorobenzoic acid (PFB). The FTA include: α,α,α-trifluoro-m-toluic acid (mTFT), α,α,α-trifluoro-o-toluic acid (oTFT), and α,α,α-trifluoro-p-toluic acid (pTFT). The FSA include: 5-fluorosalicylic acid (5FSA) and 3,5-difluorosalicylic acid (35FSA). A minimum of seven injections of each compound were made.

The retention time of each compound was multiplied by the flow rate to determine the retention volume. The mean retention volumes, standard deviations and percent relative standard deviations (%RSD) are listed in Table 1. In comparing the fluorinated organic acids to potassium bromide it can be seen that there is no significant difference in the retention time volumes; they all fall within close to one standard deviation. A comparison between the different groups of compounds is shown in Table 2. From this, it can be seen that the retention volume is not affected by the number of fluorides; there are similar results between 23DFB, 236TFB, and PFB. However, the position of the fluoride can affect the retention volume. It appears that the more polar the compound, the lower the retention volume. Each of the three groups analyzed in this study shows this pattern. The more polar the acid is, the more hydrophillic the tracer becomes. It appears that the size of the compounds is related to the retention volume as well. The more massive the basic structure of the tracer, the larger the retention volume tends to be. The benzoic acids, the less massive group, has the lowest mean retention volume while the salicylic acids, the more massive group, has the highest mean retention volume.

The results provided in this portion of the study show that the fluorinated organic acids compare very favorably to the potassium bromide. In the next quarter, the following compounds will be analyzed using the medium tuff soil: 2,4-difluorobenzoic acid, 2,5-difluorobenzoic acid, 2,6-difluorobenzoic acid, 3,5-difluorobenzoic acid, 2,3,4-trifluorobenzoic acid, 2,4,6-trifluorobenzoic acid, 2,3,4,5-tetrafluorobenzoic acid, 2,3,5,6-tetrafluorobenzoic acid, and some cinnamic acids. This will be followed by identical studies with dark and light tuffs.

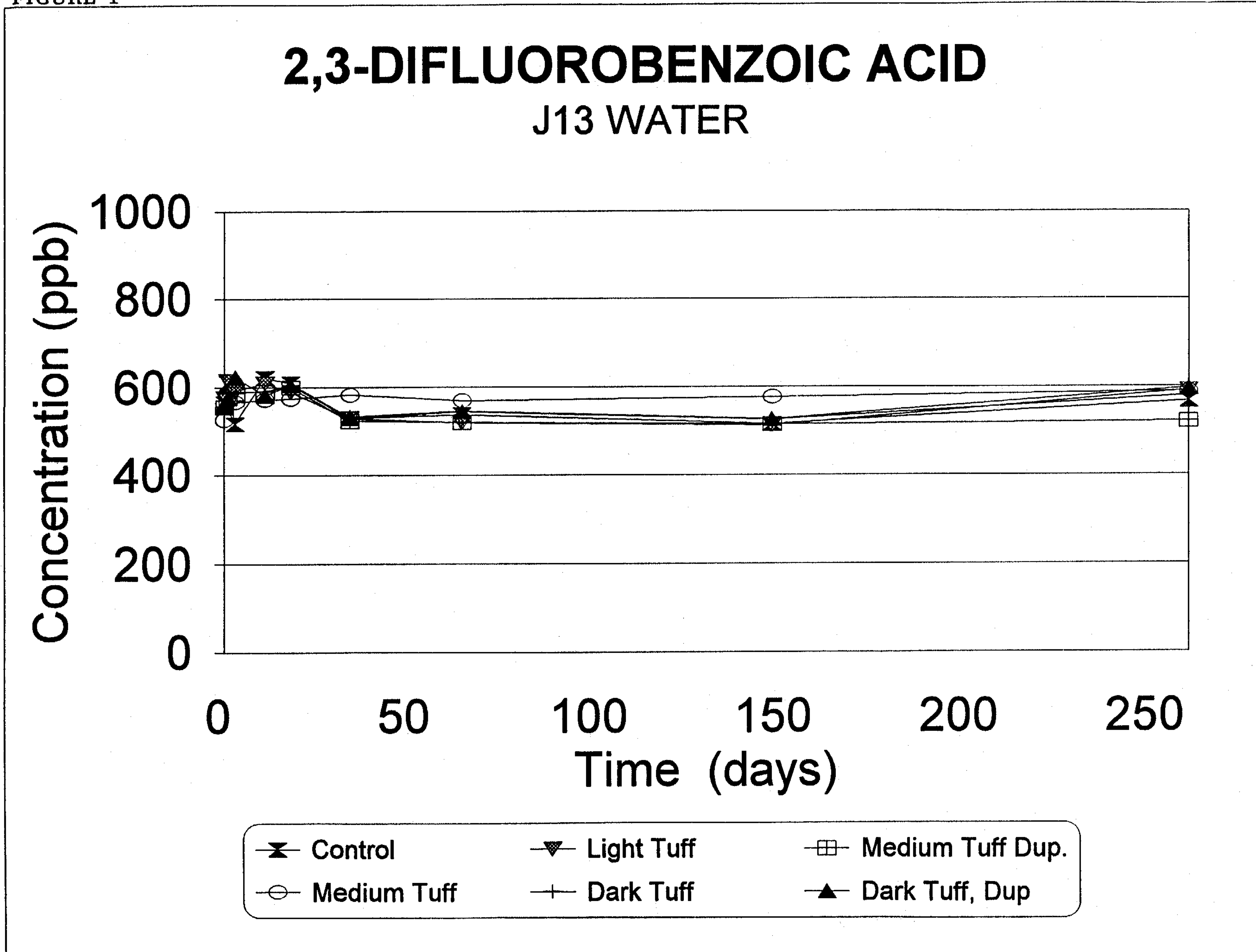
Table 1. Mean values of each compound analyzed

| Benzoic Acids: | n | Mean of Volumes (ml) | Standard Deviation | RSD (%) | Range |
|---|---|---|---|---|---|
| 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 |
| pentafluorobenzoic acid | 9 | 207.27 | 1.18 | 0.57 | 204.38-208.36 |
| Toluic Acids | | | | | |
| 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 |
| Salicylic Acids: | | | | | |
| 5-fluorosalicylic acid | 8 | 215.78 | 1.93 | 0.90 | 213.51-218.40 |
| 3,5-difluorosalicylic acid | 7 | 218.32 | 4.05 | 1.86 | 212.40-223.61 |
| Potassium Bromide | 31 | 211.15 | 3.72 | 1.76 | 205.18-218.01 |

Table 2. Comparison of the fluorinated organic acid groups

| | Mean (ml) | Standard deviation | RSD (%) |
|---|---|---|---|
| Benzoic Acids | 207.44 | 1.88 | 0.91 |
| Toluic Acids | 209.59 | 3.12 | 1.49 |
| Salicylic Acids | 217.05 | 1.80 | 0.83 |
| Difluorobenzoic acids | 207.64 | 2.04 | 0.98 |
| Trifluorobenzoic acids | 207.38 | 2.59 | 1.25 |
| Pentafluorobenzoic acid | 207.27 | 1.18 | 0.57 |
| Potassium Bromide | 211.15 | 3.72 | 1.76 |

FIGURE 1



2,3-DIFLUOROBENZOIC ACID
J13 WATER
Concentration (ppb)
1000
800
600
400
200
0
0
50
100
150
200
250
Time (days)
Control
Light Tuff
Medium Tuff Dup.
Medium Tuff
Dark Tuff
Dark Tuff, Dup

FIGURE 2

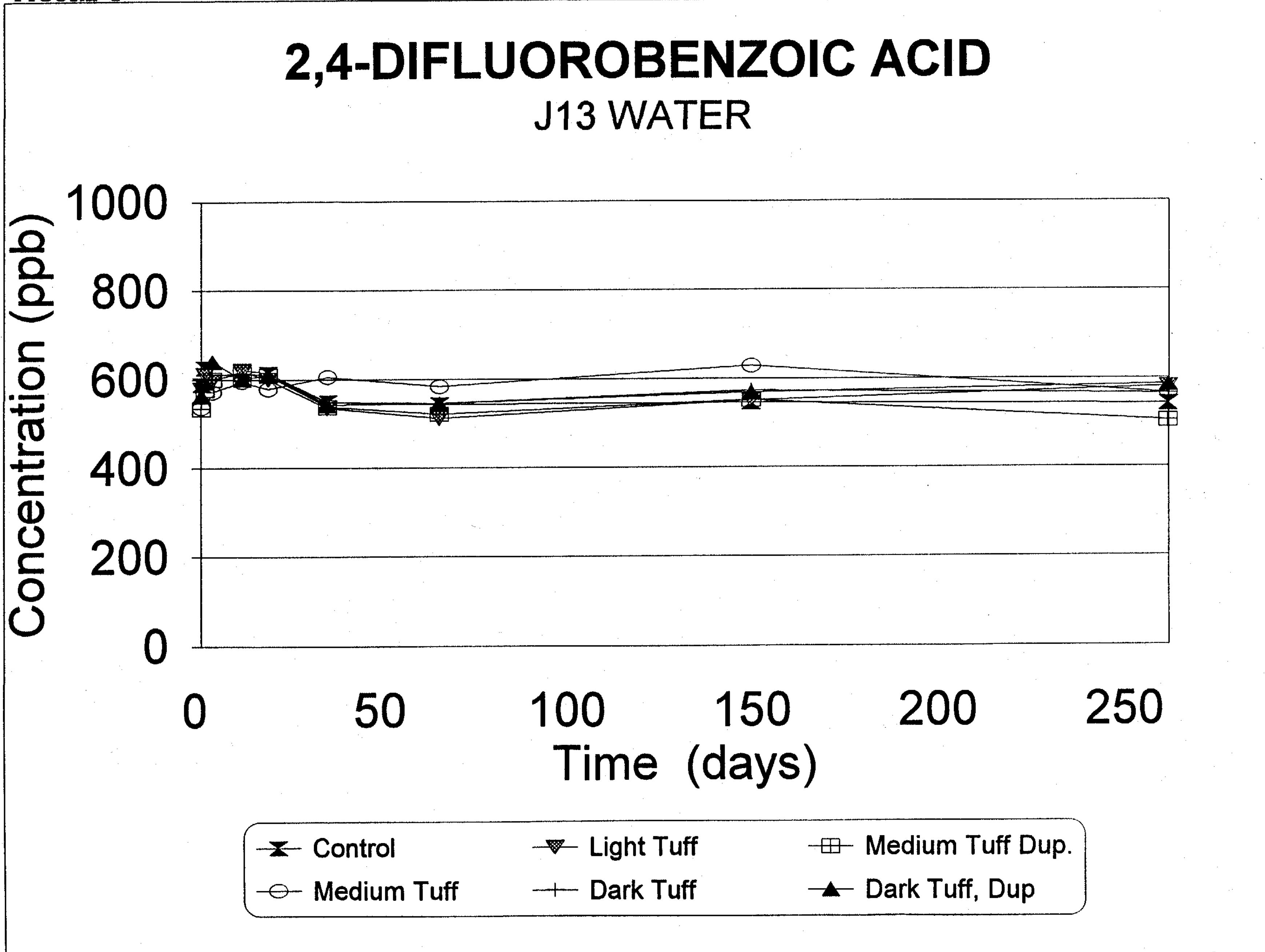

2,4-DIFLUOROBENZOIC ACID
J13 WATER
Concentration (ppb)
1000
800
600
400
200
0
0
50
100
150
200
250
Time (days)
Control
Light Tuff
Medium Tuff Dup.
Medium Tuff
Dark Tuff
Dark Tuff, Dup

