Fire Fighting Foams & Equipment

Fact Sheet on C6 Fluorinated Surfactants

More than a decade after 3M stopped production of PFOS-based AFFF agents; there is continued discussion within the fire protection industry on the environmental impact and efficacy of fire fighting foams. The discussion of environmental impact is usually focused on foams that contain fluorochemicals, while the discussion of efficacy is usually focused on foams that do not contain fluorochemicals. The first part of this fact sheet is in content and wording based on Fire Fighting Foam Coalitions fact sheet to provide you with accurate, up-to-date information about these issues. More information can be obtained from www.fffc.org. The last pages cover our own view point when it comes to efficiency and environmental friendliness of different foam types.

Key facts

- All modern AFFF agents (except some produced in China) contain telomer-based fluorosurfactants.
- Telomer-based AFFF agents are the most effective foams currently available to fight flammable liquid fires in military, industrial, aviation, and municipal applications. They provide rapid extinguishment, burnback resistance, and protection against vapour release.
- Fire test results presented at the 2011 SUPDET conference and 2013 Reebok conference showed that AFFF agents are significantly more effective at extinguishing flammable liquid fires than fluorine-free foams.
- Telomer-based foams **do not** contain or break down into PFOS (per fluorooctane sulfonate) or homologues of PFOS such as PFHxS (perfluorohexane sulfonate).
- Telomer-based foams **do not** contain or break down into any chemicals that are currently listed as persistent organic pollutants (POPs) under the Stockholm Convention.
- Telomer-based foams **are not** made with PFOA (perfluorooctanoic acid) or any PFOA-based products.
- Telomer-based foams **are not** made with any chemicals that are currently considered by environmental authorities to be persistent, bioaccumulative, and toxic (PBT).
- Telomer-based foams **are not** banned or restricted from use. We are aware of no pending legislation to regulate telomer-based foams in Australia, Canada, Europe, Japan, or the United States.
- The C6-based fluorosurfactants that have been the predominant fluorochemicals used in telomer-based AFFF for the last 25 years are low in toxicity and **not considered** to be bioaccumulative or biopersistent.
- Foam manufacturers are in the process of transitioning to the use of pure C6-based fluorosurfactants in response to the US EPA PFOA stewardship program.

Fluorinated Surfactants

All AFFF firefighting agents contain fluorinated surfactants (fluorosurfactants). They are key ingredients that provide AFFF with the required low surface tension (15 to 17 mN/m) and positive spreading coefficient that enables film formation on top of lighter fuels. It is this film formation capability that gives AFFF its name and its effectiveness against flammable liquid fires. The chemicals used to produce fluorosurfactants can be manufactured by different processes and have different chemical structures. The fluorosurfactants used in AFFF have historically been produced from fluorochemicals manufactured by two methods: electrochemical fluorination and telomerization. AFFF agents manufactured by 3M contain fluorosurfactants produced by electrochemical fluorination. All other AFFF agents contain fluorosurfactants produced by telomerization.

Dafo Fomtec AB P.O. Box 683, SE-135 26 Tyresö, Sweden
Telephone +46 8 506 405 66
Fax +46 8 506 405 29
E-mail info@fomtec.com

PFOS
In 2002, 3M voluntarily stopped production of a number of products including AFFF agents because they contain and degrade into perfluorooctane sulfonate (PFOS). PFOS is considered by environmental authorities to be persistent, bioaccumulative and toxic (PBT). Regulations in the United States, Canada, European Union, Australia, and Japan act as a ban on new production of PFOS-based products including foams. These regulations do not currently restrict the use of existing stocks of PFOS-based foam in the US, Australia, or Japan. In the EU and Canada, existing stocks of PFOS-based foam must be removed from service in 2011 and 2013, respectively. Production and sale of PFOS foams continues in China.

