DOE/NV/10872--T236

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

PROGRESS REPORT
JULY 1, 1995 to SEPTEMBER 30, 1995

DOE Cooperative Agreement
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The laboratory work to support the selection of the tracers to be used for the C-Well tracer tests has been completed. The solubilities for each of the fluorinated benzoic acids in J13 water have been determined and the stability of these compounds to both degradation and sorption on ground tuff has been measured through batch and column testing. Method development work is in progress for the analysis of low levels of 2,6-difluorobenzoic acid. The current plan is to use this compound as a tracer in a preliminary test.

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.

All commercially available fluorinated benzoic acids have been batch tested over sixty days. These compounds exhibit excellent stability with changes in concentation of less than 5% in each tuff type for most compounds. The concentrations for each of the compounds in each of the tuff types from day 0 to day 60 are shown in the following tables. These data are also presented in the graphs in Figures 1-17. These graphs not only show the high stability of these compounds but also demonstrate the excellent precision available through the HPLC/UV methods.

Table 1 Concentrations of Tracers in the Control Samples

	Concentration (ppm)						
Compound	0	1	5	10	20	30	60
2,3-Difluorobenzoic Acid	5.15	5.19	5.09	5.11	5.13	5.21	5.12
2,4-Difluorobenzoic Acid	5.33	5.32	5.35	5.38	5.25	5.34	5.37
2,5-Difluorobenzoic Acid	5.14	5.15	5.14	5.18	5.13	5.17	5.15
2,6-Difluorobenzoic Acid	4.99	4.97	5.03	5.01	5.02	5.17	5.06
3,4-Difluorobenzoic Acid	5.05	5.06	5.01	5.13	5.04	5.07	5.01
3,5-Difluorobenzoic Acid	5.06	5.20	5.01	5.15	5.05	5.20	5.03
2,3,4-Trifluorobenzoic Acid	4.95	4.92	4.92	5.06	4.90	5.01	4.98
2,3,6-Trifluorobenzoic Acid	5.10	5.13	5.04	5.07	5.06	5.18	5.13
2,4,5-Trifluorobenzoic Acid	5.92	5.94	5.94	6.03	6.08	6.02	5.90
2,4,6-Trifluorobenzoic Acid	5.74	5.77	5.79	5.78	5.84	5.75	5.72
3,4,5-Trifluorobenzoic Acid	5.14	5.16	5.02	5.06	5.31	5.20	5.06
2,3,4,5-Tetrafluorobenzoic Acid	5.74	5.71	5.66	5.70	5.73	5.65	5.60
2,3,5,6-Tetrafluorobenzoic Acid	6.20	6.22	6.29	6.26	6.21	6.27	6.24
Pentafluorobenzoic Acid	5.62	5.64	5.67	5.71	5.67	5.65	5.59
α,α,α-Trifluoro-o-toluic acid	5.14	5.15	5.00	5.07	4.96	5.09	5.05
α,α,α-Trifluoro-m-toluic acid	5.13	5.12	5.02	5.06	5.18	5.12	5.06
α,α,α-Trifluoro-p-toluic acid	5.28	5.29	5.19	5.22	5.23	5.26	5.14

Table 2 Concentrations of Tracers in the Light Tuff Samples

Compound	Concentration (ppm) 0	1	5	10	20	30	60
2,3-Difluorobenzoic Acid	5.15	5.19	5.07	5.02	5.00	5.09	5.09
2,4-Difluorobenzoic Acid	5.43	5.45	5.43	5.35	5.23	5.35	5.49
2,5-Difluorobenzoic Acid	5.19	5.18	5.19	5.18	5.10	5.19	5.28
2,6-Difluorobenzoic Acid	4.77	4.78	*	*	*	*6.58	4.96
3,4-Difluorobenzoic Acid	5.07	5.14	5.06	5.10	4.99	5.06	5.18
3,5-Difluorobenzoic Acid	5.07	5.08	5.03	5.04	5.08	5.11	5.10
2,3,4-Trifluorobenzoic Acid	4.98	5.04	5.08	5.11	4.94	5.06	5.11
2,4,5-Trifluorobenzoic Acid	5.97	5.99	5.95	5.97	6.01	6.02	6.08
3,4,5-Trifluorobenzoic Acid	5.05	5.08	5.08	5.13	5.18	5.25	5.35
2,3,4,5-Tetrafluorobenzoic Acid	5.78	5.81	5.75	5.69	5.67	5.65	5.71
Pentafluorobenzoic Acid	5.53	5.58	5.55	5.16	5.27	4.96	5.55
α,α,α-Trifluoro-o-toluic acid	4.97	5.02	4.98	5.03	4.91	5.06	5.29
α,α,α-Trifluoro-m-toluic acid	5.06	5.17	5.14	5.14	5.13	5.26	5.10
α,α,α-Trifluoro-p-toluic acid	5.16	5.28	5.25	5.28	5.23	5.33	5.31

*A large interference was observed in all of the light tuff samples. This interferred with the quantitation of 2,3,5,6-Tetrafluorobenzoic acid, 2,4,6-Trifluorobenzoic acid, 2,3,6-Trifluorobenzoic acid and t5 - t30 for 2,6-Difluorobenzoic acid. These data are therefore not reported.

Table 3 Concentrations of Tracers in the Medium Tuff Samples

Compound	Concentration (ppm) 0	1	5	10	20	30	60
2,3-Difluorobenzoic Acid	5.17	5.18	5.11	5.15	5.11	5.14	5.10
2,4-Difluorobenzoic Acid	5.41	5.41	5.37	5.39	5.25	5.36	5.45
2,5-Difluorobenzoic Acid	5.19	5.18	5.20	5.18	5.14	5.21	5.24
2,6-Difluorobenzoic Acid	5.05	5.14	5.28	5.21	5.18	5.17	4.99
3,4-Difluorobenzoic Acid	5.12	5.08	5.06	5.10	5.07	5.03	4.99
3,5-Difluorobenzoic Acid	5.18	5.10	5.08	5.10	5.06	5.13	5.11
2,3,4-Trifluorobenzoic Acid	4.98	5.01	5.02	5.13	4.96	5.10	5.11
2,3,6-Trifluorobenzoic Acid	5.05	5.15	4.97	5.02	4.94	4.99	4.53
2,4,5-Trifluorobenzoic Acid	5.99	5.97	5.96	6.04	6.12	6.11	6.09
2,4,6-Trifluorobenzoic Acid	6.01	6.03	*	6.01	5.68	5.67	5.62
3,4,5-Trifluorobenzoic Acid	5.18	5.14	5.15	5.12	5.10	5.18	5.25
2,3,4,5-Tetrafluorobenzoic Acid	5.74	5.74	5.76	5.71	5.76	5.70	5.68
2,3,5,6-Tetrafluorobenzoic Acid	6.29	6.30	6.40	6.36	6.19	6.26	6.29
Pentafluorobenzoic Acid	5.59	5.64	5.73	5.64	5.68	5.69	5.69
α,α,α-Trifluoro-o-toluic acid	5.04	5.13	5.07	5.17	5.07	5.21	5.04
α,α,α-Trifluoro-m-toluic acid	5.08	5.15	5.13	5.19	5.05	5.22	5.19
α,α,α-Trifluoro-p-toluic acid	5.25	5.30	5.25	5.34	5.19	5.31	5.34

*2,4,6-Trifluorobenzoic acid could not be quantitated at T=5 due to the presence of an interference in the chromatogram.

Table 4 Concentrations of Tracers in the Dark Tuff Samples

Compound	Concentration (ppm)						
	0	1	5	10	20	30	60
2,3-Difluorobenzoic Acid	5.26	5.23	5.10	5.12	5.13	5.10	5.15
2,4-Difluorobenzoic Acid	5.38	5.44	5.35	5.36	5.29	5.41	5.47
2,5-Difluorobenzoic Acid	5.17	5.20	5.16	5.18	5.16	5.25	5.25
2,6-Difluorobenzoic Acid	5.07	5.22	5.40	5.41	5.50	5.73	5.04
3,4-Difluorobenzoic Acid	5.07	5.09	5.09	5.10	5.09	5.06	4.98
3,5-Difluorobenzoic Acid	5.06	5.22	5.01	5.04	5.02	5.13	5.12
2,3,4-Trifluorobenzoic Acid	4.96	5.06	5.05	5.14	5.05	5.18	5.12
2,3,6-Trifluorobenzoic Acid	5.07	5.13	4.93	4.99	4.99	5.03	5.02
2,4,5-Trifluorobenzoic Acid	5.95	5.97	5.96	5.99	6.12	6.14	6.11
2,4,6-Trifluorobenzoic Acid	5.85	5.92	*	*7.00	5.67	5.65	5.70
3,4,5-Trifluorobenzoic Acid	5.07	5.10	5.08	5.16	5.20	5.13	5.39
2,3,4,5-Tetrafluorobenzoic Acid	5.74	5.76	5.80	5.68	5.79	5.72	5.62
2,3,5,6-Tetrafluorobenzoic Acid	6.29	6.33	6.22	6.13	6.18	6.23	6.32
Pentafluorobenzoic Acid	5.58	5.63	5.69	5.60	5.62	5.66	5.62
α,α,α-Trifluoro-o-toluic acid	5.00	5.08	5.04	5.04	5.02	5.04	5.09
α,α,α-Trifluoro-m-toluic acid	5.11	5.14	5.09	5.10	5.04	5.25	5.02
α,α,α-Trifluoro-p-toluic acid	5.24	5.31	5.25	5.27	5.09	5.28	5.25

*2,4,6-Trifluorobenzoic acid could not be quantitated at T=5 due to the presence of an interference in the chromatogram. The high concentration reported on T=10 is also due to an interference.

COLUMN TESTING

Another method used to measure the sorption of the tracer compounds to tuff material is the column test. The tracer is injected into a column containing ground tuff and the time required for its elution is measured. The elution volume, calculated by multiplying the elution time by the measured flow rate, is compared to that of bromide. Bromide, which is considered to be a conservative tracer, is used as a reference for each compound. All fluorinated benzoates have been tested on columns containing each of the tuffs (see the previous report for column dimensions and detection methods). The mean elution volume, the standard deviation, and the percent relative standard deviation (%RSD) for each compound are listed in Tables 5 - 7. 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 along with the mean, standard deviation (SD), and percent relative standard deviation (%RSD) for the KBr elution volumes.

