DOE/NV/10872--T204

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

PROGRESS REPORT
APRIL 1, 1995 to JUNE 3, 1995

DOE Cooperative Agreement
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The focus for this quarter has been on completing the laboratory studies in preparation for the C-Well tracer tests. These studies include measuring the solubilities for each of the fluorinated benzoic acids as well as determining the stabilities of these compounds through both batch and column testing. A batch test for four pyridone compounds was also initiated.

The Tracer QA procedures were approved by the YM USGS on May 24, 1995. The batch testing was repeated using these procedures.

BATCH TESTING

The batch tests provide information on the stabilities of the potential tracers in an environment that closely simulates that of the C Wells. Mixtures containing these compounds in J-13 water are exposed to three types of tuffs (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 light weight, 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.

A control is also prepared which contains each of the tracers in J-13 water but no tuff. The concentration of each compound is measured periodically to determine changes that occur with time. High performance liquid chromatography (HPLC) is used to separate each of the compounds within the mixture and an ultraviolet (UV) or fluorescence detector is used for detection and quantitation.

Four sets of batch tests are currently in progress. One set consists of four pyridones and the other three consist of the fluorinated benzoic acids. Three sets containing the benzoic acids are required due to the inability to separate several of the compounds using HPLC (2,3,6-trifluorobenzoic acid, 2,6-difluorobenzoic acid and 2,3,5,6-tetrafluorobenzoic acid co-elute and 3,4-difluorobenzoic acid and 3,5-difluorobenzoic acid co-elute).

Batch Test 1

The following compounds were included in the first batch test:

2,4-Difluorobenzoic acid (2,4-DFBA)
2,5-Difluorobenzoic acid (2,5-DFBA)
3,4-Difluorobenzoic acid (3,4-DFBA)
2,3,4-Trifluorobenzoic acid (2,3,4-TFBA)
2,4,5-Trifluorobenzoic acid (2,4,5-TFBA)
2,4,6-Trifluorobenzoic acid (2,4,6-TFBA)
2,3,4,5-Tetrafluorobenzoic acid (2,3,4,5-TFBA)
2,3,5,6-Tetrafluorobenzoic acid (2,3,5,6-TFBA)
Pentafluorobenzoic acid (PFBA)

Exceptional stabilities for these compounds were observed over thirty days (see Figures 1-9). A large peak observed in all of the light tuff samples interfered with the quantitation of 2,4,6-TFBA and 2,3,5,6-TFBA. The light tuff data are therefore not included for these compounds. A larger change in concentration (10%) was observed for PFBA in the light tuff. This may be due to interference by this peak as well. An attempt to extract out this interference from the sixty day samples will be made, thus, providing the final concentration for these compounds. A peak also existed in both the medium and dark tuffs at T=5 and T=10 that interfered with the quantitation of 2,4,6-TFBA. By T=20 this peak disappeared and quantitation of this compound in both the T=20 and T=30 samples was therefore possible (see Figure 6).

A duplicate sample in medium tuff was also prepared for these compounds. The two medium tuff samples agree within 1% for all compounds.

Batch Test 2

The following compounds were included in the second batch test:

2,3-Difluorobenzoic acid (2,3-DFBA)
3,5-Difluorobenzoic acid (3,5-DFBA)
2,3,6-Trifluorobenzoic acid (2,3,6-TFBA)
3,4,5-Trifluorobenzoic acid (3,4,5-TFBA)
m-Trifluoromethylbenzoic acid (m-TFMBA)
o-Trifluoromethylbenzoic acid (o-TFMBA)
p-Trifluoromethylbenzoic acid (p-TFMBA)

These compounds were also quite stable over thirty days (see Figures 10-16). An interference in the light tuff existed in these samples and resulted in the inability to quantitate 2,3,6-TFBA. The light tuff data are therefore not included for this compound. The sixty day, light tuff samples will be extracted in an attempt to remove this interference.

Duplicate samples in light and dark tuff were prepared for these compounds. These samples agree within 2% for all compounds.

Batch Test 3

The following compounds were included in the third batch test:

2,6-Difluorobenzoic acid (2,6-DFBA)
2,4,5-Trifluorobenzoic acid (2,4,5-TFBA)
2,4,6-Trifluorobenzoic acid (2,4,6-TFBA)
Pentafluorobenzoic acid (PFBA)

This batch test was required for 2,6-DFBA only. Batch testing for 2,4,6-TFBA and PFBA was repeated because of the difficulties observed during the first test. Results similar to batch test 1 were observed for these compounds. The large interfering peak in the light tuff made quantitation of 2,6-DFBA and 2,4,6-TFBA impossible. The data are therefore not included for these compounds in the light tuff. An interfering peak in the medium and dark tuff resulted in poor

quantitation of 2,4,6-TFBA in these samples as well (see Figure 19). These compounds were shown to be quite stable when accurate quantitation was possible (see Figure 17-20).

Batch Test 4

Four derivatives of 2-pyridone were included in this batch test:

3-Amide 2-Pyridone
3-Amide 2-Pyridone 1-Methyl
3-Methyl Ester 2-Pyridone
3-Carboxyl 2-Pyridone

These compounds are highly fluorescent and can therefore be detected at the low ppb levels. Because of the low detection limits, the pyridone compounds are good candidates for use in the preliminary C-Well tracer test.

Two of these compounds, 3-Amide 2-Pyridone and 3-Amide 2-Pyridone 1-Methyl, were found to be stable in both the light and dark tuff (see Figures 21 and 22). A decrease in the concentration of these compounds was observed for both the 3-Amide 2-Pyridone (19%) and 3-Amide 2-Pyridone 1-Methyl (42%) in the medium tuff. Significant variability was observed for the other two compounds over 20 days (see Figures 23 and 24). The cause of this variability is unknown at this time.

Column Tests

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 light and dark tuffs using a 28 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. Seven injections of each compound were made for each tuff. The elution volume for each compound and tuff was calculated by multiplying the retention time by the measured flow rate. The mean elution volume, the standard deviation, and the relative standard deviation (RSD) for each compound tested are listed in Tables 1 and 2. Bromide, which is considered to be a conservative tracer, was used as a reference compound for each column. Two or three injections of potassium bromide were made per day and the ratios of the elution volumes, analyte/bromide, were calculated. This ratio is also listed in Tables 1 and 2.

The ratios of all acids to bromide, except the 2,3-difluorobenzoic and o-toluic, were less than one. This indicates faster travel through the column than bromide. If it is assumed that bromide (potassium bromide) does not sorb to the tuff then all the benzoic and toluic acids also act conservatively thus confirming the results obtained from batch testing.

Table 1. Mean Elution Values of Compounds tested on Dark Tuff

Compound	Mean Elution Volume(ml)	Standard Deviation	RSD (%)	Ratio of Elution Volumes (Analyte/Bromide)
2,3-Difluorobenzoic acid	178.6	6.47	3.62	1.042
2,4-Difluorobenzoic acid	162.6	4.78	2.94	.950
2,5-Difluorobenzoic acid	152.8	7.26	4.75	.947
2,3,4-Trifluorobenzoic acid	159.6	10.8	6.79	.972
2,3,6-Trifluorobenzoic acid	170.1	2.17	1.28	.998
2,4,5-Trifluorobenzoic acid	173.8	2.09	2.09	.988
2,4,6-Trifluorobenzoic acid	134.6	3.48	2.58	.961
α,α,α-Trifluoro-*o*-toluic acid	139.4	4.04	2.90	1.003
α,α,α-Trifluoro-*p*-toluic acid	164.4	8.34	5.08	.986

Table 2. Mean Elution Values of Compounds tested on Light Tuff

Compound	Mean Elution Volume(ml)	Standard Deviation	RSD (%)	Ratio of Elution Volumes (Analyte/Bromide)
2,3-Difluorobenzoic acid	302.1	6.38	2.11	.935
2,4-Difluorobenzoic acid	285.6	11.6	4.06	.910
2,5-Difluorobenzoic acid	292.0	6.03	2.06	.984
2,6-Difluorobenzoic acid	288.0	9.04	3.14	.945
3,4-Difluorobenzoic acid	283.8	7.98	2.81	.972
3,5-Difluorobenzoic acid	303.0	9.34	3.08	.950
2,3,4-Trifluorobenzoic acid	292.5	8.59	2.94	.944
2,3,6-Trifluorobenzoic acid	292.9	6.03	2.06	.956
2,4,5-Trifluorobenzoic acid	283.3	9.13	3.22	.925
2,4,6-Trifluorobenzoic acid	286.3	17.2	6.01	.956
3,4,5-Trifluorobenzoic acid	291.7	3.34	1.15	.951
2,3,4,5-Tetrafluorobenzoic acid	291.9	10.9	3.74	.909
2,3,5,6-Tetrafluorobenzoic acid	295.9	13.2	4.45	.936
Pentafluorobenzoic acid	284.4	8.52	3.00	.923
α,α,α-Trifluoro-*o*-toluic acid	280.2	8.52	3.04	.917
α,α,α-Trifluoro-*p*-toluic acid	308.8	17.1	5.82	.950
α,α,α-Trifluoro-*m*-toluic acid	292.4	14.9	5.10	.913

Solubility Studies

The seventeen fluorinated benzoic acids were tested to insure that concentration levels of 20% (200 g/L) in J-13 could be achieved. The solubilities of these compounds are dependent on pH, requiring the addition of a strong base such as sodium hydroxide in order to obtain these highly concentrated solutions. Concentrations of 20% for all compounds in J-13 water were achieved at a pH of 14.

Future Studies

All batch testing will be completed during the next quarter. A laboratory audit will also take place. A chemist and analytical instrumentation will also be provided for the analysis of all samples collected during the preliminary C-Well tracer test. This test should occur during the next quarter.

Figure 1

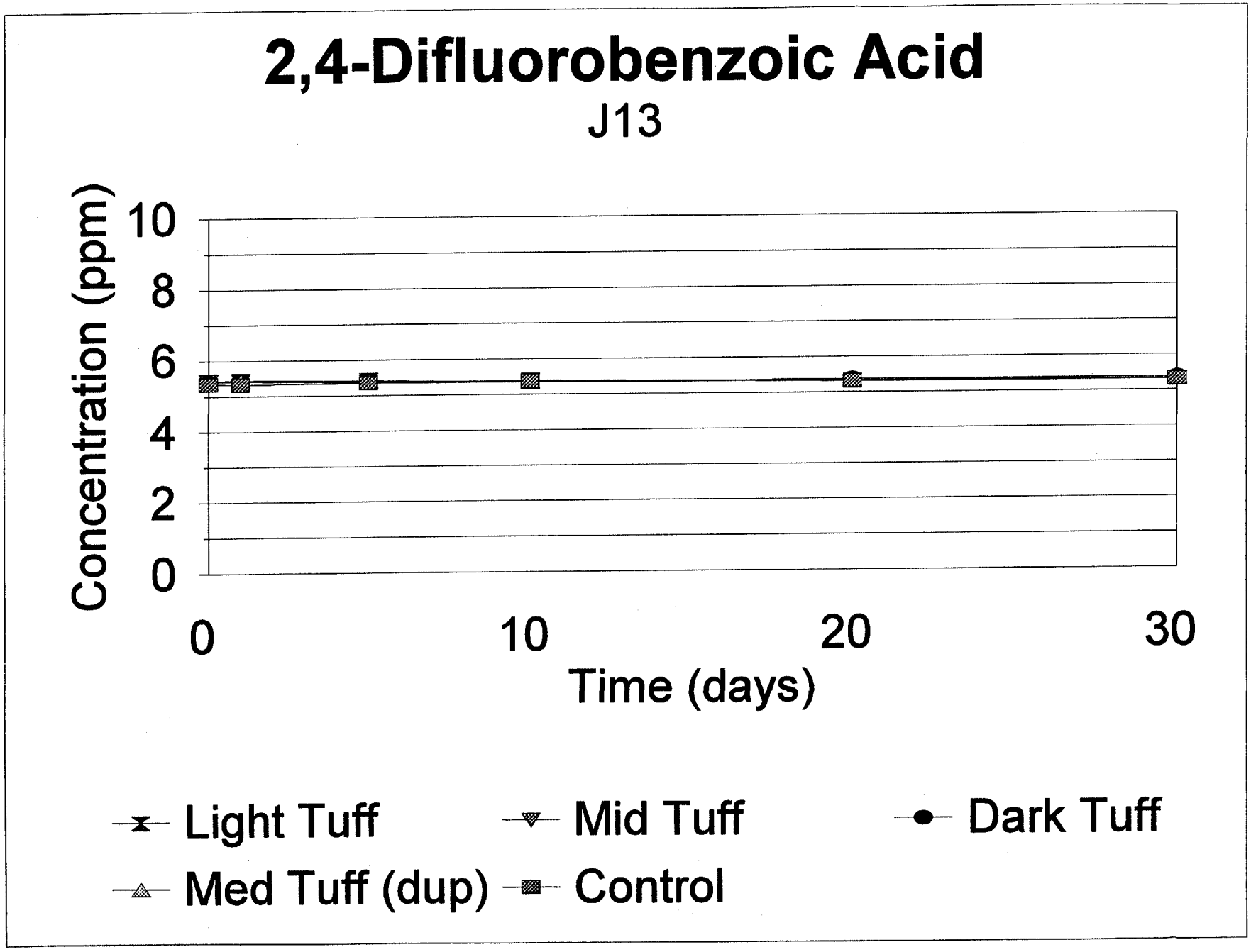

2,4-Difluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Mid Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 2

