

Study of environmental and human health impacts of firefighting agents

Draft



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CONTENT

Summary.....	4
Sammanfattning	6
Abbreviations of highly fluorinated substances	8
1. Background	9
2. Analysis of firefighting agents on the Swedish market	10
2.1 Selection of fire agents.....	10
2.2 Chemical analysis	11
2.3 Ecotoxicological analysis	13
2.4 Conclusion	22
3. Formation of by-products during extinguishing using different techniques	23
3.1 Method and execution	23
3.2 chemical analysis	25
3.3 Results	28
3.4 Conclusion	33
4. Pilot study on highly fluorinated substances in firefighter's blood	33
4.1 Method.....	34
4.2 Results	34
Acknowledgment.....	38
Literature	39
Appendices	41

Summary

A study was performed by Örebro University on behalf of the Swedish Civil Contingencies Agency, where extinguishing agents are studied from an environmental and health perspective. The purpose of the study is to gain more knowledge about the chemicals firefighters and the environment are exposed to from the use of firefighting agents, and if alternative methods results in less harmful by-products. The study can be divided into the following parts: 1) chemical and ecotoxicological analyzes of selected firefighting agents, 2) study the formation of hazardous chemicals when extinguishing using different techniques , 3) conduct an initial survey of Swedish fire fighters occupational exposure of highly fluorinated substances. This report describes the work carried out from 2014 to 2015.

Firefighting agents that were included in the study were several class A foam for fires in fibrous materials, class B foams for liquid fires, and the additive X-fog. Class A and B foams on the Swedish market contains surfactants with the characteristic hydrophobic and hydrophilic properties. All class B foams included in the study contained fluorinated surfactants. The predicted long-term effect of the identified fluorinated surfactants is that they will undergo environmental transformation in more than one step until a carboxylic acid state with a fully fluorinated carbon chain is obtained. From there no further transformation or degradation is expected. These acids are as persistent in the environment as PFOS, that is banned in EU. They are however more water soluble than PFOS meaning that elimination time in organisms including humans are reduced, uptake in water rich crops like vegetables are increased, and removal from drinking water is more difficult.

All products tested showed clear effects in all conducted ecotoxicological tests. The strongest toxic effects were found for the primary consumer *Daphnia magna* which are affected by firefighting agents at lowest concentration. Differences in toxic responses between the tested agents were observed, X-fog showed the lowest toxic response based on the concentrated product for all tests. The marine bacteria *Vibrio fischeri* actually started to grow with lower concentrations of X-fog and a high concentration of 21 vol% concentrated product was needed to obtain the effect concentration. This is probably due to the X-fog's composition of salts like ammonium and sodium which functions as nutrition. There were minor differences between the foam products with exception for One Seven A that resulted in highest toxic response (e.g. lowest effect concentration). It should be noted that acute toxic effects are seen for class A foams as well as for class B foams and there are little differences in aquatic toxicity between these foam classes.

Formation of hazardous by-products during fire extinction was studied by fire tests in containers using fog spear, cutting extinguisher, CAFS, and cutting extinguisher with additive X-fog. A general trend in the results is that cutting extinguisher with additive X-fog generated the lowest concentrations of by-products. It was also using cutting extinguisher with additive X-fog that least volume of water was used, least number of re-ignitions occurred, and no fire water could be collected from the containers on the floor. The cutting extinguisher together with X-fog resulted in the fastest extinction process and most likely resulted in least hazardous compounds in the fire gas and soot.

Highly fluorinated substances both have and are still used in Class B firefighting foams. These substances have a long residence time in the body, why it is possible to see an occupational exposure, even many years after it ceased. To study firefighter's exposure for firefighting agents a pilot study was conducted in Helsingborg. The concentrations of highly fluorinated substances are low in firefighters from Helsingborg and there are no clear

association between serum levels and years worked as a firefighter. In contrast, 10 % of the firefighters had about 2-3 times higher PFOS concentrations and / or 5-20 times higher PFHxS levels compared to the average concentrations in other studies from Sweden and the USA. This may be a sign of an occupational exposure but too few individuals are included in the study achieve statistical certainty. The reason for the general low concentrations in firefighter's could be that the exposure for firefighting agents are low and that precautions are taken when handling firefighting products. Another explanation could be that handling and usage of foams for class B fires have been rare. The historical usage of class B foams at the Helsingborg stations could not be properly elucidated.

Sammanfattning

På uppdrag av Myndigheten för Samhällsskydd och beredskap har en studie utförts av Örebro universitet där brandsläckningsmedel studeras ur ett miljö- och hälsa perspektiv. Syftet med studien är att öka kunskap om vilka kemikalier brandmän och miljön utsätts för vid användning av släckmedel samt om olika släckmetoder orsakar olika mycket skadliga kemikalier under släckning. Den här rapporten beskriver arbete som utförts 2014-2015.

Syftet med studien är få mer kunskap om vilka kemikalier brandmän och miljön utsätts för vid användning av släckmedel samt om alternativa släckmetoder orsakar mindre skadliga kemikalier. Studien kan delas upp i följande delar; 1) kemiska och ekotoxikologiska analyser av utvalda släckvätskor, 2) studera bildandet av farliga kemikalier vid släckning med olika tekniker, 3) genomföra en inledande undersökning om svenska brandmäns yrkesexponering av högfluorerade kemikalier.

Släckmedel som ingick i studien var ett antal klass A skum för fibrösa bränder, klass B skum för vätskebränder, samt tillsatsmedlet X-fog. A och B-skum på den svenska marknaden innehåller tensider med de karakteristiska hydrofoba och hydrofila egenskaperna. Alla klass B skum som ingår i studien innehöll fluorerade tensider. Den långsiktiga effekten av de identifierade fluorerade tensiderna förutspås vara en omvandling till en karboxylsyra med en helt fluorerad kolkedja erhålls. Därifrån sker ingen ytterligare omvandling eller nedbrytning. Dessa syror är extremt svårnedbrytbara i miljön på samma sätt som PFOS, som idag är förbjuden. De är dock mer vattenlösliga än PFOS vilket innebär att eliminerings tiden i organismer inklusive människor är kortare, upptag i vattenrika grödor, t.ex. grönsaker ökar, och de är svårare att rena från vatten.

Alla testade släckprodukter visade tydliga effekter i alla genomförda ekotoxikologiska tester. Den starkaste toxiska effekten konstaterades för den primära konsumenten *Daphnia magna* som påverkas av släckmedel vid lägst koncentration. Skillnader i giftighet mellan de testade släckmedlen kunde också konstateras, X-fog visade den lägsta toxiska effekten i alla test baserat på den koncentrerade produkten. Den marina bakterien *Vibrio fischeri* började faktiskt växa vid låga koncentrationer av X-fog och hela 21 vol% koncentrerad produkt krävdes för att uppnå effektkoncentrationen. Detta beror sannolikt på X-fog's innehåll av salter såsom ammonium och natrium som fungerar som näring. Det fanns endast mindre skillnader mellan skumprodukterna med undantag för One Seven A som resulterade i högsta toxisk respons (d.v.s. lägsta effektkoncentration). Det bör noteras att det inte finns skillnader i toxicitet mellan klass A skum och klass B skum.

Bildandet av miljö- och hälsofarliga biprodukter studerades genom brandtest i containrar med strålrör, skärsläckare, CAFS, och skärsläckare med tillsatsmedlet X-fog. En allmän trend i resultaten är att med skärsläckare och X-fog genereras lägst koncentration av biprodukter såsom bromerade dioxiner, VOC, och PAH. Det var också med skärsläckare och X-fog som minst volym vatten användes, minst antal återtändningar inträffade, och inget släckvatten kunde samlas från behållarna på golvet. Skärsläckaren tillsammans med X-fog hade det snabbaste släckförloppet vilket troligen är orsaken till minst farliga föreningar i gas och sot.

Högfluorerade ämnen både har och används fortfarande i klass B släckskum. Ämnena har en lång uppehållstid i kroppen varvid det går att se en yrkesexponering även många år efter den upphört. För att studera exponering av släckmedel för brandmän utfördes en undersökning av brandmän i Helsingborg. Halterna av högfluorerade ämnen är låga i brandmän från Helsingborg och det finns inte någon säkerställd koppling mellan serumnivåer och antal år som brandman. Däremot hade 10% av brandmännen ca 2-3 gånger högre PFOS-halter och /eller 5-

20 gånger högre halter PFHxS jämfört med medelvärdet i andra studier från Sverige och USA. Detta kan vara ett tecken på en yrkesexponering men för få individer ingår i studien för att säga säkert. Anledningen till de låga serumhalterna kan vara att exponeringen för släckmedel är låga och att försiktighetsåtgärder vidtas vid hantering av produkter. En annan förklaring kan vara att hantering och användning av skum för klass B bränder har varit sällsynta. Den historiska användningen av klass B skum vid Helsingborg stationer kunde inte verifieras i den här studien.

Abbreviations of highly fluorinated substances

Per- and polyfluorinated alkyl substances	PFAS
Perfluorobutanoic acid	PFBA
Perfluoropentanoic acid	PFPeA
Perfluorohexanoic acid	PFHxA
Perfluoroheptanoic acid	PFHpA
Perfluorooctanoic acid	PFOA
Perfluorononanoic acid	PFNA
Perfluorodecanoic acid	PFDA
Perfluoroundecanoic acid	PFUnDA
Perfluorododecanoic acid	PFDoDA
Perfluorotridecanoic acid	PFTTrDA
Perfluorotetradecanoic acid	PFTDA
Perfluorobutane sulfonic acid	PFBuS
Perfluorohexane sulfonic acid	PFHxS
Perfluorooctane sulfonic acid	PFOS
Perfluorodecane sulfonic acid	PFDS
6:2 Fluorotelomer Sulfonate	6:2 FTS
Perfluorooctane sulfonamide	PFOSA
N-Methylheptadecafluorooctane sulfonamide	N-MeFOSA
N-Ethylheptadecafluorooctane sulfonamide	N-EtFOSA
N-Methylheptadecafluorooctane sulfonamidoethanol	N-MeFOSE
N-Ethylheptadecafluorooctane sulfonamidoethanol	N-EtFOSE
Fluorotelomer alcohol	FTOH
1H,1H,2H,2H-perfluoro-1-octanol	6:2 FTOH
1H,1H,2H,2H-perfluoro-1-decanol	8:2 FTOH
1H,1H,2H,2H-perfluoro-1-dodecanol	10:2 FTOH
Fluorotelomer unsaturated carboxylic acid	FTUCA
Fluorotelomer carboxylic acid	FTCA
Fluorotelomermercaptoalkylamido sulfonate	6:2 FTSAS
Fluorotelomer sulfonamide alkylbetaine	6:2 FTAB

1. Background

Misuse of firefighting agents, both in real fire situations and exercises, results in a large impact on the environment and can have devastating effects on sensitive aquatic environments as well as private and municipal water supplies. An estimate made by the Swedish drinking water producers and the Swedish Water and Waste Water Association shows that 22% of the drinking water in the country is affected by fluorinated surfactants (Holmström et al 2014) which, partly originates from fire exercise areas. Converted into the number of drinking water customer's results in every fourth Swede that has a tap water impacted by fluorinated surfactants. The most known water pollution cases include Tullinge, Kallinge and Uppsala. Moreover, there is a large, yet unknown number of contaminated sites in Sweden that must be remediated. The social costs in the current, known situation cannot be estimated. Fluorinated surfactants are primarily used in firefighting agents designed for liquid fires (KEMI 2015) but it is not only the fluorine-containing foams that are potentially harmful to the environment and health. Foams and other extinguishing agents are acutely harmful and extinguishing foams have been shown to significantly elevate the levels of organic pollutants, such as dioxins, in the extinguishing water (SP 2005). Firefighting agents can more or less help to leach out and transport the toxic fire remains at risk of irreversible damage to the environment. Number of interventions per year where potential emissions can damage groundwater or environmentally sensitive areas are estimated at 10,500, of whom 3500 are car fires and 7000 are fires in buildings (MSB 2016). Add to that exercises performed by emergency services and authorities, and more rare fires such as petroleum fires and industrial fires

Hazardous substances can be formed during fire of different materials as well as in the flue gas when the fire is depleted. Depending on the extinguishing method used, different thermal conditions are created in the fire room. Different firefighting agents and techniques extinguish fires in different ways. Some lower the temperature of the fire gas, while others lower the temperature of the burning material. The firefighting agent's efficiency in lowering the temperature is crucial for reducing the formation of hazardous by-products and it should be examined whether various firefighting methods can contribute to or reduce the formation of toxic substances. If such differences exist it can cause negative effects on firefighter's health and the environment.

There is a high demand from municipalities (emergency services) and government agencies (the Swedish Civil Contingencies Agency, Swedish Armed Forces, and the Swedish Chemicals Agency) for more knowledge on environmentally friendly methods. The knowledge of what firefighting agents are made of and what environmental impact they have is low. This has contributed to a situation in where operations and exercises differs between different emergency services. As a result of the relatively low concentrations of chemical additives in the extinguishing products, market products are not subject to any legal testing or reporting requirements. Therefore a development of knowledge is needed to make firefighting efforts nationally eco-efficient and sustainable.

The present study aims at providing more knowledge on firefighting agents environmental and health impact and can be divided into three parts:

- 1) Chemical and ecotoxicological evaluation of selected fire extinguishing agents to increase knowledge on what kind of chemicals are being used and released, and what the environmental effects are.
- 2) Study the formation of hazardous chemicals during extinguishing of fires using different techniques; are there firefighting agents and/or techniques that results in less by-products?

- 3) Conduct an initial survey of Swedish fire fighters occupational exposure of highly fluorinated chemicals that are or have been present in firefighting agents

2. Analysis of firefighting agents on the Swedish market

At the request of the Swedish Contingencies Agency and the Swedish Chemical Agency, Örebro University performed several different analysis of selected firefighting agents present on the Swedish market in 2014. The aim was to increase the knowledge of the toxicity of firefighting agents and to identify the main ingredients in order to evaluate the long term toxicity to the environment and humans. A special focus were to identify the presence of per- and polyfluorinated alkyl substances (PFAS) including precursor compounds.

Producers consider the ingredients in their products as trade secrets thus firefighting agents can contain a variety of additives and the present ingredients needs to be elucidated due to environmental and health concerns. Fires in fibrous materials, e.g. building fires also called class A-fires, are today extinguished with fluorine-free foam, water or water mist, with or without additives. Fires in e.g. flammable liquids also called class B-fires are extinguished with foam that often contains highly fluorinated substances. Surfactants, or detergents, used in foams affects the surface tension of water which facilitates formation of a film. Addition of fluorine to the surfactant makes it more stable and heat resistant. The surface properties are also increases, i.e. a more efficient lowering of the water's surface tension.

There are many different techniques and extinguishing agents to choose from but an overall risk- and efficiency assessment is missing and there are no national recommendations.

Restrictions of foam containing highly fluorinated substances, albeit with significant exceptions, are proposed by the Swedish Chemical Agency however fluorine-free fire extinguishing agents are being introduced on the market without adequate environmental assessment. A complete register of the products is also lacking. A survey of the manufacturers and suppliers of firefighting foams on the Swedish market was conducted in 2014 on behalf of the Swedish Chemical Agency (KEMI 2014).

A selection of firefighting agents were studied with respect to i) chemical analysis in order to identify the main ingredients and presence of highly fluorinated substances, ii) ecotoxicological analysis to assess environmental effects.

