

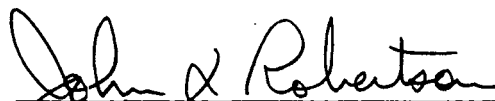
**POTENTIAL FOR ENVIRONMENTAL
IMPACT OF AFA-6 SURFACTANT**

A Report for:

**PANARCTIC OILS LTD.
CALGARY, ALBERTA**

Submitted by:

**BEAK CONSULTANTS LIMITED
MISSISSAUGA, ONTARIO**



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1.0 SUMMARY

Panarctic Oils Ltd. of Calgary has applied to the Environmental Protection Service (EPS) of Environment Canada to use Geotech AFA-6 Accelerated Freezing Additive in the construction of an ice island for exploration in the Arctic ocean. Although preliminary approval had been granted for the 1984-85 season, EPS remained concerned about potential environmental impacts. Beak Consultants Limited was retained by Panarctic to investigate the potential impacts and prepare this report addressing EPS concerns.

Panarctic plans to apply AFA-6 at a concentration of 10 mg/L down to -21°C . AFA-6 is a perfluorinated alkyl ethoxylate surface active agent manufactured from a perfluorinated alkyl sulphonate (product number FC-95) and ethylene oxide. It will biodegrade slowly, producing the original perfluorinated alkyl sulphonate, plus CO_2 and water as its final degradation products. The application concentration of AFA-6 is similar to the LC50 for representative salt water organisms. For Artemia (brine shrimp) the LC50 was 10 mg/L, while for sea-water acclimatized trout the LC50 was 4 mg/L. The degradation product (FC-95) was slightly less toxic, having LC50's of 9 mg/L and 14 mg/L, respectively.

Octanol/water partition coefficients were measured for both AFA-6 and FC-95 and were used to estimate bioconcentration potential. Estimated bioconcentration factors for AFA-6 and FC-95 were 3 and 1, respectively, indicating essentially no significant bioconcentration potential.

Beause of the limited use of AFA-6, it is estimated that a maximum of 9% of the total volume of the ice island will contain AFA-6. Consequently, it is probable that dilution during melting will reduce the under ice concentration to less than the 1-2 mg/L non-lethal concentration observed in the bioassays.

On the basis of the information available, application of AFA-6 in the concentrations and quantities proposed by Panarctic does not appear to represent an environmental hazard.

2.0 INTRODUCTION

2.1 Background

Each drilling season, Panarctic Oils Ltd. builds ice islands in the Beaufort Sea to serve as exploration platforms. The rate at which these islands can be constructed depends largely upon the temperature during construction. During the 1984-85 drilling season Panarctic used a chemical product known as AFA-6 supplied by the Geotech Corporation to enhance the rate of freezing, through surface tension reduction. Use of the AFA-6 was limited to a concentration of 10 mg/L in a specific temperature range (down to -21°C) below which it had no effect.

The Regional Office of Environment Canada had approved the use of the AFA-6 compound for the 1984-85 season, but had several concerns regarding potential environmental impacts. Because BEAK was conducting similar work on other surfactants, EPS Industrial Programs Branch Regional Office approached BEAK about inclusion of the AFA-6 in a parallel study to address some of the environmental issues. BEAK was subsequently retained by Panarctic to carry out an assessment of AFA-6 and its breakdown products.

2.2 Project Objectives and Scope

EPS has expressed concern about the following issues:

- o persistence of the surfactant and its breakdown products,
- o biodegradability, and measurement of the surfactant and breakdown products, as well as identity of the breakdown products,
- o distribution in various environmental compartments (aqueous phase, sediments, food chain, air),
- o potential for bioconcentration of the surfactant or its breakdown products,
- o acute toxicity of the surfactant and breakdown products.

The objective of this project was to acquire sufficient data to answer these concerns and establish the acceptability of the AFA-6 surfactant using these concerns as criteria. The following tasks were identified to achieve this objective:

- o Physical/Chemical characterization including chemical composition and structure, solubility, melting and boiling points, vapour pressure, octanol water partition coefficients. Data sources would include manufacturer's safety data sheet (MSDS), chemical literature, in-house testing.
- o Validation of appropriate analytical procedures including wet chemical and instrumental methods such as gas chromatography (GC) or high pressure liquid chromatography (HPLC).
- o Determination of biodegradability and identification of breakdown products. Data sources would include the chemical literature and in-house testing.
- o Determination of acute toxicity to a variety of test organisms and in particular the salt water species *Artemia* (brine shrimp), representative of the branchipoda invertebrate group which is resident in the Arctic Ocean. Organisms to be tested included *Daphnia* (fresh water), *Artemia* (salt water), rainbow trout (fresh and salt water).
- o Estimation of the potential for accumulation in sediments and biota based on the octanol/water partition coefficient (K_{ow})
- o Submit a final report detailing the test results and making a recommendation about the continued use of AFA-6.