Telomers
All modern AFFF agents (except some produced in China) contain telomer-based fluorosurfactants. Telomer-based AFFF agents do not contain or break down into PFOS and have about 30 - 60% less fluorine than PFOS-based AFFF. Telomer-based AFFF agents are not made with any chemicals that are currently considered by environmental authorities to be PBT. The US Environmental Protection Agency (EPA) has indicated that some telomer-based fluorochemicals can break down in the environment into perfluorooctanoic acid (PFOA) or other perfluorocarboxylic acids (PFCAs). Further, EPA states that their concern is focused on long-chain perfluorinated chemicals (LCPFCs) containing eight carbons or more (C8, C10, C12). Existing data shows that shorter-chain compounds (C6 and below) have a lower potential for toxicity and bioaccumulation.

EPA PFOA Stewardship Program
Under the EPA 2010/15 PFOA Stewardship Program eight fluorochemical manufacturers have voluntarily agreed to reduce by 95% by year-end 2010 and work to eliminate by year-end 2015 both plant emissions and product content of PFOA, PFOA precursors, and related higher homologue chemicals. EPA intends to propose a regulation in 2012 that would close any loopholes in the Stewardship Program such as treated article imports.

Efficacy
At the 2011 SUPDET Conference, the Naval Research Laboratories (NRL) presented the results of fire testing of AFFF agents and fluorine-free foam[1]. Although the testing was limited in scope, it provided clear evidence of the importance of film formation to foam performance. Extinguishment times for AFFF agents on 28 ft^2 (c:a 2.6 m^2) pool fires tested at full strength were on average 77% faster for gasoline, 88% faster for methyl cyclohexane (MCH), and 70% faster for heptane when compared to fluorine-free foam. For isooctane, where the tested AFFF agents were unable to form a film, fluorine-free foam extinguished the fire about 10% faster (Table 1). AFFF agents extinguished all gasoline and heptane fires in less than 30 seconds, the time required to pass the United States military specification (MilSpec). The fluorine-free foam was unable to extinguish any gasoline or heptane fire in less than 30 seconds. Foam agents must meet the requirements of the MilSpec in order to be listed on the US Department of Defence qualified products database (QPD) and used for military applications[2]. The Federal Aviation Administration (FAA) requires all US airports to carry AFFF agents that meet the MilSpec and are listed on the QPD[3].

Table 1: Extinction Times (seconds)

Foam Type	Heptane	Gasoline	MCH	Isooctane
AFFF (3%)	25	21	19, 20	32, 33
AFFF (6%)	23, 28	22	22, 23	32, 33
Fluorine-free (6%)	43	34, 41	33, 46	29, 30

Table 2: Spray Extinction Times (minutes)

Foam Type	Heptane	Gasoline	Jet A-1
AFFF (1%)	1:03	0:38	0:22
AR-AFFF 1x3	2:11	1:25	1:25
Fluorine-free (1%)	2:14	3:36	3:12
Fluorine-free (1%)	2:21	2:21	3:21
Fluorine-free (3%)	None	None	1:00

Table 3: Spray Pan out Extinction Times (seconds)

Foam Type	0.25 m^2	0.785 m^2	4.52 m^2	7.06 m^2
AFFF (1%)	0:35	1:19	2:16	2:06
Fluorine-free (1%)	0:50	1:55	2:21	None

In addition many national authorities outside of the US require the use of AFFF agents that meet the MilSpec, including the Australia Department of Defence. At the 2013 Reebok Foam Conference, a paper was presented by Manuel Acuna of VS Focum summarizing his company's development of a fluorine-free foam agent[4]. The presentation contained side-by-side test data done at the same facility under the same conditions comparing the fire performance of AFFF agents and fluorine-free foams. The results showed that AFFF agents performed significantly better than fluorine-free foams in spray extinction tests (0.785 m^2) and pan fires ranging in size from 0.25 m2 to 7.06 m^2 (Table 2 and 3).

