MEMORANDUM FOR SEE DISTRIBUTION

SUBJECT: Aqueous Film Forming (AFFF) Workshop

We would like you to attend a one day workshop to discuss the impact of the U.S. Environmental Protection Agency' s (U.S.EPA) proposed rule which has the potential to ban future production and import of perfluorooctyl sulfonates (PFOS) chemicals to the Department of Defense. The Mil Spec for AFFF allows the use of PFOS, perfluorooctanoic acid (PFOA), and telomers as foaming agents. The U.S.EPA released data this past year that indicates PFOS chemicals are persistent, bioaccumulating and toxic. PFOS has been found in the blood of the general US population, in wildlife, and in people overseas. The 3M Company, the sole United States producer of ninety PFOS chemicals, has chosen to discontinue their manufacture and sale of all uses globally by December 31, 2002, and substantially reduce their manufacture for the most widespread uses of these chemicals by December 31, 2000.

The U.S. EPA is evaluating PFOA and telomer chemicals as a substitute for PFOS. PFOA and telomer are also persistence in the environment and more toxic than PFOS. Because of this, they also may be subject to manufacturers' withdrawal from the market place (similar to 3M's action for PFOS) or future EPA rule making. AFFF is used in a number of critical life saving situations in DoD. Currently, there are no known substitutes that are as effective as the materials in the Mil Spec. We've asked the Air Force Research Laboratory, Materials and Manufacturing Directorate to present recommendations and discuss potential substitutes. We plan to discuss "high-risk" uses of PFOS and what should be done to reduce or eliminate environmental releases of PFOS. We will also determine if DoD should switched to PFOA or telomer instead of PFOS. We need a multi-disciplinary team to conduct this review and develop an AFFF replacement strategy.

The workshop will be held on March 16, 2001, from 0800hrs - 1630hrs, in the OSD Conference Center, 1E801, Room 4, Pentagon. We also requested the Defense Logistic Agency to brief DoD's uses of PFOS. Attached is the meeting agenda. My POC for this Workshop is Lt Col Isaac Atkins, Director Occupational Health Policy, ODUSD (ES)/FP. He can be reached at (703) 604-1628, if you have any questions.

Curtis Bowling
Assistant Deputy Under Secretary of Defense
Force Protection

Attachment:
As stated

Aqueous Film Forming (AFFF) Workshop

Agenda

Introduction (Overview)	Mr. Curtis Bowling
AFFF Environmental Issues	Dr. Doug Dierdorf, AFRL
Toxicity of PFOS, PFOA, Telomer	TBD, USEPA
Impact of AFFF Voluntary Production Ban on Army	TBD, DASA(ESOH)
Impact of AFFF Voluntary Production Ban on Navy	TBD, (E&S)
Impact of AFFF Voluntary Production Ban On AF	TBD, DASAF(ESOH)
Overview of AFFF Uses and Impact to Fire-fighting Operations	TBD, National Fire Protection Association
Impact AFFF Voluntary Production Ban On FAA	TBD, Federal Aviation Administration
PFOS Uses	TBD, Defense Logistics Agency
The Way Ahead	Workshop Members

Distribution

DASAF(ESOH)
DASN(E&S)
DASA(ESOH)
Defense Logistics Agency
AFRL/MMD
USEPA
Federal Aviation Administration
National Fire Protection Association

From: Toncray Bradley A NNVA
To: Bennett David C NNVA; Chapman Keith D NNVA; Hancock Donald L NNVA; Lowe Donald J NNVA; Geithmann Gary R CONT NNVA; Carty Jeffrey L NNVA; Earehart James NNVA; Korzun Joel A NNVA; Kelly Art G NNVA; Yarashus Thomas R NNVA; Wood Leesa M NNVA
Sent: 3/9/2001 2:20:08 PM
Subject: FW: Ban on AFFF
Attachments: Jeff_F-1.TIF

-----Original Message-----
From: Parish Benjamin A NNVA
Sent: Friday, March 09, 2001 8:53 AM
To: Toncray Bradley A NNVA; Michael A Turner (CNAP N4342P) (E-mail)
Subject: FW: Ban on AFFF

Just thought you would like to know.
Ben

-----Original Message-----
From: Lewis Edward A NSSC [mailto:LewisEA@NAVSEA.NAVY.MIL]
Sent: Friday, March 09, 2001 8:41 AM
To: Corley Wesley S NSSC
Cc: Plunkett R Bryan CONT NSSC; Ngo Tien M NSSC; Parish Benjamin A NNVA; Speca Aaron M NNVA; Wujick Christine A NSSC; Montgomery Mike L CONT NSSC; 'Mike Turner'
Subject: FW: Ban on AFFF

Wes,

FYI. We will continue to monitor this situation and it's potential impact to the CVN 70 RCOH.

V/R,

Ed Lewis
PEO Aircraft Carriers
RCOH Ship Design Manager
(703) 607-1818 x 331 (Voice)
(703) 607-2495 (Fax)
(703) 505-6728 (Cell)
Lewisea@navsea.navy.mil

-----Original Message-----
From: Fink Jeff E NSSC
Sent: Friday, March 09, 2001 8:05 AM
To: Raber James D NSSC; Snyder CF (Charles) NSSC; Bergner Richard L NSSC; Wujick Christine A NSSC; McAllister Keith R NSSC; Lewis Edward A NSSC; Gimbel Weldon K NSSC; Orski Gary A NSSC; Ngo Tien M NSSC; Waldman Jack S NSSC; Plunkett R Bryan CONT NSSC; Bob Morris (E-mail); Jim Counts (E-mail); Sean Kiely (E-mail)
Subject: Ban on AFFF

Just wanted to keep everyone up to date on the AFFF issue. For those of you who do not know EPA has proposed a rule which has the potential to ban future production and import of chemicals that are integral to the production of AFFF.

Background AFFF was developed by the Navy Labs in the 1960s to provide better fire protection than the older protein foam. AFFF is used in machinery rooms, flight decks and hangar bays on most Navy ships. Mil-Std AFFF is used at most airports throughout the world and is considered by the insurance industry as the premier fire fighting agent.
Some of the chemical components of AFFF are categorized as Perfluorocytl Sulfonates (PFOS) which can potentially degrade into PFOSA (acid). PFOSA is highly persistent in the environment and has a strong tendency to bioaccumulate. (which means, like lead, the body absorbs this chemical, but does not get rid of it. Over time the body can accumulate this chemical to toxic levels) Studies indicate that exposure to PFOSA is widespread and recent tests have raised concerns about long term effects in people and wildlife.
There are four manufacturers on the QPL for AFFF. 3M won the current contract to supply AFFF to DOD. This contract expires in Dec '02. 3M, worried about the potential future problems, has decided to get out of the market as soon as the contract is over. They have already stopped their production of things like ScotchGuard that have the same PFOS.
James Rudroff of N452C wrote a point paper on this issue. (see attachment)

I have been told be NAVSEA 05L4 that there is a question as to whether the other manufacturers will stay in the market knowing that 3M got out and why they got out. There is an AFFF Workshop being held on March 16th at the Pentagon sponsored by the Assistant Deputy Under Secretary of Defense Force Protection in which NAVSEA 05L4, EPA, DLA will be in attendance. If production of AFFF is discontinued there will certainly be a major impact to Carriers as well as the rest of the Navy. The scope of effort to replace AFFF will be larger than the Freon elimination program. The effort could be on the magnitude of Asbestos elimination. However it is to early to panic and to discuss corrective action. We need to let the tech community and industry experts have a chance to assess the total picture and develop a POA. The Aux and Crew Team here at PEO Carrier will be closely monitoring the situation.

Jeff_F-1.TIF
Jeff Fink
PEO - E
DSEM Aux & Crew
(703) 607-1701 x343

From: Bowling, Curtis, Mr, OSD-ATL
To: <Atkins>;<Isaac>;<LtCol>;<OSD-ATL>
Sent: 3/31/2001 6:24:00 PM
Subject: FW: Fluorotelomer Chemicals and Related Fluoroorganics

We need to talk about the occupational exposure of telomers.

```
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>From: Dierdorf Doug S Contr AFRL/MLQD
>[mailto:Doug.Dierdorf@tyndall.af.mil]
>Sent: Friday, March 30, 2001 2:08 PM
>To: Curtis Bowling (E-mail)
>Cc: Carr Virgil J Contr AFRL/MLQD; Vickers Dick N Civ
>AFRL/MLQD; Galindo
>Bob Contr AFRL/MLQD
>Subject: FW: Fluorotelomer Chemicals and Related Fluoroorganics
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>[mailto:Stephen.H.Korzeniowski@USA.dupont.com]
>Sent: Friday, March 30, 2001 12:11 PM
>To: doug.dierdorf@tyndall.af.mil
>Subject: Fluorotelomer Chemicals and Related Fluoroorganics
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>Doug, I obtained your name from Mary Dominiak of the US EPA.
>We met and
>spoke again on Tuesday at the public hearing held by the US
>EPA on Tuesday
>this week in Arlington, VA.
>I have a dual role in DuPont. One is as a business manager for a
>fluorosurfactants and additives business. And the other is an external
>company role in working with the global regulatory agencies and Telomer
>consortium (see below).
>
>You were copied on an E-mail note to Mary written by Lt. Col.
>Isaac Atkins,
>Jr on February 13, 2001referencing a AFFF Workshop held on 16
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>In addition, most of the global telomer manufacturers have
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>further study our products. I can also describe this in
>detail for you.
>
>Please let me know how you would like to proceed.
>I can be reached by E-mail by just responding to this note or using
>stephen.h.korzeniowski@usa.dupont.com. This is usually the
>easiest way to
>reach me due to my travel schedule. I can also be reached by phone on
>302-992-3672 and fax - 302-892-1135.
>
>I look forward to discussing these matters with you.
>
>Thank you in advance for your consideration.
>
>Steve
>
```

From: Phull, Kotu K COL ASA-I&E
To: <Atkins>;<Isaac>;<LtCol>;<OSD/ATL>
Sent: 3/28/2001 10:48:00 AM
Subject: FW: AFFF

Ike: Per conversation this morning.

Please call me if you have any questions.

Regards,

KOTU K (KK) PHULL
COL, MS
Office of the Deputy Assistant Secretary of the Army
for Environment, Safety, and Occupational Health
110 Army Pentagon, Room 2E577
Washington, DC 20310-0110
(703) 697-0440, DSN 227
FAX - (703) 693-8149

-----Original Message-----
From: Bowling, Curtis, Mr, OSD-ATL [mailto:Curtis.Bowling@osd.mil]
Sent: Wednesday, March 28, 2001 6:28 AM
To: Phull, Kotu K COL ASA-I&E
Subject: RE: AFFF

Thanks

>-----Original Message-----
>From: Phull, Kotu K COL ASA-I&E
>Sent: Tuesday, March 27, 2001 4:17 PM
>To: Bowling, Curtis, Mr, OSD/ATL
>Cc: Fatz, Raymond J Mr ASA-I&E
>Subject: AFFF
>
>
>Curtis:
>
>As requested at the 16 March AFFF Workshop, we feel that the
>DOD/users would
>need to answer the following questions to minimize the impact
>of a future
>AFFF ban by the EPA. I have also included a list of the potential Army
>organizations that should be considered for membership on the DOD AFFF
>Steering Group. Our response is based on limited
>coordination, due to the
>short time available. We will ensure a wider Army-wide
>coordination upon
>receiving further instructions/tasking from your Office.
>Please call me, if
>you have any questions. AFFF = All PFOS's, PFOAs, and telomers.
>
>A. QUESTIONS:
>
>
>1. Quantity of these substances used in the Army
>
>2. Quantity of AFFF that the Army can afford to store as the
>Reserves for
>continued, critical uses past the phase out
>
>3. Operations where these substances are used. Although the
>discussion at

>the Workshop focused primarily on the use of AFFF in
>firefighting, we would
>need to determine other operations/products related to the use of AFFF,
>e.g., aviation hydraulic fluids, semiconductors, etc.
>
> - Need to identify all MILSPECs/STDs, NSNs, and/or commercial
>/industry specs that define these materials.
>
>4. Critical uses. We would need to define "critical uses" to ensure
>consistency in responses received from the field.
>
>5. Areas where uses can be eliminated, e.g., training
>
>6. Quantity of AFFF that the Army can afford to store
>(COST)/must store
>(CRITICAL USES) as reserves for continued use past the phase-out
>
>7. Impact of the use of non-Aqueous Film Forming Foams -
>Operational, e.g.,
>process modifications for fire-fighting; Cost
>
>8. Environmental Impact of potential releases of AFFF into
>the environment
>
>9. Current and projected research, in-house and in partnership with
>Industry - ASA(ALT)
>Development of AFFF substitutes with AFFF-like performance;
>Technology enhancements to improve the performance of non-AFFF products
>
>10. Procurement strategies, i.e., availability and production
>capabilities
>for alternatives; how to budget and POM for increased
>reserves, if the DOD
>decides to continue the use of AFFF past the EPA ban, for
>increased costs
>associated with use of AFFF substitutes, e.g., system
>retrofitting, need for
>additional equipment, etc.; cost of disposal of excess stored
>materials that
>may have to be disposed of as "hazardous material"
>
>11. Need for occupational assessments and medical monitoring
>based on the
>review of available data
>- Exposure monitoring
>- Medical monitoring
>- Population to be monitored
>- Cost
>
>12. Environmental, Safety, and health considerations for AFFF
>substitutes
>
>B. DOD STEERING GROUP MEMBERSHIP. Some of the following
>offices/organizations should be considered for membership:
>ACSIM (Assistant
>Chief of Staff for Installation Management, ODCSLOG (Deputy
>Chief of Staff
>for Logistics, APPSO (Army Acquisition Pollution Prevention
>Support Office
>(to represent AMC (Army Materiel Command and ASA/ALT
>(Assistant Secretary of
>the Army for Acquisition, Logistics, and Technology), OTSG
>(Office of the
>Surgeon General), and this Office. ODCSLOG would appear to be
>ideal Army
>Lead.
>
>Regards,

>
>KOTU K (KK) PHULL
>COL, MS
>Office of the Deputy Assistant Secretary of the Army
> for Environment, Safety, and Occupational Health
>110 Army Pentagon, Room 2E577
>Washington, DC 20310-0110
>(703) 697-0440, DSN 227
>FAX - (703) 693-8149
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>

MEMORANDUM FOR SEE DISTRIBUTION

SUBJECT: Request Information on Usage of Perfluorooctly Sulfonates Containing Materials

We would like you to provide information on the impact of the U.S. Environmental Protection Agency's (U.S.EPA) proposed rule that calls for the phase-out of 90 perfluorooctly sulfonate (PFOS) chemicals (See attachment). The Mil Spec for Aqueous Film Forming (AFFF) allows the use of PFOS, perfluorooctanoic acid (PFOA), and telomers to produce fluorochemical surfactants which are key to helping other AFFF's agents meet low fire-fighting surface tension requirements. AFFF is used in a number of critical life saving situations in DoD and currently, there are no known substitutes that are as effective as the materials in the Mil Spec. The U.S. EPA released data this past year that indicates PFOS chemicals are persistent, bioaccumulating and toxic. PFOS has been found in the blood of the general US population, in wildlife, and in people overseas.

The U.S.EPA will prevent manufacture or import of PFOS after the phase-out period, including PFOS-based AFFF, unless a 90-day notice is filed and approved. They are also evaluating PFOA and telomer chemicals. PFOA and telomer are also persistence in the environment and may pose significant health risks. Because of this, PFOA and telomer may also be subject to manufacturers' withdrawal from the market place (similar to 3M's action for PFOS) or future EPA rule making.

Request you perform an assessment of the impact of EPA's phase-out of PFOS to your organization and provide a copy to my office **by 08 Jul 01**. This assessment should include the quantity (in lbs.) and type of materials that contain PFOS. Include the amount of AFFF or PFOS-containing material in stock, number of systems and the amount (in lbs.) used per year. Also list the operations where AFFF or PFOS-containing materials are used and identify all mission critical uses, amounts, usage rate, stockpile, and potential substitutes, if any. Mission critical uses are uses where there are no available substitutes and phase-out of PFOS will negatively impact operational effectiveness and operational suitability of combat missions or contribute significantly to the degradation of combat capability.

In addition, please explain the mission impacts if a fire suppression system is not replaced, cost of replacement options and estimate quantities needed for stockpiling for mission critical uses. Identify any operations that release PFOS-containing materials to the environment and take appropriate steps to prevent or stop these releases. We will use this information to develop a DoD AFFF and PFOS-containing material replacement strategy. My POC is Mr. Gary Hamilton.

He can be reached at (703) 604-1820, email: gary.hamilton@osd.mil. If you have any questions, please contact him

Curtis M. Bowling
Assistant Deputy Under Secretary of Defense
(Force Protection)

Attachment:
As stated

DISTRIBUTION

DASA (ESOH)
DASN (E&S)
DASAF (ESOH)
DEFENSE LOGISTICS AGENCY
DEFENSE AGENCIES' DESIGNATED AGENCY
SAFETY AND HEALTH OFFICIAL

From: Bowling, Curtis, Mr, OSD-ATL
To: <Atkins>;<Isaac>;<LtCol>;<OSD-ATL>
Sent: 3/31/2001 6:24:00 PM
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>Thank you in advance for your consideration.
>
>Steve
>

Mr. Stephen H. Korzeniowski
Business Manager
Fluorosurfactants and Additives
E. I. Dupont de Nemours & Co., Inc

Dear Mr. Korzeniowski:

Thank you for your letter to Dr. Dierdorf expressing your interest in our Aqueous Film Forming (AFFF) Workshop of March 16, 2001. The purpose of the workshop was to provide a forum for discussion of the Environmental Protection Agency's (EPA) proposed rule that calls for the voluntary phase-out of perfluorooctly sulfonate (PFOS) chemicals to the Department of Defense by 2003. DoD is concerned about the availability of PFOS for use in AFFF and the pending phase-out rule's impact on military fire-fighting capabilities. Dr. Dierdorf asked me to respond to you because I am the author of the letter mentioned in your correspondence.

The application of AFFF in firefighting is inherently dispersive and results in the distribution of AFFF's chemical components on the surface and in the groundwater. Concern about this distribution prompted Military Service Departments to investigate the biodegradation, possible remediation, toxicity, fate and transport of many of AFFF's components. These studies date back to 1983 or earlier and are on going. Based on these studies and published literature, the "Lowest Observed Adverse Effect Level" (LOAEL) for perfluorinated carboxylic acids is 0.1 mg/kg/day for mice.[1] The LOAEL for perfluorooctanyl sulfonates is 0.4 mg/kg/day.[2] My assertion that PFOA is more toxic than PFOS is based on these data. The association of this result with telomer is based on the below unpublished Air Force tests.

Several weeks after a large-scale fire-fighting operation using AFFF in Jacksonville Bay, Florida, allegations of surfactant related bird kill caused the Air Force to screen AFFF's components to determine if they were non-persistent. The perfluorinated carboxylic and sulfonic acid surfactants were known to be persistent, leaving telomer surfactants as the only potentially non-persistent, commercially available, fluorosurfactant candidates. During 1998, the Air Force Research Laboratory, Fire Technology Group at Tyndall Air Force Base, Florida conducted the screening by monitoring the changes in "Soluble Chemical Oxygen Demand" (COD) and surface tension during biodegradation. Standard procedures for measuring "Biological Oxygen Demand" over a period of 28 days were used. Purely by coincidence, the telomer-tested surfactant samples were identified as "Zonyl" branded surfactants, which were supplied by your company.

Results indicated that the telomer fluorosurfactant did biodegrade as shown by decreased soluble COD, however, the surface tension remained essentially unchanged. Control samples of hydrocarbon

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[1] **Developmental toxicity of perfluorodecanoic acid in C57BL/6N mice.** Harris MW, Birnbaum LS, Fundam Appl Toxicol, 1989, 442-8 (1989).

[2] **3M Submissions in EPA Docket AR-226.**

surfactants showed decreased soluble COD indicating biodegradation and as expected an increase in surface tension to that of water. The research staff involved in this work found the results consistent with the degradation of telomer surfactants to perfluorocarboxylic acids. In the case of Zonyl TBS, the only biodegradable segment is the 1,1,2,2 tetrahydro segment, which can only result in formation of perfluorononanoic acid. They considered this information insignificant at the time with the required documentation being extensive research notes.

I'm sure industry efforts in this area are being revived in light of the EPA's pending regulatory action. Dr. Dierdorf has been collaborating with manufacturers of fluorosurfactants to ensure non-persistent surfactants are developed and commercially available. These chemicals provide the properties essential to effective AFFF fire fighting. If you want a copy of the Air Force's unpublished experimental data, please contact Mr. Dick Vickers at (850) 283-3707, Dick.Vickers@tyndall.af.mil.

Curtis M. Bowling
Assistant Deputy Under Secretary of Defense
(Force Protection

AN ABSTRACT OF THE THESIS OF

Cheryl Moody Bartel for the degree of Doctor of Philosophy in Chemistry
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Surfactants in Groundwater Contaminated by Fire-Fighting Activity

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Jennifer A. Field

Aqueous film forming foams (AFFFs) are used to extinguish hydrocarbon-fuel fires and repetitive use, particularly at military sites, has led to AFFF-laden wastewater and subsequent groundwater contamination. Perfluorinated surfactants are an important class of specialty chemicals that are used in AFFF agents and have physio-chemical properties that differentiate them from hydrocarbon surfactants. In the past, the environmental behavior of perfluorinated surfactants has received little attention, and how the unique properties affect the behavior of perfluorinated surfactants in the environment and their potential impact on co-contaminant transport and biodegradation are unknown. An analytical method was developed to determine perfluorocarboxylates in groundwater. Solid-phase extraction and in-vial derivatization techniques were used to form the methyl esters of perfluorocarboxylates that were then analyzed by gas chromatography/mass spectrometry. Perfluorocarboxylates containing 6 to 8 carbons were detected in groundwater samples collected from Naval Air Station Fallon, NV, Tyndall Air Force Base, FL, and Wurtsmith Air Force Base, MI, with total concentrations

ranging from 3 to 7,090 µg/L. The homologous series of perfluorocarboxylates observed in groundwater from the three military sites as well as in commercial AFFF mixtures consisted of even and odd number perfluorinated carboxylates, which is indicative of the electrochemical fluorination synthesis process. At Wurtsmith Air Force Base, MI, perfluorocarboxylates detected 500 m from the source area were estimated to have a minimum residence time of 5 to 15 years. Additionally, the perfluorocarboxylate concentrations observed in groundwater are significantly lower than the corresponding methylene blue active substances concentrations, which indicates that there are additional anionic surfactant species present in the groundwater. Perfluorinated carboxylates measured at Naval Air Station Fallon, NV, Tyndall Air Force Base, FL, and Wurtsmith Air Force Base, MI, which have not been used since 1988, 1992, and 1986, respectively, provide direct field evidence that this class of perfluorinated surfactants persist under prevailing groundwater conditions and potentially could be used as unique tracers of groundwater impacted by repetitive fire-training exercises.

Occurrence and Distribution of Perfluorinated Surfactants in Groundwater Contaminated by Fire-Fighting Activity

by

Cheryl Moody Bartel

A THESIS

submitted to

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the requirements for the
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Cheryl Moody Bartel, Author

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PREFACE

Chapter 1 provides an introduction to aqueous film forming foams (AFFFs), which are used to extinguish hydrocarbon-fuel fires. Their repetitive use, particularly at military sites, has led to AFFF-laden wastewater and subsequent groundwater contamination. Perfluorinated surfactants are an important class of specialty chemicals that are used in AFFF agents and in the past, the environmental behavior of perfluorinated surfactants has received little attention.

The second chapter of this study describes the isolation, identification and quantification of perfluorinated carboxylates in groundwater impacted by fire-training activities at Naval Air Station Fallon, NV and Tyndall Air Force Base, FL. Strong anion exchange disks were used to extract perfluorocarboxylates from groundwater collected from fire-training sites located at the two military facilities. The developed method is the primary tool that was then used to quantitatively determine perfluorocarboxylates in groundwater samples collected for a more extensive groundwater study described in Chapter 3.

The work presented in Chapter 3 aids in the understanding of the environmental behavior of one class of perfluorinated surfactants, perfluorocarboxylates, since virtually no information exists on their occurrence, transport, and biodegradability in the environment. Commercial AFFF mixtures containing perfluorinated surfactants were applied at Wurtsmith Air Force Base, Oscoda, MI, including the Fire-Training Area 2 and a site where an airplane crashed. Comparison of the perfluorocarboxylate concentrations to other bulk chemical indicators such as specific conductance, total organic carbon, and methylene blue active substances, add context to the environmental occurrence and distribution of perfluorocarboxylate surfactants.

Occurrence and Distribution of Perfluorinated Surfactants in Groundwater Contaminated by Fire-Fighting Activity

Chapter 1

Introduction: Perfluorinated Surfactants and the Environmental Implications of their Use in Fire-Fighting Foams

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Abstract

The recent identification of one class of fluorinated surfactants in groundwater impacted by fire-fighting activity has created an awareness of the potential environmental issues resulting from the use of aqueous film forming foam (AFFF) agents. Aqueous film forming foams are used to extinguish hydrocarbon-fuel fires and their repeated usage particularly at military sites has led to AFFF-contaminated groundwater. Formulations of AFFF agents include fluorinated surfactants, which are an important class of specialty chemicals that have physio-chemical properties that differentiate them from hydrocarbon surfactants. Little is known about the occurrence, transport, biodegradation and toxicity of fluorinated surfactants in the environment. The fact that fluorinated surfactants as well as other AFFF components co-occur with priority pollutants (e.g., jet fuel components and chlorinated solvents) complicates studies on their fate and effect in the environment. Research is needed to sufficiently characterize the structures and environmental properties of fluorinated surfactants. Additionally, the environmental behavior of the AFFF mixtures and complex AFFF-wastewaters needs to be investigated.

Introduction

Fluorinated surfactants constitute an important class of fluorinated compounds that are utilized in fire-fighting applications, herbicide and insecticide formulations, cosmetics, greases and lubricants, paints, polishes, and adhesives *(1-4)*. For example, perfluorooctane sulfonate is an important surfactant itself as well as a precursor to other fluorinated surfactants and pesticides *(5)*. The Organization for Economic Cooperation and Development (OECD) lists perfluorinated C5-C18 compounds, which includes most perfluorinated surfactants, as high-production-volume (HPV) chemicals. High-production volume chemicals are those chemicals manufactured or imported in the U.S. in volumes exceeding 1 million pounds *(6)*.

Fluorinated surfactants are distinctly different from hydrocarbon surfactants. Although the polar head groups may be similar between hydrocarbon and fluorocarbon surfactants, the non-polar perfluorocarbon tail is both *hydrophobic* and *oleophobic* (oil-repelling), which is in contrast to the tail group of hydrocarbon surfactants, which are only considered hydrophobic in nature. For this reason, fluorinated surfactants exhibit both hydrophobic and oleophobic characteristics, which accounts for their unique physio-chemical properties as will later be addressed *(1)*. Fluorinated surfactants may be classified as either perfluorinated, in which all hydrogen atoms are substituted by fluorine atoms, or as partially-fluorinated where some carbons contain hydrogen atoms. Like other surfactant classes, fluorinated surfactants generally are classified into one of four categories: nonionic, anionic, cationic, and amphoteric, with anionic fluorinated surfactants being the most important class *(1)*.

Fluorinated surfactants comprise a unique class of specialty chemicals whose environmental behavior has received little attention. Consequently little information is available to permit a complete life-cycle analysis. The focus of this review is to 1) characterize the unique properties of fluorinated surfactants, 2) describe how the unique properties are utilized for the purpose of fighting fires, and 3) evaluate how the unique properties might affect the behavior of perfluorinated surfactants in the environment and their potential impact on co-contaminant transport and biodegradation. Finally, the need for new analytical methods to measure perfluorinated surfactants is highlighted as a requirement for addressing questions about the occurrence, behavior, and impact of this specialty chemical class in the environment.

Perfluorinated Surfactant Synthesis and Properties

Two principal processes used in the manufacturing of fluorinated surfactants are electrochemical fluorination and telomerization *(1)*. With electrochemical fluorination, the substance to be fluorinated is dissolved in hydrofluoric acid and an electric current is passed through the media *(1, 7)*. All hydrogen molecules are replaced by fluorine and perfluorinated molecules result. Despite low to moderate yields of perfluorinated compounds and many side products, electrochemical fluorination is economically attractive because of the relatively low cost of electricity as well as that of the hydrogen fluoride reagent *(7)*. With the electrochemical fluorination process, perfluorinated compounds with homologous series of even and odd number perfluorocarbons are generated *(1, 8)*. In contrast, the telomerization process reacts a molecule called a telogen, with two or more unsaturated molecules called taxogens, which creates a telomer that contains only an even number of carbon atoms *(1)*. Because odd and even number perfluorocarbons result from electrochemical fluorination, the occurrence of odd *and* even carbon perfluorinated surfactants in the environment can potentially be traced to manufacturers that use the electrochemical fluorination process *(9)*.

When fluorine is a substituent in organic compounds, unique chemical properties are observed due to the electronegativity of fluorine as well as the overlap between the 2s and 2p orbitals of fluorine and the corresponding orbitals of carbon *(1, 7)*. The presence of fluorine atoms contributes to the rigidity of perfluorocarbon chains *(2,3)* relative to hydrocarbon chains. The highly polarized carbon fluorine bond is the strongest of known covalent bonds *(1)* with the average C-F bond approximately 25 kcal/mole stronger than the corresponding C-Cl bond in monochloroalkanes *(7)*. Additionally, fluorination usually strengthens the adjacent C-C bonds *(7)*.

The properties of hydrocarbons and, therefore, surfactants, are altered significantly when fluorine atoms are substituted for hydrogen atoms *(1)*. Perfluorinated surfactants are more thermally-stable than their corresponding hydrocarbon analogues. In particular, perfluorocarboxylic acids and perfluoroalkanesulfonic acids are considered the most thermally-stable fluorinated surfactants *(1)*. In addition to thermal stability, perfluorinated surfactants are stable to acids, bases, oxidants and reductants *(1)*. This stability allows fluorinated surfactants to remain intact in environments where hydrocarbon surfactants are degraded.

Perfluorinated anionic surfactants have high-acid strength relative to their hydrocarbon analogs due to the electron-withdrawing effects of fluorine substitution. For example, the replacement of hydrogen atoms by fluorine atoms on octanoic acid to form perfluorooctanoic acid decreases the pKa from 4.89 to 2.80 (Table 1.1) *(1, 7)*. Perfluorinated surfactants are much more surface active than hydrocarbon surfactants *(1, 10)*. The substitution of fluorine atoms for hydrogen atoms decreases their surface activity for aqueous solutions, which promotes micellization at lower concentrations (i.e., the critical micelle concentration (CMC)) and lowers the surface tension relative to that of other hydrocarbon analogs *(1)*. For example, the surface tension of perfluorooctanoic acid has been reported as 15.2 dynes/cm *(1)*. The CMC values for C7 and C8 fluorinated surfactants (i.e., perfluorocarboxylates and perfluoroalkane sulfonates) are approximately equal to those of C11 and C12 hydrocarbon surfactants *(1)*.

The cost of fluorinated surfactants is higher relative to that of hydrocarbon surfactants. Because of the high prices of fluorinated surfactants, fluorosurfactant applications are limited to problems that conventional, lower-priced surfactants can not address *(4, 11)*. Within a specific application, fluorinated surfactants are typically cost effective because their relatively high price is offset by the low concentrations needed to achieve the reduction in interfacial tension or to form micellar solutions *(1)*. In some applications such as AFFF, a mixture of a fluorinated surfactant and a hydrocarbon-based surfactant are more cost effective and/or perform better than either surfactant separately *(1)*.

Perfluorinated Surfactants in Aqueous Film Forming Foams

Hydrocarbon-fuel fires pose a serious threat to life and property, and require immediate response. To enable a quick response to hydrocarbon-fuel fires, effective and

Table 1.1. Properties of perfluorooctanoic acid.

Property	Perfluorooctanoic acid
pKa[1]	2.80
Critical micelle concentration[2]	8.7-9.0
Interfacial tension[3]	15.2

[1] *(1)*.

[2] Units for critical micelle concentrations are mMoles/L *(1)*.

[3] Units for surface tension are dynes/cm *(10)*.

efficient fire-extinguishing agents are needed to prevent damage and re-ignition of the fires. Aqueous film forming foams (AFFFs) were developed in the 1960s as important tools for extinguishing fires involving flammable liquid fuels (i.e., gasoline, kerosene) *(12)*.

Due to the presence of large quantities of flammable liquids, municipal (i.e., fire departments), hydrocarbon-processing industry (i.e., oil refineries), and military sectors utilize AFFFs (Figure 1.1), with the military comprising 75% of the total market, while the municipal and hydrocarbon-processing industry represents 13% and 5%, respectively *(13)*. In 1985, the United States market for AFFF products (i.e., 3% and 6% concentrates) was 6.8 million L with a total revenue of 10 million dollars in U. S. sales *(13)*. The military was the single largest consumer of AFFF agents in 1985, with consumption totaling 5.1 million L *(13)*. For historical reasons, the U. S. Department of Defense Military Specifications Regulations have driven the requirements for AFFF performance by establishing performance criteria.

Commercial AFFF formulations are complex proprietary mixtures whose major components include a solvent, which is typically butyl carbitol; fluorocarbon (perfluorinated anionic and partially-fluorinated amphoteric) surfactants; and hydrocarbon-based surfactants (Table 1.2). Fluorinated surfactants in AFFF mixtures contribute to the performance of foams as the primary fire extinguishing chemical and as vapor sealants that prevent re-ignition of fuel and solvents *(1, 14, 15)*. To evaluate the spreading of AFFFs and the spontaneous formation of films, a spreading coefficient can be calculated. The spreading coefficient (SC) *(16)* evaluates the reduction in surface and

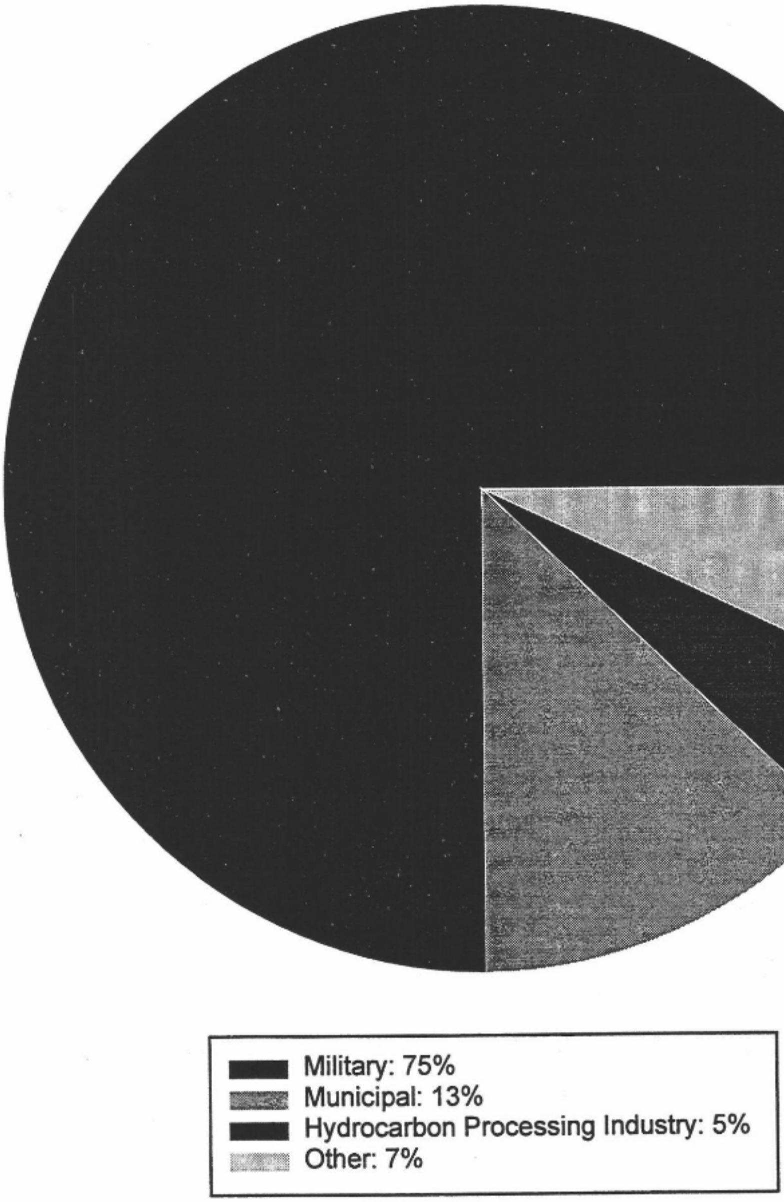

Figure 1.1. Percentage breakdown of United States consumers of AFFF products, where the hydrocarbon processing industry and municipal represent entities such as oil refineries and fire departments, respectively *(13)*.

interfacial tension and is defined as the difference between the surface tension of a model hydrocarbon phase ($\gamma_{cyclohexane}$) (such as cyclohexane at 25 dynes/cm), the surface tension of the aqueous solution ($\gamma_{aqeuous}$), and the interfacial tension between the aqueous solution and hydrocarbon phase($\gamma_{interfacial}$) *(17)*.

$$SC_{(aqueous/cyclohexane)} = \gamma_{cyclohexane} - \gamma_{aqeuous} - \gamma_{interfacial} \qquad (1)$$

For military specifications the spreading coefficient of the mixture calculated from Equation (1) must be positive *(18)*. For example, the fluorinated surfactant components in AFFFs lower the surface tension of the aqueous solution to 15-20 dynes/cm while hydrocarbon surfactants lower the interfacial tension between the aqueous solution and the hydrocarbon phase (i.e., burning fuel) to 0-2 dynes/cm *(19)*. Thus, the films formed by fluorocarbon and hydrocarbon solutions consist of two-mixed monolayers of surfactants where the air-aqueous phase monolayer is dominated by the fluorocarbon surfactant and the aqueous-hydrocarbon phase monolayer is dominated by the hydrocarbon surfactant (Figure 1.2) *(19)*.