The elution volumes for all acids are very similar to bromide and are generally within one standard deviation. The ratios, Tracer/KBr, are also very close to one, and in fact in the light and medium tuff most are less than one. This indicates faster travel through the column than bromide. The Tracer/KBr in the dark tuff are slightly higher than in the light and medium tuff, but, the elution volumes for KBr injections are still within one standard deviation of the benzoates. If it is assumed that bromide (potassium bromide) does not sorb to the tuff then all the benzoic and toluic acids also act conservatively.

Table 5 Column Test Results for the Medium Tuff

Compound	Mean (ml)	Standard Deviation	Tracer %RSD	Tracer/ Kbr	KBr Mean	KBr SD	KBr %RSD
2,3-difluorobenzoic acid	206.6	2.00	0.97	0.99	208.1	0.82	0.39
2,4-difluorobenzoic acid	162.6	4.77	2.93	0.96	169.5	2.52	1.49
2,5-difluorobenzoic acid	158.2	7.74	4.89	0.98	161.5	2.64	1.64
2,6-difluorobenzoic acid	161.0	5.81	3.61	1.00	160.6	2.53	1.58
3,4-difluorobenzoic acid	209.3	5.48	2.62	0.98	212.9	4.05	1.90
2,3,4-trifluorobenzoic acid	156.4	1.65	1.05	0.99	157.5	6.18	3.92
2,3,6-trifluorobenzoic acid	206.6	3.74	1.81	0.99	208.6	3.08	1.48
2,4,5-trifluorobenzoic acid	201.4	1.67	0.83	0.98	205.5	1.60	0.78
2,4,6-trifluorobenzoic acid	158.3	9.81	6.20	0.98	161.5	3.73	2.31
3,4,5-trifluorobenzoic acid	210.8	2.02	0.96	1.00	211.7	2.34	1.11
2,3,4,5-tetrafluorobenzoic acid	191.6	7.83	4.09	0.99	193.7	0.00	0.00
2,3,5,6-tetrafluorobenzoic acid	213.0	1.44	0.68	1.00	212.4	2.38	1.12
pentafluorobenzoic acid	207.4	1.26	0.61	1.00	206.5	1.41	0.68
m-toluic acid	210.4	3.34	1.59	0.97	215.9	4.45	2.06
o-toluic acid	205.7	1.20	0.58	0.98	209.7	0.52	0.25
p-toluic acid	212.5	2.42	1.14	1.01	210.5	0.60	0.29

Table 6 Column Test Results for the Light Tuff

Compound	Mean (ml)	Standard Deviation	Tracer %RSD	Tracer/ KBr	KBr mean	KBr SD	KBr %RSD
2,3-difluorobenzoic acid	301.7	6.16	2.04	0.95	316.4	7.91	2.50
2,4-difluorobenzoic acid	288.4	13.0	4.51	0.92	312.0	21.3	6.84
2,5-difluorobenzoic acid	292.7	5.34	1.82	0.99	296.7	3.30	1.11
2,6-difluorobenzoic acid	287.0	10.2	3.56	0.95	302.3	3.74	1.24
3,4-difluorobenzoic acid	292.6	14.7	5.04	0.98	298.2	12.7	4.26
3,5-difluorobenzoic acid	302.5	5.13	1.70	0.95	317.8	11.4	3.59
2,3,4-trifluorobenzoic acid	292.7	7.31	2.50	0.95	309.5	7.02	2.27
2,3,6-trifluorobenzoic acid	292.9	5.54	1.89	0.94	312.9	14.1	4.51
2,4,5-trifluorobenzoic acid	282.0	9.07	3.21	0.92	305.1	3.65	1.20
2,4,6-trifluorobenzoic acid	287.1	13.9	4.84	0.95	302.8	3.64	1.20
3,4,5-trifluorobenzoic acid	292.8	3.77	1.29	0.95	308.0	3.76	1.22
2,3,4,5-tetrafluorobenzoic acid	292.1	13.9	4.77	0.93	315.2	12.4	3.95
2,3,5,6-tetrafluorobenzoic acid	292.4	10.3	3.51	0.92	316.3	18.0	5.70
pentafluorobenzoic acid	292.6	28.3	9.67	0.98	299.1	19.9	6.66
m-toluic acid	294.3	12.3	4.19	0.96	306.0	25.6	8.36
o-toluic acid	287.4	11.9	4.14	0.93	309.2	3.85	1.25
p-toluic acid	285.5	13.9	4.87	0.90	316.1	16.8	5.30

Table 7 Column Test Results for the Dark Tuff

Compound	Mean (ml)	Standard Deviation	Tracer %RSD	Tracer/ KBr	KBr mean	KBr SD	KBr %RSD
2,3-difluorobenzoic acid	177.4	7.29	4.11	1.03	171.4	2.49	1.46
2,4-difluorobenzoic acid	269.9	6.55	2.43	1.01	266.5	9.96	3.73
2,5-difluorobenzoic acid	237.6	20.2	8.51	0.98	242.1	28.9	11.9
2,6-difluorobenzoic acid	152.8	4.68	3.06	1.00	152.8	3.79	2.48
3,4-difluorobenzoic acid	159.1	0.56	1.61	1.02	155.4	0.85	0.55
3,5-difluorobenzoic acid	245.1	10.3	4.22	1.02	240.2	6.74	2.81
2,3,4-trifluorobenzoic acid	250.2	9.55	3.82	1.04	240.0	14.0	5.82
2,3,6-trifluorobenzoic acid	152.8	4.68	3.06	1.00	152.8	3.79	2.48
2,4,5-trifluorobenzoic acid	163.0	6.05	3.71	1.00	162.2	10.5	6.47
2,4,6-trifluorobenzoic acid	135.2	3.49	2.58	0.96	140.5	4.05	2.88
3,4,5-trifluorobenzoic acid	169.4	1.51	0.89	1.01	168.0	0.21	0.12
2,3,4,5-tetrafluorobenzoic acid	162.2	2.51	1.54	0.99	164.7	3.43	2.08
2,3,5,6-tetrafluorobenzoic acid	170.9	1.07	0.63	1.01	169.7	2.23	1.31
pentafluorobenzoic acid	241.9	10.3	4.22	1.05	230.2	9.72	4.22
m-toluic acid	243.1	2.96	1.22	1.06	230.4	4.65	2.02
o-toluic acid	138.4	3.19	2.31	0.98	141.4	5.96	4.22
p-toluic acid	165.5	9.18	5.55	0.99	167.0	13.1	7.85

METHOD DEVELOPMENT

At this time, the degree of dilution that will occur during the tracer test is largely unknown. A dilution of at least 6 orders of magnitude is expected due to the large distance and high pumping rate involved with these tests. It was therefore recommended by HRC that a preliminary tracer test be performed This will allow all aspects of the test to be examined and further optimized prior to the larger more costly testing.

It is the current plan to inject 2,6-difluorobenzoic acid. Method development to optimize the analysis of this compound is therefore in progress. We are currently investigating the effects of injecting larger sample volumes into the HPLC. We also plan to develop concentrating procedures using solid phase extraction.