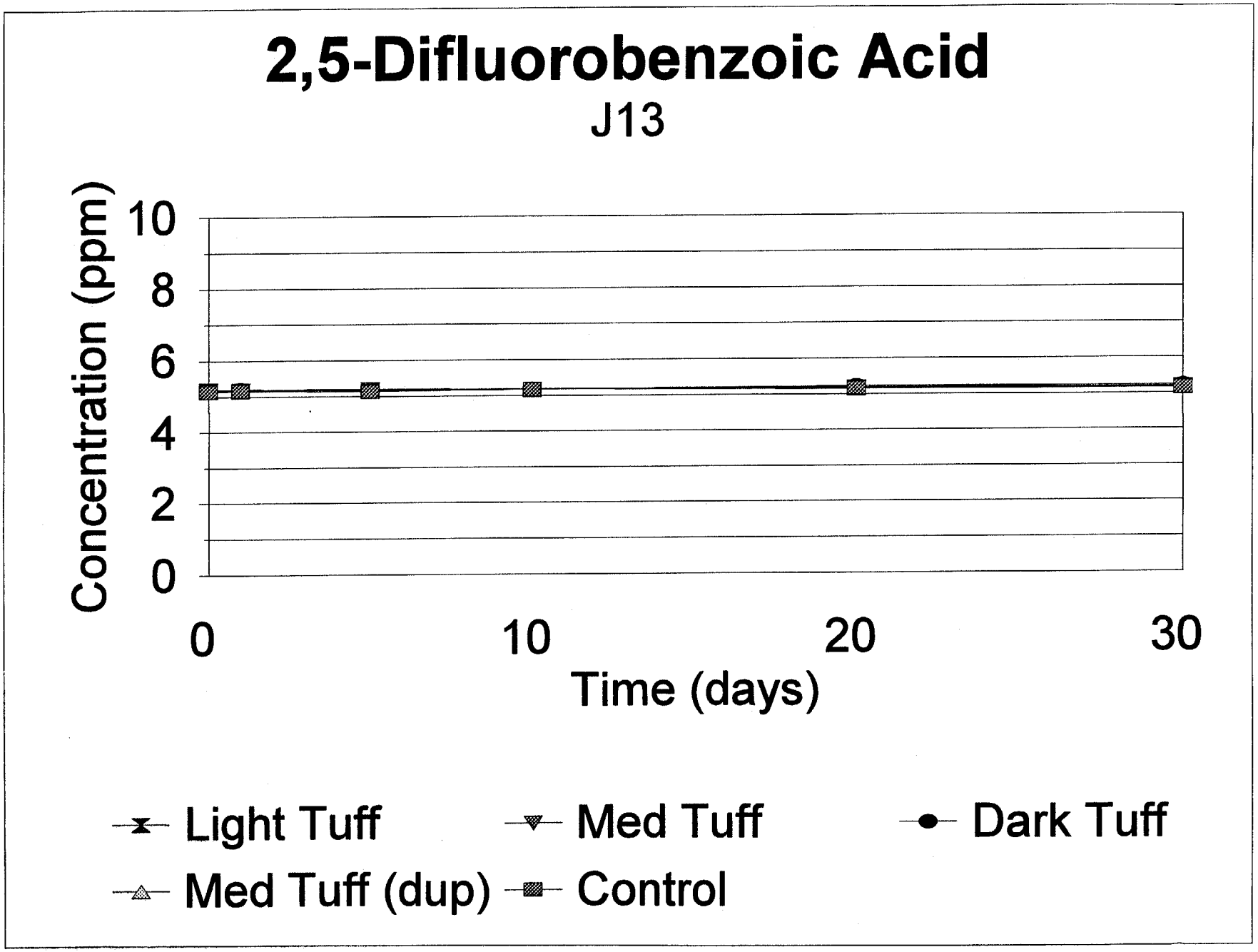

2,5-Difluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 3

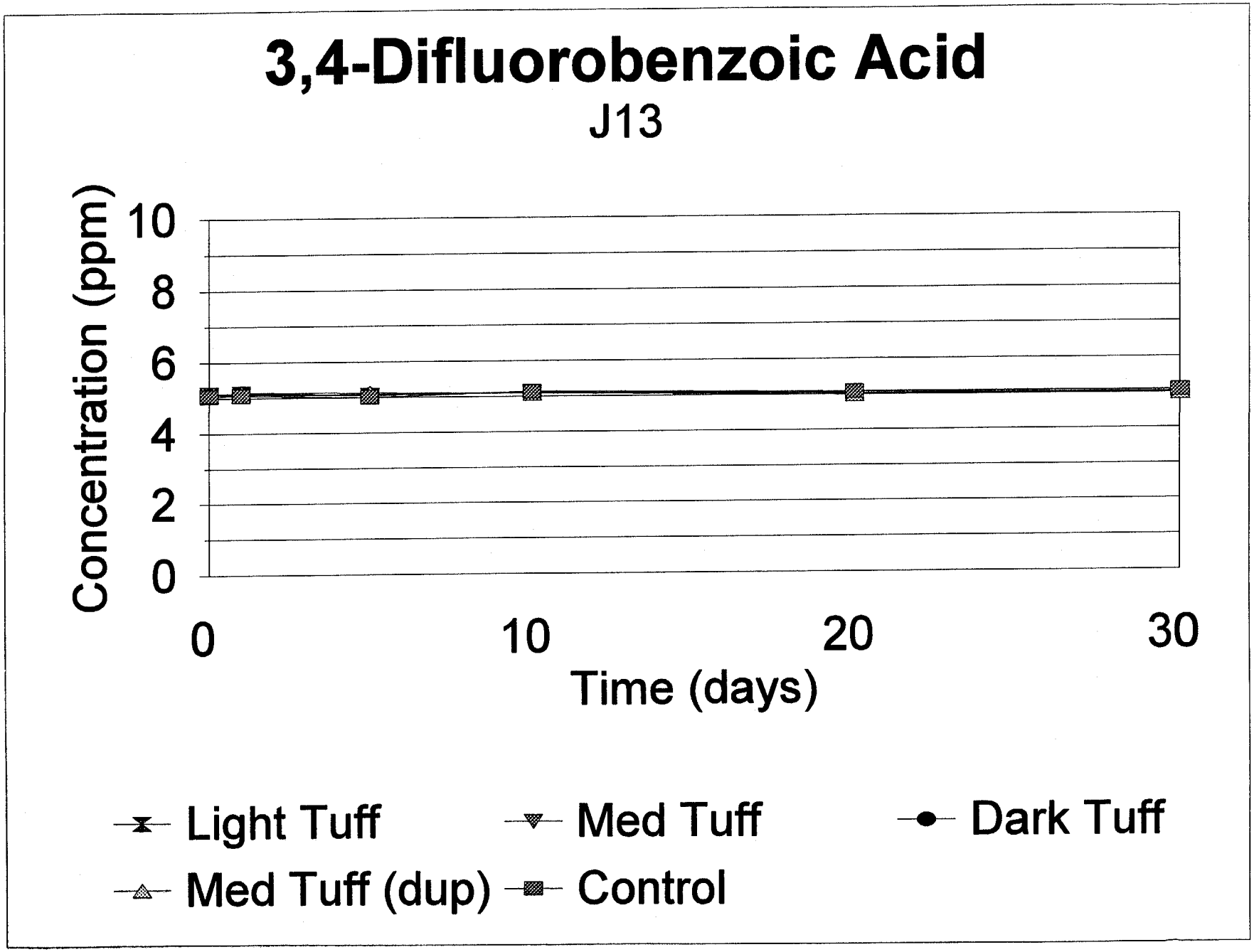

3,4-Difluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 4

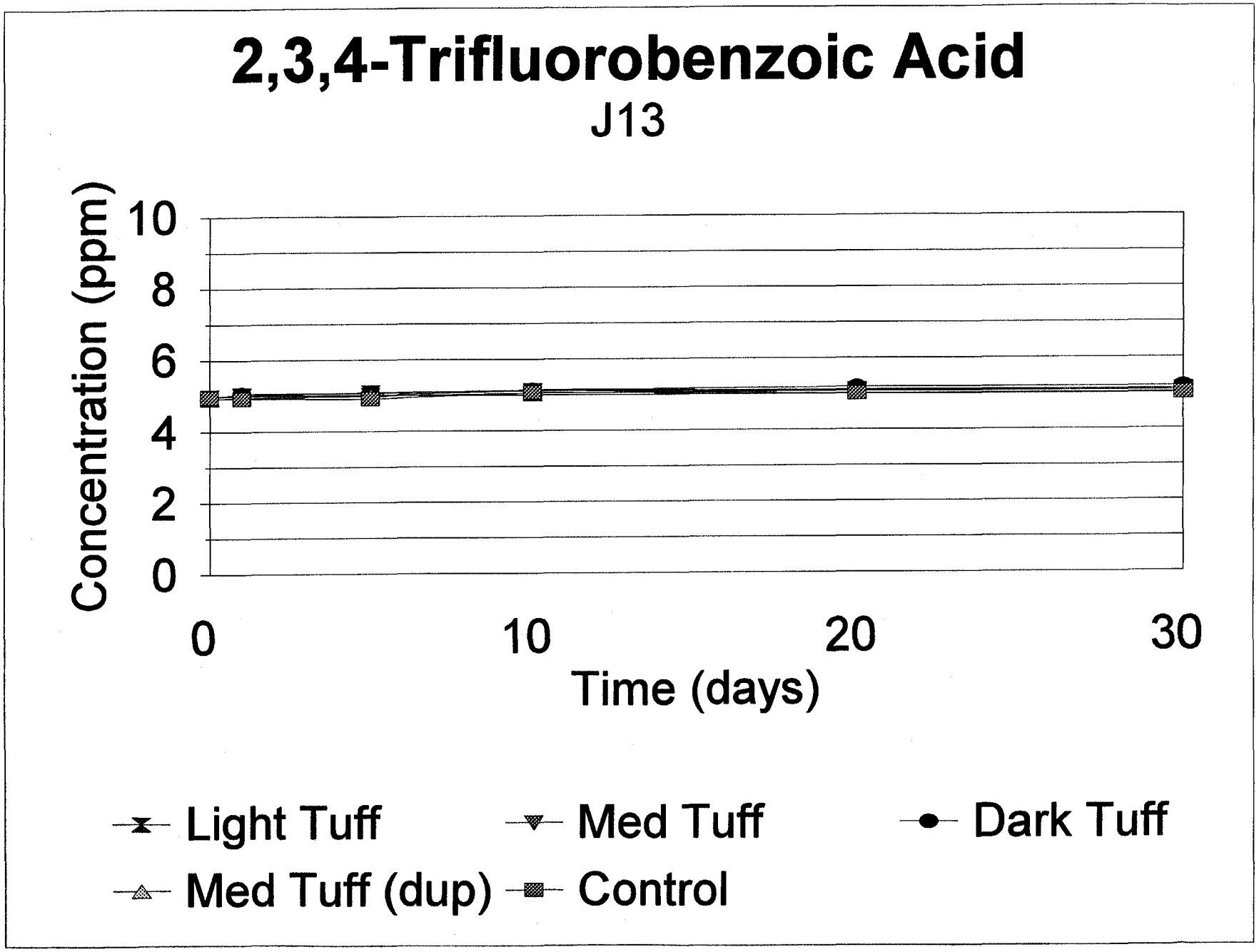

2,3,4-Trifluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 5

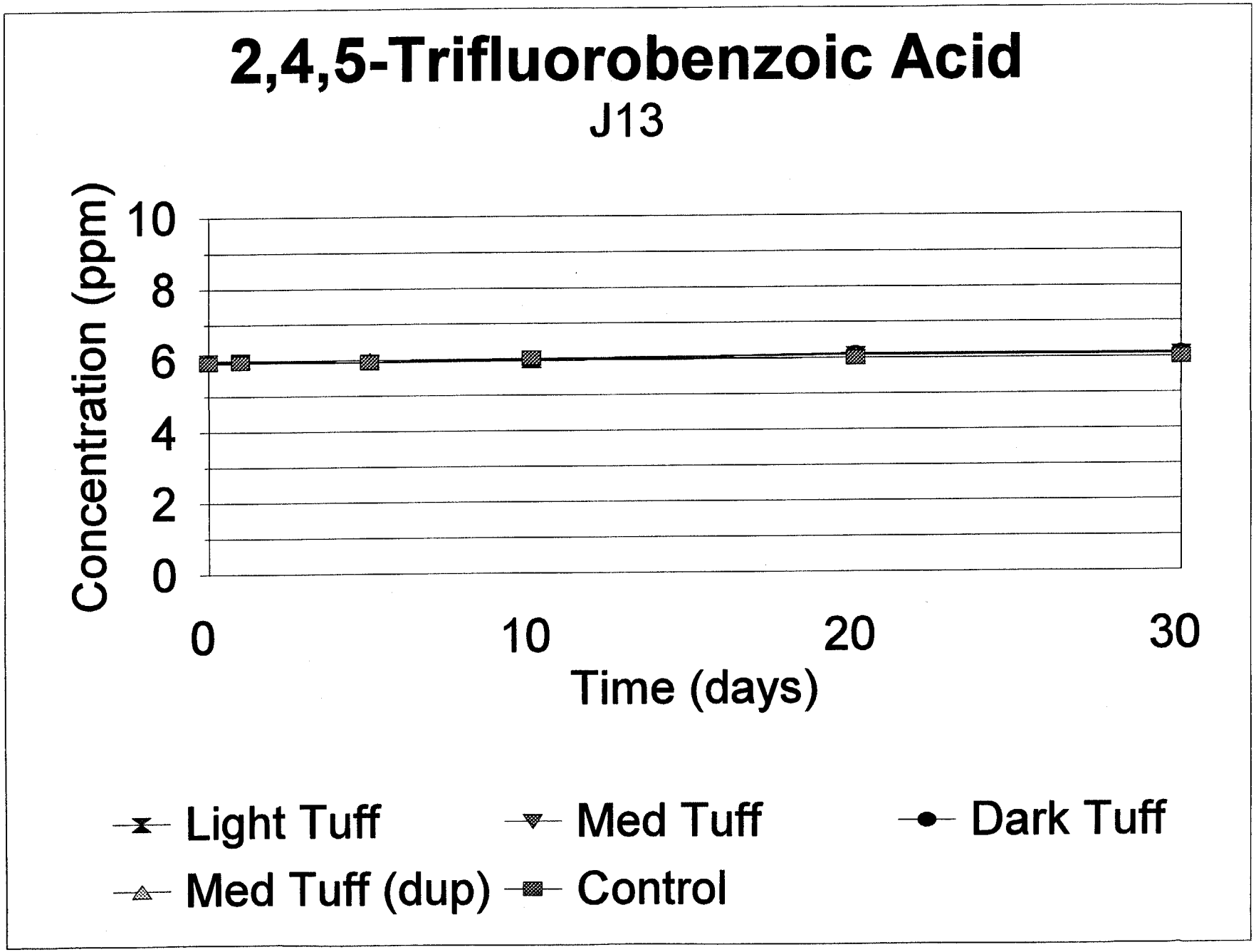
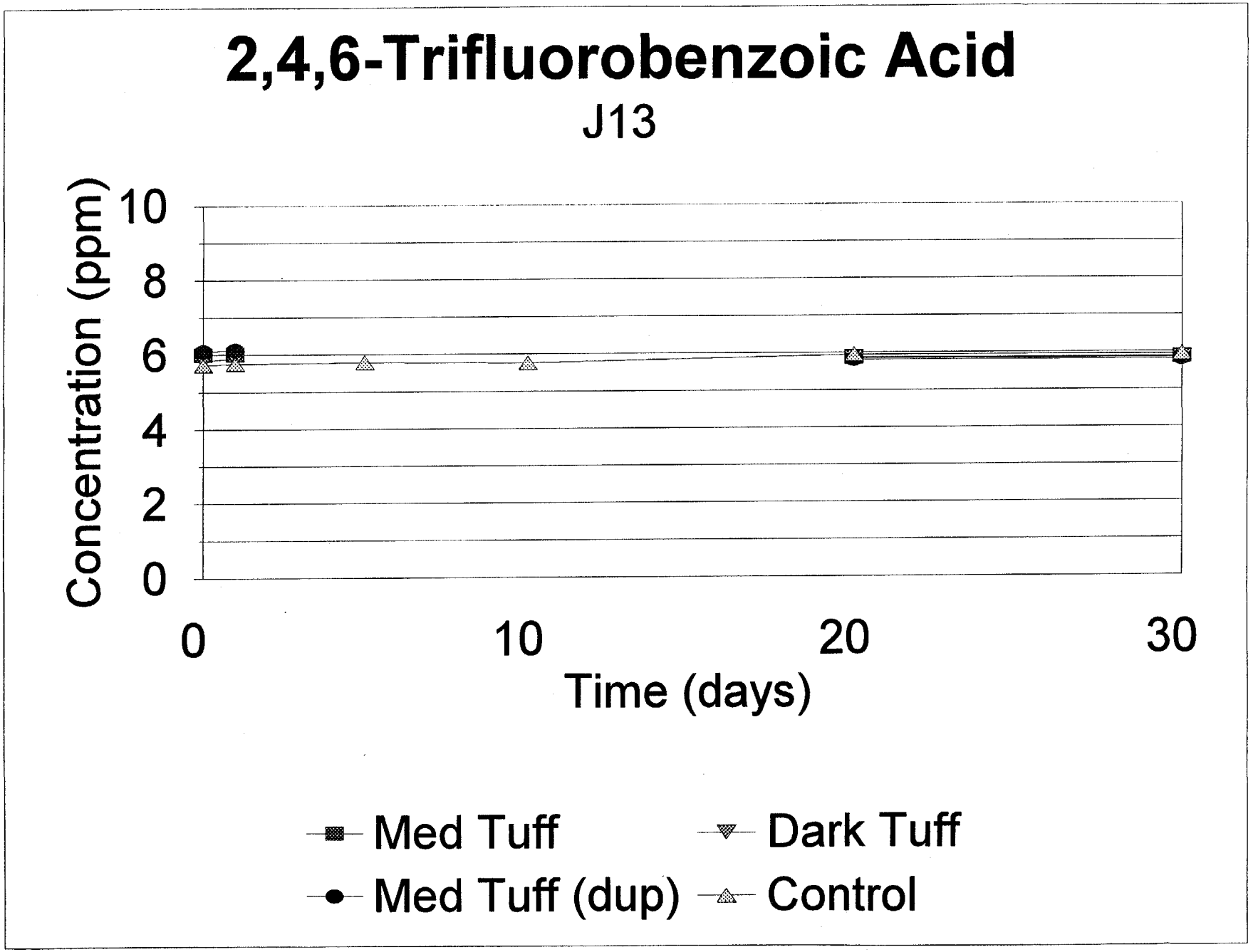

2,4,5-Trifluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 6


2,4,6-Trifluorobenzoic Acid
J13
Concentration (ppm)
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8
6
4
2
0
0
10
20
30
Time (days)
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 7