This report presents and summarizes all the information gathered, together with a recommendation regarding the continued use of AFA-6.

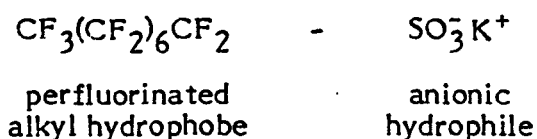
3.0 ENVIRONMENTAL CHEMISTRY OF AFA-6

3.1 General

The designation AFA-6 is the Geotech product number for a perfluorinated alkyl ethoxylate manufactured by 3-M (Minnesota Mining and Manufacturing). The 3-M product numbers for this type of compound are FC-171 or FC-760. The compound can be classified generally as a nonionic surface active agent (surfactant) manufactured from a potassium perfluoroalkylsulphonate and ethylene oxide. The perfluoro-alkylsulphonate starting material is an anionic surfactant also manufactured by 3-M, and designated as FC-95.

All organic surfactants contain both a hydrophilic and a hydrophobic moiety in the same molecule. With modern chemical processes, surfactants can essentially be "tailor-made" to exhibit specific properties. In general, the hydrophobic portion of a surfactant molecule is derived from a C_8 to C_{20} hydrocarbon, selected on the basis of the particular properties desired.

Hydrophilic groups can be divided into two groups: those that ionize in aqueous solution (anionic and cationic) and those that do not (non-ionic). FC-95, the starting material for AFA-6, is an anionic surfactant compound containing a fluorinated alkyl hydrophobe and a hydrophilic sulphonate group as shown below.



To manufacture AFA-6, a polyoxyethylene (polyether) chain is added on to the sulphonate group using ethylene oxide. The polyether chain is non-ionic and confers somewhat different properties on the molecule as compared to the anionic starting material. The polyether chain length in most non-ionic surfactants can be varied simply by continuing the introduction of ethylene oxide into the reaction mixture (Swisher, 1970). The rate-controlling step is the formation of the "mono-adduct", an intermediate product containing only one ethylene oxide unit. Thereafter, polymerization occurs rapidly, independent of chain length (Kirk-Othmer). Consequently, the polyether chain is built up before all the starting material is reacted and the final product is polydisperse with

respect to chain length. This is illustrated by the structure of the AFA-6 shown below, where the mean polyether chain length is 7.2 ethoxylate units. The chain length probably varies from 5 to 9 units with the predominant length being 7 with a mean of 7.2.



perfluoroalkyl sulphonate ethoxylate (polyether) chain

Table 3.1 summarizes the physical/chemical properties of AFA-6 and its precursor compound FC-95. Water solubility for AFA-6 is reported by Geotech as "negligible". In the toxicity tests reported in Chapter 4.0, solutions of up to 100 mg/L were prepared. However, the AFA-6 would not readily dissolve at room temperature and had to be heated to 40-50°C with vigorous stirring to produce a stable solution.

3.2 Analytical Protocols

Two analytical techniques were evaluated for analysis of the AFA-6 surfactant. The Cobalt Thiocyanate Active Substances (CTAS) test for non-ionic surfactants was evaluated and refined to allow detection of 0.2 mg/L. This is adequate to allow detection of the compound at concentrations lower than the lowest reported LC50 (0.4 mg/L to Daphnia). Although the method is not specific to AFA-6, it is unlikely that any other non-ionic surfactants will be present in Arctic waters or in test solutions. The method will also detect nonionic surfactant breakdown products containing more than 3 ethoxylate units.

Analysis of the surfactant was attempted by GC/EC (gas chromatography with electron capture detection) to provide a highly sensitive, specific analysis of the AFA-6. Initially, direct analysis under various column conditions was assessed but none was unsuccessful. Subsequently, an HBr cleavage technique used for analysis of linear alcohol ethoxylate nonionic surfactants was tested. While the technique showed typical ethoxylate unit cleavage and bromination response, the balance of the molecule did not chromatograph well. As the AFA-6 compound is an ethoxylated perfluoroalkyl sulphonate, the chromatographic problems encountered in method development can be attributed to the highly polar sulphonate group in the cleavage product and its associated high boiling point.

**TABLE 3.1: PHYSICAL/CHEMICAL PROPERTIES OF AFA-6
AND FC-95 FLUOROCHEMICAL SURFACTANTS**

Property	AFA-6	FC-95
Form	Clean, yellowish liquid	Free-flowing white powder
Composition	100% active	100% active
Ionic Type	Non-ionic	Anionic
pH (0.1% Aqueous Solution)	-	7 - 8
Melting Point (°C)	-	Decomposes at 390°C
Boiling Point (°C)	L 300°C	Decomposes at 390°C
Water Solubility (at 25°C)	Negligible*	2,000 mg/L
Specific Gravity	1.4	approx. 0.6 (bulk density)

* Solutions of up to 100 mg/L were prepared for bioassay tests, indicating significant solubility in environmental terms.