Figure 1

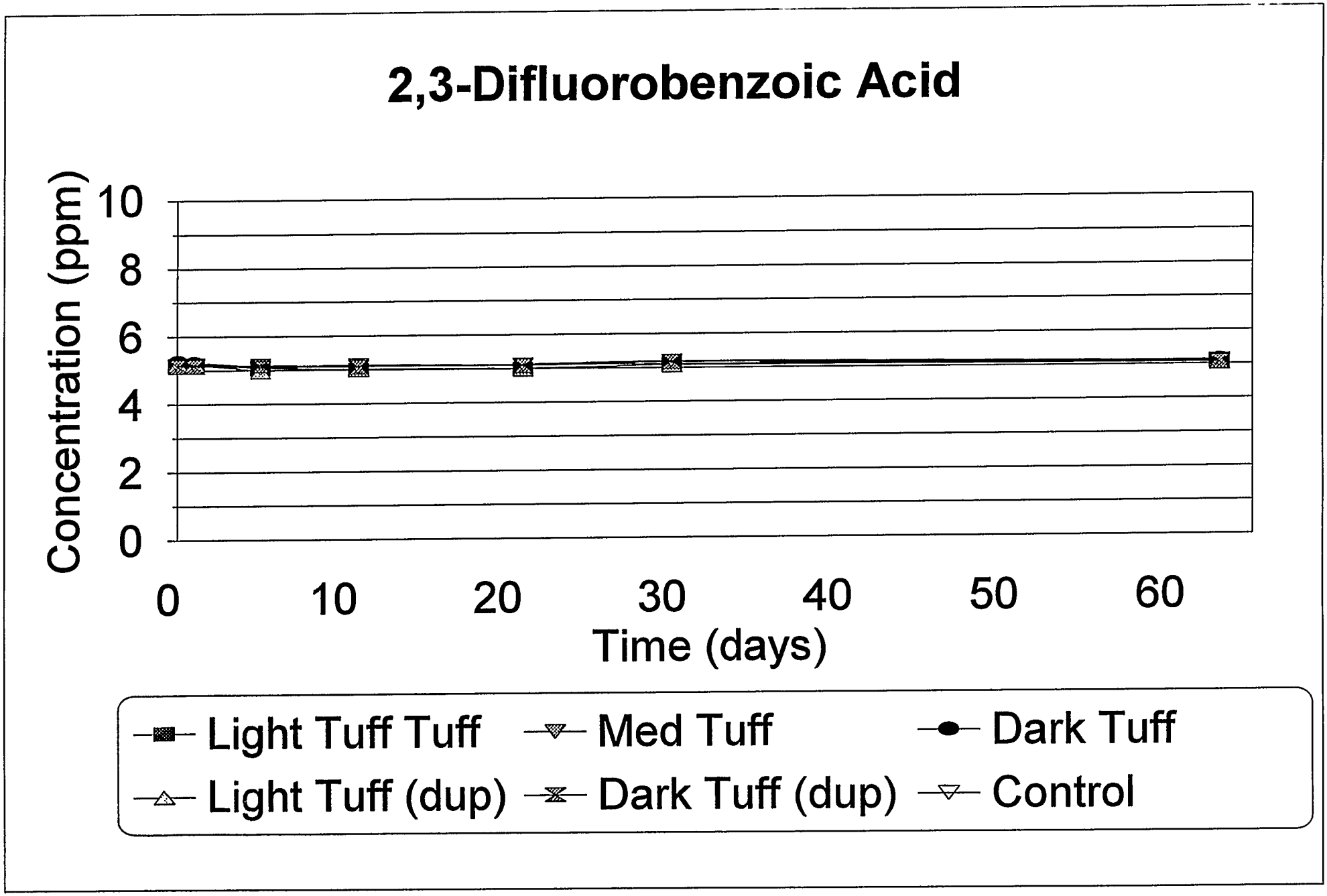

2,3-Difluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 2

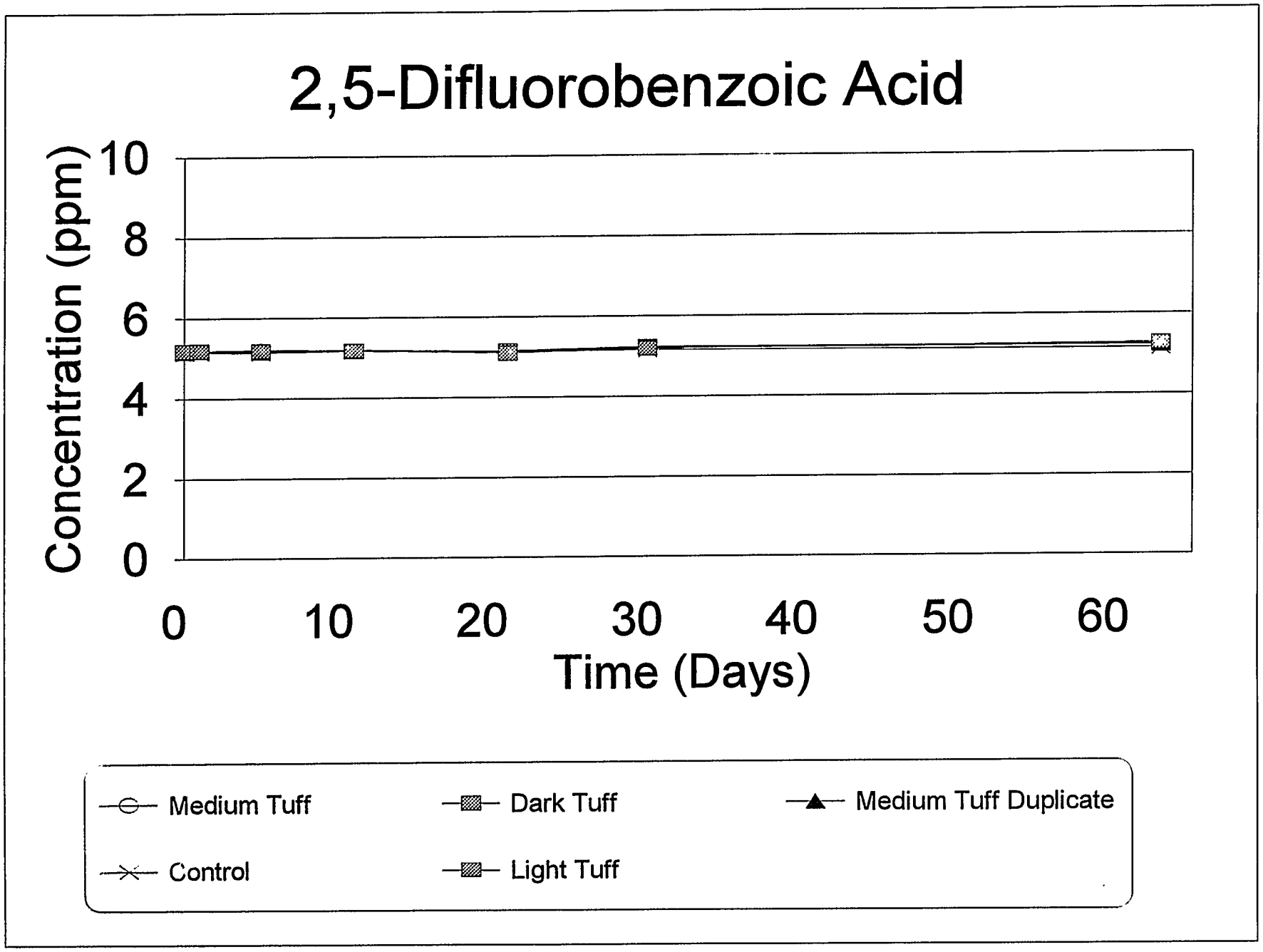

2,5-Difluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff

Figure 3

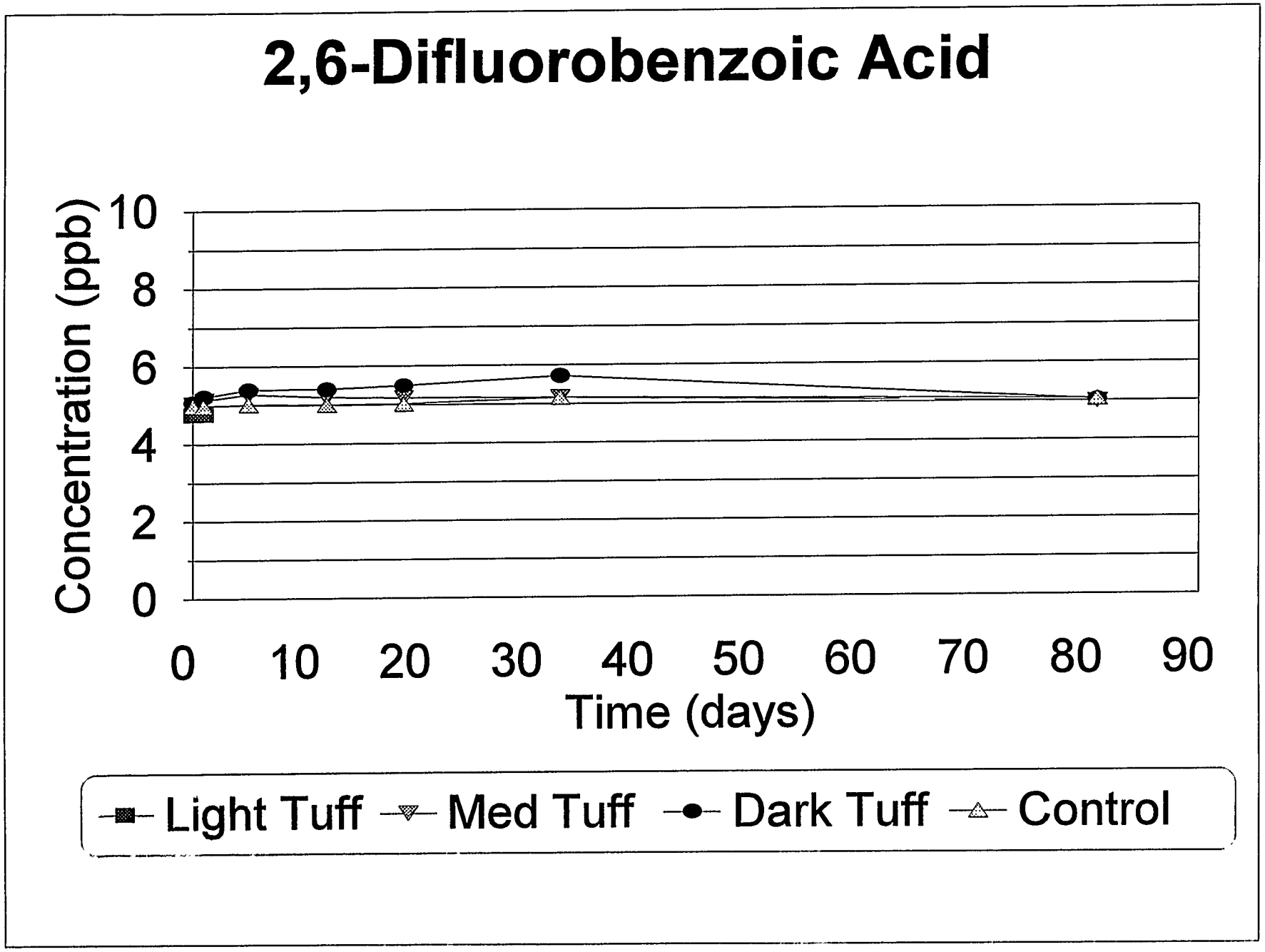

2,6-Difluorobenzoic Acid
Concentration (ppb)
10
8
6
4
2
0
0
10
20
30
40
50
60
70
80
90
Time (days)
Light Tuff
Med Tuff
Dark Tuff
Control