FIGURE 3

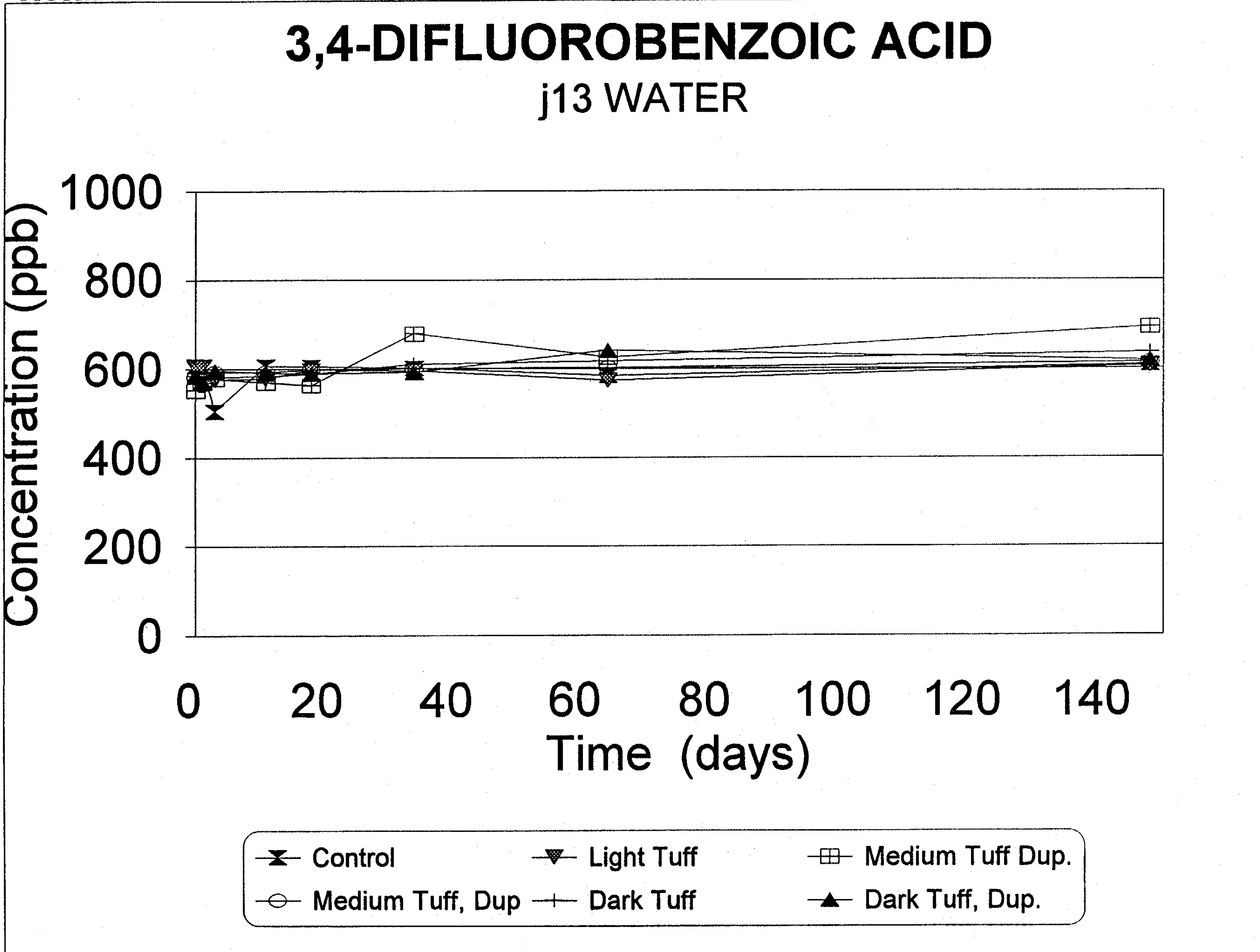

3,4-DIFLUOROBENZOIC ACID
j13 WATER
Concentration (ppb)
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
Time (days)
Control
Light Tuff
Medium Tuff Dup.
Medium Tuff, Dup
Dark Tuff
Dark Tuff, Dup.

FIGURE 4

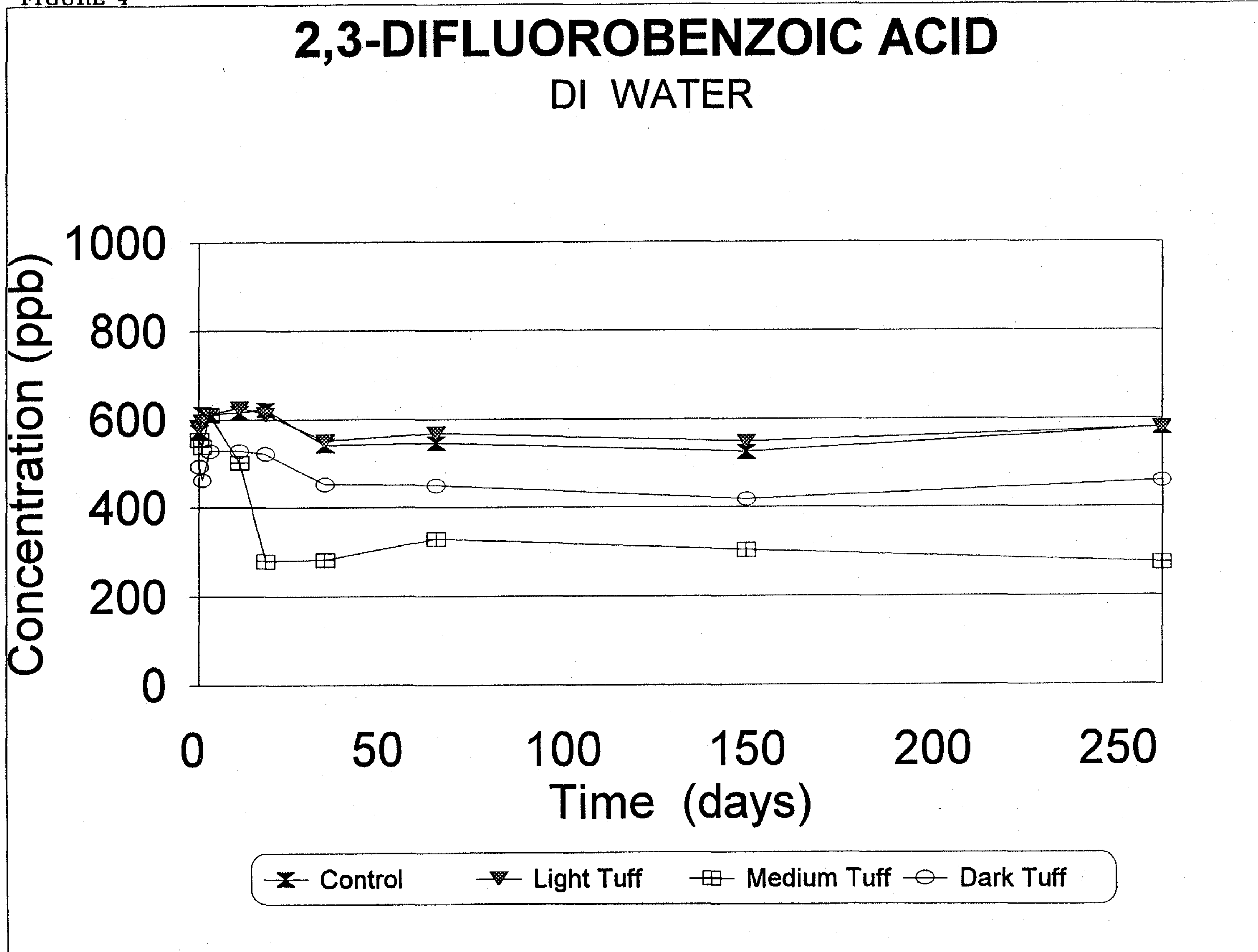

2,3-DIFLUOROBENZOIC ACID
DI WATER
Concentration (ppb)
1000
800
600
400
200
0
0
50
100
150
200
250
Time (days)
Control
Light Tuff
Medium Tuff
Dark Tuff