Environmental Impact

The environmental impact of AFFF-type fluorosurfactants has been extensively studied and a large body of data is available in the peer-reviewed scientific literature. The bulk of this data continues to show that C6-based AFFF fluorosurfactants and their likely breakdown products are low in toxicity and not considered to be bioaccumulative or biopersistent. Groundwater monitoring studies have shown the predominant breakdown product of the short-chain C6 fluorosurfactants contained in telomer-based AFFF to be 6:2 fluorotelomer sulfonate (6:2 FTS)[5]. A broad range of existing data on 6:2 FTS indicate that it is not similar to PFOS in either its physical or ecotoxicologicalproperties[6,7,8,9]. Recent studies on AFFF fluorosurfactants likely to break down to 6:2 FTS show it to be generally low in acute, sub-chronic, and aquatic toxicity, and neither a genetic nor developmental toxicant. Both the AFFF fluorosurfactant and 6:2 FTS were significantly lower than PFOS when tested in bio-persistence screening studies that provide a relative measure of bio up-take and clearance[10]. Aerobic biodegradation studies of 6:2 FTS in activated sludge have been conducted to better understand its environmental fate[11]. These studies show that the rate of 6:2 FTS biotransformation was relatively slow and the yield of all stable transformation products was 19 times lower than 6:2 fluorotelomer alcohol (6:2 FTOH) in aerobic soil. In particular, it was shown that 6:2 FTS is not likely to be a major source of perfluorocarboxylic acids or polyfluorinated acids in wastewater treatment plants. Importantly neither 6:2 FTOH nor PFHpA (perfluoroheptanoic acid) were seen in this study. PFHxA is a possible breakdown product and contaminant that may be found in trace quantities in telomer based AFFF. Extensive data on PFHxA presented in 2006 and 2007 gave a very favourable initial toxicology (hazard) profile[12,13,14]. Testing was done on four major toxicology end points: sub-chronic toxicity in rats, reproductive toxicity in rats, developmental toxicity in rats, and genetic toxicity. Results show that PFHxA was neither a selective reproductive nor a selective developmental toxicant. In addition it was clearly shown to be neither genotoxic nor mutagenic. In 2011 results were published from a 24-month combined chronic toxicity and carcinogenicity study, which demonstrated that under the conditions of this study PFHxA is not carcinogenic in rats and its chronic toxicity was low[15].

Conclusions

Telomer-based AFFF agents are the most effective agents currently available to fight class B, flammable liquid fires. They do not contain or breakdown into PFOS and are not likely to be a significant source of long-chain perfluorochemicals. They do contain fluorosurfactants that are persistent, but are not generally considered to be environmental toxins. AFFF and fluorochemical manufacturers are in position to meet the goals of national stewardship programs with pure short-chain fluorosurfactants that provide the same fire protection characteristics with reduced environmental impacts.

References

1 Extinguishment and Burnback Tests of Fluorinated and Fluorine-free Firefighting Foams with and without Film Formation, Bradley Williams, Timothy Murray, Christopher Butterworth, Zachary Burger, Ronald Sheinson, James Fleming, Clarence Whitehurst, and John Farley, Naval Research Laboratory, Washington, DC, presented on March 25, 2011, at the SUPDET Conference.

2 United States Department of Defense Military Specification, Mil-F-24385, "Fire Extinguishing Agent, Aqueous Film Forming Foam"

3 FAA Advisory Cautionary Non-directive (CertAlert), Aqueous Film Forming Foam meeting MIL-F-24385, No. 06-02, February 8, 2006 and Federal Aviation Administration, National Part 139 CertAlert No. 11-02, Identifying Mil-Spec Aqueous Film Forming Foam (AFFF), February 15, 2011

4 A New High Performance Newtonian Fluorine-Free Foam, Manual Acuna, VS Focum, presented on March 19, 2013 at the 5th Reebok International Foam Conference.

5 Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS, Melissa M. Schultz, Douglas F. Barofsky and Jennifer Field, Environmental. Sci. Technol. 2004, 38, 1828-1835

6 DuPont 2007a. H-27901: Static, Acute 96-Hour Toxicity Test with Rainbow Trout, Oncorhynchus mykiss. Unpublished report, DuPont-21909.

