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TOXICITY OF AQUEOUS FILMFORMING FOAMS TO MARINE ORGANISMS: LITERATURE REVIEW AND BIOLOGICAL ASSESSMENT

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INTRODUCTION

Aqueous filmforming foams (AFFF) are used regularly by the Air Force and Navy in training exercises at fire-fighting schools and, when necessary, for fuel/oil fire control aboard ship. These AFFF agents work by producing a flame-quenching blanket that floats on the surface of fuel and/or water. This blanketing results in complete surface vapor-proofing, cooling the fuel, and preventing reflash or reburning of the extinguished surface. These agents are also effective on unburned fuels, rendering them fireproof to future ignition.

The are a combination of AFFFs fluorocarbons, surfactants, and solubilizers. They have an exceptional resistance to thermal. chemical, electrical, and biological attack (Chan, 1982). The AFFF agents a oduced by only a few different manufacturers under the guidelines and spec .cations given in MIL-F-24385C (Military Specification, 1981). Approximately / million gallons of AFFF are produced for Naval and Air Force use annually. Depending on the formulation being used, the concentrate is diluted to either an optimum 3- or 6-percent/solution with freshwater, seawater, or bilge water before using in fire-fighting systems. Wastewater resulting from training exercises generally contains less than half the original AFFF concentration. About 200 million gallons of AFFF wastewater are being generated annually by the Navy and the Air Force.

The usage of AFFF and the disposal of AFFF-laden wastewater have the potential for an adverse impact on the environment. These foams are potentially toxic due to the fluorocarbons and surfactants. Additionally, the wastewater contains other contaminants such as residual fuel and combustion products, which could add to the toxicity. The use of seawater or bilge water as the dilutor yields other potentially toxic contaminants from the high concentrations of chlorides and sulfides (Chan, 1982).

The possible adverse effects of AFFF and AFFF-laden wastewater are divided into two categories: (1) the toxic effects to the aquatic/marine environment and (2) the effects on biological processes in sewage treatment plants. There is a potential for adverse effects on sewage treatment organisms if these wastewaters are discharged directly into the sewage system. Possible impacts are (1) inhibition of microbial oxygen uptake, (2) toxicity to microbial organisms, (3) foaming in aeration basins, and (4) development of sludge settling problems in clarifiers.

The toxicity of AFFF to various freshwater and marine organisms has been assessed. The 3-M Company (manufacturer of several "Lightwater" AFFF agents) has tested each of its products for toxicity to freshwater and/or marine organisms. Product Environmental Data Sheets prepared by the 3-M Company are presented in Appendix A. These reports provide information on the toxicity of AFFF agents to freshwater and marine organisms as well as information regarding possible effects on conventional biological treatment facilities. The USAF Environmental Health Laboratory, Kelly AFB, Texas, performed assays on AFFF agents manufactured by Ansul Company (Ansul K74-100); National Foam Systems, Inc. (Aer-O-Water 3 and Aer-O-Water 6); and 3-M Company (Lightwater FC-199, FC-200, and FC-206). Their toxicity data along with information regarding recommended levels to sewage treatment facilities and direct stream discharge are presented in Appendix B. A compilation of toxicity data from the available literature has been assembled and is presented as Table 1.

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Agent/Species Assessed (Fre	reshwater/Marine)	2) Results of Study	Source
FC-199: Fathead Minnow (Pimephales promelas)	(FW)	96 hr LC ₅₀ = 398 mg/l	LeFebvre & Thomas, 1973
<u>FC-200</u> : Fathead Minnow (<u>Pimephales promelas</u>)	(FW)	96 hr LC ₅₀ = 97 mg/l	LeFebvre & Thomas, 1973
<u>FC-203</u> : Fathead Minnow (<u>Fimephales promelas</u>)	(FW)	96 hr LC ₅₀ = 750 mg/l	3M Co., 1980a
Rainbow Trout (<u>Salmo gairdneri</u>)	(FW)	96 hr LC ₅₀ = 1300 mg/l	3M Co., 1980a
Water Flea (<u>Daphnia magna</u>)	(FW)	48 hr LC ₅₀ = 1600 mg/l	3M Co., 1980a
Scud (Gammarus fasciatus)	(FW)	48 hr LC ₅₀ = 1100 mg/l	3M Co., 1980a
Green Algae (Chlorella pyrenoidosa)	(FW)	No growth inhibition @ 1000 mg/l	3M Co., 1980a
Blue-green Algae (Phormidium inundatum)	(FW)	No growth inhibition @ 1000 mg/l	3M Co., 1980a
Oyster larvae (<u>Crassostrea</u> <u>virginica</u>)	(W)	$48 \text{ hr } \text{LC}_{5,0} = 47 \text{ mg}/1$	3M Co., 1980a
Killifish (Fundulus heteroclitus)	*(W)	95 hr LC ₅₀ = 2500 mg/l	3M Co., 1980a
Grass Shrimp (Palaemonetes pugio)	(W)	$96 \text{ hr } \text{LC}_{50} = 510 \text{ mg/l}$	3M Co., 1980a
FC-203A: Fathead Minnow (<u>Pimephales promelas</u>)	(FW)	96 hr LC ₅₀ = 300 mg/l	3M Co., 1980a
FC-203C: <u>Killifi</u> sh (Fundulus heteroclitus)	*(H)	96 hr LC ₅₀ = 1400 mg/l	3M Co., 1982a
Fathead Minnow (<u>Pimephales</u> promelas)	(FW)		
Green Algae (Selenastrum capricornatum)	(FW)	$96 \text{ hr } \text{LC}_{50}^{\circ} = 408 \text{ mg/l}$	3M Co., 1982a
FC-206: Fathead Minnow (<u>Pimephales</u> promelas)	(FW)	96 hr LC _{EO} = 3000 mg/l	3M Co., 1980b
Fathead Minnow (P. promelas) juveniles	(FW)	96 hr $LC_{5,0} = 1080 \ \mu l/l$	LeFebvre & Inman, 1974
Fathead Minnow (P. promelas) fry	(FW)	96 hr $LC_{50} = 170 \ \mu l/l$	LeFebvre & Inman, 1974
Rainbow Trout (Salmo gairdneri)	(FW)	96 hr $LC_{5,0}^{2} = 1800 \text{ mg/l}$	3M Co., 1980b
Killifish (Fundulus heteroclitus)	*(W)	96 hr LC ₅₀ = 1820 mg/l	3M Co., 1980b
Grass Shrimp (Palaemonetes vulgaris)	(M)	96 hr 1.0 = 280 me/l	3M Co 1080b

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 $\stackrel{\scriptstyle\scriptscriptstyle +}{\scriptstyle\scriptscriptstyle +}$ Found in brackish to saltwater environments.