FIGURE 5

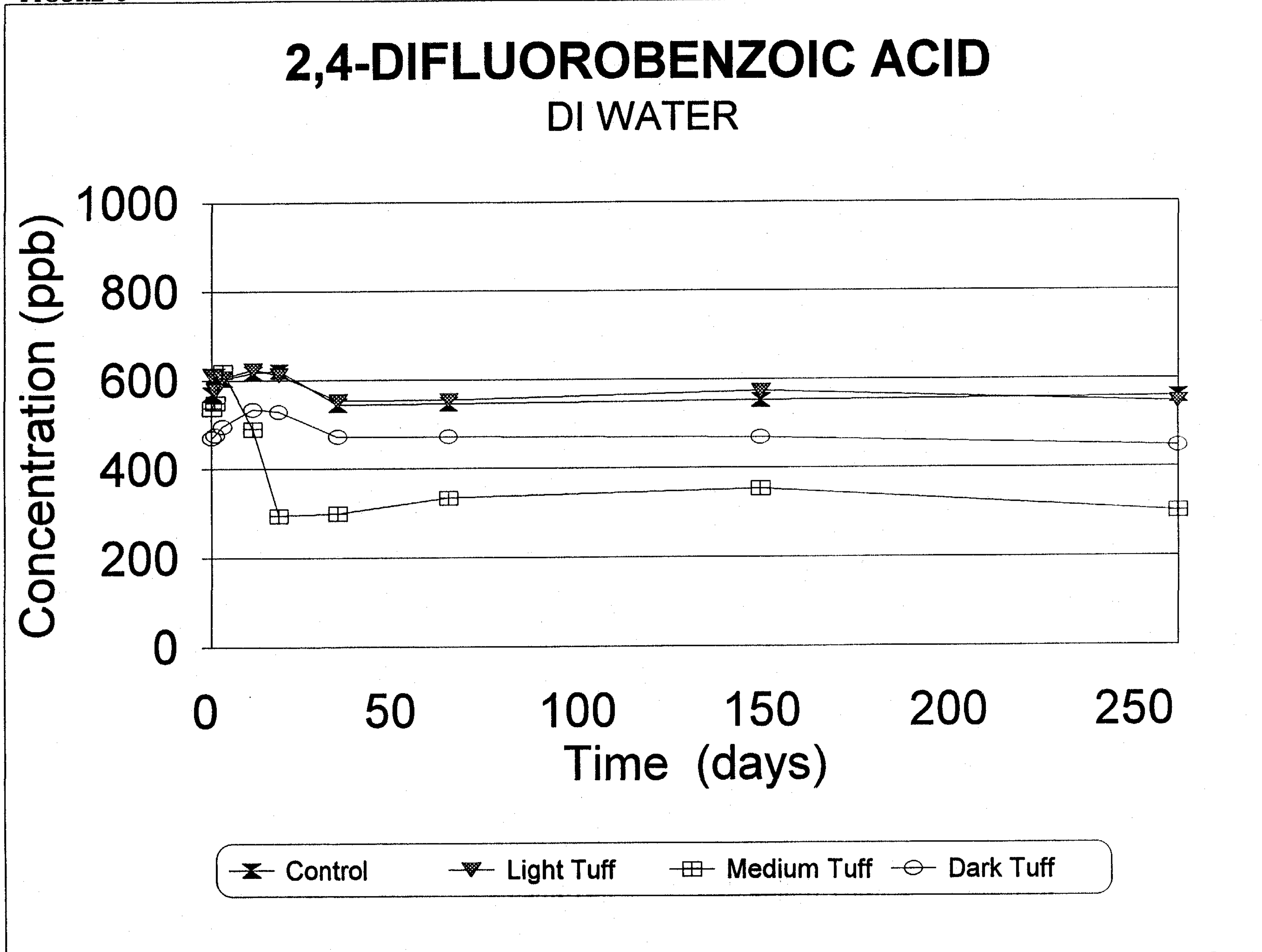

2,4-DIFLUOROBENZOIC ACID
DI WATER
Concentration (ppb)
1000
800
600
400
200
0
0
50
100
150
200
250
Time (days)
Control
Light Tuff
Medium Tuff
Dark Tuff

FIGURE 6

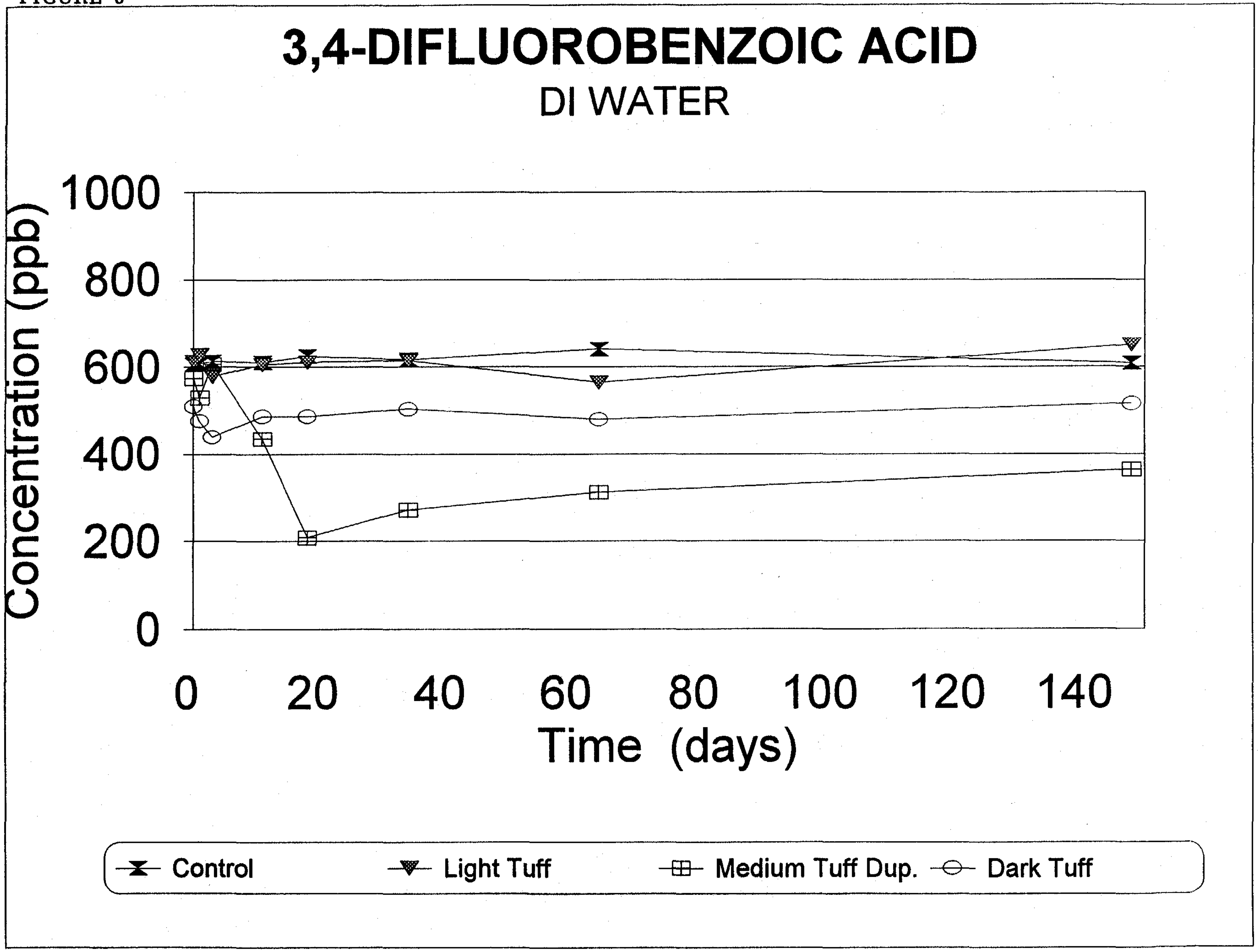
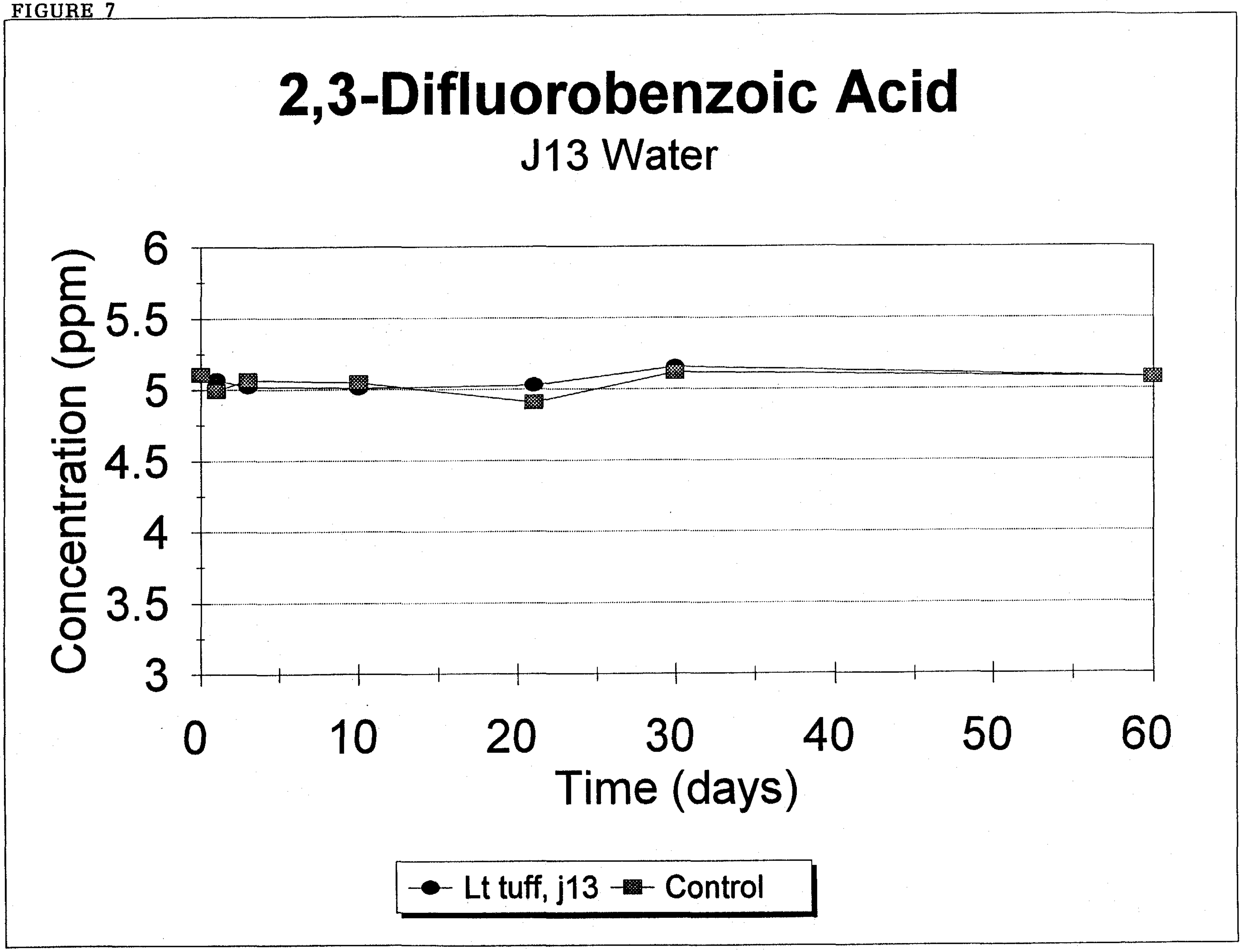
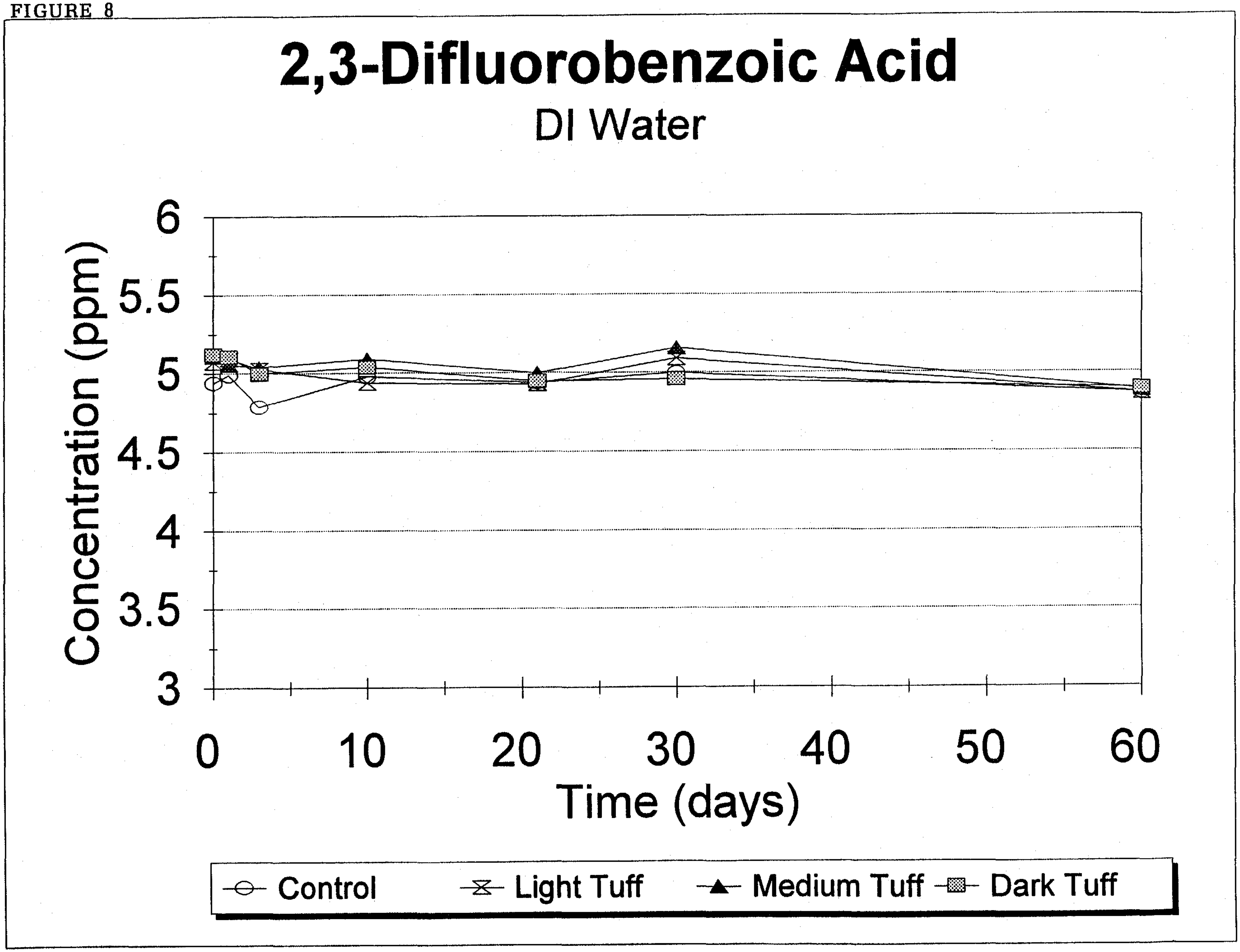