L = less than

The FC-95 compound could not be analysed by the CTAS method, but was found to be responsive to the Methylene Blue Active Substance (MBAS) tests used for anionic surfactants. As with the AFA-6 in the CTAS test, FC-95 was less responsive in the MBAS test than other anionic surfactants. However, the response was sufficient to allow detection in 0.2-0.5 mg/L range as well.

3.3 Octanol/Water Partition Coefficients

The partition coefficient (P) may be determined empirically or calculated (Leo, 1971) and represents the partitioning of a compound into the n-octanol phase of an octanol/water mixture. The octanol/water interface models biological membrane systems and the P value can be related to lipid solubility. High P values are representative of lipid soluble persistent chlorinated hydrocarbons (e.g., PCB, DDT, mirex) and low P values are associated with non-lipid-soluble non-persistent compounds (e.g., phenols). Octanol/water partition coefficients can be used to predict bio-magnification potential and potential for accumulation in sediments (Veith et al., (1979); Neely et al. (1974); Mackay (1982); Karickhoff et al. (1979)).

No data on octanol/water partitioning for either AFA-6 or FC-95 was available from 3-M or the chemical literature. Consequently, octanol/water partition coefficients were measured in the laboratory. The method used is essentially that presented by Leo et al. (1971). Analytical methods were the CTAS and MBAS methods indicated in Section 3.2.

Table 3.2 summarizes the partition coefficients (P) and their base 10 logarithms (log P) for both AFA-6 and FC-95. Bioconcentration factors (BCF) have been calculated for both using the equation developed by Veith et al. (1979).

3.4 Biodegradation and Breakdown Products

The study of surfactant biodegradability first began in England in the 1950's, when many of the general principles of surfactant biodegradation were established during research on anionic surfactants. These principles were later extended to other surfactant classes. In the case of non-ionic surfactants, additional work was required on the effect of the hydrophilic group because, unlike the anionics, it is potentially biodegradable as well.

FC-171

Calculated Bioconcentration potential
of FC-171 based on its reported
water solubility in CCD Technical Brochure of
1000 mg/l and Jun Kenzawa, Prediction of
Biological Concentration Potential of Pesticides in
Aquatic Organisms, Rev. Plant. Protec. Res. 13, 1980 p 27-36

$$\log BCF = 4.68 - 0.59 \log S_{aq}$$

(Solubility in ppb)

$$= 4.68 - 0.59 \cdot \log 10^6$$

$$= 4.68 -$$

$$= 1.14$$

$$BCF = 13.8$$

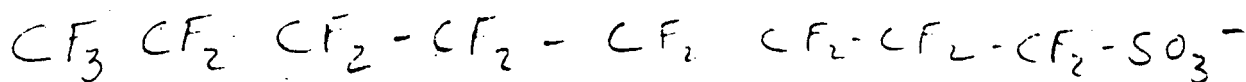
Too small to be
of concern

TABLE 3.2: OCTANOL/WATER PARTITION COEFFICIENTS
AND DERIVED DATA FOR AFA-6 AND FC-95

Compound	P	log P	BCF
AFA-6	25	1.4	3
FC-95	6.0	0.8	1

NOTES: P = octanol/water partition coefficient; also known as K_{ow}
 log P = base 10 logarithm of P or K_{ow}
 BCF = bioconcentration factor (from equation in Veith, 1979)

Calculation of F_{C-95}



f - SO ₃ ⁻	1 (-5.87)	-5.87
f C	8 (0.70)	1.6
f F	17 (-0.38)	-6.46
F _b	24 (-0.12)	-2.88
	7 C bonds 1 C-S bond 17 C-F bonds 25 n-1 = 24	
3 FmhG ₃	3 (0.53)	1.59
14 FmhG ₂	14 (0.30)	4.2
16 FmhV ₁₇	16 (0.28)	4.48
F _{H/SP₂} (2 F α to SO ₃ ⁻) (?)	No values are tabulated for SO ₂ and F but by analogy with other fragments a value of 2-3 would seem reasonable as the contribution from the 2 α F. ∴ assume 2.5	2.5

Calculated log P for FC-95

-0.84

Ref. Chapter IV, The Fragment Method of Calculating Partition Coefficients, Substituent Constants for Correlation Analysis in Chemistry and Biology, by Corwin Hansch and Albert Leo (1979) John Wiley & Sons, Inc.

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The following generalizations relating structure and biodegradation of nonionic surfactants have been reasonably well documented.

- i) **Hydrophobe Structure:** biodegradation is enhanced by hydrophobe linearity and deterred by branching or chemical substitution (e.g., replacement of H by F);
- ii) **Nature of Hydrophile:** generally has only a minor effect; in polyethoxylate non-ionics shorter chain length promotes complete conversion to carbon dioxide and water (ultimate biodegradability); and
- iii) **Distance Principle:** generally, the greater the distance between hydrophile and the far end of the hydrophobe increases the speed of the primary biodegradation. This is particularly true for ABS.