AFFF Wastewater and its Impact on Wastewater Treatment Facilities

At installations, such as military bases, fire-training exercises are part of emergency preparedness plans and therefore are conducted with some frequency. A fire-training exercise typically consists of flooding a fire pit with flammable liquids (e.g., off-

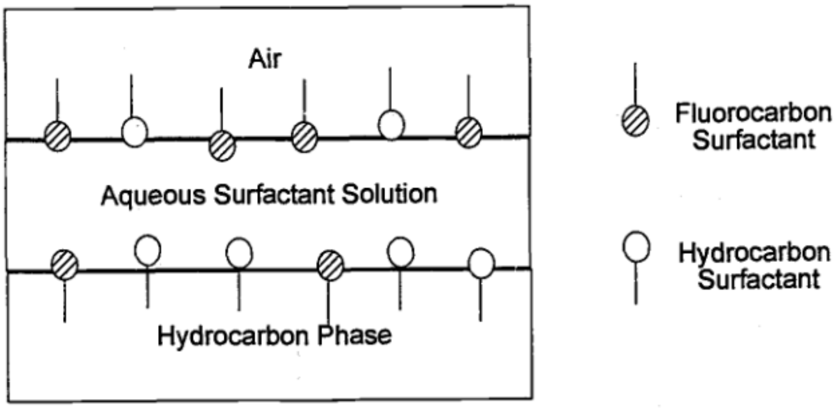

Figure 1.2. Mixed monolayers at the air-aqueous and aqueous-hydrocarbon phase interfaces. Adapted from Reference *(19)*.

specification jet fuel and waste solvents such as chlorinated solvents *(20-22)*), igniting the fluids, and subsequently extinguishing the fire with fire-fighting agents *(21)*. For example, training exercises occurred on a weekly to monthly basis *(9)* at Naval Air Station (NAS) Fallon, NV, and consisted of igniting fuel (average 3000 L/week) *(21)* and extinguishing the fire with 1200-3200 L (3%-6%) of aqueous AFFF solutions. Typically, at this site and others, disposal options for AFFF wastewater included discharge into a wastewater treatment facility and/or directly onto the ground adjacent to the training facilities.

If too much fire-fighting foam is discharged to a wastewater treatment facility at one time, excess foaming may occur, which results in aesthetic and operational problems in sewers and wastewater treatment facilities. Another concern for wastewater treatment facilities is that in-coming AFFF wastewaters have high biological (BOD) and chemical oxygen demands (COD) *(23)*. For example, for 3M Light Water™ AFFF product FC-203 as a 3% solution, the BOD_5 (5 day biological oxygen demand), BOD_{20} (20 day biological oxygen demand) and COD are 1.7×10^4 mg/L, 3.2×10^4 mg/L, and 3.2×10^4 mg/L, respectively, and can lead to significantly higher values than those normally found at treatment plants (100-400 mg/L BOD_5 *(23)*) *(23, 24)*. One of the principle contributors to the high BOD and COD of AFFF is the organic solvent component, butyl carbitol (Table 1.2).

In addition to the foaming BOD and COD problems associated with AFFF, residual fuel is part of AFFF wastewater *(12, 25)*. Residual fuel in combination with AFFF components and potential combustion products complicates the characterization of AFFF wastewater and thus its disposal in an economically-and environmentally-

Table 1.2. Chemical Composition of 3M FC-203CF Light Water™ Aqueous Film Forming Foam Concentrate (St. Paul, MN) *(73)*.

Chemical Name	Percent of Total Composition
Water	69.0-71.0
Diethylene glycol butyl ether (butyl carbitol)	20.0
Amphoteric fluoroalkylamide derivative	1-5
Alkylsulfate salts	1.0-5.0
Perfluoroalkyl sulfonate salts	0.5-1.5
Triethanolamine	0.5-1.5
Tolyltriazole (corrosion inhibitor)	0.05

acceptable manner *(26)*. Solutions containing free and emulsified oil, fuel, and AFFF components were shown to adversely affect activated sludge processes *(12, 25)* and the performance of anaerobic sludge digestors *(27)* in wastewater treatment facilities. Because of the potential problems at wastewater treatment facilities, characterization of AFFF wastewater is required in some instances prior to gaining approval to discharge the waste to a wastewater treatment facility. Characterization methods generally are lacking, and thus some fire-training facilities have had to impound AFFF wastewater over extended periods of time.

Aqueous film forming foam wastewater and its treatment have been the focus of investigative studies by the U. S. Department of Defense *(26)*. Several pre-treatments such as precipitation, coagulation, adsorption on activated carbon and ultrafiltration *(12, 26)* are being evaluated for the treatment of AFFF wastewater before dispensing it to a wastewater treatment facility *(23, 25, 28-30)*; however, few pre-treatment strategies are being implemented. Currently, treatment efficiency is judged using only general, non-specific parameters such as methylene blue active substances (MBAS) and total organic carbon. Unfortunately, analytical methods are not yet widely available that permit the specific assessment of the effectiveness of treatment technology efficiency on fluorinated surfactant removal.

Perfluorinated Surfactants in Groundwater

Plumes of contaminated groundwater are associated with past fire-training sites at several military bases in the United States *(20-22, 31-33)* including NAS Fallon, NV, Tyndall Air Force Base, FL, and Wurtsmith Air Force Base, MI, where AFFF wastewater has entered groundwater without prior treatment. Most of these plumes have been characterized with respect to fuel and solvent components unlike the surfactant components, which have received little attention primarily due to the lack of appropriate analytical techniques.

A few early reports tentatively identified the presence of fluorinated surfactants in groundwater impacted by fire-fighting activities at Tyndall Air Force Base, FL *(31, 34)*. A recent report described the development of an analytical method that permitted the definitive identification of perfluorocarboxylates surfactants in groundwater at NAS Fallon, NV, and Tyndall Air Force Base, FL, at concentrations ranging from 125 to 7090 μg/L *(9)*. A current study at Wurtsmith Air Force Base, MI, has revealed a plume of perfluorocarboxylates 500 m in length with concentrations ranging from 3 to 110 μg/L *(35, 36)*.

At each field site both even- and odd-numbered carbon perfluorocarboxylates were identified, which is indicative of product formulations manufactured by the electrochemical fluorination process *(9)*. This finding is consistent with the fact that the 3M Co., a company that uses electrochemical fluorination to manufacture perfluorinated surfactants, has held the military contract to supply AFFF for the last 25 years.

Laboratory and field data regarding the transport of fluorinated surfactants in groundwater are virtually nonexistent. In an attempt to address this data gap, we performed a single-well push-pull test *(37)* using perfluorooctane sulfonate in order to obtain *in-situ* transport information. The push-pull test consisted of the injection of a prepared test solution into the saturated zone of an aquifer using an existing monitoring well, followed by the extraction of the test solution/groundwater mixture from the same location. For this experiment, 50 L of injectate containing 97 mg/L bromide (non-reactive tracer) and 26 mg/L potassium perfluorooctane sulfonate, which is one of the major perfluorinated surfactants present in some AFFF mixtures, was injected into a well over a period of 4 hr. Immediately after injection, a total of 98 L was extracted from the well over a 9-hr period. Samples were taken during the extraction phase and analyzed for bromide and perfluorooctane sulfonate by ion chromatography and MBAS, respectively. It should be noted that the MBAS test is non-specific and does not allow for the detection and quantitation of individual anionic surfactant classes. However, for this field study where only a single perfluorinated surfactant was present in the injectate solution and none was present in the background groundwater, the limitations of MBAS did not hinder its application as the analytical method for perfluorooctane sulfonate.

Breakthrough curves were constructed for bromide and perfluorooctane sulfonate (Figure 1.3) by plotting the relative concentration C/C_o for each solute, where C is the measured concentration and C_o is the injected concentration, versus the cumulative extracted volume divided by the total injected volume of the test solution. Identical breakthrough curves for bromide and perfluorooctane sulfonate were observed indicating that perfluorooctane sulfonate was transported conservatively in this aquifer. In contrast, breakthrough curves for a mixture C10-C13 linear alkylbenzene sulfonate (LAS) obtained from a separate single-well push-pull test conducted in the same aquifer (data not shown) indicates the retardation of C10-C13 LAS relative to that of bromide *(38)*. Preliminary data indicates for a given site, perfluorooctane sulfonate (C8) is conservatively transported while its hydrocarbon surfactant analog of 2 to 5 more carbon atoms is

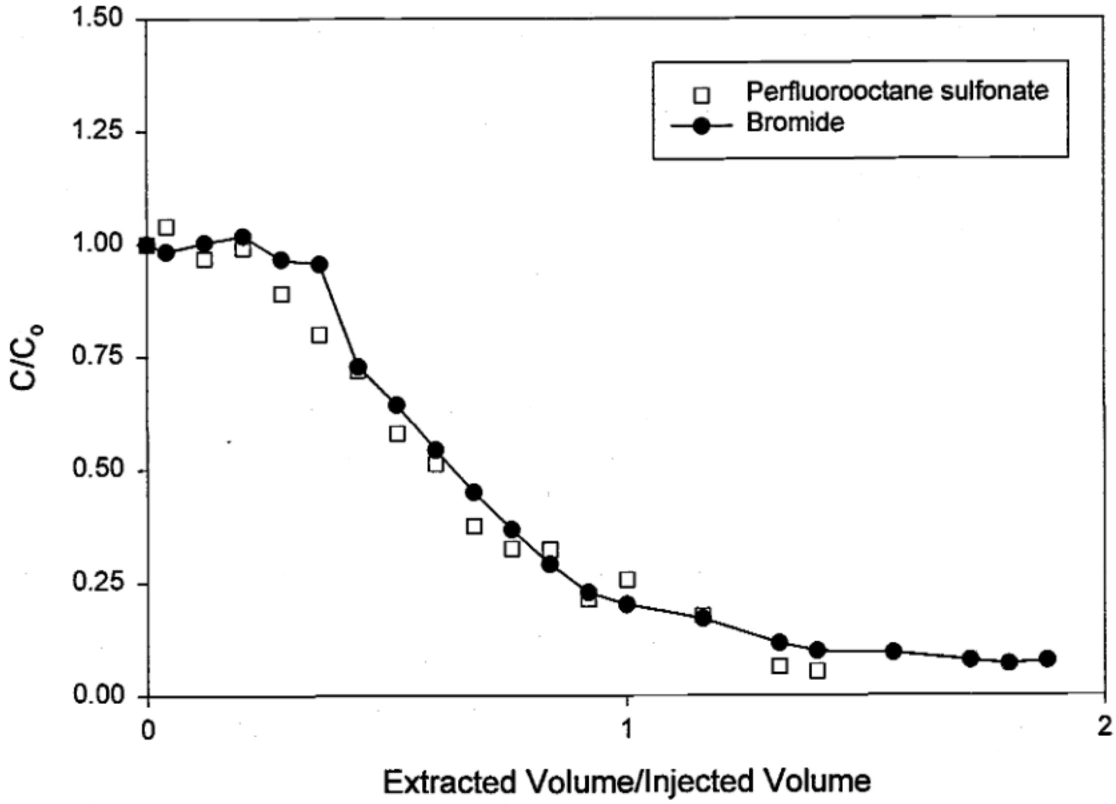

Figure 1.3. Breakthrough curves for bromide and perfluorooctane sulfonate obtained from a push-pull field test.

retarded. Because perfluorocarboxylates are weaker acids, their transport may be affected by pH and ionic strength. Therefore, research is required to fully investigate the transport behavior of the perfluorinated surfactants present in AFFF. However, the conservative transport perfluorooctane sulfonate observed in the field study indicates that perfluorinated surfactants may be good tracers for AFFF-contaminated groundwater.

Biodegradation

The extent to which AFFF components and priority pollutants in AFFF wastewater biodegrade is quite varied. A material safety data sheet for a current AFFF product states that the product contains one or more organic fluorochemicals that have the potential to resist degradation and persist in the environment *(39)*. The detection of perfluorocarboxylates in groundwater at NAS Fallon, NV, and Tyndall Air Force Base, FL, which have not been used for 7-11 years *(9)* is consistent with both AFFF product labeling and the widely-held view that perfluorinated surfactants are not biodegradable.

Few studies have been conducted to investigate the biodegradability of perfluorinated or partially-fluorinated surfactants *(2, 3, 12, 40)*. Perfluorooctane sulfonic acid was not degraded under aerobic or anaerobic conditions *(27)*, while a partially-fluorinated surfactant, 1H, 1H, 2H, 2H-perfluorooctane sulfonic acid, was partially degraded both aerobically and under sulfur-limiting conditions *(2, 3, 5)*. Biodegradation of partially-fluorinated surfactants appears to be limited to the non-fluorinated portion of the molecule *(2, 5, 41)*. For example, 1H, 1H, 2H, 2H-perfluorodecanol was biotransformed to perfluorooctanoate *(41)*. The recalcitrant nature of perfluorinated compounds is attributed, in part, to the strength of the carbon–fluorine bond *(1, 2, 42)* as well as the rigidity of the perfluorocarbon chain *(2, 43)*.

In contrast to the recalcitrant nature of the fluorinated surfactant components present in AFFF mixtures, the alkyl sulfate hydrocarbon surfactants (Table 1.2) *(26)* present in some AFFF formulations is considered biodegradable under aerobic and anaerobic conditions *(44)*. As mentioned previously, the solvent component of AFFF formulations is also biodegradable as indicated by high BOD values. As a result, the high BOD of butyl carbitol may influence the biogeochemical conditions of groundwater by consuming oxygen and thus driving systems anaerobic. Corrosion inhibitors (i.e., tolyltriazole) are a component found in AFFF formulations that have been shown to persist in the environment *(45, 46)*. While some information is available on individual AFFF components, virtually nothing is known about the biodegradation of this complex mixture and any synergistic effects of AFFF components upon priority pollutants biodegradation under actual subsurface conditions. Additional research is required to understand the biodegradation of AFFF components.

Co-Contaminant Transport and Degradation

Because some perfluorinated surfactants appear to persist in groundwater they may affect the environmental fate and transport of other co-contaminants (i.e., jet fuel and trichloroethylene) that are present in AFFF wastewater. Unfortunately, the physical character (e.g., number of liquid phases) and chemical composition of AFFF wastewaters have not been widely characterized. However, it is likely that AFFF wastewaters resulting from the application of AFFF on burning solvents, some of which form dense non-aqueous phase liquids or DNAPLs, are multi-phased systems. Due to the complex nature of AFFF wastewater there are a number of potential interactions between AFFF components and co-contaminants that can affect co-contaminant transport and biodegradation. For example, some hydrocarbon surfactants above their CMC are known to enhance the apparent solubility and/or the mobility of DNAPL in contaminated aquifers *(47-49)*. Because surfactants can cause large reductions in water-DNAPL interfacial tension, surfactants may promote the displacement of residual DNAPL and hence its more rapid migration in the subsurface. The ability of hydrocarbon surfactants to increase the solubility or mobility of DNAPLs is dependent on the physical properties of the particular surfactant. Given the oleophobic nature of the perfluorocarbon chain, it is likely that on a per carbon basis, perfluorocarbon surfactants are less effective in increasing the solubility of DNAPL than hydrocarbon surfactants as well as less effective in lowering aqueous-DNAPL interfacial tensions *(1)*. However, to date studies have not been conducted to determine the extent to which fluorinated surfactants can increase the solubility and/or mobility of DNAPL in the subsurface.

By analogy to wastewater treatment systems where AFFF wastewater adversely affected the performance, perfluorinated surfactants may have an effect on groundwater microbial populations and their ability to degrade co-contaminants *(12, 25, 27)*. No information exists on the potential impact of perfluorinated surfactants on microbial populations. Recent studies with hydrocarbon surfactants have indicated either inhibition *(50-52)* or promotion *(53-55)* of organic contaminant degradation *(47)*. The ability of a surfactant to promote or inhibit co-contaminant biodegradation also appears structure specific. Unfortunately, structure-activity relations have not been established for fluorinated surfactants. Therefore, it is not yet possible to predict *a priori* the effect that perfluorinated surfactants will have upon the biodegradation of other contaminants in AFFF-contaminated groundwater.

Toxicity

The toxicity of AFFF formulations to marine and freshwater organisms has been tested in laboratory studies *(24)*. Various diluted AFFF agents were considered mildly toxic to marine life at concentrations near 6.0 g/L *(24)*. Additional components of interest found in AFFF concentrate formulations are the corrosion inhibitors such as tolyltriazole. Recent toxicological studies on toyltriazoles have shown that these compounds have moderate to high toxicity *(45, 46)*. However, realistic toxicity evaluations of AFFF mixtures and AFFF wastewater in the environment are difficult because AFFF wastewaters are complex mixtures that contain AFFF components, primary pollutants, as well as toxic burn products. In addition, differential degradation during transport of AFFF wastewater components will change the mixtures composition and toxicity over distance and time. Finally, the toxicity of these types of complex mixtures is difficult to assess because of the potential synergistic effects between mixture components, making it difficult to predict *a priori* the toxicity of these mixtures in the environment.

Release of fluorinated surfactants to surface waters is not a recommended by AFFF manufacturers as a route of disposal for AFFF wastewater *(56)*. Fortunately, reports of AFFF wastewater discharge to surface waters are limited. However, AFFF wastewater released to a Florida river in 1993 has been the subject of investigation as a possible cause of sea bird illnesses and deaths in the region *(57, 58)*. By analogy to hydrocarbon surfactants, perfluorinated surfactants in AFFF wastewater can potentially cause birds to loose their natural oils, thus causing birds to die from hypothermia *(59)*.

Analytical Considerations

The determination of perfluorinated surfactants is problematic *(12)*, in part, because the surfactants are nonvolatile and generally do not contain chromophores, which limits their detection using commonly available analytical detectors. The scarcity of analytical methods for fluorinated surfactants is in sharp contrast to numerous methods available on hydrocarbon surfactant analysis *(11, 60-62)*. Creating an analytical method to isolate perfluorinated surfactants from environmental samples is complicated due to the proprietary nature of AFFF formulations and therefore, the lack of knowledge regarding the specific structure of perfluorinated surfactants. Furthermore, the isolation of perfluorinated surfactants from water is complicated by their high water solubility.

The non-specific determination of the total organofluorine content of a water sample may be obtained using the oxyhydrogen combustion method *(1, 63)*. A water sample (e.g., 10 mL) introduced into the oxyhydrogen torch for combustion is completely mineralized to the fluoride ion, which is then trapped in an aqueous solution *(1, 64, 65)*. The fluoride ion is then measured by an ion selective electrode *(1, 64, 66)*. As little as 20-40 μg/L fluorinated surfactant can be detected without the need to concentrate the water sample before combustion *(1)*. Although this method determines the total organofluorine content of a water sample, it does not provide structure-specific information. In addition, the mixtures of oxygen and hydrogen present a potentially significant safety hazard.

The methylene blue active substances test was used to detect the presence of anionic surfactants in groundwater at a fire-training area at Tyndall Air Force Base *(31)*. With the MBAS test, anionic surfactants form ion pairs with the methylene blue cation, which then are extracted into chloroform and determined spectrophotometrically *(67)*. However, the use of MBAS as a reliable means of detecting fluorinated surfactants in environmental wastewaters is limited because the MBAS test is non-specific and does not allow for the individual identification of anionic surfactants nor for the differentiation between anionic hydrocarbon and fluorocarbon surfactants.

When structural information is required to obtain definite identification of fluorinated surfactants in environmental samples, mass spectrometry is the method of choice. Chemical derivatization was combined with gas chromatography/mass spectrometry (GC/MS) for the determination of perfluorinated surfactants in groundwater at Tyndall Air Force Base, FL *(9, 34)*. Perfluorocarboxylates were quantitatively determined in groundwater by derivatizing the carboxylates to their methyl esters, which were detected and quantified by electron impact GC/MS and electron capture negative chemical ionization GC/MS. Perfluorooctane sulfonate, which is present in AFFF formulations, was not detected by this method. Although perfluoroalkanesulfonate esters may have been formed during the derivatization step, the esters are unstable due to excellent leaving group properties of the perfluoroalkanesulfonic group *(7, 68)*. In fact, perfluorooctane sulfonate esters are sold as *alkylating* reagents for the derivatization of *other* analytes. Therefore, derivatization with gas chromatography has limited utility for determining a broad range of perfluorinated surfactants.

Liquid chromatography/mass spectrometry (LC/MS) is an attractive option for the sensitive and quantitative analysis of non-volatile analytes such as perfluorinated surfactants. Liquid chromatography/mass spectrometry was used to qualitatively identify perfluorooctane sulfonate in groundwater from Tyndall Air Force Base, FL, NAS Fallon, NV, and Wurtsmith Air Force Base, MI *(35)*. To the best of our knowledge, only one other report characterizes the determination of fluorinated surfactants in water and wastewater by high performance liquid chromatography (HPLC) together with a thermospray interface and a tandem mass spectrometer *(69)*. Liquid chromatography/mass spectrometry will most likely prove to be the most useful tool for characterizing the compositions and concentrations of a range of perfluorinated surfactants in environmental samples.

Future Challenges

Hydrocarbon-fuel fires pose a serious threat to life and property and therefore the issue of fire safety must be balanced against the risks that AFFF and their perfluorinated surfactants potentially pose to the environment. Fluorinated surfactants are a unique class of chemicals that are directly discharged to natural and engineered aquatic systems. The variety of applications for these types of surfactants is increasing yet little information on the environmental behavior is available. Fluorinated surfactants differ significantly from hydrocarbon surfactants such that direct analogies can not be drawn between the two types of surfactants. Therefore, the environmental behavior of fluorinated surfactants is worthy of independent investigation.

Because commercial formulations of AFFF are complex mixtures, the employment of these mixtures in fire-training situations introduces both priority and non-priority pollutants into the environment. There are significant gaps in the knowledge of how chromatographic separation during transport affects these complicated mixtures. Because perfluorinated surfactants persist in the environment, they may impact the biogeochemical processes affecting the distribution and bioavailability of co-contaminants. The effect that AFFF components has upon subsurface microbial ecology and activity is unknown.

Several different technologies are being evaluated to solve current problems resulting from AFFF usage, including the development of products to replace AFFF. The 1998 Presidential Green Chemistry Challenge Award was recently presented to a company for the development of a biodegradable fire-extinguishing agent that does not contain glycol ethers or fluorinated surfactants *(70, 71)*. Another approach to addressing the problems associated with fluorinated surfactants is to discontinue their use in AFFF agents and to return to prior technology such as protein-based foams.

In a related issue, advances in fire-fighting product development includes the development and marketing of training foams that are designed to be used during training exercises in lieu of AFFF products that contain fluorinated surfactants. Training products are attractive for their cost savings due to the absence of expensive fluorinated surfactant components. Training products have the added benefit of being readily treated by conventional wastewater treatment facilities due to the increased biodegradability of the non-perfluorinated surfactant mixture and its reduced foaming properties. Such training foams eliminate the common environmental concern associated with AFFF and reduce training costs while still allowing for actual practice with fire-training equipment *(72)*. While training foams are designed to provide expansion characteristics similar to AFFF, they are inadequate fire extinguishing materials if used in an actual hydrocarbon-fuel fire. Because the possibility exists that training foams may be mistaken in an emergency for AFFF, some AFFF users do not employ training foams.

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Chapter 2

Analytical Method for the Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity

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Abstract

Perfluorinated surfactants are used in aqueous film forming foam (AFFF) formulations, which are used to extinguish hydrocarbon-fuel fires. Virtually nothing is known about the occurrence of perfluorinated surfactants in the environment, in particular, at fire-training areas and emergency response sites where AFFF entered groundwater without prior treatment. Strong anion exchange Empore disks were used to extract perfluorocarboxylates from groundwater collected from fire-training facilities located on Naval Air Station Fallon, NV, and Tyndall Air Force Base, FL. The carboxylates were simultaneously eluted from the disks and derivatized to their methyl esters for direct analysis by gas chromatography/mass spectrometry. Perfluorocarboxylates containing 6-8 carbons were detected in groundwater collected from the two field sites with total concentrations ranging from 125 to 7,090 μg/L. The detection of perfluorocarboxylates at field sites after 7 to 10 years of inactivity indicates their potential utility as markers for delineating groundwater impacted by fire-fighting activity.

Introduction

Aqueous film forming foams (AFFF) are complex mixtures of surfactants and other components used to extinguish hydrocarbon-fuel fires that occur at fire-training sites as well as in emergency situations. Aqueous film forming foams have been commercially available for fire-fighting applications since their development by the United States Navy and 3M Co. in the mid-1960s *(1)*. At fire-training areas that routinely used AFFF mixtures and military emergency response sites, AFFF-laden wastewater that entered surface water and groundwater without treatment has led to groundwater and soil contamination. For example, perfluorinated compounds were tentatively identified in groundwater impacted by fire-training activities at Tyndall Air Force Base *(2)*. Unfortunately, definitive identifications of the perfluorinated compounds were not reported.

Commercial AFFF mixtures are propreitary in nature and typically contain fluorinated and non-fluorinated surfactants *(1, 3-5)*. Due to the proprietary nature of AFFF formulations, the chemical structures of the actual perfluorinated surfactants used in commercial AFFFs are not known outside the companies that manufacture them *(5)*. Moreover, the analysis of anionic perfluorinated surfactants that are known to occur in AFFF formulations *(6)* is problematic because the surfactants are non-volatile and may not contain chromophores. As a result, analytical methods for AFFF formulation components are lacking and therefore it is difficult to assess their occurrence, fate, and transport in AFFF-contaminated groundwater. Because perfluorinated surfactants co-occur with other pollutants (e.g. fuel components, solvents, etc.) in groundwater, it is important to determine if perfluorinated surfactants affect the transport and biodegradation of other contaminants. Free and emulsified oil, fuel, and AFFF components were shown to adversely affect activated sludge processes *(6, 7)* and the performance of anaerobic sludge digestors *(8)* in wastewater treatment facilities. For this reason, perfluorinated surfactants may have an adverse affect on groundwater microbial populations and their ability to degrade co-contaminants present in AFFF-contaminated groundwater.

In addition to fluorinated surfactants use in fire-fighting foams, they are also utilized in herbicides and insecticides, cosmetics, greases and lubricants, and adhesives *(3)*. Fluorinated carboxylic acids of industrial significance include perfluorooctanoic acid (PFC8) and perfluorodecanoic acid (PFC10) *(9)*. There is concern regarding the potential toxicity of perfluorinated carboxylic acids. An in vivo study of rat liver response to PFC10 indicated the rapid onset of a low-level heptatotoxicity but no detectable damage to the DNA *(10)*. Perfluorodecanoic acid and PFC8 have been found to inhibit gap junction intercellular communication in rat liver epithelial cells *(11)* and may be involved in tumor promotion *(9)*.

In this paper, we describe the isolation, identification and quantification of perfluorinated carboxylates in groundwater impacted by fire-training activities at Naval Air Station (NAS) Fallon, NV, and Tyndall Air Force Base, FL. The development of analytical methods is necessary before investigating the occurrence and distribution of perfluorinated surfactants in AFFF-contaminated groundwater and their effect on co-contaminant transport and biodegradation.

Experimental Section

Standards and Reagents. Standards of PFC8 (98%), perfluorododecanoic acid (PFC12) (95%), and the internal standard, 2-chlorolepidine (99%) were purchased from Aldrich Chemical (Milwaukee, WI). Methyl iodide (neat) was used as purchased from Aldrich Chemical.

Field Sites and Sample Collection. From the mid-1950s to 1988, the crash crew training area at NAS Fallon, NV, (Figure 2.1a) was used to conduct fire-training activities, which consisted of flooding a fire pit with flammable liquids, igniting the fluids, and subsequently extinguishing the fire with fire-fighting agents including AFFF *(12)*. For a typical training exercise, approximately 75-100 L of AFFF concentrate were diluted with 1200-3200 L of water according to specifications (3% or 6% solution) and subsequently employed. During the years of activity at the NAS Fallon site, training exercises occurred on a weekly to monthly basis. At the NAS Fallon site, groundwater samples were collected from four monitoring wells located within a 120 m radius of the fire pit where the water table is located between 2 to 3 m below the land surface.

The Tyndall Air Force Base Fire-training Area FT-23 was used from 1980 to 1992 for similar activities (Figure 2.1b) *(13)*. Four groundwater samples were obtained from wells surrounding the fire-training area; the water table is located between 1 and 2 m below the land surface. All samples were collected in high density polyethylene brown bottles because perfluorinated carboxylates adsorb to glass *(14)*. Samples were shipped on ice without preservation and stored at 4 °C prior to analysis.

Solid-Phase Extraction and Derivatization. Samples (55-200 mL) were extracted through 25 mm strong anion exchange (SAX) disks in a manner similar to that

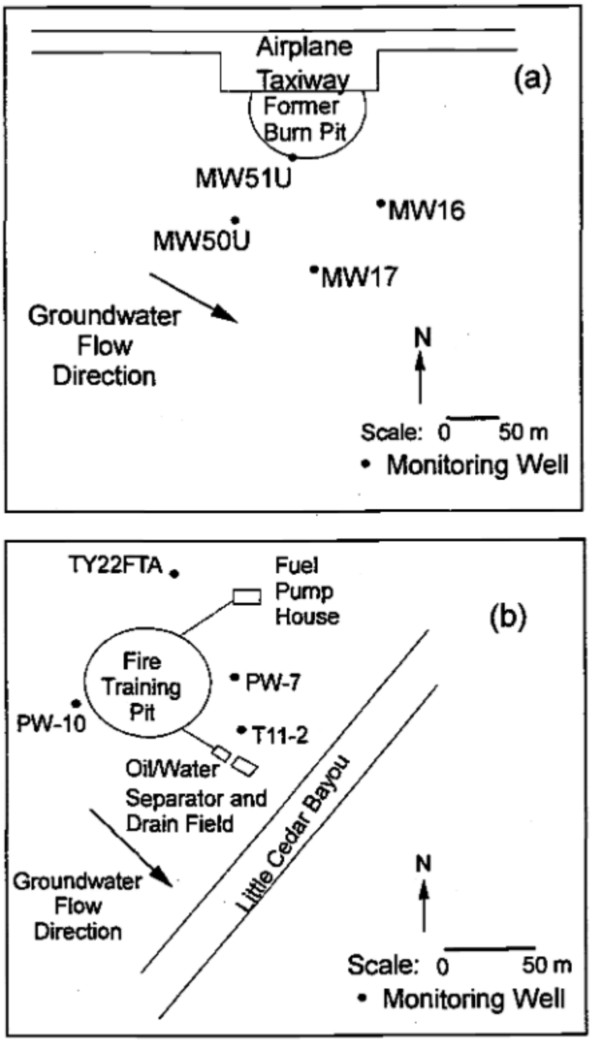

Figure 2.1. Map of (a) Naval Air Station Fallon, NV, and (b) Tyndall Air Force Base, FL, field sites indicating location of groundwater wells and direction of regional groundwater flow.

described by Field and Reed *(15)* with the exception that the SAX disks were pre-treated prior to use to remove interfering disk impurities. Pre-treatment consisted of soaking the disks in 12 mM HCl/acetonitrile for 2 days after which the disks soaked in pure acetonitrile for several hours. Just prior to use the disks were rinsed with a minimum of 350 mL of deionized water in order to sufficiently rinse the HCl from the disks and wet them prior to passing groundwater samples through them. Samples (55-200 mL) were passed through the disks under full vacuum and the disks were then allowed to dry. The disks containing the exchanged analytes were placed in a 2 mL autosampler vial together with 1 mL of acetonitrile, 51.2 μg of internal standard, and 100 μL of methyl iodide. When heated at 80 °C for 1 h, the acids were simultaneously eluted from the disk and derivatized to their methyl esters.

Spike and Recovery. Spike and recovery experiments were performed to determine the precision and accuracy of the SAX disk extraction and in-vial elution method. A set of experiments was performed on groundwater samples from NAS Fallon MW 50U and MW 17 that had been previously determined to contain neither PFC8 nor PFC12 above detection. Duplicate groundwater samples from wells MW 50U and MW 17 were spiked to contain a final concentration of 1,240 μg/L of PFC8 and 560 μg/L of PFC12.

Standard addition analyses were performed with NAS Fallon groundwater samples that contained measurable quantities of PFC8; the samples did not contain PFC12 above detection. Known amounts of PFC8 were added to samples to give a final concentration twice that of the background concentration. For example, groundwater from MW 51U and MW 16, which contained background concentrations of 6,570 μg/L and 460 μg/L, respectively, were spiked to give a final concentration of 12,900 μg/L and 1,000 μg/L of PFC8, respectively. Each sample also was spiked with 56.4 μg of PFC12. To determine the detection limit of the method, single samples of groundwater that contained no perfluorinated carboxylates above detection were spiked to give a range of final PFC8 concentrations from 18 to 54 μg/L.

Gas Chromatography/ Mass Spectrometry. Extracts were analyzed using a Hewlett Packard Model 5890 Series II Plus gas chromatograph (GC) equipped with a 30 m x 0.32 mm x 4.00 μm SPB-1 SULFUR column (Supelco Inc., Bellefonte, PA). An injection volume of 1 μL was used under splitless conditions with an injector temperature of 200 °C. The GC oven temperature was initially held for 6 min at 60 °C, increased by 6 °C/min to 190 °C, increased further by 30 °C/min to 270 °C, and then held for 5 min.

Quantification of perfluorocarboxylate methyl esters was performed using a Hewlett Packard Model 5972 mass selective detector operated in electron impact (EI) mode (70 eV). The mass selective detector was operated in full scan (50-450 amu) mode and in selected ion monitoring (SIM) mode using a dwell time of 100 ms for each ion. The scanning mode was used for qualitative identification while SIM mode was used for quantification. The ions of m/z 131 $[C_3F_5]^{-}$, m/z 169 $[C_3F_7]^+$, and m/z 219 $[C_4F_9]^+$, which are characteristic fragments of perfluorocarbons *(16-18)*, were used to identify and quantify the methyl esters of perfluorohexanoic acid (PFC6), perfluoroheptanoic acid (PFC7), PFC8 and PFC12. The internal standard, 2-chlorolepidine, was quantified with the ions m/z 177 and 115.

The identification of perfluorocarboxylate methyl esters was confirmed by electron capture negative ionization (ECNI) GC/MS, which gave unique molecular ions for each of the perfluorinated carboxylate methyl esters (e.g. m/z 328 for PFC6, m/z 378 for PFC7, m/z 428 for PFC8, and m/z 628 for PFC12). These measurements were performed with a Varian 3400 gas chromatograph interfaced with a Finnigan Model 4023 mass spectrometer. Methane was used as the reagent gas and the mass spectrometer was operated in full scan mode (100-650 amu). The gas chromatograph was operated with a column and temperature program identical to that used for the EI GC/MS.