3,4-DIFLUOROBENZOIC ACID
DI WATER
Concentration (ppb)
1000
800
600
400
200
0
0
20
40
60
80
100
120
140
Time (days)
Control
Light Tuff
Medium Tuff Dup.
Dark Tuff

FIGURE 7



2,3-Difluorobenzoic Acid
J13 Water
Concentration (ppm)
6
5.5
5
4.5
4
3.5
3
0
10
20
30
40
50
60
Time (days)
Lt tuff, j13
Control

FIGURE 8



2,3-Difluorobenzoic Acid
DI Water
Concentration (ppm)
6
5.5
5
4.5
4
3.5
3
0
10
20
30
40
50
60
Time (days)
Control
Light Tuff
Medium Tuff
Dark Tuff

FIGURE 9

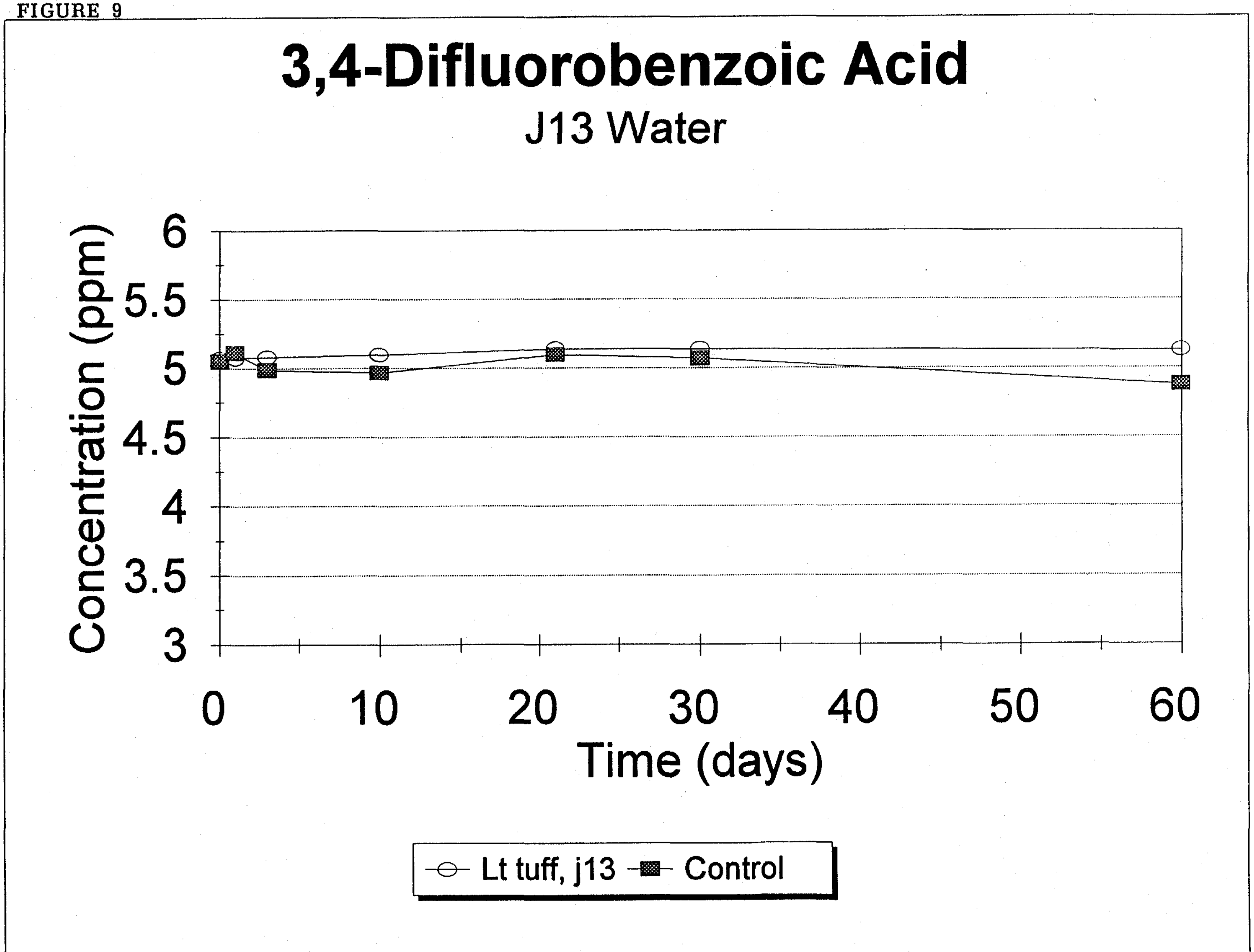

3,4-Difluorobenzoic Acid
J13 Water
Concentration (ppm)
6
5.5
5
4.5
4
3.5
3
0
10
20
30
40
50
60
Time (days)
Lt tuff, j13
Control

FIGURE 10

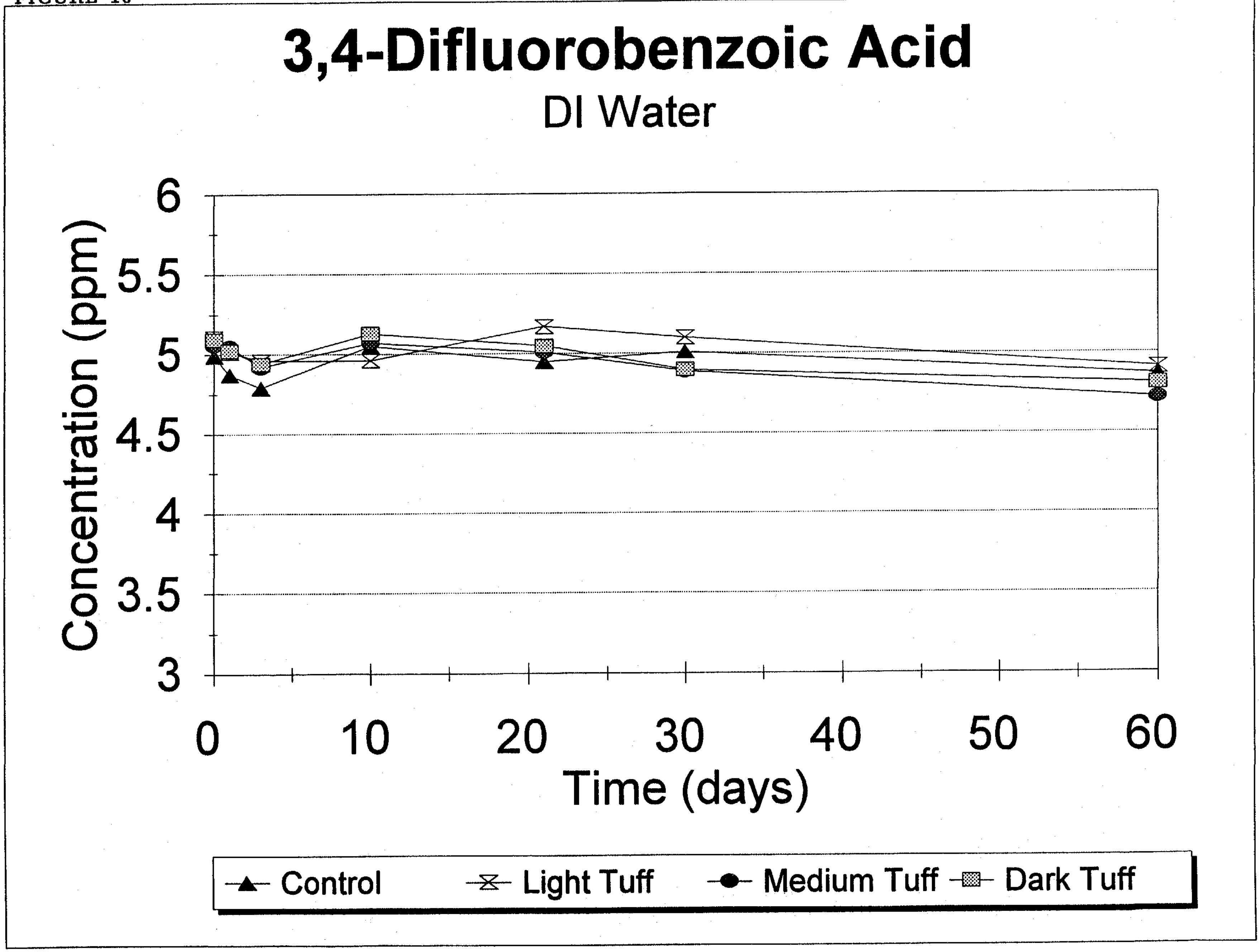

3,4-Difluorobenzoic Acid
DI Water
Concentration (ppm)
6
5.5
5
4.5
4
3.5
3
0
10
20
30
40
50
60
Time (days)
Control
Light Tuff
Medium Tuff
Dark Tuff