Figure 4

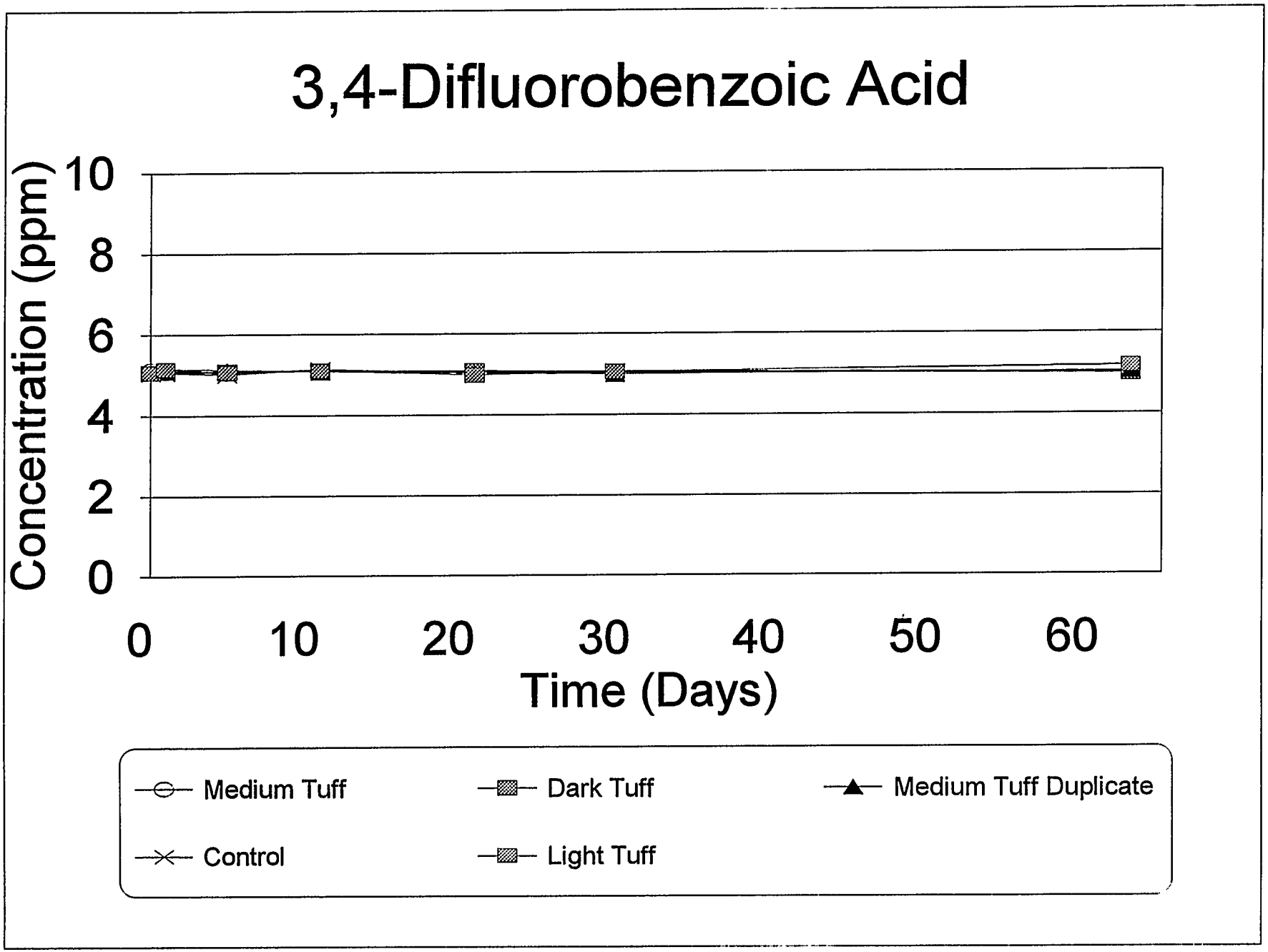

3,4-Difluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff

Figure 5

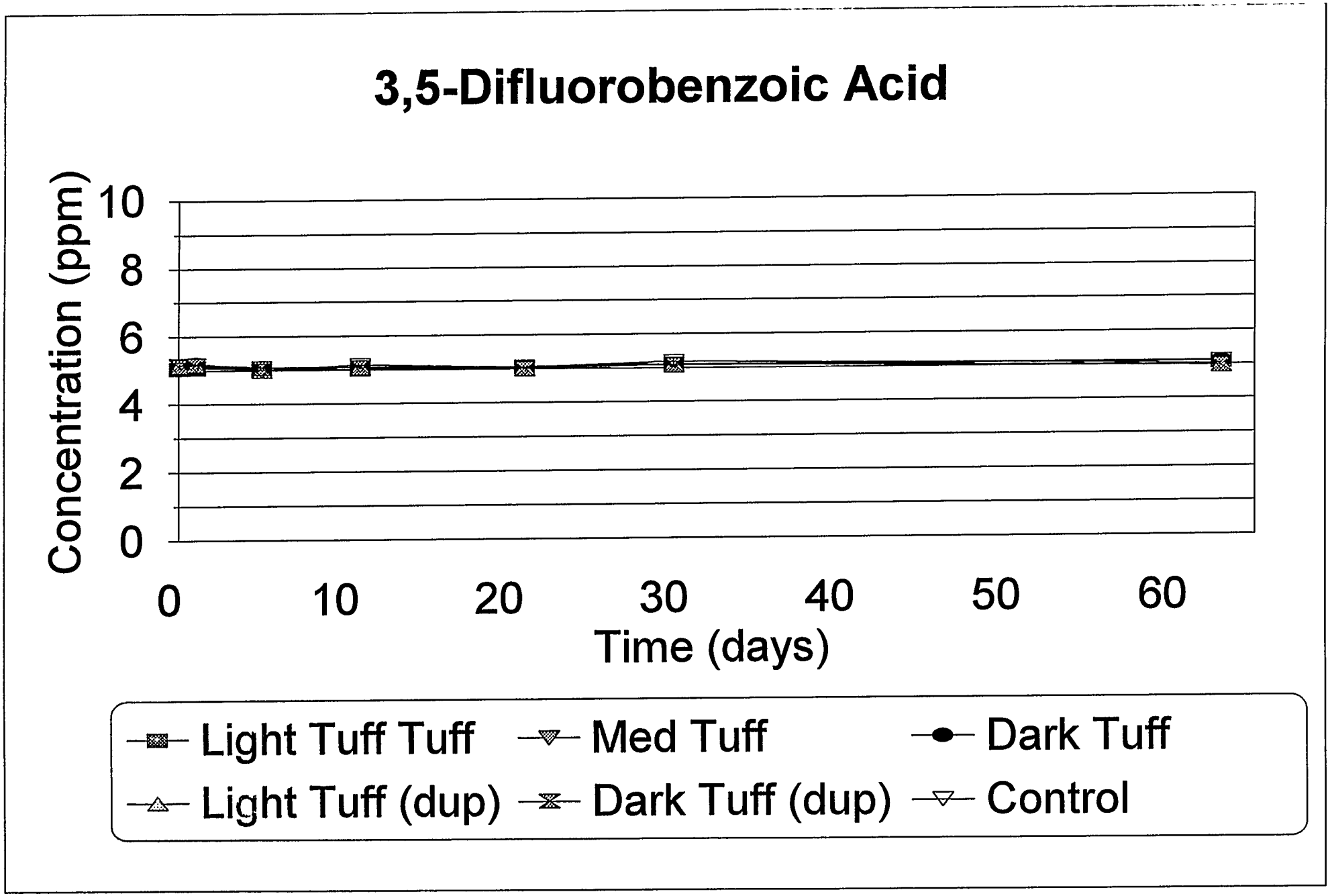

3,5-Difluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 6

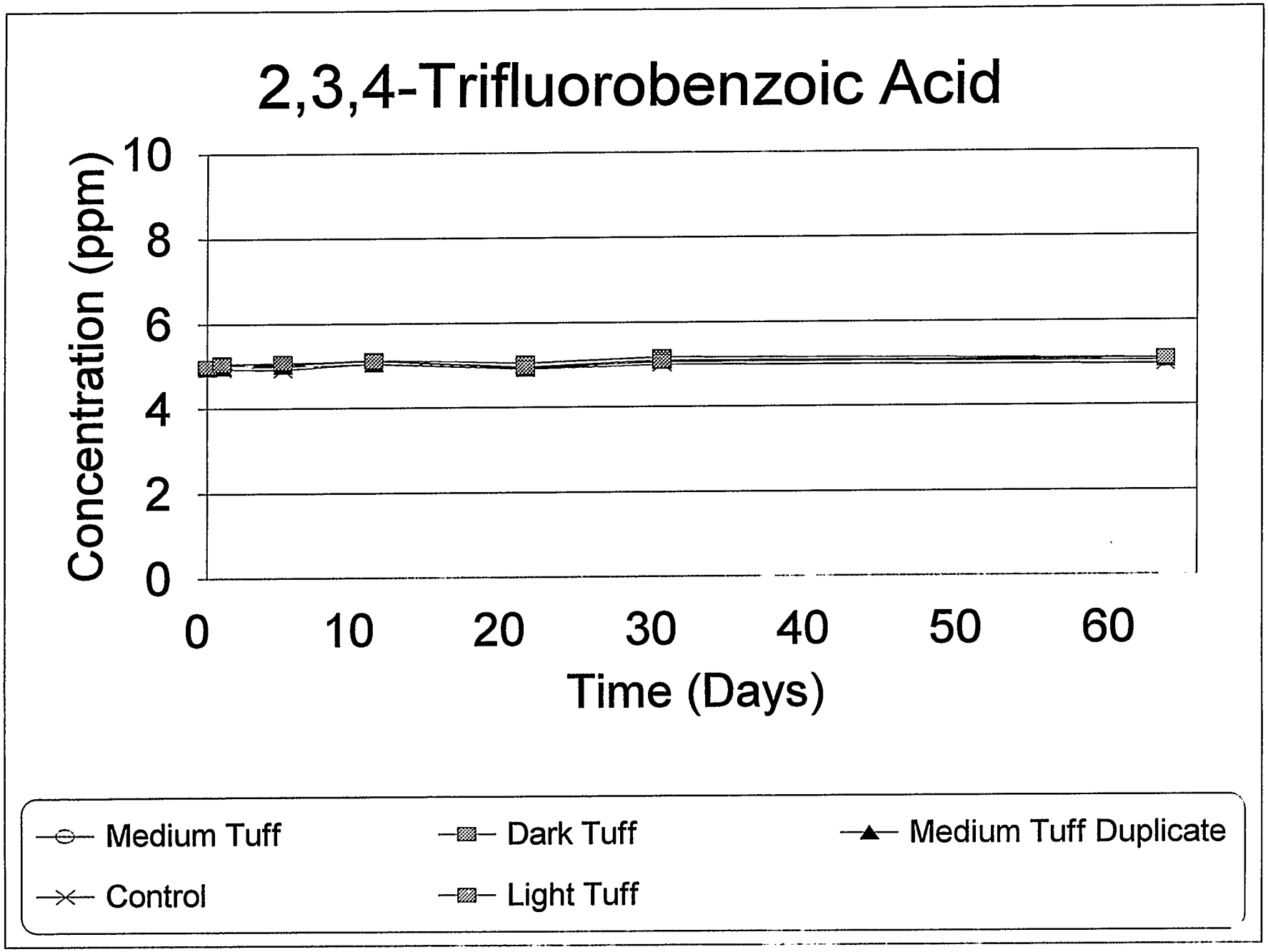

2,3,4-Trifluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff

Figure 7

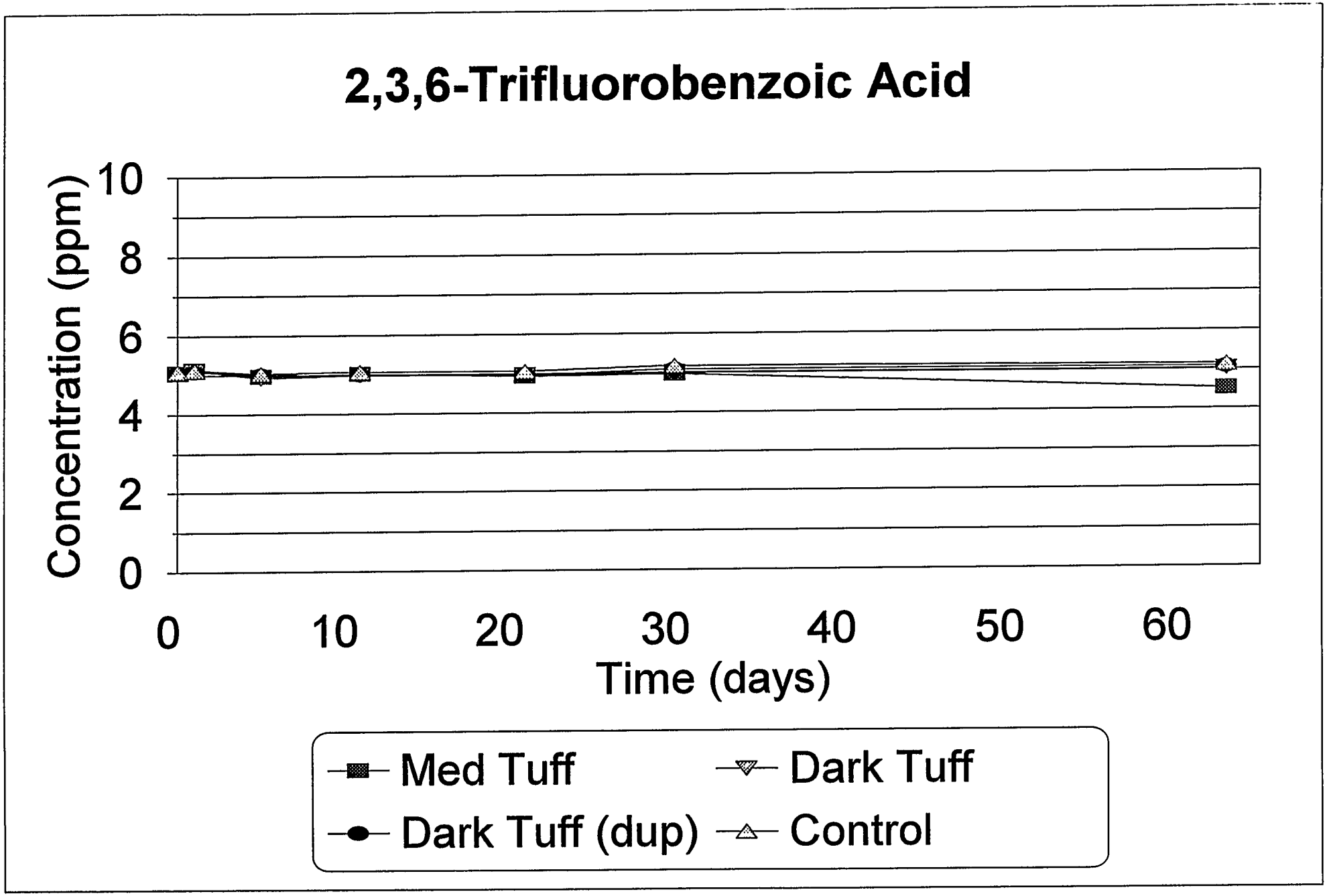

2,3,6-Trifluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Med Tuff
Dark Tuff
Dark Tuff (dup)
Control