The structure and composition of the AFA-6 surfactant permits only partial biodegradation, as discussed below.

- i) **Hydrophobe Structure:** This portion of the molecule is completely fluorinated. consequently, it will be essentially non-biodegradable, but will also be chemically and biologically inert, as it has a structure and composition much like teflon.
- ii) **Hydrophile:** the polyether chain which solubilizes the AFA-6 molecule, will be biodegradable. Birch (1982) used standard OECD biodegradation procedures to demonstrate that alcohol ethoxylates with up to 20 ethoxylate units can be readily and completely degraded. With only about 7 ethoxylate units biodegradation of the polyether chain in AFA-6 will occur.

In general, biodegradation of ethoxylated non-ionic surfactants can occur at the hydrophobic or hydrophilic group. A non-ionic surfactant may undergo "complete primary biodegradation" as measured by changes in surface tension, foaming capacity, CTAS or other chemical analysis based on the presence of the ethoxylate group. However, "ultimate biodegradation" i.e., conversion to CO_2 and water may be only partially achieved, or may be achieved at a much slower rate. This implies the formation of intermediate products of potential environmental significance. That is, by-products may be formed which also have surface active properties, which may exert toxicity, which may bioaccumulate, or which may persist in the environment for some time.

Using an HBr cleavage/GC analysis technique developed for the determination of the hydrophobe/hydrophile ratios in commercial non-ionic surfactants, Tobin et al. (1976a) showed that the alkyl portion of a readily degradable alcohol ethoxylate was degraded rapidly, whereas the ethoxylate portion was degraded much more slowly. The polyethylene glycol (PEG) like by-products from the ethoxylate portion were only 45% degraded in 530 hours, by which time, analysis for the surfactant itself and the alkyl portion of the surfactant showed 100% degradation. Testing a similar surfactant at the same starting concentration (20 mg/L) Kravetz (1982) showed that the fish toxicity of the shake flask solution was reduced to less than the surfactant LC50 in less than 15 days (360 hours) and to zero in about 600 hours. This suggests that the PEG-like by-products are less toxic than the original surfactant. However, no specific dose-response data were presented for the PEG-like products.

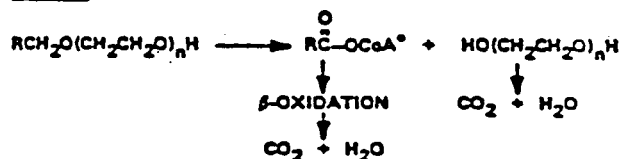
In a subsequent paper, Tobin et al. (1976b) showed a similar pattern in lake water degradation studies conducted in-situ on the same surfactant. The previous experiments were further expanded to include CO₂ production as a comparative parameter. Anthony and Tobin (1977) subsequently used a sequential extraction scheme to demonstrate the rapid formation of polyglycol which is then slowly degraded.

Cook (1979) used both HBr cleavage and trimethylsilylation with GC analysis to demonstrate that similar reactions occurred in the activated sludge degradation of a similar linear alcohol ethoxylate.

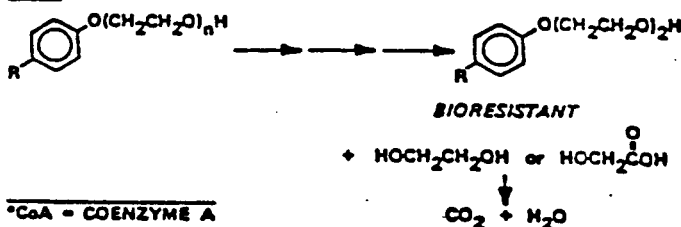
Kravetz et al. (1982) used radio-labelling techniques to demonstrate that both alcohol ethoxylates and alkylphenol ethoxylates produce soluble organic intermediate by-products from the hydrophilic polyethoxylate group, with the alkylphenol producing substantially more. Similarly, the hydrophobic alkylphenol portion produced metabolites as well. In contrast, the alcohol produced very little hydrophobe metabolite, as expected from the work of Tobin et al. (1976a,b).

Kravetz et al. (1982) proposed the following mechanisms for the degradation of alcohol and alkylphenol ethoxylates.

AE 25-9



NPE-9



Later in 1982, Stephanou and Giger confirmed this mechanism with the identification of nonylphenol mono - and di-ethoxylates in sewage treatment plant effluents.

In AFA-6, only the ethoxylate portion of the molecule should be biodegradable, because of the complete fluorination of the alkyl hydrophobe. As yet unpublished work by 3-M using radio-carbon tracer techniques in mice has demonstrated that the ultimate degradation product of AFA-6 is a perfluoralkyl sulphonate similar to FC-95.