Initially, samples prepared in deionized water were used as the matrix for constructing calibration curves and standard recoveries were low. However, when samples prepared in tap water, which contains inorganic cations and anions, were used as the matrix for constructing calibration curves quantitative recovery of standards was obtained. It is proposed that the 350 mL of deionzed water does not sufficiently rinse the disks of residual HCl and tap water is required to completely rinse the disks and obtain quantitative recovery of standards. Therefore, calibration curves for quantification of PFC8 were constructed by passing 100 mL tap water samples that had been spiked with 3.6 μg to 1,080 μg PFC8 through 25 mm SAX disks and derivatizing the acids to their methyl esters using the in-vial elution and derivatization technique. The calibration curve for PFC12 was constructed in a similar manner by adding 7.5 μg to 113 μg of PFC12 standard to 100 mL tap water. For all quantitation standards, a total of 51.2 μg of the 2-chlorolepidine internal standard was added to the autosampler vial just prior to the addition of methyl iodide. Both calibration curves were linear with r^2 typically greater than 0.99. Quantification of PFC6 and PFC7 was performed assuming a response factor equal to an equimolar amount of PFC8.

Results and Discussion

Gas Chromatography/Mass Spectrometry. A film thickness of 4 μm (30 m x 0.32 mm SPB-1 SULFUR; Supelco, Bellefonte, PA) was necessary to obtain sufficient retention times for the methyl esters of PFC8 and PFC12 to allow for the separation and quantification (Figure 2.2a). Initial attempts to separate and quantify the perfluorinated carboxylate methyl esters on a thin film (0.25 μm), 30 m x 0.25 mm DB-1 (J&W Scientific, Folsom, CA) column were unsuccessful regardless of the initial column temperature. Note that the stationary phases in the SPB-1 SULFUR and DB-1 columns are comparable. A standard of perfluorobutyric acid was not observed under any of the described GC conditions; it is most likely that an initial oven temperature less than 40 °C would be required.

The EI mass spectra of methyl PFC8 (Figure 2.3a) and PFC12 indicate characteristic perfluorocarbon fragmentation *(16, 17)* in which the major ions (e.g., 69, 119, 169, 219, etc.) differ by 50 amu, which corresponds to the mass of CF_2. Molecular ions were not observed for any of the perfluorinated carboxylate methyl esters under EI conditions; however, molecular ions $[M]^-$ were observed under ECNI conditions. For example m/z 428 (in Figure 2.3b) corresponds to the molecular ion of methyl PFC8.

Solid-Phase Extraction. Prior to developing a solid-phase extraction method, initial experiments were conducted using diazomethane as the derivatization reagent.

When perfluorinated carboxylates were derivatized using ethanol-based diazomethane, multiple peaks corresponding to methyl and ethyl esters were detected (unpublished data). Because EI GC/MS did not produce molecular ions, ECNI GC/MS was used to verify the formation of both methyl and ethyl esters. Consequently, if ethanol-based diazomethane was used for derivatization in conjunction with EI GC/MS, multiple peaks in a chromatogram could be erroneously interpreted as a greater number of perfluorinated compounds than are actually present. In contrast, only the methyl ester was obtained when butyl carbitol (2-(2-butoxyethoxy)ethanol) was used to prepare the diazomethane reagent. However, because of the hazards associated with the use of diazomethane and the time-consuming nature of diazomethane derivatization, an alternative method was desired.

Derivatization of the perfluorocarboxylates by the solid-phase extraction and the in-vial elution and derivatization technique gave only a single peak that corresponded to the methyl ester of each perfluorinated carboxylate standard; the identification of each methyl ester was confirmed by ECNI GC/MS. In addition, the solid-phase extraction approach combined the steps of isolation and derivatization, which greatly simplified the procedure and eliminated the use of diazomethane. Six replicate analyses of blank 25 mm SAX disks that had not been pre-rinsed with 12 mM HCl/acetonitrile prior to use, yielded an average of 21 ± 1 μg (4.8% relative standard deviation (RSD)) of PFC8 per disk. No other perfluorinated carboxylates were present in the disks above the detection limit. The PFC8 is associated with the Teflon matrix and not the embedded anion exchange particles (unpublished data). The background PFC8 was successfully removed

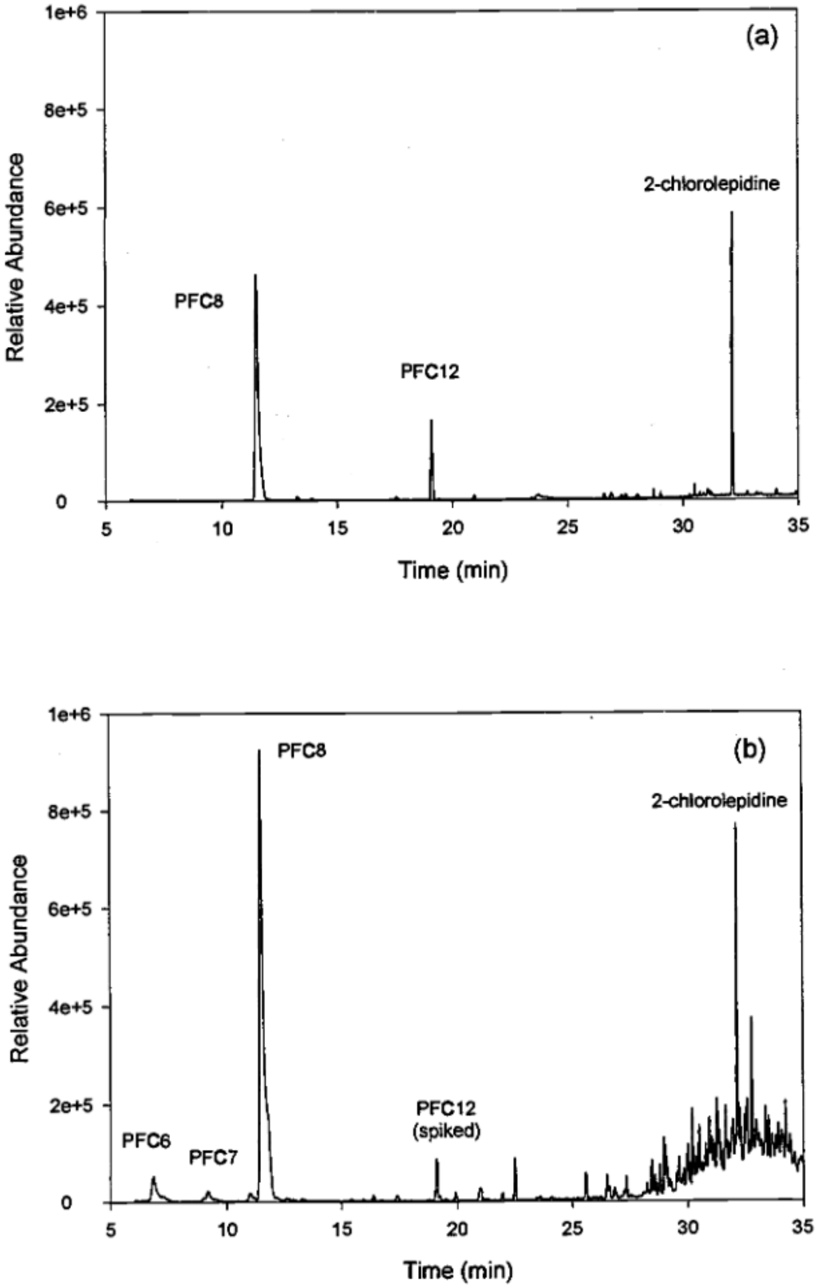

Figure 2.2. (a) Typical EI GC/MS chromatogram of PFC8 and PFC12 standards and (b) perfluorinated carboxylates, including PFC6, PFC7, PFC8 and PFC12 (spiked) in Naval Air Station Fallon, NV, groundwater.

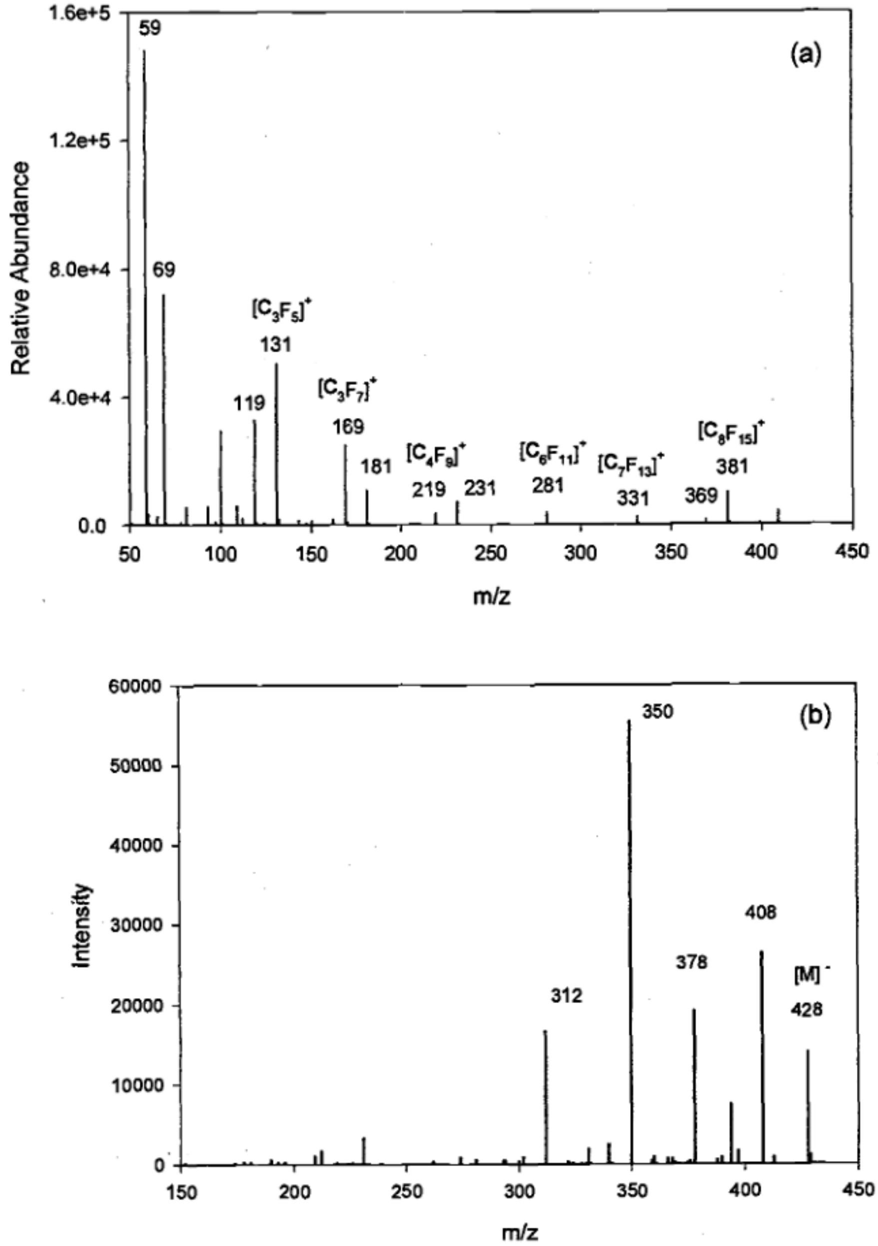

Figure 2.3. (a) EI mass spectrum of methyl PFC8 and (b) an ECNI mass spectrum of methyl PFC8.

by rinsing the disks prior to use with 12 mM HCl/acetonitrile followed by 350 mL of deionized water. It should be noted that benzoic acid and ethylhexylphthalic acid are also present in the disks as artifacts and are removed by the HCl/acetonitrile pre-rinse step.

Accuracy, Precision and Detection Limits. The recoveries of PFC8 from blank groundwater samples obtained from NAS Fallon wells MW 50U and MW 17 were 73 and 74%, respectively, while the recoveries of PFC12 were 77 and 88%, respectively (Table 2.1). Because detectable levels of PFC8 occurred in groundwater from MW 51U and MW 16, standard addition experiments were performed to determine the recoveries of PFC8. The recoveries of the PFC8 spiked into MW 51U and MW 16 groundwater to give a final concentration double that of the background concentration were 83 and 90%, respectively (Table 2.1). The recoveries of PFC12 from MW 51U and MW 16 groundwater, which did not contain background concentrations of PFC12, were 35 and 85%, respectively (Table 1). Although the recovery of PFC8 (83%) differs significantly from that of PFC12 (35%) in groundwater from MW 51U, the recoveries of PFC8 and PFC12 were nearly equivalent for the other groundwater samples. Monitoring well 51U is located closest to the fire pit where AFFF agents where applied to burning mixtures of fuels and solvents. Due to its proximity to the fire pit, the groundwater from MW 51U most likely contains the greatest diversity of inorganic and organic constituents, which may adversely affect PFC12 recoveries relative to that of PFC8. Therefore, although the original intent was to use the PFC12 as a surrogate standard because it did not occur in the groundwater samples, PFC12 appears more sensitive to matrix interferences

Table 2.1. Recovery of PFC8 and PFC12 spiked into groundwater samples from Naval Air Station Fallon, NV.[a]

Sample	PFC8 % recovery	PFC12 % recovery
NAS Fallon MW 51U[b]	83[c]	35
NAS Fallon MW 16	90[d]	85
NAS Fallon MW 50U	73	77
NAS Fallon MW 17	74	88

[a] Duplicate samples were analyzed. Sample volume was 100 mL unless otherwise noted.

[b] Sample volume was 55 mL.

[c] Calculated as the final measured concentration divided by background concentration plus spike concentration and multiplied by 100. The background concentration was 6,570 μg/L.

[d] Calculated as the final measured concentration divided by background concentration plus spike concentration and multiplied by 100. The background concentration was 460 μg/L.

compared to PFC8 so that it is an inappropriate choice for a surrogate standard. For this reason, all subsequent quantification was based on the 2-chlorolepidine internal standard.

The precision, indicated by the RSD, calculated from five replicate analyses each of groundwater from NAS Fallon MW 16 and Tyndall AFB T11-2 ranged from 3.7 to 14% (Table 2.2). The detection and quantitation limit of the method was defined as those concentrations of PFC8 needed to produce a signal to noise (S/N) of 3:1 and 10:1, respectively. The detection and quantitation limits for PFC8 were 18 μg/L and 36 μg/L, respectively.

Application to Groundwater Samples. Four groundwater samples from both NAS Fallon and Tyndall AFB were analyzed for perfluorinated carboxylates. Chromatograms obtained by EI GC/MS indicated the presence of multiple perfluorinated compounds all having characteristic perfluorocarbon fragmentation (Figure 2.2b). Analysis by ECNI GC/MS established the identification of PFC6, PFC7 and PFC8 in groundwater obtained from wells MW 51U and MW 16 from NAS Fallon. The molecular ions $[M]^-$ for methyl PFC6 (m/z 328) and methyl PFC7 (m/z 378) were observed for peaks eluting 4.7 and 2.3 min before that of PFC8 (Figure 2.4a and 2.4b). The ECNI mass spectrum for methyl PFC8 in MW 51U was similar to that of the PFC8 standard (Figure 2.2b).

The groundwater samples from NAS Fallon MW 51U and MW 16 had total perfluorinated carboxylate concentrations of 7,090 μg/L and 540 μg/L, respectively (Table 2). The PFC6 detected in NAS Fallon groundwater samples from MW 51U and MW 16 comprised 5.2% and 11%, respectively, of the total perfluorocarboxylates

Table 2.2. Concentrations of perfluorinated carboxylates in groundwater samples from Naval Air Station Fallon, NV, and Tyndall Air Force Base, FL.[a,b]

Sample	n	PFC6 (µg/L)	PFC7 (µg/L)	PFC8 (µg/L)	Total (µg/L)
NAS Fallon MW 51U	3	372 ± 4	149 ± 5	6,570 ± 150	7,090 ± 160
		(1.1%)	(3.4%)	(2.3%)	(2.3%)
NAS Fallon MW 16	5	57 ± 8	18 ± 2	460 ± 20	540 ± 20
		(14%)	(11%)[c]	(4.3%)	(3.7%)
NAS Fallon MW 50U	3	nd	nd	nd	nd
NAS Fallon MW 17	3	nd	nd	nd	nd
Tyndall AFB PW-10	2	144	38	116	298
Tyndall AFB PW-07	2	73	22 [c]	64	159
Tyndall AFB T11-2	5	64 ± 4	19 ± 1	42 ± 2	124 ± 8
		(6.3%)	(5.3%)[c]	(4.8%)	(6.5%)
Tyndall AFB TY22FTA	2	nd	nd	nd	nd

[a] The relative standard deviation is given in parentheses.

[b] nd, not detected above the detection limit.

[c] The reported value is near the detection limit ($S/N \leq 3$) and less than the quantitation limit ($S/N \leq 10$). The value has been included in the reported total concentration.

detected. The PFC7 was 2.1% and 3.3% respectively, of the total perfluorinated carboxylates detected in these wells. The dominant perfluorinated carboxylate, PFC8, accounted for 93% and 85%, respectively, of the total perfluorocarboxylate concentration.

The highest concentrations of perfluorocarboxylates were observed in groundwater collected from NAS Fallon MW 51U, which is the well located closest to the fire-training pit (Figure 2.1a). Monitoring well 16, which is located downgradient of MW 51U and the fire-training pit, had lower but detectable concentrations of perfluorocarboxylates. Groundwater from MW 50U and MW 17, which are located off gradient from the fire-training pit, contained no detectable perfluorinated carboxylates. Over the approximate 100 m distance between MW 51U and MW 16, the concentrations of the perfluorinated carboxylates decreased with increasing number of carbons. For example, the concentration of PFC6 decreased 85% over the 100 m compared to decreases of 88% and 93% for PFC7 and PFC8, respectively.

The groundwater samples from Tyndall AFB PW-10, PW-07 and T11-2 contained total perfluorinated carboxylate concentrations of 298 μg/L, 159 μg/L and 124 μg/L, respectively (Table 2.2). The compositions of Tyndall AFB groundwater collected from the three wells ranged from 46 to 52% for PFC6, 13 to 15% for PFC7 and 34 to 40% for PFC8. In contrast to the groundwater samples from NAS Fallon, the dominant perfluorinated carboxylate in Tyndall AFB groundwater was PFC6.

The highest concentrations of perfluorocarboxylates among the groundwater samples from Tyndall AFB were observed in PW-10 and PW-07, which are the two wells located closest to the fire-training pit (Figure 2.1b). Monitoring well T11-2, which is

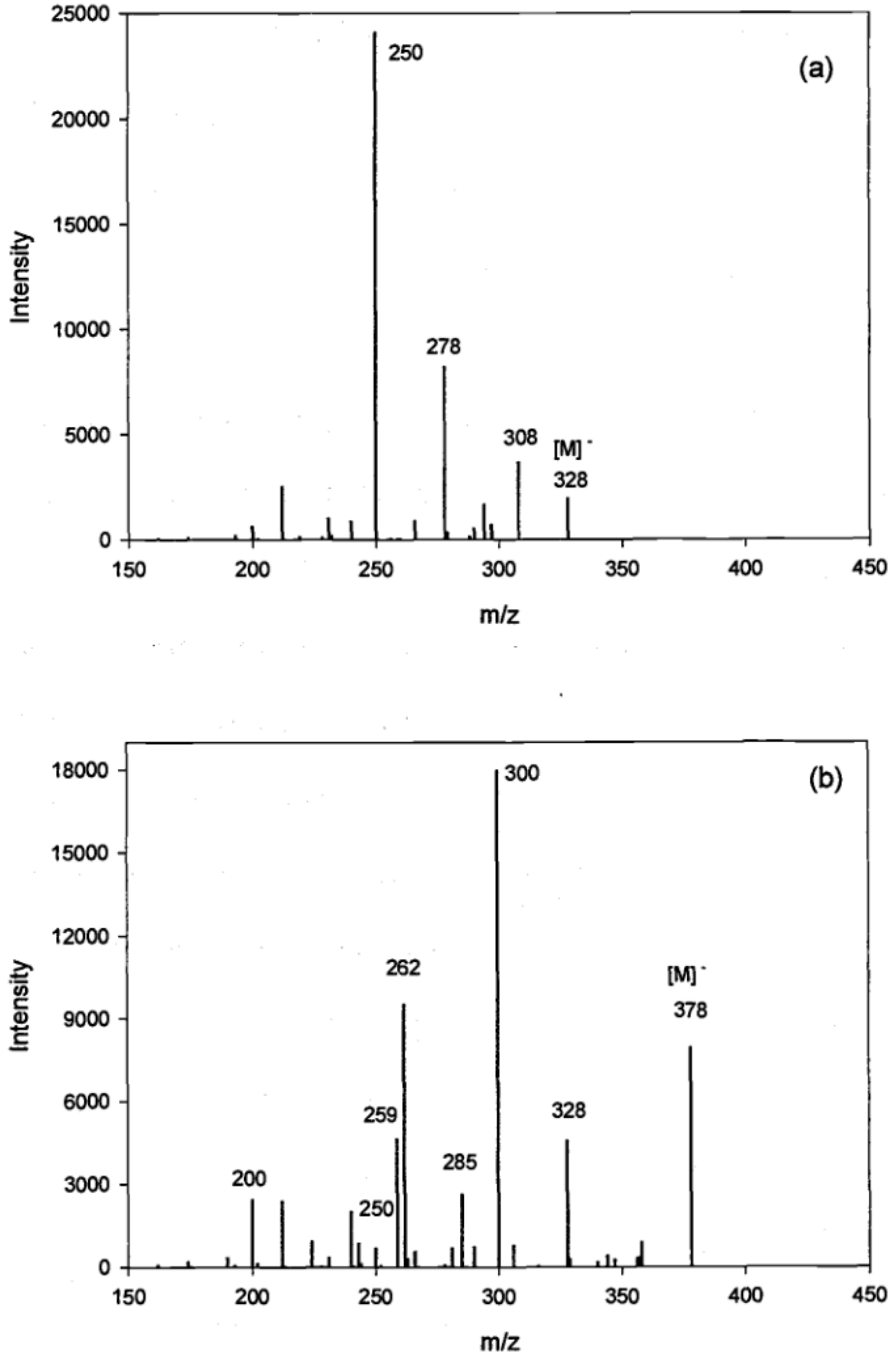

Figure 2.4. (a) ECNI mass spectrum of methyl PFC6 and (b) methyl PFC7.

located downgradient of the fire-training pit, had lower but detectable groundwater concentrations of perfluorocarboxylates. The groundwater collected from a well located north of the fire-training pit, TY22FTA, contained no perfluorinated carboxylates above the detection limit (18 μg/L).

It is not surprising to observe a suite of perfluorinated carboxylates since the raw materials used in the synthesis of perfluorinated organic compounds are mixtures *(3, 19)*. Different ratios of PFC6, PFC7 and PFC8 may result from the use of different AFFF formulations at the two fire-training areas. The observed homologous series consisting of even and odd number perfluorinated carboxylates is indicative of the electrochemical fluorination process used by 3M Co. *(3)*. Other fluorination processes, such as telomerization, produce only even number homologues *(3)*. Because of the proprietary nature of AFFFs, it is not known if perfluorinated carboxylates are present as one of the major surface active agents in AFFF formulations or as unreacted starting materials used in the synthesis of the principal perfluorinated surfactants used in AFFF formulations. In addition, the carboxylates may be combustion, biological or non-biological degradation products of the principal perfluorinated components in AFFF mixtures. Unfortunately, the exact source and history of AFFF applications at the two field sites are unknown, and, therefore, the relationship between the observed perfluorocarboxylate ratios and that of the original AFFF mixtures is unknown.

To the best of our knowledge, very little is known regarding the transport and fate of perfluorocarboxylates in groundwater. Adsorption to sludge at wastewater treatment facilities is considered a significant process for the removal of perfluorinated surfactants during treatment *(3)*. However, detection of perfluorinated carboxylates at the NAS Fallon and Tyndall AFB sites, which have not been used since 1988 and 1992, respectively, is consistent with the view that biodegradation of the long chain perfluorocarbon hydrophobe is unlikely *(6, 9, 19)*. The recalcitrant nature of perfluorinated compounds is attributed in part to the rigidity of the perfluorocarbon chain *(9, 20)* as well as the strength of the carbon – fluorine bond *(3, 9, 21)*.

To the best of our knowledge this is the first definitive identification of perfluorinated carboxylates in groundwater impacted by fire-fighting activity. Further work is needed to determine if additional perfluorinated components are present, such as perfluorooctane sulfonic acid, which is thought to be one of the principle components in some commercial AFFF formulations. In addition, it is of interest to relate the occurrence and distribution of perfluorinated compounds to other site characterization parameters such as dissolved organic carbon, inorganic constituents, and the distribution of co-contaminants and to understand the potential influence of perfluorinated compounds on the biotransformation and transport of other co-contaminants.

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Chapter 3

Occurrence and Distribution of Perfluorinated Surfactants in Groundwater at the Wurtsmith Air Force Base Fire-Training Area Two and KC-135 Crash Site

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Abstract

Perfluorinated surfactants are a major component in aqueous film forming foam (AFFF) formulations, which are used to extinguish hydrocarbon-fuel fires. As a result of past fire-training exercises, as well as response to emergency situations, AFFF-laden wastewater containing fuels, solvents, and other materials directly entered groundwater without prior treatment. Historically, AFFF mixtures containing perfluorinated surfactants were applied at Wurtsmith Air Force Base, MI, including at Fire-Training Area Two and a location where a KC-135 airplane crashed. Perfluorocarboxylate (containing 6 to 8 carbons) concentrations ranging from the detection limit (3 μg/L) to 110 μg/L were measured in groundwater sampled over an extensive well array at Fire-Training Area Two where as none were detected at the airplane crash site. Perfluorocarboxylates detected over 500 m from the source area have an approximate minimum residence time of 5 to 15 years, and provide direct field evidence that this class of perfluorinated surfactants persists under prevailing groundwater conditions. Significantly higher concentrations (e.g., 400-3600 μg/L) of methylene blue active substances which is an indirect measurement of anionic surfactants, indicates that the perfluorocarboxylates are only a small fraction of the anionic surfactant species present in the groundwater. The transport of perfluorocarboxylates in groundwater was not fully characterized such that additional research is needed to characterize the transport of perfluorocarboxylates in groundwater.

Introduction

In fluorinated surfactants, the hydrophobic portion of the surfactant molecule contains fluorine. To classify a surfactant as perfluorinated, all hydrogen atoms in the hydrophobic segment are replaced by fluorine atoms. The substitution of fluorine for hydrogen in fluorinated surfactants differentiates these surfactants from hydrocarbon surfactants. For example, fluorinated surfactants have unique wetting and spreading characteristics that make them better suited than hydrocartbon surfactants in coating, paint, ink, and polish applications *(1, 2)*. Because of the fluorocarbon hydrophobe, fluorinated surfactants are usually more physically, chemically, and biologically stable than hydrocarbon surfactants *(2)*.

Hydrocarbon-fuel fires pose serious threats to life and property, and aqueous film forming foams (AFFFs) are employed to extinguish these types of fires. Fluorinated surfactants are a major component in AFFF formulations *(3)*. Physical characteristics, such as the ability to lower surface tension, aid in the formation of a water film that forms over the surface of a hydrocarbon (e.g., fuel), which makes fluorinated surfactants well-suited for AFFF applications. While the stability of perfluorinated surfactants make them suitable for applications that involve extreme environments, it also leads to their apparent persistence in the environment *(4)*.

Due to the presence of large quantities of flammable liquids, municipal (i.e., fire departments), hydrocarbon-processing industry (i.e., oil refineries), and military sectors utilize AFFFs, with the military comprising 75% of the total market, while the municipal and hydrocarbon-processing industry represents 13% and 5%, respectively *(5)*. In 1985, the United States market for AFFF products (i.e., 3% and 6% concentrates) was 6.8

million L with a total revenue of 10 million dollars in U. S. sales *(5)*. The military was the single largest consumer of AFFF agents in 1985, with consumption totaling 5.1 million L *(5)*.

Currently, the Organization for Economic Cooperation and Development (OECD) classifies perfluorinated C5 to C18 compounds as high-production-volume (HPV) chemicals, where HPV chemicals are those chemicals manufactured or imported in the U.S. in quantities exceeding 1 million pounds *(6)*. This class of chemicals encompasses the perfluorinated and partially-fluorinated surfactants used in AFFF. Data is needed for an environmental and toxicological database that will be developed for HPV chemicals under a voluntary program led by the U.S. Environmental Protection Agency and the Chemical Manufacturer's Association. Planned database entries for the HPV chemical testing program include physical and chemical properties, environmental fate and pathways, fate and environmental distribution assessment, and mammalian toxicity *(7)*; currently much of this information for perfluorinated surfactants is either unknown or unavailable.

In preparation for hydrocarbon-fuel fires, training exercises at military bases often are conducted. As a result, at military emergency response sites and fire-training areas, the repetitive use of AFFF and release of AFFF-laden wastewater to the environment has led to groundwater contamination. Positive identification of one class of perfluorinated surfactants, perfluorocarboxylates, was reported for a limited number of groundwater samples obtained from Naval Air Station (NAS) Fallon, NV, and Tyndall Air Force Base, FL *(4)*. Although not listed as a component in material safety data sheets from AFFF manufacturers, the perfluorocarboxylates were found in some commercially-available

AFFF products (unpublished data). An additional report tentatively identifies perfluorinated compounds in groundwater impacted by fire-training activities at Tyndall Air Force Base *(8)*.

Few publications report the occurrence of perfluorinated surfactants in the environment, primarily due to the lack of sensitive and specific analytical methods. The methylene blue active substances (MBAS) test has been used as an indicator of hydrocarbon anionic surfactants in soils *(9)* and groundwater *(10-14)*. A study at Tyndall Air Force Base used MBAS to qualitatively identify the presence of anionic surfactants in groundwater *(15)*. With the MBAS test, anionic surfactants form ion pairs with the methylene blue cation, which then are extracted into chloroform and determined spectrophotometrically. Reasons for employing the MBAS test include that it is inexpensive, relatively simple, and field-ready. However, the MBAS method is non-specific and does not allow for the detection and quantitiation of the individual surfactants present. In the case of AFFF–contaminated groundwater, a number of anonic surfactants could be present including perfluorinated and non-fluorinated surfactants *(16-18)*. For these reasons, the use of MBAS should be limited to that of a screening tool for environmental samples *(13)*.

This field study addresses the gap in information concerning the occurrence, distribution, and transport of perfluorinated surfactants in the environment, specifically in AFFF-contaminated groundwater at Wurtsmith Air Force Base (WAFB) in Oscoda, MI. The concentrations of perfluorinated carboxylates detected in groundwater impacted by fire-training activities at WAFB provide information regarding the movement and persistence of perfluorinated surfactants in groundwater at Fire-Training Area Two.

Additionally, general chemical indicators, such as specific conductance, total organic carbon (TOC) and MBAS were measured for the study to further delineate the distribution of perfluorinated surfactants in groundwater contaminated by fire-training activities at this site.

Experimental Section

Field Site Descriptions. Wurtsmith Air Force Base is located in northeast Michigan and was decommissioned in June of 1993. Historically, Fire-Training Area Two (FTA-02) (Figure 3.1) at WAFB was used for U. S. military personnel training in fire-fighting procedures. The site was used from 1952-1986 for training exercises that consisted of flooding a fire pad with flammable liquids, igniting the fluids, and subsequently extinguishing the fire with fire-fighting agents including AFFF *(19, 20)*. Before the concrete pad was installed in 1982, as well as an oil/water separator, fuel was dumped directly onto a gravel area and ignited for each fire-training exercise *(19)*.

The aquifer at WAFB is comprised of alternating eolian sands and glacial out wash material that is highly permeable and exhibits hydraulic conductivities on the order of 30 m/day *(21-23)*. The water table is located between 5 and 8 m below land surface. Aquifer solids are comprised of greater than 85% quartz minerals, with organic carbon and inorganic carbon contents below 0.1% and approximately 6.0%, respectively *(21, 22)*. Flow in the sand and gravel upper aquifer is generally eastward towards Lake Van Etten and south-southeast to the Au Sable River discharge areas at average rates of 0.1 to 0.3 m/day *(22-24)*. Direction of groundwater flow at WAFB does not change significantly from season to season *(23)*.

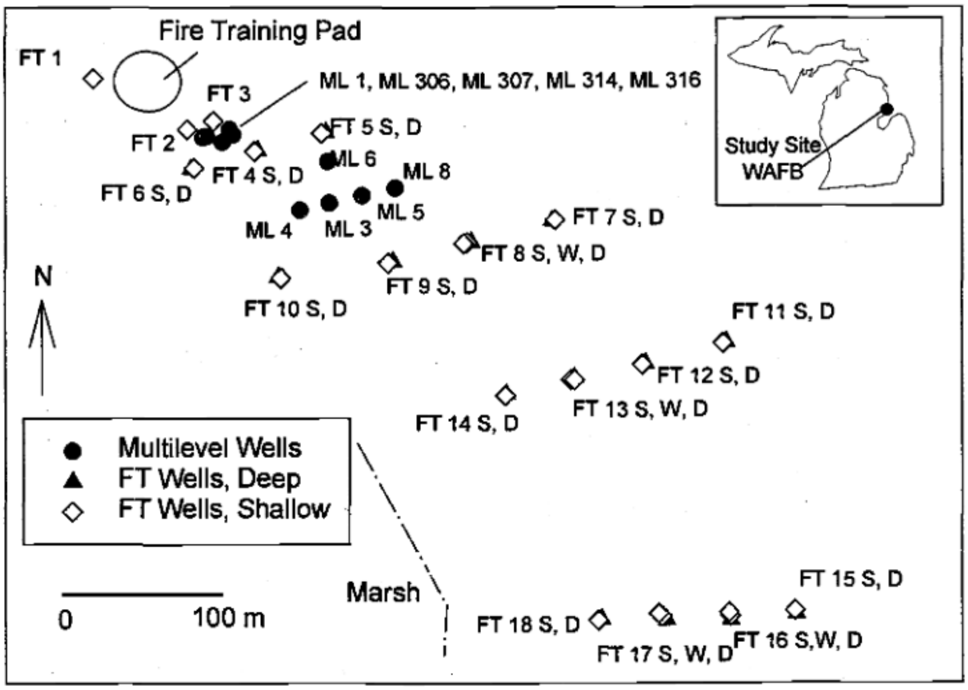

Figure 3.1. Map of Wurtsmith Air Force Base field site Fire-Training Area Two indicating locations of groundwater wells and direction of regional groundwater flow. The study site location is highlighted on the map of Michigan (inset).

At FTA-02, two types of monitoring wells have been installed over time. Monitoring wells with the identifier FT denote iron-cased 10 cm inner diameter wells with 1 to 6 m screened intervals. These wells consist of shallow wells with a screen set 3 to 6 m below the water table, and deep wells with screens set near the base of the aquifer *(23)*. Wells with ML notation describe multilevel sampling wells constructed from 2.5 cm inner diameter PVC casing with 0.3 m screened intervals that are vertically spaced from 0.5 to 2 m *(21)*.

Contaminants detected in WAFB groundwater include petroleum hydrocarbon-fuels, oils, and lubricants; chlorinated solvents (e.g., trichloroethylene and dichloroethylene); combustion products (e.g., napthalene and phenanthrene); and chlorinated aromatic compounds *(22)*. At FTA-02, concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) range from about 20 to 1000 μg/L in the contaminated plume *(21)*.

A second field site, the KC-135 Crash Site, is located near the main runway at WAFB. Contamination by JP-4 fuel resulted from the crash of a KC-135 fuel tanker in October 1988. The crash site had one-time application of AFFFs, which is in contrast to the repeated applications of fire-fighting materials associated with fire-training exercises at FTA-02. Several multilevel sampling wells (2.5 cm inner diameter, 0.3 m screen intervals) have been installed at this site *(25, 26)*.

Sample Collection. Groundwater was sampled from monitoring wells from FTA-02 and the KC-135 Crash Site in November 1998 and June 1999, and February 1998, respectively. As groundwater was removed from the monitoring well it was circulated through a closed cell and continuously monitored for pH and specific conductance (Purge Saver Model FC 2000, QED Environmental Systems, Inc. Ann Arbor, MI). Samples for MBAS and perfluorocarboxylate determinations were collected in high-density polyethylene bottles. Polyethylene was used due to a report that indicated perfluorinated carboxylates adsorb to glass *(27)*. For the FT wells at FTA-02, an additional sample from each well was collected in glass for TOC analysis. Samples were shipped on ice without preservation and stored at 4 °C prior to analysis.