7 DuPont 2007b. H-27901: Static, Acute 48-Hour Toxicity Test with Daphnia magna. Unpublished report, DuPont-21910

8 DuPont 2007c. H-27901: Static, 72-Hour Growth Inhibition Toxicity Test with the Green Alga, Pseudokirchneriella subcapitata. Unpublished report, DuPont-22048.

9 DuPont 2007d. H-27901: Early Life-Stage Toxicity to the Rainbow Trout, Oncorhynchus mykiss. Unpublished report, DuPont 22219

10 Serex, T. et al, 2008. Evaluation of Biopersistence Potential Among Classes of Polyfluorinated Chemicals using a Mammalian Screening Method. SOT 2008 Poster #958

11 6:2 Fluorotelomer sulfonate aerobic biotransformation in activated sludge of waste water treatment plants, Ning Wang, Jinxia Liu, Robert C. Buck, Stephen H Korzeniowski, Barry W. Wolstenholme, Patrick W. Folsom, Lisa M. Sulecki, Chemosphere 2011, 82(6), 853-858

12 Chengalis, C.P., Kirkpatrick, J.B., Radovsky, A., Shinohara, M., 2009a A 90-day repeated dose oral gavage toxicity study of perfluorohexanoic acid (PFHxA) in rats (with functional observational battery and motor activity determinations). Reprod. Toxicol. 27, 342-351

13 Chengalis, C.P., Kirkpatrick, J.B., Myers, N.R., Shinohara, M., Stetson, P.I., Sved, D.W., 2009b Comparison of the toxicokinetic behavior of perfluorohexanoic acid (PFHxA) and nonafluorobutane -1-sulfonic acid (PFBS) in monkeys and rats. Reprod. Toxicol. 27, 400-406

14 Loveless, S.E., Slezak, B., Serex, T., Lewis, J., Mukerji, P., O'Connor, J.C., Donner, E.M., Frame, S.R., Korzeniowski, S.H., Buck, R.C., Toxicological evaluation of sodium perfluorohexanoate. Toxicology 264 (2009) 32–44

15 A 24-Month Combined Chronic Toxicity/Carcinogenicity Study of Perfuorohexanoic Acid (PFHxA) in Rats, H. Iwai, M. Shinohara, J.Kirkpatrick, J.E. Klaunig, Poster Session, Society of Toxicologic Pathology, June 2011

Our own experience

Dafo Fomtec has worked for many years developing both AFFF-type of foam concentrates as well as fluorine free types (FFF-types). In this work we have gained a lot of experiences on how these kinds of foam works – both regarding fire performance and environmentally aspects.

In our mind fire performance is paramount in order to save life, assets and environment. A fire is a very dangerous situation that can change from small and controllable to a huge uncontrolled firestorm within a blink of an eye. In a fire scenario people's life are at risk both civilians trapped in the flames and firefighters combating the fire. A fire is destroying assets for huge values – the longer the fire is allowed to continue the higher the value is literarily spoken going up in smoke. Moreover, a fire is a heavy pollutant, unless it is a controlled fire where it is optimised to give a more or less full combustion at high temperatures – like a power plant where the chemical reaction yielding more or less water and carbon dioxide. I fire is on the contrary often going on with depletion of oxygen – incomplete combustion (pyrolysis) – and forms severe pollutants. Just a few examples, polycyclic aromatic hydrocarbons (i.e. benzopyren) that are mutagenic and carcinogenic are formed from incomplete combustion of organic materials. One of the most utilized plastics, PVC, is forming dioxins (to be more accurate: polychlorinated dibenzodioxin) when combusted – also a well know environmental pollutant. Hence, the longer a fire is ongoing, the more pollutants are formed – generating thick black smoke that spreads widely. It is also worth to point out that a lot of these pollutants are contaminating the run-off water used for extinguishing the fire. This is just another reason it is important to extinguish as fast as possible – to minimize run-off water that needs to be collected afterwards.