Data from 3-M show that the 20 day BOD of FC-760 (AFA-6) is 170,000 mg/L while the COD is 700,000 mg/L indicating only 25% decomposition. Assuming the chemical composition and structure shown in Section 3.1, and assuming that the fluorinated alkyl portion of the molecule is inert, the theoretical oxygen demand of AFA-6 is 1,050,000 mg/L. This indicates only partial biodegradation and a relatively low rate of degradation. No inhibitory effect on activated sludge respiration rate was noted at 1,000 mg/L, indicating no bacterial toxicity.

Biodegradation tests undertaken in brine solution in BEAK's laboratories showed a similar slow degradation. Using a low initial concentration of 14.5 mg/L as dissolved organic carbon (DOC), no significant degradation had occurred after 9 days. At 57 days, the DOC had been reduced to 6.0 mg/L. Based on the relative carbon contents of the fluorinated alkyl sulphonate and the average ethoxylate chain length, this indicates that biodegradation of the ethoxylate chain was approaching completion. That is, 59% DOC removal had been achieved as compared to 64% for complete ethoxylate degradation. The DOC removal suggests an average of one ethoxylate group remaining undegraded.

Test conditions were set up similar to the ISO standard aerobic shake flask test with nutrient salts in a brine (sea water) solution. Although ISO recommends use of low concentrations of various organic growth factors, the AFA-6 was used as the sole organic substrate to simplify DOC measurements, and to simulate pristine Arctic water conditions. This may have contributed to the nine-day lag observed.

It is clear from the data presented above that AFA-6 does biodegrade and that it does so relatively slowly. With an applied concentration of 10 mg/L concentration, no measureable effect on dissolved oxygen will be observed.

4.0 TOXICOLOGY

4.1 Exposure Protocols

Rainbow trout (Salmo gairdneri), water flea (Daphnia magna) and brine shrimp (Artemia salina) were used as the bioassay organisms to determine the toxicity of the AFA-6 and FC-95 compounds. Exposure protocols followed the guidelines outlined in "Standard Procedures for Testing Acute Lethality of Liquid Effluents" (Environment Canada, 1980). for rainbow trout, the International Standards Organization (1982) protocol for daphnia and the International Standards Organization (Vanhaecke and Persoone, 1981) draft protocol for artemia.

Both rainbow trout and daphnia are widely recognized as standard test organisms for fresh water toxicity assessments and therefore provide an excellent basis of comparison to establish relative toxicity to other compounds. Acclimation of rainbow trout to saline conditions is also an accepted means to estimate toxicity of compounds in marine environments.

Artemia are native to inland saltwater lakes and are physiologically adapted to a salt environment. The species has been adopted as a representative marine organism for toxicity screening tests by European member countries of the International Standards Organization (ISO). The use of Artemia provides a practical and standardized means of toxicological assessment and meets all of the requirements of biological testing. Culture and maintenance are well documented, standardized methods have been developed, and tests are reproducible and comparable among laboratories. The strength of incorporating artemia data is that marine invertebrate information is provided. The genus is within the crustacean family which includes crabs, shrimp and lobsters. The artemia data can therefore be considered to be representative of marine crustacean sensitivities in the absence of specific species test data.

All protocols were similar in that they required test organisms to be exposed to a logarithmic concentration series of test product for a set period (fish - 4 days, invertebrates - 2 days). Mortality, dissolved oxygen and pH were recorded daily and the cumulative mortality-concentration plot was used to estimate the concentration producing 50% mortality (LC50).

TABLE 4.1: DILUTION WATER CHARACTERISTICS
(Dechlorinated Mississauga Tap Water)

Chemical Parameter*	mg/L
pH	7.94
Conductivity (umhos/cm)	377
Alkalinity	88
Hardness (as CaCO ₃)	137
Ammonia-N	< 0.06
Chlorine	< 0.05
<u>Anion Scan</u>	
Chloride	28.0
Fluoride	1.1
Sulphate	0.74
O-Phosphate	0.1
Nitrate	0.46
Nitrite	0.1
<u>DCP Scan</u>	
Beryllium	< 0.005
Molybdenum	0.015
Calcium	40
Vanadium	< 0.005
Aluminum	0.15
Magnesium	8.6
Borium	0.02
Potassium	1.7
Strontium	0.19
Sodium	12.6
Zinc	< 0.005
Cadmium	< 0.005
Manganese	< 0.005
Cobalt	< 0.005
Copper	< 0.005
Silver	< 0.01
Iron	< 0.005
Lead	< 0.01
Chromium	< 0.005
Nickel	< 0.005

* Results in mg/L unless otherwise indicated.

Tests were static, continuously aerated and at a constant temperature (fish - 15°C; invertebrates - 22°C). Due to the size of the fish the exposure solution was replaced after 48 hours to maintain an acceptable loading rate. Photoperiod was 12 hours light, 12 hours dark.

Rainbow trout were purchased from a certified disease free hatchery (Rainbow Springs, Thamesford) and acclimated for 28 days in Mississauga dechlorinated tap water (Table 4.1).