Standards and Reagents for Laboratory Analyses. Standards of perfluorobutyric acid (PFC4) (99%), perfluorooctanoic acid (PFC8) (98%), and the internal standard, 2-chlorolepidine (99%) were purchased from Aldrich Chemical (Milwaukee, WI). Methyl iodide (neat) was used as purchased from Aldrich Chemical. Methylene blue was purchased from Mallinckrodt Chemical (Paris, KY). Standards for pH measurements were purchased from Micro Essential Laboratory (Brooklyn, NY).

Laboratory Analyses. Quantitative perfluorocarboxylate concentrations were measured by the method of Moody and Field *(4)*. Strong anion exchange Empore disks were used to extract perfluorocarboxylates from groundwater. The perfluorocarboxylates were simultaneously eluted from the disks and derivatized to their methyl esters for direct analysis by electron impact (EI) and electron capture negative ionization (ECNI) gas chromatography/mass spectrometry (GC/MS). The detection limit (defined as signal to noise greater than 3) and quantitation limit (defined as signal to noise greater than 10) for perfluorocarboxylates were 3 and 13 μg/L, respectively. Quantification of perfluorohexanoic acid (PFC6) was performed assuming a response factor equal to an equimolar amount of PFC8.

To semi-quantitatively determine MBAS present in groundwater, a 10 mL groundwater sample aliquot was placed in a 50 mL plastic centrifuge tube with 4 mL of chloroform and 0.5 mL of 3mM methylene blue. The mixture was shaken vigorously for 1 min and the aqueous phase removed. The chloroform layer was rinsed by adding 5 mL of deionized water to the tube containing the chloroform and shaking again for 1 min. After removing the wash-aqueous phase, the chloroform layer was measured spectrophotometrically at 652 nm *(28-30)*. Calibration standards were made using PFC8 and MBAS values are reported as μg/L (calculated as PFC8, molecular weight 414). The detection limit of the MBAS analysis was 200 μg/L. Unlike with more conventional MBAS methods, groundwater samples were not acidified to prevent underestimation of perfluorocarboxylates. For example, acidification protonates PFC8, which has a pKa of 2.8; the free acid partitions into the chloroform layer without the MBAS cation and therefore goes undetected. At the pH of the groundwater at FTA-02 which ranged from 5.5 to 8.6 (Table 3.1). MBAS concentrations measured potentially represent the cumulative concentration of all anionic surfactant species present. The response of amphoteric surfactants, which are known to occur in some AFFF formulations, to MBAS is not well understood.

Samples were analyzed for non-volatile total organic carbon using a TOC analyzer (Model Dohrman DC-190, Rosemount Analytical, Santa Clara, CA). The TOC analyzer separately measures total carbon (TC) and inorganic carbon (IC); the TOC concentration is obtained as the difference between TC and IC. The detection limit of the TOC method was 1.0 mg/L. Because perfluorinated surfactant are reportedly stable to oxidants *(2)*, standards of PFC4 and PFC8 were analyzed for TOC, where PFC4 was completely oxidized and PFC8 gave 85% of the expected response (unpublished data).

Results and Discussion

Fire-Training Area Two Groundwater Samples. At FTA-02, thirty groundwater samples collected from ML wells (multilevel wells screened over 0.3 m interval made of PVC materials) and thirty-eight groundwater samples collected from FT wells (single depth iron-cased wells screened over a 1 to 6 m interval) were evaluated. The data collected for some of the multilevel monitoring wells, ML 306, ML 307, ML 314, and ML 316 (Figure 3.1), were omitted for this study because these wells are thought to be influenced by a bioreactor-remediation process ongoing at FTA-02, which re-injects treated water near these ML wells. The ML samples were collected in November 1998 and the FT samples were collected in June 1999. Although the wells were sampled several months apart, the groundwater velocity was used to calculate travel distance over that elapsed time period. The small distance (approximately 20 m) indicates that combining the data from the two different sampling times does not affect interpolation of the data.

Because one class of perfluorinated surfactants, perfluorocarboxylates, was detected in a limited number of groundwater samples from two other U. S. military fire-training areas *(4)* as well as in commercial AFFF mixtures (unpublished data), the groundwater from FTA-02 was analyzed for these specific compounds. The groundwater samples from FTA-02 had total perfluorinated carboxylate concentrations ranging from below the detection limit (3 μg/L) to 110 μg/L (Table 3.1). Perfluorocarboxylates containing 6 (PFC6), 7 (PFC7) and 8 (PFC8) carbons in the perfluorocarbon chain were observed in 38 of the 68 groundwater samples analyzed.

The highest concentrations of perfluorocarboxylates were observed in groundwater collected from FT 2 and FT 3 which are two monitoring wells located close to the fire-training pad (Figure 3.2a), an established source point for jet fuel components, chlorinated solvents, and AFFF *(22)*. Groundwater collected from wells located down gradient of FT 2 and FT 3 wells (and the fire-training pad), had lower concentrations of perfluorocarboxylates (less than the detection limit to 26 μg/L). Groundwater collected from FT 18, which is 500 m from the fire-training pad, had total perfluorocarboxylate concentrations of 10 μg/L. Groundwater from a background well at WAFB contained no detectable perfluorinated carboxylates (less than 3 μg/L), indicating that the occurrence of perfluorocarboxylates in groundwater downgradient from the fire-training pad at FTA-02 is the result of AFFF applications and discharge during fire-training exercises.

In comparison, the total perfluorocarboxylate concentrations measured at FTA-02 are generally lower than those previously observed at Tyndall Air Force Base and NAS Fallon (124 to 298 μg/L and 54 to 7090 μg/L, respectively) *(4)*. The differences in total concentrations of perfluorocarboxylates observed in groundwater are apparent when comparing the concentrations observed near the source at three military sites. For example, the total perfluorocarboxylate concentration in groundwater sampled near the source at NAS Fallon was 7090 μg/L where groundwater concentrations observed near the source at Tyndall Air Force Base and WAFB were 298 and 110 μg/L, respectively *(4)*. Additionally, the frequency with which fire-training tests were conducted at the individual sites undoubtedly varied and is poorly documented. Over several years, testing conducted on a weekly basis versus a monthly basis could cause the observed differences in groundwater perfluorocarboxylate concentrations.

The dominant perfluorocarboxylate detected in the FTA-02 groundwater, PFC8, generally accounted for greater than 90% of the total perfluorocarboxylate concentration and is consistent with the relative abundance of PFC8 (93%) observed at the NAS Fallon fire-training facility *(4)*. Qualitative results from the analysis of commercial AFFF products indicate that PFC8 is the dominant perfluorocarboxylate homologue (65%) where PFC7 and PFC6 comprise 10% and 25%, respectively, of total perfluorocarboxylates (unpublished data). Perfluoroheptanoic acid (PFC7) was observed in a few of the FTA-02 groundwater samples and only at the detection limit (3 μg/L). Perfluorohexanoic acid concentrations represented less than 10% of the total perfluorocarboxylate concentration. This is in contrast to Tyndall AFB groundwater where PFC6 was the most abundant perfluorocarboxylate. Electron capture negative ionization GC/MS was used to confirm the identity of PFC6, PFC7 and PFC8. The presence of PFC6 to PFC8 homologues of perfluorocarboxylates in groundwater from three U. S. military sites indicates the potential for using these unique chemicals as markers of AFFF-contaminated groundwater.

Table 3.1. Summary of groundwater data from FTA-02 sampled wells in November 1998 and June 1999.

Parameter (units)	Range
pH	5.5-8.6
Total Perfluorocarboxylates (μg/L)[3]	d. l.-110
Methylene Blue Active Substances (μg/L)[2]	400-3600
Total Organic Carbon (mg/L)[1]	d. l.–69
Specific Conductance (μS/cm)	110–810

[1] Total organic carbon detection limit is 1 mg/L.

[2] MBAS detection limit is 200 μg/L and is reported as equivalent to PFC8.

[3] Total perfluorocarboxylate concentrations reported represent the summation of PFC6 and PFC8 concentrations. The detection limit is 3 μg/L.

The observation of a suite of perfluorocarboxylates was expected since the raw materials (i.e., carboxylates) used in the synthesis of perfluorinated organic compounds are mixtures *(2, 31)*. The homologous (even and odd number) series of perfluorinated carboxylates is indicative of the electrochemical fluorination synthesis process *(4, 32)*. Furthermore, the electrochemical fluorination technique is employed by the 3M Company, which has supplied AFFF agents to the U. S. military for the past two decades *(3, 4)*. In contrast, telomerization, one alternative technique for fluorocarbon synthesis, produces only even-numbered carbon perfluorocarbons.

In addition to perfluorocarboxylates, other anionic surfactants such as alkylsulfates and perfluoroalkylsulfonates are present in commercial AFFF formulations *(16-18)*. Because our GC/MS method does not detect additional anionic species, we used MBAS as a semi-quantitiative tool to detect all anionic surfactants (of which perfluorocarboxylates are one component) present in FTA-02 groundwater. The MBAS concentrations measured in groundwater from FTA-02 ranged from 400-3600 μg/L for all wells (Table 3.1). As was the case with perfluorocarboxylates, high MBAS concentrations were predominantly centered around the fire-training pad area (Figure 3.2b) while lower MBAS concentrations extended downgradient from the source. The MBAS concentrations above background (400 μg/L) indicate the presence of additional anionic surfactant components associated with past AFFF applications at FTA-02. The observation of anionic surfactant species in groundwater several hundred meters downgradient from the fire-training pad area indicates that the unidentified anionic

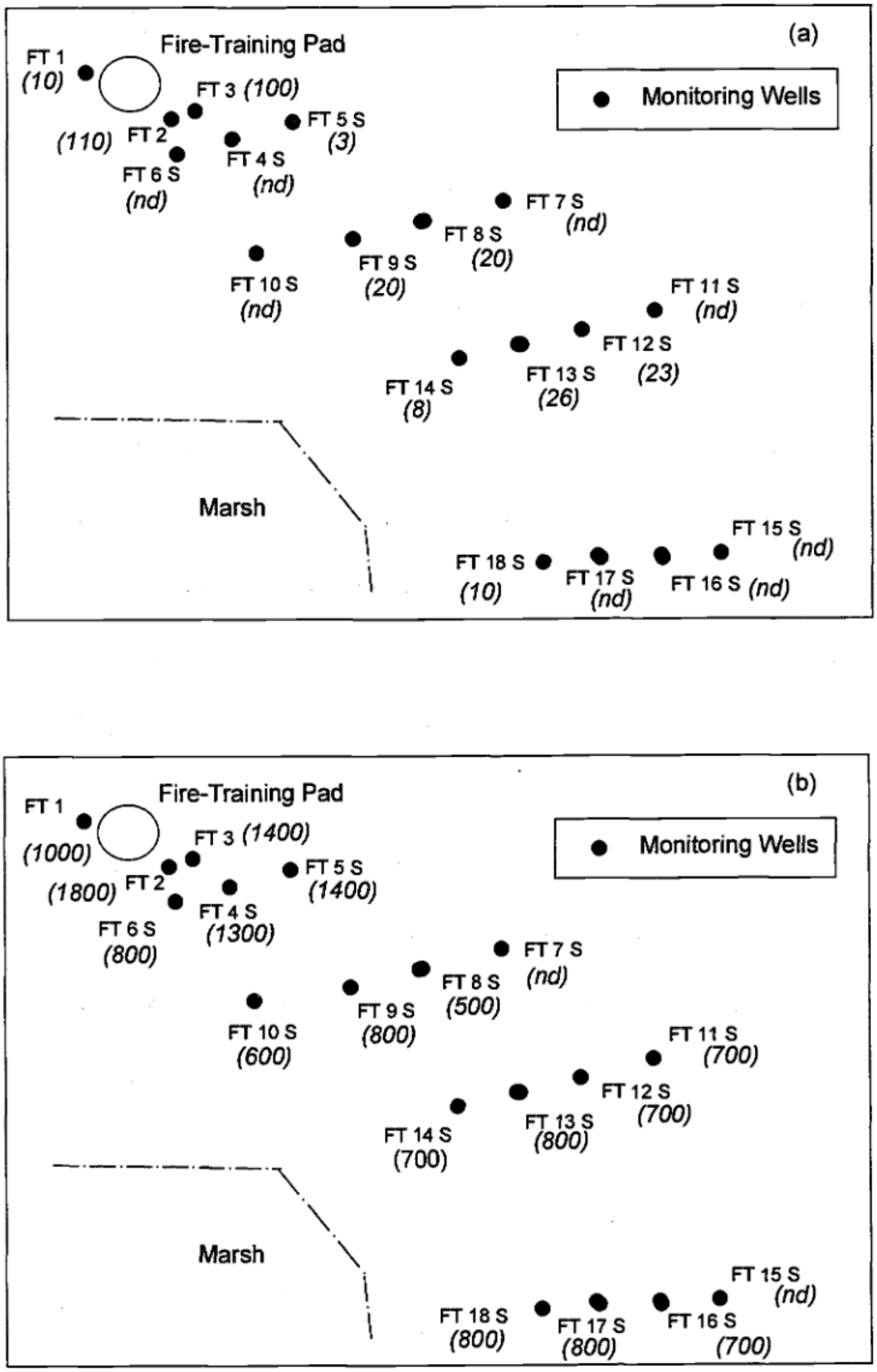

Figure 3.2. Distribution of (a) perfluorocarboxylate concentrations (μg/L) and (b) methylene blue active substances concentrations (μg/L) in shallow FT monitoring wells.

surfactants are transported by WAFB groundwater. The MBAS concentrations measured in groundwater at FTA-02 are of similar magnitude in concentration to those reported for sewage contaminated groundwater, which ranged from 300 to 2300 μg/L *(13)*.

The perfluorocarboxylate concentrations observed in groundwater from FTA-02 are significantly lower than the MBAS concentrations indicating that perfluorocarboxylate concentrations account for only a fraction of the anionic surfactants present in the groundwater at FTA-02. For example, the perfluorocarboxylates account for 6.1% and 1.3% of the MBAS concentrations measured in groundwater from FT 2 and FT 18, respectively. Liquid chromatography/mass spectrometry (LC/MS) was used to tentatively identify an additional class of perfluorinated surfactants, perfluorooctane sulfonate, in groundwater from FTA-02 *(33)*. Perfluoroalkylsulfonates are one of the major perfluorinated surfactant classes present in commercial AFFF formulations, which is indicated in product material safety data sheets. Additional method development is necessary to quantify perfluorooctane sulfonate and to identify other classes of fluorinated surfactants (such as amphoteric) potentially present in AFFF-contaminated groundwater.

Total organic carbon measurements were made to quantify all carbon containing compounds in the groundwater water at this site, which includes volatile contaminants (e.g., fuel components and chlorinated solvents) and non-volatile contaminants (e.g., AFFF components, including fluorocarbon- and hydrocarbon-based surfactants). The TOC values for the groundwater sampled from the wells sampled at FTA-02 ranged from the detection limit (1 mg/L) to 69 mg/L (Table 3.1) with high TOC values (i.e., 69 mg/L and 55 mg/L) close to the fire-training pad. The groundwater from the background well had a TOC value of 2 mg/L. Interestingly, perfluorocarboxylate and MBAS concentrations comprised only a small fraction of the measured TOC values. For example, near the fire-training pad perfluorocarboxylate and MBAS concentrations represent 0.2% and 2%, respectively, of the TOC concentration measured in monitoring well FT 2.

Despite a minimum of 13 years of inactivity at this site, significant concentrations of perfluorocarboxylates, MBAS, and TOC are still detected near the source. The soils in the vicinity of the fire-training pad could have a sorbed organic solid phase or a separate liquid phase. For example, FTA-02 sediments have total petroleum hydrocarbon concentrations of 13,650 mg/kg between 4.5 and 5.7 m below the ground surface *(34)*. This is likely a result of fire-training exercises at FTA-02 where unburned fuel and other priority pollutants as well as AFFF entered the subsurface. In addition, at several locations near the pad, a discontinuous layer of black, tar-like substance was observed at 0.3 to 0.9 m below the land surface. This layer is approximately 0.1 m thick, and is detected downgradient as far as monitoring well FT 4 (Figure 3.1) *(19)*, which is approximately 50 meters from the fire-training pad. A free/residual non-aqueous phase liquid (NAPL) plume comprised of jet fuel components and/or chlorinated solvents has been suggested by others to be present in the fire-training pad area *(24)*. The association, if any, between the perfluorinated and non-perfluorinated surfactants with NAPL is unknown.

In order to make a judgment about the transport of perfluorocarboxylates as well as other anionic perfluorinated surfactants in groundwater at FTA-02, a commonly used approach is to compare the distribution of perfluorinated compounds to that of a conservative plume component such as those that are measured by specific conductance. Specific conductance measurements at FTA-02 ranged from 110 to 810 μS/cm (Table 3.1) with the highest values measured near the fire-training pad area. The specific conductance of groundwater sampled from a well representing background conditions was 250 μS/cm. The distribution of specific conductance at FTA-02 (Figure 3.3) is consistent with previous reports of groundwater contamination at this site *(19, 21, 22, 34)* and indicates that the plume of contaminants may be turning to the southwest direction, away from FT wells 15-18 (Figure 3.1), and discharging into a marshy area. Unfortunately, no groundwater or surface water samples were collected from the marsh area for this investigation.

Because the terminus of the contaminant plume is undefined at this field site, the spatial relationship of perfluorocarboxylates to specific conductance can not be evaluated and therefore it is difficult to estimate perfluorocarboxylate transport relative to conservative components of the plume. If a well-defined terminus of the plume had been present, the transport distance of measured parameters combined with the time of operation of activities at the training area could be used to estimate flow rates as well as retardation factors for perfluorocarboxylates (and MBAS). It is known that perfluorocarboxylates present in groundwater 500 m from the fire-training area is approximately 5-15 years old assuming a 0.1-0.3 m/day groundwater velocity *(22-24)*.

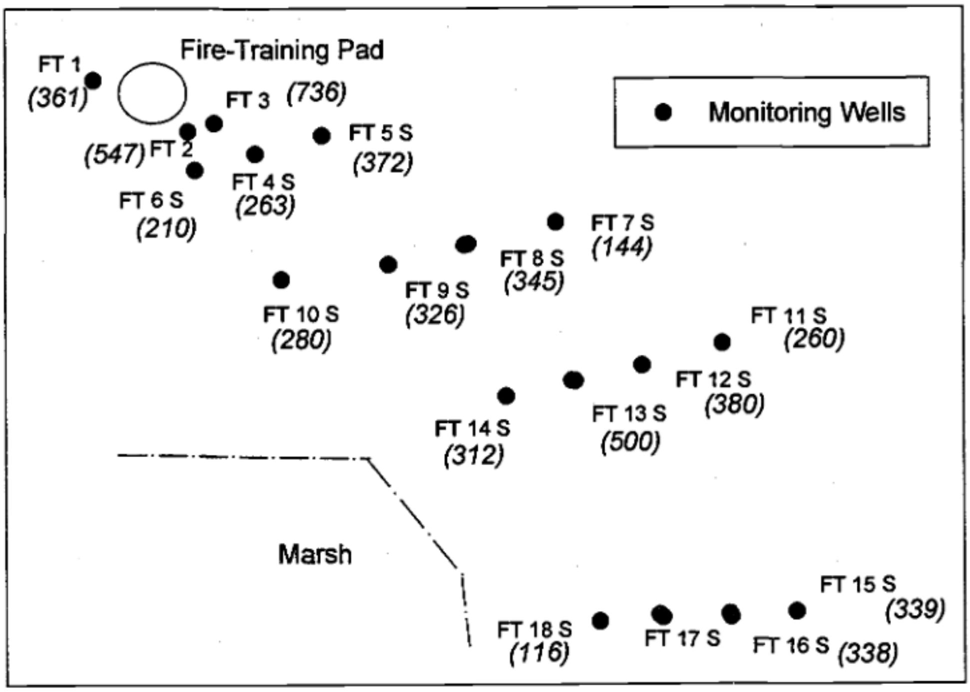

Figure 3.3. Distribution of specific conductance measurements (μS/cm) in shallow FT monitoring wells.

A minimum residence time of 5 years for perfluorocarboxylates in groundwater indicates the resistance of perfluorinated compounds to degradation under the prevailing groundwater conditions at this site. If perfluorocarboxylates moved conservatively away from the source, the edge of the contaminant plume should be 475-1425 m downgradient. However, the groundwater discharges to a marshy area at approximately 500 m from the fire-training pad area.

To accurately describe the transport of perfluorinated surfactants in groundwater at FTA-02 an independent measure of retardation such as an *in-situ* tracer test could be performed at this site. A single-well push-pull test can provide *in-situ* transport information *(35)*. At a different field site located in Corvallis, OR, a single-well push-pull test was performed with perfluorooctane sulfonate and bromide as the conservative tracer. Identical breakthrough curves for bromide and perfluorooctane sulfonate were obtained indicating that perfluorooctane sulfonate was conservatively transported *(3)*. Because conservative transport of perfluorooctane sulfonate was observed in that field study, perfluorinated surfactants also may be conservative tracers for AFFF-contaminated groundwater. Clearly more research is required to fully investigate the transport behavior of perfluorinated surfactants.

Implications. Perfluorocarboxylate concentrations measured at FTA-02 as well as at other U. S. military sites, indicate that this class of specialty chemicals is a potentially unique tracer for groundwater impacted by repetitive fire-training exercises. The detection of perfluorocarboxylates at the NAS Fallon and Tyndall Air Force Base military sites, which have not been used since 1988 and 1992, respectively, *(4)* as well as the detection of perfluorocarboxylates at FTA-02 after 13 years of fire-training inactivity is consistent with the widely-held AFFF-industry view that biodegradation of the long-chain perfluorocarbon hydrophobe does not occur *(31, 36-39)*. The strength of the carbon–fluorine bond *(2, 37, 40)* as well as the rigidity of the perfluorocarbon chain *(37, 41)* are thought to contribute to the recalcitrant nature of perfluorinated compounds.

In contrast to repetitive application of AFFF at fire-training areas such as FTA-02, the site of a KC-135 airplane crash at WAFB had a one-time application of fire-fighting agents. High TOC values were observed in groundwater from monitoring wells located closest to the crash site/point source, and are attributed to the estimated 3,000 gallons of JP-4 fuel *(25, 26)* spilled at the site as a result of the crash. Alternatively, perfluorocarboxylates as well as MBAS-responsive components were not detected in the sampled groundwater; this is not surprising since the impacted area had a one-time application of fire-fighting materials over ten years ago. By evaluating groundwater from these two different field sites, there appears to be little impact from a single application of AFFF (i.e., an emergency response situation) relative to long-term repetitive applications for training purposes at FTA-02. Because hydrocarbon-fuel fires pose a serious threat to life and property, the issue of fire safety must be balanced against the risks that these products, particularly perfluorinated surfactants, potentially pose to the environment.

Three U. S. military sites *(4)* have been identified to have the presence of what appears to be a biologically-stable specialty chemical. The occurrence of perfluorocarboxylates, and potentially other perfluorinated surfactants raises issues for military bases and other facilities where fire-training exercises are conducted routinely and wastewater is disposed of improperly. Because perfluorinated surfactants co-occur with other pollutants (e.g., fuel components, solvents, etc.) in groundwater, it is important to determine if perfluorinated surfactants affect the transport and biodegradation of other contaminants. Additionally, research is needed to further examine the possible presence of NAPLs and their influence of AFFF components on the solubility and transport of NAPLs in the subsurface at WAFB.

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Chapter 4

Summary

Aqueous film forming foam formulations are used to extinguish hydrocarbon-fuel fires that pose a serious threat to life and property. In preparation for such fires, training exercises are often conducted. Because of past fire-training exercises at military bases, as well as response to emergency situations, AFFF-laden wastewater containing fuels, solvents, and other materials directly entered groundwater without prior treatment, and has led to groundwater contamination. Fluorinated surfactants are a unique class of chemicals present in AFFFs that are directly discharged to the environment. Fluorinated surfactants differ significantly from hydrocarbon surfactants such that direct analogies can not be drawn between the two types of surfactants. The information contained in this thesis addresses the gap in knowledge regarding the occurrence, distribution, and transport of perfluorinated surfactants in the subsurface.

An analytical method based on the use of solid-phase extraction and followed by an in-vial elution and derivatization was used to quantitatively determine a suite of perfluorinated carboxylates (PFC6 to PFC8) in groundwater. Concentrations of perfluorocarboxylates ranged from 125 to 7,090 μg/L in a limited number of groundwater samples collected from NAS Fallon, NV, and Tyndall AFB, FL.

Historically, AFFF mixtures were applied at Wurtsmith Air Force Base (Oscoda, MI), at various locations including the Fire-Training Area Two and at the site of an airplane crash. Total perfluorocarboxylate concentrations (PFC6 to PFC8) ranging from near the detection limit (3 μg/L) to 110 μg/L were measured in groundwater sampled from an extensive well array at Fire-Training Area Two. Perfluorocarboxylate concentrations detected over 500 m from the source area have an approximate minimum residence time of 5 to 15 years. The observed methylene blue active substances concentrations indicate that perfluorocarboxylates are only a small fraction of the anionic surfactants present in the groundwater. This finding highlights the need for further analytical method development in order to fully characterize the contaminated groundwater.

In contrast to the repetitive application of AFFF at fire-training areas such as Fire-Training Area Two, the airplane crash site at Wurtsmith Air Force Base had a one-time application of fire-fighting agents. Not surprisingly, the MBAS concentrations were below the detection limit (0.2 mg/L) and total perfluorocarboxylate concentrations also were below the detection limit (0.3 μg/L). The analysis of groundwater from two sites with different AFFF application histories indicates a disparity between a single deployment of AFFFs (i.e., an emergency response situation) and repetitive applications for fire-training purposes.

The observed suites of perfluorocarboxylates containing 6 to 8 carbons in groundwater from the three military sites is consistent with the manufacture of these specialty chemicals, since the raw materials used in the synthesis of perfluorinated organic compounds are themselves mixtures. The specific ratios of perfluorohexanoic, perfluoroheptanoic, and perfluorooctanoic acids observed at the three military sites may be the result of different AFFF formulations used at each of the sites. The observed homologous series consisting of even and odd number perfluorinated carboxylates is indicative of the electrochemical fluorination process. In contrast, other fluorination processes, such as telomerization, produce only even-numbered homologues. The detection of perfluorinated carboxylates at NAS Fallon, NV, Tyndall Air Force Base, FL, and Wurtsmith Air Force Base, MI, military sites that have not been used since 1988, 1992, and 1986, respectively, is consistent with the view that long chain perfluorocarbon hydrophobes do not biodegrade. Because perfluorocarboxylates persist in the environment, they may serve as unique tracers of groundwater impacted by repetitive fire-training exercises.

Because commercial formulations of AFFF are complex mixtures, the employment of these mixtures in fire-training situations introduces both priority and non-priority pollutants into the environment. Questions remain regarding how chromatographic separation during transport affects these complicated mixtures. Because perfluorinated surfactants persist in the environment, they may impact the biogeochemical processes that affect the distribution and bioavailability of co-contaminants. Moreover, the effect, if any, that biodegradation of AFFF components has upon the microbial ecology and activity of the subsurface is unexplored. Finally, the need for additional analytical methods to measure perfluorinated surfactants is necessary to address questions about the occurrence, environmental behavior, and impact of these classes of specialty chemicals.

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Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity

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Abstract:

Perfluorinated surfactants are used in aqueous film forming foam (AFFF) formulations, which are used to extinguish hydrocarbon-fuel fires. Virtually nothing is known about the occurrence of perfluorinated surfactants in the environment, in particular, at fire-training areas and emergency response sites where AFFF entered groundwater without prior treatment. Strong anion exchange Empore disks were used to extract perfluorocarboxylates from groundwater collected from fire-training facilities located on Naval Air Station Fallon, NV, and Tyndall Air Force Base, FL. The carboxylates were simultaneously eluted from the disks and derivatized to their methyl esters for direct analysis by gas chromatography/mass spectrometry. Perfluorocarboxylates containing six to eight carbons were detected in groundwater collected from the two field sites with total concentrations ranging from 125 to 7090 μg/L. The detection of perfluorocarboxylates at field sites after 7-10 years of inactivity indicates their potential utility as markers for delineating groundwater impacted by fire-fighting activity.

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What is significance of findings?
Is this a bad thing?

Test site is trg ground.

Significance is it was funded by EPA. Indicates their getting interested in AFFF.

7/99

Determination of Perfluorocarboxylates in Groundwater Impacted by Fire-Fighting Activity

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Perfluorinated surfactants are used in aqueous film forming foam (AFFF) formulations, which are used to extinguish hydrocarbon–fuel fires. Virtually nothing is known about the occurrence of perfluorinated surfactants in the environment, in particular, at fire-training areas and emergency response sites where AFFF entered groundwater without prior treatment. Strong anion exchange Empore disks were used to extract perfluorocarboxylates from groundwater collected from fire-training facilities located on Naval Air Station Fallon, NV, and Tyndall Air Force Base, FL. The carboxylates were simultaneously eluted from the disks and derivatized to their methyl esters for direct analysis by gas chromatography/mass spectrometry. Perfluorocarboxylates containing six to eight carbons were detected in groundwater collected from the two field sites with total concentrations ranging from 125 to 7090 μg/L. The detection of perfluorocarboxylates at field sites after 7–10 years of inactivity indicates their potential utility as markers for delineating groundwater impacted by fire-fighting activity.

Introduction

Aqueous film forming foams (AFFF) are complex mixtures of surfactants and other components used to extinguish hydrocarbon–fuel fires that occur at fire-training sites as well as in emergency situations. Aqueous film forming foams have been commercially available for fire-fighting applications since their development by the United States Navy and 3M Co. in the mid-1960s (*1*). At fire-training areas that routinely used AFFF mixtures and military emergency response sites, AFFF-laden wastewater that entered surface water and groundwater without treatment has led to groundwater and soil contamination. For example, perfluorinated compounds were tentatively identified in groundwater impacted by fire-training activities at Tyndall Air Force Base (*2*). Unfortunately, definitive identifications of the perfluorinated compounds were not reported.

Commercial AFFF mixtures are proprietary in nature and typically contain fluorinated and nonfluorinated surfactants (*1, 3–5*). Due to the proprietary nature of AFFF formulations, the chemical structures of the actual perfluorinated surfactants used in commercial AFFFs are not known outside the companies that manufacture them (*5*). Moreover, the analysis of anionic perfluorinated surfactants that are known to occur in AFFF formulations (*6*) is problematic because the surfactants are nonvolatile and may not contain chromophores. As a result, analytical methods for AFFF formulation components are lacking, and therefore it is difficult to assess their occurrence, fate, and transport in AFFF-contaminated groundwater. Because perfluorinated surfactants co-occur with other pollutants (e.g. fuel components, solvents, etc.) in groundwater, it is important to determine if perfluorinated surfactants affect the transport and biodegradation of other contaminants. Free and emulsified oil, fuel, and AFFF components were shown to adversely affect activated sludge processes (*6, 7*) and the performance of anaerobic sludge digestors (*8*) in wastewater treatment facilities. For this reason, perfluorinated surfactants may have an adverse affect on groundwater microbial populations and their ability to degrade co-contaminants present in AFFF-contaminated groundwater.

In addition to fluorinated surfactants use in fire-fighting foams, they are also utilized in herbicides and insecticides, cosmetics, greases and lubricants, and adhesives (*3*). Fluorinated carboxylic acids of industrial significance include perfluorooctanoic acid (PFC8) and perfluorodecanoic acid (PFC10) (*9*). There is concern regarding the potential toxicity of perfluorinated carboxylic acids. An in vivo study of rat liver response to PFC10 indicated the rapid onset of a low-level heptatotoxicity but no detectable damage to the DNA (*10*). Perfluorodecanoic acid and PFC8 have been found to inhibit gap junction intercellular communication in rat liver epithelial cells (*11*) and may be involved in tumor promotion (*9*).

In this paper, we describe the isolation, identification and quantification of perfluorinated carboxylates in groundwater impacted by fire-training activities at Naval Air Station (NAS) Fallon, NV, and Tyndall Air Force Base, FL. The development of analytical methods is necessary before investigating the occurrence and distribution of perfluorinated surfactants in AFFF-contaminated groundwater and their effect on co-contaminant transport and biodegradation.

Experimental Section

Standards and Reagents. Standards of PFC8 (98%), perfluorododecanoic acid (PFC12) (95%), and the internal standard, 2-chlorolepidine (99%), were purchased from Aldrich Chemical (Milwaukee, WI). Methyl iodide (neat) was used as purchased from Aldrich Chemical.

Field Sites and Sample Collection. From the mid-1950s to 1988, the crash crew training area at NAS Fallon, NV (Figure 1a), was used to conduct fire-training activities, which consisted of flooding a fire pit with flammable liquids, igniting the fluids, and subsequently extinguishing the fire with fire-fighting agents including AFFF (*12*). For a typical training exercise, approximately 75–100 L of AFFF concentrate were diluted with 1200–3200 L of water according to specifications (3% or 6% solution) and subsequently employed. During the years of activity at the NAS Fallon site, training exercises occurred on a weekly to monthly basis. At the NAS Fallon site, groundwater samples were collected from four monitoring wells located within a 120 m radius of the fire pit where the water table is located between 2 and 3 m below the land surface.

The Tyndall Air Force Base Fire-Training Area FT-23 was used from 1980 to 1992 for similar activities (Figure 1b) (*13*). Four groundwater samples were obtained from wells surrounding the fire-training area; the water table is located between 1 and 2 m below the land surface. All samples were collected in high-density polyethylene brown bottles because

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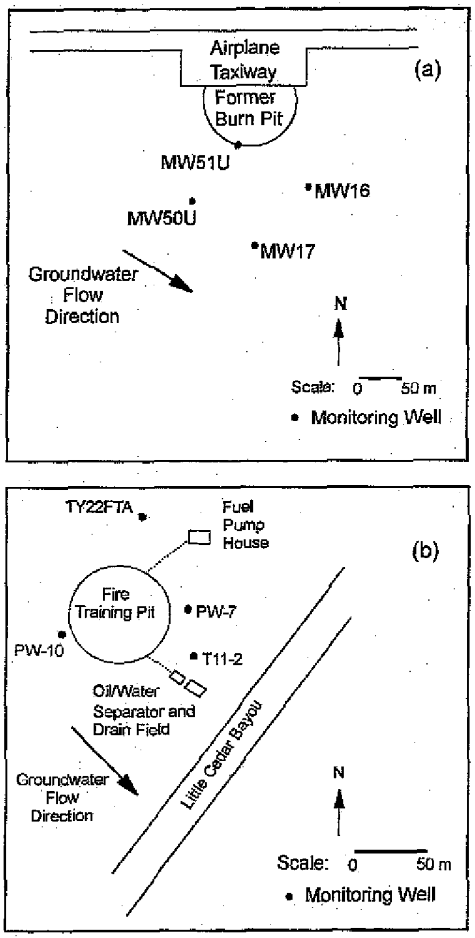

FIGURE 1. Map of (a) Naval Air Station Fallon and (b) Tyndall Air Force Base field sites indicating location of groundwater wells and direction of regional groundwater flow.

perfluorinated carboxylates adsorb to glass (*14*). Samples were shipped on ice without preservation and stored at 4 °C prior to analysis.

Solid-Phase Extraction and Derivatization. Samples (55–200 mL) were extracted through 25 mm strong anion exchange (SAX) disks in a manner similar to that described by Field and Reed (*15*) with the exception that the SAX disks were pretreated prior to use to remove interfering disk impurities. Pretreatment consisted of soaking the disks in 12 mM HCl/acetonitrile for 2 days after which the disks were soaked in pure acetonitrile for several hours. Just prior to use, the disks were rinsed with a minimum of 350 mL of deionized water in order to sufficiently rinse the HCl from the disks and wet them prior to passing groundwater samples through them. Samples (55–200 mL) were passed through the disks under full vacuum, and the disks were then allowed to dry. The disks containing the exchanged analytes were placed in a 2 mL autosampler vial together with 1 mL of acetonitrile, 51.2 μg of internal standard, and 100 μL of methyl iodide. When heated at 80 °C for 1 h, the acids were simultaneously eluted from the disk and derivatized to their methyl esters.