2.1 SELECTION OF FIRE AGENTS

The firefighting agents included in the present study was selected based on the above mentioned survey report and available public registers on imported and used volumes from 2012 (KEMI 2014). One additive for water mist extinguishing was also included in the study. The agents included were:

A-class foams for fires in fibrous materials (name(distributor)):

- Forest (Dafo), OneSeven A (NFRS), Unifoam Bioyellow (Kempartner)

B-class foams for fires in flammable liquids:

- Sthamex AFFF 3% (Dr Sthamer/Presto), Alcoséal 3-6% (Angus/Kidde), AFFF 3% (Dafo), Towalex AFFF (Tyco), OneSeven B-AR (NFRS), ARC Miljö (Dafo)

Additive for water mist:

- X-fog (X-fire AB)

Selected products were kindly donated from distributors and users. Firefighting products were provided from the different sources and were sampled by the provider, between 200 mL – 5000 mL, in clean plastic containers (not containing Teflon or other fluoropolymers) during fall 2014.

2.2 CHEMICAL ANALYSIS

The firefighting products were sub-sampled and diluted (between 100 to 10000 times) with laboratory produced water (MilliQ-quality) and methanol (LC-MS grade) and was filtered (GHP filters, 0.2 μ m) before analysis. Detailed information on the analytical procedure are described elsewhere (KEMI 2015).

Chemical analysis with the aim to identify main ingredients in firefighting agents was performed using non-target screening using liquid chromatography coupled to mass spectrometry (Acquity UPLC Xevo Synapt qToF (Waters Corporation, Milford, USA) with atmospheric electrospray). This technique is suitable for identifying unknown substances that are highly to moderately water soluble substances and that relatively easily can be transformed into an ionized state. A diluted solution (10000 times) of the products was analyzed. Non-target screening was done in both positive and negative mode and by the MS^E-technology that maximize the information obtained from a single analysis by switching low collision energy mode, to obtain precursor ion data, with a high collision energy ramp to obtain fragment ion data. Tentatively identification of unknown compounds was performed using softwares from Waters Corporation (MassLynx, MarkerLynx, UNIFI) elemental composition and by matching structures with the database ChempSpider.

Target analysis of highly fluorinated substances was also performed using liquid chromatography and gas chromatography coupled to mass spectrometry. Approximately 30 highly fluorinated substances for which authentic standards are available were analyzed in firefighting agents using different instrumentations (Acquity UPLC Xevo TQ-S MS/MS (Waters Corporation, Milford, USA) and 7890A GC system with a 5975C MSD (Agilent Technologies, Palo Alto, CA). Quantification of target compounds was performed by adding labeled internal standards to the diluted (approximately 10 mg to 1 mL) products. Interferences in the analysis from sample matrix were corrected for by the labeled standards. Labeled internal standards were added to clean methanol/water and were analyzed as a blank control. Several blank injections were performed to monitor possible system carry-over or memory effects.

2.2.1 Results

Non-target analysis

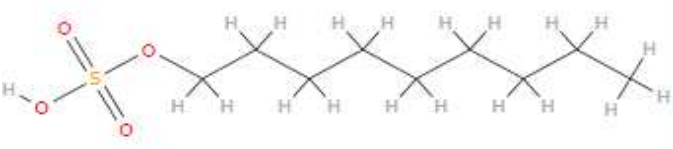
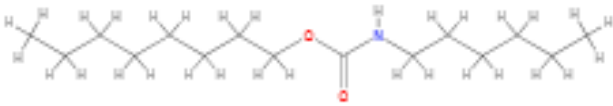
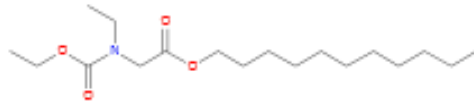
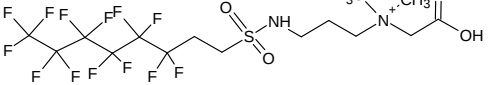
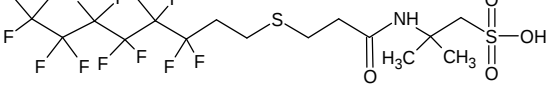
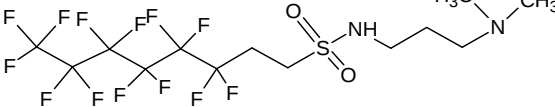
Foams are complex mixtures of additives such as surfactants and a mixture of chemicals are present in the products. The process of identifying ingredients is therefore a tedious and difficult task. Both class A and B foams resulted in complex mixtures of signals. Tentative identification was made when the structure could be confirmed by the presence of the molecular ion and at least two product ions. Moreover, any organic component that for some reason does not ionize under the used analytical conditions (positive and negative atmospheric electrospray ionization together with water/methanol/ammonium acetate or formic acid) cannot be detected. The signal intensity may not be representative of the actual concentration and the homogeneity of the foam samples have not been studied which may be a source of uncertainty both in the non-target and target analysis. For unequivocal identification of unknowns reference standards are required. Examples of structures found in different firefighting foams can be seen in table 1. Special focus was on identification of unknown highly fluorinated substances. All class B foams and none of the class A foams contained highly fluorinated substances.

The found structures containing organofluorine were compared to literature and could be confirmed to be present in firefighting foams included in other studies (D'Agostino and Mabury 2014; Moe et al. 2012; Weiner et al. 2013) (1-4) for all cases except for ARC Miljö.

A list of abbreviations of fluorinated substances mentioned here is found on page 6.

Fluorotelomermercaptoalkylamido sulfonate with six fluorinated carbons (6:2 FTSAS) was identified in Towalex master, Alco seal 3-6%, and Skum AFFF3%. Fluorotelomer sulfonamide alkylbetaine (6:2 FTAB) was identified in Sthamex, Alco seal 3-6% and Towalex Master 3%. ARC Miljö also contains the 6:2 fluorotelomer chemistry which could be identified as 6:2 fluorotelomer sulfonamide amine however one of the main signals represented a structure in where the amine group connected to the sulfonyl group bears one oxygen. 6:2 FTSAS has previously been reported to be present in AFFFs with product names F-500, Tridol S3%, Anslite 3% AFFF-DC-3, Niagara 1-3, and Ansul Anslite ARC (Weiner et al. 2013). 6:2 FTAB has been reported to be present in Forafac 1157, F-500, Niagara 1-3, and Tridol S (D'Agostino and Mabury 2014; Moe et al. 2012).

Table 1. Ingredients tentatively identified in different firefighting foam products by qToF analysis

Nonyl hydrogen sulfate	
Octyl hexylcarbamate	
Undecyl N-(ethoxycarbonyl)-N-ethylglycinate	
N-tetradecylacrylamide	
6:2 FTAB fluorotelomer sulfonamide alkylbetaine	
6:2 FTSAS fluorotelomermercaptoalkylamido sulfonate	
6:2 fluorotelomer sulfonamide amine	

Presence and levels of known fluorinated substances

Highly fluorinated substances were detected in all class B foams and none of the class A foams. Known PFAS was found in all products analyzed, most commonly detected were short chain perfluorinated carboxylates, from low ppb levels up to ppm levels. Perfluorohexanoic acid (PFHxA, C6) was found in highest concentrations, up to 14 000 µg/kg. Fluorotelomer sulfonic acid with six fluorinated carbons (6:2 FTS) was quantified in all studied

products up to 10 000 µg/kg. Bioaccumulating perfluorinated acids ($C \geq 7$) and perfluorinated sulfonic acids were detected less frequent and in lower concentrations. Perfluorooctane sulfonic acid (PFOS) was found in two different products from users, but not in the corresponding samples from sealed containers or distributors indicating probable site contamination from previous firefighting products. The presence of PFHxA and 6:2 FTS can be residues from the manufacturing process or due to storage degradation. The connection between the PFAS-profile (target analysis) and the identified structures is clear, traces of C6 carboxylic acid and 6:2 fluorotelomer sulfonate in the mg/kg range are present in products that has the 6:2 telomer configuration as part of one of the major organic molecules.

Other PFAS-profiles in samples collected from users can be due to contamination from previously used products. There is also a possibility that users keep older products that has the same name as current products but in where the ingredients have been replaced over time.

More information regarding class B firefighting foams are available elsewhere (KEMI 2015).

The six selected products for non-target analysis all contained fluorinated telomer products with 6:2 configuration including mercaptoalkylamido sulfonate, sulfonamide amine, and sulfonamide alkylbetaine. The connection between the PFAS-profile (target analysis) and the identified structures is clear, residues of C6 and shorter carboxylic acids and C6 fluorotelomer sulfonate in the mg/range are present in products that has the 6:2 telomer configuration as part of the precursor molecule. Other PFAS-profiles in products obtained from users can be due to contamination from previously used products and/or equipment. The results from this limited study indicates that contamination from previously used products might be widespread.

Water mist additive X-fog

Using previously described methodology did not result in any information regarding the additive X-fog. The conclusion from the analysis is that X-fog does not contain organic structures that are ionized under electrospray conditions. This does not however rule out presence of organic structures but the content of X-fog is much different compared to the foam products. Further analysis on a more elementary basis was therefore made; analysis using ICP-MS showed high concentrations of sodium and calcium and ion chromatography showed high levels of for example chloride, acetate, and ammonium.

2.3 ECOTOXICOLOGICAL ANALYSIS

Environmental effects can occur both acute and/or on a more long term basis. Acute effects occurs immediately in the discharge area for a short time after the emission and usually close to the source. Chemical's causing only acute effects may lead to additional impacts if they reach the groundwater. Long term effects on the other hand can occur during some time after the release. Long-term effects can be related to a chemical's persistence, e.g. slow or non-existing degradation in the environment and/or metabolism in organisms. Accumulation in organisms, e.g. higher concentration in the organism compared to its surrounding, is also an example of long term effects. Distribution to other areas, sometimes far from the contamination source can be a consequence of a chemical's persistence.

Different negative effects can occur in different environmental compartments. For example release of chemicals into air gives a different effect scenario compared to chemicals released into a water stream or soil. The

measured environmental effect is depending on the property of the chemical, concentration of the chemical, time of exposure, and type of organisms that comes in contact with the chemical.

In the present study a selection of firefighting agents were evaluated based on acute effects in the aquatic environment. The selection of organisms from the aquatic environment were made based on the fact that firefighting agents are water soluble and there is a risk that emissions will reach the aquatic environment. Aquatic organisms are also among the most sensitive organisms and are therefore suitable for evaluation of environmental effects. The test systems included in the present study are algae, fish embryos, and daphnia magna.

2.3.1 Algae growth inhibition test

To assess effects towards primary producers, ARC Miljö, One Seven, Sthamex and Towalex were investigated in the algae growth inhibition test using unicellular green algae *Desmodesmus subspicatus*. These freshwater algae belong to the phylum *Chlorophyta*. Primary producers like green algae are important food sources for many other aquatic organisms, thus they have a fundamental position in aquatic food webs.

In the algae test the inhibition of growth of unicellular algae strains is used to quantify the effects of chemicals in aqueous solutions. For this purpose the growth rates of exposed algae populations are compared to those of unexposed negative controls. Due to short generation cycles of the used test organism there are multiple generations of algae cells produced throughout the test duration (72 hours). Hence the algae growth inhibition test can be denoted as a chronic assay.

The algae growth inhibition test was conducted according to OECD Guideline 201 (2011) using OECD medium. The test organism *Desmodesmus subspicatus* CHODAT (SAG 86.81) originated from the Culture Collection of Algae at Göttingen University, Germany (SAG). The strain is cultivated at the Institute for Environmental Research (RWTH Aachen University).

Each substance was examined in three independent tests using five concentrations which are shown in Table 2.

Table 2. Concentrations (in volume %) prepared for the algae growth inhibition tests using *Desmodesmus subspicatus*.

ARC Miljö	Tests 1, 2, 3	0.031	0.063	0.125	0.25	0.5
One Seven A	Test 1	0.0001	0.0005	0.001	0.005	0.01
	Tests 2.3	0.001	0.005	0.01	0.05	0.1
Sthamex	Tests 1.3	0.005	0.01	0.05	0.1	0.5
	Test 2	0.0005	0.001	0.005	0.01	0.05
Towalex	Tests 1.2.3	0.01	0.05	0.1	0.5	1
X-fog	Tests 1.	0.031	0.063	0.125	0.250	0.500
	Tests 1.2.3	0.125	0.250	0.500	0.750	1.000

The tests were conducted in 24 well plates (TPP AG. Trasadingen. Swiss). For each test concentrations and negative control were inoculated with about 5×10^3 cells/mL and tested in three replicates (wells) containing 2 mL. The well plates were incubated at 23 ± 2 °C under suitable light conditions and continuous shaking. Chlorophyll fluorescence was measured at the beginning of the test and after 24, 48 and 72 hours using an Infinite M200 microplate reader (Tecan Group Ltd., Männedorf, Swiss). The statistical evaluation was conducted using the software ToxRat (ToxRat Solutions GmbH, Alsdorf, Germany). The software performed probit analysis using maximum-likelihood regression to compute concentration-response curves and $EC_{50}(72h)$ values.

Results

Each substance was investigated in three independent algae growth inhibition tests (named as Test 1, 2, and 3). Examples of the concentration-response curves of the tests are shown in Figure 1 and the complete curves are shown in Figures A1-A5 in the appendices. The corresponding $EC_{50}(72h)$ -values calculated mean values and standard deviations are summarized in Table 3.

Table 3: $EC_{50}(72h)$ -values (mean values and standard deviations (SD)) determined from three independent algae growth inhibition tests using *Desmodesmus subspicatus*.

	$EC_{50}(72h)$ [vol%] mean $\pm$ SD
ARC Miljö	0.168 ± 0.031
One Seven A	0.010 ± 0.004
Sthamex	0.036 ± 0.023
Towalex	0.260 ± 0.218
X-fog	0.442 ± 0.238

In the algae growth inhibition test the lowest mean $EC_{50}(72h)$ indicating the highest toxic potential for primary producers was found for One Seven A (0.010 ± 0.004 vol%). The mean $EC_{50}(72h)$ of Sthamex (0.036 ± 0.023 vol%) and ARC Miljö (0.168 ± 0.031 vol%) were higher. Towalex showed the highest variability between the three conducted tests (0.083 vol%, 0.193 vol%, and 0.504 vol%). With 0.442 ± 0.238 vol% the highest mean $EC_{50}(72h)$ was found for X-fog. The highest concentration for X-fog (1.000 vol%) did not completely inhibit algal growth in all three conducted tests. The maximum averaged growth inhibition for this concentration was observed in Test 3 with a mean value of 82.8 % inhibition (Appendix Table A1).

All conducted tests complied with the validity criteria stated in OECD 201 (2011). The pH-values were monitored according to OECD 201. Major pH-shifts of more than 1.5 units were measured for Sthamex at 0.5 vol% and for One Seven at 0.1 vol% and 0.05 vol%, the other tests showed no abnormalities.