FIGURE 11

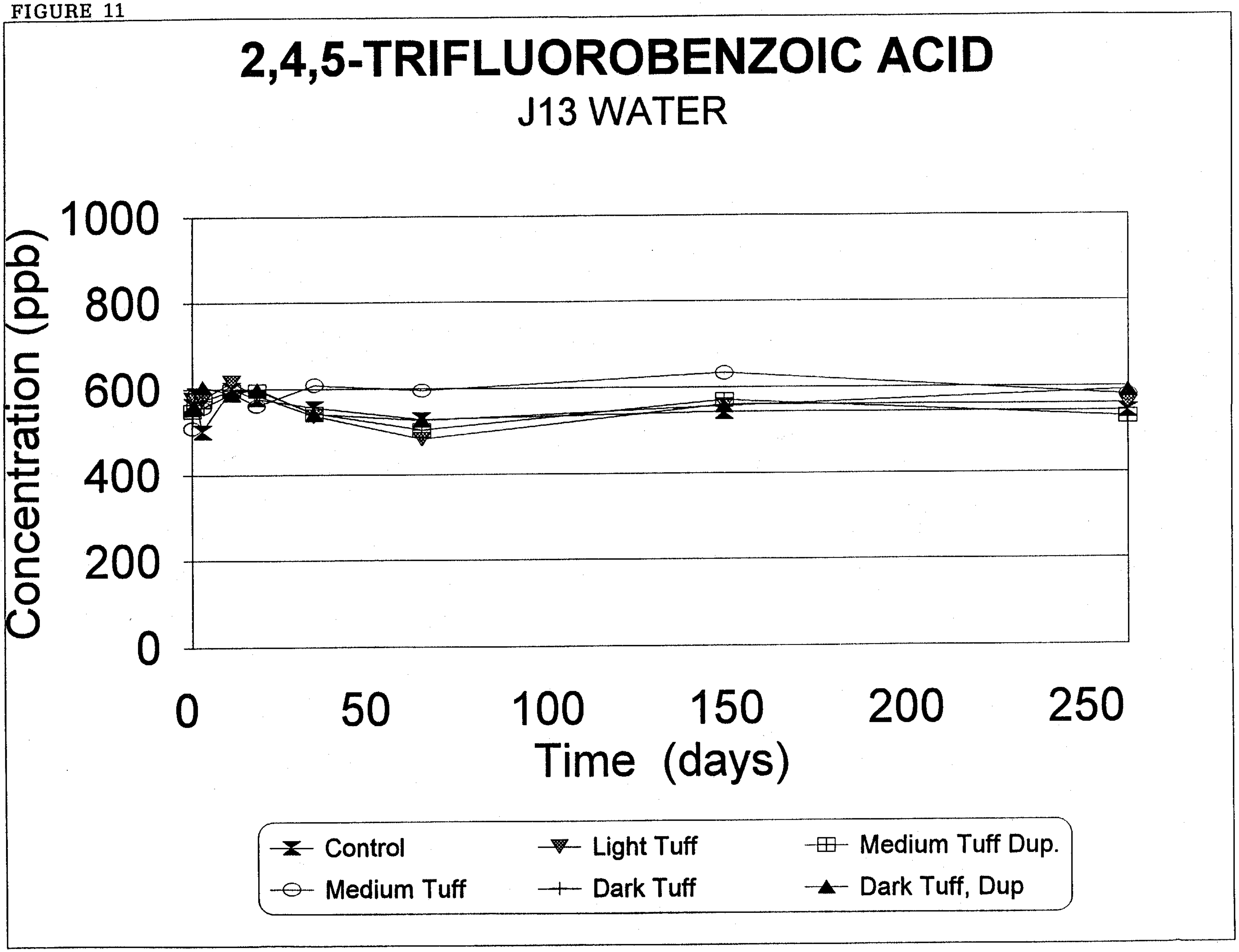
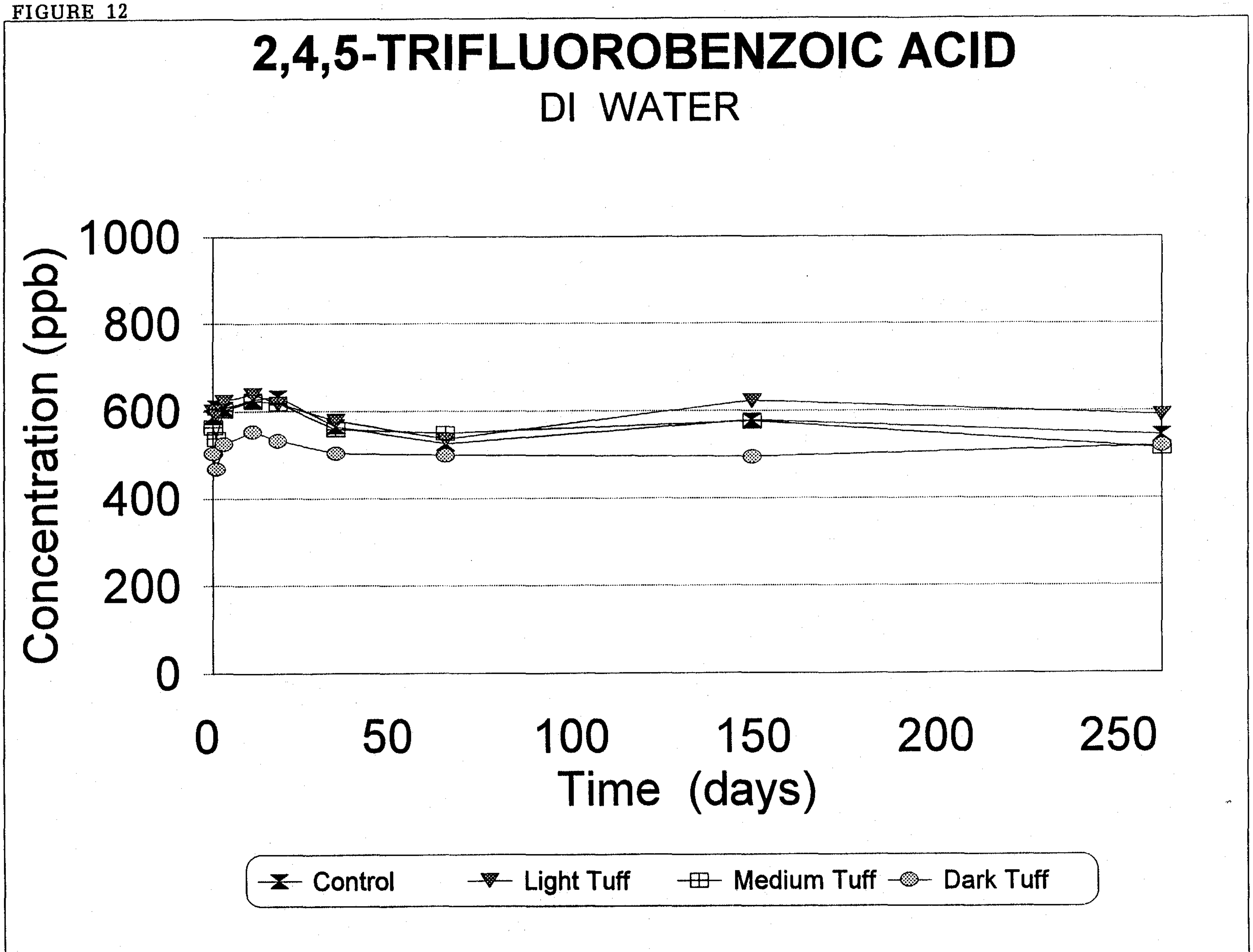

2,4,5-TRIFLUOROBENZOIC ACID
J13 WATER
Concentration (ppb)
1000
800
600
400
200
0
0
50
100
150
200
250
Time (days)
Control
Medium Tuff
Light Tuff
Dark Tuff
Medium Tuff Dup.
Dark Tuff, Dup

FIGURE 12



2,4,5-TRIFLUOROBENZOIC ACID
DI WATER
Concentration (ppb)
1000
800
600
400
200
0
0
50
100
150
200
250
Time (days)
Control
Light Tuff
Medium Tuff
Dark Tuff