Spike and Recovery. Spike and recovery experiments were performed to determine the precision and accuracy of the SAX disk extraction and in-vial elution method. A set of experiments was performed on groundwater samples from NAS Fallon MW 50U and MW 17 that had been previously determined to contain neither PFC8 nor PFC12 above detection. Duplicate groundwater samples from wells MW 50U and MW 17 were spiked to contain a final concentration of 1240 μg/L of PFC8 and 560 μg/L of PFC12.

Standard addition analyses were performed with NAS Fallon groundwater samples that contained measurable quantities of PFC8; the samples did not contain PFC12 above detection. Known amounts of PFC8 were added to samples to give a final concentration twice that of the background concentration. For example, groundwater from MW 51U and MW 16, which contained background concentrations of 6570 and 460 μg/L, respectively, were spiked to give final concentrations of 12900 and 1000 μg/L of PFC8, respectively. Each sample also was spiked with 56.4 μg of PFC12. To determine the detection limit of the method, single samples of groundwater that contained no perfluorinated carboxylates above detection were spiked to give a range of final PFC8 concentrations from 18 to 54 μg/L.

Gas Chromatography/Mass Spectrometry. Extracts were analyzed using a Hewlett-Packard Model 5890 Series II Plus gas chromatograph (GC) equipped with a 30 m × 0.32 mm × 4.00 μm SPB-1 SULFUR column (Supelco Inc., Bellefonte, PA). An injection volume of 1 μL was used under splitless conditions with an injector temperature of 200 °C. The GC oven temperature was initially held for 6 min at 60 °C, increased by 6 °C/min to 190 °C, increased further by 30 °C/min to 270 °C, and then held for 5 min.

Quantification of perfluorocarboxylate methyl esters was performed using a Hewlett-Packard Model 5972 mass selective detector operated in electron impact (EI) mode (70 eV). The mass selective detector was operated in full scan (50–450 amu) mode and in selected ion monitoring (SIM) mode using a dwell time of 100 ms for each ion. The scanning mode was used for qualitative identification while SIM mode was used for quantification. The ions of m/z 131 $[C_3F_5]^+$, m/z 169 $[C_3F_7]^+$, and m/z 219 $[C_4F_9]^+$, which are characteristic fragments of perfluorocarbons (*16–18*), were used to identify and quantify the methyl esters of perfluorohexanoic acid (PFC6), perfluoroheptanoic acid (PFC7), PFC8, and PFC12. The internal standard, 2-chlorolepidine, was quantified with the ions at m/z 177 and m/z 115.

The identification of perfluorocarboxylate methyl esters was confirmed by electron capture negative ionization (ECNI) GC/MS, which gave unique molecular ions for each of the perfluorinated carboxylate methyl esters (e.g. m/z 328 for PFC6, m/z 378 for PFC7, m/z 428 for PFC8, and m/z 628 for PFC12). These measurements were performed with a Varian 3400 gas chromatograph interfaced with a Finnigan Model 4023 mass spectrometer. Methane was used as the reagent gas, and the mass spectrometer was operated in full scan mode (100–650 amu). The gas chromatograph was operated with a column and temperature program identical to that used for the EI GC/MS.

Initially, samples prepared in deionized water were used as the matrix for constructing calibration curves, and standard recoveries were low. However, when samples prepared in tap water, which contains inorganic cations and anions, were used as the matrix for constructing calibration curves, quantitative recovery of standards was obtained. It is proposed that the 350 mL of deionzed water does not sufficiently rinse the disks of residual HCl and tap water is required to completely rinse the disks and obtain quantitative recovery of standards. Therefore, calibration curves for quantification of PFC8 were constructed by passing 100 mL of tap water samples that had been spiked with 3.6–1080 μg of PFC8 through 25 mm SAX disks and derivatizing the acids to their methyl esters using the in-vial elution and derivatization technique. The calibration curve for PFC12 was constructed in a similar manner by adding 7.5–113 μg of PFC12 standard to 100 mL of tap water. For all quantitation

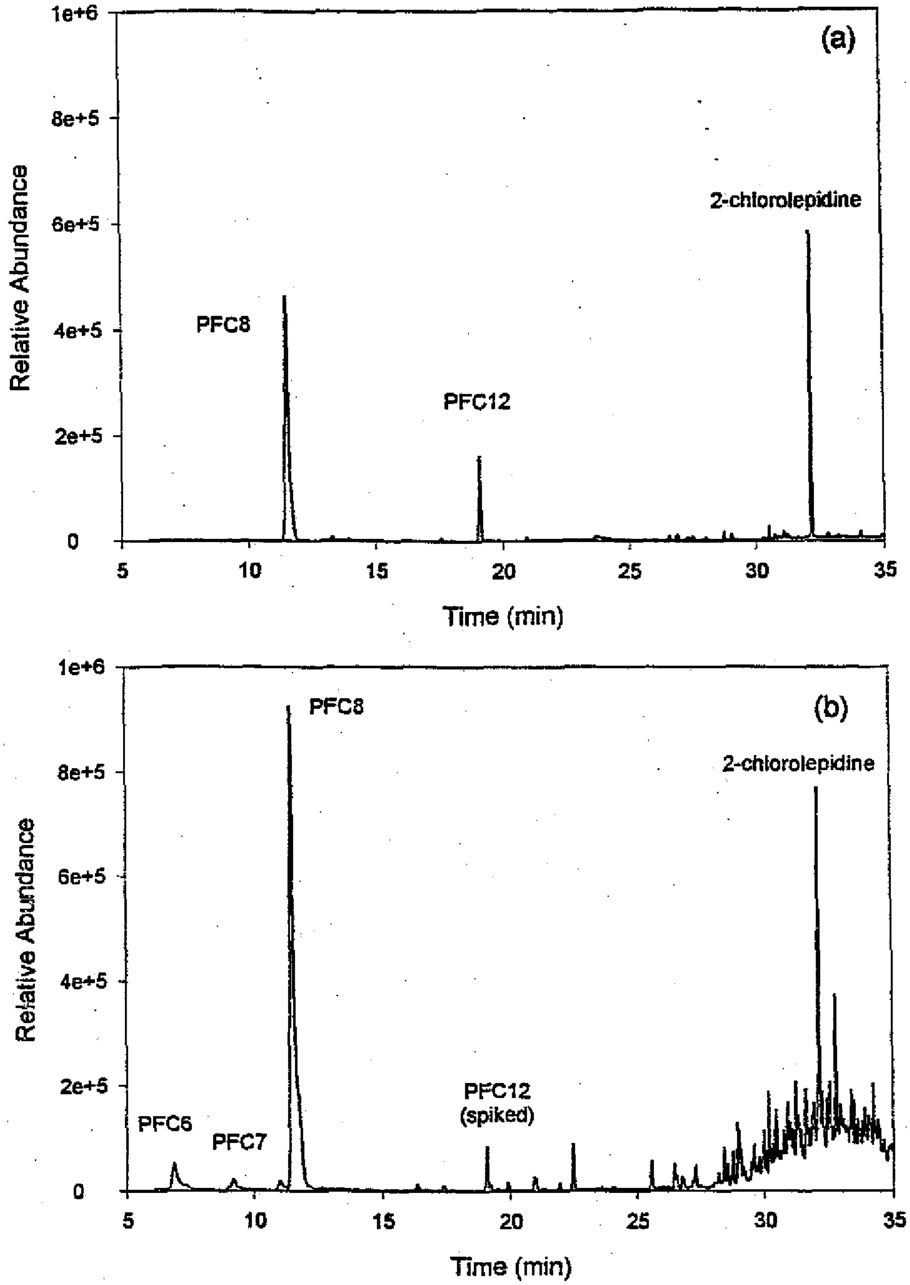

FIGURE 2. (a) Typical EI GC/MS chromatogram of PFC8 and PFC12 standards and (b) perfluorinated carboxylates, including PFC6, PFC7, PFC8, and PFC12 (spiked) in Naval Air Station Fallon groundwater.

standards, a total of 51.2 μg of the 2-chlorolepidine internal standard was added to the autosampler vial just prior to the addition of methyl iodide. Both calibration curves were linear with r^2 typically greater than 0.99. Quantification of PFC6 and PFC7 was performed assuming a response factor equal to an equimolar amount of PFC8.

Results and Discussion

Gas Chromatography/Mass Spectrometry. A film thickness of 4 μm (30 m × 0.32 mm SPB-1 SULFUR; Supelco, Bellefonte, PA) was necessary to obtain sufficient retention times for the methyl esters of PFC8 and PFC12 to allow for the separation and quantification (Figure 2a). Initial attempts to separate and quantify the perfluorinated carboxylate methyl esters on a thin film (0.25 μm), 30 m × 0.25 mm DB-1 (J&W Scientific, Folsom, CA) column were unsuccessful regardless of the initial column temperature. Note that the stationary phases in the SPB-1 SULFUR and DB-1 columns are comparable. A standard of perfluorobutyric acid was not observed under any of the described GC conditions; it is most likely that an initial oven temperature less than 40 °C would be required.

The EI mass spectra of methyl PFC8 (Figure 3a) and PFC12 indicate characteristic perfluorocarbon fragmentation *(16, 17)* in which the major ions (e.g., 69, 119, 169, 219, etc.) differ by 50 amu, which corresponds to the mass of CF_2. Molecular ions were not observed for any of the perfluorinated carboxylate methyl esters under EI conditions; however, molecular ions $[M]^-$ were observed under ECNI conditions. For example *m/z* 428 (in Figure 3b) corresponds to the molecular ion of methyl PFC8.

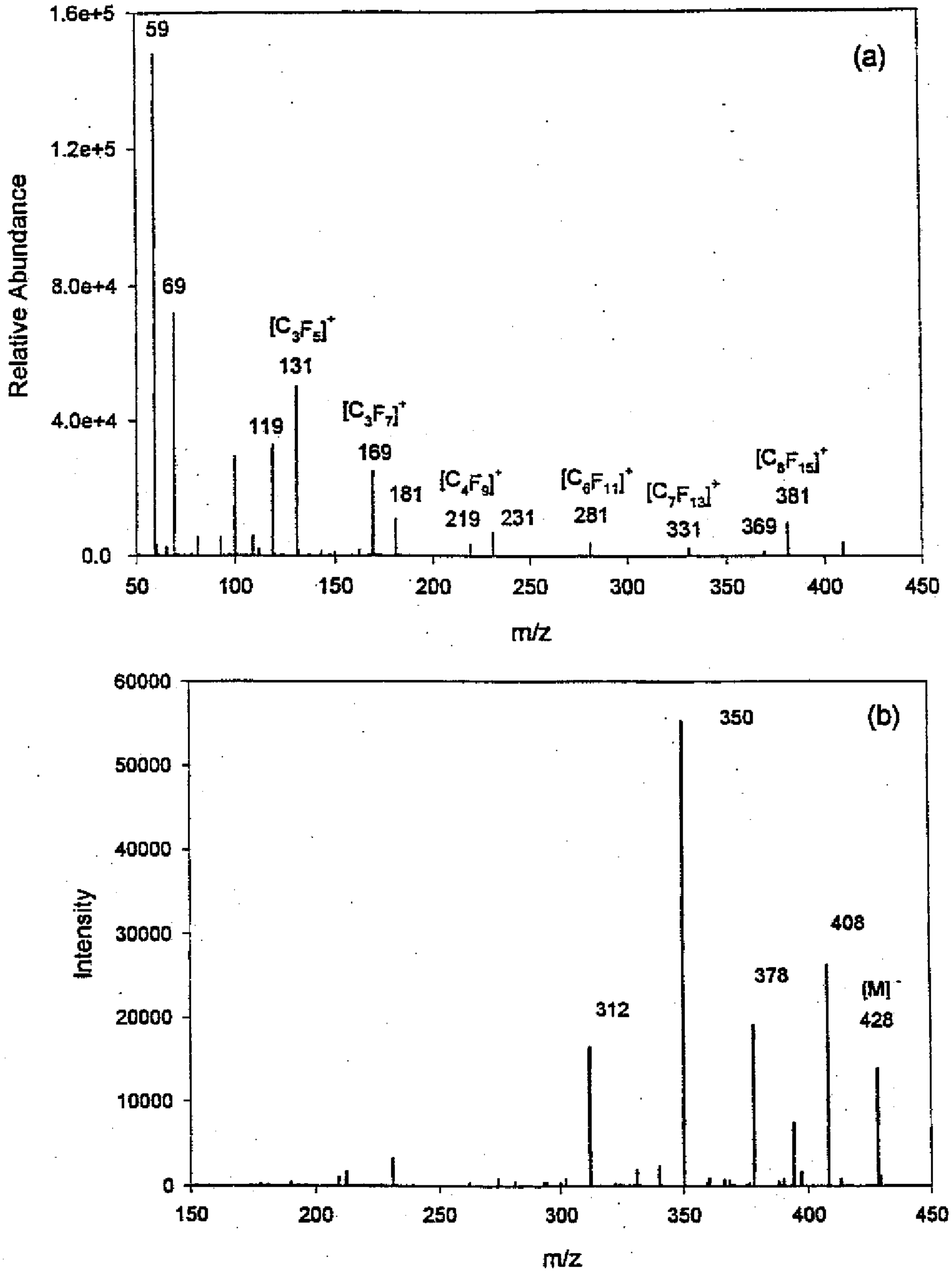

FIGURE 3. (a) EI mass spectrum of methyl PFC8. (b) ECNI mass spectrum of methyl PFC8.

Solid-Phase Extraction. Prior to developing a solid-phase extraction method, initial experiments were conducted using diazomethane as the derivatization reagent. When perfluorinated carboxylates were derivatized using ethanol-based diazomethane, multiple peaks corresponding to methyl and ethyl esters were detected (unpublished data). Because EI GC/MS did not produce molecular ions, ECNI GC/MS was used to verify the formation of both methyl and ethyl esters. Consequently, if ethanol-based diazomethane was used for derivatization in conjunction with EI GC/MS, multiple peaks in a chromatogram could be erroneously interpreted as a greater number of perfluorinated compounds than are actually present. In contrast, only the methyl ester was obtained when butyl carbitol (2-(2-butoxyethoxy)ethanol) was used to prepare the diazomethane reagent. However, because of the hazards associated with the use of diazomethane and the time-consuming nature of diazomethane derivatization, an alternative method was desired.

Derivatization of the perfluorocarboxylates by solid-phase extraction and the in-vial elution and derivatization technique gave only a single peak that corresponded to the methyl ester of each perfluorinated carboxylate standard; the identification of each methyl ester was confirmed by ECNI GC/MS. In addition, the solid-phase extraction approach combined the steps of isolation and derivatization, which greatly simplified the procedure and eliminated the use of diazomethane.

Six replicate analyses of blank 25 mm SAX disks that had not been prerinsed with 12 mM HCl/acetonitrile prior to use, yielded an average of 21 ± 1 μg (4.8% relative standard deviation (RSD)) of PFC8 per disk. No other perfluorinated carboxylates were present in the disks above the detection limit. The PFC8 is associated with the Teflon matrix and not

TABLE 1. Recovery of PFC8 and PFC12 Spiked into Groundwater Samples from Naval Air Station Fallon[a]

sample	% recovery PFC8	% recovery PFC12
NAS Fallon MW 51U[b]	83[c]	35
NAS Fallon MW 16	90[d]	85
NAS Fallon MW 50U	73	77
NAS Fallon MW 17	74	88

[a] Duplicate samples were analyzed. Sample volume was 100 mL unless otherwise noted. [b] Sample volume was 55 mL. [c] Calculated as the final measured concentration divided by background concentration plus spike concentration and multiplied by 100. The background concentration was 6,570 μg/L. [d] Calculated as the final measured concentration divided by background concentration plus spike concentration and multiplied by 100. The background concentration was 460 μg/L.

the embedded anion exchange particles (unpublished data). The background PFC8 was successfully removed by rinsing the disks prior to use with 12 mM HCl/acetonitrile followed by 350 mL of deionized water. It should be noted that benzoic acid and ethylhexylphthalic acid are also present in the disks as artifacts and are removed by the HCl/acetonitrile prerinse step.

Accuracy, Precision, and Detection Limits. The recoveries of PFC8 from blank groundwater samples obtained from NAS Fallon wells MW 50U and MW 17 were 73 and 74%, respectively, while the recoveries of PFC12 were 77 and 88%, respectively (Table 1). Because detectable levels of PFC8 occurred in groundwater from MW 51U and MW 16, standard addition experiments were performed to determine the recoveries of PFC8. The recoveries of the PFC8 spiked into MW 51U and MW 16 groundwater to give a final concentration double that of the background concentration were 83 and 90%, respectively (Table 1). The recoveries of PFC12 from MW 51U and MW 16 groundwater, which did not contain background concentrations of PFC12, were 35 and 85%, respectively (Table 1). Although the recovery of PFC8 (83%) differs significantly from that of PFC12 (35%) in groundwater from MW 51U, the recoveries of PFC8 and PFC12 were nearly equivalent for the other groundwater samples. Monitoring well 51U is located closest to the fire pit where AFFF agents where applied to burning mixtures of fuels and solvents. Due to its proximity to the fire pit, the groundwater from MW 51U most likely contains the greatest diversity of inorganic and organic constituents, which may adversely affect PFC12 recoveries relative to that of PFC8. Therefore, although the original intent was to use the PFC12 as a surrogate standard because it did not occur in the groundwater samples, PFC12 appears more sensitive to matrix interferences compared to PFC8 so that it is an inappropriate choice for a surrogate standard. For this reason, all subsequent quantification was based on the 2-chlorolepidine internal standard.

The precision, indicated by the RSD, calculated from five replicate analyses each of groundwater from NAS Fallon MW 16 and Tyndall AFB T11-2 ranged from 3.7 to 14% (Table 2). The detection and quantitation limit of the method was defined as those concentrations of PFC8 needed to produce a signal-to-noise (S/N) of 3:1 and 10:1, respectively. The detection and quantitation limits for PFC8 were 18 and 36 μg/L, respectively.

Application to Groundwater Samples. Four groundwater samples from both NAS Fallon and Tyndall AFB were analyzed for perfluorinated carboxylates. Chromatograms obtained by EI GC/MS indicated the presence of multiple perfluorinated compounds all having characteristic perfluorocarbon fragmentation (Figure 2b). Analysis by ECNI GC/MS established the identification of PFC6, PFC7 and PFC8 in groundwater obtained from wells MW 51U and MW 16 from NAS Fallon. The molecular ions $[M]^-$ for methyl PFC6 (m/z 328) and methyl PFC7 (m/z 378) were observed for peaks eluting 4.7 and 2.3 min before that of PFC8 (Figure 4a,b). The ECNI mass spectrum for methyl PFC8 in MW 51U was similar to that of the PFC8 standard (Figure 2b).

The groundwater samples from NAS Fallon MW 51U and MW 16 had total perfluorinated carboxylate concentrations of 7090 and 540 μg/L, respectively (Table 2). The PFC6 detected in NAS Fallon groundwater samples from MW 51U and MW 16 comprised 5.2% and 11%, respectively, of the total perfluorocarboxylates detected. The PFC7 was 2.1% and 3.3% respectively, of the total perfluorinated carboxylates detected in these wells. The dominant perfluorinated carboxylate, PFC8, accounted for 93% and 85%, respectively, of the total perfluorocarboxylate concentration.

The highest concentrations of perfluorocarboxylates were observed in groundwater collected from NAS Fallon MW 51U, which is the well located closest to the fire-training pit (Figure 1a). Monitoring well 16, which is located downgradient of MW 51U and the fire-training pit, had lower but detectable concentrations of perfluorocarboxylates. Groundwater from MW 50U and MW 17, which are located off gradient from the fire-training pit, contained no detectable perfluorinated carboxylates. Over the approximate 100 m distance between MW 51U and MW 16, the concentrations of the perfluorinated carboxylates decreased with increasing number of carbons. For example, the concentration of PFC6 decreased 85% over the 100 m compared to decreases of 88% and 93% for PFC7 and PFC8, respectively.

The groundwater samples from Tyndall AFB PW-10, PW-07, and T11-2 contained total perfluorinated carboxylate concentrations of 298, 159, and 124 μg/L, respectively (Table 2). The compositions of Tyndall AFB groundwater collected from the three wells ranged from 46 to 52% for PFC6, from 13 to 15% for PFC7 and from 34 to 40% for PFC8. In contrast to the groundwater samples from NAS Fallon, the dominant perfluorinated carboxylate in Tyndall AFB groundwater was PFC6.

TABLE 2. Concentrations of Perfluorinated Carboxylates in Groundwater Samples from Naval Air Station Fallon and Tyndall Air Force Base[a,b]

sample	n	PFC6 (μg/L)	PFC7 (μg/L)	PFC8 (μg/L)	total (μg/L)
NAS Fallon MW 51U	3	372 ± 4 (1.1%)	149 ± 5 (3.4%)	6570 ± 150 (2.3%)	7090 ± 160 (2.3%)
NAS Fallon MW 16	5	57 ± 8 (14%)	18 ± 2 (11%)[c]	460 ± 20 (4.3%)	540 ± 20 (3.7%)
NAS Fallon MW 50U	3	nd	nd	nd	nd
NAS Fallon MW 17	3	nd	nd	nd	nd
Tyndall AFB PW-10	2	144	38	116	298
Tyndall AFB PW-07	2	73	22[c]	64	159
Tyndall AFB T11-2	5	64 ± 4 (6.3%)	19 ± 1 (5.3%)[c]	42 ± 2 (4.8%)	124 ± 8 (6.5%)
Tyndall AFB TY22FTA	2	nd	nd	nd	nd

[a] The relative standard deviation is given in parentheses. [b] nd: not detected above the detection limit. [c] The reported value is near the detection limit ($S/N \leq 3$) and less than the quantitation limit ($S/N \leq 10$). The value has been included in the reported total concentration.

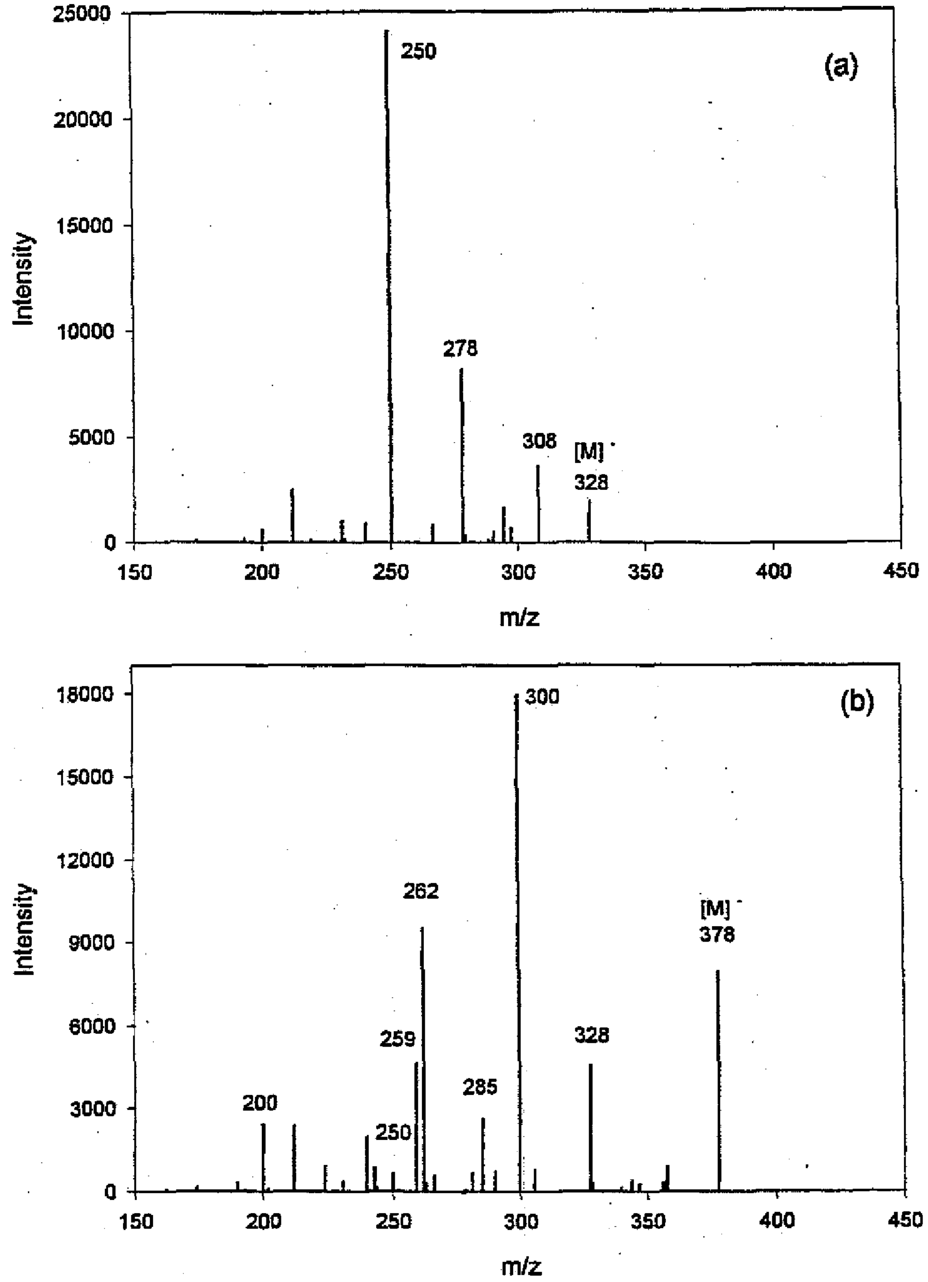

FIGURE 4. ECNI mass spectra of (a) methyl PFC6 and (b) methyl PFC7.

The highest concentrations of perfluorocarboxylates among the groundwater samples from Tyndall AFB were observed in PW-10 and PW-07, which are the two wells located closest to the fire-training pit (Figure 1b). Monitoring well T11-2, which is located downgradient of the fire-training pit, had lower but detectable groundwater concentrations of perfluorocarboxylates. The groundwater collected from a well located north of the fire-training pit, TY22FTA, contained no perfluorinated carboxylates above the detection limit (18 μg/L).

It is not surprising to observe a suite of perfluorinated carboxylates since the raw materials used in the synthesis of perfluorinated organic compounds are mixtures (*3, 19*). Different ratios of PFC6, PFC7, and PFC8 may result from the use of different AFFF formulations at the two fire-training areas. The observed homologous series consisting of even and odd number perfluorinated carboxylates is indicative of the electrochemical fluorination process used by 3M Co. (*3*). Other fluorination processes, such as telomerization, produce only even number homologues (*3*). Because of the proprietary nature of AFFFs, it is not known if perfluorinated carboxylates are present as one of the major surface active agents in AFFF formulations or as unreacted starting materials used in the synthesis of the principal perfluorinated surfactants used in AFFF formulations. In addition, the carboxylates may be combustion, biological, or nonbiological degradation products of the principal perfluorinated components in AFFF mixtures. Unfortunately, the exact source and history of AFFF applications at the two field sites are unknown, and therefore, the relationship between the observed perfluorocarboxylate ratios and that of the original AFFF mixtures is unknown.

To the best of our knowledge, very little is known regarding the transport and fate of perfluorocarboxylates in groundwater. Adsorption to sludge at wastewater treatment facilities is considered a significant process for the removal of perfluorinated surfactants during treatment (*3*). However, detection of perfluorinated carboxylates at the NAS Fallon and Tyndall AFB sites, which have not been used since 1988 and 1992, respectively, is consistent with the view that biodegradation of the long chain perfluorocarbon hydrophobe is unlikely (*6, 9, 19*). The recalcitrant nature of perfluorinated compounds is attributed in part to the rigidity of the perfluorocarbon chain (*9, 20*) as well as the strength of the carbon–fluorine bond (*3, 9, 21*).

To the best of our knowledge this is the first definitive identification of perfluorinated carboxylates in groundwater impacted by fire-fighting activity. Further work is needed to determine if additional perfluorinated components are present, such as perfluorooctane sulfonic acid, which is thought to be one of the principle components in some commercial AFFF formulations. In addition, it is of interest to relate the occurrence and distribution of perfluorinated compounds to other site characterization parameters such as dissolved organic carbon, inorganic constituents, and the distribution of co-contaminants and to understand the potential influence of perfluorinated compounds on the biotransformation and transport of other co-contaminants.

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Encl: (1) Minutes of subject meeting

1. The Navy Technology Center for Safety and Survivability of the Naval Research Laboratory hosted the DOD AFFF Environmental Meeting on 2-3 August 2000. The meeting was held to exchange information on environmental issues surrounding AFFF. The meeting was sponsored jointly by The Naval Facilities Engineering Command and the Naval Air Systems Command.

2. Enclosure (1) is a copy of the minutes of the meeting.

3. The NRL point of contact for this program is Dr. Frederick W. Williams, Code 6180, (202) 767-2476, email: fwilliam@ccs.nrl.navy.mil.

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Minutes
Of the
DOD AFFF Environmental Meeting

Held at the Naval Research Laboratory
Navy Technology Center for Safety and Survivability
Washington, D.C.
On
2-3 August 2000

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Minutes of
DOD AFFF Environmental Meeting
Naval Research Laboratory
2-3 August 2000

Summary

A meeting to discuss AFFF environmental issues within the Department of Defense (DoD) was held at the Naval Research Laboratory (NRL), Washington, D.C., on 2-3 August 2000. The meeting was hosted by Dr. Fred Williams, NRL, Director, Navy Technology Center for Safety and Survivability. The meeting was jointly sponsored by the Naval Facilities Engineering Command (NAVFAC) and the Naval Air Systems Command (NAVAIR). The agenda for the meeting is shown in Appendix (1). A list of attendees is provided in Appendix (2), along with a photo of attendees present at the opening general session on 2 August 2000. To facilitate future exchanges of information on this subject, Appendix (2) includes mailing addresses, phone numbers and E-Mail addresses for each attendee.

Objective

The overall objective of the meeting was to provide a forum for open discussion on AFFF environmental issues within DoD. Additionally, the meeting was called to address three specific objectives:

(1) Assist NAVFAC in the development of a DoD design policy for AFFF systems in aircraft hangars and other shore facilities to minimize adverse environmental impact.

(2) Obtain information to assist NAVAIR in finalizing their AFFF Environmental Safety and Health Need Assessment Summary (ESH NAS) and in preparing the follow-on Development Plan.

(3) Provide information for attendees on the relevant issues surrounding the decision by the 3M Company to phase-out production of AFFF and other products containing perfluorooctyl sulfonate (PFOS).

Background

There has been growing concern in the past few years about the potential adverse environmental impact of AFFF. This concern has been spawned by a number of factors:

- The establishment by EPA in 1994 of threshold quantities for reporting spills of AFFF due to the butyl carbitol commonly used as a solvent in AFFF
- Inadvertent activations of AFFF systems in hangars and the resultant clean-up and disposal
- Reports of problems created by the discharge of AFFF to waste water treatment facilities

- Limitations on overboard discharges of AFFF by ships under the Uniform National Discharge Standards (UNDS) of the Clean Water Act
- Anecdotal reports of damage to aquatic life by discharge of AFFF to streams and waterways
- Various designations of AFFF waste, necessitating expensive disposal by specialty contractors
- Recognition of the persistence and limited biodegradability of the fluorocarbon surfactants in AFFF
- Publicity surrounding 3M's decision to phase-out production of AFFF and other chemicals containing perfluorooctyl sulfonate (PFOS)
- Claims by vendors of so-called "environmentally-friendly" AFFF alternatives

As a result of these concerns, the affected Navy Systems Commands have undertaken various actions:

- NAVFAC, under the auspices of the DoD Fire Protection Coordinating Committee, has started the development of design policy for shore facility AFFF systems to minimize discharges and to address environmental issues.
- NAVAIR has funded Concurrent Technologies Corporation to draft an ESH Need Assessment Study on AFFF, to be followed by a Development Plan that will recommend future action to alleviate identified problems.
- NAVSEA has reduced the frequency of testing of shipboard AFFF systems to minimize overboard AFFF discharge in compliance with the UNDS regulations.

The meeting was called to share recent information and discuss issues relevant to the above concerns and on-going actions.

Meeting Scope/Presentations

The meeting consisted of general session discussions and presentations as well as two specifically focused breakout sessions. Copies of the general session presentations are provided as Appendices (3) – (10). Presentations given at the Hangar Facility breakout session are contained in Appendices (11) and (12). Overall summaries of each breakout session are provided in Appendices (13) and (14).

Significant Discussion and Presentation Points

There were many important points raised during discussion sessions or contained in formal presentations. Those considered to be the most significant are summarized below (additional details are contained in the appendices):

- AFFF is a vital fire fighting agent for controlling and extinguishing flammable liquid fires. Within DoD, it is especially critical for fire scenarios where life safety is paramount, where ordnance is exposed or high value assets are threatened.

- The AFFF military specification (Mil Spec) is considerably more demanding than the applicable UL standard relative to speed of extinguishment of a flammable liquid pool fire.
- The AFFF Mil Spec is widely cited in procurement specifications in the civil sector, especially at municipal airports.
- There are currently 5 manufacturers that have AFFFs on the Mil Spec Qualified Products List.
- There are many fire fighting foams that are commercially available. However, no non-AFFFs have been able to match the rapid fire extinguishment performance of AFFF.
- At present there is no regulation or directive to modify the AFFF Mil Spec.
- There is no recognized or universally accepted definition of "environmentally friendly" fire fighting foam.
- NAVSEA is the designated DoD technical custodian of the existing AFFF Mil Spec. Only NAVSEA can formally change the Mil Spec, though it may be possible to develop a separate specification just for shore-based applications.
- Inconsistent policy and guidance have led to expensive and questionable secondary containment designs in recent shore facility projects.
- 3M is voluntarily phasing-out production of AFFF because the fluorocarbon surfactant in their AFFF biodegrades to perfluorooctyl sulfonate (PFOS). PFOS has been identified by EPA as environmentally persistent, bio-accumulative in blood, and toxic to aquatic life and laboratory animals (the degree varies by species).
- Levels of PFOS measured in humans and found in blood banks is not considered to present a heath hazard at present levels. Concern is the potential for build-up over time.
- Other AFFF manufacturers do not produce AFFF that is currently believed to biodegrade to PFOS.
- It is not known if other AFFFs have a similar problem. EPA is currently in a fact-finding mode relative to other AFFFs.
- At present the EPA does not prohibit or limit specifically the manufacturing of AFFF.
- A comprehensive review of federal and local environmental regulations applicable to AFFF (and other foam agents) has just been completed (see Appendix (8)).
- All fire fighting foams have environmental properties and/or constituents that are regulated.
- Adverse impact on waste water treatment facilities is a major concern, primarily due to foaming.
- A "risk based" approach, using the Frequency Vs Severity concepts in Military Standard 882C, has been shown to be feasible for managing AFFF environmental issues in shore facilities. Such an approach may be applicable to other AFFF applications as well.
- The NAVFAC Facility AFFF Management Working Group will continue development of policy, with a completion goal of approximately 6 months.

The next meeting of the NAVFAC Working Group is scheduled for October 12, 2000.

- NAVAIR will complete the AFFF Need Assessment Study and prepare the Development Plan to recommend a future course of action.
- There was a general consensus that a second follow-on DoD meeting should be held (host, location, dates – TBD). Depending on developments between now and the next meeting, a decision could be made to establish a governing charter for a DoD AFFF Environmental Steering Group and perhaps to designate a formal DoD "advocate" for the effort.