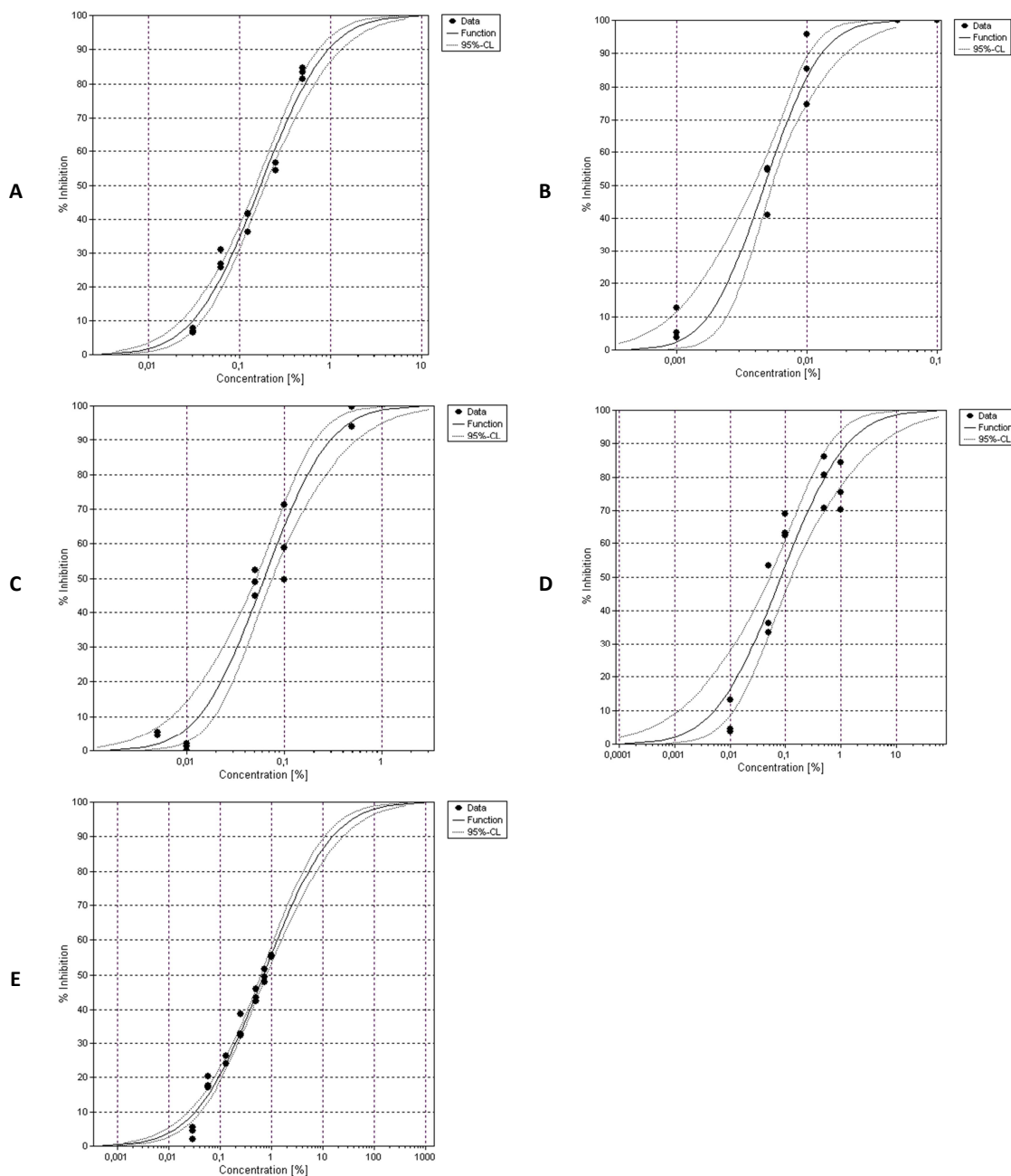


Fig. 1: Examples of concentration-response curves in the algae growth inhibition assay for **A:** ARC Miljö, **B:** OneSeven, **C:** Sthamex, **D:** Towalex, **E:** X-fog after 72 hours. The dots represent the single replicate values. The solid line shows the fitted concentration-response curve while the dashed lines illustrate the 95 %-confidence limits.

2.3.2 Fish Embryo Acute Toxicity Test with *Danio rerio*

The acute toxicity test on fish (OECD 203) is today an internationally acknowledged and standardized method within chemical risk assessment. During the last years chemical testing on fish and other vertebrates has raised ethical concerns as the animals may experience pain and distress (Braunbeck et al. 2005) which is not in line with current animal welfare legislation. Focusing on ethical considerations, Russell and Burch (1959) were the first to suggest that proper experimental design should include methods that refine techniques to lessen pain or distress of animals, reduce the number of animals necessary for a particular test, or replace animals with non-

animal models. This concept became known as the ‘Three Rs’ of alternative methods: refinement, reduction, and replacement and is now embedded in national and international legislation regulating the use of animals in scientific procedures. Animal alternative considerations have also been incorporated into new European REACH regulations through strong advocacy for the reduction of testing with live animals. One of the most promising alternative approaches to classical acute fish toxicity testing with live fish is the Fish Embryo Acute Toxicity (FET) test. The FET test has been standardized at the international level as DIN EN ISO 15088 and OECD guideline 236 for the determination of the acute toxicity of waste water and chemicals, respectively.

The test organism used in the OECD guideline is the zebrafish (*Danio rerio*), a tropical freshwater fish belonging to the minnow family (Cyprinidae). It is native to the southeast of Asia where it lives in stagnant or flowing water; e.g. paddy fields or rivers. Zebrafish grow rapidly and have a short generation cycle of about 2-3 months (Bresch 1991. Scholz et al. 2008). Within favorable conditions female fish are able to spawn a large amount of eggs with a transparent chorion year round every 2-3 days. This characteristic makes them a very suitable test organism in environmental science as toxic effects on their larval development can easily be observed (Scholz et al. 2008). Apical observations performed on each tested embryo include: coagulation of embryos, lack of somite formation, non-detachment of the tail, and lack of heartbeat. These observations are used for the determination of lethality. Any positive outcome in one of these observations means that the zebrafish embryo is considered as dead. Additionally, hatching is recorded in treatment and control groups on a daily basis starting from 48 hours post fertilization. Observations are recorded every 24 hours until the end of the test.

The fish embryo toxicity test was conducted according to DIN EN ISO 15088 (2009), but the test duration was prolonged to 96 hours for all firefighting agents except X-fog. Each substance was examined in three independent tests using five concentrations which were based on pre-test results and are shown in Table 4.

Table 4. Concentrations (in vol%) prepared for the fish embryo toxicity test using *Danio rerio*

ARC Miljö	0.100	0.200	0.300	0.400	0.500
One Seven A	0.0003	0.0006	0.0013	0.0025	0.005
Sthamex	0.020	0.030	0.040	0.050	0.060
Towalex	0.060	0.070	0.080	0.090	1.00
X-fog	0.063	0.125	0.250	0.500	0.750

The eggs used in the tests originated from spawning groups (sex ratio 3:2 male/female) cultivated in the Institute for Environmental Research (RWTH Aachen University). The spawning groups were fed ad libitum on a daily basis using commercial flake food for fish (TetraMin™ Flockenfutter, Tetra GmbH, Melle, Germany) and living nauplius larvae (*Artemia spec.*). Spawning was stimulated using artificial plants. As *Danio rerio* are spawn predators, the spawn was collected in glass trays covered with mesh to prevent predation. The trays were inserted into fish tanks shortly after power up of the illumination in the morning of a test day and retrieved after about 30 minutes.

Immediately after fertilization and before exposure the eggs were selected using a binocular microscope with at least 25-fold magnification. Only fertilized eggs between 8-cell stage and 128-cell stage were chosen. 10 eggs were used for each concentration. Each egg was exposed in a volume of 2 mL. For each test negative controls

(40 eggs in artificial water) and positive controls (20 eggs in 3.75 mg/L 3,4-dichloroaniline) were entrained. The fish eggs were exposed in 24 well plates (TPP AG, Trasadingen, Swiss) and incubated at 26 ± 1 °C. The evaluation of the test was carried out using an inverted microscope at magnifications of 40x and 100x. After an exposure time of 48 and 96 hours, lethal (coagulation of the embryo, non-detachment of the tail, non-detection of the heartbeat, lack of somite formation, the latter added according to OECD 236 (2013)) and sublethal (weak heartbeat, incomplete blood circulation, weak blood circulation, edemas on pericardium, edemas on tail, weak or absent pigmentation, lack of eye pigmentation, absence of eyes, underdevelopment, malformations, deformed or curved backbone, epiboly, absence or truncation of fins) endpoints were recorded. The statistical evaluation of 48- and 96 h-data was conducted using the software Prism (GraphPad Software, La Jolla, USA). The software combined the results from the three independent test replicates per substance to compute collective sigmoidal concentration-response curves and LC_{50} values using the method of least squares.

Results

In order to calculate a collective LC_{50} value the results of three independent fish embryo toxicity tests were used to create a collective sigmoidal concentration-response curve (Figure 2). The highest concentration for all tests and firefighting agents resulted in complete mortality and the concentrations in between revealed a concentration-response pattern.

The LC_{50} (96h) were nearly identically compared to the LC_{50} s found after 48 hours (Table 5). In all cases the concentration-response curves determined after 48 hours and 96 hours were also very similar (Figure 2 and Appendix X). For each sample, at least the highest examined concentration (Table 4) resulted in complete mortality after 48 and 96 hours in all three tests conducted per sample. Notable large deviations between the tests were mainly found for Sthamex (concentrations 0.3 vol% and 0.4 vol% in Fig. 2).

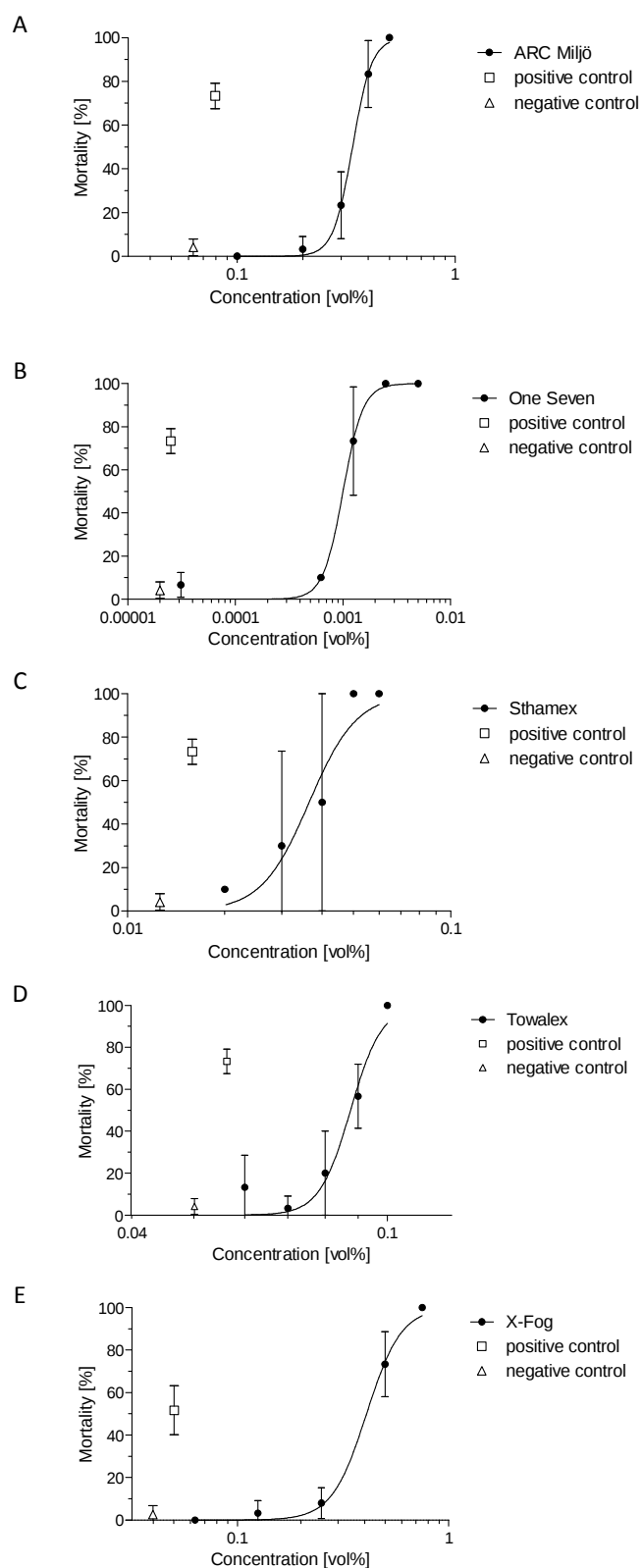


Fig. 2. Concentration-response curve for A: ARC Miljö, B: One Seven, C: Sthamex, D: Towalex, E: X-Fog determined in the fish embryo toxicity test (*Danio rerio*) after 48 hours as well as results of positive ($\square$) and negative (Δ) controls. Each symbol represents the mean of three independent tests while error bars indicate the standard deviation.

The lowest LC₅₀(48h), indicating the highest toxic potential, was found for One Seven and the highest LC₅₀(48h), indicating the lowest toxic potential, was found for X-fog.

Table 5: LC₅₀(48/96h)-values and 95 %-confidence limits (95 %-c.l.) determined for ARC Miljö, One Seven A, Sthamex, Towalex, and X-fog in the fish embryo toxicity test.

	LC ₅₀ (48h)	95 %-c.l. [vol%]		LC ₅₀ (96h)	95 %-c.l. [vol%]	
	[vol%]	lower limit	upper limit	[vol%]	lower limit	upper limit
ARC Miljö	0.3386	0.3219	0.3560	0.3318	0.3178	0.3464
One Seven A	0.0010	0.0008	0.0012	0.0010	0.0008	0.0011
Sthamex	0.0365	0.0302	0.0440	0.0360	0.0299	0.0434
Towalex	0.0876	0.0845	0.0908	0.0864	0.0818	0.0912
X-fog	0.409	0.368	0.453	-	-	-

The negative control in each case resulted in a mortality lower than 10 % while the positive control (3.75 mg/L 3,4-dichloroaniline) always resulted in a mortality clearly higher than 10 %. Thus the validity criteria were fulfilled for all tests.

The additional lethal effect “lack of somite formation” (according to OECD 236 (2013)) was not observed in any case. Furthermore absence of pigmentation was the only sub-lethal effect found. This effect was just observed in one of the three tests in one concentration (0.5 vol%) on two embryos.

Overall the data revealed just slight deviations among the three tests and the results were well reproducible.

2.3.3 Acute immobilization test with *Daphnia Magna*

To determine acute effects towards primary consumers. X-Fog was tested in the acute immobilization test using the freshwater water flea *Daphnia magna*. This Crustacean from the genus *Daphnia* belongs to the order *Cladocera* and is a widely used model organism for assessing effects of chemicals and complex mixtures towards aquatic invertebrates. Daphnids are filter feeders and have an important position in aquatic food webs. As primary consumers they are a link between primary producers such as algae and higher-order consumers like fish.

In the acute toxicity test the immobilization of daphnids is used to quantify the hazard potential of substances in aqueous solutions. This acute test is one of the most commonly used bioassays for assessing the effects of chemicals. Some reasons for this are fast exposition-caused response, short generation cycles and easy rearing of daphnids under lab conditions.

The acute toxicity test was conducted according to OECD Guideline 202 (2004) using M4 medium. The test organism *Daphnia magna* STRAUS (clone 5) originated from the continuous-breeding of the Institute for Environmental Research (RWTH Aachen University).

X-Fog was examined in three independent tests using seven concentrations shown in table 6 with four replicates per concentration. A replicate contained five neonate (younger than 24 hours) *Daphnia magna* in a volume of 10 mL. Additionally four control replicates were entrained. The daphnids were incubated in darkness at 20±1 °C and

were not fed during the duration of the test. After 24 and 48 hours the numbers of immobile animals were determined by counting. The statistical evaluation was conducted using the software Prism (GraphPad Software, La Jolla, USA). The software combined the results from the three independent tests to compute one collective concentration-response curve (figure 3) and EC_{50} value using the model $\log(\text{agonist})$ vs. normalized response with variable slope.

Table 6. Concentrations (in vol%) prepared for the toxicity test using *Daphnia magna*

X-fog	0.017	0.031	0.063	0.125	0.250	0.500	1.000
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Results

In order to calculate a collective $EC_{50}(48h)$ value the results of three independent daphnia acute immobilization tests were used to create a collective concentration-response curve (Fig. 3).