Table 1. Data available from the literature on the organisms (continued).	on the toxicity of AFFF agents to freshwater and marine	and marine
Agent/Species Assessed (Freshwater/Marine)	Marine) Results of Study	Source
	96 hr LC ₅₀ = 3260 mg/l	3M Co., 1980b
Oyster Larvae (<u>Crassostrea</u> <u>virginica</u>) (M)	$48 \text{ hr } \text{LC}_{50} = > 100 < 240 \text{ mg/l}$	3M Co., 1980b
Water Flea (<u>Daphnia magna</u>) (FW)	$48 \text{ hr } \text{LC}_{50} \approx 5850 \text{ mg/l}$	3M Co., 1980b
Scud (Gammarus fasciatus) (FW)	$48 \text{ hr } \text{LC}_{50} = 5170 \text{ mg/l}$	3M Co., 1980b
Green Algae (Chlorella pyrenoidosa) (FW)	Growth inhibited at 1:1000 dilution Chan 1982	ition Chan 1982
Blue-green Algae (<u>Phormidium</u> inundatum) (FW)	Growth inhibited at 1:1000 dilution Chan, 1982	ition Chan, 1982
FC-206A:		
Bluegill Sunfish (Lepomis macrochirus) (FW)	96 hr LC ₅₀ = 1200 mg/l	3M Co., 1980c
Fathead Minnow (Pimephales promelas) (FW)	96 hr LC ₅₀ > 3000 mg/l	3M Co., 1980c
Water Flea (<u>Daphnia magna</u>) (FW)	48 hr LC ₅₀ = 2300 mg/l	3M Co., 1980c
FC-206C:		
Killifish (Fundulus heteroclitus) (M)*	96 hr LC ₅₀ > 2000 mg/l	3M Co., 1982b
Fathead Minnow (Pimephales promelas) (FW)	96 hr LC ₅₀ > 2000 mg/l	3M Co., 1982b
Green Algae (<u>Selenastrum capricornutum</u>) (FW)	96 hr LC ₅₀ = 345 mg/l	3M Co., 1982b
FC-780: Killifish (Fundulus <u>heteroclitus</u>) (M)*	96 hr LC ₅₀ > 5000 mg/l	3M Co., 1982c
FC-780B: Bluegill Sunfish (Leponis machrochirus) (FW)	96 hr LC _{co} = 1600 mg/l	3M Co., 1981
Killifish (Fundulus heteroclitus) (M)*	96 hr LC ₅₀ = 3900 mg/l	3M Co., 1981
<u>AOW-3</u> : Fathead Minnow (<u>Pimephales promelas</u>) (FW)	96 hr LC ₅₀ = 600 mg/l	LeFebvre & Thomas, 1973
AOW-6: Fathead Minnow (<u>Pimephales</u> promelas) (FW)	96 hr LC ₅₀ = 225 mg/l	LeFebvre & Thomas, 1973
ANSUL K74-100: Fathead Minnow (<u>Pimephale</u> aelas) (FW)	96 hr LC ₅₀ = 1100 mg/l	LeFebvre & Inman, 1975

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These earlier studies demonstrated that a wide range of toxic concentrations exist for a variety of organisms. Larvae of the Eastern oyster (Crassostrea virginica) were the most sensitive organisms tested, with a 48-hour EC_{50} of 47 mg/liter to the FC-203 formulation (manufactured by the 3-N Company). All species of fish tested showed a high tolerance to the various AFFF agents tested with an average LC_{50} near 1500 mg/liter. In general, these data suggest the available AFFF formulations are mildly toxic or nontoxic.

The second area of concern is the impact of AFFF on sewage treatment organisms. The 3-M Company has performed biodegradation tests, microbial respiration inhibition tests, and activated sludge pilot plant studies on many of its AFFF products. These results, along with the recommended treatment concentrations, are summarized in Table 2. Information for AFFF agents produced by the Ansul Company and the National Foam Systems Company are also included in this table. These data suggest that there is little potential for toxicity from AFFF introduced to the sewage treatment facilities. There is a potential problem, however, with excessive foaming for some of the agents. The recommended treatment concentrations reflect these precautions.

The vast majority of the available toxicity data has come from studies performed on freshwater organisms. Since there is a high potential for dispersion of AFFF in the marine environment and this is a prime Navy operating area, more studies on the toxicity to marine organisms should be conducted before a final assessment can be made. The purpose of this study was to collect information from the literature regarding the toxicity of AFFF and conduct supplementary toxicity tests using AFFF and appropriate marine organisms. This work was performed during October 1982 at the Naval Ocean Systems Center by personnel in the Marine Sciences Division with funding from the Naval Facilities Engineering Command.

METHODS

The FC-780B AFFF agent manufactured by the 3-N Company is the formulation currently being used by the Navy. It is routinely diluted to a 6-percent solution for fire-fighting purposes. It was assessed for toxicity to marine phytoplankton and crustaceans. The 96-hour definitive toxicity tests were preceded with a series of range-finding tests to identify the approximate toxic concentration. Conditions and procedures were the same for both range-finding and definitive toxicity tests. The species selected for these tests are routinely used for bioassays and toxicity testing.

TOXICITY TO PHYTOPLANKTON

The toxicity of this AFFF agent to marine phytoplankton was determined by monitoring in vivo fluorescence (IVF) and 3-(3,4-dichlorophenyl)-1, 1dimethylurea (DCMU)-induced fluorescence (DCMU-F). The IVF measurements were used to estimate growth rates according to the procedures given in Lockheed (1979), with minor modifications. The ratios of DCMU-F to IVF were calculated for phytoplankton under the various test conditions and used as a measure of photosynthetic efficiency (Roy & Legendre, 1979, 1980).

2. ed i	Effects of various AFFF agents in the literature.	s on sewage treatment facilities.	lities. Information collected from data	ed from data
AFFF Agent/ 20 Day BOD (mg/l)	Effects on Microbial Respiration	Effects on Microbial Activity	Activated Sludge Pilot Plant Studies	Recommended Treatment Concentration/Source
FC-200: 339,000	N/A	N/A	N/A	5 µ1/1 ***********************************
FC-203: 1,060,000 FC-203A·	No inhibition @ conc. up to 1000 mg/l	No inhibition @ conc. up to 1000 mg/l	N/A	N/A 3M Co., 1980a
427,000	N/A	N/A	N/A	N/A 3M Co., 1980a
<u>FC-203C</u> : 580,000 FC-206:	No inhibition @ conc. up to 1000 mg/l.	N/A	N/A	25 mg/l 3M Co., 1982a
210,000	No inhibition @ conc. up to 1000 mg/l.	No inhibition @ conc. up to 1000 mg/l.	Acceptable treatability below 1000 mg/l; 1000 mg/l does cause foaming.	100 mg/l 3M Co., 1980b
330,000	No inhibition @ conc. up to 1000 mg/l.	No inhitition @ conc. up to 1v60 mg/l.	No foaming or sludge settling problems during testing.	N/А ЗМ Со., 1980с
<u>FC-206C:</u> 330,000 FC-780R.	No inhibition @ conc. up to 1000 mg/l.	N/A	N/A	50/mg/l 3M Co., 1982b
372,000	N/A	N/A	N/A	100 mg/l 3M Co., 1981
338,000	N/A	N/A	N/A	60 µl/l LeFebvre & Thomas, 1973
287,000	N/A	N/A	N/A	22.5 μ1/l LeFebvre & Thomas, 1973
154,000	N/A	N/A	N/A	55 μ/l LeFebvre & Inman, 1975
NA = Not annlicable	Q			

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NA = Not applicable

The phytoplankton <u>Dunaliella</u> sp. (Division Chlorophyta) was selected as the test species for this study. Stock cultures of <u>Dunaliella</u> were maintained in exponential-phase growth on Guillard's F/2 medium (Guillard & Ryther, 1962) at constant temperature (18 °C) and illumination (1.9 milliwatts/cm²).