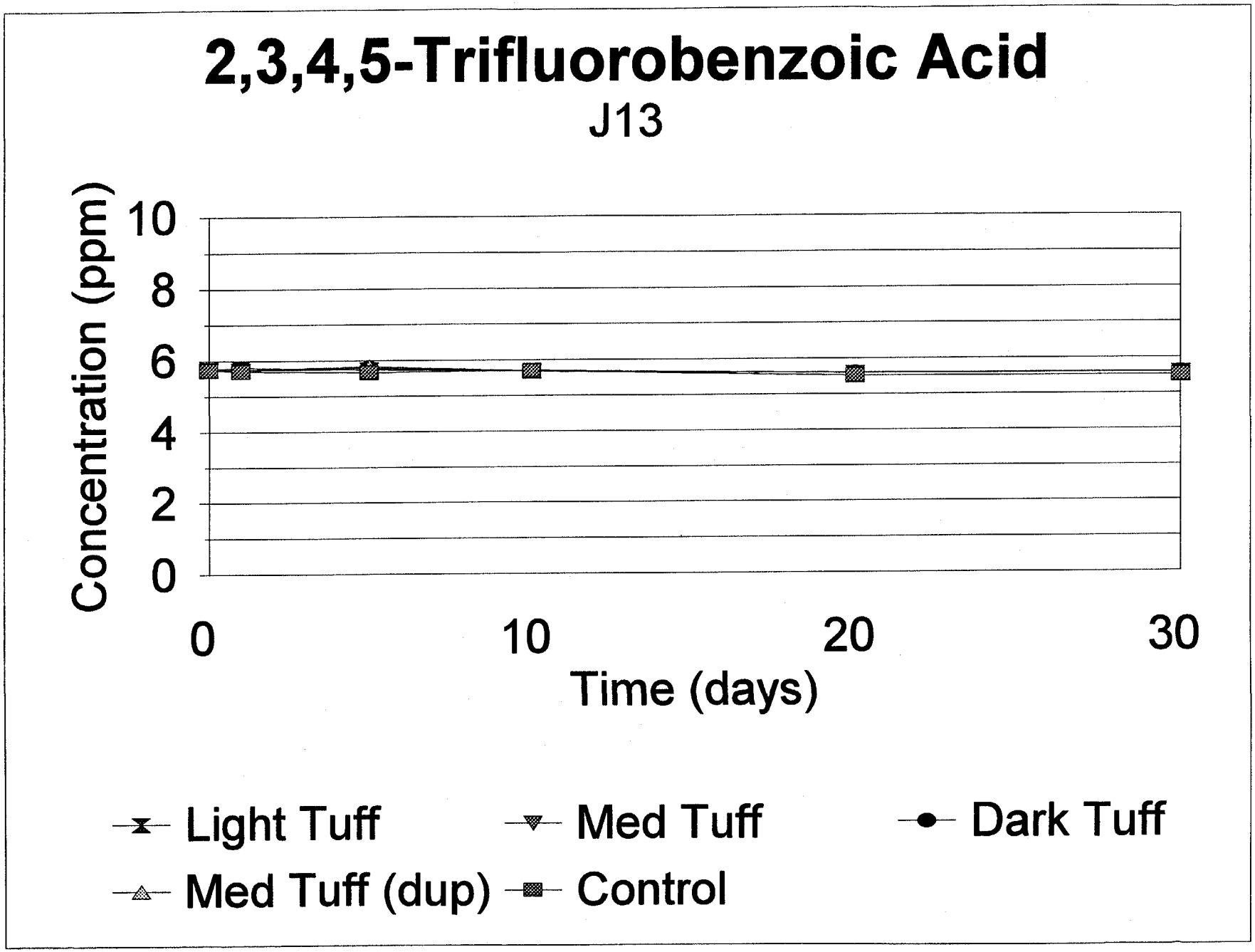

2,3,4,5-Trifluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 8

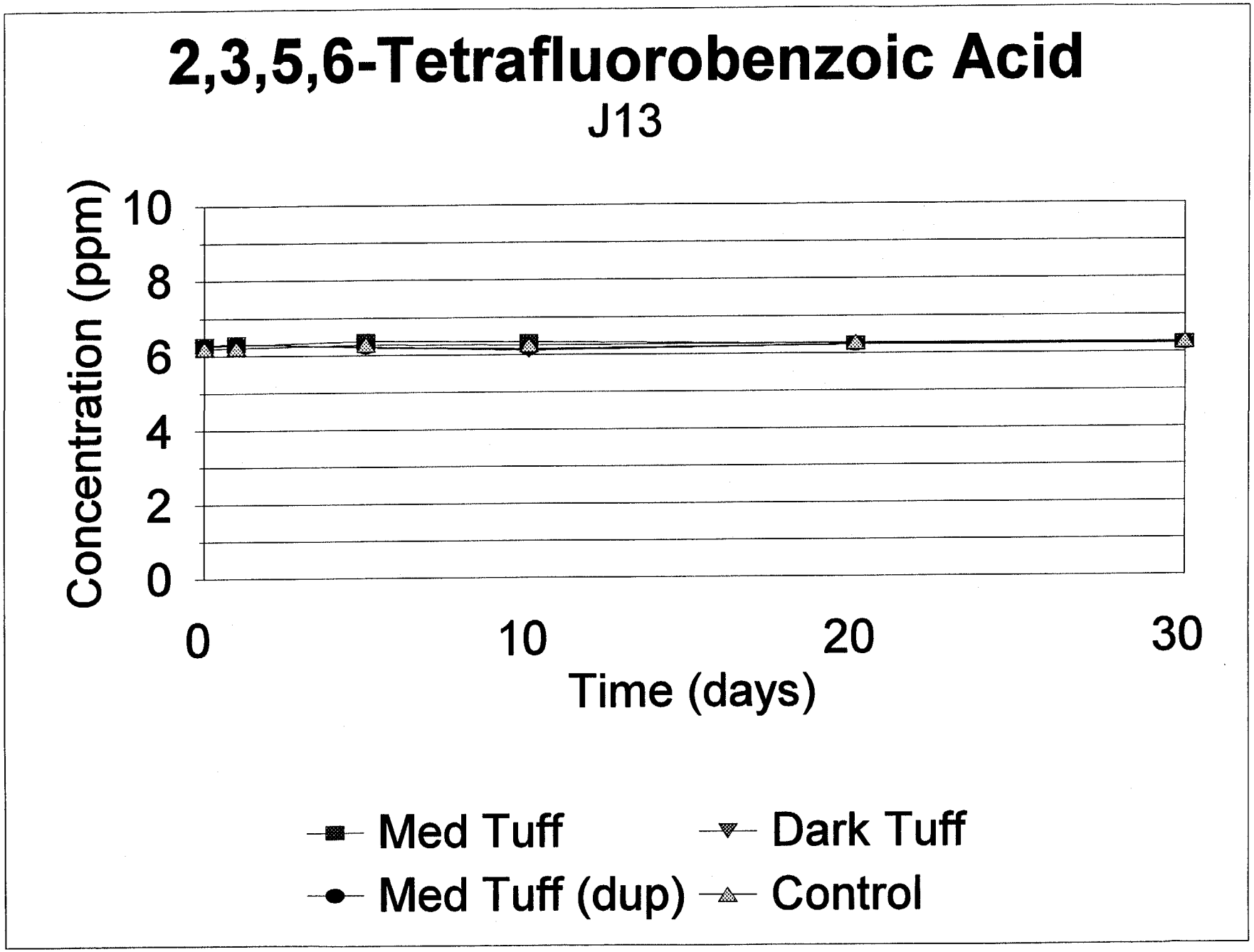

2,3,5,6-Tetrafluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 9

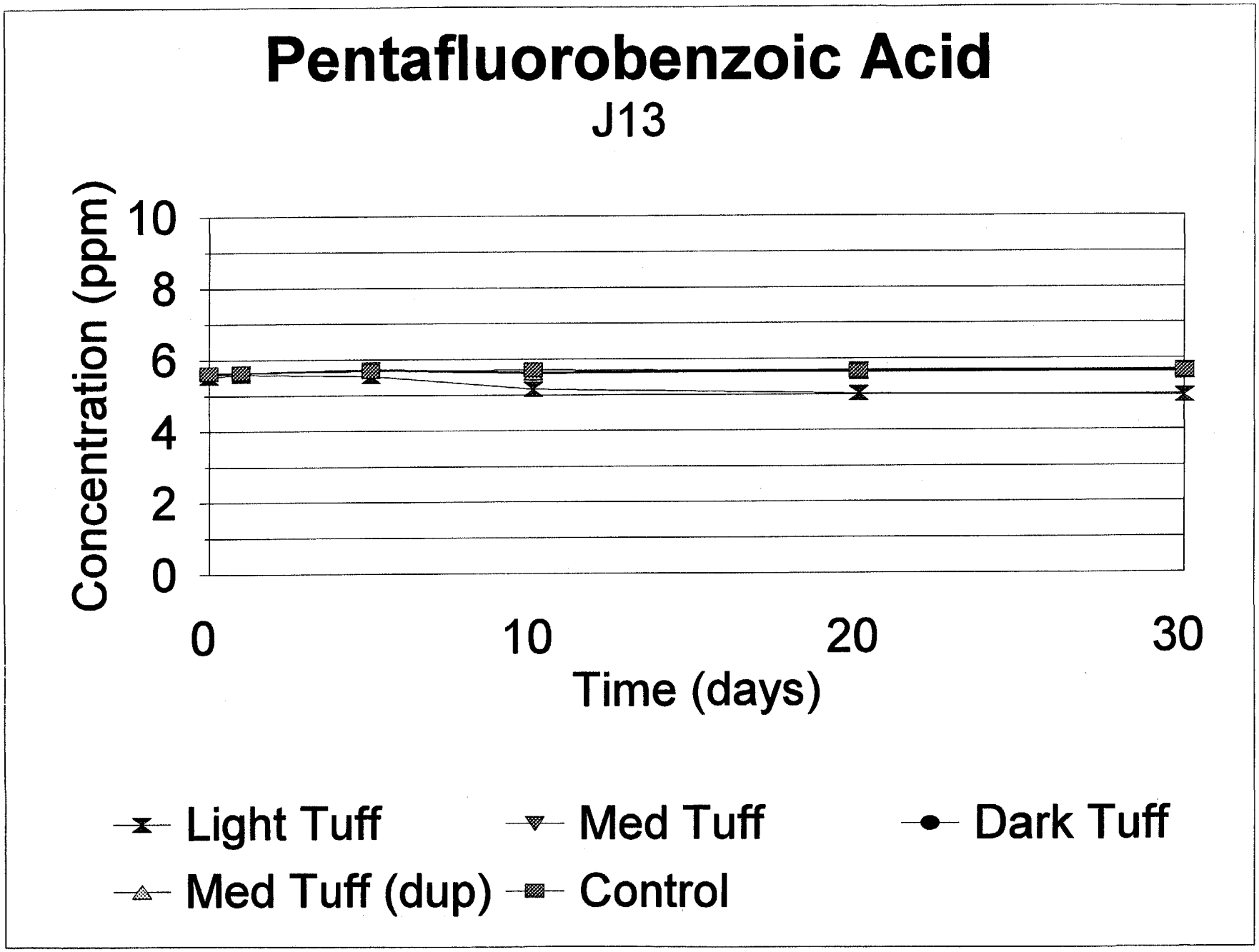

Pentafluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Med Tuff (dup)
Control