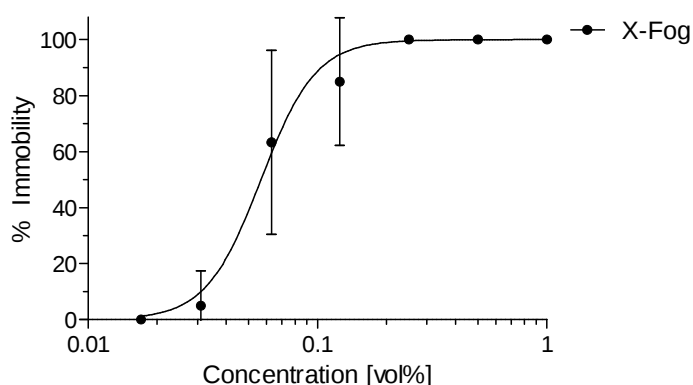


Fig. 3. Concentration-response curve determined in the daphnia acute immobilization assay for X-Fog after 48 hours. . Each symbol represents the mean of three independent tests while error bars indicate the standard deviation. This does not apply to the lowest concentration (0.017 vol%), for this concentration the results of one test were discarded due to clearly non substance related immobilization of the daphnids.

At the lowest concentration (0.017 vol%) no immobilization was observed in two of the three tests. The high immobilization (65 %) found for this concentration in one of the tests was clearly non-substance related and therefore excluded from statistical analysis. The three highest concentrations (0.250 vol%, 0.500 vol% and 1.000 vol%) led to total immobilization in all cases. The concentrations in between revealed a concentration-response pattern. The $EC_{50}(48h)$ was 0.057 vol% (95% confidence interval: 0.051 to 0.062 vol%). There was no immobilization observed in the negative control in each case. Oxygen concentrations and pH-values were monitored according to OECD Guideline 202. The pH-values did not change more than 1.5 units during incubation. Extraordinary low oxygen concentrations were found just for two single replicates in one of the three independent tests. These values seem to be outliers as for both concentrations the parallel replicate values were found to have normal oxygen concentrations.

Table 7. $EC_{50}(48h)$ -values and 95 %-confidence limits (95 %-c.l.) in the *Daphnia magna* toxicity test.

	EC ₅₀ (48h)	95 %-c.l. [vol%]	
	[vol%]	lower limit	upper limit
X-fog	0.057	0.051	0.062

2.3.4 Microtox

A standard method for toxicity testing is Microtox, which is an *in vitro* bioassay that uses a marine bacteria, *Vibrio fischeri*. The bacteria is natural luminesce, that is it sends out light as a part of its metabolism. When exposed to a toxic substance the function changes and a reduced output of light can be measured. Due to its simplicity the method has become a standard toxicity test for water, soil, and sediment.

The before mentioned firefighting agents together with additional agents were tested in this bioassay. The toxicity for *Vibrio fischeri* (stock 9) was measured according to standard method SS-EN ISO 11348-3:2008. Zink (II) was used as control was monitored together with pH, temperature and oxygen concentration and were all within control levels according to the method standard.

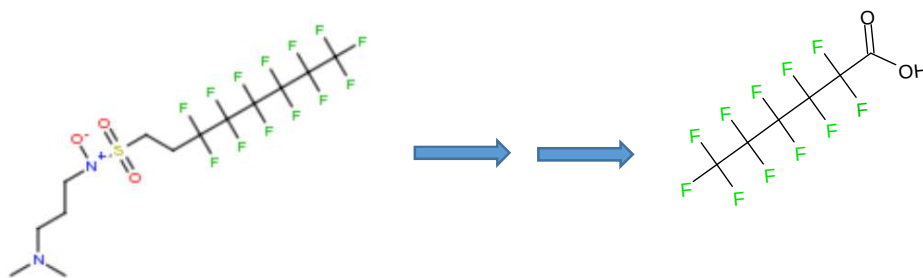
The test was evaluated statistically using regression analysis (curve fit) and the measured EC₅₀ values can be seen in table 8. The lowest toxicity for the marine bacteria *Vibrio fischeri*, e.g. the highest EC₅₀ value was observed for X-fog while the foam products showed approximately the same toxicity, up to 1000 times higher toxic response compared to X-fog.

Table 8. EC₅₀(15min) in vol% for several firefighting agents in the *Vibrio fischeri* (Microtox) toxicity test. The exposure time was prolonged to 30 min for X-fog due to low toxicity.

	Vol%
X-fog (30 min)	21
One Seven A	0.030
Bioyellow	0.020
Forest	0.020
Towalex master	0.095
One Seven B-AR	0.049
ARC Miljö	0.016
Sthamex	0.085
X-foam	0.033

2.4 CONCLUSION

Class A and B foams on the Swedish market contains surfactants with the characteristic hydrophobic and hydrophilic properties. All class B foams included in the study contained fluorinated surfactants. The predicted long-term effect of the identified fluorinated surfactants is that they will undergo environmental transformation in more than one step until a carboxylic acid state with a fully fluorinated carbon chain is obtained, as illustrated below. From there no further transformation or degradation is happening. These acids are as persistent in the environment as PFOS. They are however more water soluble than PFOS meaning that elimination time in organisms including humans are reduced, uptake in water rich crops like vegetables are increased, and removal from drinking water is more difficult.



All products tested showed clear effects in all conducted bioassays. The strongest toxic effects were found for acute immobilisation test using the primary consumer *Daphnia magna* which are affected by firefighting agents at lowest concentration. The toxicity towards the green alga *Desmodesmus subspicatus* and embryos of *Danio rerio* was found to be lower. Differences in toxic responses between the tested agents were observed, X-fog showed the lowest toxic response based on concentrated product for all tests. The marine bacteria *Vibrio fischeri* actually started to grow by lower concentrations of X-fog and a high concentration of 21 vol% concentrated product was needed to obtain the effect concentration. This is probably due to the X-fog's composition of salts like ammonium and sodium which functions as nutrition. There were minor differences between the foam products with exception for One Seven A that resulted in highest toxic response (e.g. lowest effect concentration). It should be noted that acute toxic effects are seen for class A foams as well as for class B foams and there are no differences in aquatic toxicity between these foam classes.

Addition of foam and surfactants to water, both of which reduce the surface tension does not only lead to a higher toxic response but have also been shown to increase the solubility of the particular polyaromatics formed under fire in porous materials and may thereby contribute to increased pollution of the extinguishing water than if only water is used (Pablo et al 2011).

3. Formation of by-products during extinguishing using different techniques

Materials like wood, plastic, fabrics, rubber, paper etc. generates hazardous substances when burning. The formation of hazardous by-products is not only determined by the material burning but also by the thermal conditions during extinguishing. Different firefighting agents and techniques help to extinguish fires in different ways. Some lower the temperature of the fire gas, while others lower the temperature of the burning material. The firefighting agent's efficiency in lowering the temperature is crucial for reducing the formation of hazardous by-products. Depending on the composition of the firefighting agent, it is also possible that the agent itself can generate hazardous chemicals on contact with flames and hot surfaces. Another important parameter is how the extinguishing agent is introduced and distributed into the fire area.

A series of fire extinguishing tests were performed in order to study different firefighting agents and techniques influence on formation of hazardous by-products. The objective of the tests was to measure the formation of hazardous chemicals in gas and soot particles during fire extinguishing.

3.1 METHOD AND EXECUTION

Method and execution were focused on creating identical fire tests in where the only difference between tests should be the extinguishing technique. Fire extinguishing efficiency was not included in the evaluated. Two water-based systems and one foam system, commonly used for fires in buildings, were used:

- Fog spear with water
- Cutting extinguishing with water
- Compressed air foam system (CAFS) with One Seven A
- Cutting extinguishing with water and additive X-fog

Fire tests were performed in containers that were equipped with identical interior consisting of double plasterboards, wooden studs, and identical furniture including sofa, carpet, mattress, pillows, table, lamp, electric cables, TV, computers and a plastic chair (figure 4). Most of the interior and furniture were newly purchased. Ignition was done in a standardized way, shown in figure 4, and quenching started about 10s after flashover. One and the same person, trained on all included techniques, extinguished all fires with the only instruction to put out the fires as if a normal firefighting incident. A heat camera was at the fire fighters disposal. Steel collectors were placed on the floor to retain firefighting water.



Figure 4. Picture of the container interior and the standardized ignition set-up (small picture)

Several samples and measurements were taken during the fire and extinguishing. Temperature were monitored by three different temperature probes situated at different positions in the container. Fire gas was sampled by low volume pumps (GSA SG4000. Messgerätebau GmbH. Gut Vellbrüggen. Germany) operated at air flows of 0.4-1 L/min connected to glass tubes, about 20 cm long, which were inserted through the wall of the container. One set of pump and tube was used to collect gases from the fire (until flashover) and another set was used to collect gases during the fire extinguishing phase until 5 minutes after the start of the extinguishing. Fire soot was sampled on stainless steel plates (length 500 mm. width 420 mm. thickness 1 mm); one mounted on the wall next to the gas sample glass tubes and one mounted in the opening of the container. Stainless steel plates were burned clean before usage and was not re-used. Fire gas samples and soot from the container opening was taken before and during extinguishing, respectively.

The four tests of the different techniques were performed during three days at the facility Guttasjön, Södra Älvsborgs Räddnings Förbund (SERF). Container interiors including furniture were kept dry between mounting and fire test by a gas heater. Changes in conditions occurred however and it cannot be ruled out that outer circumstances influence the formation of by-products during extinguishing. In order to study bias from uncontrolled variables one test was performed twice with the aim to identify variables that differs due to weather circumstances rather than the extinguishing technique. The cutting extinguishing with water and

additive X-fog was therefore repeated. Pictures from the five fire tests are shown in figure 5, together with notes on weather conditions.



1. Fog spear with water. Varying winds, partly away from the container opening



2. Cutting extinguishing with water. Varying winds, partly towards container opening



3. CAFS with One Seven A. Winds directed towards container opening



4. Cutting extinguishing with water and additive X-fog. Winds directed towards container opening



5. Cutting extinguishing with water and additive X-fog. Calm weather.

Figure 5. Pictures at the start of each of the five fire tests together with weather notes for each test.

3.2 CHEMICAL ANALYSIS

It is relatively well known what by-products are formed during fire of different materials (Bengtsson and Antonsson 1993). A wide selection of parameters were chosen in this study to evaluate differences in formation of by-products depending on different extinguishing techniques.

Fire gas was sampled during the fires and during the extinguishing, separately, with respect to following parameters:

- Organic, non-polar substances (for example chlorinated and brominated dioxins and furans, polyaromatic hydrocarbons (PAHs))
- Isocyanates
- Volatile Organic Carbons (VOCs)
- Inhalable dust and metals
- Ammonia
- Aldehydes
- Carbon monoxide
- Inorganic and organic acids

Fire soot was sampled on the pre-cleaned stainless steel plate mounted inside the container at the same height as the glass tube used for gas sampling, reflecting both fire and extinguishing, and at the container opening. The plate mounted at the opening was changed before extinguishing thus resulting in two soot samples, one during fire and one during extinguishing. After each test the soot were wiped off of the plates using Kleenex tissues. To minimize the risk of contamination each plate was used only once. The Kleenex tissues were analyzed with respect to:

- Organic, non-polar substances (for example chlorinated and brominated dioxins and furans, polyaromatic hydrocarbons (PAHs))

Sampling and analysis of inhalable dust

Inhalable dust was collected using an IOM sampler (SKC Inc., PA 15330 USA) with a 25 mm nitrocellulose membrane filter (Merk Millipore Ltd. Cork, Ireland, 3 µm pore size) connected to a pump (GSA SG4000, Messgerätebau GmbH, Gut Vellbrüggen, Germany) operated at an air flow of 0.5 L/min. Determination of deposited amount of dust on the filters was made gravimetrically.

Analysis of element composition in inhalable dust

A standard analytical procedure of metal analysis on each filter was performed with inductively coupled plasma mass spectrometry (HP 4500 ICP-MS, Agilent Technologies Inc.) (NIOSH 1994a).

Aldehydes

Aldehydes in air were collected using an aldehyde sampler (Sep-Pak XPoSure Aldehyde Sampler, Waters Corp., Millford, MA, USA) consisting of silica impregnated with 2,4-dinitrophenyl-hydrazine (2,4-DNPH). The sampler was connected to a pump (GSA SG4000, Messgerätebau GmbH, Gut Vellbrüggen, Germany) operated at an air flow of 0.2 L/min. Aldehydes were analyzed by High Performance Liquid Chromatography (HPLC) with UV detection at 365 nm.

Ammonia in air

Ammonia in air was sampled using sorbent tubes filled with silica gel treated with sulfuric acid (SKC Inc., PA 15330 USA). The sorbent tubes were connected to a pump (GSA SG4000, Messgerätebau GmbH, Gut

Vellbrüggen. Germany) operated at an air flow of 0.2 L/min. Ammonia was extracted using Milli-Q water and then analysed with ion chromatography according to NIOSH method 6016 (NIOSH 1994b).

VOC in air

VOCs in air were sampled using Tenax TA adsorbent tubes (Markes International. Llanstrisant. Wales. UK) connected to a pump (GSA SG4000. Messgerätebau GmbH. Gut Vellbrüggen. Germany) operated at an air flow of 0.1 L/min. Prior to analysis an internal standard (3-methylpyridine) was added to the sorbent tubes. VOCs were desorbed and analysed using a thermal desorber (Markes International) coupled to GC/MS (Agilent 7890B Agilent Technologies Inc.).

Organic and inorganic acids

Organic and inorganic acids in air were sampled using sorbent tubes filled with washed silica gel (SKC Inc.. PA 15330 USA) connected to pump (GSA SG4000. Messgerätebau GmbH. Gut Vellbrüggen. Germany) operated at an air flow of 0.1 L/min. Organic and inorganic acids were extracted using water as a solvent. Organic acids were analysed using ion chromatography according to NIOSH method 2011 (NIOSH 1994c). Inorganic acids were analysed using ion chromatography according to NIOSH method 7903 (NIOSH 1994d).

Isocyanates

Isocyanates in air were collected using EZ4-NCO samplers (Supelco ASSETTM. Bellafonte. PA. USA) connected to pump (GSA SG4000. Messgerätebau GmbH. Gut Vellbrüggen. Germany) operated at an air flow of 0.2 L/min. Isocyanates were extracted and analyzed using LC/MS/MS according to Marand et al. (Marand et al. 2005).

Chlorinated and brominated dioxins and furans (PCDD/Fs and PBDD/Fs)

ORBO 609 Amberlite XAD-2 (20/50) 400/200 mg (Sigma-Aldrich. Steinheim, Germany) was connected to pumps (GSA SG4000. Messgerätebau GmbH. Gut Vellbrüggen. Germany) operated at air flows of 0.4-1 L/min. The compounds were extracted during 24 hours with Soxhlet and toluene. The extract was split into two; one for dioxin analysis and one for PAHs. Clean-up was performed by using three different open columns (multilayer silica. AlOx and active carbon). To avoid photolytic degradation amber colored glassware or glassware covered with aluminum foil was used. PCDD/Fs and PBDD/Fs were analyzed on a Micromass Autospec Ultima operating at 10 000 resolution using EI ionization at 35 eV. All measurements were performed in the selective ion recording mode (SIR) monitoring the two most abundant ions of the molecular bromine or chlorine cluster. Quantification was performed using isotope dilution. For PCDD/Fs splitless injection was used to inject 1 µL of the extract on a 30 meter (0.25 mm i.d. 25 µm) DB-5MS column (J&W Scientific; Folsom. CA. USA). For PBDD/Fs a Programmed Temperature Vaporiser (PTV) injector was used and 7 µL of the extract was injected on a 15 meter (0.25 mm i.d. 10 µm) DB-5MS column (J&W Scientific; Folsom. CA. USA).