There has been a lot of focus on the environmental aspect of fluorine containing foam concentrates, like in AFFF-type and fluorine free foam concentrates. In literature we have seen commercials where firefighters are shooting flowers from their foam generators, plants are flourishing and are greener than ever. This is, however, to simplify things too much. It is not that simple, just taking out one component makes things environmentally friendly. As has been shown above, the new short chain fluorosurfactants have a very good environmental, health and safety profile. They and their breakdown products have been proven to be virtually non-toxic. They are not considered bioaccumulative or persistent. On the other hand they add incredible fire performance to a foam concentrate.

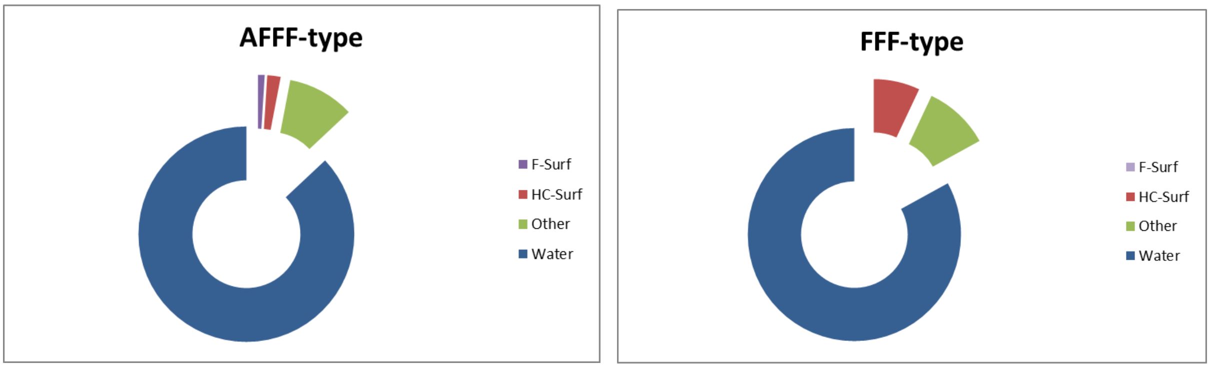

Figure 1 *The above diagrams represents the difference in composition between an average AFFF-type foam and a FFF-type of foam. The major part of the composition is water and just minor parts are surfactants. Note that the hydrocarbon surfactants are at a much higher level in the FFF-type compared to the AFFF-type.*

Looking at general representation of the compositions of the two foam types as concentrates in figure 1, there are three striking things to note (i) the major part is water, (ii) there are no fluorosurfactants present in the FFF-type of foam and (iii) the amount of hydrocarbon surfactant is a lot higher compared to an AFFF-type of foam. It is not possible to take away the fluorosurfactants without any kind of compensation to keep fire performance at a decent level.

However, this is in the concentrate, but this is not how it is used. It is diluted with water to a premix, and that changes the situation dramatically. In figure 2 below show the composition of the above foam types as premixes. Even though the additions are minute, they are crucial for the fire performance – for both types of foam.

Dafo Fomtec AB **Telephone** **Fax** **E-mail**
P.O. Box 683, SE-135 26 Tyresö, Sweden +46 8 506 405 66 +46 8 506 405 29 info@fomtec.com