Figure 10

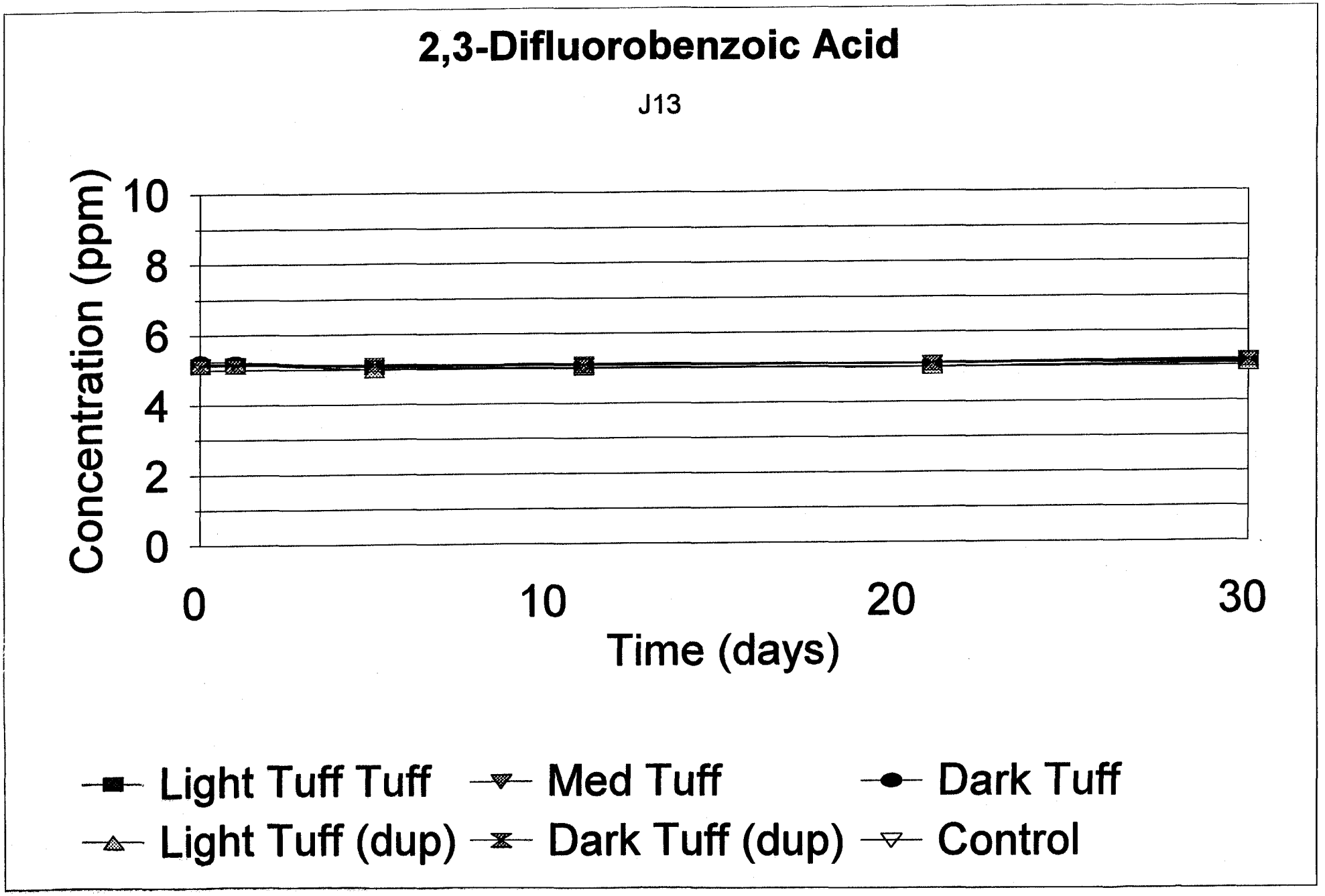

2,3-Difluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 11

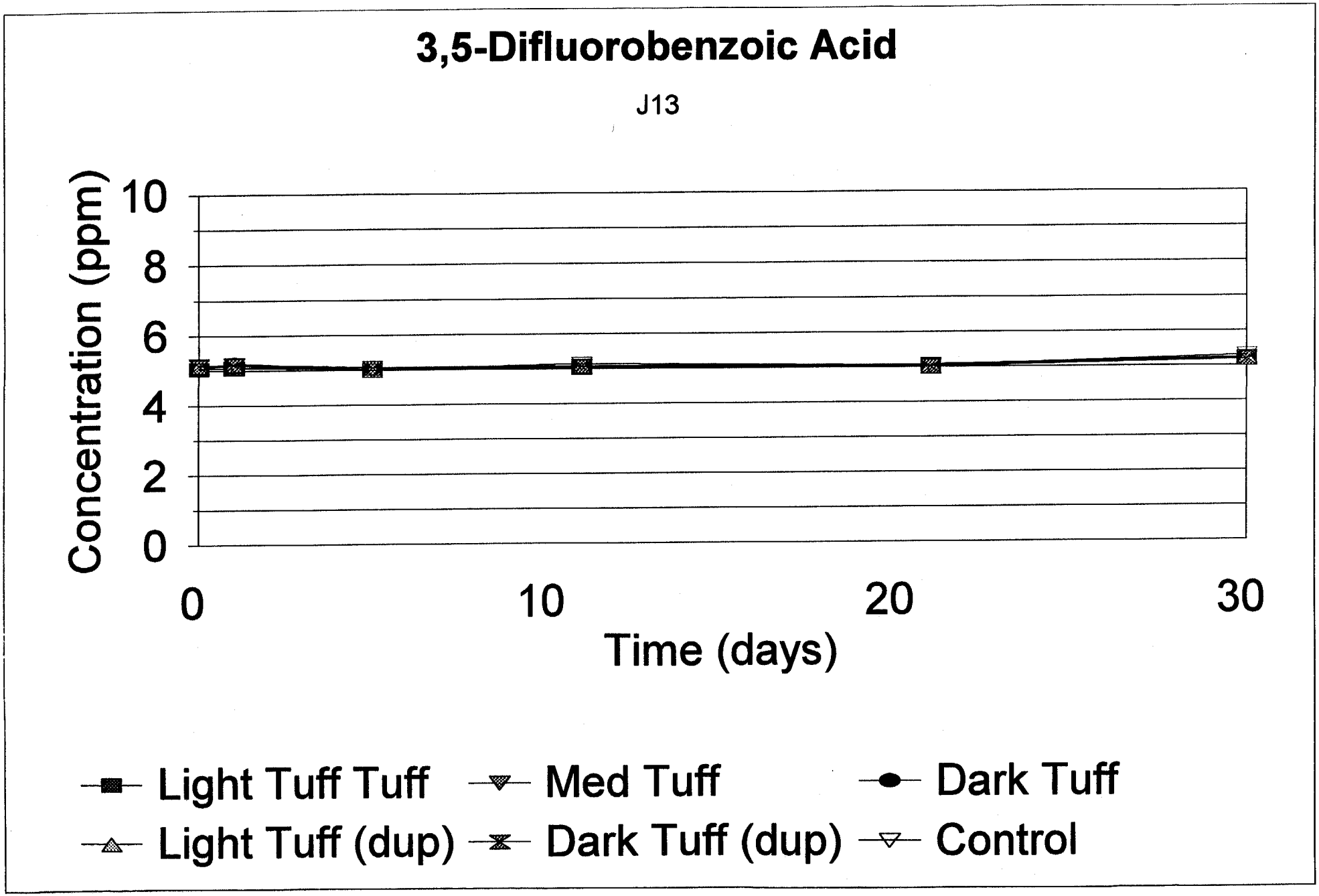
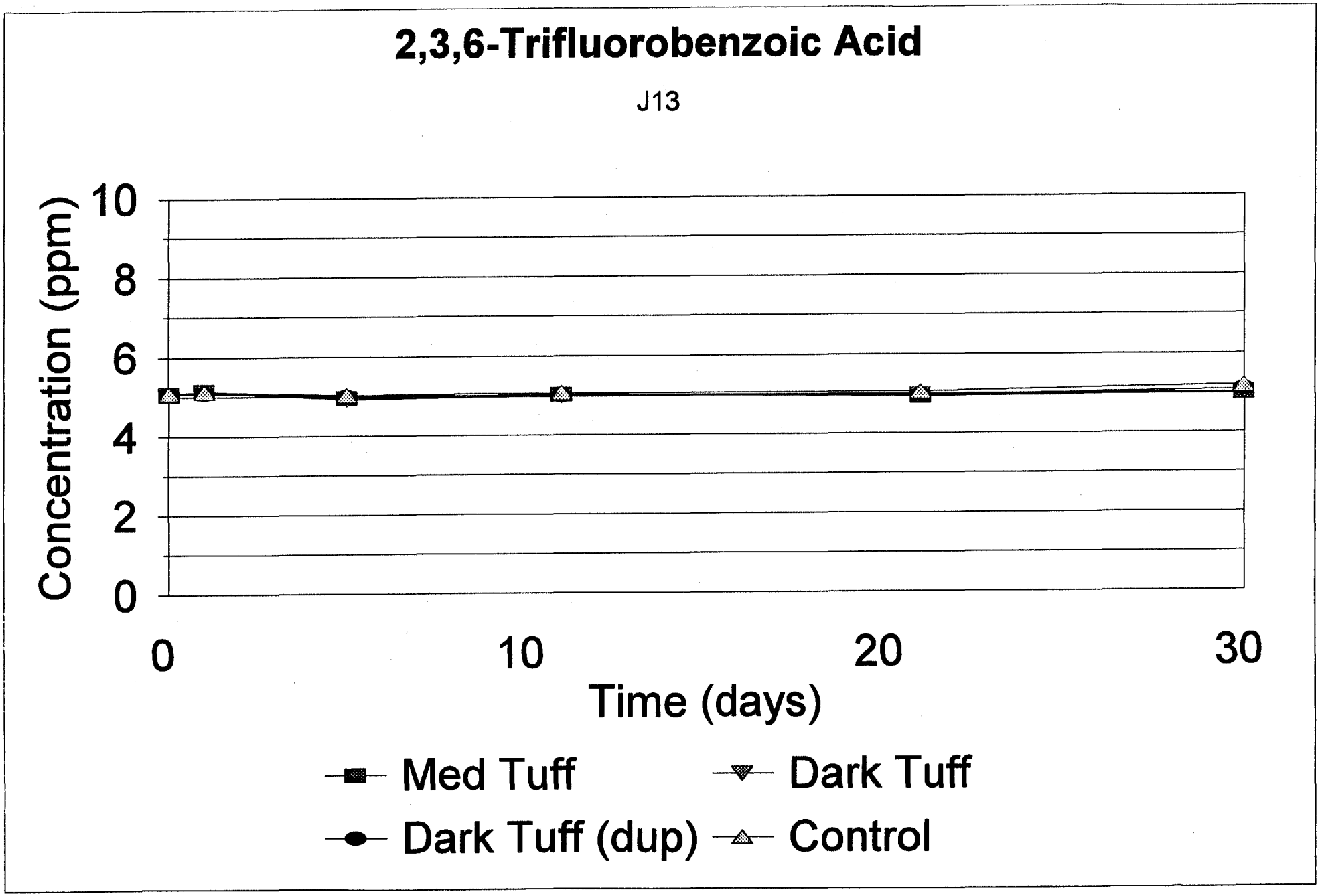

3,5-Difluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 12


2,3,6-Trifluorobenzoic Acid
J13
Concentration (ppm)
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8
6
4
2
0
0
10
20
30
Time (days)
Med Tuff
Dark Tuff
Dark Tuff (dup)
Control