PAHs

Sampling and extraction was identical with that of PCDD/Fs and PBDD/Fs and clean-up was performed using acidic silica. An Agilent 7890A gas chromatograph coupled to a 5975 low-resolution mass spectrometer using electron ionization (EI) at 70 eV was used for analysis. The separation capillary column was a Select PAH column, 30m x 0.25 mm, df = 0.15 µm provided by Agilent. Detection was made in single ion monitoring mode (SIM) and quantification was performed by isotope dilution.

3.3 RESULTS

The fire tests were performed by allowing the fire gases to ignite, making all flammable material being involved in the fire before starting the extinction. Sampling continued five minutes after start of extinguishing regardless when the fire was put out. Time to flashover varied from approximately 260s to 500s. Several steel containers on the container floor were used to collect remaining water after extinction. Table 9 shows descriptive data for the five fire tests.

Table 9. Descriptive data from the five fire tests.

Test	Number of re-ignitions	Water consumption	Firefighting water collected
1. Fog spear with water	22	121 litres	2 litres
2. Cutting extinguishing with water	4	62 liters	0.3 litres
3. Compressed air foam system (CAFS) with One Seven A	1	45 liters	0.2 litres
4. Cutting extinguishing with water and additive X-fog	0	21 liters	0 litres
5. Cutting extinguishing with water and additive X-fog	0	28 liters	0 litres

Time between first application and the fire was completely put down varied, and for test number 1 the sofa was still on fire after 5 minutes. The temperature decrease from the first application until five minutes passed can be seen in figure 6. Test 5 is not displayed for clarity reasons however the temperature curve was similar to test 4.

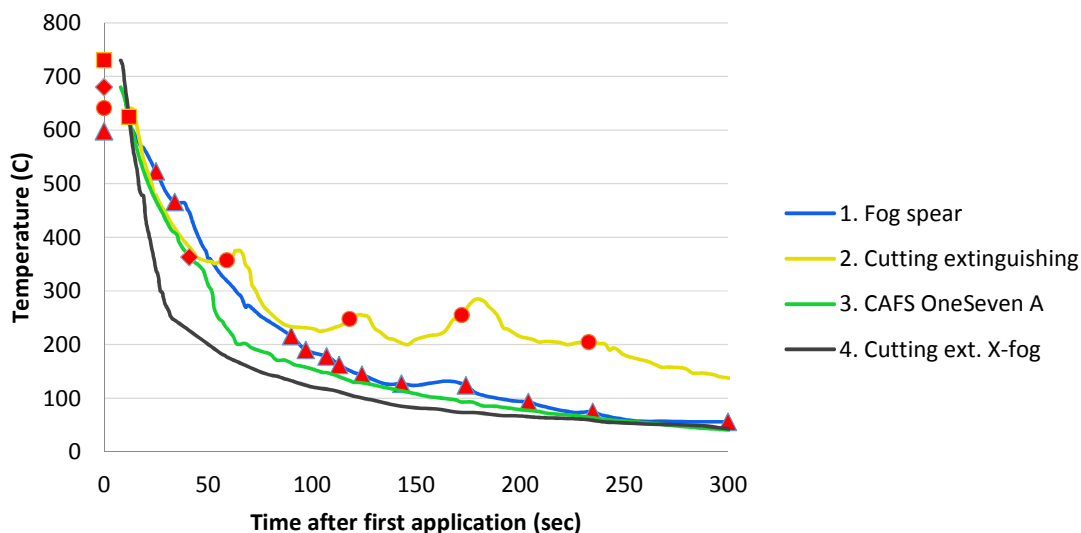


Figure 6. Temperature decrease in the container after the first application of firefighting agents (time 0 sec) until 5 minutes have passed. Filled symbols represents an application of firefighting agent. (Note: the starting temperature at 0sec could not be properly measured due to technical difficulties).

Inhalable dust and element composition

Low levels of inhalable dust was sampled in fire gas during fire extinguishing. Test 1 (fog spear) and test 2 (cutting extinguisher) generated particles that affected the sampling thus leading to underestimation of the inhalable dust fraction. Concentrations of 82, 185, and 320 $\mu\text{g}/\text{m}^3$ was measured for test 1, 2 and 3, respectively. The inhalable dust fraction for test 4-5 could not be measured and was set to less than detection limit (Table A2). Metals detected in the inhalable dust fraction can be seen in table A3. Magnesium (Mg), Manganese (Mn) and Antimony (Sb) were detected in test 1-3 but were less than LOD in test 4-5.

Aldehydes

Aldehydes measured and detected in fire gas are shown in table A4. Concentrations were generally low however the pattern reveals that other variables than the firefighting agent/technique influence the formation and measurement of aldehydes. Illustrated in figure 7 is the measured concentrations of acetaldehyde, two measurements (A and B) were performed for each test and a large variation between duplicates are seen. Moreover, test 4 and 5 uses the same firefighting agent/technique (cutting extinguisher with additive X-fog) and the concentration of acetaldehyde varies between 36 and 206 μL . Clearly, aldehydes are not suitable to use for evaluation of differences between firefighting agents.

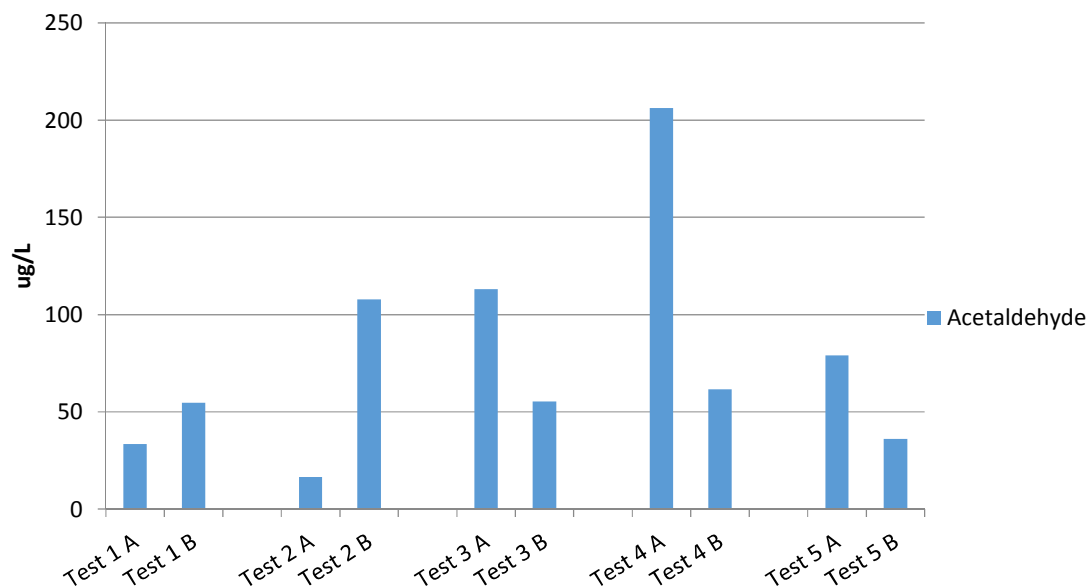


Figure 7. Acetaldehyde in fire gas during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates, A and B are duplicate measurement for each test).

Ammonia in air

Ammonia could be detected in fire gas in three tests, all which used the cutting extinguisher (test 2, 4 and 5, see table A5). Concentration in test 3, for which only water was used, was 7.6 mg/m^3 while test 4 and 5 measured 39 and 38 mg/m^3 , respectively. Ammonia is probably formed in test 4 and 5 as a result of the additive X-fog, that contains salts like ammonium salts.

VOC

Table A6 shows individual and sum of VOCs in fire gas sampled during the 5 fire tests. There is a clear trend with highest concentrations for tests 1-3 compared to tests 4-5. Figure 8 illustrates concentrations of sum of VOCs and sum of VOCs including semivolatile organic carbons. Highest concentrations were measured for test 3, CAFS with One Seven A.

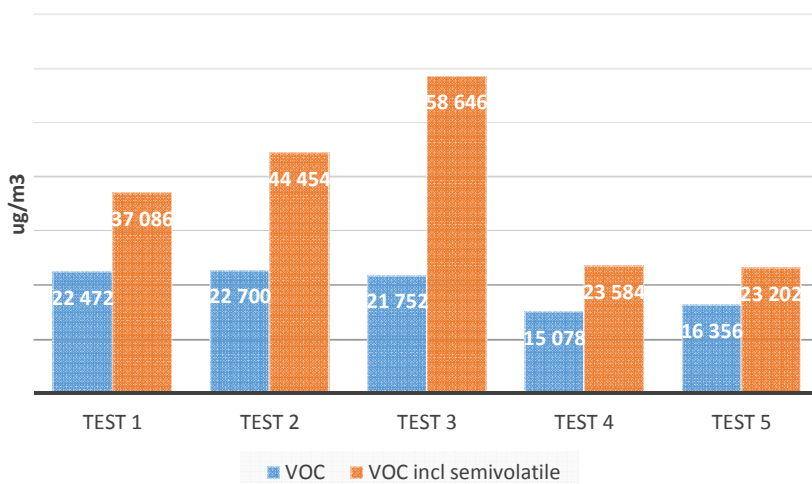


Figure 8. Sum of VOC ($\mu\text{g}/\text{m}^3$) in fire gas during extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are replicates).

Organic and inorganic acids

Organic and inorganic acids in fire gas (mg/m^3) could only be quantified in low concentrations as can be seen in Table A7. No trend between the different firefighting agents could be seen.

Isocyanates

A number of different isocyanates could be detected in fire gas as can be seen in table 10. Test 2 (cutting extinguisher with water) showed the highest concentration for several isocyanates.

Table 10. Isocyanates (mg/m^3) in fire gas during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are replicates).

$\mu\text{g}/\text{m}^3$	Test 1	Test 2	Test 3	Test 4	Test 5
isocyano acid (ICA)	460	5700	610	140	350
methyl isocyanate (MIC)	650	930	470	210	270
ethyl isocyanate (EIC)	14	38	18	7	7
fenylisocyanat (FI)	<LOD	53	60	<LOD	24
hexamethylene diisocyanate (HDI)	<LOD	<LOD	<LOD	<LOD	<LOD
toluene diisocyanate (TDI)	45	2400	720	140	420
methylene diphenyl diisocyanate (MDI)	<LOD	100	<LOD	<LOD	<LOD
isophorone diisocyanate (IPDI)	<LOD	<LOD	<LOD	<LOD	<LOD

Chlorinated and brominated dioxins and furans (PCDD/Fs and PBDD/Fs)

Dioxins and furans are formed during combustion if organic materials and chlorine or bromine are present. Chlorinated dioxins and furans (PCDD/Fs) could not be detected in fire gas samples in present study nor in soot taken from inside the container (table A8 and A9). A few congeners of chlorinated dioxins could be detected in low concentrations in soot from the plate in the opening of the container during fire extinguishing (table A10).

Brominated dioxins were detected in both gas and soot samples. Fire gas samples contained several congeners of foremost furans however a pattern among the different tests is hard to see (table A11). Soot samples also contained mostly brominated furans, the soot swipe from inside the container contained less congeners and at lower concentrations compared to the other soot sample (table A12 and A13). Brominated furans in soot sampled during the extinguishing showed a clearer pattern and was also present in higher concentration. It is clear that the steel plate mounted in the opening of the container acted as a better condensation surface for brominated furans. The concentration of brominated furans in soot during extinguishing can be seen in figure 9. The pattern is that test 1 (fog spear) generated higher concentrations followed by test 3, CAFS with One Seven A.

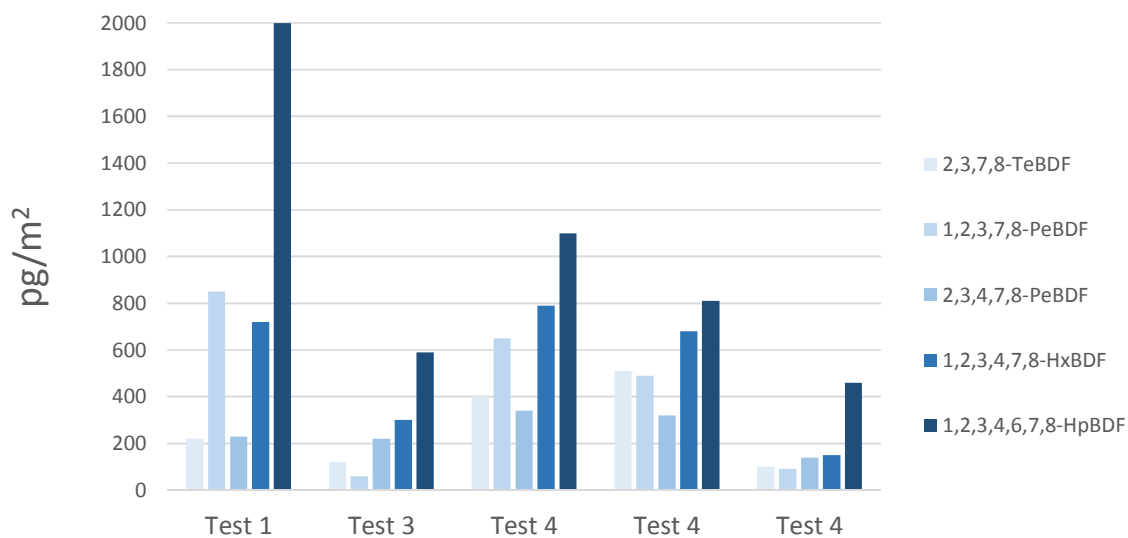


Figure 9. Brominated furans (PBDFs) in fire soot (pg/m^2) collected from the stainless steel plate mounted in the container opening during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

PAHs

PAHs were detected in both fire gas and soot at relatively high concentrations. Figure 10 illustrates the PAH profile in fire gas sampled during fire extinguishing. A general trend is that lowest concentrations are found in test 4-5 with cutting extinguisher and X-fog.

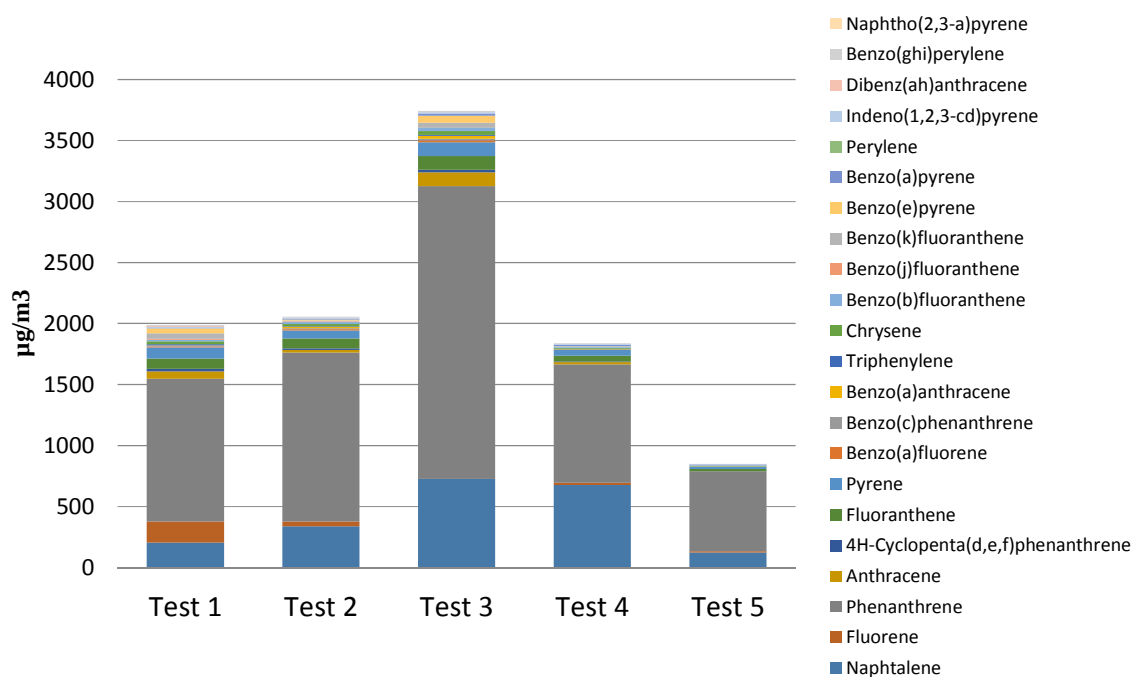


Figure 9. PAHs in fire gas ($\mu\text{g}/\text{m}^3$) sampled during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are fire test replicates).