Determination of Test Concentrations

Two range-finding tests were done prior to the definitive toxicity test with <u>Dunaliella</u>. In the first range-finding test, FC-780B AFFF concentrations of 0.01, 0.10, and 1.00 gm/liter were assessed over a 96-hour period. No deleterious effects were observed in phytoplankton at these concentrations of this AFFF agent. The second range-finding test, a 72-hour assay, resulted in no effect at either a 1.0- or a 2.0-gm/liter exposure. Complete cessation of growth and death of cells were observed at the 10.0-gm/liter exposure after 72 hours. A concentration of 60.0-gm/liter (equal to the 6-percent dilution) resulted in immediate death of the exposed phytoplankton. The AFFF concentrations used in the definitive toxicity test, 2.0, 4.0, 8.0, and 10.0 gm/liter plus controls, were selected from the results obtained in the second range-finding test.

Test Procedures

For all toxicity tests, 1.5 liters of culture media were inoculated with stock phytoplankton 5 days prior to the start of the test. After this 5-day period, the cells had entered exponential-phase growth. Cell density was approximately 6.0 times 10^4 cells/ml. Test solutions were prepared by adding 100 ml of this culture to 100 ml of each AFFF test solution. A final cell density of 3 times 10^4 cells/ml was achieved. Control samples were prepared by combining 100 ml of the phytoplankton culture with 100 ml of filtered seawater.

The AFFF test solutions were prepared by weighing aliquots of AFFF concentrate to the nearest 0.001 gm. These known amounts of concentrate were diluted with appropriate volumes of 0.45- μ filtered seawater to achieve the desired AFFF concentrations.

Twenty replicates were prepared for the controls and for each FC-780B AFFF concentration assessed. A 6.5-ml aliquot of phytoplankton/AFFF solution was delivered to the test containers. Ten-ml (13 by 100 mm) glass-stoppered KIMAS glass tubes were used for the test containers. These tubes fit directly into the fluorometer.

All tubes were cleaned and conditioned in the following manner. They were first soaked for 24 hours in RBS-35 biological cleaning solution. This solution was decanted, and the tubes were rinsed six times in hot tap water followed by six rinses with deionized water. A 24-hour soak in filtered seawater followed the washing regime. The seawater soak was decanted just prior to the start of the test. Immediately after combining algae and AFFF, the tubes were filled with the test solutions and IVF measurements were made on all replicates. Fluorescence measurements were made with a Turner Designs model 10-000R fluorometer. Following these IVF measurements, DCMU-F measurements were made on three replicates selected randomly from each treatment condition. DCMU-F measurements were made approximately 1 minute after adding 50 μ 1 deionized water saturated with DCMU to the phytoplankton samples. The samples containing DCMU were discarded after measurement; remaining samples were maintained in a constant temperature incubator (18 °C) under constant illumination (1.9 milliwatts/cm²). Tubes were held in a wire mesh rack suspended approximately 18 cm above eight "Cool White" fluorescent bulbs.

The IVF and DCMU-F measurements were made at 24-hour intervals over a 96-hour period. All samples were placed on a Vortex mixer for 15 seconds prior to measurement to assure sample homogeneity.

Data Analysis

The data obtained over the 96-hour period were used to assess differences in growth rates and photosynthetic efficiencies in phytoplankton. Growth rates were determined from the IVF data. Using the IVF data as the dependent variable and time as the independent variable, linear regression equations were generated for phytoplankton grown under each condition. Since growth rate is approximated by the slope of the regression line, similar slopes indicate similar growth rates. An analysis of covariance on these linear regression equations was used to compare growth rates (slopes) of controls and treatments. The data were also displayed graphically to depict subtle changes in IVF over time, since the regression equations and the statistical analyses did not show where such changes occurred.

The productivity efficiency of phytoplankton was computed as the ratio of DCMU-F to IVF. These values were determined for each 24-hour period over the 96 hours. As with the IVF data, the productivity efficiency data were plotted against time to depict subtle trends. The Kruskal-Wallis test was used to determine if differences existed among treatments at each sampling period. This statistical test compares each sample with all remaining samples to maximize the number of possible comparisons. If a significant difference was detected by the kruskal-Wallis test, the nonparametric multiple range test (Zar, 1974) was used to determine where differences occurred. Control versus "Treatment" comparisons are reported here. All statistical tests were performed at the 95-percent confidence level.

TOXICITY TO BRINE SHRIMP

The second species selected for AFFF toxicity testing was <u>Artemia salina</u>, commonly known as brine shrimp. Toxicity to brine shrimp was determined by calculating the percent survival after a 96-hour exposure period. <u>Ten-day-old</u> larvae were used in this series of tests. Larvae were obtained by hatching brine shrimp eggs in the laboratory. San Francisco Bay brand eggs were mixed with seawater and aerated to assure continual mixing of the solution. The brine shrimp hatched 48-72 hours later. At this time, larvae were separated from egg cases and maintained on the green alga <u>Dunaliella</u> for 10 days. Brine shrimp were held in the constant temperature (18 °C) and illumination (1.9 milliwatts/cm²) incubator during the rearing phase and toxicity testing.

Determination of Test Concentrations

Previous experiments in this laboratory with brine shrimp have indicated their tolerance to toxic materials to be equal to or greater than that demonstrated by Dunaliella. For this reason, the first range-finding test with brine shrimp assessed AFFF concentrations of 0.10, 0.50, and 1.0 gm/liter. After 72 hours, survival was 100 percent for the controls and 88 percent for shrimp exposed to the highest concentration of AFFF (1.0 gm/liter). Since this test demonstrated no toxicity, a second test was run in which AFFF concentrations of 1.0, 3.0, and 9.0 gm/liter were assessed. Onehundred-percent mortality was observed at the highest concentration after 96 hours. Survival at 1.0 and 3.0 gm/liter was 86 and 52 percent, respectively. Survival for the control organisms was 80 percent after 96 hours. Because of this low control survival, these test results could not be used in determining LC₅₀ values for brine shrimp exposed to AFFF. However, apparently AFFF concentrations ranging from 1.0 to 9.0 gm/liter should bracket the LC_{50} . Therefore, these same concentrations were used in the definitive toxicity test.

Test Procedures

Test solutions of the desired concentrations were prepared by adding known amounts of AFFF concentrate to appropriate volumes of 0.45 μ filtered seawater. Five replicates per concentration were prepared, each consisting of 40 ml. Five controls were also prepared, each containing 40 ml of 0.45 μ filtered seawater. The test containers used were 50-ml glass test tubes, cleaned and conditioned as previously described for glassware used in the phytoplankton tests. After the tubes were filled with test solutions, 10

larval brine shrimp were fed <u>Dunaliella</u> (approximately 4 times 10^5 cells/shrimp/day). The samples were maintained for 96 hours in the incubator. The number of live shrimp per replicate was recorded at 24-hour intervals.

Data Analysis

The survival data for eac treatment were plotted against time to examine trends. The 96-hour survival data were compared statistically with the Kruskall-Wallis test to determine if differences existed among treatments. If differences were detected, the nonparametric multiple range test was used to identify where these differences existed. The data were evaluated at the 95percent confidence level.