Figure 8

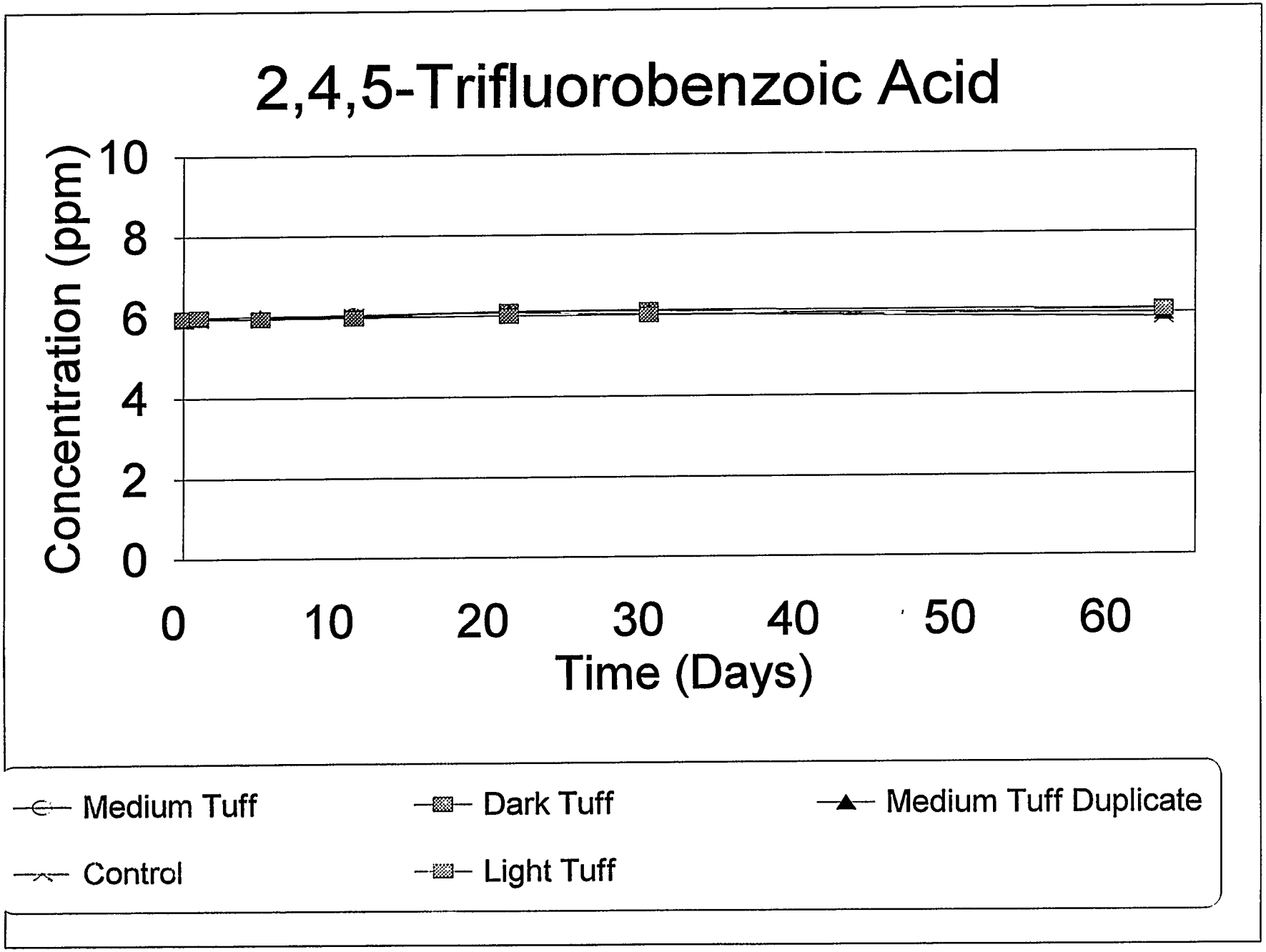

2,4,5-Trifluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff

Figure 9

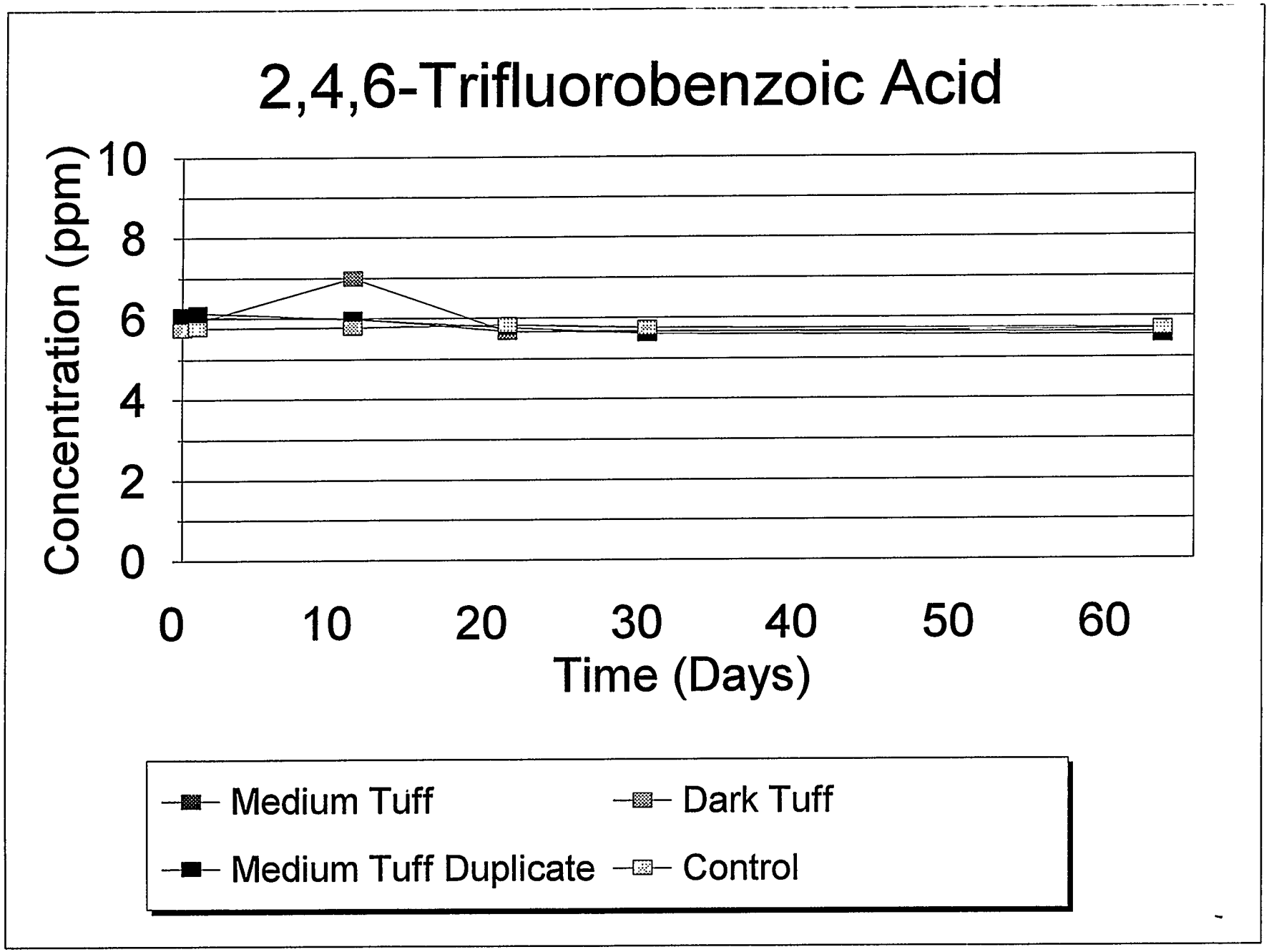

2,4,6-Trifluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control

Figure 10

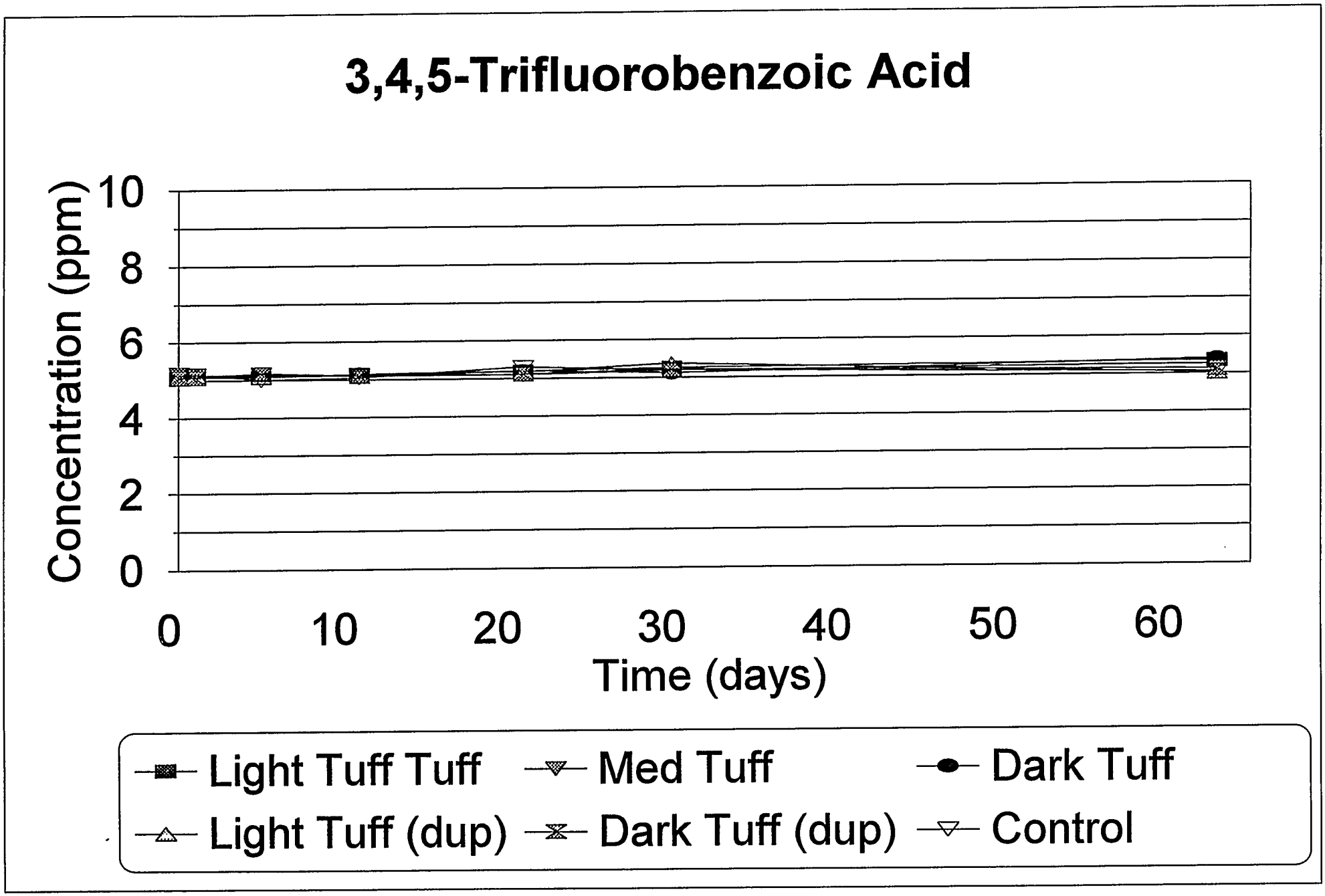

3,4,5-Trifluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 11