FIGURE 13

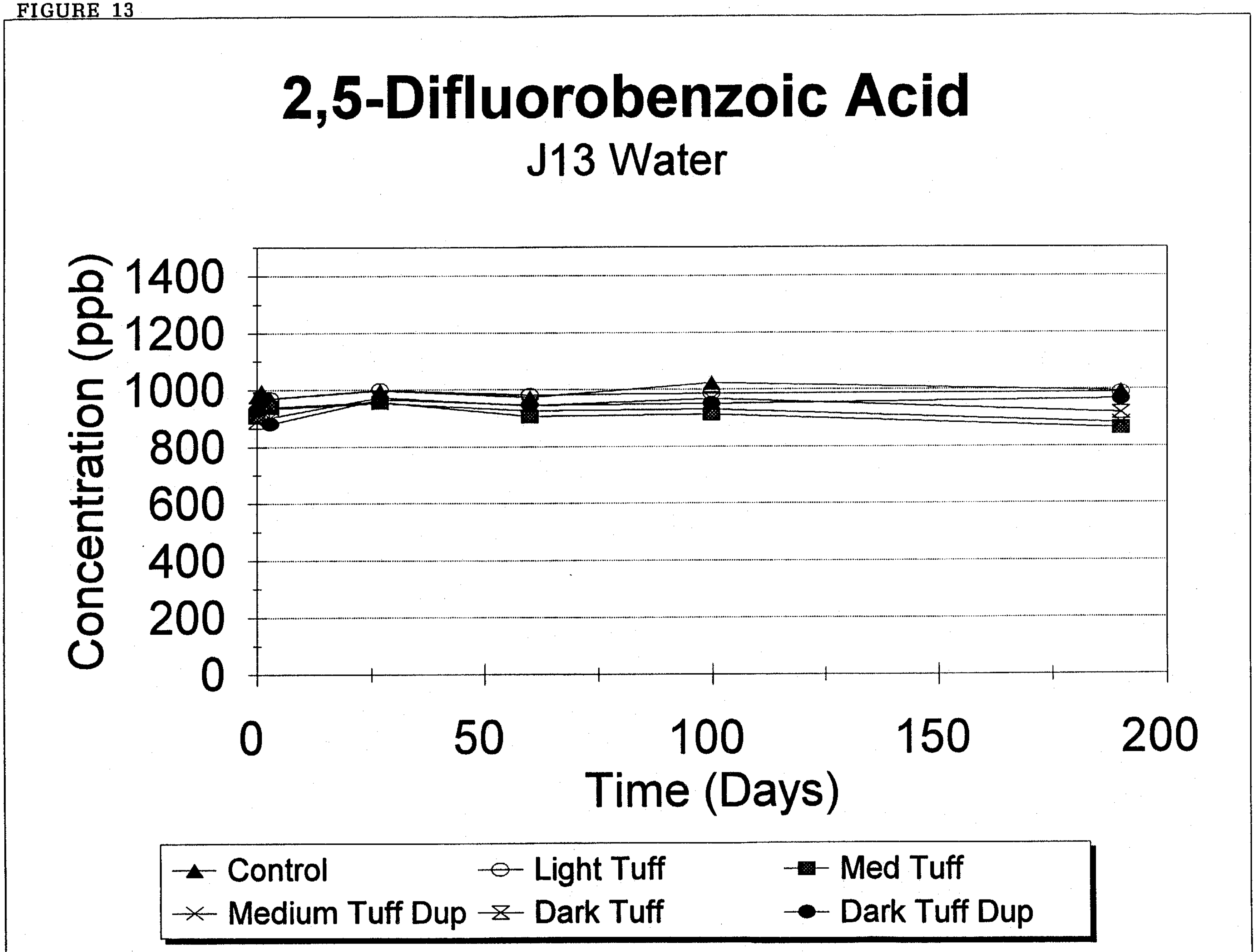
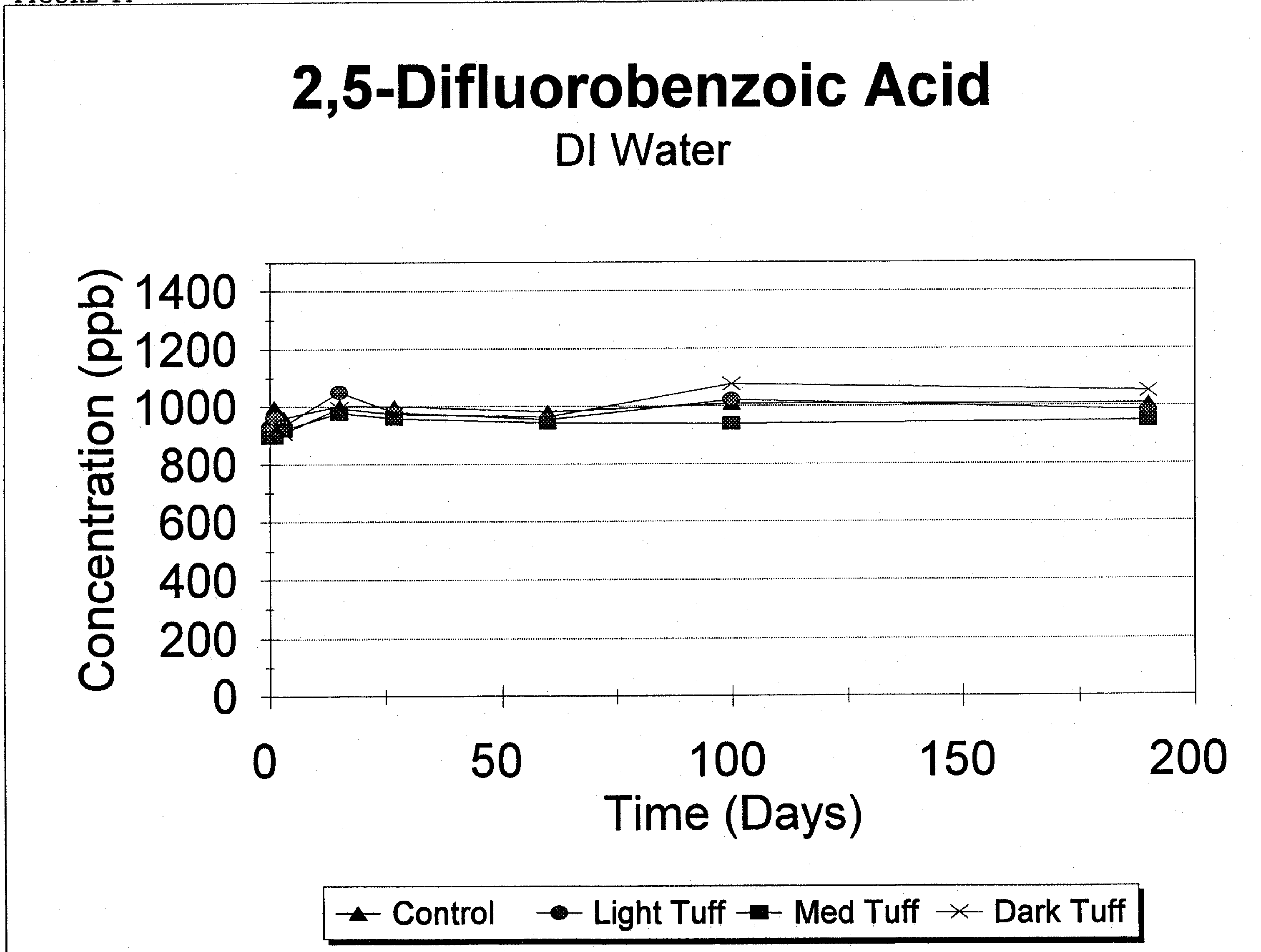
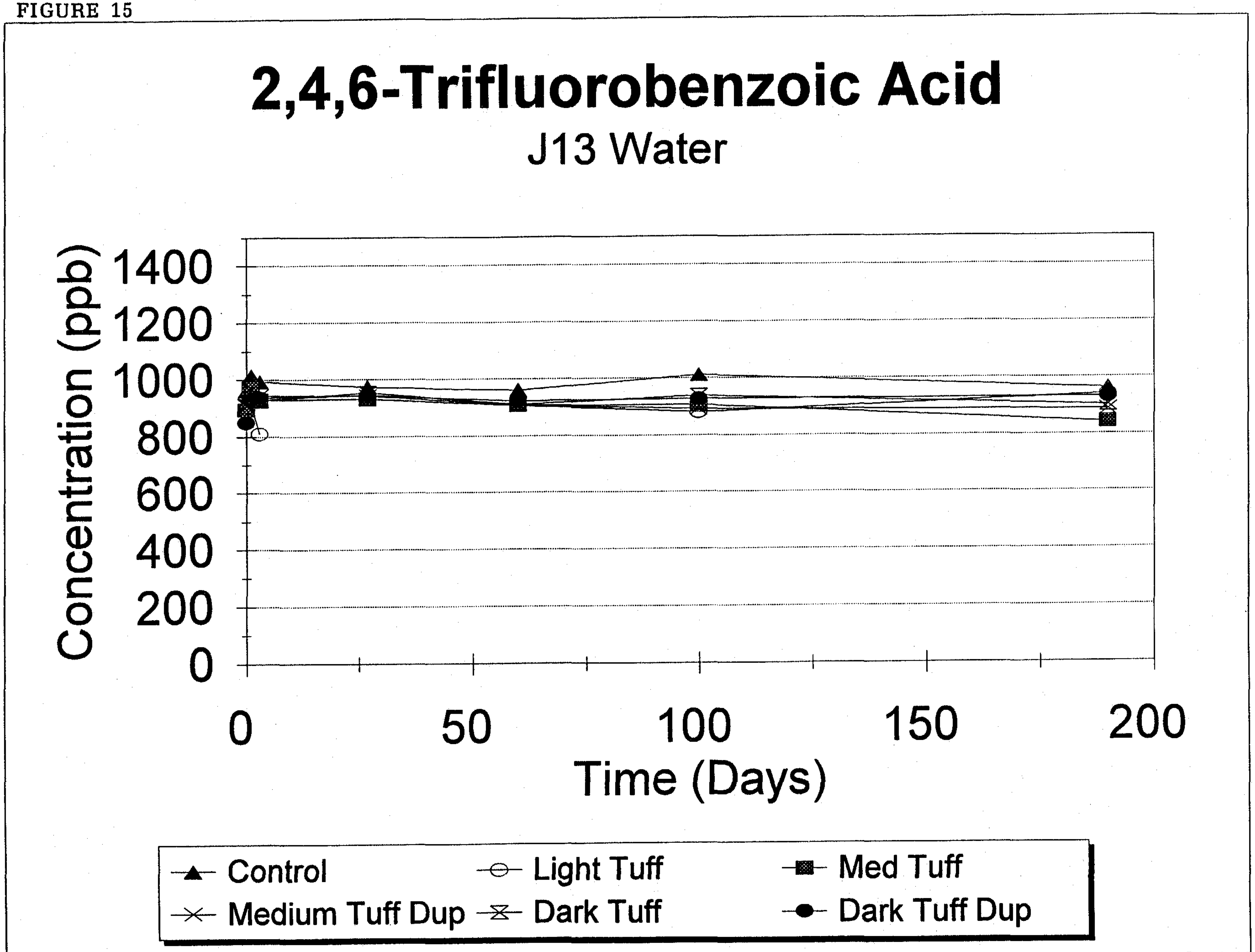

2,5-Difluorobenzoic Acid
J13 Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Medium Tuff Dup
Dark Tuff
Dark Tuff Dup

FIGURE 14



2,5-Difluorobenzoic Acid
DI Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Dark Tuff

FIGURE 15



2,4,6-Trifluorobenzoic Acid
J13 Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Medium Tuff Dup
Dark Tuff
Dark Tuff Dup