RESULTS

PHYTOPLANKTON

Growth curves were generated from the IVF data for the control algae and for algae exposed to various concentrations of AFFF (Figure 1). Changes in IVF over time are quite similar for the controls and the 2.0-gm/liter exposure. <u>Dunaliella</u> at the 2.0-gm/liter exposure had a slightly higher IVF output than the controls. With 4.0-gm/liter AFFF, IVF was lower than the controls only during the first 48 hours. After 48 hours this treatment series demonstrated increased IVF. This suggests that the cells were only affected initially and later recovered. There was no change in IVF for <u>Dunaliella</u> at the 8.0-gm/liter exposure over the first 72 hours. A very short increase in IVF was seen with the 96-hour measurement. There was essentially no change in IVF over time for Dunaliella at the 10.0-gm/liter exposure.



Figure 1. Effects of AFFF on the in vivo fluorescence of *Dunaliella* during the 96-hour exposure period.

These growth curves were analyzed with a linear regression analysis and an analysis of covariance (Table 3). The results of these statistical tests indicated significant differences in slopes between the controls and both the 2.0-gm/liter and the 4.0-gm/liter treatments. In both cases, the growth rates for exposed phytoplankton were significantly higher than the growth rate for the controls. This suggests there was possible growth stimulation in Dunaliella due to AFFF exposure. Table 3. Linear regression equations generated from the in vivo fluorescence data and the results of statistical analyses on these data. Data evaluated at the 95-percent confidence level.

	Linear Regression Equation	$\underline{\mathbf{r}}^{\mathbf{Z}}$
Control	Y = 0.0098X - 0.030	0.9606
2.0 gm/liter	Y = 0.0120X - 0.0382	0.9604
4.0 gm/liter	Y = 0.0140X - 0.1401	0.8905
8.0 gm/liter	Y = 0.0013X - 0.0133	0.4280
10.0 gm/liter	Y = 0.000067X - 0.0377	0.0140

Analysis of Covariance Test Results

 $F_{calc} = 14.31$ $F_{crit} = 3.09$

Yes, there is a significant difference among slopes.

Multiple Comparison Test Results

	\underline{Q}_{calc}	<u>0</u> _crit	Conclusion
Control vs 2.0	5.99	2.00	Significant difference
Control vs 4.0	6.76	3.35	Significant difference
2.0 vs 4.0	3.16	2.80	Significant difference
Control vs 8.0			Significant difference*
Control vs 10.0			Significant difference*

* Significant difference determined by visual examination of data and resulting linear regression equations.

When compared to the controls, both the 8.0- and 10.0-gm/liter AFFF treatments had significantly lower growth rates (Figure 1). These differences are obvious from the graphical data. The data from these treatments were not analyzed statistically because they did not meet the necessary criteria of significant regressions. Regression equations for these two data sets had slopes of essentially zero. Both data sets had negative growth rates for the first 2 days of the experiment. Low levels of IVF exhibited by the 8.0- and 10.0-gm/liter exposures indicate that growth in <u>Dunaliella</u> was inhibited at these AFFF concentrations.

The ratios of DCMU-F/IVF obtained for the controls and <u>Dunaliella</u> exposed to four concentrations of the FC-780B AFFF over the 96-hour period are shown in Figure 2. The relationships observed in the IVF data between controls and AFFF-exposed phytoplankton are also present in these ratios. First, the ratios for the 2.0-gm/liter exposure parallel the control values throughout the test, with the values for the treatments being slightly lower than the controls. The 4.0-gm/liter exposure resulted in decreasing ratios over the first 72 hours and increasing ratios over the next 48 hours. After 96 hours, the ratios were quite similar to the controls. This increase may be an indication of recovery by <u>Dunaliella</u>. Exposure of <u>Dunaliella</u> to 8.0- and 10.0-gm/liter AFFF resulted in ratios that declined from 2.0 to approximately 1.0 during the first 48 hours. A ratio of 1.0 is characteristic of dead or near-dead cultures. A slight increase in the DCMU-F/IVF ratio was observed during the last 24 hours for phytoplankton as the 8.0-gm/liter exposure. Phytoplankton exposed to 10.0-gm/liter AFFF did not show signs of recovery over the entire test period.



Figure 2. Effects of the FC-780B AFFF on the ratio of DCMU-fluorescence to in vivo fluorescence for *Dunaliella* during the 96-hour exposure period.

The Kruskal-Wallis tests applied to the DCMU-F/IVF ratios resulted in significant intergroup differences at each sampling period. Multiple range tests (Table 4) indicated the ratios for phytoplankton at the 2.0-gm/liter exposure were similar to those of the control phytoplankton throughout the 96 hours. The ratios for phytoplankton at the 8.0- and 10.0-gm/liter exposures were significantly different from the control values over the same period. Significant differences in ratios between the controls and phytoplankton at the 4.0-gm/liter exposure were found to exist at the 24- and 48-hour sampling periods.

Table 4. Results of the nonparametric multiple comparisons performed on productivity efficiency data. All evaluations were made at the 95-percent confidence level.

Time of Measurement	Significantly Similar	Significantly Different
Initial - T _o	Control = 2.0 gm/l Control = 4.0	Control ≠ 8.0 gm/i Control ≠ 10.0
24 Hours	Control = 2.0 gm/l	Control ≠ 4.0 gm/l Control ≠ 8.0 Control ≠ 10.0
48 Hours	Control = 2.0 gm/l	Control ≠ 4.0 gm/l Control ≠ 8.0 Control ≠ 10.0
72 Hours	Control = 2.0 gm/l Control = 4.0	Control ≠ 8.0 gm/l Control ≠ 10.0
96 Hours	Control = 2.0 gm/l Control = 4.0	Control ≠ 8.0 gm/l Control ≠ 10.0

Nonparametric Multiple Comparison Test Results

The phytoplankton were examined for cellular abnormalities, activity, and general appearance at the end of the test. A Zeiss light microscope was used. Algal cells from the controls and the 2.0-gm/liter treatment appeared active with normal shapes and sizes. Very little detrital material was present. Cells from the 4.0-gm/liter exposure were also active and of normal shape and size, but the density was slightly depressed. The 8.0-gm/liter exposure resulted in both suppressed densities and activity. Surviving cells were of the normal shape and size; however, much detrital material was observed. Very few live cells were found in the 10.0-gm/liter exposure. The sample media for this treatment contained a high level of particulates.

BRINE SHRIMP

The survival data obtained for 10-day-old larval brine shrimp are given in Figure 3. Control survival was 98 percent after 96 hours. Treatment survival after 96 hours for the 1.0- and 3.0-gm/liter AFFF exposures were 92 and 96 percent, respectively. No significant differences were found between controls and treatments. The results suggest 9.0-gm/liter AFFF is toxic to these organisms. Survival was 46 percent at 48 hours, 10 percent at 72 hours, and 0 percent at 96 hours.





The brine shrimp were actively swimming throughout the test in the controls, 1.0-, and 3.0-gm/liter exposures. Phytoplankton added as the food source increased slightly in density over time for the same three conditions. Brine shrimp in the 9.0-gm/liter exposure were inactive after the first 24 hours with the majority laying on the bottom of the test tubes. Phytoplankton supplied to these samples did not increase in density over time. These samples turned slightly cloudy after 48 hours.