List of Appendices

(1) Meeting Agenda

(2) List of attendees and photo

(3) Presentation: "AFFF Performance Perspective," R. Darwin, Hughes Associates

(4) Presentation: "NAVSEA Comments on the AFFF Mil Spec", R. Williams, NAVSEA

(5) Presentation: "Hangar Facility AFFF Management Breakout Session Introduction", J. Gott, NAVFAC

(6) Presentation: "AFFF Environmental Impact Breakout Session Introduction", J. Hoover, NAWCWD China Lake

(7) Presentation: "Issues With 3M's Withdrawal from the Market", C. Hanauska, Hughes Associates

(8) Presentation: "AFFF Environmental Impact Review", W. Ruppert, Hughes Associates

(9) Presentation: "AFFF Management – Risk Based Approach", D. Verdonik, Hughes Associates

(10) Presentation: "Phasing out a Problem: Perfluorooctyl Sulfonate", M. Dominiak, EPA

(11) Presentation: Facilities Background and AFFF Issues", J. Simone, NAVFAC

(12) Presentation: "AFFF Risk Assessment", A. Wakelin, Hughes Associates

(13) Presentation: "Summary of Shore Facility AFFF Management Breakout Session", D. Verdonik, Hughes Associates

(14) Presentation: "Summary of AFFF Environmental Breakout Session", J. Hoover NAWCWD China Lake and R. Darwin, Hughes Associates

APPENDIX (1)

Meeting Agenda

DOD AFFF Environmental Meeting

Location:

Building 207 (Chemistry Building)
Naval Research Laboratory,
4555 Overlook Ave,
Washington DC, 20735

Agenda:

Wednesday August 2nd

0830 – 0845	Welcome and Introduction – Dr Fredrick Williams, NRL, Director, Navy Technology Center for Safety and Survivability.
0845 – 0915	AFFF Performance Perspective – Robert Darwin, Senior Engineer, Hughes Associates, Inc.
0915 – 0925	NAVSEA Comments on the AFFF Military Specification - Robert Williams, NAVSEA Fire Protection and Damage Control Division
0925 – 0935	Hangar Facility AFFF Management Breakout Session Introduction – Joseph Gott, NAVFAC, Director, Navy Facilities Safety and Health Office
0935 – 0945	AFFF Environmental Impact Breakout Session Introduction – Dr. Jim Hoover, NAWCWD, Head, Combustion Research Branch
0945 – 1000	Break
1000 – 1015	Issues Surrounding 3M Withdrawal from the Market – Chris Hanauska, Senior Engineer, Hughes Associates, Inc.
1015 – 1100	Presentation of AFFF Environmental Regulatory Aspects – Bill Ruppert, Senior Environmental Engineer, Hughes Associates, Inc.
1100 – 1130	Summary Presentation on Risk Assessment for Hangar Facilities – Dr. Dan Verdonik, Hughes Associates, Inc.
1130 – 1230	Lunch
1230 – 1600	Breakout sessions

Thursday August 3rd

0830 – 0930	3M Withdrawal from Market – Mary Dominiak, EPA, Chemical Control Division, Office of Prevention, Pesticides & Toxic Substances.
0930 – 1230	Presentation of Breakout Session Conclusions. Discussion of any further requirements to complete breakout session action items.

Hangar Facility AFFF Management Breakout Session

Session Objectives and Details:

The objectives of the Naval Facility Engineering Command (NAVFAC) hangar facility AFFF Management breakout session are:

- To begin efforts toward developing a policy that details requirements for hangar facilities that will provide "adequate measures" to:
  - (a) prevent an accidental AFFF discharge,
  - (b) limit any adverse environmental impacts from a release.
- To achieve an agreement on the definition of "adequate measures" and to begin to establish design criteria to meet them.

Initial draft design criteria and costs of specific engineering solutions will be presented and discussed as a starting point.

Agenda

1230 – 1315	Facility Background and Issues – Joe Simone, Head Fire Protection Engineer, Naval Facilities Engineering Command
1315 – 1430	Risk Assessment for Hangar Facilities – Alison Wakelin, Fire Protection Engineer, Hughes Associates, Inc.
1430 – 1600	Design Criteria Discussion and Development

List of Breakout Session Attendees:

D. Verdonik (Chair)
J. Gott
W. Ruppert
A. Wakelin
J. Simone
V. Donnally
T. Ruffini
D. Roderique
G. Sadler
L. Wolf
K. Ellis
M. Doherty
K. Kochar
B. Scott
R. Talbot
R. Hansen
J. Shah
F. Williams

AFFF Environmental Impact Breakout Session

Session Objectives and Details:

The objective of this meeting is to share the technical data related to the environmental impact, status and the planned future use of AFFF. NAVAIR will use output from this session to ensure their Environmental Safety and Health (ESH) Need Assessment Summary (the where we are today) is accurate and complete, and to ensure their Development Plan (the where we go from here) is consistent with the need to provide sound fire protection in an environmentally responsible manner.

The AFFF Environmental Impact working group will address the following questions:

- What current and future environmental regulations impact AFFF use and why (data and politics)?
- What data do we have (or lack) on the environmental impact of AFFF?
- What technology or products exist that could help reduce AFFF releases into our environment or mitigate the impact of those releases?
- What technology or products could be applied to recycle or reuse AFFF?
- What alternatives to AFFF currently exist and how do they compare in effectiveness, cost, environmental impact, availability, etc?

List of Breakout Session Attendees:

J. Hoover (Chair)
R. Darwin
J. Scheffey
C. Hanauska
W. Leach
D. McCrory
R. Williams
S. Wade
M. Wade
K. Bagot
R. Morris
B. Parks
S. Johnson
P. Bungcayo
R. Lee
R. DiAngelo
D. Dierdorf
J. LaPoint
I. Young

APPENDIX (2)

List of Attendees and Photo

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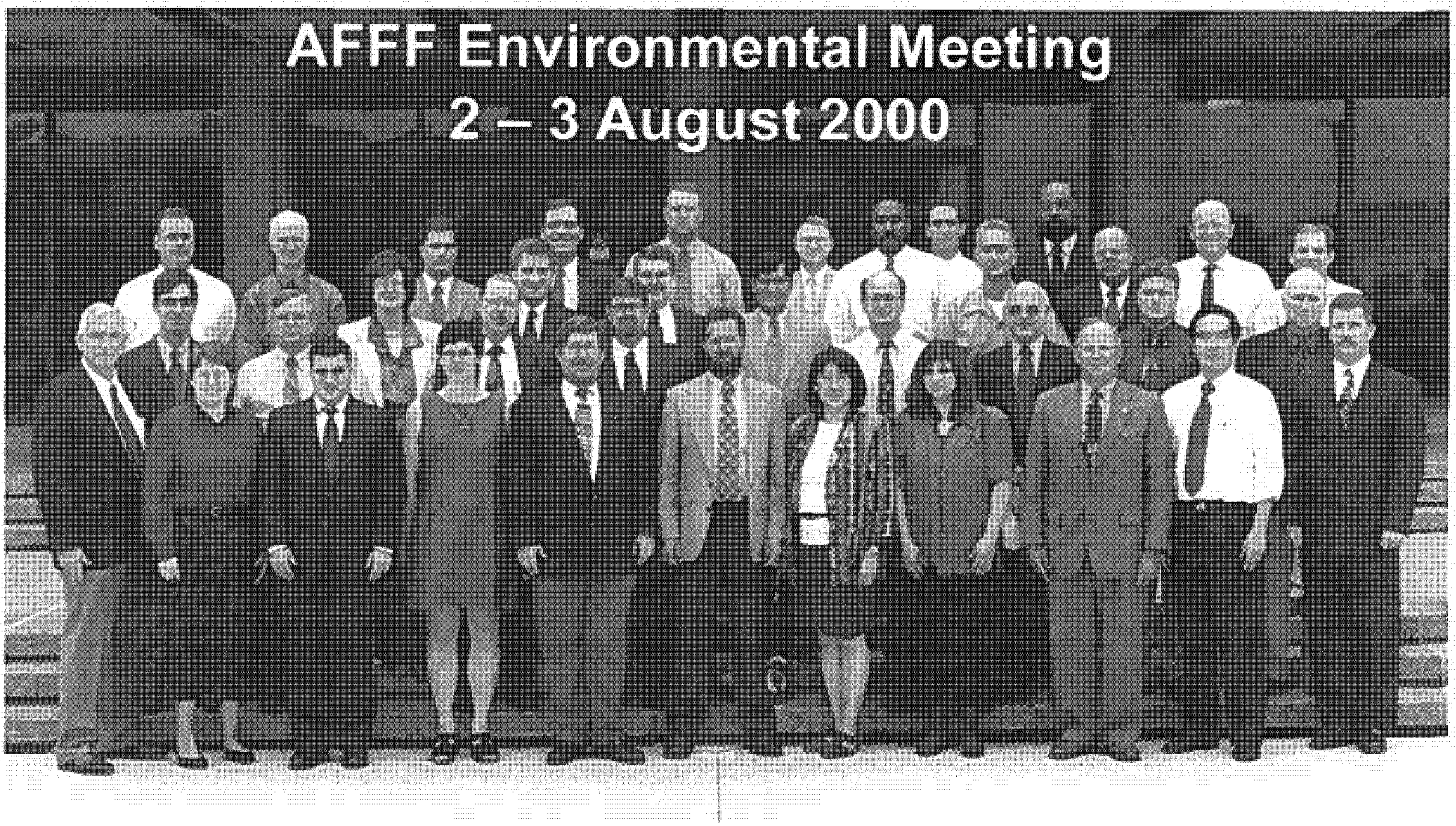

AFFF Environmental Meeting
2 – 3 August 2000

Top Row: C. Hanauska, D. McCrory, J. Simone, L. Wolf, K. Bagot, M. Doherty, B. Parks, J. LaPoint, S. Johnson, R. Hansen, R. DiAngelo

Middle Row: W. Ruppert, B. Williams, D. Roderique, J. Hoover, J. Gott, J. Scheffey, D.Verdonik, J. Shah, W. Leach, P. Bungcayo, R. Darwin, K. Kochar, R. Talbot, S. Wade

Bottom Row: F. Williams, R. Morris, T. Ruffini, A. Wakelin, D. Dierdorf, B.R. Scott, I. Young, K. Ellis, G. Sandler, R. Lee, M. Wade

APPENDIX (3)

Presentation: "AFFF Performance Perspective"

R. Darwin,
Hughes Associates, Inc.
Baltimore MD

AFFF

Performance Perspective

Robert L. Darwin, PE
Senior Engineer
Hughes Associates, Inc.

2 August 2000

History of Foam

1920-40	Chemical Foam
1940-70	Protein Foam (Air Foam)
1970- 2000	AFFF

<u>AFFF Key Events:</u>

1961 First experiments with fluorocarbon surfactants at NRL

1962 First Mil-Spec (Mil-F-23905, 1 Nov 63)
25 % concentration (fresh water only)
Emphasis on twin agent application

1963 Large scale tests at NAS pensacola
Led to procurement of 100 twin agent units

1964 Helo air borne TAU tests at NAS Miramar

1965	6 % concentration developed by 3M (FC-194)
1966	Testing of FC-194 in airfield crash trucks Selective conversion of some crash trucks
1967	Flight deck conflagration on USS Forrestal TAUs to aircraft carriers Push to develop seawater-compatible AFFF
1967	Seawater –compatible AFFF developed by 3M/NRL
1968	Additional crash truck tests at NAS Miramar
1968	Shipboard equipment tests w/ seawater at NAS Jacksonville First edition of seawater/AFFF mil spec (Mill-F-24385)
1969	Flight deck conflagration on USS Enterprise Push to convert ships to AFFF
1970	Navy starts comprehensive conversion of ship systems and crash trucks
1973	USAF starts converting all USAF crash trucks

UL Listed Foams

(Per UL 162-"Foam Equipment & Liquid Concentrates")

AFFF – Aqueous Film Forming Foam
FFFP – Film Forming Fluoroprotein
FP – Fluoroprotein
PF – Protein Foam

	Manufacturers	Concentrates
AFFF	24	110
FFFP	5	16
FP	12	26
PF	5	6

Mil Spec Qualified Product List (QPL)

Ansul

Ansulite 3 (AFC-5A) *	Type 3
Ansulite 6 (AFC-5) *	Type 6

3M

FC-203C	Type 3
FC-203CE *	
FC-203CF *	
FC-206C	Type 6
FC-206CE	
FC-206CF *	

Chemguard

C-301MS *	Type 3

National Foam

Aer-O-Water 3-EM *	Type 3
Aer-O-Water 6-EM *	Type 6

Angus

Tridol M	Type 3

* Also UL Listed

“Application Density” (Defined as the Gallons of Agent Per Unit Area of Pool Fire Size) is the best measure of effectiveness for a flammable liquid pool fire

Application Rate = GPM/Sq Ft of fire area

Application Rate x Ext Time = Application Density

GPM/Sq Ft x Minutes = Gals/Sq Ft

<u>Example</u>

Fire Area = 1000 Sq Ft
Appl Rate of Agent = 200 GPM
Ext Time = 0.5 minutes

Appl Rate = 200 GPM/1000 Sq Ft = 0.2 GPM/Sq Ft

Appl Density = Appl Rate x Time
= 0.2 GPM/SqFt x 0.5 minutes
= 0.1 Gals/SqFt

AFFF Performance Requirements

Mil Spec (Mil-F-24385):

Max Appl Density

2 gpm/28 sq ft x 30/60 minutes = .036 gal/sq ft

2 gpm/50 sq ft x 50/60 minutes = .033 gal/sq ft

Underwriters Laboratory:

2 gpm/50 sq ft x 3 minutes = .12 gal/sq ft

(Maximum extinguishment time is 5 minutes for fluoroprotein and protein foam)

Rapid Extinguishment of Pool Fires is Critical When:

- Pool fire threatens high value assets (such as an aircraft hangar)
- Pool fire under an occupied aircraft (must maintain fuselage integrity and rescue occupants)
- Pool fire exposes weapons to potential “cook off”

Relative Performance of Foam Agents on Pool Fires

(Best) AFFF (Mil-Spec)

AFFF (UL listed, non Mil-Spec)

AFFF (non UL, non Mil-Spec)

FFFP

FP

PF

(Worse) Wetting Agents

UL Listed Wetting Agents
(Based on NFPA 18)

" A liquid concentrate for addition to water to produce a solution having a <u>greater fire extinguishing efficiency than plain water</u>"

Manufacturers:	11
Agents:	13

If Use Non-Film Formers:

- Extinguishment time will be slower, unless application rate is increased

- Higher application rate causes

    Greater system cost

    Greater quantity of agent emitted

- Must consider possible need for "air aspiration"

    Replace nozzles

    Less reach than "non air aspirated"

AFFF Environmental Issue - 1994

Glycol Ethers (Butyl Carbitol), solvent in most AFFFs, placed on EPA list of hazardous air pollutants.

Since no reporting threshold had been established, a default quantity of one pound per day was established for required reporting under CERCLA.

Because Diethylene Glycol Butyl Ether (DGBE) typically comprises about 20 % of AFFF, spills of just a few gallons of AFFF had to be reported to the National Response Center and to State and local officials.

One pound per day reporting requirement dropped in 1996.

Some manufacturers substituted Propylene Glycol for Ethylene Glycol and declared their foam to be “environmentally friendly”.

DOD Uses of AFFF

- Shipboard Foam Systems
- CFR Vehicles at Airfields
- Aircraft Hangar Foam Systems
- Misc Shore Facilities
  - Hush Houses
  - Jet Engine Test Facilities
  - Hardened Aircraft Shelters
  - Aircraft Fueling Stations
  - Fuel Farms
- Foam Sytems on Structural Pumpers

DOD AFFF Discharges

- Fires
- Training Evolutions
- System Tests and Maintenance
- Accidental/Malicious Discharges
- Research and Development

There is a Need to Quantify and Characterize:

- All DOD AFFF applications (What precisely do we use it for ?)
- Precise quantities in service and in reserve stocks (How much do we have ?)
- Annual emmisions (type and quantity) (How much do we discharge ?)

APPENDIX (4)

Presentation: ‘NAVSEA Comments on the AFFF Mil Spec”

R. Williams,
Naval Sea Systems Command

NAVSEA Comments
On the
AFFF Military Specification
Mil-F-24385F
(Amendment 1 of 8/94)

(Talking Points)

Presentation to DOD AFFF Environmental Meeting
2 August 2000

Robert B. Williams
Fire Protection & Damage Control Division
Naval Sea Systems Command
(Technical Custodian of the AFFF Mil-Spec)

1. I would like to express appreciation to NAVFAC and NAVAIR for sponsorship of this Conference. Also, I appreciate the opportunity to establish the NAVSEA perspective up front.

2. This conference is important and timely:

Recently there has been a proliferation of Navy groups active in AFFF; usually with no focus, some scattered and uncoordinated EPA contacts.

Recently there has been aggressive commercial marketing of so-called "environmentally friendly foams"; yet there is no established definition of "environmentally friendly foam".

AFFF is subject of considerable hype: effect on sewage plants, danger to aquatic life, exposure results in mutant first born, etc.

AFFF spills are media friendly- very visible, makes for good "films at 11", photos provide permanent record, helps stir up environmental activists

Real issues from my perspective:

  3M withdrawal and fall out relative to other QPL AFFFs

  Restrictions by AHJs; technical basis or not

  Unknown forthcoming EPA activity

  All are on agenda to be addressed

3. The product I personally desire of this conference is to specifically identify what the problems are regarding MILSPEC AFFF, and problems that are inherent to any foam alternative (visible, wastewater treatment plants).

Appears money is & will be directed at AFFF.

My concern is that funding needs to be attached to a focus on specifics that are documented as requiring resolution.

Navy labs and contractors see a golden egg out there on this topic; I personally don't want to see them going off into the sunset with a generic task to find an environmentally friendly firefighting agent. (whatever friendly means).
The specific problems to be resolved require documentation before charging onto a search for solutions; doesn't always happen in correct order.

The agenda appears to support what I hope is the conference objective.

4. A few quick comments about the MILSPEC and shipboard applications:

NAVSEA is custodian; only NAVSEA can revise. Self appointed cannot.

However, an alternate extinguishing agent specification under someone else's cognizance could be created.

For example, it might be feasible to develop a separate specification just for shore facility use (fresh water only, one percent, universal foam, no refractive index requirement, etc).

NAVSEA goal regarding the spec: Satisfy environmental requirements without degradation of firefighting effectiveness. If maintaining performance requirements is not possible, then where do we draw the trade-off line in the sand? (fish vs. sailors; national defense vs. environment)

MILSPEC contents - shipboard oriented, even though it is essentially the national standard ashore and afloat:
AFFF is for two dimensional shallow spill fires, rapid control and extinguishment are essential. No "foam-of-the-month" has matched the performance of mil-spec AFFF.
Environmental provisions in spec; fish kill, BOD/COD limits, chemical restrictions.
Compatibility: seawater effectiveness, intermixing of products from different manufacturers on QPL.
It is an integrated match with our capital investment in hardware: viscosity, corrosion, pipe & tank materials, effect on seals/gaskets, a refractive index, container size & strength.

5. Our primary environmental involvement has been with the Uniform National Discharge Standards (UNDS) program which is relative to overboard discharge of liquids; basically a Clean Water Act action item.

Our imput to EPA, which has been accepted thus far, is discharge management:

New construction/alterations - no repeat testing, at sea

Preventative Maintenance - reliable hardware, reduced testing periodicity

Fewer ships

Geographic restrictions: no discharges within 3 miles of coast, must be making at least 10 knots for discharges within 3-12 miles, preference for only discharging when greater than 12 miles out

6. In closing, I pass along that as custodian of the MILSPEC, I have no direction, pressure, or formal or informal tasking to conduct an environmental review of MILSPEC AFFF aside from the UNS. At NFPA aviation committee meetings I have queried major airport fire chiefs, all of whom stated no direction to pursue an alternative to MILSPEC AFFF. However, we at NAVSEA know whether politically, technically, or regulatory driven, environmental restrictions on AFFF may be coming. We fully support this conference, identification of problems & potential problems, and initiation of remedial research/actions.

APPENDIX (5)

Presentation: "Hangar Facility AFFF Management Breakout Session Introduction"

J. Gott,
Naval Facilities Engineering Command

Hangar Facility AFFF Management Breakout Session Introduction

(Talking Points)

Presentation to AFFF Environmental Meeting
2 August 2000

Joseph Gott
Director, Navy Facilities Safety and Health Office
Naval Facilities Engineering Command

AFFF DOD Meeting Talking Points

- Need a consistent DOD position on AFFF management
- If we are not proactive, AFFF will become our next halon 1301
- AFFF is only product on market right now that meets our needs
- Time for the design engineers, and environmental engineers to come together
- The services have already done this with the Unified Design Guidance Group
- As past chair of DOD FPE committee, we wrote the first tri-service design criteria
- Fixed containment systems are affecting our mission because they have already caused the omission of AFFF from some hangars resulting in the air wings inability to perform their mission
- This is the beginning of a working group to address this important issue
- Need to get all the right players
- Need to address AFFF management from a risk assessment approach
- Need to dismiss all the myths and fears and address the facts
- Need to give the local regulators something to reference as adequate protection
- Need to determine if additional research is needed to produce a different AFFF
- Discuss changes to NFPA 409 - mandatory drains, reduced AFFF, various protection options
- NAVFAC has long history in fixed AFFF systems, their behavior, problems, and design characteristics

APPENDIX (6)

Presentation: "AFFF Environmental Impact Breakout Session Introduction"

J. Hoover,
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China Lake CA

AFFF Environmental Impact Breakout Session Introduction

(Talking Points)

Presentation to DOD AFFF Environmental Meeting
2 August 2000

Dr. Jim Hoover
Head, Combustion Research Branch
NAWCWD China Lake

The purpose of the AFFF Environmental Impact Breakout Session will be to share technical information within the DoD on AFFF use and environmental impact. This information will be used to assist the completion of two environmental planning documents used by the Naval Air Systems Command (NAVAIR) - an Environmental Safety and Health Needs Assessment Summary (NAS) and a Development Plan. The NAS will provide a "snap-shot" of technical issues surrounding AFFF use and environmental impact, and the Development Plan will recommend a strategy for future efforts within NAVAIR.

Background: The importance of AFFF in protecting Navy personnel and assets must not be understated. Likewise, public safety and commercial assets are highly dependent on AFFF for fire protection. Its firefighting performance remains unmatched and much remains unknown about its human health and environmental effects.

Other services and agencies have data and experiences with AFFF that could assist the Navy in future decision making, so a forum for technical information exchange is needed. In planning for the future, all aspects of technical knowledge about AFFF (and all of its formulated components) should be considered. These should include costs, performance/function, human health and environmental effects, availability, inventory, alternatives, etc.

Break-out Session Format:

The following questions will be asked of the participants to promote discussion and information exchange. Participants will be invited to provide other questions.

1. What current and future environmental regulations impact AFFF use and why (data and politics)?

2. What data do we have (or lack) on the environmental impact of AFFF?

3. What technology or products exist that could help reduce AFFF releases into our environment or mitigate the impact of those releases?

4. What technology or products could be applied to recycle or reuse AFFF?

5. What alternatives to AFFF currently exist and how do they compare in effectiveness, cost, environmental impact, availability, etc?

6. What related planning documents exist with other services or agencies?

7. What follow-on strategies should be considered?

APPENDIX (7)

"Issues With 3M's Withdrawal From the Market"

C. Hanauska
Hughes Associates, Inc.
Baltimore MD

Issues with 3M's Withdrawal from the Market

AFFF DoD Meeting

Christopher Hanauska

HUGHES ASSOCIATES, INC.
FIRE SCIENCE & ENGINEERING

August 2, 2000

Purpose of this Presentation

- Mary Dominiak of EPA will provide more detailed information tomorrow
- Provide some background for her presentation
- Frame the issue relative to the subjects of this meeting
- *This presentation is only an executive summary*

Fluorochemical Surfactants (FC's)

- FC's are a component of AFFF
  - One of several components in AFFF
  - FC's are difficult and expensive to make
  - Formulators have minimized (and attempted to eliminate) the FC content for 30 years
  - Necessary for performance (especially for CFR)
    - rapid fire knockdown
    - relatively low application rates

What is an FC?

- C8F17-functional group
- Length of carbon chain varies
- Fluoronated carbon chain is very stable
- Functional group gives different properties

FC's for AFFF Do Not Fully Biodegrade

- 3M's FC's => PFOS (Perfluorooctyl Sulfonate)
- Other FC's => ?
- Functional group may biodegrade, but something is always left
- Ultimate fate unknown
- "Persistent"

3M Performed Testing

(Last 2 Years)

- Found PFOS
  - in blood banks around the US
  - in fish and birds
- Discovered toxicity issues
  - reproductive sub-chronic studies
- “Bioaccumulative” and “Toxic”

3M Voluntarily Phasing Out PFOS Related Chemicals

- Scotchguard, Scotchban, industrial uses, AFFF
- About 2 years for complete halt of production
- Decision made at highest level of 3M
  - were in discussion with EPA at the time
- An unexpected and extreme action

If Only 3M PFOS FC's are a Problem

- Other non-PFOS FC based AFFF's are on the QPL
- Possibly a short term supply issue
- Should not be a major fire protection/environmental concern

Do Non-PFOS FC's Have a Problem?

- EPA has asked manufacturers to examine and test
- What constitutes a "problem" uncertain
  - "Bioaccumulative" "Toxic"
- EPA will do risk/benefit and risk/risk analysis
  - Understanding of importance of AFFF to fire protection

Conclusions

- No FC specific regulations exist
- No apparent short term (1 year) problems
- Mid-term (2-3 years) problems related to supply only
  - as 3M withdraws from market
- Potentially no long term problems (3+ years)
- *Unless other FC's have significant problems*

APPENDIX (8)

Presentation: "AFFF Environmental Impact Review"

W. Ruppert
Hughes Associates, Inc.
Baltimore MD

Aqueous Film Forming Foam (AFFF) ENVIRONMENTAL IMPACT REVIEW

Bill Ruppert

HUGHES ASSOCIATES, INC.
FIRE SCIENCE & ENGINEERING

Background:
AFFF Constituents

- MILSPEC based on Performance, not Constituents
- Must be on Qualified Products List - QPL
- Main Ingredients in Firefighting Strength Foam:
  - WATER = 98%-99%
  - Butyl Carbitol (Glycol Ether) = 0.5%–1.1%
  - Fluorosurfactants & Hydrocarbon Surfactants = 0.03%–0.45%
  - Ethylene Glycol (Not in all formulations) = 0.34%–0.60%
  - Urea (Not in all formulations) = 0.2–0.4%

Background:
AFFF 'Environmental' Properties

- MIL-F-24385F Requirements
  - Chemical Oxygen Demand
    - 3% Concentrate - 1,000,000 mg/L Max
    - 6% Concentrate - 500,000 mg/L Max
    - Calculated Firefighting Strength ~ 30,000 mg/L Max
  - Biochemical Oxygen Demand (20 Day)
    - =(0.65 X COD) or greater
  - Aquatic Toxicity (LC50, Killiefish)
    - 3% Concentrate - 500 mg/L Min
    - 6% Concentrate - 1000 mg/L Min
    - Calculated Firefighting Strength ~ 16,667 mg/L Min
- Persistence and Bioaccumulation
  - Only Fluorosurfactants - Not in other constituents
  - example: Butyl Carbitol log BCF = 0.46
- Foams

Background: AFFF Properties

MILSPEC vs. Typical QPL Product

Property	MIL-F-24385F Requirements			Typical QPL Product		
	3%	6%	FF	3%	6%	FF
Chemical Oxygen Demand (mg/L)	1,000,000 Max	500,000 Max	30,000 Max	750,000	341,000	22,500
Biochemical Oxygen Demand (mg/L)	$BOD_{20} > 0.65 \times COD$			720,000 (0.96*COD)	274,000 (0.80*COD)	21,600
Aquatic Toxicity (Killiefish) (mg/L)	500 Min	1000 Min	16,667	>1000	>1000	>16,777 or >33,333

Codes and Standards Survey

Approach

- Electronic Review
- Federal Environmental Regulations
  - “AFFF”
  - MILSPEC AFFF Constituents (19)
    - Surfactants
    - Fluorosurfactants
    - Glycol Ethers
    - Urea, etc.
  - AFFF “Environmental” Properties
    - Biochemical And Chemical Oxygen Demands
    - Aquatic Toxicity
    - Foaming
- DOD, State And Local Regulations
  - “AFFF”
  - MILSPEC AFFF Constituents

Codes and Standards Survey

Federal Environmental Regulations

- Clean Air Act (CAA)
    - Air Emissions
    - Air Discharge Permits
- Emergency Planning and Community Right-to-Know Act (EPCRA)
    - Toxics Release Inventory (TRI)
    - Chemical Storage and Use
- Comprehensive Environmental Response, Compensation, & Liability Act (CERCLA)
    - Superfund Amendments and Re-authorization Act (SARA)
    - Spills and Clean-up Of Spills
- Resource Conservation and Recovery Act (RCRA)
    - Hazardous Waste
- Safe Drinking Water Act (SDWA)
    - Regulates Contaminants in Treated Drinking Water
- Clean Water Act (CWA)
    - Water Discharges
    - Water Discharge Permits

Federal Environmental Regulations
Results

- Clean Air Act (CAA)
  - Glycol Ethers In AFFF Are Hazardous Air Pollutants (HAPs)
  - HAP Releases Are Regulated by the Installation Air Permit
    - Major Sources for HAPs Might Have Potential Permit Issue
- EPCRA and TRI
  - Glycol Ethers are Covered Because CAA Defines them as HAPs
  - Chemicals Released Above a Reportable Quantity (RQ) Must Be Reported
    - Default RQ was One (1) Pound
    - EPA Established a No RQ
  - AFFF Discharges Do Not Currently Need to Be Reported Under EPCRA and TRI
  - Ethylene Glycol Specifically Listed
  - No Other Constituent is Currently Regulated by EPCRA and TRI

Federal Environmental Regulations

Results

- CERCLA and SARA
  - Glycol Ethers are Covered Because CAA Defines them as HAPs
  - Glycol Ethers May Need to Be “Cleaned Up” After a Spill
    - Air Pollutants So Expected to be Volatile
      - Are not volatile when mixed with water
    - Biodegradable So Might Be “Cleaned Up” Naturally
- Resource Conservation And Recovery Act (RCRA)
  - AFFF and Its Constituents are Not Classified as Hazardous Waste
  - RCRA Does Not Apply
- Safe Drinking Water Act:
  - Primary Drinking Water Regulations (Health Properties)
    - Does not regulate AFFF or its constituents
  - Secondary Drinking Water Regulations (Aesthetic Properties):
    - Foaming Agents <0.5 mg/L in drinking water
    - Do not regulate foaming agents in source water
    - Guideline for State Regulations Only (Not Federally Enforceable)

Federal Environmental Regulations

Results (Continued)

- Clean Water Act (CWA)
  - Installations Require Discharge Permits
    - Storm Water
    - Treated Sewage from Installation Wastewater Treatment Plant
    - Raw Sewage to Public Wastewater Treatment Plant (Locale Specific)
  - Regulates Wastewater that:
    - Foam
    - Remove Oxygen From Water
    - Disrupt Wastewater Treatment Plants, etc.
  - AFFF
    - Persistent Foam
    - Removes High Amounts of Oxygen From Water (High BOD and/or COD)
    - Untreated, Undiluted AFFF Will Disrupt Wastewater Treatment Plant
    - (Even Diluted AFFF Can Disrupt Wastewater Treatment Plant) SDWA

Codes and Standards Survey

State/Local Environmental Regulations

- State Regulations Can be More Strict Than Federal
  - No Specific Instances Found for AFFF
  - Storm Sewer Regulations Emphasized
- Nothing Additional in County and City Regulations
- Representative Jurisdictions
  - Telephone Surveys
  - Focused on Jurisdictions In:
    - Virginia
    - Hawaii
    - Florida
    - California
- Local Anecdotal AFFF ‘Problems’
  - Sewage Treatment Plants Becoming ‘Bubble Baths’
  - Pump Stations ‘Burned-up’
  - Storm Sewer Overflowing With Foam

State/Local Environmental Regulations
(Continued)

- Foaming the Greatest Concern
- Perception:
  - Foam Is Highly Toxic to Everything
  - No Concentration is Okay for a WWTP
- Results
  - Local Jurisdictions **CAN** and **DO** Regulate AFFF by Name
  - Have Water Discharge Permit Authority
  - Local Waste Water Treatment Plants Often Ban AFFF
    - Based on Direct Experience with a Disruption
    - High Oxygen Demand
    - Foaming

Environmental Consequences

- Media Considered
  - Air
  - Groundwater
  - Soil
  - Surface Water
    - Via storm water
    - Via wastewater treatment plant
- Both Constituent Characteristics and AFFF Solution Properties

Environmental Consequences

Media: Air

- HAPS: Butyl Carbitol, Ethylene Glycol
- Low Migration Potential (All Constituents)
  - Highly Soluble in Water
    - Tends to stay with liquid water
    - Not very volatile
  - If Volatilized, Half-lives in Air 4 Hr - 3.5 Days

Environmental Consequences
Media: Groundwater

- Consequence Varies Depending on Subsurface Conditions
- Fluorosurfactants: Not Mobile
- All Other Constituents:
  - Highly Soluble, Highly Mobile
  - Degrades Rapidly in Soil
    - 30% Degradation Over 24 Hour Period
- Drinking Water Wells ‘Under the Influence of Surface Water’ Could Receive Undegraded AFFF Constituents

Environmental Consequences

Media: Soil

- Consequence varies depending on soil type
- Fluorosurfactants and break-down products
  - Persistent in soil
  - No quantified environmental impact
  - EPA will discuss further tomorrow
- Other constituents highly mobile in water, will not adsorb to soil

Environmental Consequences

Media: Surface Water Via Storm Water

- Foaming:
  - Aesthetic Concern
- Oxygen Demand
  - Robs Oxygen from Water
  - Usually near water's surface
- Aquatic Toxicity
  - Considered 'Practically Nontoxic' by the US Fish and Wildlife Service.
  - Lowest toxicity value in 40 CFR 300
    - LC50 > 1000 mg/L in concentrate
    - ~160 mg/L in most sensitive species
    - Much Lower Toxicity in Firefighting Strength
  - Anecdotal Reports of Higher Toxicity
- Surface Water May influence Groundwater
- 'Environmental' Threat
  - Depends on Sensitivity of Receiving Water: Worst Cases
    - Kaneohe Bay, HI Risk Analysis - "Potential for significant ecological damage … relatively small"
    - Wetlands
      - Waterfowl-Fluorosurfactant Interaction being studied in St. Johns River Basin in Florida.