3.4 CONCLUSION

A general trend in the results is that test 3 and 4 generated the lowest concentrations of by-products. It was also in test 4 and 5 that least volume of water was used, least number of re-ignitions occurred, and no fire water could be collected from the containers on the container floor. The cutting extinguisher together with X-fog resulted in the fastest extinction process and most likely resulted in least hazardous compounds in the fire gas and soot. The significance of the results obtained in the present study is difficult to know since the tests were only performed once with exception of the cutting extinguisher together with X-fog that was performed twice. Some parameters included in the study showed a high variability between replicates, for examples aldehydes, and should therefore not be included in conclusions regarding differences caused by using different firefighting methods. Test 4 and 5 generated ammonia in the fire gas probably as a result of the ammonium salt originating from X-fog. X-fog also contains chlorine salts however this does not seem to cause unwanted by-products like chlorinated dioxins.

4. Pilot study on highly fluorinated substances in firefighter's blood

Aqueous film-forming foams (AFFFs) are complex mixtures containing fluorocarbon- and hydrocarbon- based surfactants used to extinguish fires involving highly flammable liquids. Fluorinated surfactants in AFFF are made up of per- and polyfluorinated alkyl substances (PFAS) which are both hydrophobic and oleophobic as opposed to hydrocarbon surfactants that are merely hydrophobic in nature. The use of PFOS and other perfluoroalkyl acids (PFAAs) in AFFF formulations has been linked to environmental contamination related to handling, storage,

and usage. Substantially elevated levels of PFOS have been reported in water and biological samples such as molluscs, turtles, wild mink, and fish downstream from airports with a history of firefighting training activities. PFASs are inherently environmentally persistent and the estimated human half-lives widely vary (2-29 years for different compounds) thus meaning that historical exposure can still be detected several years later (Olsen et al. 2007; Zhang et al. 2013). PFASs have recently been linked to a number of negative health effects in humans. Large human epidemiological studies like the C8 health study in the US show association between a population exposed to drinking water contaminated with PFASs (most notably PFOS and PFOA) and elevated cholesterol, delayed puberty in girls, ulcerative colitis, early menopause, thyroid disease in women, and osteoarthritis (Frisbee et al. 2009; Innes et al. 2011; Knox et al. 2011; Steenland et al. 2009; Steenland et al. 2013).

Perfluoroalkyl carboxylic acids (PFCAs) such as PFOA and PFNA and perfluoroalkane sulfonic acids (PFSA)s such as PFOS and PFHxS. are among the most concentrated perfluoroalkyl substances (PFASs) found in human blood. These persistent and toxic compounds are ubiquitous in our environment as a result of various commercial applications. The level of PFAS exposure can be influenced by a number of factors including ingestion of food, water, air, and dust. In addition, a person's level of exposure may also be influenced by their occupation. For example the level of selected PFASs may be higher in blood from firefighters compared to the general population due to their increased exposure to firefighting foams and inhalation of burning materials impregnated with PFASs. Thus a pilot study was performed to determine the concentration of 18 PFASs (carbon chain length C₄-C₁₈) in 50 firefighters from 5 different stations in Helsingborg. Sweden.

The objectives were to analyze 14 PFASs including PFOS from 50 Helsingborg firefighter's blood serum and compare the PFAS concentrations to the general public. If possible, association with levels and working years will be studied.

4.1 METHOD

Blood samples were collected in 2015 by venipuncture and the serum fraction was immediately isolated. Samples were stored at ≤ 20°C until further analysis. The study was approved by the Ethics Committee of the University of Uppsala and the participants gave a written informed consent.

The sample preparation and instrumental analysis methods used in this study were previously developed and validated in terms of recovery, accuracy, and precision (Salihovic et al. 2013). Briefly, the method includes solvent protein precipitation and sample filtration using 96-well plates followed by instrumental analyses on an Acquity UPLC coupled to a Quattro Premier XE MS/MS system (Waters Corporation. Milford. USA) operating in negative ion mode. Target PFASs were quantified via a matrix matched calibration curve and isotope dilution, where the mean relative response factors (RRFs) obtained from the calibration curve and internal standard response from each sample were used for concentration determination.

A list of abbreviations of fluorinated substances mentioned here is found on page 6.

4.2 RESULTS

By using a previously developed robust, high sample throughput sample preparation with Ostro 96-well plates and selective UPLC-MS/MS detection technique we were able to identify and quantify 14 of the 18 PFASs in all of the firefighter's blood serum. The four substances detected in highest concentrations were PFOS (median 4.3 ng/mL), PFOA (median 1.6 ng/mL), PFHxS (median 1.2 ng/mL) and PFNA (median 0.66 ng/mL) (Figure 10). The results of the three highest PFASs concentrations found in the firefighter's serum, PFOS, PFOA, and PFHxS were compared to the geometric mean and median values of the NHANES's U.S. male serum concentrations sampled

from 2011 to 2012 (3) and to median levels of PFASs in fifty 18 year old Swedish males sampled from 2009 to 2010 (4) (table 11).

The majority of the firefighter's serum levels are either lower than or similar to the U.S. males (n=966) and the Swedish males (n=50). 10% of the firefighters have approximately 2-3 times higher levels of PFOS and/or 5-20 times higher levels of PFHxS compared to the geometric mean and median of U.S. males. 22% of the firefighters have approximately 5-50 times higher levels of PFHxS and 6% have 2-3 times higher levels of PFOS compared to the median value of Swedish males.

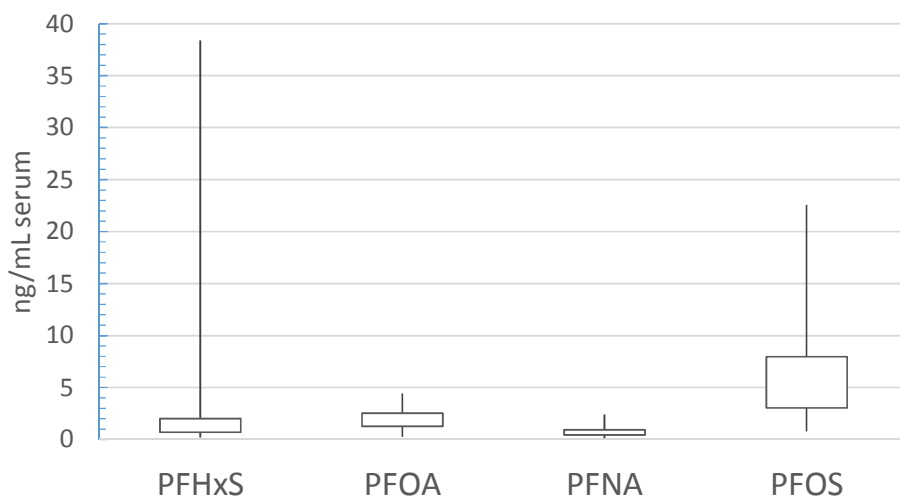


Figure 10. Concentrations (ng/mL) of four highly fluorinated substances in serum Helsingborg firefighters (n=50), 2015. Boxes indicate the range in where 50% of the participants have their results and whiskers show the entire concentration range (min-max).

Table 11. Concentrations of PFOA, PFOS, and PFHxS (ng/mL) in present study compared to U.S. males (NHANES) and Swedish young men (S-EPA)

	PFOA			PFOS			PFHxS		
	This study	NHANES	S-EPA	This study	NHANES	S-EPA	This study	NHANES	S-EPA
Geometric mean	1.7	2.37	-	4.9	7.91	-	1.3	1.68	-
Confidence interval	+/-0.2	+/-0.16	-	+/-1.2	+/-0.79	-	+/-1.5	+/-0.21	-
50th percentile	1.7	2.38	1.9	4.4	8.31	6.9	1.2	1.73	0.78
75th	2.5	3.25	-	8.0	12.5	-	2.1	2.75	-

percentile									
95th percentile	3.6	5.62	-	15.0	24.1	-	10.2	6.90	-
Range (ng/mL)	0.3-4.4	-	1.2-3.3	0.8-23	-	3.7-19	0.2-39	-	0.38-2.5

No significant correlation to the number of years worked as a firefighter (figure 11) or the firefighter's age (not shown) was found. Overall there is a normal distribution of the target PFAS concentrations among the firefighters but the elevated levels of PFOS and PFHxS in the few number of firefighters may be an indication of an exposure to these compounds through firefighting foams or ineffective preventative practices.

The concentrations of highly fluorinated substances are low in firefighters from Helsingborg and there does not seem to be any association between serum levels and years worked as firefighter. The reason for this could be that the exposure for firefighting agents are low and that precautions are taken when handling firefighting products. Another explanation could be that handling and usage of foams for class B fires have been rare. A study from Australia showed that firefighters known to handle class B foams had clearly elevated levels of PFOS and PFHxS (table 12) and a clear trend with increasing serum levels with increasing number of working years. Since highly fluorinated substances are difficult to eliminate historical exposure are seen for many years and higher concentrations are therefore detected in those highest number of working years. The historical usage of class B foams at the Helsingborg stations could not be properly elucidated.

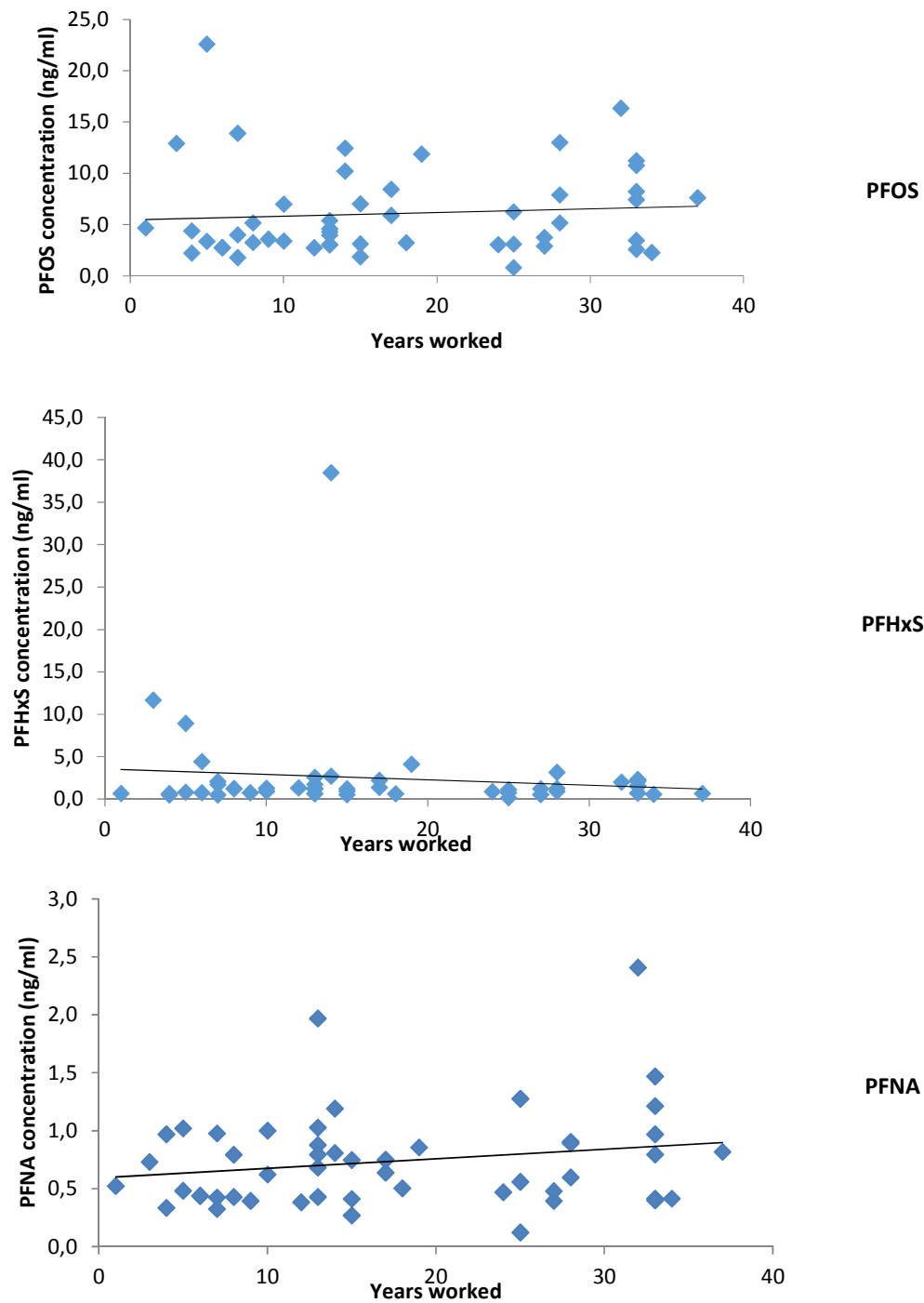


Figure 11. Serum concentrations of PFOS, PFHxS, and PFNA in relation to number or years worked as firefighters. A linear model is plotted (solid line) by least square regression analysis.

Table 12. Median values (ng/mL) of selected PFAS in serum from this study in comparison with firefighters from Australia

	Helsingborg firefighters 2015 (n=50)	Firefighters Australia 2013 (n=149)
PFOS	4.3	66
PFHxS	1.2	25
PFOA	1.6	4.2
PFNA	0.66	0.69
PFDA	0.26	0.27
PFUnDA	0.25	0.14

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Appendices

Table A1 EC₅₀(72h)-values and 95 %-confidence limits determined for ARC Miljö, One Seven A, Sthamex, Towalex, and X-fog in three independent algae growth inhibition tests using *Desmodesmus subspicatus* as well as mean values and standard deviations (SD) calculated from the three replicate values. n.d.: not determined.