DISCUSSION

FC-780B AFFF was not toxic to the marine alga <u>Dunaliella</u> at concentrations up to 4.0-gm/liter (40,000 ppm). Based on data from this study, the 96-hour EC₅₀ for <u>Dunaliella</u> for FC-780B AFFF is between 4.0- and 8.0-gm/liter. It is not clear whether the actual EC₅₀ is closer to 4.0- or 8.0-gm/liter, but based on the fact that 4.0-gm/liter did have a slight effect at 48 hours and the 8.0-gm/liter killed almost everything, it is likely that the actual EC₅₀ is closer to 4.0-gm/liter.

Similarly, there was no significant toxicity to brine shrimp nauplii (Artemia salina) at concentrations of 3.0-gm/liter (30,000 ppm). There was a significant difference in survival between the 3.0-gm/liter exposure and the

9.0-gm/liter exposure. The estimated 96-hour LC_{50} is between 4.0 and 6.0-gm/liter. The 96-hour LC_{50} estimated for brine shrimp is in the range of those reported by the 3-M Company (1981) for Bluegill sunfish (1.6 gm/liter) and Killifish (3.9 gm/liter).

From the available literature, the 96-hour LC_{50} concentrations for the majority of organisms appear to be equal to or slightly greater than 1.0 gm/liter. The results obtained in this and previous studies show that the various AFFF agents can be considered mildly toxic to marine life at concentrations near 6.0 gm/liter. This is within a factor of 10 from concentrations actually used in fire-fighting operations (60 gm/liter). Between 3.0 and 4.0 gm/liters there may be a sublethal effect, but both Dunaliella and A. salina appear to recover from these effects. AFFF concentrations below 1.0 gm/liter are not toxic to the marine organisms tested here.

The increase in phytoplankton density upon exposure to the lower concentrations of AFFF suggests algal blooms may result from dumping this material into seawater. The reason for enhanced growth is unclear at this time. However, they may not be a significant problem since concentrated AFFF will not remain in the water column very long. Tidal cycles, wave activity, and currents will aid in dispersing and diluting the AFFF.

The recovery capability of phytoplankton after exposure to AFFF concentrations approaching the EC_{50} is an indication of the organisms' ability to avoid significant environmental impacts. This recovery was observed in both cell density and productivity efficiency for <u>Dunaliella</u> exposed to AFFF concentrations of 4.0 gm/liter. As the concentration decreases due to initial mixing in the water column, exposed phytoplankton have the capability of recovering from the initial shock and reproducing normally.

The potential problems in sewage treatment facilities have not been addressed in depth in this study. The 3-M Company suggests diluting the FC-780B AFFF formulation at a rate of 1 gallon per 10,000 gallons sewage (see the Product Environmental Data Sheet for the FC-780B AFFF agent, Appendix A). This dilution rate prevents serious foaming in aeration basins as well as settling problems in the clarifiers. The data reported in the available literature show that the problems of disposal and introduction into sewage treatment systems have been adequately covered.

In addition to the retention times and treatment procedures in disposal operations being worked out for several AFFF agents, an alternative method of disposal has been investigated. The Naval Civil Engineering Laboratory (NCEL) has developed an oil/water separation system based on ultrafiltration and reverse osmosis processes. This system is capable of separating unburned oil and AFFF from the wastewater (Chan, 1982). Both oil and AFFF are reclaimed and used again rather than being dumped into the sewage system or seawater. Only after complete separation is the wastewater dumped. NCEL tested the system at the San Diego Navy Firefighting School during 1979. The results of these studies were very promising. It is a very feasible method of reclaiming fuel and AFFF as well as eliminating potential adverse environmental impacts resulting from ocean or sewage system disposal.

CONCLUSIONS

/contid

The results of this study suggest that the dispersion of AFFF agents in the marine environment should not have a significant impact on marine life. Dilution of the 6-percent solution used for fire-fighting operations by wave and tidal activity results in concentrations that can be considered mildly toxic or nontoxic to marine life. The FC-780B AFFF is not toxic to the marine alga <u>Dunaliella</u> at concentrations up to 4.0 gm/liter. The estimated 96-hour LC_{50} for brine shrimp, <u>Artemia salina</u>, is between 4.0 and 6.0 gm/liter. These LC_{50} concentrations are in the range of those reported for other marine and freshwater organisms.

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APPENDIX A

62

3-M PRODUCT

ENVIRONMENTAL DATA SHEETS



Environmental Laboratory Environmental Engineering and Pollution Control

900 Bush Avenue PO Box 33331 St. Paul, MN 55133 612/778 5104

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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATES FC-203 AND FC-203A

DESCRIPTION: Water-miscible fire extinguishing agents.

APPEARANCE: Clear, amber liquids.

- USAGE: Foams, containing 3% FC-203 or FC-203A in water, cover and thus extinguish hydrocarbon liquid-based fires. For more detailed usage information, see your technical service representative.
- WASTE DISCHARGE: Facilities which use "LIGHT WATER" Brand AFFF agents in actual or simulated firefighting activities usually direct the resulting wastes to wastewater treatment systems. Whenever possible, 3M recommends disposing of FC-203 and FC-203A wastes in this manner. However, aquatic and soil environments sometimes receive these wastes untreated.

AQUATIC TOXICITY DATA:

Freshwater Organisms Fish	Static 96-H	<u>r. LC</u> 50
	FC-203	FC-203A
Fathead minnow (<u>Pimephales</u> promelas)	750 mg/l	300 mg/l
Rainbow trout (<u>Salmo gairdneri</u>)	1300 mg/1	
Invertebrates	Static 48-H	r. LC50
Water flea (<u>Daphnia magna</u>)	1600 mg/1 (1300-2100 :	mg/l)*
Scud (<u>Gammarus</u> <u>fasciatus</u>)	1100 mg∕1 (840-1300 m	g/l)*
<u> Algae</u> - FC-203 concentrations <u><</u> 1000	mg/l did no	t prevent the

- growth of <u>Chlorella pyrenoidosa</u> and <u>Phormidium inundatum</u>.
- Date: 7/29/80 (Supersedes 3/4/80)

Page 1 of 3

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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATES FC-203 AND FC-203A

(continued)

AQUATIC TOXICITY DATA (continued)

Marine Organisms

Species

48-Hr. EC50** (FC-203)

Eastern Oyster embryo-larvae (Crassostrea virginica)

47 mg/l (10-234 mg/l)*

<u>96-Hr. LC50</u> (FC-203)

Common mummichog (Fundulus heteroclitus)

Grașs shrimp (<u>Palaemonetes pugio</u>) (1700-3600 mg/l)* 510 mg/l

(360-710 mg/l)*

2500 mg/1

Low DO could have contributed to the toxicity of FC-203 to shrimp.

- * 95% confidence limits
- ** The effect measured was the reduction of the number of embryo-larvae developing to the straight-hinged veliger stage.

TOTAL ORGANIC CARBON (TOC): 264,000 mg/l

BIODEGRADATION AND TREATABILITY DATA:

Biodegradation	FC-203	FC-203A
BOD ₅	560,000 mg/1	72,000 mg/l
BOD ₂₀	1,060,000 mg/1	427,000 mg/l
COD	1,070,000 mg/1	648,000 mg/l

Date: 7/29/80 (Supersedes 3/4/80)

Page 2 of 3

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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATES FC--203 AND FC--203A

(continued)

Effect on Microbial Respiration

Dissolved oxygen concentration measurements, performed by placing a dissolved oxygen probe in activated sludge mixed liquor and ceasing aeration, showed no inhibition of microbial oxygen uptake rates at FC-203 concentrations up to 1000 mg/l.