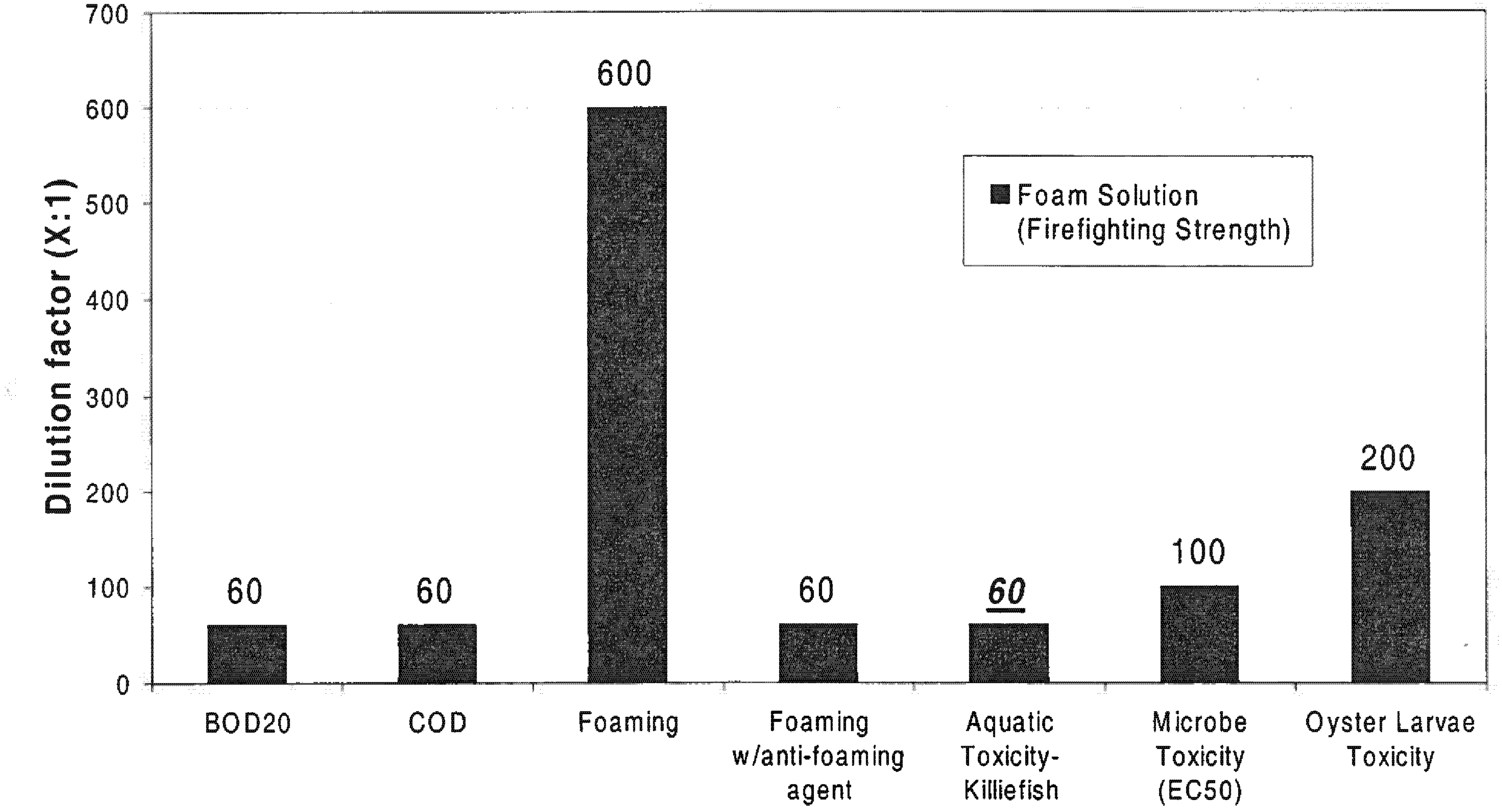
Environmental Consequences

Media: Surface Water Via Direct Discharge to WWTP

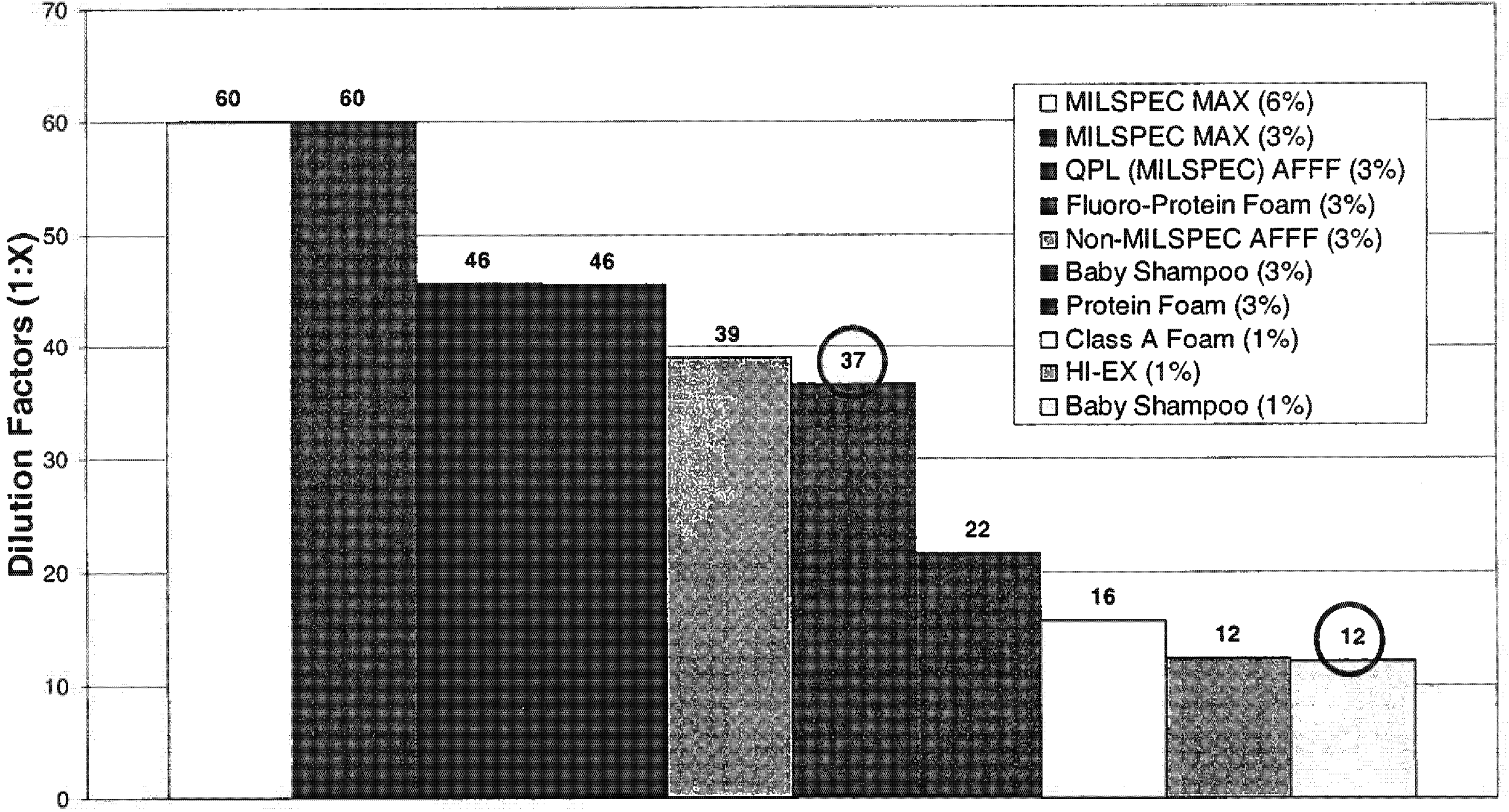
- Disrupts plant through:
  - Foaming
    - Disrupts mechanical devices
    - Causes ‘sludge bulking’
    - Causes Froth
  - High Oxygen Demand
    - Removes all oxygen - killing microorganisms used to treat sewage
    - Causes ‘sludge bulking’.
  - Aquatic Toxicity
    - Of lower concern than Foaming and Oxygen Demand
    - May cause ‘sloughing’ of organisms from certain processes

- Disrupted plant:
  - Contaminates receiving water
  - Could cause fish kill
  - Makes water unfit for:
    - Drinking
    - Recreation, etc.

Representative Dilution Factors for Treatment of MAX MILSPEC AFFF at a WWTP



Representative Dilution Factors for COD of Foam Solution (Firefighting Strength)



Summary

- Under Context of Current Laws/Regulations, AFFF and all other Foams Regulated Based On:
  - Properties
    - BOD, COD, Foaming and Aquatic Toxicity
  - "Listed" Chemical Constituents
    - Butyl Carbitol, Surfactants, Ethylene Glycol, Urea, etc.
  - Water Issues are Most Prevalent
  - Foaming is Major Issue for WWTP
- Potential Environmental Impacts Generally Low
  - Impacts Consequence of
    - Foaming
    - O_2 Demand
    - Aquatic Toxicity
  - Upset of WWTP Creates Greatest Impact

APPENDIX (9)

Presentation: AFFF Management – Risk Based Approach"

D. Verdonik
Hughes Associates, Inc.
Baltimore MD

AFFF Management
Risk Based Approach

Dr. Dan Verdonik

HUGHES ASSOCIATES, INC.
FIRE SCIENCE & ENGINEERING

Why a Risk Based Approach?

- From Environmental Review
  - AFFF / Foams have Similar Environmental Impacts
    - Based on the Properties of Foams in General
    - Worst Impact for WWTP
  - Hazard Exists
  - Cannot Alter What Would Happen IF Released
- Can Reduce the If or Likelihood of Release
  - Example - Double Hulled Oil Tankers
    - Hazard Exists from Potential Oil Spill
    - Double Hull Reduces Probability of Having the Oil Spill
    - Double Hull Does Not Reduce Environmental Impact IF Have Oil Spill
    - Reducing Probability Reduces the Risk to the Environment
- Need to Evaluate Probability of Foam Release
- Probability + Severity = Risk

Risk and Risk Assessments

- Military Standard 882C: System Safety Program Requirements
  - Define Terms
    - Risk - Combination of hazard severity AND hazard probability
    - Hazard Probability: <u>Aggregate</u> probability of the <u>individual events</u>
    - Hazard Severity: Consequences of worst credible mishap
    - Control: Action to Eliminate Hazard or Reduce Risk
  - Applicable to All DOD Systems and Facilities
  - Identify the Hazards and Impose Design Requirements and Management Controls to Prevent Mishaps
  - Tailor to Application
    - AFFF/Foam Discharge from Facility Fixed Fire Suppression System
    - Accidental Discharge
    - Pre-planned testing
- Have Hazard Severity, Need Hazard Probability
  - Determine Risk
  - Risk Decision

MIL-STD-882C
4.5.2 Hazard Probability

- Potential occurrences per unit of time, events, population, items, or activity
  - Quantitative probability for potential design generally not possible
  - Qualitative probability
    - Derived from research, analysis, and evaluation of historical data
- Given for Specific Individual Item or Fleet / Inventory
- Assign Probability of Having Environmental Consequence

Qualitative Probability Levels
Specific Individual Item

FREQUENT	(A)	Likely to occur frequently
PROBABLE	(B)	Will occur several times in the life of an item
OCCASIONAL	(C)	Likely to occur some time in the life of an item
REMOTE	(D)	Unlikely but possible to occur in the life of an item
IMPROBABLE	(E)	So unlikely, it can be assumed occurrence may not be experienced

MIL-STD-882C

4.5.1 Hazard Severity

- Hazard Severity Category Definition
  - Provide Qualitative Measure of Worst Credible Mishap
  - Result of:
    - Personnel Error
    - Environmental Conditions
    - Design Inadequacies
    - Procedural Deficiencies
    - System, Subsystem or Component Failure or Malfunction

Qualitative Hazard Severity Categories

CATASTROPHIC	(1)	Death, System Loss, or Severe Environmental Damage
CRITICAL	(2)	Severe Injury, Severe Occupational Illness, Major System or Environmental Damage
MARGINAL	(3)	Minor Injury, Minor Occupational Illness, Minor System or Environmental Damage
NEGLIGIBLE	(4)	Less Than Minor Injury, Occupational Illness, Less Than Minor System or Environmental Damage

Risk Assessment and Acceptance

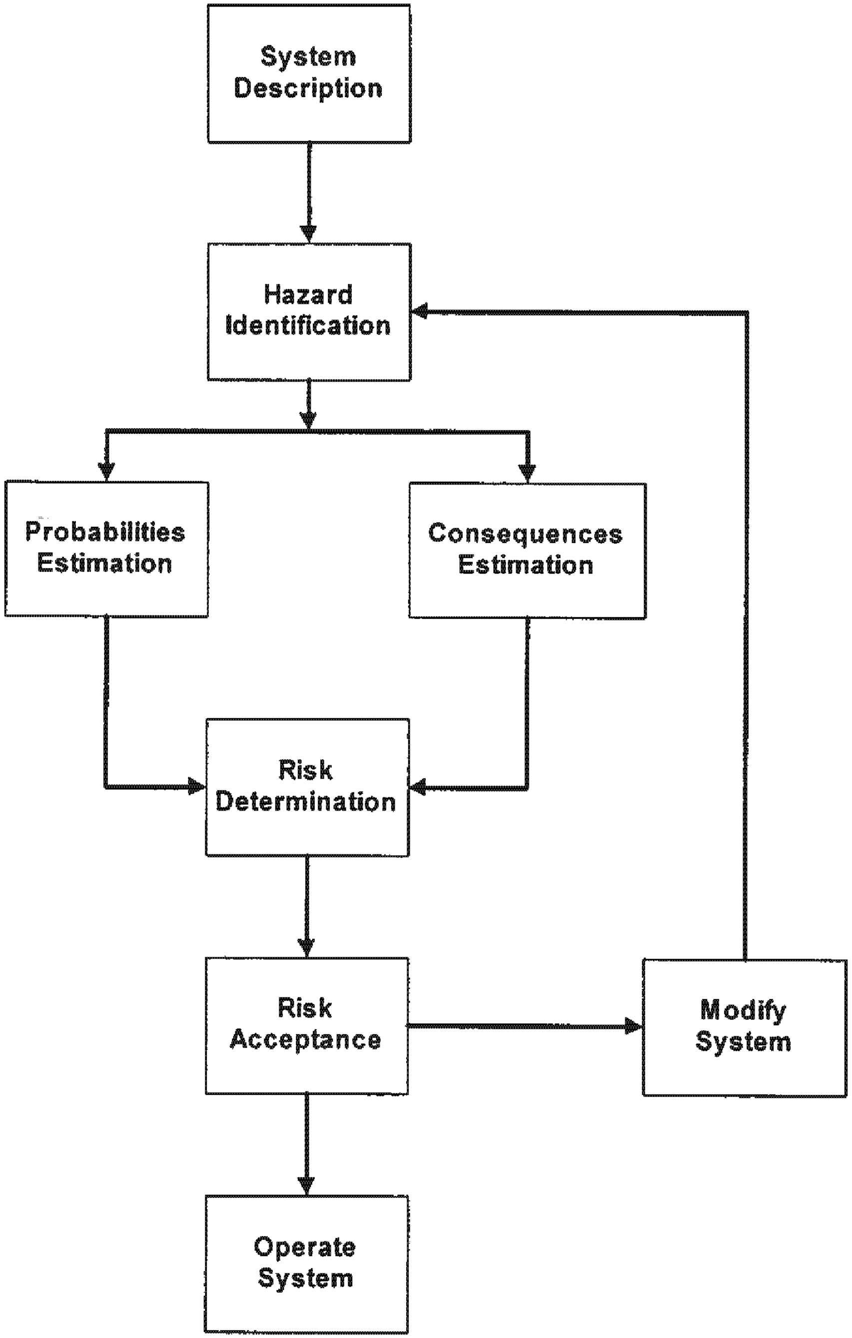
CATEGORY FREQUENCY	1 CATASTROPHIC	2 CRITICAL	3 MARGINAL	4 NEGLIGIBLE
A – FREQUENT	1A	2A	3A	4A
B – PROBABLE	1B	2B	3B	4B
C – OCCASIONAL	1C	2C	3C	4C
D – REMOTE	1D	2D	3D	4D
E - IMPROBABLE	1E	2E	3E	4E

- Risk Index - Suggested Acceptance Criteria in MIL-STD-882C

Unacceptable:	1A, 1B, 1C, 2A, 2B, 3A
Undesirable:	1D, 2C, 2D, 3B, 3C
Acceptable w/ Review by Managing Activity:	1E, 2E, 3D, 3E, 4A, 4B
Acceptable w/out Review:	4C, 4D, 4E

Design Criteria

- Design for minimum risk
  - Review design criteria for inadequate or overly restrictive requirements
  - Design to eliminate hazards
  - If hazard cannot be eliminated
    - Reduce risk to an acceptable level through design selection
    - Interlocks, redundancy, fail safe design, system protection, fire suppression, and protective clothing, equipment, devices, and procedures
- Recommend new design criteria supported by study, analyses, or test data



System Description

Hazard Identification

Probabilities Estimation

Consequences Estimation

Risk Determination

Risk Acceptance

Modify System

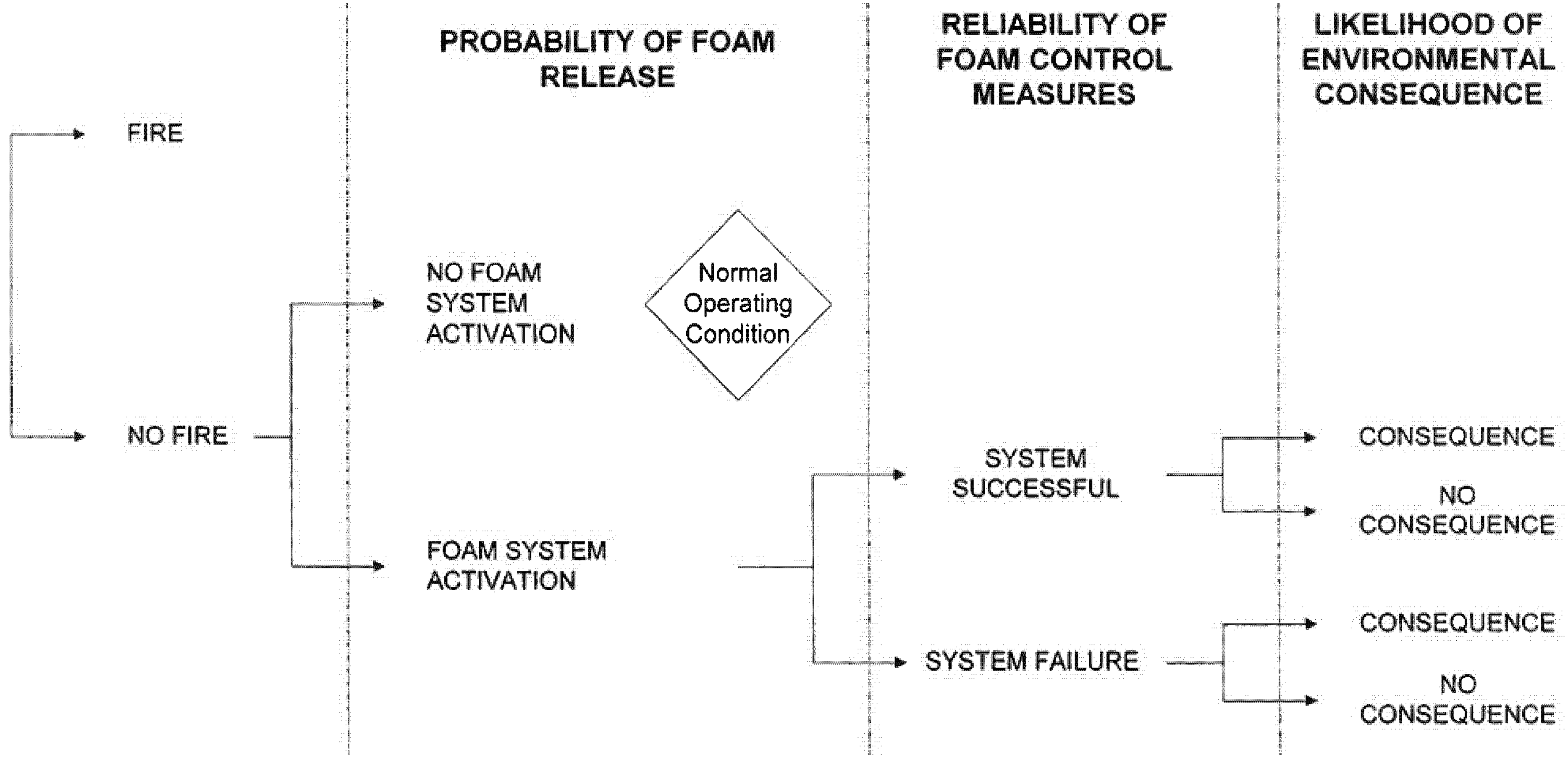
Operate System

Probability Estimation

3 Parts to Probability Estimation

- **Probability of foam release**
- **Reliability of system controlling foam movement**
- **Likelihood of environmental consequence**

Probability Estimation



PROBABILITY OF FOAM RELEASE

RELIABILITY OF FOAM CONTROL MEASURES

LIKELIHOOD OF ENVIRONMENTAL CONSEQUENCE

FIRE

NO FIRE

NO FOAM SYSTEM ACTIVATION

Normal Operating Condition

FOAM SYSTEM ACTIVATION

SYSTEM SUCCESSFUL

SYSTEM FAILURE

CONSEQUENCE

NO CONSEQUENCE

CONSEQUENCE

NO CONSEQUENCE

Accident Probability Estimation Of Environmental Consequence

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP	E	C	E	C
2. Segregated Storm Sewer	E	C	E	E
3. Plugged, Storm Sewer	E	D	E	D
4. Pavement, Plugged Storm Sewer/drains	E	D	E	E
5. Pavement, Plugged Combined Sewer/drains	E	D	E	D
6. Pavement, Combined Sewer WWTP	E	C	E	C
7. Pavement, Storm Sewer	E	C	E	E
8. Unlined Pond, Percolates	E	E	E	E
9. Lined Pond, Pump Off-Site	E	E	E	E
10 Lined Pond, evaporate	E	E	E	E
11. Lined Pond, Meter WWTP	E	D	E	D
12. Lined Pond, Meter Storm Sewer	E	C	E	D
13. Lined Pond, Degrade WWTP	E	D	E	D
14. Lined Pond, Degrade Storm Sewer	E	D	E	D
15. Tank, Pump Off-Site	E	E	E	E
16. Tank, Meter WWTP	E	D	E	D
17. Tank Meter Storm Sewer	E	C	E	D
18. Tank, Degrade WWTP	E	D	E	D
19. Tank, Degrade Storm Sewer	E	D	E	D

Consequence Estimation

Severity of Environmental Impact

Air → Negligible/Marginal*

Sensitive Body of Water → Marginal

Soil Ground Water → Marginal

WWTP → Critical

*Air becomes marginal if foam in WWTP

Risk Assessment and Acceptance

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP	3E	3C	3E	2C
2. Segregated Storm Sewer	4E	3C	3E	2E
3. Plugged, Storm Sewer	4E	3D	3E	2D
4. Pavement, Plugged Storm Sewer/drains	4E	3D	3E	2E
5. Pavement, Plugged Combined Sewer/drains	4E	3D	3E	2D
6. Pavement, Combined Sewer WWTP	3E	3C	3E	2C
7. Pavement, Storm Sewer	4E	3C	3E	2E
8. Unlined Pond, Percolates	4E	3E	3E	2E
9. Lined Pond, Pump Off-Site	4E	3E	3E	2E
10 Lined Pond, evaporate	4E	3E	3E	2E
11. Lined Pond, Meter WWTP	3E	3D	3E	2D
12. Lined Pond, Meter Storm Sewer	4E	3C	3E	2D
13. Lined Pond, Degrade WWTP	3E	3D	3E	2D
14. Lined Pond, Degrade Storm Sewer	4E	3D	3E	2D
15. Tank, Pump Off-Site	4E	3E	3E	2E
16. Tank, Meter WWTP	3E	3D	3E	2D
17. Tank Meter Storm Sewer	4E	3C	3E	2D
18. Tank, Degrade WWTP	3E	3D	3E	2D
19. Tank, Degrade Storm Sewer	4E	3D	3E	2D

Summary

- Control and Management of AFFF Solutions
  - Based on Risk of Environmental Consequence
    - Risk Decision
    - Probability AND Severity
  - No "Unacceptable" Risks from Accidental Discharge
  - "Undesirable" Risks Avoidable through Design
  - Remaining Options All have Equivocal Residual Risk
- Basis for Design Criteria
  - Ensure Risk is "Acceptable w/ Review by Managing Activity" Category
  - Minimizes Risk to the Environment
  - Does Not Increase Risk to Life-Safety/ Fire Loss

APPENDIX (10)

Presentation: "Phasing Out a Problem: Perfluorooctyl Sulfonate"

M. Dominiak
Environmental Protection Agency

Phasing Out a Problem: Perfluorooctyl Sulfonate (PFOS)

Mary F. Dominiak
U.S. Environmental Protection Agency
Naval Research Laboratory
3 August 2000

What is PFOS?

- Perfluorooctyl sulfonates; *acids, salts, halides, etc.*
- Man-made: do not occur in nature
- Produced since 1950's for use in surface treatment, paper protection, and performance chemical (surfactant and insecticide) products
- Also produced by breakdown/degradation of other sulfonyl-based fluorochemicals
- Made mostly by 3M Company

What is PFOS used for?

- Soil and stain resistant coatings on textiles, carpets, leather (2.3 million lbs/year)
- Oil, grease, and water resistance on paper products, including paperboard and food contact papers (2.6 million lbs/year)
- Performance chemicals: fire fighting foams, industrial surfactants, acid mist suppression, etc. (1.5 million lbs/year)

Why is PFOS a problem?

- PFOS is a PBT chemical:

  <u>P</u>ersistent

  <u>B</u>ioaccumulative

  <u>T</u>oxic

- PFOS has been found in the blood of the general US population, in wildlife, and in people overseas

Why is PFOS a problem?

- Persistent:
  - PFOS is a very stable chemical that does not break down or degrade in the environment; *once it's there, it stays*
- Bioaccumulative:
  - PFOS can build up over time; *its half-life in human blood is about 4 years*
  - Higher-ups in the food chain are exposed to the full dose of what has built up in their food

Why is PFOS a problem?

- Toxicity:
  - PFOS is only moderately toxic via acute oral exposure; *rat LD_{50} of 251 mg/kg*
  - In repeat oral dose subchronic and reproductive toxicity studies, however, serious effects seen
    - *Post-natal deaths in rats at 3.2 and 1.6 mg/kg/day*
    - *In repeat-dose treated Rhesus monkeys, death within 3 weeks at 10 mg/kg/day; within 7 weeks at 4.5 mg/kg/day. Adverse effects in cynomolgus monkeys at 0.75 mg/kg/day*

Why is PFOS a problem?

- Detected in blood not only in workers handling the chemical, but in the general US population and in wildlife
  - *High as 12.83 ppm in manufacturing workers*
  - *In pooled serum from general population, 30-40 ppb; small sample of children, mean 54 ppb*
  - *In eagles, wild birds, and fish, in ppb range*

How did PFOS get in people?

- We don't know the precise exposure route, but studies are underway
- Possibilities include:
  - Dietary intake from food wrapped in papers treated with PFOS derivatives
  - Inhalation from aerosol applications
  - Inhalation, dietary, or dermal exposures during manufacturing, use, or disposal of chemicals and treated products

Why haven't PFOS problems been addressed before?

- PFOS was always known to be persistent, but much information on bioaccumulation and toxicity is recent
  - Improved detection technologies find PFOS at much lower levels in humans, wildlife
  - PFOS doesn't fit normal bioaccumulation model; *partitions to blood, not fat*
  - Newest toxicity tests raise greatest concerns

How big a risk is PFOS?

- EPA does not believe that the current situation presents an imminent health risk to the general US population; *blood levels low, concentration in surface-treated products (carpets/textiles) low*
- However, serious concern for potential future risk to humans and wildlife if PFOS continues to be produced, released, built up in the environment
- Studies underway to determine relationship of current blood levels to potential for adverse effects
- Questions/concerns on occupational exposures

What is being done about PFOS?

- 3M conducted studies, shared results with EPA, and discussed concerns
- On 5/16/2000, 3M publicly announced voluntary phase-out of perfluorooctanyl chemistries, most by end of 2000
- 3M submitted phase-out plan to EPA on 6/16/2000, amended on 7/7/2000
- 3M continues aggressive research program

What does the 3M PFOS phaseout plan involve?

- 3M will stop manufacture of PFOS for surface treatment products by 12/31/2000; *includes fabric/carpet/leather soil and stain resistance and paper coating products, including food contact*
- 3M will phase out manufacture of PFOS for performance products by 12/31/2002
- *Caveat:* May request permission for extended production for specific performance uses for which adequate substitutes do not exist or can't be qualified in time; *risk/risk tradeoffs, national security, technical performance issues*

What does EPA think of 3M's PFOS phaseout plan?

- EPA agrees that continued manufacture and use of PFOS represents an unacceptable technology that should be eliminated to protect human health and the environment from long term consequences
- 3M's voluntary phaseout will accomplish this goal more quickly than regulation could
- EPA may use regulation to "close the door" on PFOS after 3M's exit; *concerned parties will be able to comment and to dialogue with EPA*

What does this mean for fire fighters using PFOS foams?

- Fire fighting foams are in the performance category of products; continue through 2002
- 3M and EPA will be assessing health, safety and environmental implications of possible substitutes; *will welcome dialogue!*
- If qualified substitutes not available by end of 2002, 3M may request continued PFOS production for specific uses

What about using chemicals other than PFOS?

- Initial actions and phaseout apply to PFOS chemicals only
- EPA will be expanding review to assess other perfluorinated chemicals and related chemistries; *PFOA, telomers*
- Assessment activities will be international
- Industry group already proposing voluntary two-year research effort on some major telomers to begin 9/2000
- Too early to anticipate outcomes

How will EPA make decisions on PFOS issues?

- Toxic Substances Control Act (TSCA)
- Risk/benefit balancing requirements allow flexibility; *TSCA lets EPA take risk/risk tradeoffs, economic issues into account*
- Possible actions include:
  - Bans
  - Restrictions on uses
  - Production volume limits
  - Data collection and new testing requirements
  - Labeling, hazard communication

Where can I find information on PFOS and EPA actions?

- All documents on PFOS in public EPA Administrative Record, File AR-226
  - Includes all health studies submitted on PFOS
  - Available in hard copy or on CD-ROM
  - 401 M St, SW, Room NE B-607, Wash., DC, noon to 4 PM Eastern, Monday-Friday; telephone 202-260-7099
- Working on website; *not up yet, stay tuned*
- Interim EPA "Voice of PFOS:" Mary Dominiak, phone 202-260-7768; *dominiak.mary@epa.gov*

APPENDIX (11)

Presentation: "Facilities Background and AFFF Issues"

J. Simone
Naval Facilities Engineering Command

Facilities Background
And
AFFF Issues

Presentation to Hangar Facilities Breakout Session
DOD AFFF Environmental Meeting
2 August 2000

Joe Simone
Naval Facilities Engineering Command

FACILITIES BACKROUND

- Facilities that use AFFF - Aircraft Hangars, HAZ/FLAM Buildings, Fire Fighters Test Facilities, Hush Houses, and others
- Variety of Fire Protection Criteria in the Last 10 Years
- Variety of Containment Requirements
- No Risk Analysis with respect to Environmental
- Budget Proposals Guess or Don't Address Funding

NAVAIR/NAVFAC HANGAR PROJECTS

- Evaluated Detector & Sprinkler Response Time in Hangars
- Evaluated Removing AFFF from Overhead Sprinkler Systems
  - Evaluated Using Lower AFFF Application Rate
- Evaluated New Low Level AFFF Distribution Systems
- Evaluated Variety of Optical Flame Detectors
- Developed New Fire Protection Criteria

DESIGN

PREVIOUS DESIGNS	CURRENT DESIGNS
• Deluge AFFF Sprinklers	• Closed Head, Water only Sprinklers
• High Volume AFFF System (20,000 sq.ft. => 5,000 gpm AFFF)	• Low Volume AFFF System (20,000 sq.ft. => 2,000 gpm AFFF & 3,000 gpm water)
• AFFF is used in the Ceiling <u>and</u> Low Level Systems	• AFFF is used in the Low Level System <u>only</u>
• Full Discharge Testing	• Test Ports for Discharge Testing
• May or May not have Drainage System	• Drainage
	• Detection Technology
	• Can Include Abort Switches

AFFF MANAGEMENT ISSUES

- Environmental Hazard is Not Quantified
  - Toxicity?, Air?, Water?
- No Uniform Criteria for AFFF Management (site specific)
- Current Containment Requirements are Based on Worst Case
- Cost of Containment Exceeds Project Funding
- Exceeding Project Funding Results in Removal of Fire Protection Systems from Hangars - Impaired Mission

CONTAINMENT ISSUES

If Containment is Required:

- Manual Intervention or Fixed Containment?
- How Do You Size Containment (10 minutes of AFFF supply)?
- Disposal - Is it necessary?

APPENDIX (12)

Presentation: "AFFF Risk Assessment"