Figure 13

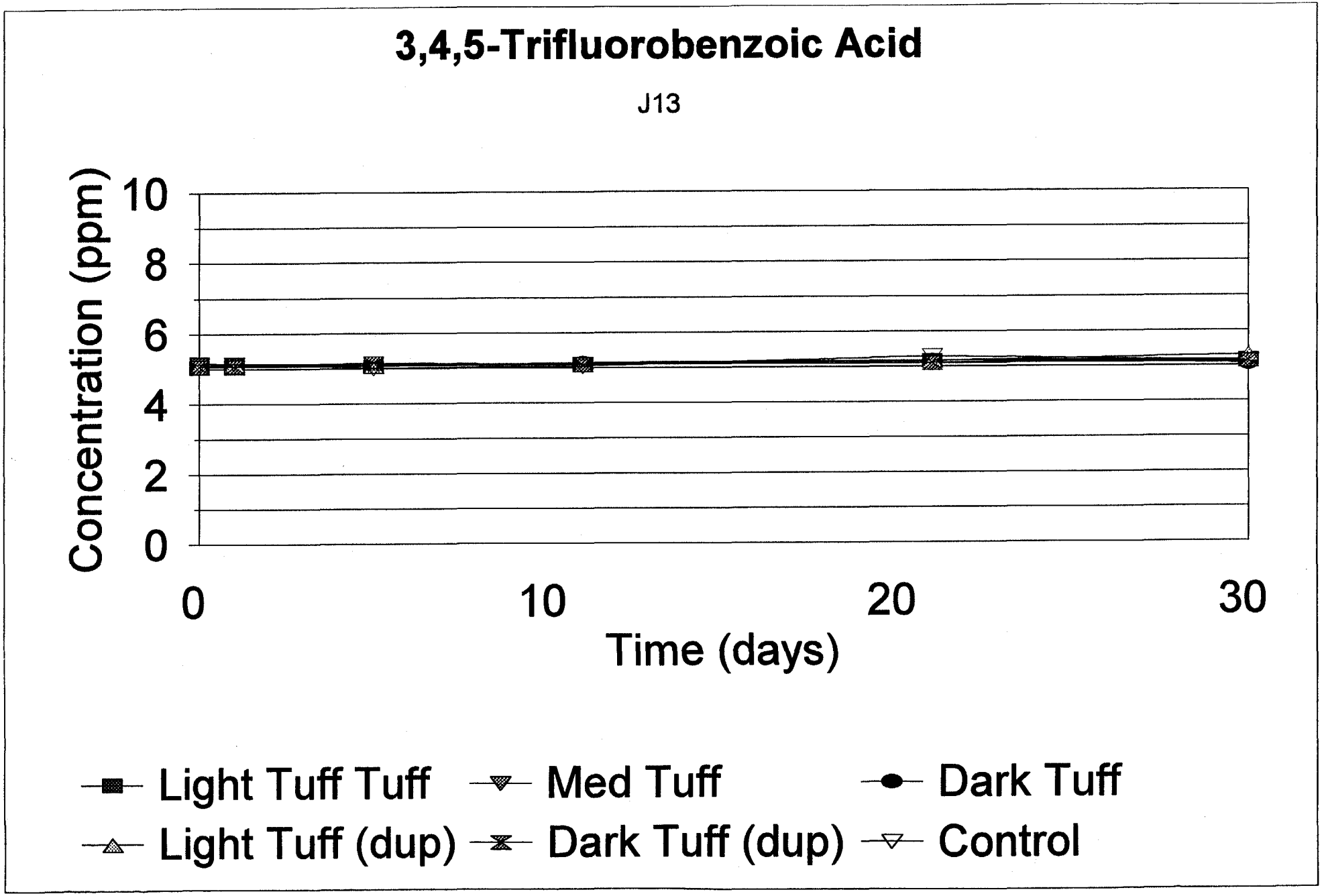

3,4,5-Trifluorobenzoic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 14

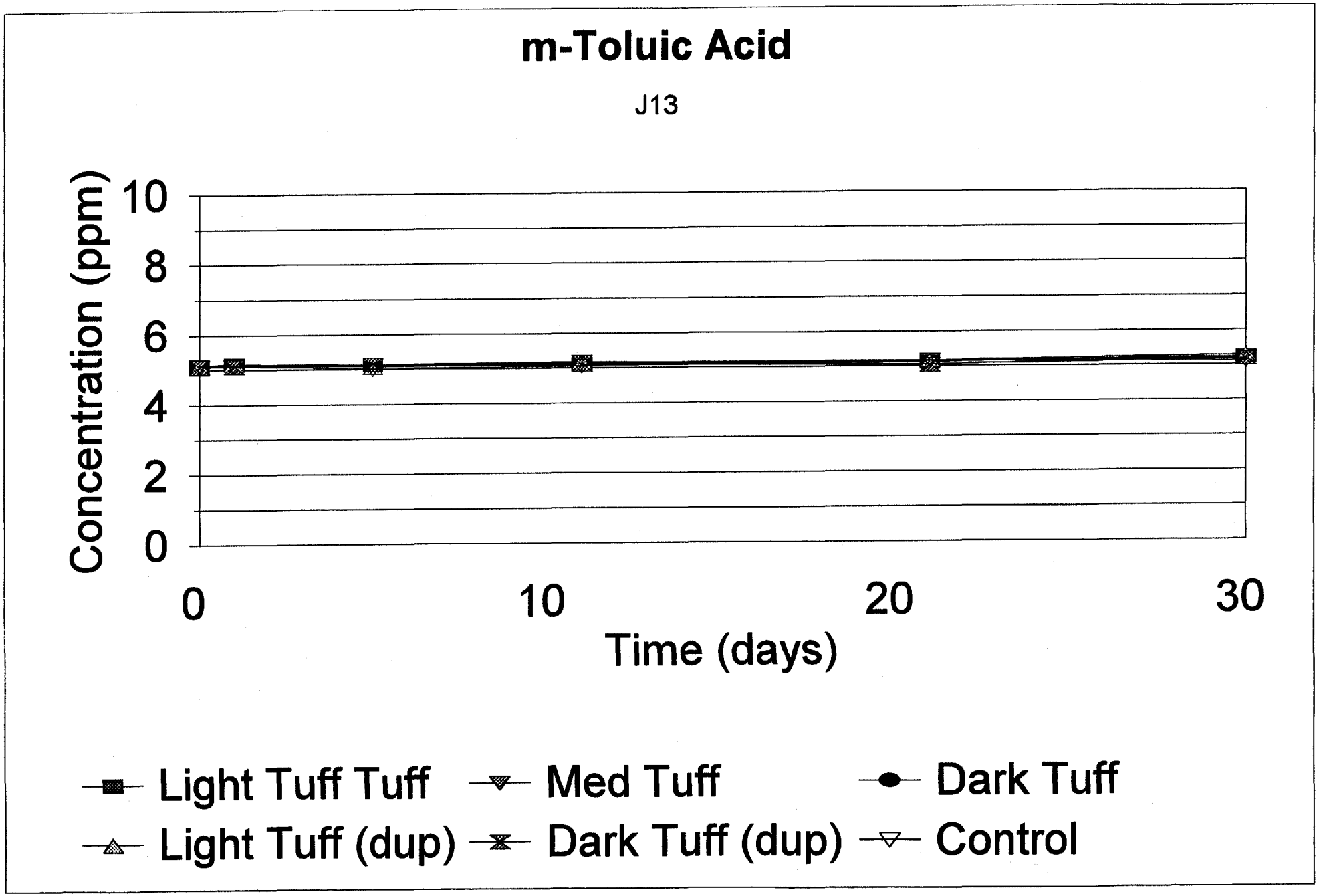

m-Toluic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 15

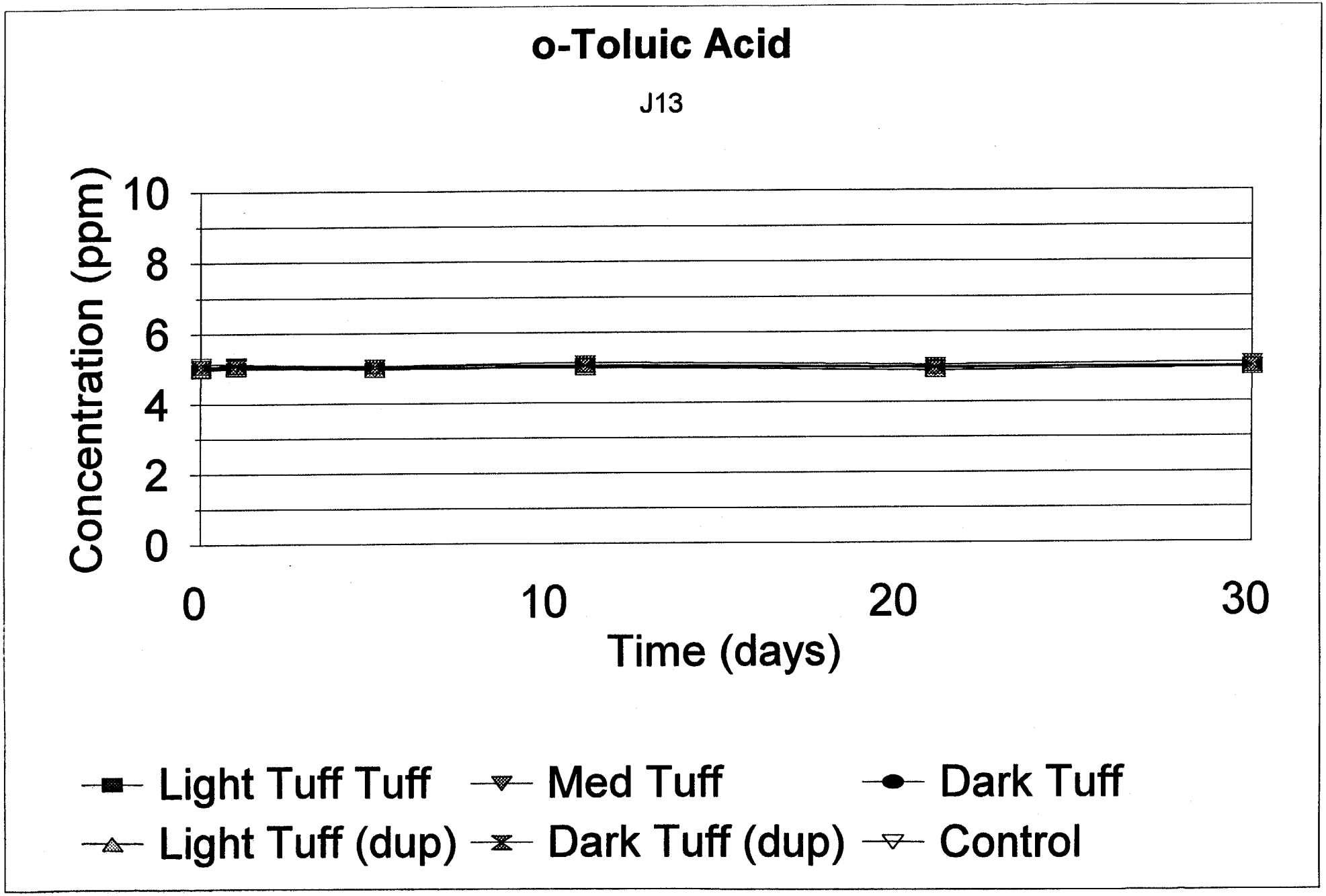

o-Toluic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 16