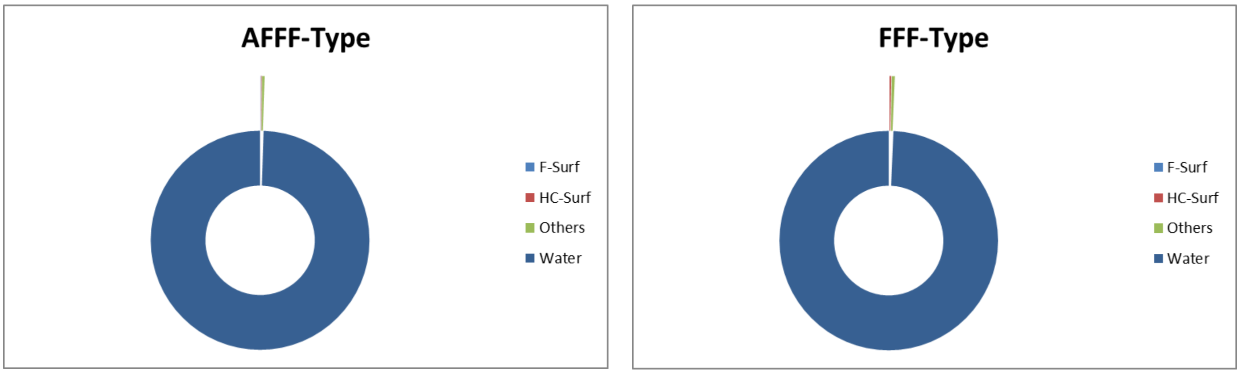

Figure 2 *The composition of a ready to use premix of water and foam concentrate. Note that all active ingredients are less than 1% of the composition.*

If we consider fire performance between the two types of foam our experience is the following. A good FFF-type of foam can pass the EN1568-3 test with good fire rating. Our Enviro 3x3 Ultra have Class IB, which means that it extinguish within three minutes and pass the burnback test with more than 15 minute. Looking at a good AFFF-type of foam we also achieve Class IB, but with one huge difference. In the former case we extinguish just at the end of the 3-minute mark but with the AFFF-type we extinguish within the first 1½ minute, more or less half the time. The burnback remains the same but the crucial part – fast and efficient extinguishment is a lot different.

There have been many tests done where the FFF-types have been tested according to different fire protocols with varying results. Sometimes they pass sometimes they fail – mainly in the extinction phase. One explanation for this can be that they are borderline to pass the criteria whilst the AFFF-types are well within the allowed extinction time.

At the end this means that an AFFF-type of foam is about twice as fast as FFF-type in extinction. In a real situation this means that at least double amount of water and foam concentrate will be needed, resulting in a lot more of contaminated run-off water to collect that needs to be cleaned. This brings us in to the environmental discussion.

As have been demonstrated above the fluorosurfactants based on C6-telomers are not considered as toxic, bioaccumulative or persistent according to POP. There are not much that differ these surfactants from ordinary hydrocarbon surfactants in this respect. In fact, there are hydrocarbon surfactants that are a lot worse in this respect, not too far from PFOS – but these are surprisingly never discussed in this context. As an example of such hydrocarbon surfactant we can take ethoxylated nonylphenols. These types degrades to nonylphenol which is persistent, bioaccumulative and not biodegradable. But worst of all, nonylphenol is endocrine disruptor an mimics the hormone oestrogen causing feminization of organisms. It is worth to point out that nonylphenol surfactants are strongly restricted to be used in Europe but it is still possible to buy. Dafo Fomtec has never used such kind of surfactants.

As we have touched earlier FFF-foams are frequently marketed with highly exaggerated statements making the world a lot better place just because they are fluorine free. As we have seen, it is not necessarily giving the full picture. Real life is much more complicated than just the presence or not of one substance in a formulation. Instead of arguing about this, let's have a look at real figures regarding aquatic toxicity and see how this correlates to the components in the formulation. Data like this has been published in literature and we decided to do our own investigation where we can correlate the results to the components in the formulation. The aquatic toxicity was determined with Rainbow Trout at a independent lab. The foams selected were a high performing FFF-type, high performing ARC- and AFFF-types, an ordinary AFFF-type and a Class A type. The latter for class A fires for porous and fibrous materials.