Effect on Microbial Activity

The TTC* test, which measures microbial toxicity by assaying dehydrogenase enzyme activity in microbial cultures, showed no enzyme inhibition at FC-203 concentrations up to 1000 mg/l. This indicates an absence of microbial toxicity at this concentration.

*TTC (2,3,5-Triphenyltetrazolium Chloride) Re: "Dehydrogenase Enzyme as a Parameter of Activated Sludge Activities," Ford, et al. Proceedings of the 21st Industrial Waste Conference, Purdue, May 3, 4, and 5, 1966.

When possible, tests were performed in accordance with <u>Standard Methods for</u> the Examination of Water and Wastewater, American Public Health Association, 1740 Broadway, New York, 10019.

Date: 7/29/80 (Supersedes 3/4/80)

Page 3 of 3

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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE FC-206

DESCRIPTION: Water-miscible fire extinguishing agent.

APPEARANCE: Clear, amber liquid.

- USAGE: Foams, containing 6% FC-206 in water, cover and thus extinguish hydrocarbon liquid-based fires. For more detailed usage information, see your technical service representative.
- WASTE DISCHARGE: Facilities which use FC-206 in actual or simulated firefighting activities usually direct the resulting wastes to wastewater treatment systems. Whenever possible, 3M recommends disposing of FC-206 wastes in this manner. However, aquatic and soil environments sometimes receive these wastes untreated.

AQUATIC TOXICITY DATA:

Freshwater Organisms

Species

Invertebrates	<u>48-Hr. LC50</u>
Water flea (<u>Daphnia magna</u>) Scud (<u>Gammarus fasciatus</u>)	5850 mg/l 5170 mg/l
Fish	96-Hr. LC50
Fathead minnow (<u>Pimephales</u> promelas)	3000 mg/l Continuous Flow Test 1500 mg/l Static Test
Rainbow trout (<u>Salmo gairdneri</u>)	1800 mg/l Static Test
Marine Organisms	<u>96-Hr. LC50</u>
Mummichog (<u>Fundulus heteroclitus</u>) Grass shrimp (<u>Palaemonetes vulgaris</u>) Fiddler Crab (<u>Uca pugilator</u>)	1820 mg/l Static Test 280 mg/l Static Test 3260 mg/l Static Test
12/11/80 (Supersedes 4/4/79)	Page 1 of 4

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Form 14705-C PWO

Date:



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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE FC-206

(continued)

AQUATIC TOXICITY DATA (continued)

Marine Organisms

48-Hr. EC50

Atlantic oyster larvae (Crassostrea virginica)

>100 <240 mg/l

SOIL SORPTION STUDIES:

Effect of Soil on Toxicity

Soil contact with FC-206 solutions reduces their aquatic toxicity. In the absence of soil, only 60% of fathead minnows (<u>Pimephales promelas</u>) survived 48-hr. static exposure to 2500 mg/l of FC-206. None survived for 72 hours. Mixing 10 g/l of 2% organic soil containing 56% sand, 21% silt, and 23% clay into the same FC-206 solution increased fish survival to 100% at 48 hours and 50% at 72 hours. Suspended soil components in natural waters are expected to similarly reduce FC-206 toxicity.

Soil COD Removal

Shaking 100-ml aqueous solutions of FC-206 for 24 hours with 100 g of soil reduced the soluble COD. The soil used was 57% sand, 36% silt, and 7% clay. It had a 2.5% organic matter content and a cation exchange capacity of 15.3 meq/100 g. The results summarized in the following table suggest that at low concentrations of FC-206, soil contact may also reduce the COD of wastewater.

Concentration of	% of COD
FC-206 in Initial	Removed From
Aqueous Solution (mg/l)	Aqueous Phase
600	30
6,000	7
60,000	ŝ

Date:

-12/11/80 (Supersedes 4/4/79)

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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE FC-206

(continued)

BIODEGRADATION AND TREATABILITY DATA:

5-Day Biochemical Oxygen Demand (BC	$OD_5)$ 210,000	mg/l
20-Day Biochemical Oxygen Demand (BC		mg/l
Chemical Oxygen Demand (COD)	420,000	mg/1
Total Organic Carbon (TOC)	94,000	mg/kg

OECD Biodegradation Test

The "Modified OECD Screening Test with DOC Analysis" and supplemental parallel sterile controls conclusively demonstrated the extensive biodegradability of FC-206. In 14 days, the dissolved organic carbon (DOC) levels of FC-206 degraded by 90%. The parallel sterile controls proved that this DOC loss was not due to chemical or physical processes such as adsorption, volatilization, or precipitation of the parent material.

Effect on Microbial Respiration

Dissolved oxygen concentration measurements, performed by placing a dissolved oxygen probe in activated sludge mixed liquor and ceasing aeration, showed no inhibition of microbial oxygen uptake rates at FC-206 concentrations up to 1000 mg/l.

Effect on Microbial Activity

The TTC* test, which measures microbial toxicity by assaying dehydrogenase enzyme activity in microbial cultures, showed no enzyme inhibition at FC-206 concentrations up to 1000 mg/l. This indicates an absence of microbial toxicity at this concentration.

*TTC (2,3,5-Triphenyltetrazolium Chloride) Re: "Dehydrogenase Enzyme as a Parameter of Activated Sludge Activities," Ford, et al. Proceedings of the 21st Industrial Waste Conference, Purdue, May 3, 4, and 5, 1966.

Date:

12/11/80 (Supersedes 4/4/79)

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COMMERCIAL CHEMICALS DIVISION "LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE FC-206

(continued)

Activated Sludge Pilot Plant Studies

Operation of a conventional activated sludge pilot plant demonstrated the biological treatability of FC-206-containing wastes at concentrations below 1000 mg/l. This system, when operated on a mixture of settled domestic sewage and 1000 mg/l of FC-206, gave average BOD and COD reduction of 86% and 73%, respectively. The average BOD₅ in the effluent was 18 mg/l.

Although not toxic, treating wastes containing 1000 mg/l of FC-206 per liter is not recommended because of foaming. Laboratory tests have shown that foaming is reduced at concentrations below 100 mg/l and eliminated at 10 mg/l.

When possible, tests were performed in accordance with <u>Standard Methods for</u> the <u>Examination of Water and Wastewater</u>, American Public Health Association, 1740 Broadway, New York, 10019.

Date:

12/11/80 (Supersedes 4/4/79)

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900 Bush Avenue PO Box 33331 St. Paul, MN 55133	COMMERCIAL CHEMICALS DIVISION	
612/778 5104	"LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE, FC-206A	
DESCRIPTION:	Water-miscible fire extinguishing agent.	

APPEARANCE: Light yellow liquid.

USAGE: Foams containing 6% FC-206A in water cover and thus extinguish hydrocarbon liquid-based fires. For more detailed usage information, see your technical service representative.

AQUATIC TOXICITY DATA:

<u>Test Organisms</u>	Conditions	96-Hr. LC50
Bluegill sunfish (Lepomis macrochiru		1,2 g/l (1.1 - 1.3 g/l)*
Fathead minnow (<u>Pimephales</u> promela	<u>s</u>)(Continuous flow)	>3.0 g/l
		48 Hr. EC50
Water flea (<u>Daphnia magna</u>)	(Static)	2.3 g/l (l.9 - 2.9 g/l)*

Effect on Microbial Respiration

Dissolved oxygen concentration measurements, performed by placing a dissolved oxygen probe in activated sludge mixed liquor and ceasing aeration, showed no inhibition of microbial oxygen uptake rates at FC-206A concentrations up to 1000 mg/1.