Daphnia were originally obtained from a culture maintained at the Canadian Centre for Inland Waters, Burlington and have been successfully reproducing for 1 year. Daphnia first instars (less than 24 hours old) were collected from adults and used in the tests.

Artemia eggs (Salt Lake Brine Shrimp Inc.) were incubated at 22°C in 30 parts per thousand (ppth) NaCl solution and hatched naupuli (less than 24 hours old) were collected for exposure. The same 30 ppth NaCl solution was used to dilute the AFA-6 and FC-95.

Fish and daphnia tests were conducted in duplicate, while artemia tests were completed in triplicate.

Specific test conditions appear in Table 4.2.

4.2 Saltwater Acclimation of Rainbow Trout

Rainbow trout ($4.2 \text{ g} \pm 0.9 \text{ sd}$) were transferred into a 350 L holding tank containing a 15 ppth salt solution of dechlorinated tap water. Each day for the following four days the salt concentration was increased 3 ppth by the addition of a stock salt solution. The ionic composition of the final salt solution appears in Table 4.3. The salinity was further increased by 2 ppth/day until a final salinity of 30 ppth was reached. The fish were held at this salinity for 8 days before testing. The entire reservoir of saline acclimation water was changed every 2 days. A 30 ppth solution which was considered representative of arctic marine conditions was used as dilution water in the tests.

TABLE 4.2:

ACUTE STATIC TEST CONDITIONS USING
RAINBOW TROUT, DAPHNIA AND ARTEMIA

Test Organism	Rainbow Trout		Daphnia	Artemia
	Fresh water	Salt water		
Acclimation Period (days)	28	8 d at 30 ppth	24 hr	24 hr
Organism Size (g)	4.2 ± 0.9 (sd)	4.4 ± 1.9 (sd)	0.01 ?	0.001
Number Org/Vessel	6	6	10	10
Exposure Test Volume (L)	35	35	0.2	0.01
Loading Rate (L/g/d)	0.69*	0.66*	1.0	0.5
Test Temperature (°C)	15	15	22	22
Exposure Period (Hrs)	96*	96*	48	48
Replicates	2	2	2	3

* - 96 hr static test with 48 hr renewal

TABLE 4.3: COMPOSITION OF SYNTHETIC SEAWATER (30 ppt)
USED FOR ACCLIMATION AND TESTING OF RAINBOW TROUT

Ion	Concentration (g/L)
Calcium	0.4
Magnesium	1.3
Sodium	10.8
Chloride	19.6

Dilution water was Mississauga dechlorinated tap water (see Table 3.1).

4.3 Acute Toxicity

Mortality data for rainbow trout, daphnia, and artemia appears in Appendix 1 and is summarized in Table 4.4 for both AFA-6 and FC-95.

Rainbow trout appeared to be slightly more sensitive to the AFA-6 in saltwater compared to freshwater while the degradation product FC-95 appeared slightly more toxic to fish in freshwater. The difference in toxicity between fresh and salt water conditions for the two products is not biologically significant. The average LC50 value of 5.2 mg/L for AFA-6 and 11.3 mg/L for FC-95 suggests that the parent product AFA-6 is about twice the toxicity of the degradation product.

Artemia, the representative marine invertebrate, displays twice the tolerance to AFA-6 as rainbow trout while sensitivity to the FC-95 was comparable to rainbow trout.

Daphnia, a freshwater invertebrate, is twenty fold more sensitive to AFA-6 than rainbow trout, but is about five fold more tolerant to the FC-95 than rainbow trout. The reduction in toxicity to daphnia between the parent and degradation product is about 150 times, which represents a major response difference compared to the other two organisms. This serves to underline the importance of using test results for representative marine organisms to estimate marine toxicity rather than develop projections entirely from fresh water data.

Recognizing that the AFA-6 will be released into seawater during melting of the ice it would be important to know what concentrations would not be lethal during short-term (24 hr) exposure. Table 4.5 summarizes the range of highest concentrations that were observed to be non-lethal to rainbow trout and artemia.

Since the estimated degradation half-life is about 30 days acute exposure (24 hrs) of AFA-6 to fish will represent the most critical potential impact. Once diffusion of the AFA-6 decreases the concentration below 2 mg/L, acute effects should not occur.