	EC ₅₀ (72h) [vol%]	95 %-confidence limits [vol%]	
		lower limit	upper limit
ARC Miljö Test 1	0.136	0.104	0.180
ARC Miljö Test 2	0.172	0.153	0.193
ARC Miljö Test 3	0.197	0.142	0.291
mean ± SD	0.168±0.031		
One Seven Test 1	0.013	0.009	0.025
One Seven Test 2	0.005	0.004	0.005
One Seven Test 3	0.012	0.009	0.017
mean ± SD	0.010±0.004		
Sthamex Test 1	0.062	0.051	0.075
Sthamex Test 2	0.022	n.d.	n.d.
Sthamex Test 3	0.023	0.017	0.032
mean ± SD	0.036±0.023		
Towalex Test 1	0.504	n.d.	n.d.
Towalex Test 2	0.083	0.052	0.128
Towalex Test 3	0.193	0.124	0.305
mean ± SD	0.260±0.218		
X-fog Test 1	0.714	0.634	0.816
X-fog Test 2	0.336	0.260	0.419
X-fog Test 3	0.276	0.206	0.346
mean ± SD	0.442±0.238		

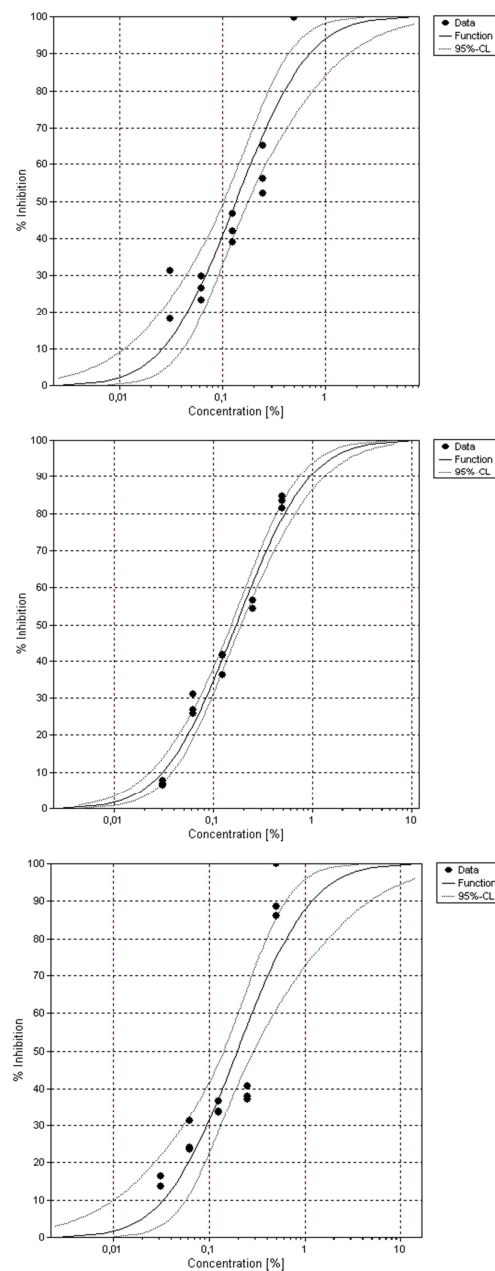


Figure A1 Concentration-response curves in the algae growth inhibition assay for ARC Miljö after 72 hours (Test1, 2, 3 from above). The dots represent the single replicate values. The solid line shows the fitted concentration-response curve while the dashed lines illustrate the 95 %-confidence limits.

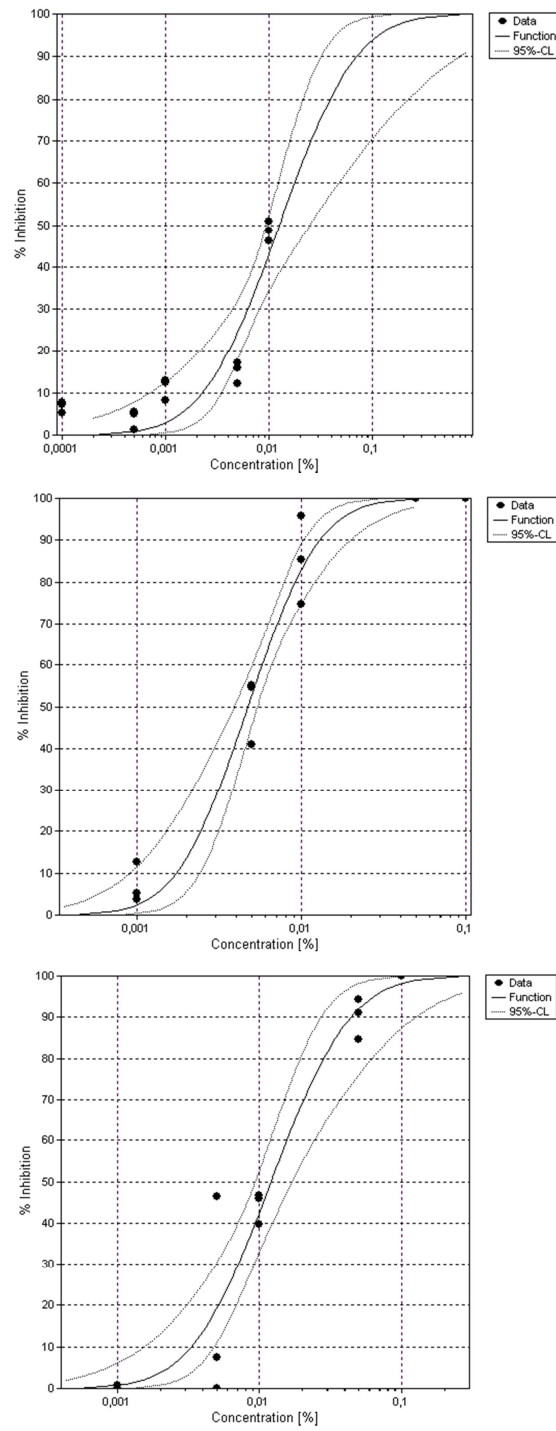


Figure A2: Concentration-response curves in the algae growth inhibition assay for One Seven after 72 hours (Test 1, 2, 3 from above). The dots represent the single replicate values. The solid line shows the fitted concentration-response curve while the dashed lines illustrate the 95 %-confidence limits.

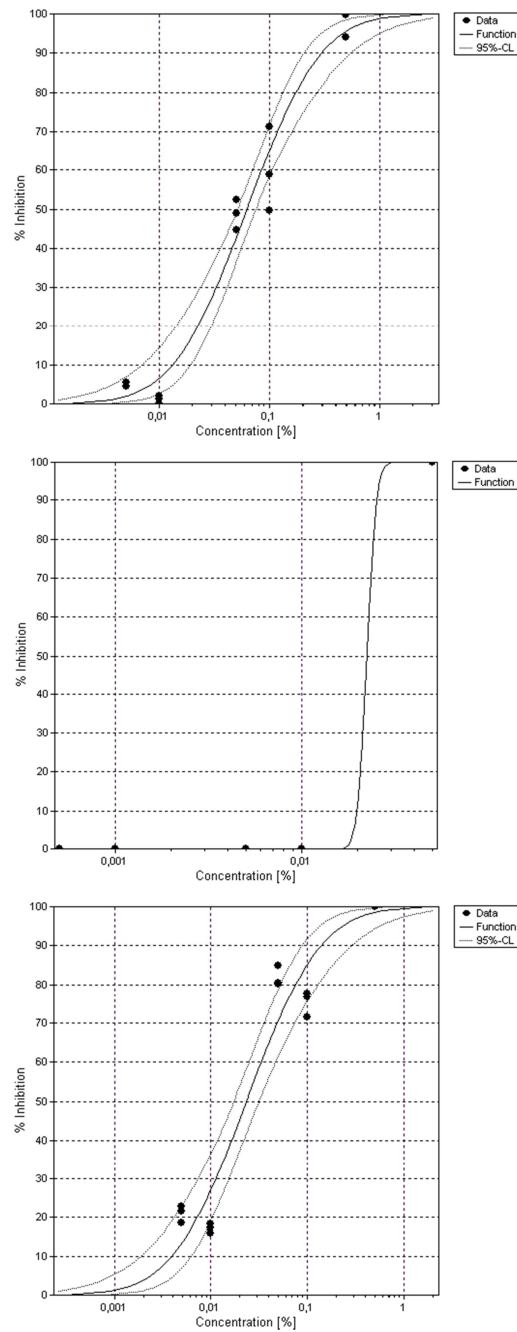


Figure A3 Concentration-response curves in the algae growth inhibition assay for Sthamex after 72 hours (Test 1, 2, 3 from above). The dots represent the single replicate values. The solid line shows the fitted concentration-response curve while the dashed lines illustrate the 95 %-confidence limits.

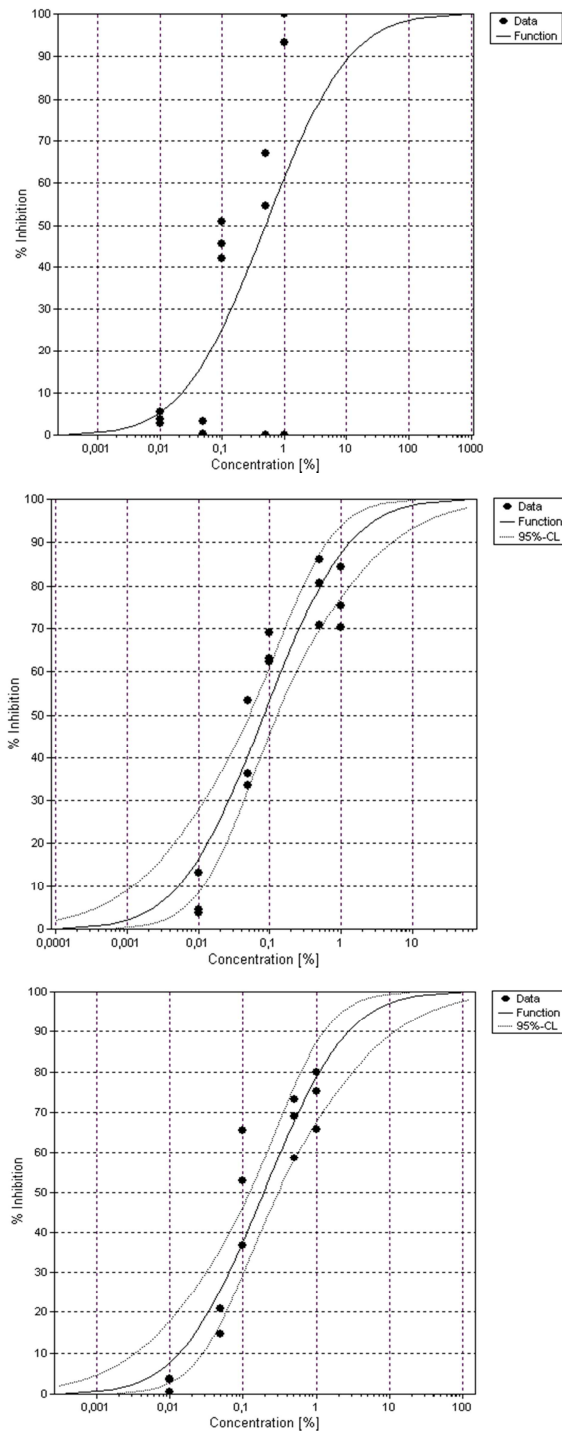


Figure A4 Concentration-response curves in the algae growth inhibition assay for Towalex after 72 hours (Test 1, 2, 3 from above). The dots represent the single replicate values. The solid line shows the fitted concentration-response curve while the dashed lines illustrate the 95 %-confidence limits.

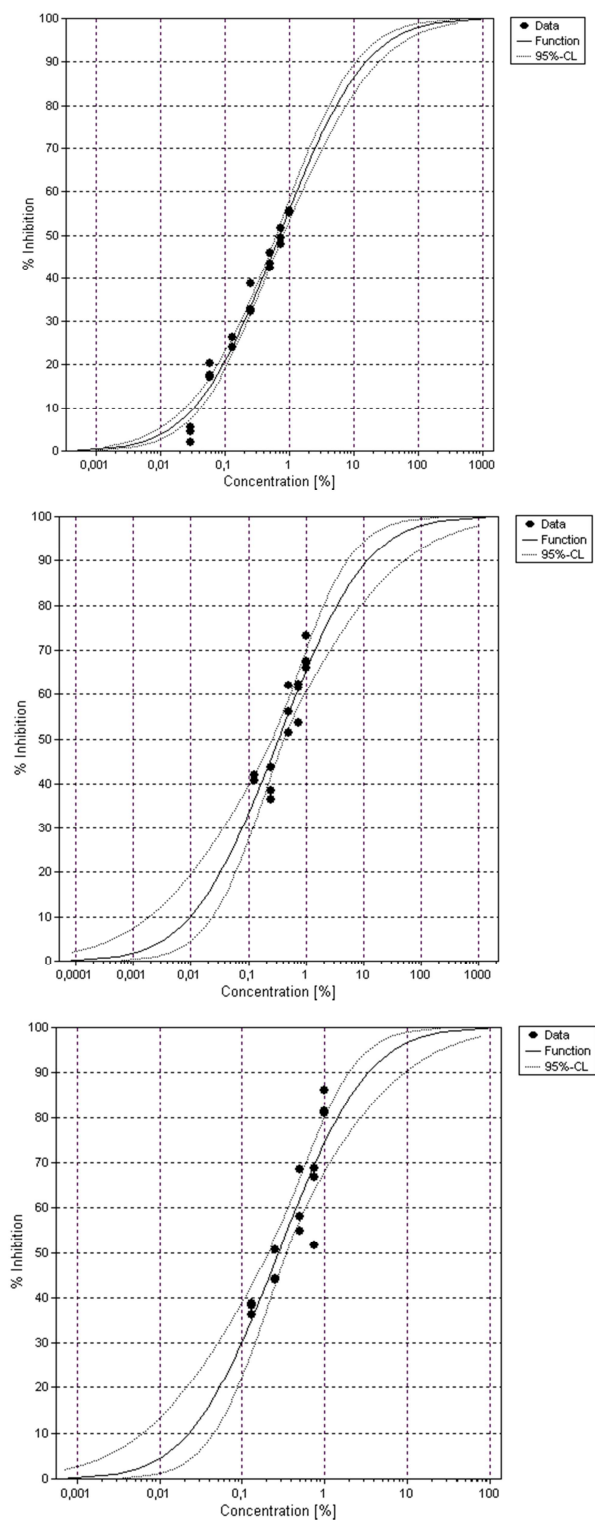


Figure A5 Concentration-response curve in the algae growth inhibition assay for X-Fog after 72 hours (Test 1, 2, 3). The dots represent the single replicate values. The solid line shows the fitted concentration-response curve while the dashed lines illustrate the 95 %-confidence limits.

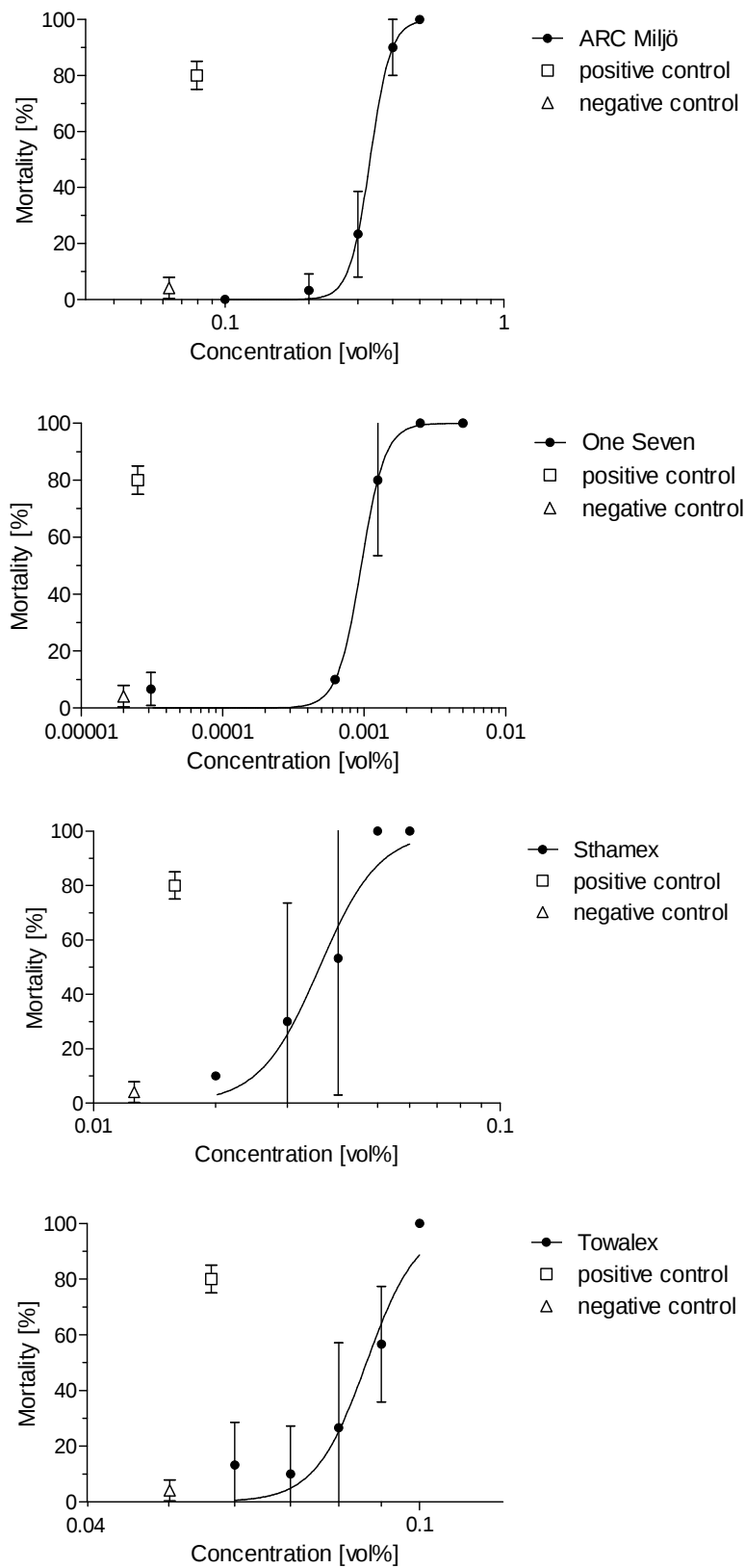


Figure A6 Concentration-response curve for ARC Miljö, One Seven A, Sthamex, and Towalex determined in the in the fish embryo toxicity test (*Danio rerio*) after 96 hours, as well as results of positive (□) and negative (Δ) controls. Each symbol represents the mean of three independent tests while error bars indicate the standard deviation

Table A2. Inhalable dust concentrations in fire gas and sampling data during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are replicates).