FIGURE 16

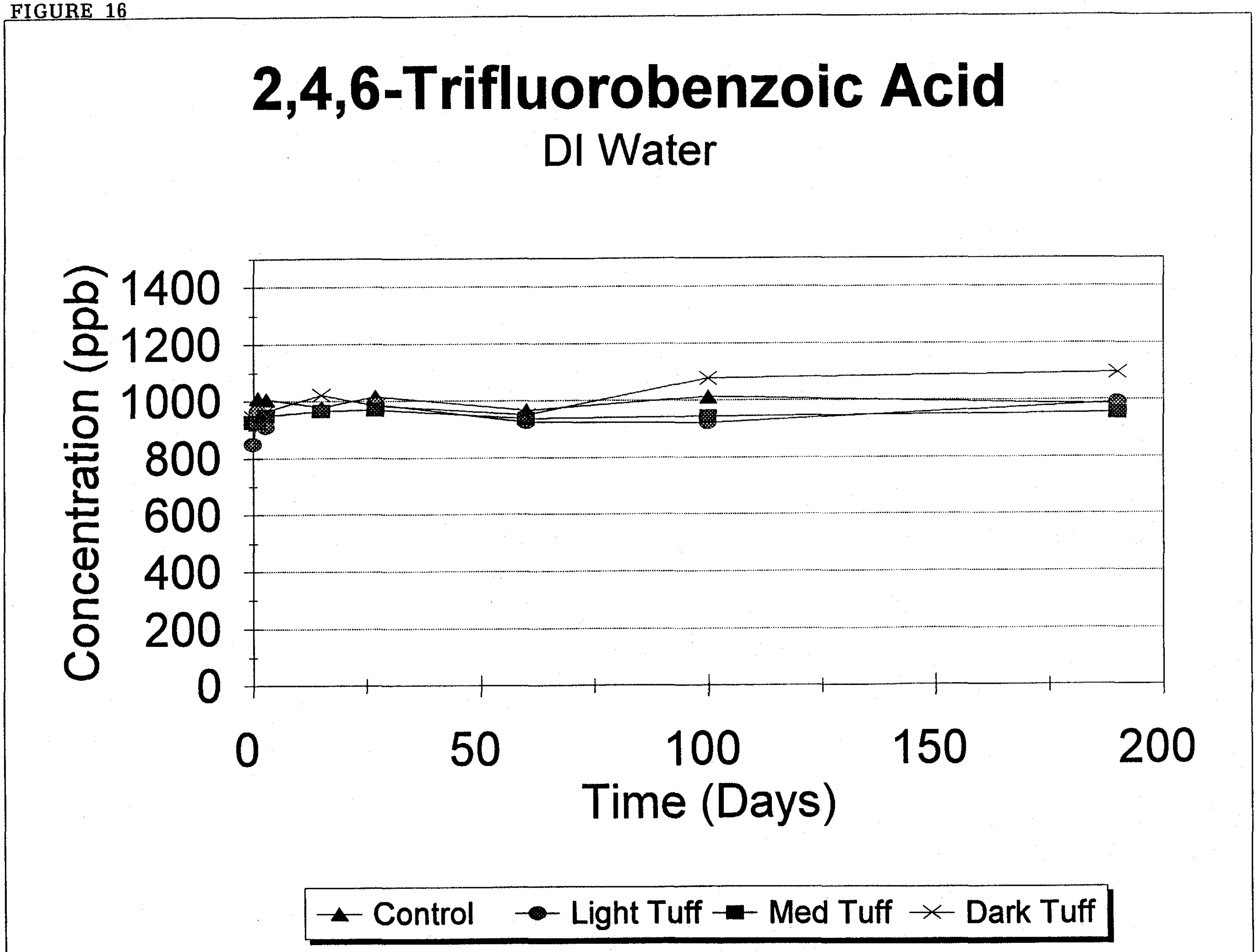

2,4,6-Trifluorobenzoic Acid
DI Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Dark Tuff

FIGURE 17

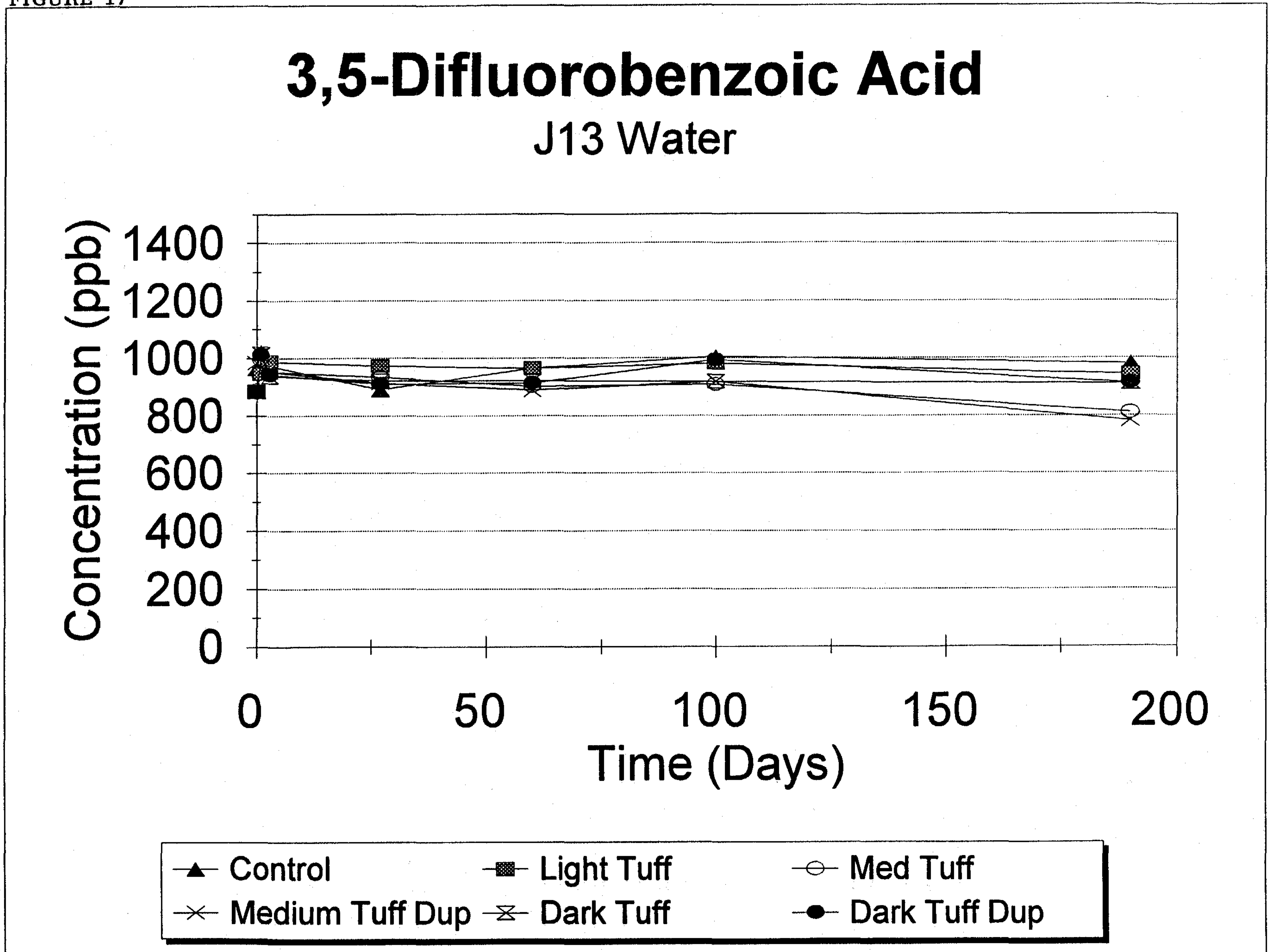

3,5-Difluorobenzoic Acid
J13 Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Medium Tuff Dup
Dark Tuff
Dark Tuff Dup