TABLE 4.4: ACUTE LC50 VALUES (mg/L) AND 95% CONFIDENCE LIMITS () FOR RAINBOW TROUT, DAPHNIA AND ARTEMIA EXPOSED TO AFA-6 AND FC-95 UNDER FRESHWATER AND SALTWATER CONDITIONS

Species	LC50s (95% Confidence Limits)	
	Freshwater (mg/L)	Saltwater (mg/L)
AFA-6		
Rainbow Trout	6.4 (4.9 - 8.4)	4.6 (3.6 - 5.9)
	6.1 (4.8 - 7.8)	3.7 (3.2 - 4.3)
Artemia	N/A	9.7 (7.5 - 12.7)
	N/A	10.3 (7.9 - 12.5)
	N/A	9.1 (7.2 - 11.4)
Daphnia Magna	0.29 (0.23 - 0.35)	N/A
	0.27 (0.22 - 0.33)	N/A
FC-95		
Rainbow Trout	7.8 (6.2 - 9.8)	13.7 (10.7 - 17.7)
	9.9 (7.5 - 13.4)	13.7 (10.7 - 17.8)
Artemia	N/A	9.4 (7.4 - 12.1)
	N/A	9.4 (7.3 - 12.2)
	N/A	8.9 (6.7 - 11.9)
Daphnia	58 (46 - 72)	N/A
	67 (48 - 92)	N/A

N/A - Not Applicable

**TABLE 4.5: HIGHEST NON-LETHAL CONCENTRATIONS OF
AFA-6 & FC-95 *
(mg/L)**

	AFA-6	FC-95
Rainbow Trout	2 - 3	5 - 30
Artemia	3 - 5	1 - 2

* Exposure Period = 24 hours

4.4 Sublethal Effects

In addition to direct toxic effects, chemical compounds can also impair growth, reproduction, or behaviour of organisms. This affects the viability of the population without causing mortality. These sublethal effects generally occur at lower exposure concentrations over longer periods of time than acute toxic (lethal) effects. The potential chronic sublethal effects of chemical compounds can be estimated using acute lethality data.

Various safety factors have been adopted for application to acute toxicity data when information on chronic effects was unavailable. The ratio between acute and chronic toxicity data for similar compounds has been used to provide a safety factor. The application of an appropriate acute/chronic ratio to acute data then provides an estimate of chronic effect concentrations.

In a review of non-ionic surfactant toxicity (BEAK, 1985) the LC50 values for non-ionic surfactants containing 5-10 ethoxylate groups ranged between 1 to 10 mg/L bracketing the LC50 values reported in this study. However, no sublethal effect levels for the former compounds were found in the literature. Drawing on data generated for lauryl alkyl sulfonate, albeit an anionic surfactant but having a similar level of fish toxicity (LC50 about 4 mg/L) and probably a similar mode of action, it would not be unreasonable to use the chronic/acute ratio developed for LAS (0.2) to estimate a chronic effect concentration for AFA-6 and FC-95. It would appear then that an ambient value 0.2 of the acute AFA-6 and FC-95 LC50 concentration would protect against chronic effects in aquatic biota.

4.5 Bioconcentration Factors

The level to which a compound accumulates in aquatic organisms compared to the ambient concentration is referred to as the bioconcentration factor (BCF). Considerable research has been devoted to estimating BCF's based on the octanol water partition coefficient (P). The more lipid soluble a compound (high P value) the greater the propensity for the compound to be sequestered in fat tissues and therefore be isolated from metabolic breakdown and excretion. During periods of organism stress (migration, reproduction, starvation) compounds in fat tissue can be mobilized and exert an effect.

The bioconcentration factor can be expressed in terms of the P value of a compound according to the relationship developed by Veith et al. (1979),

$$\log \text{BCF} = 0.85 \log P - 0.70$$

The importance of the BCF derivation is that it can be used to estimate the exposed organism's toxicant dose from ambient exposure concentrations. Knowing that ambient concentrations produce a toxic response, the equivalent dose per unit body weight can be determined. To provide sufficient protection to aquatic organisms so they are not exposed to critical (effect) concentrations, ambient concentrations can be limited so that they do not exceed predicted equivalent organism dose concentrations and thereby ensure biological effects are not produced.

Limiting the exposure concentration to the inverse of the BCF value ensures that the dose concentration (body burden concentration) does not exceed the ambient effect concentration equivalent. Incorporating the chronic/acute ratio into the exposure limit ensures that the organism concentration does not exceed the ambient chronic effect concentration, thereby providing additional safety in developing a chronic exposure limit.

The BCF values and inverse functions for AFA-6 and FC-95 which would be used to develop exposure limits are as follows:

	<u>log P</u>	<u>BCF</u>	<u>1/BCF</u>
AFA-6	1.4	3	0.32
FC-95	0.8	1	1.01

The above values indicate that both AFA-6 and FC-95 would have very limited levels of accumulation in biota compared to recognized persistent highly accumulative compounds (e.g., BCF for PCB = 1.5×10^5 ; DDT = 1.5×10^4).

4.6 Exposure Limits

The acute toxicity concentrations provide the basis of exposure limit derivation and the mean LC50 values will be used to select the most sensitive representative trophic group from fish and invertebrates.