	Test 1	Test 2	Test 3	Test 4	Test 5
dust (mg/sample)	0.9	1.1	0.8	<LOD	<LOD
flow (L/min)	2.5*	1.5*	0.5	0.5	0.5
time (min)	4.4	4.0	5.0	5.0	5.0
volume (L)	11.0*	6.0*	2.5	2.5	2.5
volume (m ³)	0.011	0.0060	0.0025	0.0025	0.0025
dust (µg/m ³)	82*	185*	320	<LOD	<LOD

* Dust concentration underestimated due to flow difficulties during sampling

Table A3. Metal concentrations (µg/m³) in inhalable dust (table X) during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are replicates)

ug/m ³	Test 1	Test 2	Test 3	Test 4	Test 5
Be	<LOD	20	<LOD	<LOD	<LOD
Mg	529	975	1680	<LOD	<LOD
Al	<LOD	<LOD	<LOD	<LOD	<LOD
Ca	<LOD	<LOD	<LOD	<LOD	<LOD
V	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	<LOD	<LOD	<LOD	<LOD	<LOD
Fe	<LOD	<LOD	<LOD	<LOD	<LOD
Mn	11	24	40	<LOD	<LOD
Co	<LOD	<LOD	<LOD	<LOD	<LOD
Ni	<LOD	<LOD	<LOD	<LOD	<LOD
Cu	<LOD	<LOD	<LOD	<LOD	<LOD
Zn	<LOD	<LOD	<LOD	<LOD	<LOD
As	<LOD	<LOD	<LOD	<LOD	<LOD
Mo	<LOD	<LOD	<LOD	<LOD	<LOD
Cd	<LOD	<LOD	<LOD	<LOD	<LOD
Sb	374	303	800	<LOD	<LOD
Ba	<LOD	<LOD	<LOD	<LOD	<LOD
Tl	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	<LOD	<LOD	<LOD

Table A4. Aldehydes ($\mu\text{g/L}$) in fire gas during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates and A and B are duplicate measurement for each test).

<i>ug/Liter</i>	Test 1A	Test 1B	Test 2A	Test 2B	Test 3A	Test 3B	Test 4A	Test 4B	Test 5A	Test 5B
Formaldehyde	5.7	2.2	5.9	2.9	0.9	1.2	1.4	0.8	1.5	0.3
Acetaldehyde	34	55	16	108	113	55.3	206	61.6	79.0	36.0
Acetone	5.5	23.6	7.9	12.4	17.3	25.8	29.5	25.6	10.1	17.3
Acrolein	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propanal	3.3	12.6	4.6	12.3	13.3	10.1	24.4	10.3	8.3	6.6
Crotonaldehyde	2.8	0.4	1.0	0.8	1.3	1.0	4.6	1.5	0.5	0.3
Butanal	0.5	2.1	0.7	1.8	0.9	1.6	3.3	0.6	0.4	2.4
Bensaldehyde	0.8	1.7	1.2	1.6	<LOD	2.6	2.3	3.1	0.6	1.0
Pentanal	1.0	0.5	1.4	1.5	2.5	0.6	2.3	0.5	0.6	0.3
Hexanal	0.6	0.8	1.6	3.2	8.5	1.5	9.7	1.0	2.9	0.5
Heptanal	0.6	1.5	0.1	0.7	1.3	1.7	1.1	1.6	0.2	1.5
Octanal	0.3	0.3	0.1	0.5	1.1	0.1	0.8	0.5	0.1	0.3
Nonanal	<LOD	<LOD	<LOD	<LOD	<LOD	0.5	<LOD	<LOD	<LOD	<LOD
Decanal	<LOD	<LOD	<LOD	<LOD	0.3	<LOD	<LOD	<LOD	<LOD	<LOD
Total ($\mu\text{g/L}$)	54.6	100	40.9	145	161	102	286	107	104	66.5

Table A5. Ammonia (NH_3 , mg/m^3) in fire gas during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are replicates).

mg/m^3	Test 1	Test 2	Test 3	Test 4	Test 5
NH_3	<LOD	7.6	<LOD	39	38

Table A6. Individual and sum of volatile organic compounds (VOCs, $\mu\text{g/m}^3$) in fire gas during extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are replicates).

	Test 1 ($\mu\text{g/m}^3$)	Test 2 ($\mu\text{g/m}^3$)	Test 3 ($\mu\text{g/m}^3$)	Test 4 ($\mu\text{g/m}^3$)	Test 5 ($\mu\text{g/m}^3$)
VOC	22 472	22 700	21 752	15 078	16 356
VOC -including semivolatile VOCs	37 086	44 454	58 646	23 584	23 202
2,3-butanedion				302	304
Alken C6/2-Methyl-1-pentene				268	240
Methylethylketone (MEK)					148
Metaacrylonitrile					156
Methylfuran				240	238
Benzene (*overloaded)	3286*	3252*	2860*	4266*	3860*
Methylacrylate	2890*	976	270	458	742
2,2,4-Trimethyl-1,3-dioxolane	320	368	266	254	228
Pyridine					250
Toluene	888	742	920	892	994
Silicone substance / hexamethylcyclotrisiloxane		296	284	266	338
1-(1-Methyletoxi)-2-propanon	562	578	446	398	352
Furfural	440	342	326	334	456
Alken C9	558	422	508	496	532

Styrene	676	382	1458	732	1686
Phenol (+ traces of bensaldehyde)		420	288		272
Bensoic acid	1254	1204	566	276	194

Table A7. Inorganic and organic acids in fire gas (mg/m³) during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

mg/m ³	Test 1	Test 2	Test 3	Test 4	Test 5
HF	<LOD	<LOD	<LOD	<LOD	<LOD
HCl	8.6	6.3	8.2	8.2	<LOD
H ₂ SO ₄	6.8	4.7	6.1	6.1	6.1
HBr	5.1	4.7	<LOD	<LOD	<LOD
HNO ₃	<LOD	4.7	<LOD	<LOD	<LOD
H ₃ PO ₄	<LOD	<LOD	<LOD	<LOD	<LOD
Acetic acid	<LOD	<LOD	<LOD	<LOD	<LOD
Formic acid	<LOD	<LOD	<LOD	<LOD	<LOD

Table A8. Chlorinated dioxins and furans (PCDD/Fs) in fire gas (pg/m³) sampled during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

pg/m ³	Test 1	Test 2	Test 3	Test 4	Test 5
2378-TCDF	< 100	< 100	< 100	< 100	< 100
12378-PeCDF	< 410	< 410	< 410	< 410	< 410
23478-PeCDF	< 330	< 330	< 330	< 330	< 330
123478-HxCDF	< 180	< 180	< 180	< 180	< 180
123678-HxCDF	< 196	< 196	< 196	< 196	< 196
234678-HxCDF	< 240	< 240	< 240	< 240	< 240
123789-HxCDF	< 420	< 420	< 420	< 420	< 420
1234678-HpCDF	< 1200	< 1200	< 1200	< 1200	< 1200
1234789-HpCDF	< 1600	< 1600	< 1600	< 1600	< 1600
OCDF	< 2000	< 2000	< 2000	< 2000	< 2000
2378-TCDD	< 100	< 100	< 100	< 100	< 100
12378-PeCDD	< 420	< 420	< 420	< 420	< 420
123478-HxCDD	< 300	< 300	< 300	< 300	< 300
123678-HxCDD	< 250	< 250	< 250	< 250	< 250
123789-HxCDD	< 390	< 390	< 390	< 390	< 390
1234678-HpCDD	< 1500	< 1500	< 1500	< 1500	< 1500
OCDD	< 5700	< 5700	< 5700	< 5700	< 5700

Table A9. Chlorinated dioxins and furans (PCDD/Fs) in soot (pg/m²) collected from the stainless steel plate mounted inside the container during the fire and fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

Amount pg/m ²	Test 1	Test 2	Test 3	Test 4	Test 5
2378-TCDF	< 1	< 1	< 1	< 1	< 1
12378-PeCDF	< 4	< 4	< 4	< 4	< 4
23478-PeCDF	< 3	< 3	< 3	< 3	< 3
123478-HxCDF	< 2	< 2	< 2	< 2	< 2
123678-HxCDF	< 2	< 2	< 2	< 2	< 2
234678-HxCDF	< 2	< 2	< 2	< 2	< 2
123789-HxCDF	< 4	< 4	< 4	< 4	< 4
1234678-HpCDF	< 12	< 12	< 12	< 12	< 12
1234789-HpCDF	< 15	< 15	< 15	< 15	< 15
OCDF	< 20	< 20	< 20	< 20	< 20
2378-TCDD	< 1	< 1	< 1	< 1	< 1
12378-PeCDD	< 4	< 4	< 4	< 4	< 4
123478-HxCDD	< 3	< 3	< 3	< 3	< 3
123678-HxCDD	< 2	< 2	< 2	< 2	< 2
123789-HxCDD	< 4	< 4	< 4	< 4	< 4
1234678-HpCDD	< 15	< 15	< 15	< 15	< 15
OCDD	< 55	69	< 55	< 55	< 55

Table A10. Chlorinated dioxins and furans (PCDD/Fs) in soot (pg/m²) collected from the stainless steel plate mounted in the container opening during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

pg/m ²	Test 1	Test 2	Test 3	Test 4	Test 5
2378-TCDF	< 1	19	20	< 1	7
12378-PeCDF	< 4	< 4	< 4	< 4	< 4
23478-PeCDF	< 3	< 3	< 3	< 3	< 3
123478-HxCDF	< 2	< 2	< 2	< 2	< 2
123678-HxCDF	< 2	< 2	< 2	< 2	< 2
234678-HxCDF	4*	< 2	< 2	< 2	< 2
123789-HxCDF	< 4	< 4	< 4	< 4	< 4
1234678-HpCDF	< 12	< 12	13	< 12	< 12
1234789-HpCDF	< 15	< 15	< 15	< 15	< 15
OCDF	< 20	< 20	< 20	39	< 20
2378-TCDD	< 1	< 1	< 1	< 1	< 1
12378-PeCDD	< 4	< 4	< 4	< 4	< 4
123478-HxCDD	< 3	< 3	< 3	< 3	< 3
123678-HxCDD	8*	< 2	< 2	19	< 2
123789-HxCDD	6*	< 4	< 4	13	6
1234678-HpCDD	80*	31	120*	190	100
OCDD	250	110	380	600	240

Table A11. Brominated dioxins and furans (PBDD/Fs) in fire gas (pg/m³) sampled during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

pg/m ³	Test 1	Test 2	Test 3	Test 4	Test 5	Test 1
2,3,7,8-TeBDF	< 220	460*	220	< 190	< 190	< 190
1,2,3,7,8-PeBDF	< 550	600	1590	< 490	< 490	< 490
2,3,4,7,8-PeBDF	< 360	< 160	1660	580	< 320	< 320
1,2,3,4,7,8-HxBDF	< 710	1340	< 710	< 640	< 640	< 640
1,2,3,4,6,7,8-HpBDF	9210	7420	86000*	20000	17000*	12000
OBDF	NA	NA	NA	NA	NA	NA
2,3,7,8-TeBDD	< 38	< 17	7100	< 34	< 34	< 34
1,2,3,7,8-PeBDD	< 93	< 42	860	240	< 83	< 83
1,2,3,4,7,8-HxBDD / 1,2,3,6,7,8-HxBDD	790	< 360	< 810	< 730	< 730	< 730
1,2,3,7,8,9-HxBDD	680	< 300	< 680	< 600	< 600	< 600
1,2,3,4,6,7,8-HpBDD	5120	3730	< 5120	< 4600	< 4600	< 4600
OBDD	NA	NA	NA	NA	NA	NA

Table A12. Brominated dioxins and furans (PBDD/Fs) in soot (pg/m²) collected from the stainless steel plate mounted inside the container during the fire and fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

pg/m ³	Test 1	Test 2	Test 3	Test 4	Test 5
2,3,7,8-TeBDF	4	6	6	5	2
1,2,3,7,8-PeBDF	< 15	< 15	< 20	21	< 15
2,3,4,7,8-PeBDF	< 17	< 17	< 20	< 17	< 16
1,2,3,4,7,8-HxBDF	< 8	21	20	23	18
1,2,3,4,6,7,8-HpBDF	73	193	124	151	116
OBDF	NA	NA	NA	NA	NA
2,3,7,8-TeBDD	< 3	< 5	< 2	< 3	< 3
1,2,3,7,8-PeBDD	< 3	< 3	< 4	< 3	< 3
1,2,3,4,7,8-HxBDD / 1,2,3,6,7,8-HxBDD	< 8	< 7	< 13	12	< 8
1,2,3,7,8,9-HxBDD	< 8	< 8	< 13	12	< 8
1,2,3,4,6,7,8-HpBDD	< 57	< 56	61	89	< 55
OBDD	NA	NA	NA	NA	NA

Table A13. Brominated dioxins and furans (PCDD/Fs) in soot (pg/m²) collected from the stainless steel plate mounted in the container opening during fire extinguishing using 4 different firefighting agents/techniques (test 4 and 5 are test replicates)

pg/m ³	Test 1	Test 2	Test 3	Test 4	Test 5
2,3,7,8-TeBDF	220*	120**	400	510	100
1,2,3,7,8-PeBDF	850*	60*	650	490	92
2,3,4,7,8-PeBDF	230	220	340	320	140
1,2,3,4,7,8-HxBDF	720	300	790	680	150
1,2,3,4,6,7,8-HpBDF	2000	590	1100	810	460

OBDF	NA	NA	NA	NA	NA
2,3,7,8-TeBDD	< 7	11**	< 11	< 7	9
1,2,3,7,8-PeBDD	< 3	< 1	< 6	10	< 3
1,2,3,4,7,8-HxBDD / 1,2,3,6,7,8-HxBDD	< 16	18	< 23	< 16	< 16
1,2,3,7,8,9-HxBDD	< 16	< 9	< 23	< 16	< 16
1,2,3,4,6,7,8-HpBDD	72	140	< 81	68	130
OBDD	NA	NA	NA	NA	NA