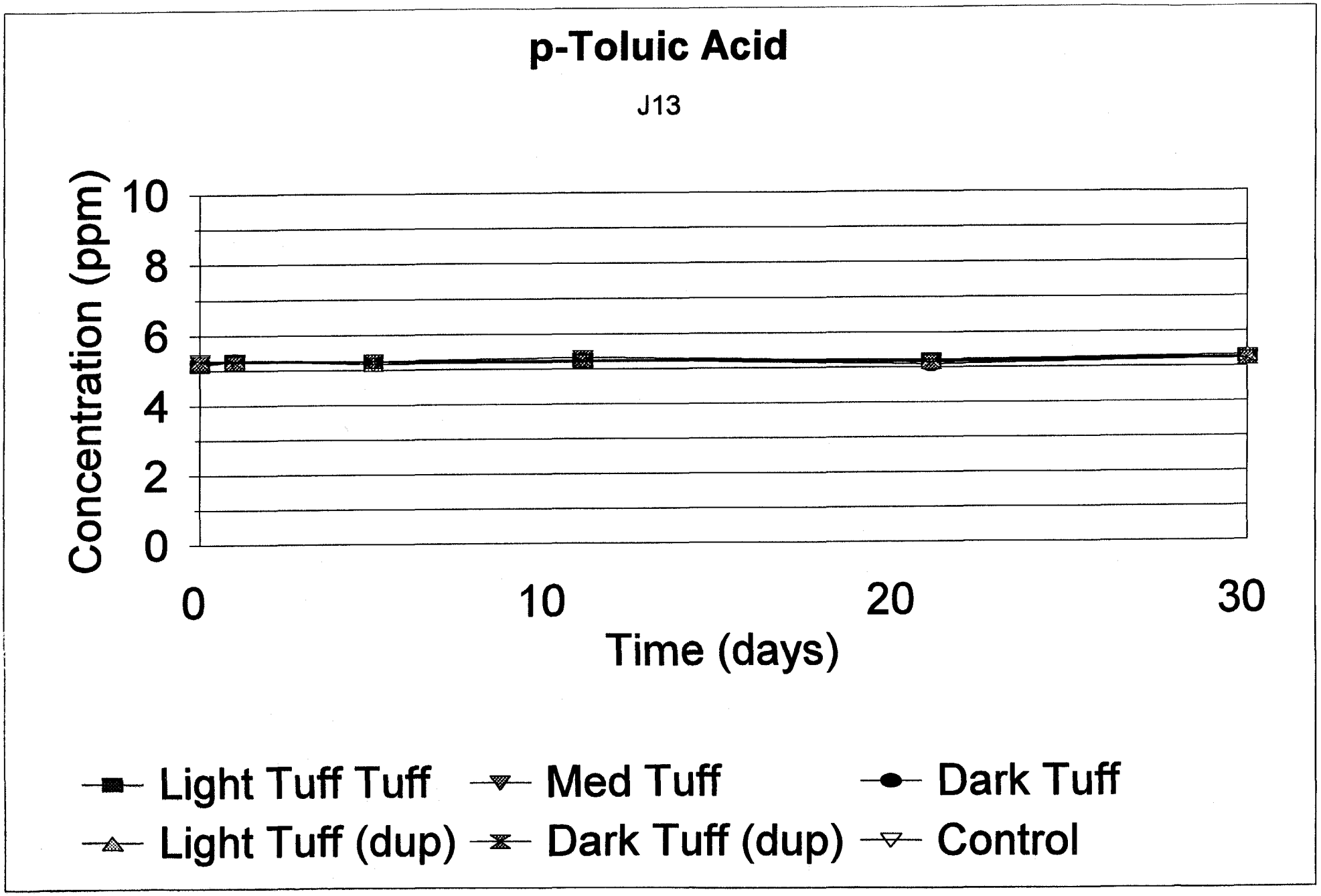

p-Toluic Acid
J13
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 17

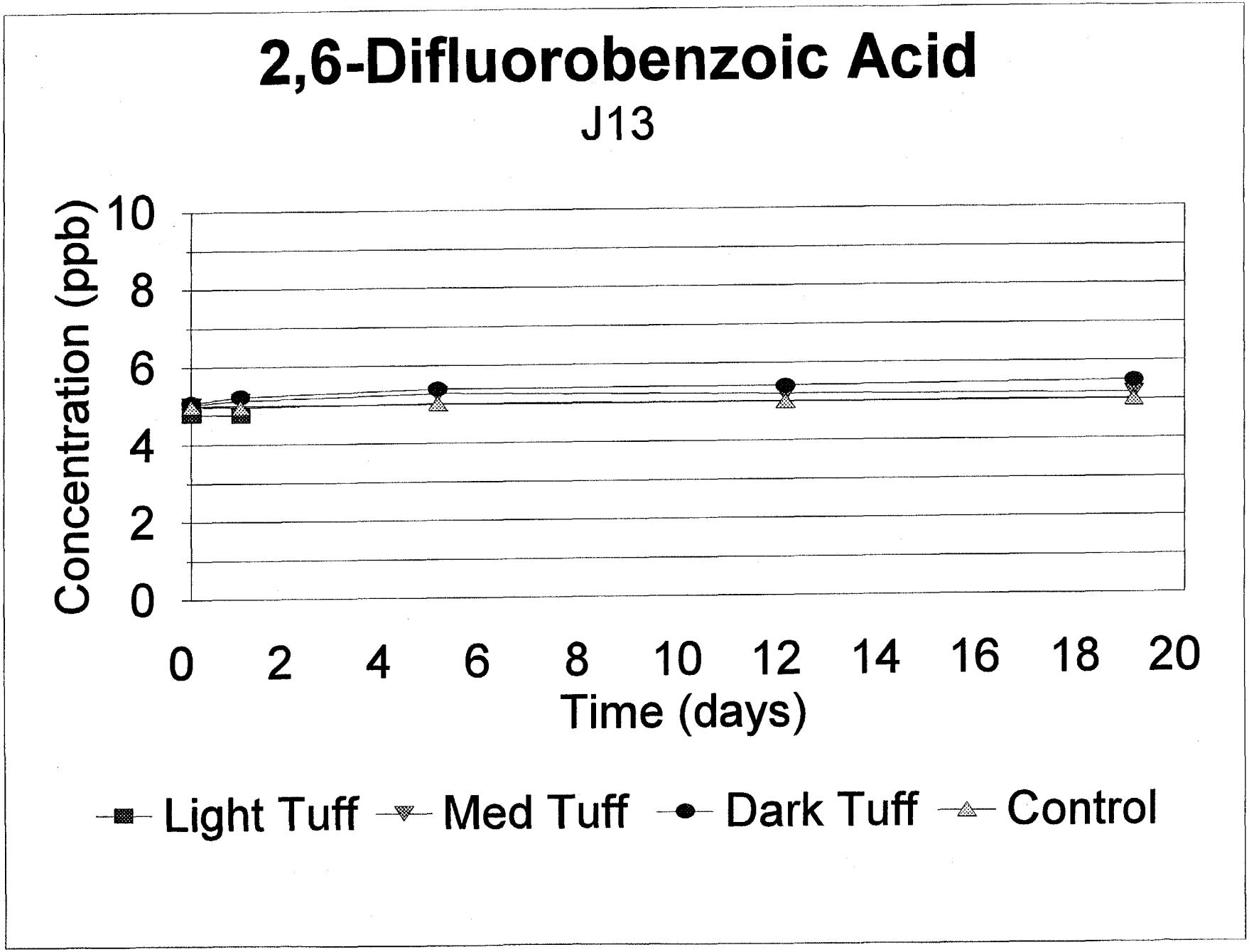

2,6-Difluorobenzoic Acid
J13
Concentration (ppb)
10
8
6
4
2
0
0
2
4
6
8
10
12
14
16
18
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 18