FIGURE 18

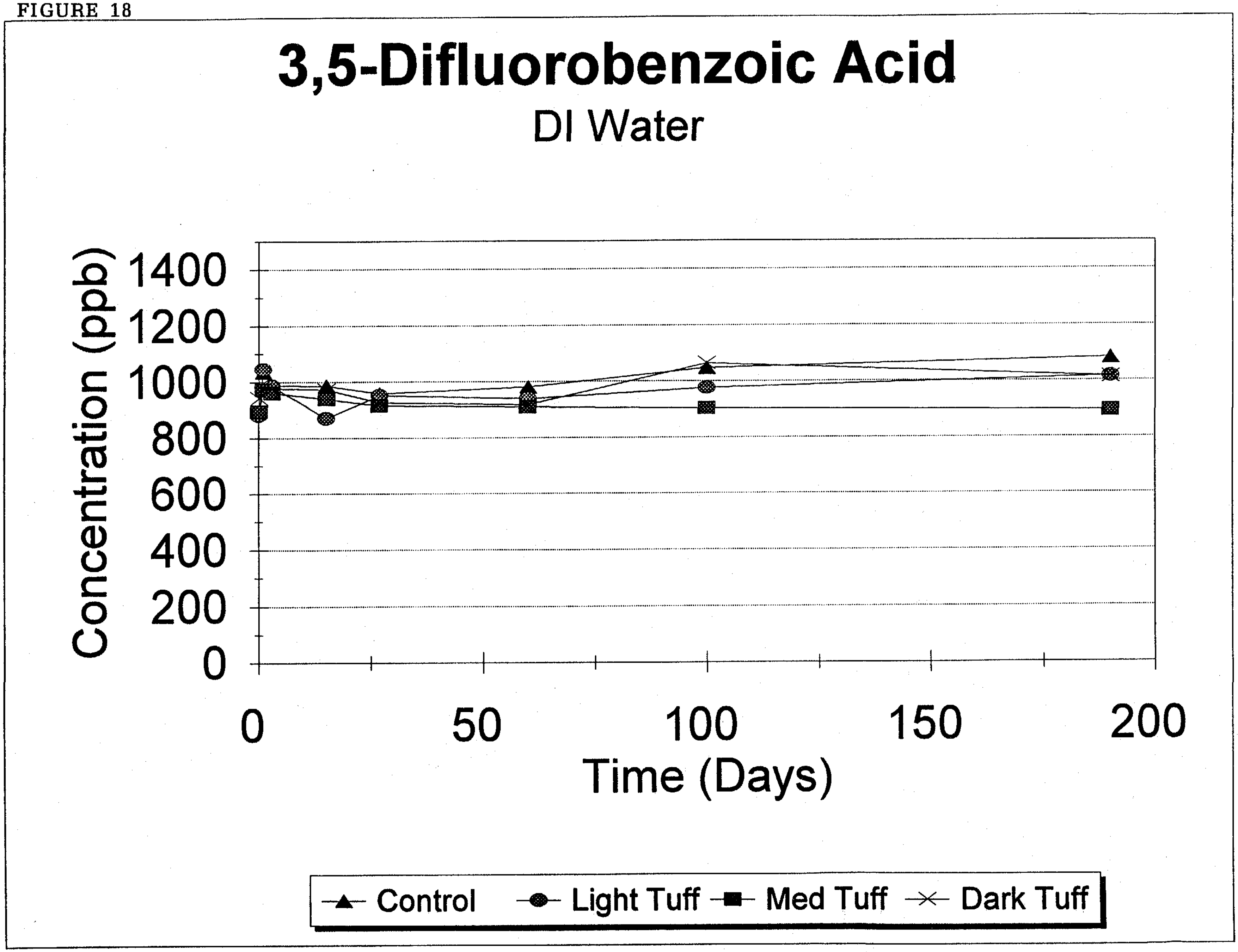
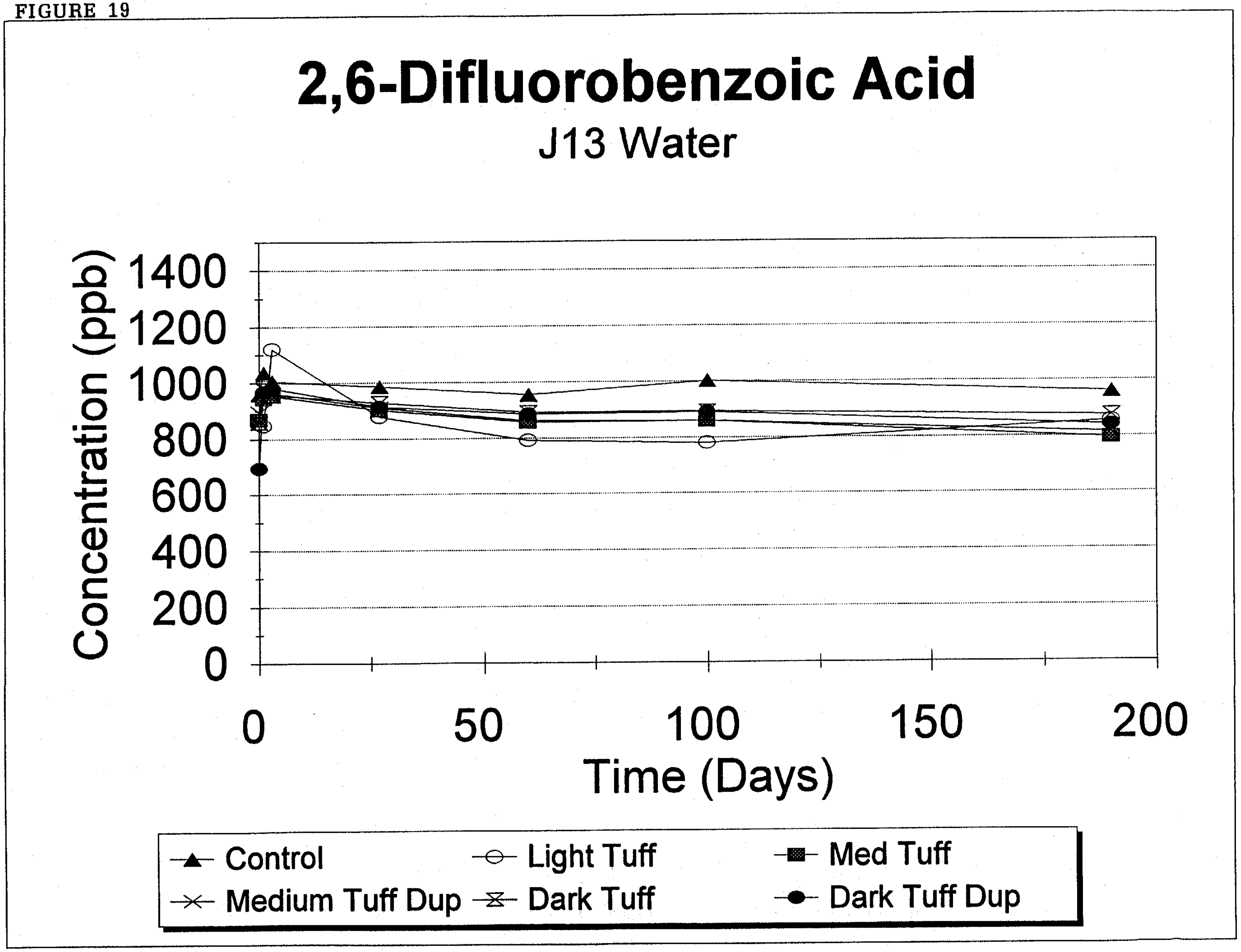
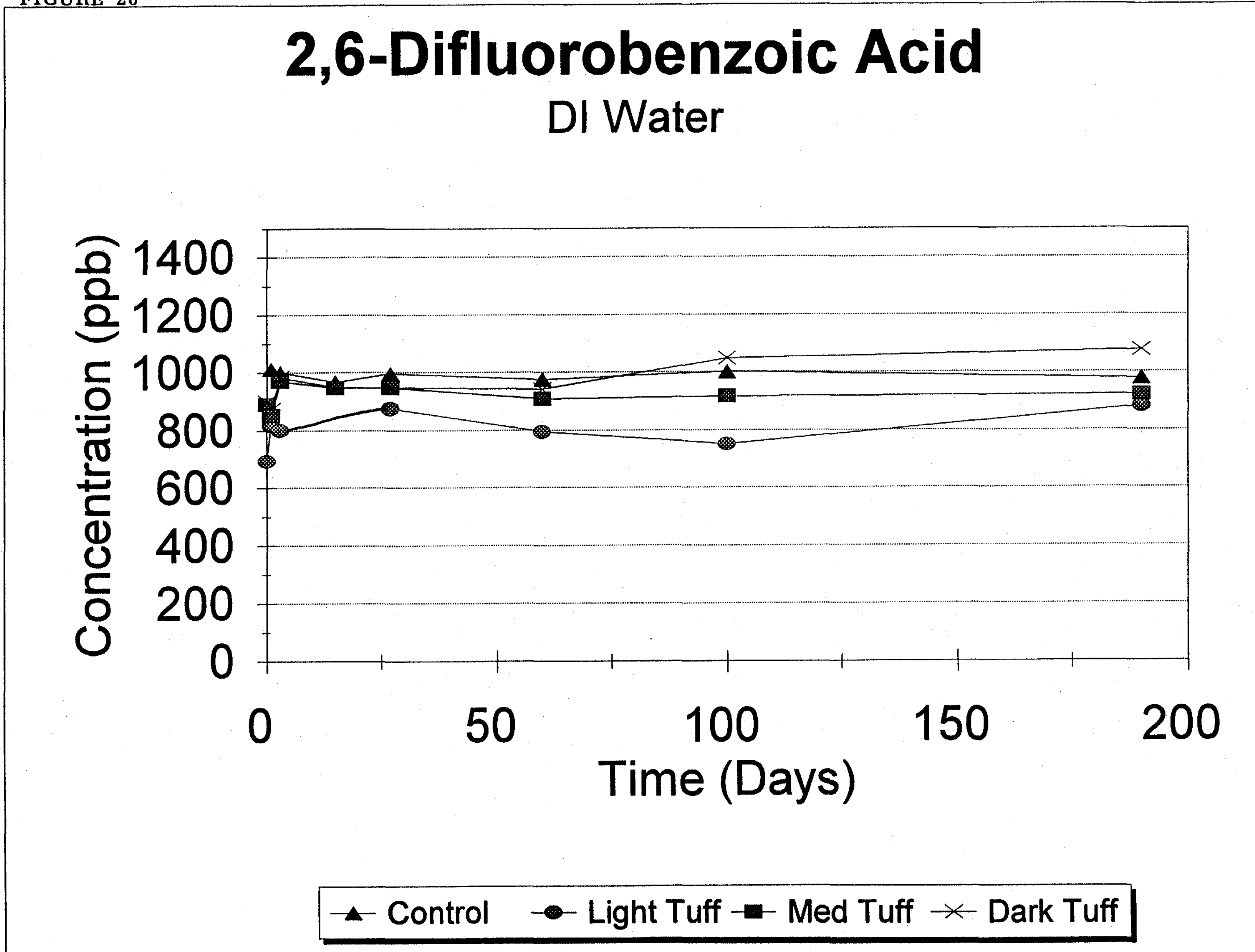

3,5-Difluorobenzoic Acid
DI Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Dark Tuff

FIGURE 19



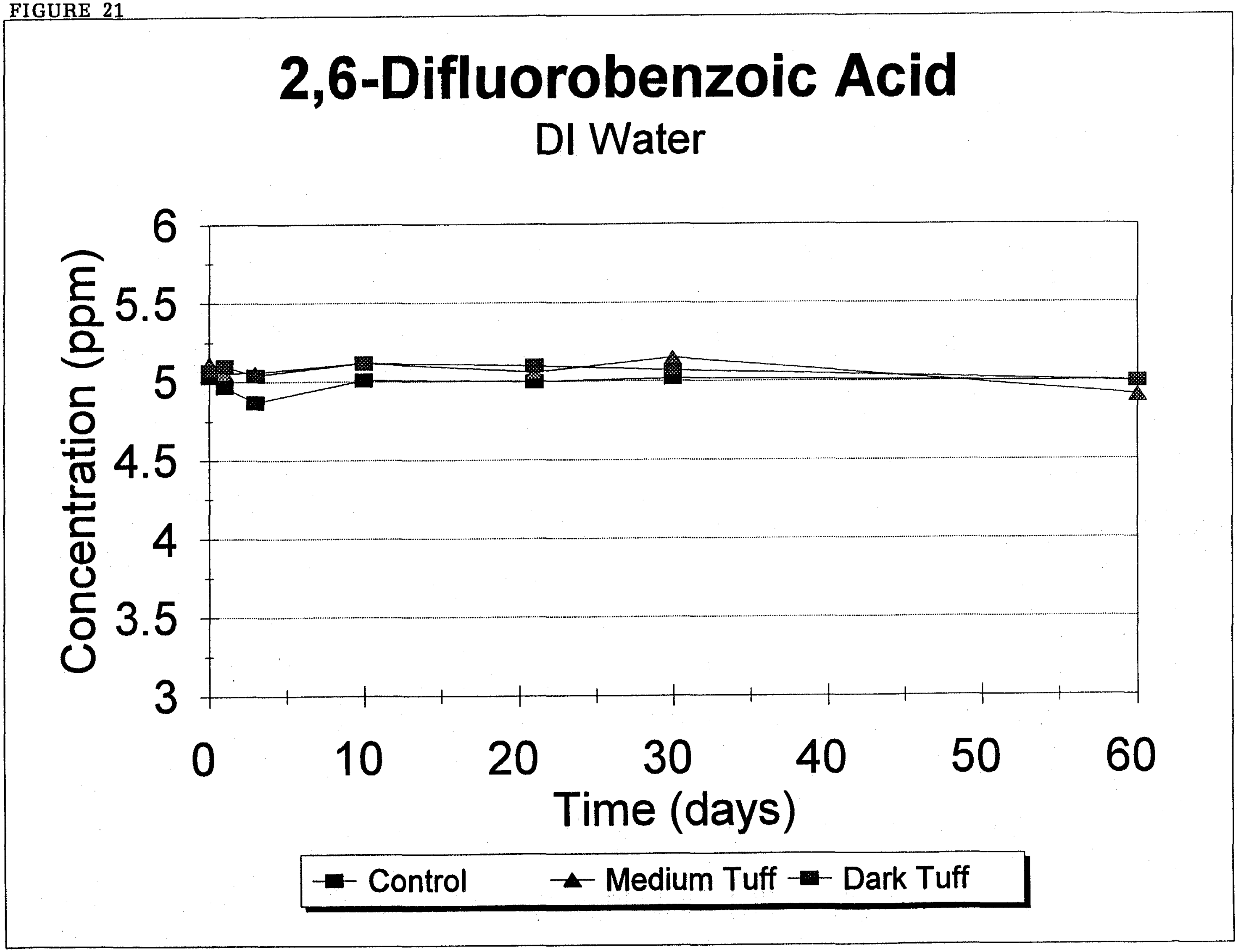
2,6-Difluorobenzoic Acid
J13 Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Medium Tuff Dup
Dark Tuff
Dark Tuff Dup

FIGURE 20



2,6-Difluorobenzoic Acid
DI Water
Concentration (ppb)
1400
1200
1000
800
600
400
200
0
0
50
100
150
200
Time (Days)
Control
Light Tuff
Med Tuff
Dark Tuff

FIGURE 21


2,6-Difluorobenzoic Acid
DI Water
Concentration (ppm)
6
5.5
5
4.5
4
3.5
3
0
10
20
30
40
50
60
Time (days)
Control
Medium Tuff
Dark Tuff