95% confidence limit.

Date: 1/4/80

Page 1 of 2

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COMMERCIAL CHEMICALS DIVISION

"LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE, FC-206A

(continued)

Effect on Microbial Activity

The TTC** test, which measures microbial toxicity by assaying dehydrogenase enzyme activity in microbial cultures, showed no enzyme inhibition at FC-206A concentrations up to 10,000 mg/l. This indicates an absence of microbial toxicity at this concentration

BIODEGRADATION:

Chemical Oxygen Demand (COD)	451,000 mg/1
Biochemical Oxygen Demand (BOD)	
BOD ₅	200,000 mg/l
BOD20	330,000 mg/l

WASTE DISCHARGE:

Facilities which use FC-206A in actual or simulated firefighting activities usually direct the resulting wastes to wastewater treatment systems. Whenever possible. 3M recommends disposing of FC-206A wastes in this manner. However, aquatic and soil environments sometimes receive these wastes untreated.

DISPOSAL: May be bled to wastewater system with a treatment plant in accordance with local regulations.

**TTC (2,3,5-Triphenyltetrazolium Chloride) Re: "Dehydrogenase Enzyme as a Parameter of Activated Sludge Activities," Ford, et al. Proceedings of the 21st Industrial Waste Conference, Purdue, May 3, 4, and 5, 1966.

1/4/80 Date

Page 2 of 2

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Environmental Laboratory

Environmental Engineering and Pollution Control

900 Bush Avenus PO Box 33331 St. Paul. MN 55133 612/778 5104

COMMERCIAL CHEMICALS DIVISION MILITARY SPEC. TYPE AFFF 6% CONCENTRATE FC-780B

Wt. 8

DESCRIPTION: Fire extinguishing agent.

APPEARANCE: Clear amber liquid.

COMPOSITION:

	a status and a statu
	•
Water	75
Butyl Carbitol	15
Synthetic Detergents	<5
Fluoroalkyl Surfactants	< 5
Urea	5

- USAGE: FC-780B is employed at a 6% level (i.e., 94 parts water to 6 parts FC-780B) to extinguish fires involving liquid fuels and other liquid organic compounds.
- WASTE DISCHARGE: Facilities which use FC-780B in actual or simulated firefighting activities usually direct the resulting wastes to wastewater treatment systems. Whenever possible, 3M recommends disposing of FC-780B wastes in this manner. However, aquatic and soil environments sometimes receive these wastes untreated.
- DISPOSAL: Bleed to wastewater treatment system in accordance with local regulations. Diluting 1 gallon of FC-780B in >10,000 gallons of sewage prevents the product from causing serious foaming in aeration basins and prevents it from causing sludge settling problems in clarifiers. USEPA Hazardous Waste Number: None.

AQUATIC TOXICITY:

Test Organism	96-Hr. LC50 95% C.I.
(Lepomis macrochirus)	Tul: (1,300-1,800 mg/l)
(Fundulus heteroclitus)	(3,400-4,600 mg/l)
2/9/81 (Supersedes 1/8/80)	Page 1 of 2

Date:

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Environmental Laboratory Environmental Engineering and Pollution Control

900 Bush Avenue PO Box 33331 St. Paul, MN 55133 612/778 5104

SSAL BUTTONS

COMMERCIAL CHEMICALS DIVISION MILITARY SPEC. TYPE AFFF 6% CONCENTRATE FC-780B

(continued)

TREATABILITY:

Neither foaming nor sludge settling problems developed as a result of aeration in laboratory scale activated sludge reactors containing 100 mg/l of FC-780B. Based on these results, no serious foaming or settling problems are anticipated in waste treatment systems containing less than 100 mg/1 of FC-780B.

BIODEGRADATION: **

Chemical Oxygen Demand (COD) 387,000 mg/l

Ratio of Twenty-Day Biochemical Oxygen Demand to Chemical Oxygen Demand (BOD_{20}/COD)

0.96

- 95% confidence interval.
- As reported by the Naval Research Laboratory, Fire Suppression Section, Washington, DC.

Date:

2/9/81 (Supersedes 1/8/80)

Page 2 of 2

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Environmental Laboratory

Environmental Engineering and Pollution Control 900 Bush Avenue PO Box 33331 St. Paul, MN 55133 612/778 5104 COMMERC

COMMERCIAL CHEMICALS DIVISION

"LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE, FC-203C

DESCRIPTION: Water-miscible fire control agent.

APPEARANCE: Clear, amber colored liquid.

USAGE: Foams containing 3% FC-203C in water cover and thus extinguish hydrocarbon liquid-based fires. For more detailed usage information, see your technical service representative.

AQUATIC TOXICITY DATA:

<u>Test Organisms</u>	Conditions	<u>96-Hr. LC</u> 50
Killifish (<u>Fundulus</u> <u>heterocl</u>	itus)(continuous flow)	1,400 mg/l (1,000-2,000 mg/l)*
Fathead minnow (<u>Pimephales</u> promel	<u>as</u>)(Continuous flow)	>2,000 mg/l
		96-Hr. EC50**
Single cell green (Selenastrum capri	algae cornatum)	408 mg/l (156-995 mg/l)*

*95% confidence limits. **Concentration inhibiting growth (measured as cell dry weight) by 50%.

Effect on Microbial Respiration

Dissolved oxygen concentration measurements, performed by placing a dissolved oxygen probe in activated sludge mixed liquor containing 1,000 mg/l of FC-203C and ceasing aeration, showed an increased oxygen uptake rate. This indicates an absence of acute microbial toxicity at this concentration and suggests that biodegradable portions of this product are utilized by nonacclimated microbial populations.

Date:

5/26/82

Page 1 of 2

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Environmental Engineering and Pollution Control 900 Bush Avenue PO Box 33331 St. Paul. MN 55133 612/778 5104 COMMERC

COMMERCIAL CHEMICALS DIVISION

"LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE, FC-203C

(continued)

BIODEGRADATION:

Chemical Oxygen Demand (COD)	0.78 g/g
20-Day Biochemical Oxygen Demand (BOD)	0.58 g/g
20-Day Carbonaceous Biochemical Oxygen Demand	0.59 g/g

DISPOSAL OF FIREFIGHTING WASTES:

If possible, 3M recommends handling wastes resulting from actual or simulated firefighting activities by pretreating in an oil-water separator followed by bleeding to a wastewater treatment system. Serious foaming can be prevented by adjusting the discharge rate so that the FC-203C concentration reaching the aeration basin will be $\leq 25 \text{ mg/l}$ (1 gallon of FC-203C concentrate in $\geq 40,000$ gallons of sewage).

DISPOSAL OF PRODUCT:

Bleed to a wastewater treatment system in accordance with local regulations. Adjusting discharge rates as described in the section above should reduce serious foaming problems in the receiving treatment system.

5/26/82

Page 2 of 2

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Form 14705-C PWO

Date:



Environmental Laboratory Environmental Engineering and Pollution Control

900 Bush Avenue PO Box 33331 St. Paul, MN 55133 612/778 5104

COMMERCIAL CHEMICALS DIVISION

"LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE, FC-206C

DESCRIPTION: Water-miscible fire control agent.