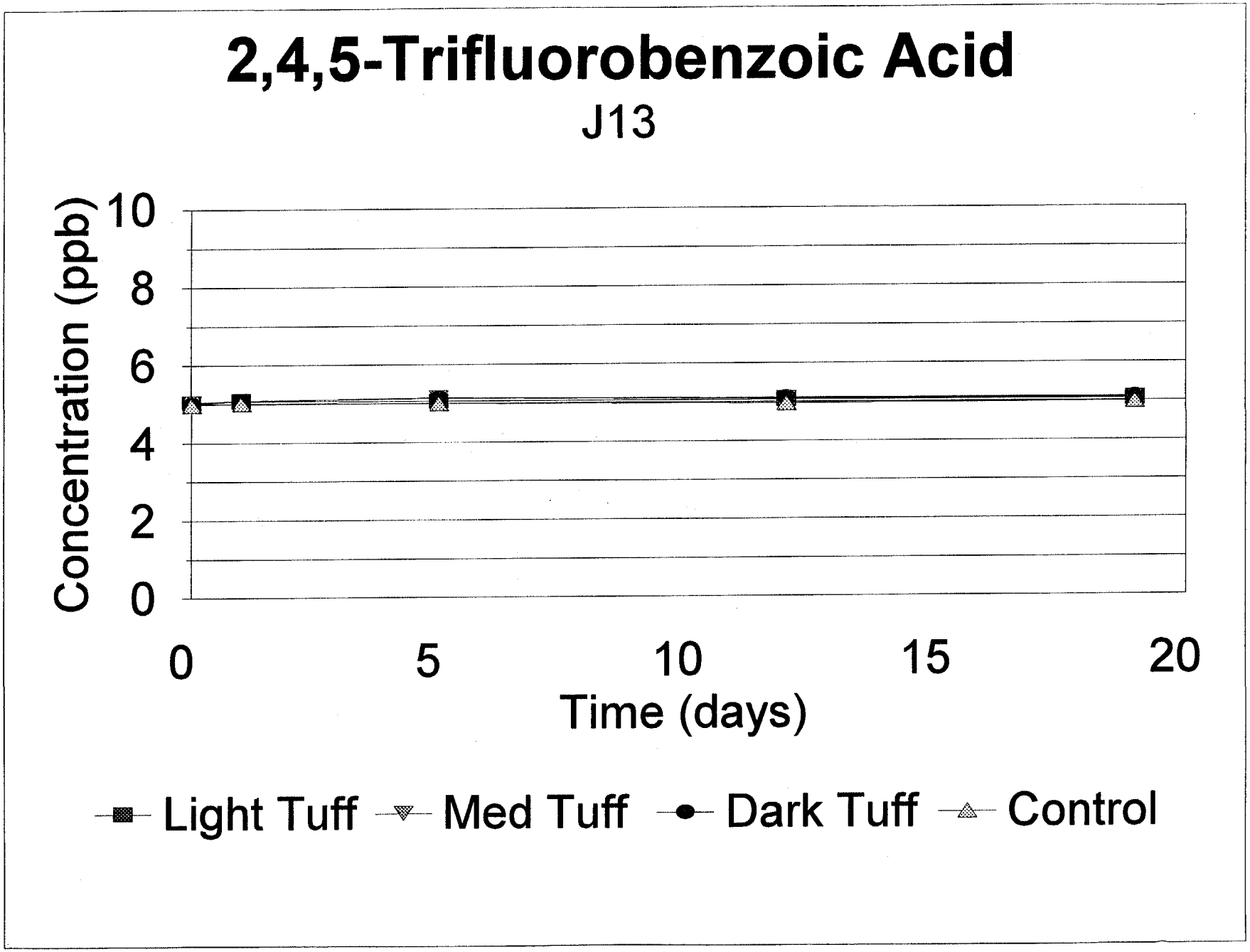

2,4,5-Trifluorobenzoic Acid
J13
Concentration (ppb)
10
8
6
4
2
0
0
5
10
15
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 19

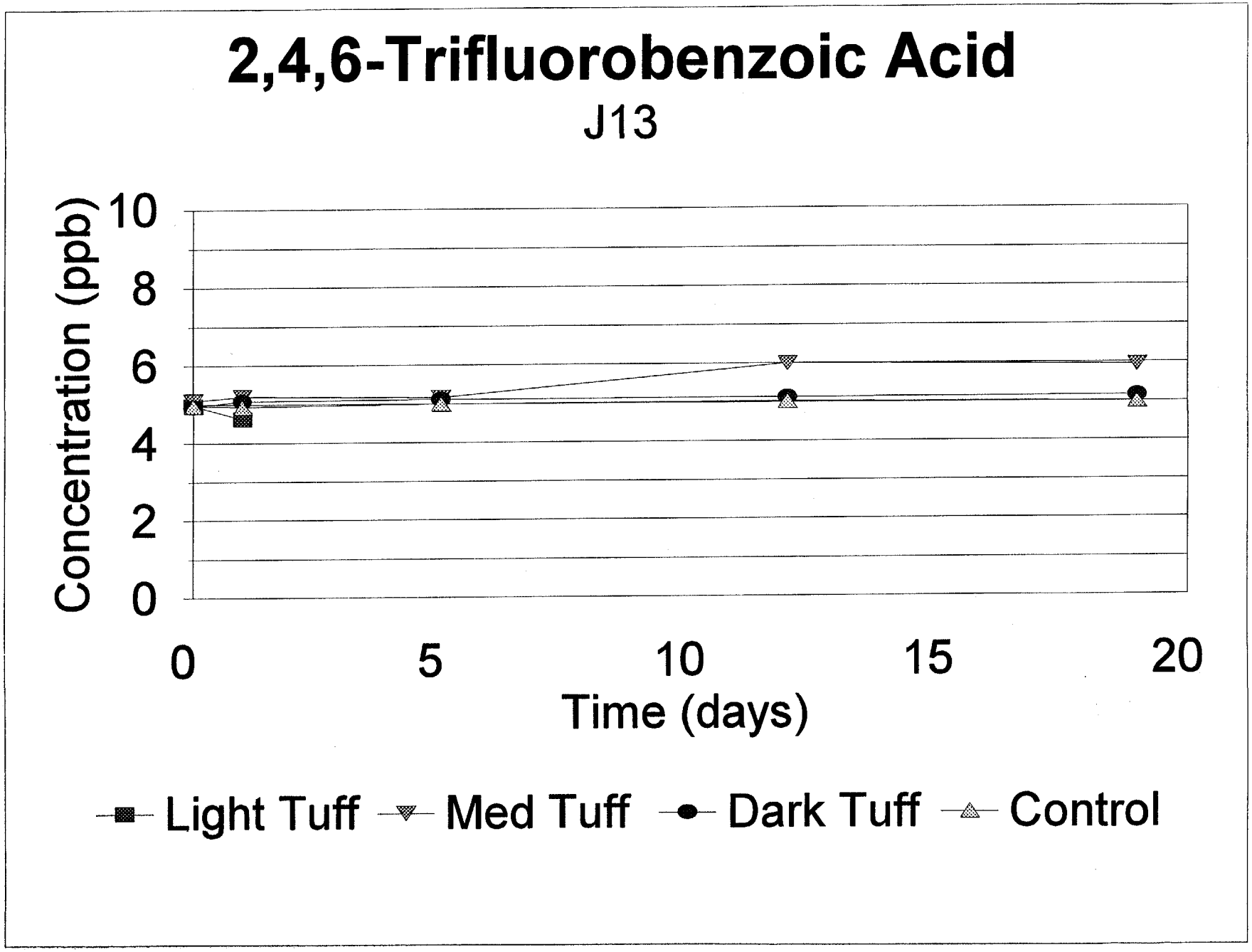

2,4,6-Trifluorobenzoic Acid
J13
Concentration (ppb)
10
8
6
4
2
0
0
5
10
15
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 20

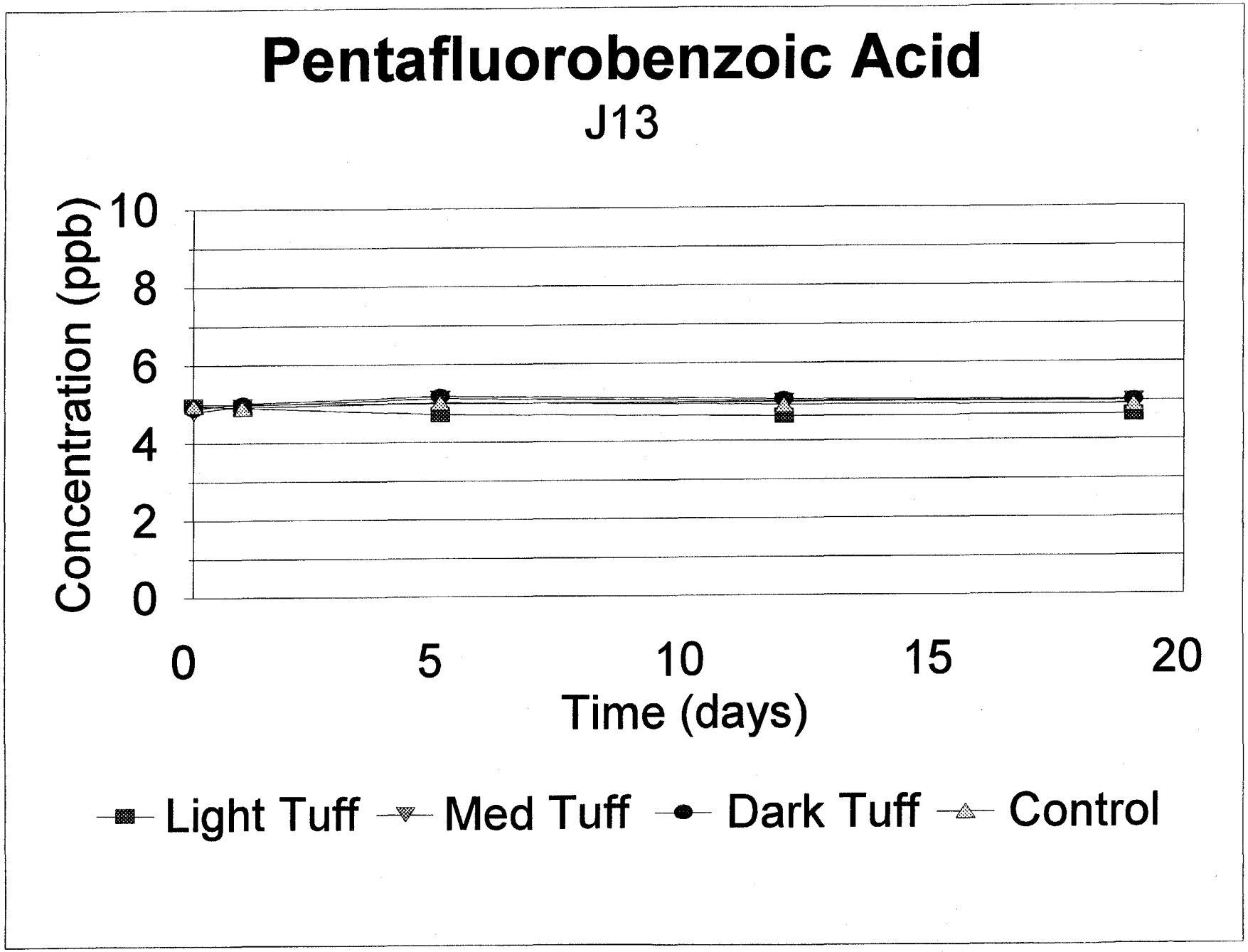

Pentafluorobenzoic Acid
J13
Concentration (ppb)
10
8
6
4
2
0
0
5
10
15
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 21

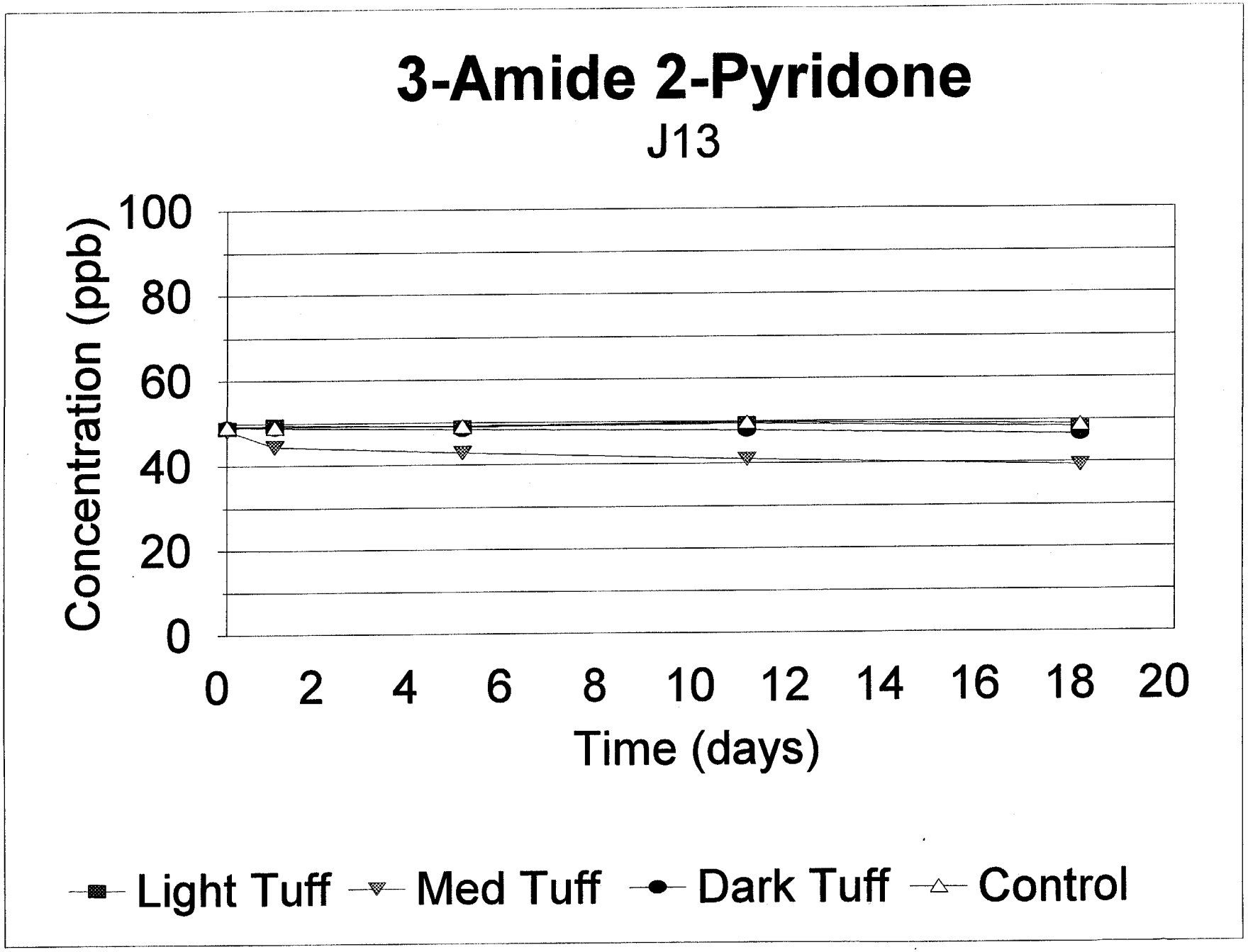

3-Amide 2-Pyridone
J13
Concentration (ppb)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
18
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 22