	A	B	C	Exposure Limit (mg/L)
	Mean LC50 (mg/L)	Chronic/Acute Ratio	1/BCF	A x B x C
<u>Rainow Trout</u>				
AFA-6	4.15	0.2	0.32	0.27
FC-95	13.70	0.2	1.0	2.74
<u>Artemia</u>				
AFA-6	9.69	0.2	0.32	0.62
FC-95	9.23	0.2	1.0	1.85

Based on application of the chronic acute ratio and 1/BCF to the acute effect level the maximum exposure limit of AFA-6 to protect against chronic sublethal effects in fish would be 0.27 mg/L. Inclusion of additional safety and rounding down to single decimal place accuracy would suggest a maximum level of 0.2 mg/L of AFA-6 should not be exceeded.

This would afford threefold greater protection to invertebrates due to their greater tolerance and would provide tenfold protection against degradation product FC-95 effects due to its lower toxicity.

5.0 FATE IN THE ARCTIC OCEAN ENVIRONMENT

5.1 Ice Island Construction

Panarctic plans to use a maximum of 500 L of AFA-6 in the coming winter exploration season. Use last year amounted to only 120 L due to temperature conditions.

Typical ice island dimensions are 7 m thick at the centre by 400 m in diameter and about 2-3 m thick at the edges. This includes about 1 m of natural ice. An additional 0.5 m of snow would typically accumulate on the surface. Total volume of the completed island is 690,000,000 L, of which 565,000,000 L is ice laid down in construction. At an application rate of 10 mg/L, the maximum volume of water (ice) containing AFA-6 will be 50,000,000 L or about 9% of the total volume. This is likely to be applied relatively early in the season and therefore will be interlayered into the ice below the surface.

5.2 Dilution, Dispersion, and Potential Impacts

As indicated in Section 4.3, the observed level of no lethal effect for AFA-6 in the toxicity tests was 1-2 mg/L. Assuming a 10 mg/L application rate, dilution by a factor of 5-10 will reduce the AFA-6 concentration to the non-lethal level. As indicated in Section 5.1, only 9% or less of the ice in the island will contain AFA-6. Therefore, dilution of 5- to 10-fold (or greater) may occur within the ice-island itself as a result of mixing of clean and "contaminated" melt-waters as they flow through the cracks and fissures or pond on the surface. Consequently, little or no lethal effect may be observed under the ice.

In the summer months, Panarctic has observed that up to 2 m of the 7 to 8 m ice thickness melts, and the island may drift up to 60 miles depending on wind and currents. As a rule more island movement is observed when melting is extensive. The melt-waters are likely to be less dense than the underlying seawater because of higher temperature, and the slightly lower salt content from snowmelt and "old" ice. Consequently, horizontal dispersion immediately under the ice will likely be considerably more prevalent than vertical dispersion. Further dilution should occur rapidly as a result of currents and ice island movement.

Based on the above, only those aquatic species which have the top of the water column and the undersurface of the ice as their natural habitat could be affected. This would include such relatively abundant species as the branchipoda, of which *Artemia* is a member. Free-swimming species such as fish would not be affected, as their natural avoidance responses would tend to keep them out of the area.

6.0 CONCLUSIONS

Investigations on the chemical nature and potential biological effects of AFA-6 and its starting degradation product FC-95 have led to the following conclusions.

- o AFA-6 is slowly biodegradable to its slightly less toxic starting material FC-95.
- o FC-95 is chemically essentially inert, having a hydrocarbon structure similar to teflon.
- o Bioassay tests on two salt water species (the brine shrimp *Artemia*, and rainbow trout) show acute (24 hr) toxicity in the 5-10 mg/L range.
- o The non-lethal concentration (no mortality of test species) was in the range 1-2 mg/L.
- o Dilution by melt-water in the ice island itself, may prevent under ice concentrations from exceeding the toxic threshold of 1-2 mg/L.
- o The recommended chronic no-effect concentration of AFA-6 was 0.2 mg/L based octanol/water partition coefficients and chronic/acute effect ratios for similar surfactant compounds.
- o Only those aquatic species which have the top of the water column and the underside of the ice as their natural habitat are likely to be affected.
- o Because of the low octanol/water partition coefficients, neither AFA-6 nor FC-95 will biomagnify significantly.
- o Based on current knowledge there do not appear to be any other long-term biological effects (e.g., teratogenicity).

On the basis of the information presented in this report, application of AFA-6 in the concentrations and quantities proposed by Panarctic does not appear to represent an environmental hazard.

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GLOSSARY

CTAS:	cobalt thiocyanate active substances - a non-specific test for all non-ionic surfactants of the polyethxylate type.
EC:	electron capture detector for gas chromatography
EPS:	Enviromental Protection Service of Environment Canada.
GC:	gas chromatography; also called GLC or gas-liquid chromatography
HPLC:	high pressure liquid chromatography
LC-50:	"lethal concentration" at which 50% of an aquatic species dies when exposed for a specified time period (e.g., 24 hours, 96 hours).
MBAS:	methylene blue active substances - a non-specific test for anionic surfatants of the alkyl sulphonate type.
surfactant:	a contraction of the phrase "surface active agent".