Clear, amber colored liquid. **APPEARANCE:**

Foams containing 6% FC-206C in water cover and thus extinguish **USAGE:** hydrocarbon liquid-based fires. for more detailed usage information, see your technical service representative.

AOUATIC TOXICITY DATA:

Test Organisms	Conditions	<u>96-Hr, LC50</u>
Killifish (<u>Fundulus</u> <u>heteroc</u>	litus)(continuous flow)	>2,000 mg/l
Fathead minnow (Pimephales prome	las)(Continuous flow)	>2,000 mg/l
		96-Hr. EC50**
Single cell green (Selenastrum capr		345 mg/l (34-1630)*

*95% confidence limits. **Concentration inhibiting growth (measured as cell dry weight) by 50%.

Effect on Microbial Respiration

Dissolved oxygen concentration measurements, performed by placing a dissolved oxygen probe in activated sludge mixed liquor containing 1,000 mg/l of FC-206C and ceasing aeration, showed an increased oxygen uptake rate. This indicates an absence of acute microbial toxicity at this concentration and suggests that biodegradable portions of this product are utilized by nonacclimated microbial populations.

Date:

5/26/82

Page 1 of 2

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COMMERCIAL CHEMICALS DIVISION

"LIGHT WATER" BRAND AQUEOUS FILM FORMING FOAM CONCENTRATE, FC-206C

(continued)

BIODEGRADATION:

Chemical Oxygen Demand (COD)	0 .40 g/g
20-Day Biochemical Oxygen Demand (BOD)	0.33 g/g
20-Day Carbonaceous Biochemical Oxygen Demand	0.34 g/g

DISPOSAL OF FIREFIGHTING WASTES:

If possible, 3M recommends handling wastes resulting from actual or simulated firefighting activities by pretreating in an oil-water separator followed by bleeding to a wastewater treatment system. Serious foaming can be prevented by adjusting the discharge rate so that the FC-206C concentration reaching the aeration basin will be $\leq 50 \text{ mg/l}$ (1 gallon of FC-206C concentrate in $\geq 20,000 \text{ gallons of sewage}$).

DISPOSAL OF PRODUCT:

Bleed to a wastewater treatment system in accordance with local regulations. Adjusting discharge rates as described in the section above should reduce serious foaming problems in the receiving treatment system.

Date:

5/26/82

Page 2 of 2

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Environmental Engineering and Pollution Control

900 Bush Avenue PO Box 33331 St. Paul, MN 55133 612/778 5104

COMMERCIAL CHEMICALS DIVISION

3M BRAND COMMERCIAL GRADE AFFF 6% CONCENTRATE FC-780

DESCRIPTION: Fire extinguishing agent.

APPEARANCE: Clear amber liquid.

COMPOSITION:

Percent by Weight

Diethylene glycol monobutyl ether (Butyl Carbitol®)	14
Water	77
Fluoroaliphatic surfactants	<5
Organic surfactants	<5
Urea	6

USAGE: FC-780 is employed at a 6% level (e.g., 94 parts water to 6 parts FC-780) to extinguish fires involving liquid fuels and other liquid organic compounds.

AQUATIC TOXICITY:

Test Organism	<u>96-Hr. LC</u> 50
	FC-780

(Fundulus heteroclitus)

BIODEGRADATION: *

Chemical Oxygen Demand (COD)0.32 g/gRatio of Twenty-Day Biochemical0xygen Demand to ChemicalOxygen Demand (BOD20/COD)0.98

* As reported by the Naval Research Laboratory, Fire Suppression Section, Washington, DC.

Date: 6/11/82 (Supersedes 1/8/80)

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APPENDIX B

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AFFF ASSAY DATA

Data taken from: D.B. Chan, 1982. Draft initial feasibility report on AFFF-laden wartewater treatment/ recovery. Technical Meino 54-82-06.

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D. Biological Treatment

Provide Apply Provide Concerned

The Air Force performed four biodegradability and toxicity studies respectively for AER-O-Water (AOW) 3 and 6 (Ref 3), FC-200 (Ref 2), FC-206 (Ref 4), and ANSUL K74-100 (Ref 5) AFFF. Results from these studies are summarized in Table 3.

	Operation Parameters		Organic Removal, %			
AFFF Agent	Detention Time	Influent Feed	COD	BOD	Remarks	
1. AOW-3	7.6 hrs.	50-2400 ppm (V/V)	94 down to 66 in 94 days Continu- ous Ex- periment	97 down to 66 in 94 days	Ethylene Glycol not biodegradable. Plant did not recover after 1,700 ppm feed	
2. AOW-6	7.5 hrs.	50-2400 ppm (V/V)	86 down to 50 in 94 days	96 down to 74 in 94 days	Plant did not recover after 1,700 ppm feed	
3. FC-200	6-8 hrs.	50-250 ppm	89 down to 45 in 53 days	Main- tained at 96 in 53 days	Efficiency degraded after 100 ppm feed	
4. FC-206	6-8 hrs.	50-300 ppm (V/V)	Main- tained 96 - 98	98 down to 96.5 in 51 days	Efficiency degraded after 250 ppm feed	
5. ANSUL K74-	6-8 hrs.	50-3500 ppm (V/V)		98 down to 75 in 98 days	Efficiency degraded after 250 ppm feed	

Table 3. Biological Treatment of AFFF

All experiments were conducted under the following conditions:

a. Using bench-scale, continuous feed activated sludge process

- b. Employing pure AFFF concentrate and synthetic sewage as feeding substrate
- c. Acclimating activated sludge with synthetic sewage before AFFF was gradually (dosage increased with time) fed to the process

Table 1.	Changes in toxicity of AFFF's to Fathead Minnows with
	increase in time of exposure (From LeFebvre and Inman,
	1975).

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	<u> 3M - Light Water</u>			Nat'l Foam	ANSUL Co.	
	FC-199	FC-200	FC-206	AOW3	AOW6	K74-100
24 Hours 48 Hours	650 588	* 135	2100 1810	1030 820	635 255	1725 1425
72 Hours	450	97	1300	630	245	1150
96 Hours	398	97	1080	600	225	1100

LC₅₀ Concentration (µl/1)

*No mortality in 24 hours in one bioassay but 50% in highest concentration (150 $\mu l/l)$ in duplicate bioassay.

Tab. 3 5.	Comparison of concentrations of AFFF in synthetic sewage
	amenable to biological treatment (From LeFebvre and Inman, 1975).

1	3M - LIGHT WATER			NAT'L FOAM	ANSUL	
	FC199	FC200	FC206	AOW3	AOW6	K74-100
Maximum to Sewage Treatment Plant Recommended for	250 μ 1/1	10 µ1/1	200 µ1/1	1700 µ1/1	1700 µ1/1	250 µ1/1
Treatment	25 µl/l	10 µ1/1	20 µ1/1	<u>150 µ1/1</u>	150 µ1/1	25 µ]/1

Table 6. Recommended maximum concentration of AFF for direct discharge to stream containing aquatic life. (From LeFebvre and Inman, 1975).

			NAT'L FOAM	SYSTEMS	ANSUL
FC199	FC200	FC206	AOU3	A0%6	K74-100
20 µ]/]	5 µ]/]	54 µ]/]	60 µ]/]	22.5 µ]/]	55 μ ì/]