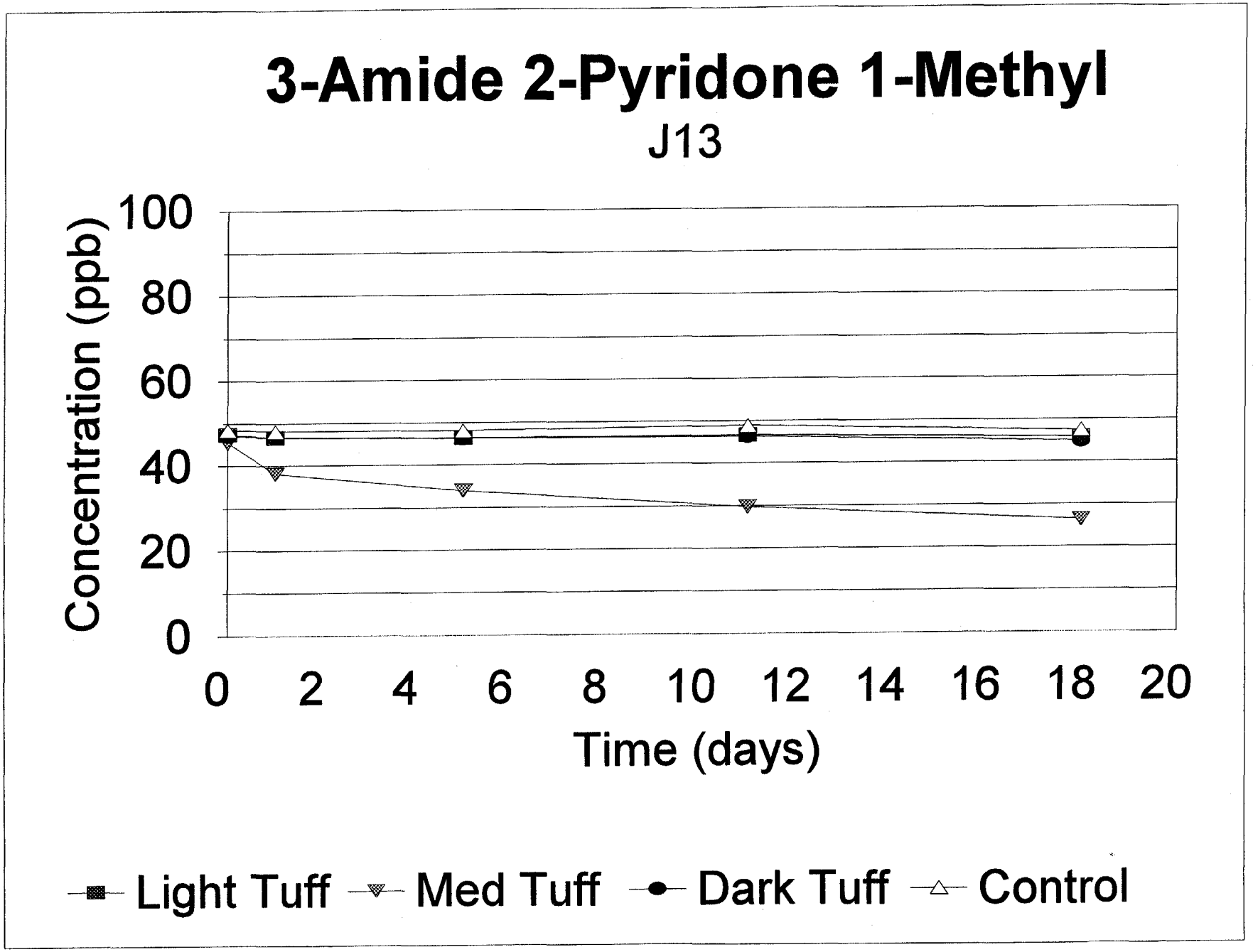

3-Amide 2-Pyridone 1-Methyl
J13
Concentration (ppb)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
18
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 23

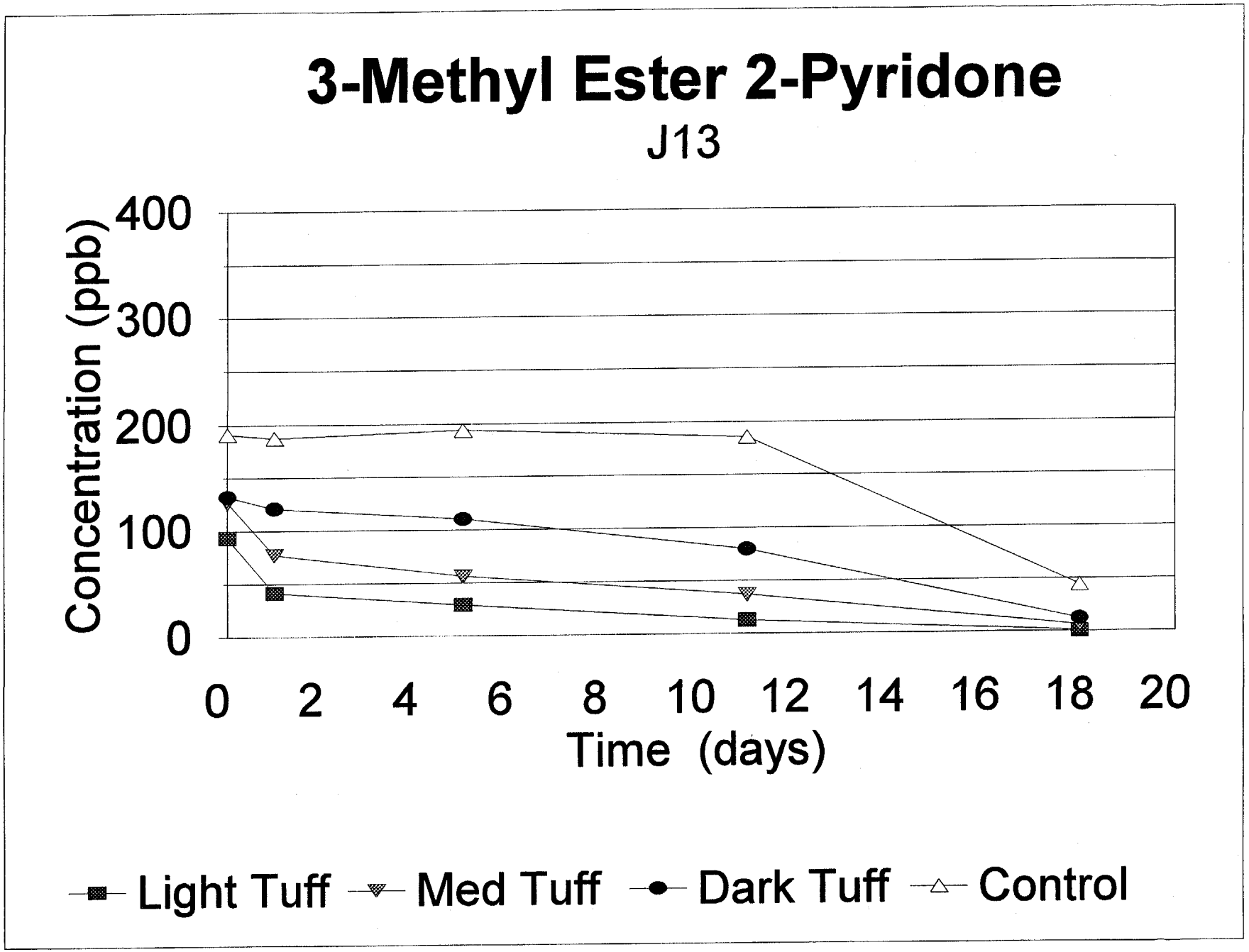
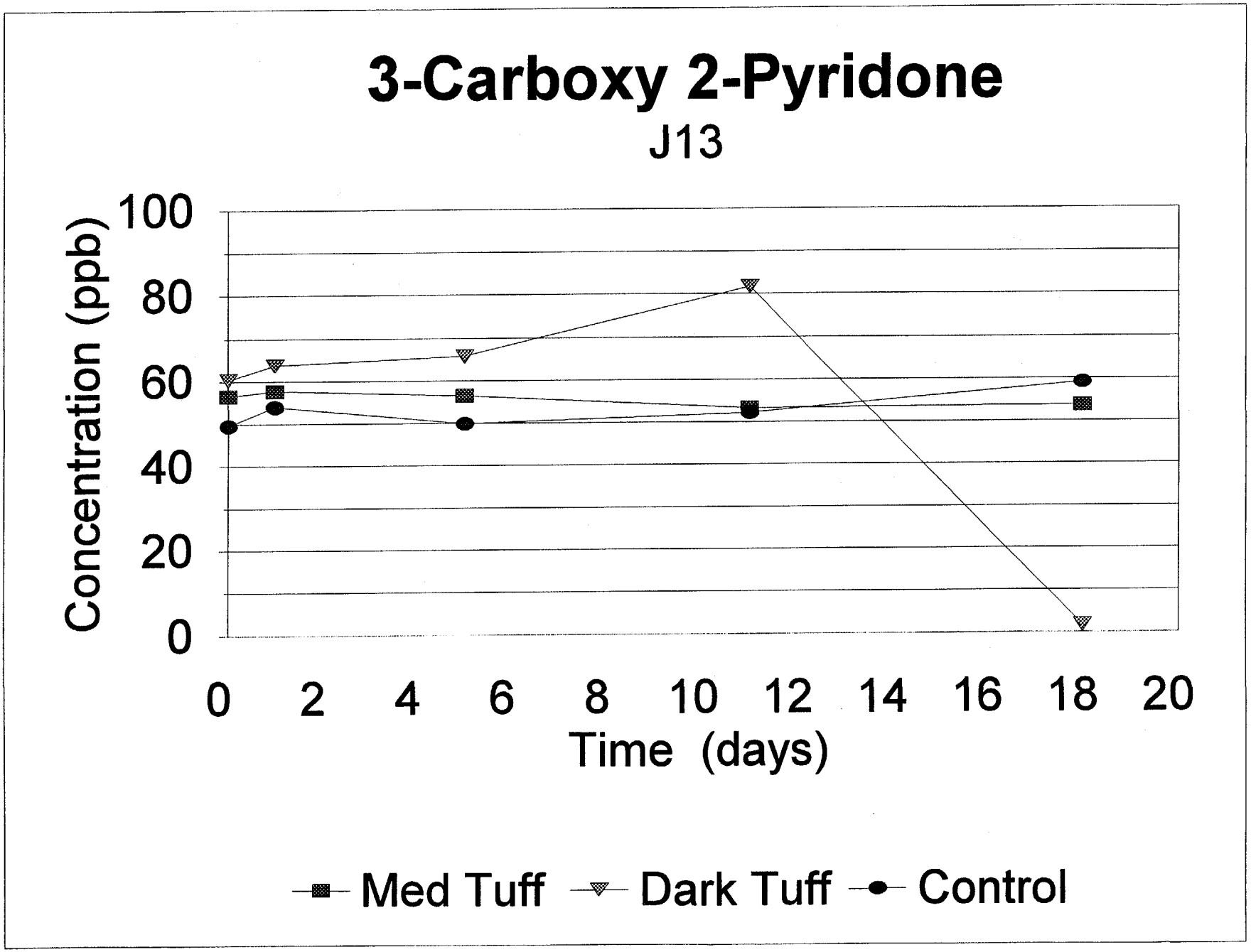

3-Methyl Ester 2-Pyridone
J13
Concentration (ppb)
400
300
200
100
0
0
2
4
6
8
10
12
14
16
18
20
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 24


3-Carboxy 2-Pyridone
J13
Concentration (ppb)
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
18
20
Time (days)
Med Tuff
Dark Tuff
Control