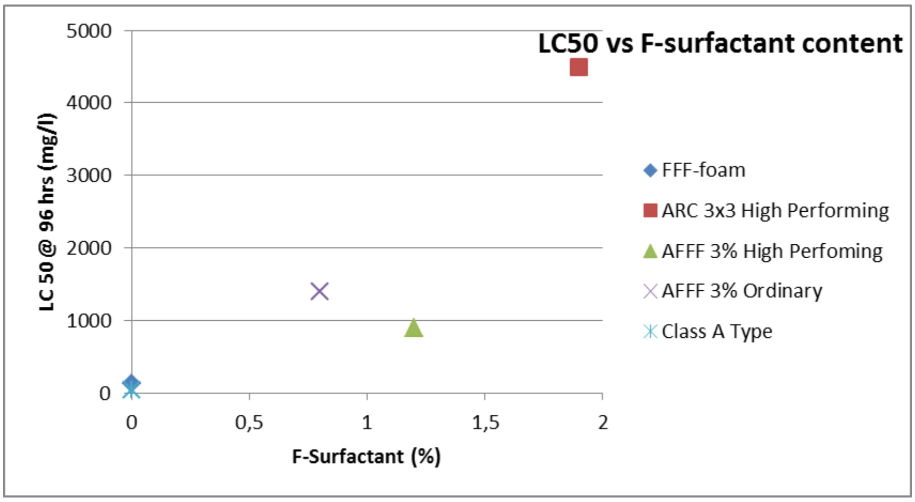

Figure 3 *Toxicity vs the concentration of fluorosurfactants in the formulations.*

In figure 3 the aquatic toxicity is shown as a function of the amount of fluorinated surfactants in the formulation. In order to interpret the results correctly it is important to know that a high value is better. Then one can add more of the substance before it affects an aquatic population. In this case we measure the LC_{50}-value – which means the concentration (in mg/litre) needed to kill 50% of the population. As can be seen there are no correlation at all.

Figure 4 shows the aquatic toxicity plotted versus the concentration of hydrocarbon surfactants in the formulation. In this case we can see a very strong correlation between the aquatic toxicity and HC-surfactants. The more HC-surfactants that are present in the formulation the lower the value for aquatic toxicity. This indicates strongly that it is the hydrocarbon surfactants and not the fluorosurfactants that are responsible for the aquatic toxicity. Note that the one of the highest LC_{50}-values obtained was with a formulation containing the highest concentration of fluorosurfactants.

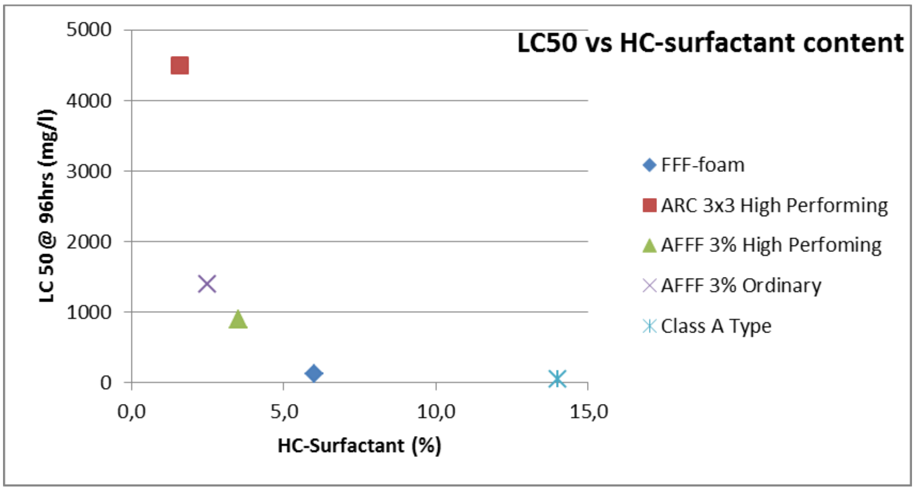

Figure 4 *Toxicity vs the concentration of hydrocarbon surfactants in the formulations.*

Conclusively, components that are always present in any formulation regardless if they are fluorine free or not are the most problematic ones regarding fish toxicity. These hydrocarbon surfactants are necessary in order to give the foam its main properties regarding expansion and drainage time. Hence, we cannot be without them. And as we discussed above, the FFF-type of foams (Class A foam is also fluorine free) have a lot higher concentration of HC-surfactants.