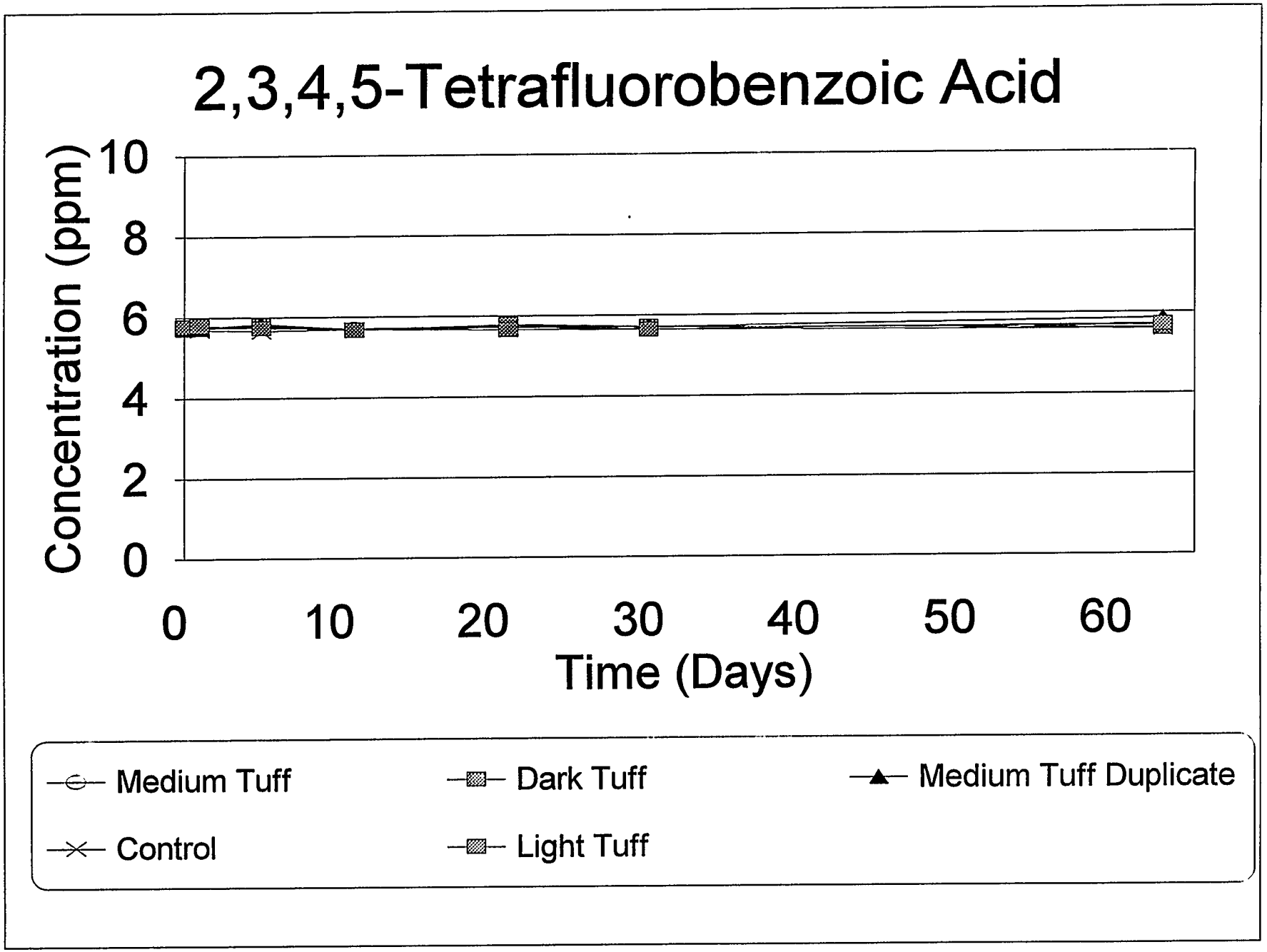

2,3,4,5-Tetrafluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff

Figure 12

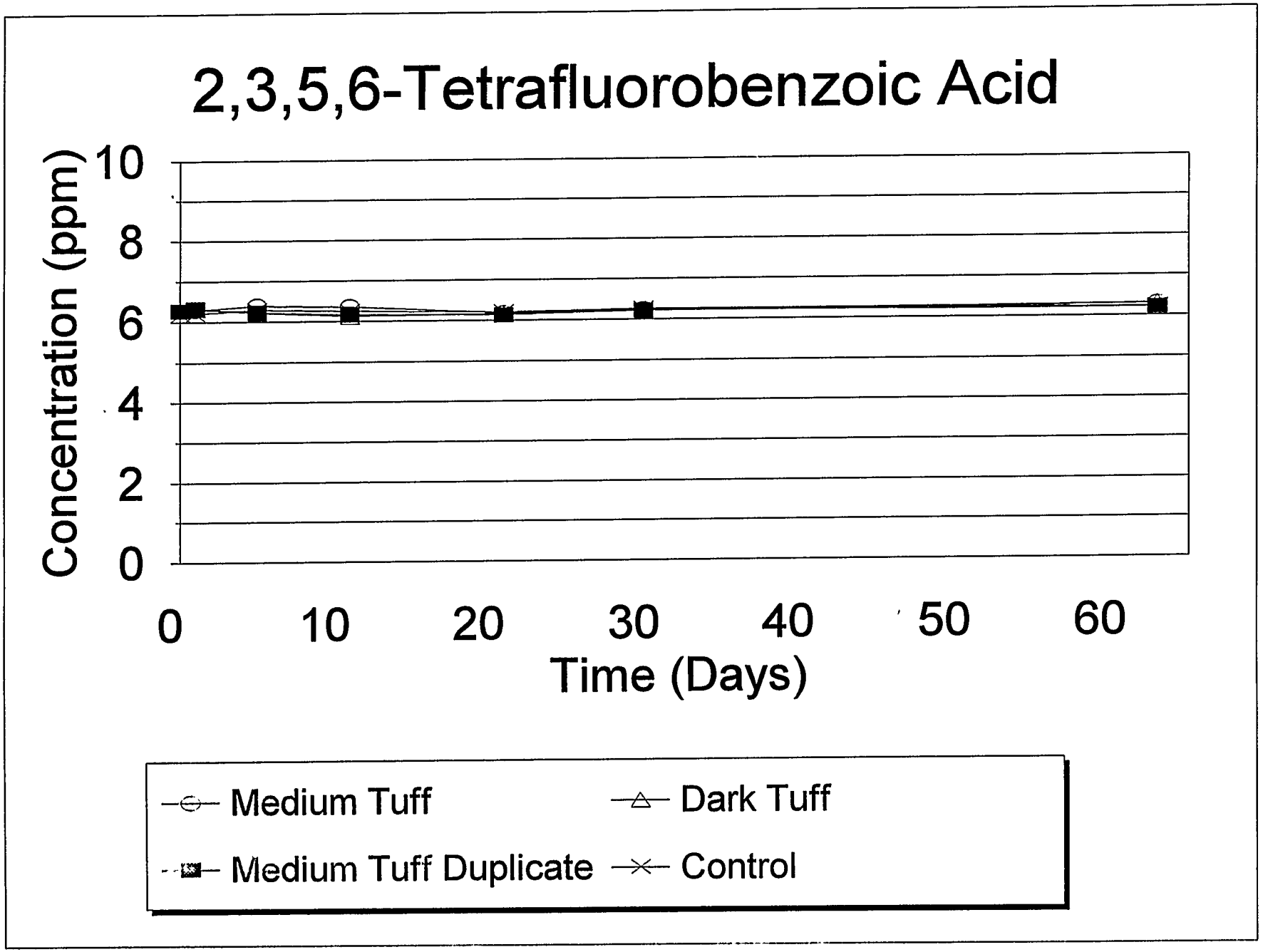

2,3,5,6-Tetrafluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control

Figure 13

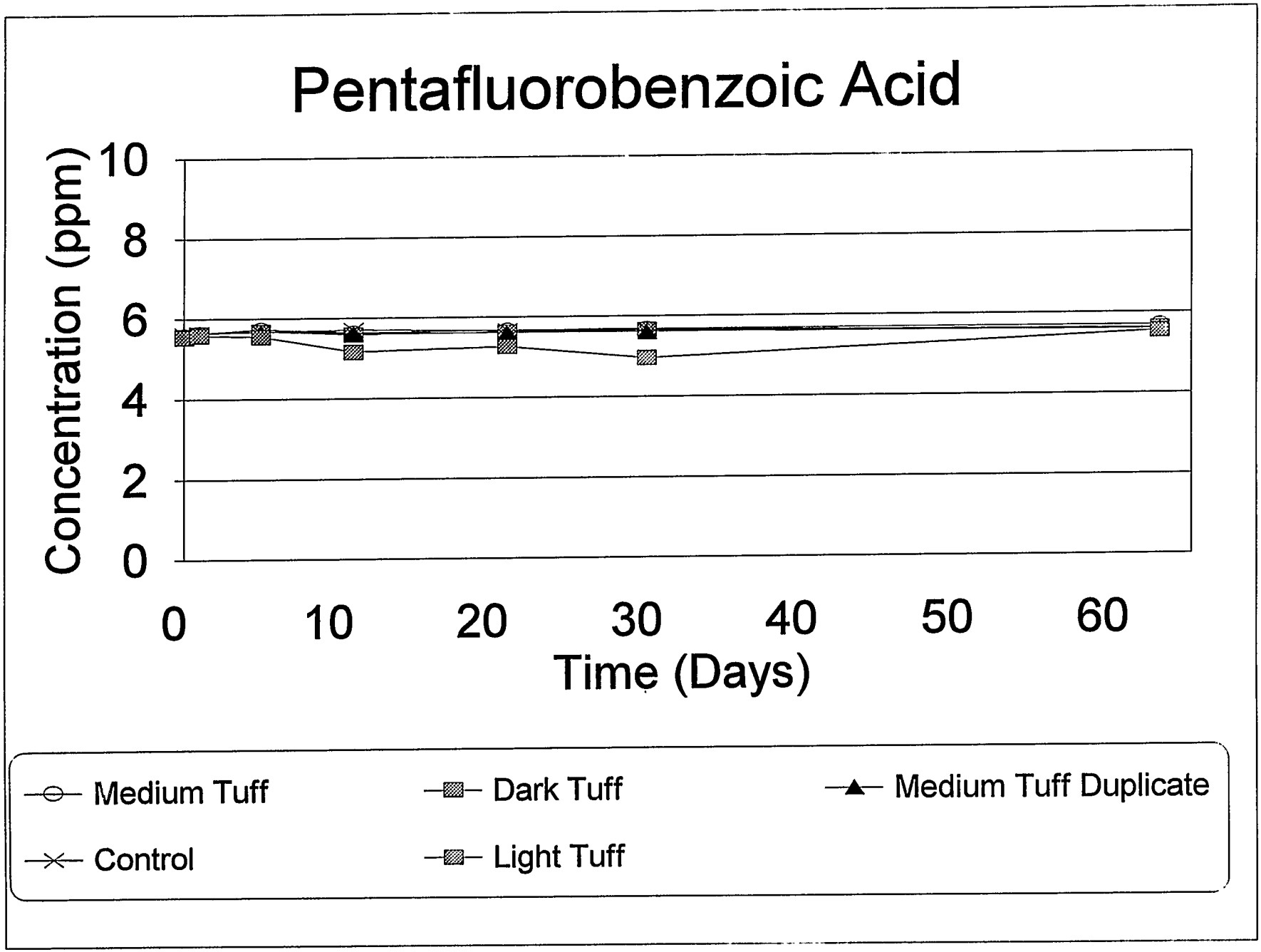

Pentafluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff

Figure 14

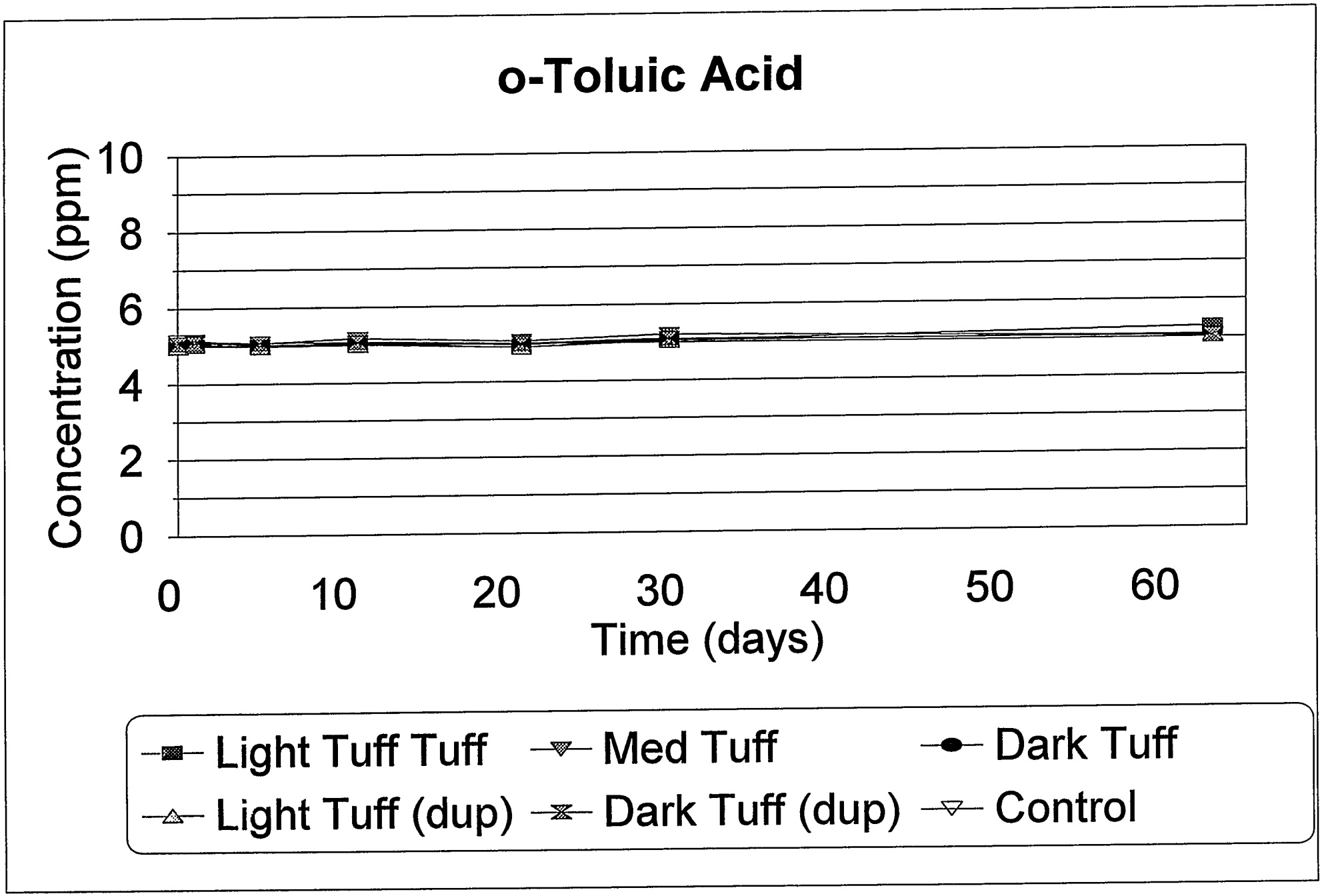

o-Toluic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 15

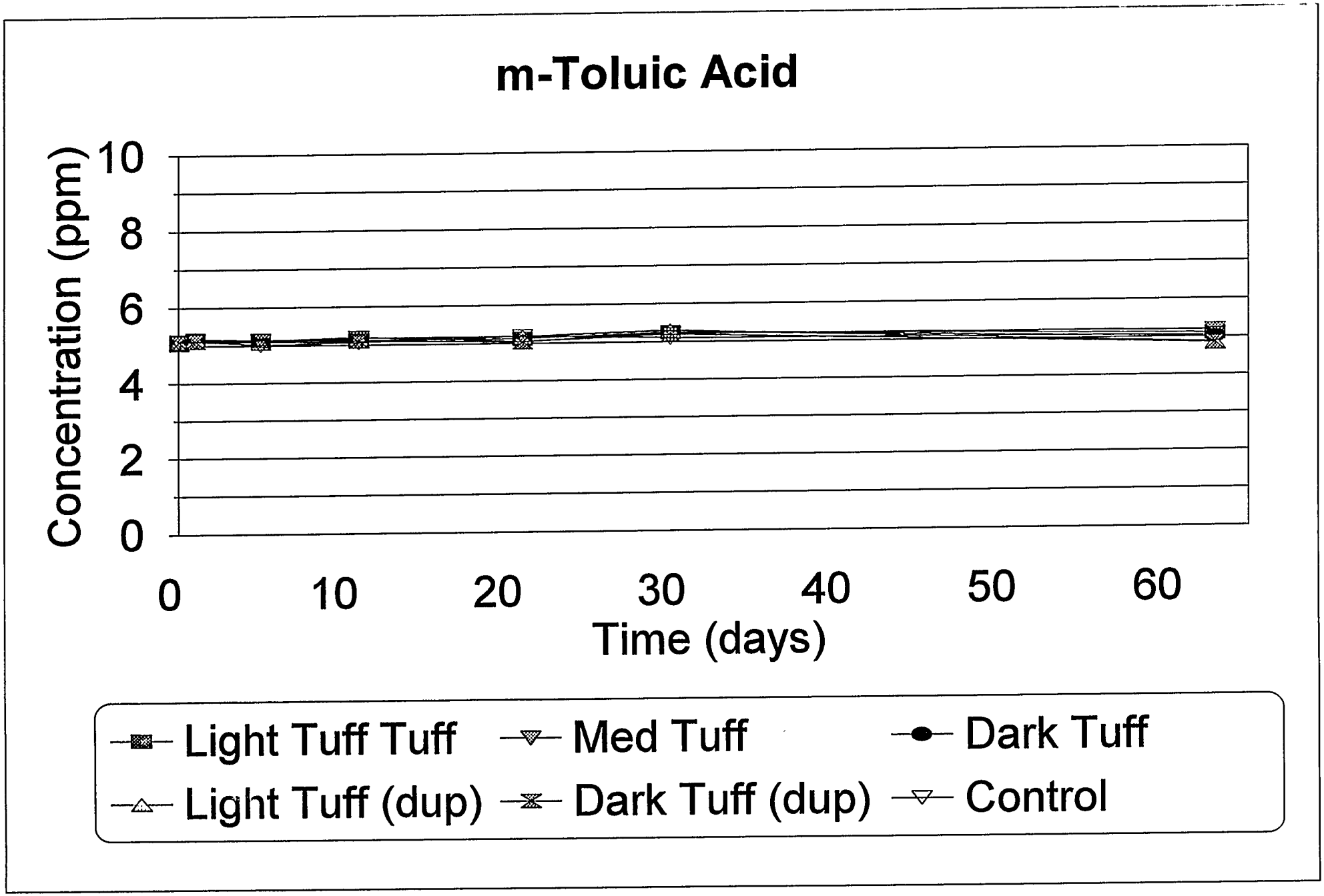

m-Toluic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 16

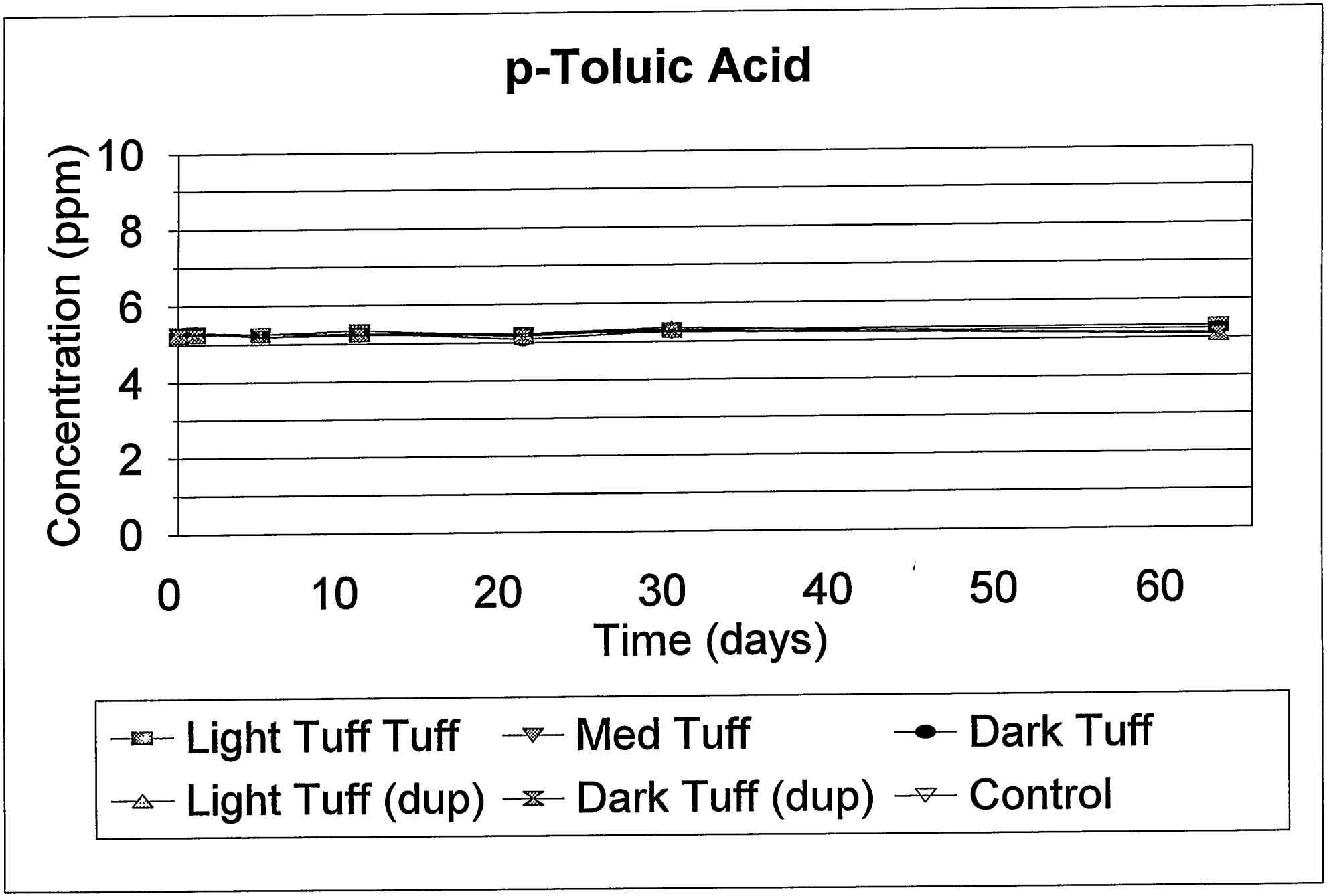