Remember, the LC_{50}-values presented above were on the foam concentrates as is. This is not how they are used. All concentrates are diluted with water to a premix that is the ready-to-use solution. Roughly, the concentrates are diluted 100 times. That means that we roughly can estimate the LC_{50}-value of the premixes from the values on the concentrates – simply speaking they will be about 100 times higher. This means that even the foam concentrate with the lowest LC_{50}-value will increase from around 40 mg/litre to 4000 making it ranked from slightly toxic to relatively harmless according the classification used world-wide, see table below.

Relative Toxicity	Aquatic EC50 or LC50 (mg/liter)
Super Toxic	< 0.01
Extremely Toxic	0.01 - 0.1
Highly Toxic	0.1 - 1.0
Moderately Toxic	1.0 - 10
Slightly Toxic	10 - 100
Practically Nontoxic	100 - 1000
Relatively Harmless	> 1000

FWS Acute Toxicity Rating Scales

FWS: *United States Fish and Wildlife Service*

This rises a relevant question, which LC_{50}-values shall be used? The values determined on the concentrates or the values of the premixes? It makes a huge difference on the assessment. Logically, it would be most relevant to use the values on the premixes since this is the intended formulation when used. The only reason to use the values on the concentrates itself is when there is an accidental release of the concentrate in nature and especially into a water system.

To wrap things up, we can summarize the fire performance and the environmental performance in a graph where we plot the different foam types with arbitrary units, see figure 5.

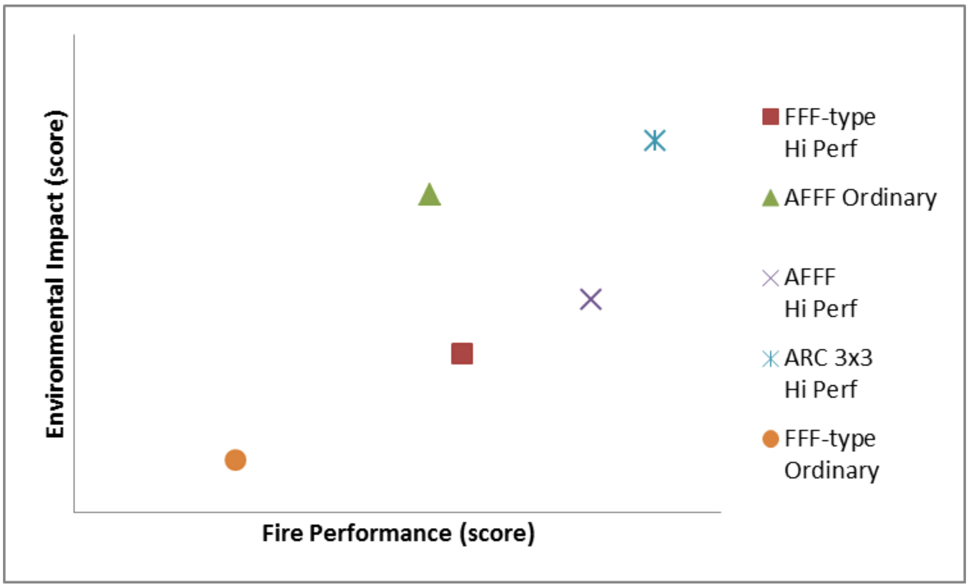

Figure 5 *Arbitrary plot of fire- and environmental performance for some selected foam types.*

This plot ranks all fluorosurfactants containing formulations higher than fluorine free formulations. This is based on LC50-values measured on the concentrates. If we change to LC50-values for premixes they will be on the same level and only fire performance will differ.