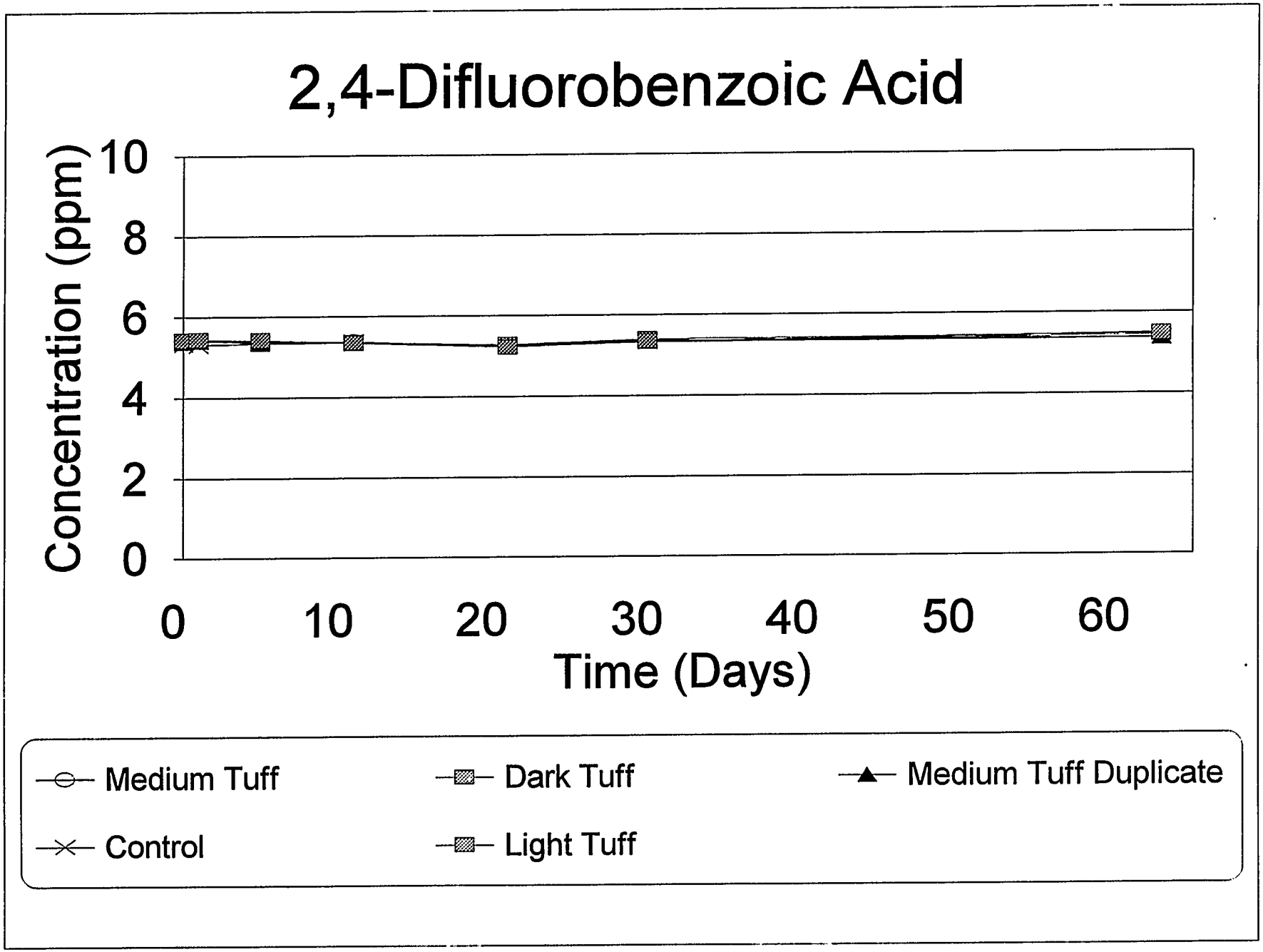

p-Toluic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (days)
Light Tuff Tuff
Med Tuff
Dark Tuff
Light Tuff (dup)
Dark Tuff (dup)
Control

Figure 17


2,4-Difluorobenzoic Acid
Concentration (ppm)
10
8
6
4
2
0
0
10
20
30
40
50
60
Time (Days)
Medium Tuff
Dark Tuff
Medium Tuff Duplicate
Control
Light Tuff