A. Wakelin
Hughes Associates, Inc.
Baltimore MD

Aqueous Film Forming Foam (AFFF) Risk Assessment

For discharges of AFFF from fixed fire protection systems in shore facilities

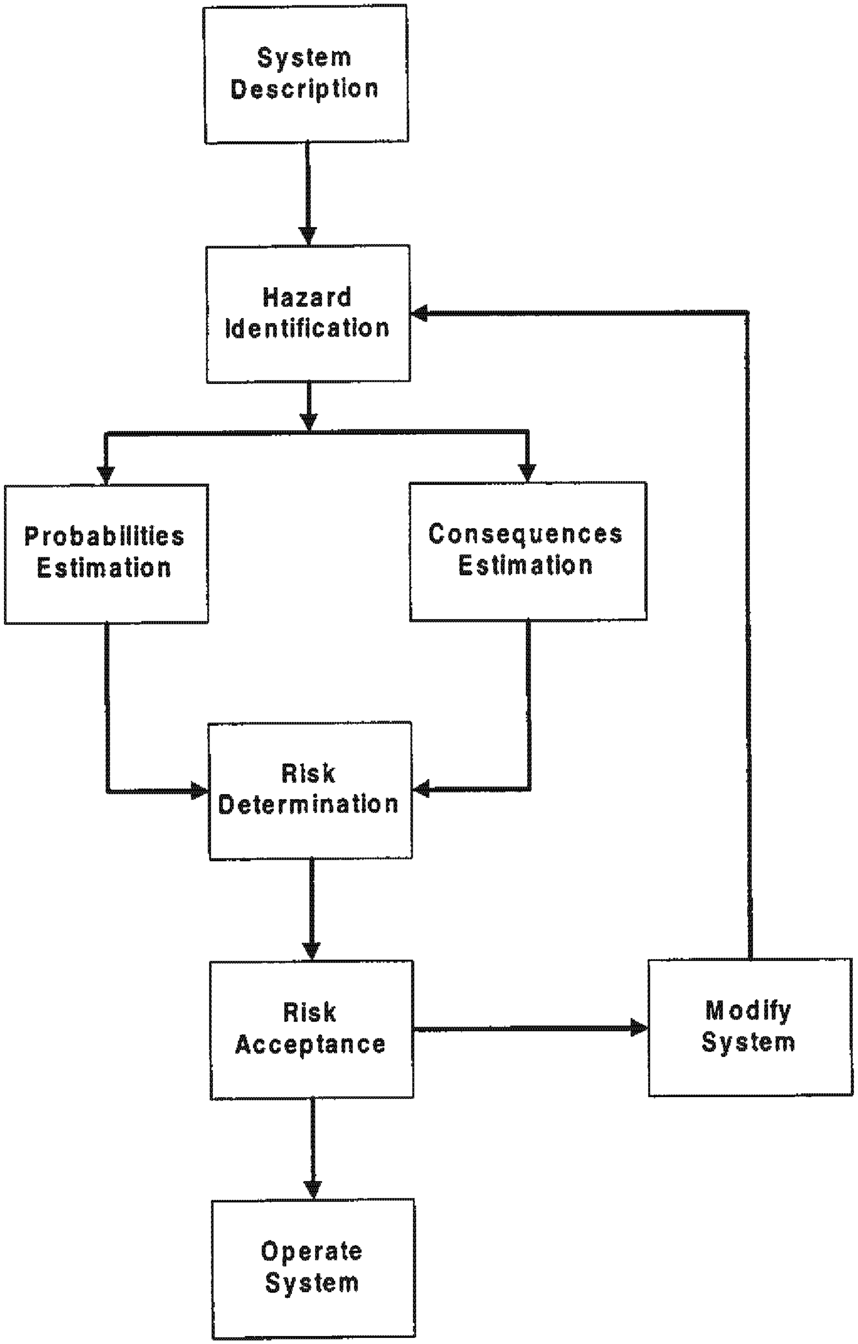
Alison Wakelin

HUGHES ASSOCIATES, INC.
FIRE SCIENCE & ENGINEERING

August 2, 2000

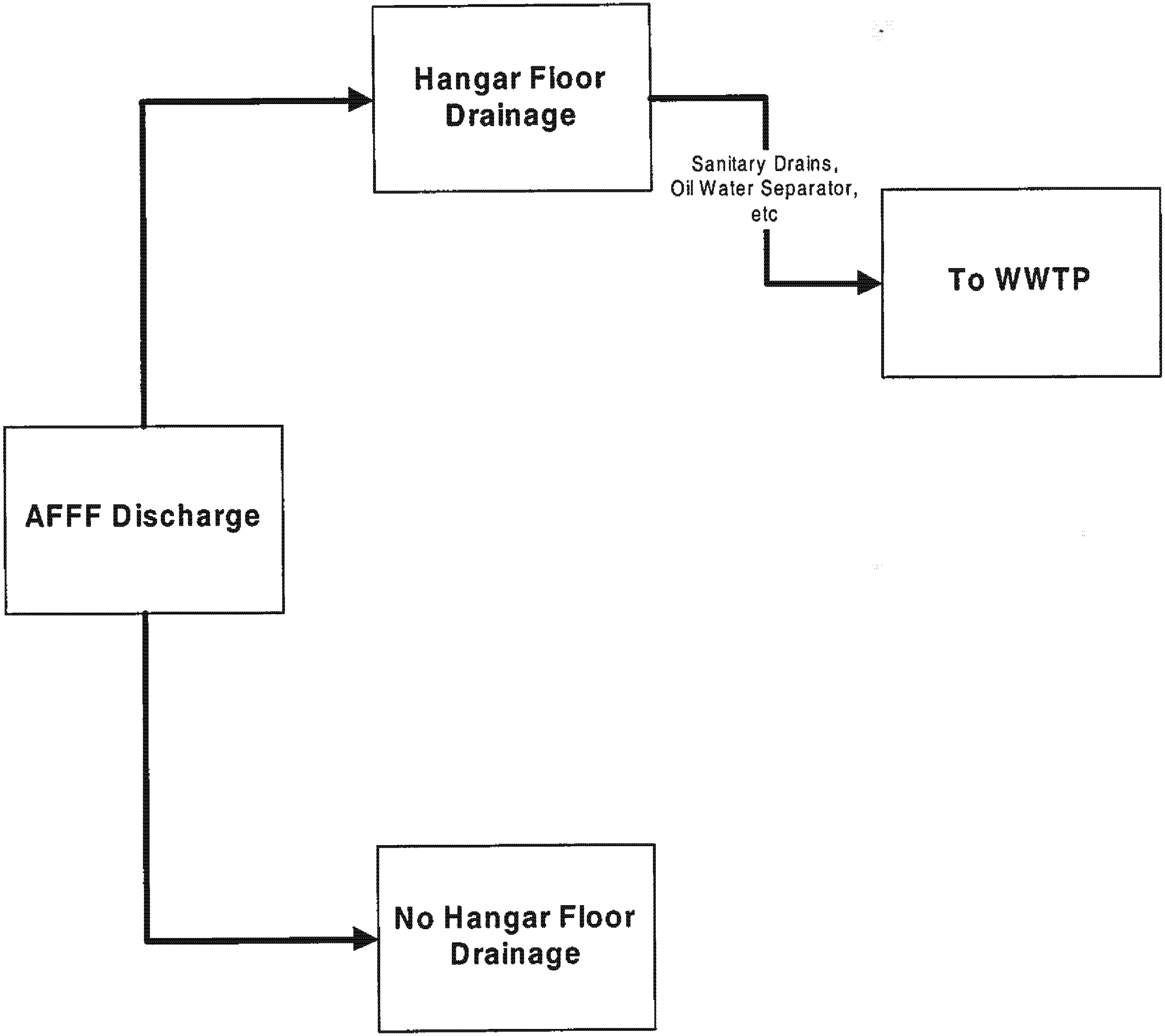
Overview

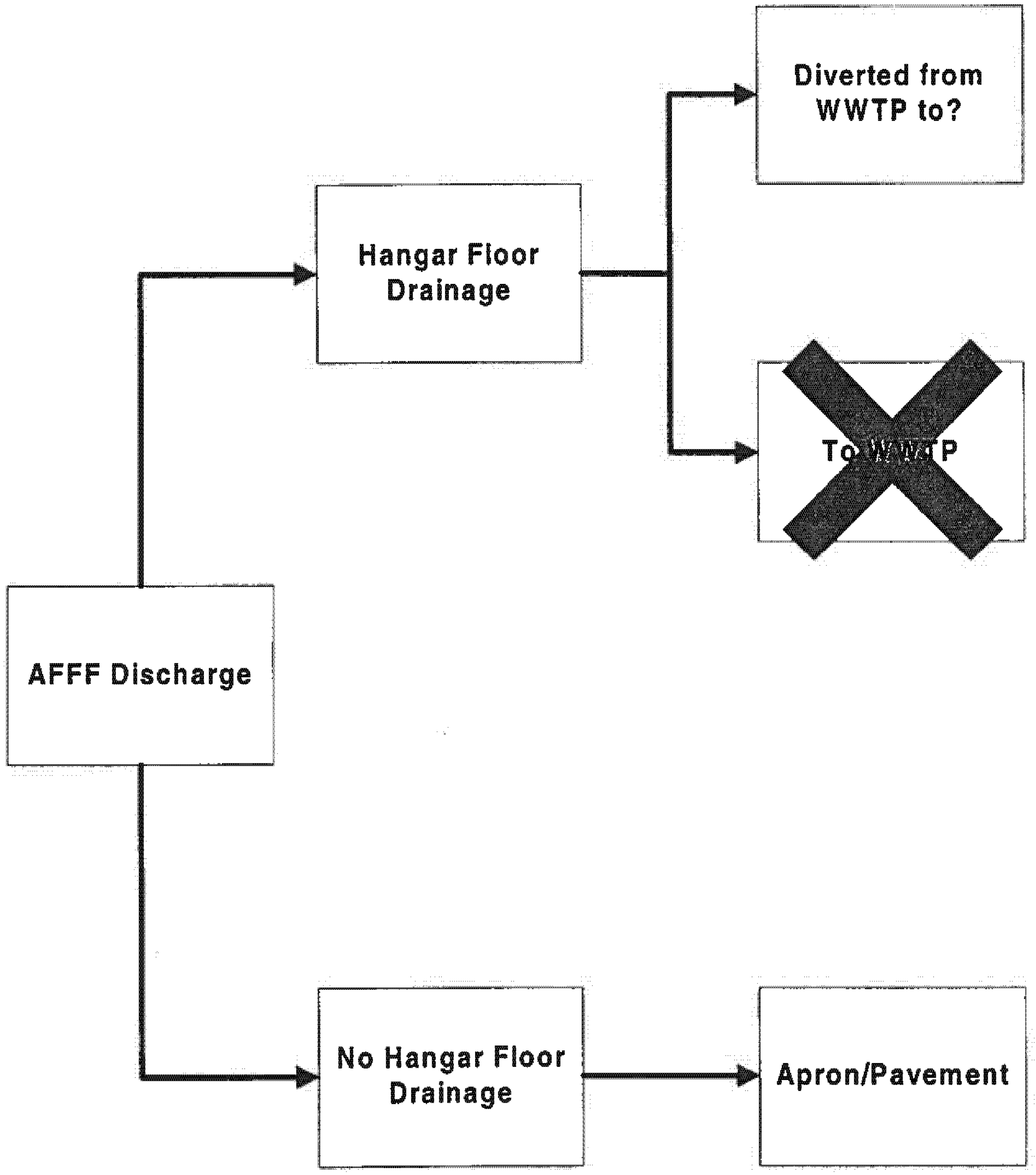
- Develop physical control options
  - Performance Criteria
- Probability Estimation
- Consequence Estimation
- Risk Assessment

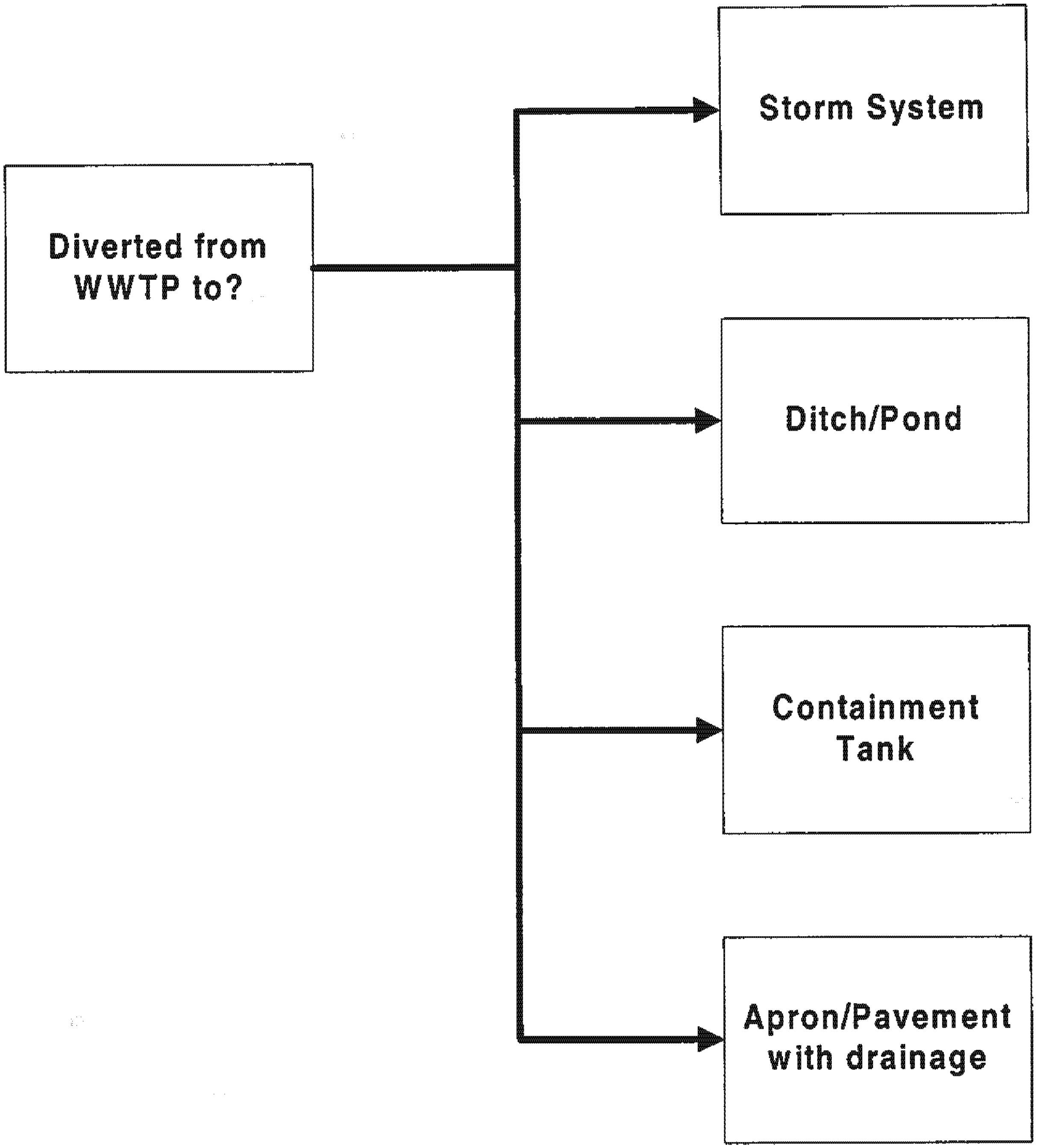

System Description
Hazard Identification
Probabilities Estimation
Consequences Estimation
Risk Determination
Risk Acceptance
Modify System
Operate System

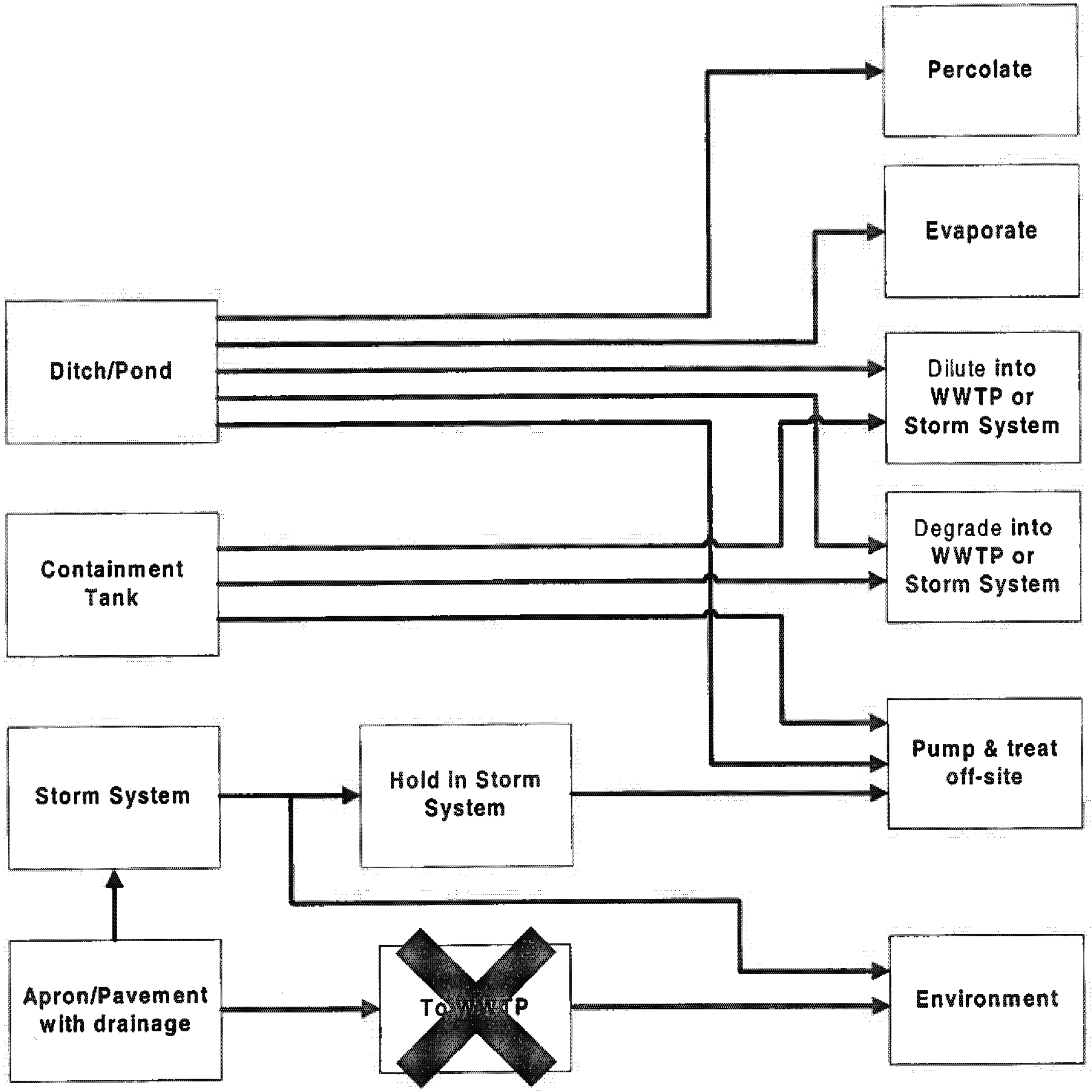
Develop Physical Control Options

- Hangar drainage requirements (NFPA 409)
- Foam to the WWTP?
- Other options for maintaining positive control of foam


AFFF Discharge
Hangar Floor Drainage
Sanitary Drains, Oil Water Separator, etc
To WWTP
No Hangar Floor Drainage


Diverted from WWTP to?
Hangar Floor Drainage
~~To WWTP~~
AFFF Discharge
No Hangar Floor Drainage
Apron/Pavement


Diverted from WWTP to?
Storm System
Ditch/Pond
Containment Tank
Apron/Pavement with drainage


Percolate
Evaporate
Ditch/Pond
Dilute into WWTP or Storm System
Degrade into WWTP or Storm System
Containment Tank
Storm System
Hold in Storm System
Pump & treat off-site
Apron/Pavement with drainage
~~To WWTP~~
Environment

Physical Control Options

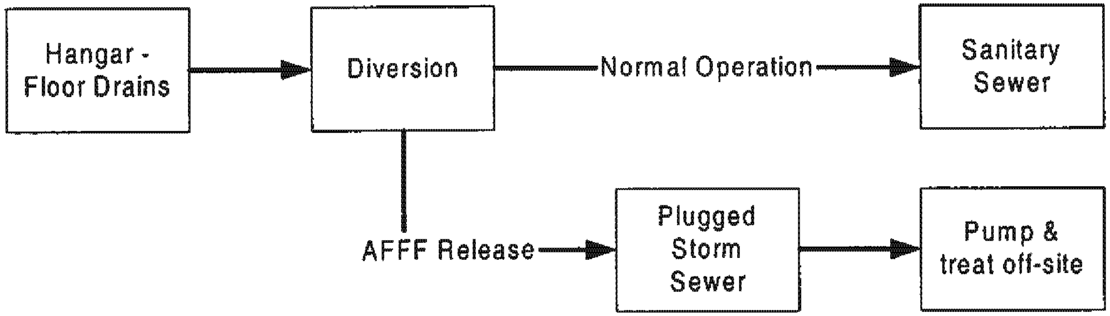
- 19 different control options
- Sufficient number to show range of risks
- Three options will be presented
  - data from all available on request

Example Physical Control Options

1. Sanitary sewer with direct access to WWTP

Hangar - Floor Drains → Sanitary System → WWTP

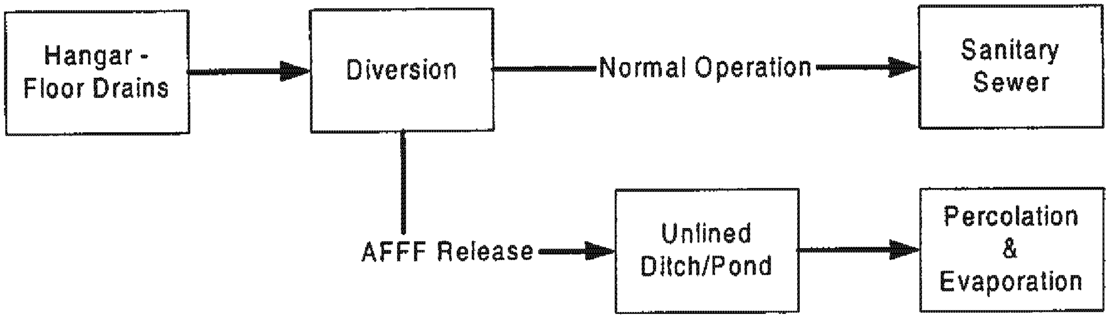
2. Plugged, totally segregated storm sewer



Hangar - Floor Drains → Diversion —Normal Operation→ Sanitary Sewer

Diversion — AFFF Release → Plugged Storm Sewer → Pump & treat off-site

3. Pond, Percolate (drains into soil)



Hangar - Floor Drains → Diversion —Normal Operation→ Sanitary Sewer

Diversion — AFFF Release → Unlined Ditch/Pond → Percolation & Evaporation

Performance Criteria

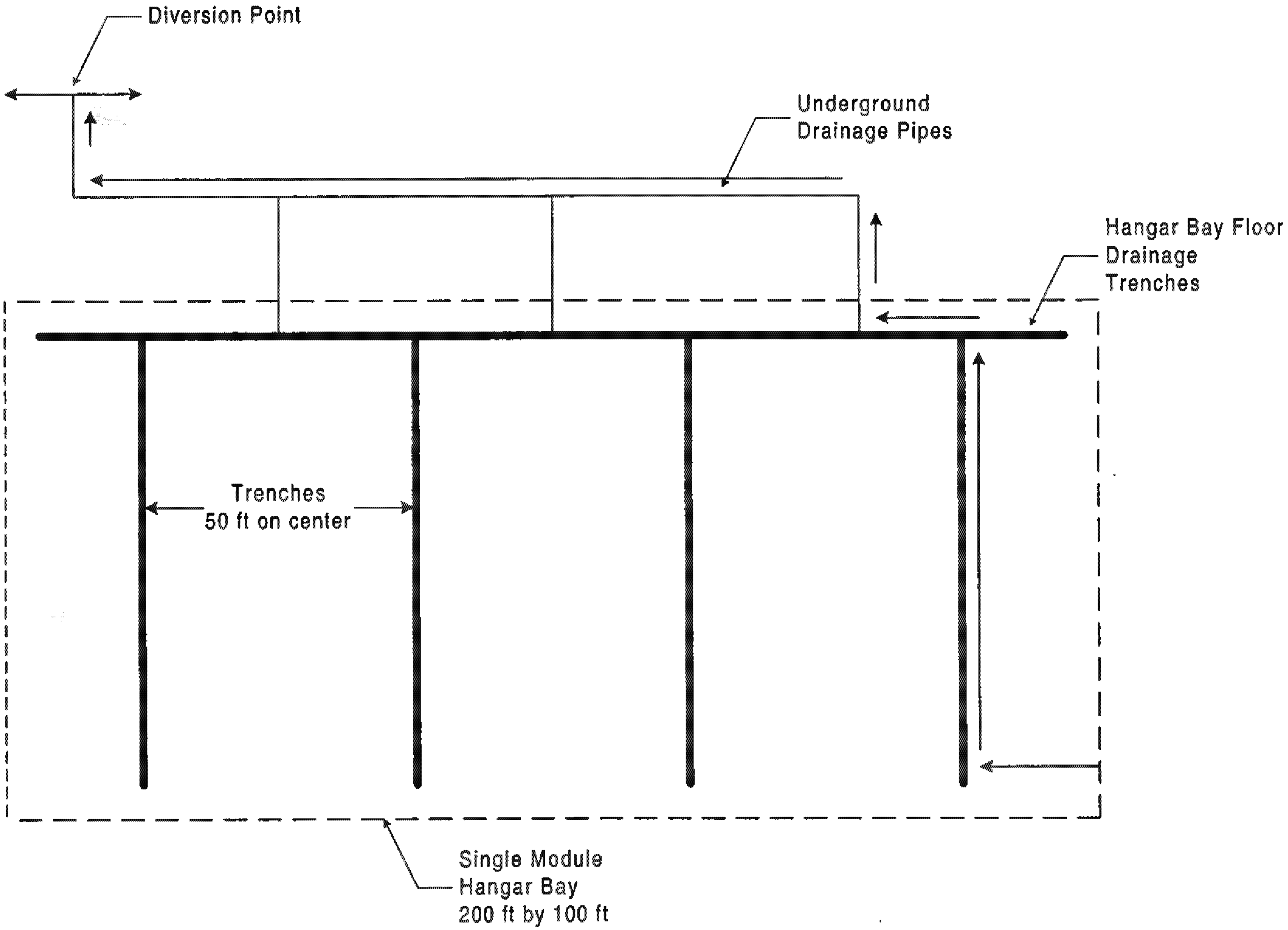
- Detailed investigation of control options
- What are performance goals of control options?
  - How much of a discharge needs to be controlled?
- Accidental discharge shut-off in 3 mins?
- Accidental discharge of all foam?

Proposed Foam Control Criteria

- Conservative approach all foam has drained to beyond diversion point
- No emergency shut-off
- 6 min drainage time
- Single "module" hangar 100 ft by 200 ft
- Total flow
  - 16 min @ 2000 gpm = 32,000 gal

Proposed Foam Control Criteria

Drainage

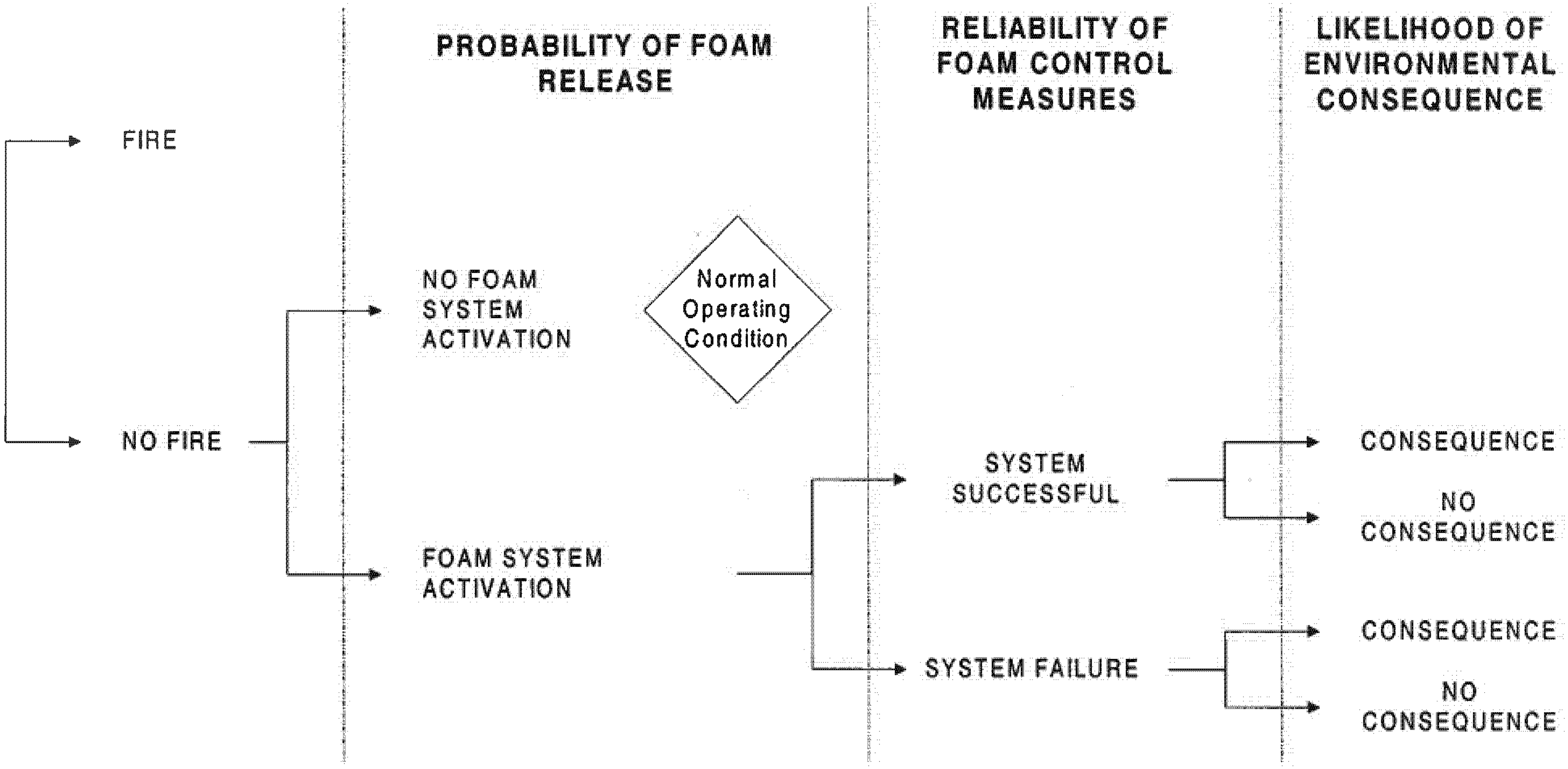


Probability Estimation

3 Parts to Probability Estimation

- Probability of foam release
- Reliability of system controlling foam movement
- Likelihood of environmental consequence

Probability Estimation

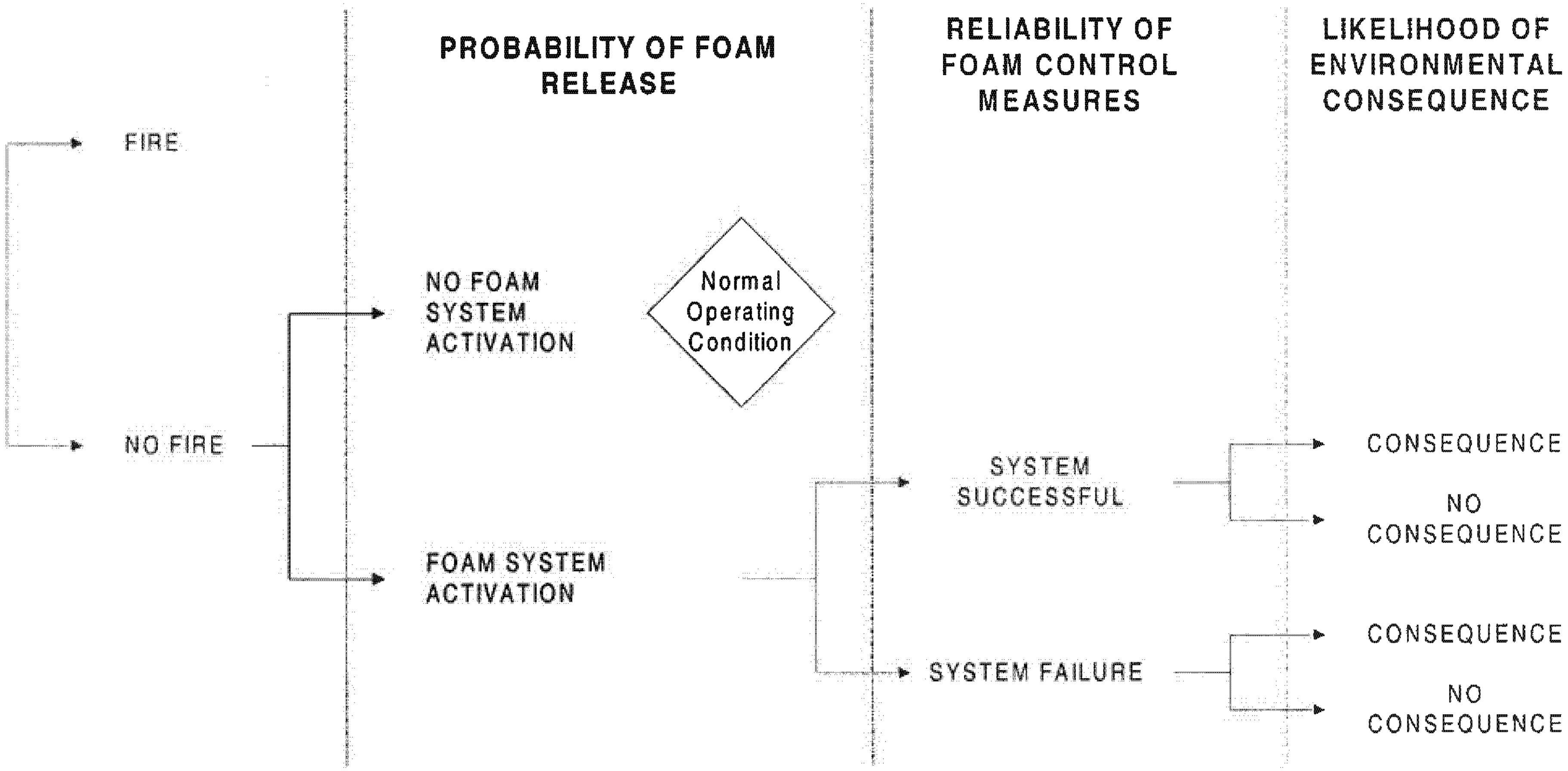


Probability Estimation

A	FREQUENT	Likely to occur frequently
B	PROBABLE	Will occur several times in the life of an item
C	OCCASIONAL	Likely to occur some time in the life of an item
D	REMOTE	Unlikely but possible to occur in the life of an item
E	IMPROBABLE	So unlikely, it can be assumed occurrence may not be experienced

Probability Estimation

Foam System Activation



PROBABILITY OF FOAM RELEASE

RELIABILITY OF FOAM CONTROL MEASURES

LIKELIHOOD OF ENVIRONMENTAL CONSEQUENCE

FIRE

NO FIRE

NO FOAM SYSTEM ACTIVATION

Normal Operating Condition

FOAM SYSTEM ACTIVATION

SYSTEM SUCCESSFUL

SYSTEM FAILURE

CONSEQUENCE

NO CONSEQUENCE

CONSEQUENCE

NO CONSEQUENCE

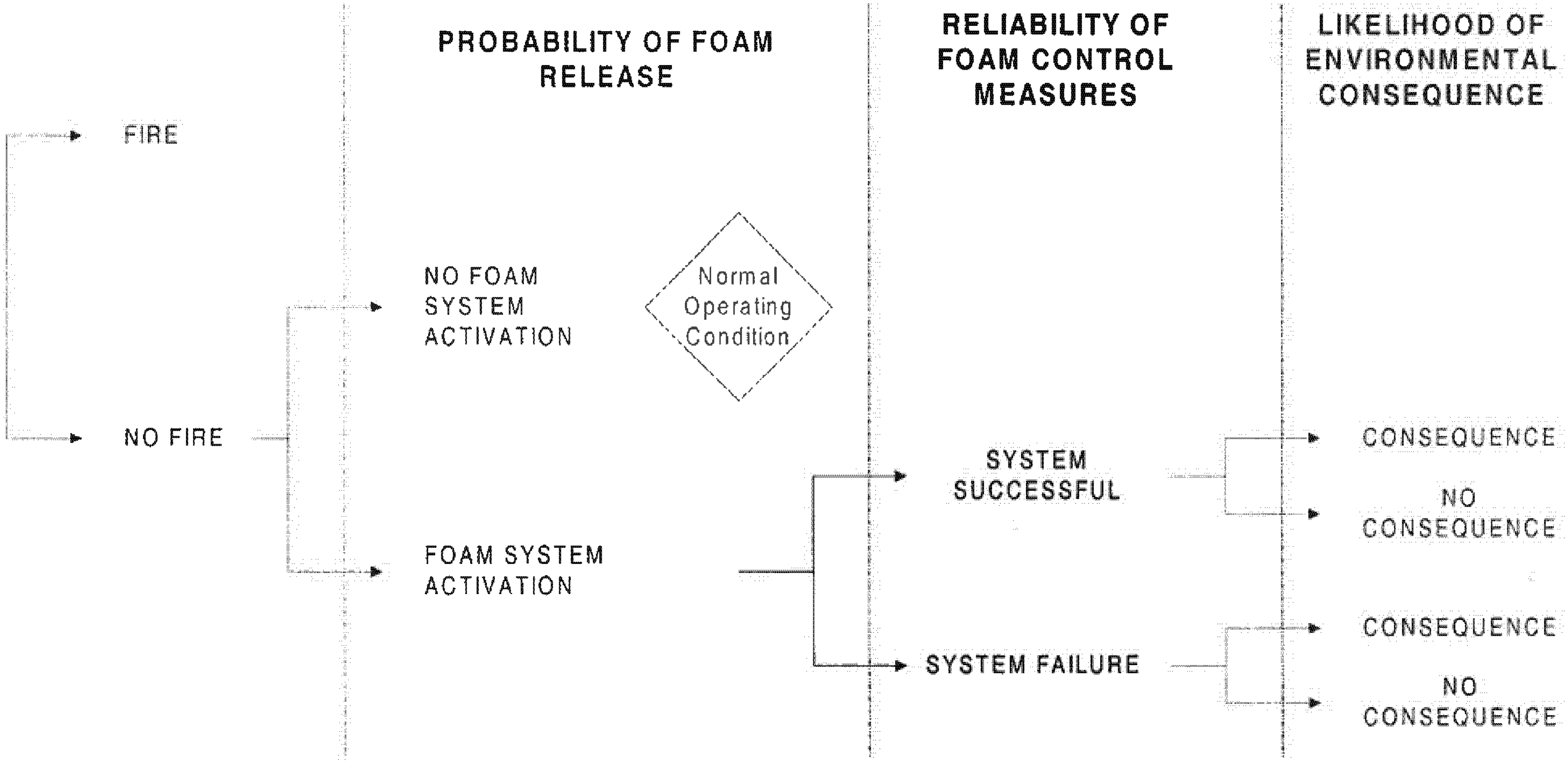
Probability Estimation
Foam System Activation

- Accidental activation of a low level foam system
- Likely to occur some time in the life of an item

⇒ Occasional C

Probability Estimation

Foam Control Measures



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Normal Operating Condition

FOAM SYSTEM ACTIVATION

SYSTEM SUCCESSFUL

SYSTEM FAILURE

CONSEQUENCE

NO CONSEQUENCE

CONSEQUENCE

NO CONSEQUENCE

Probability Estimation

Foam Control Measures

- An engineered design of each control measure is evaluated for:
  - Reliability
    - Likelihood of Control System Failure is Established
    - Failure based on complexity of system

Probability Estimation

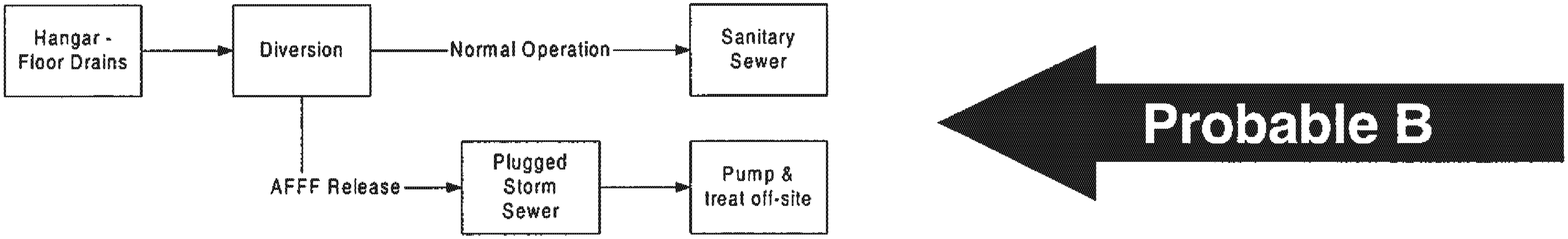
Likelihood of system failure

1. Sanitary sewer with direct access to WWTP

Hangar - Floor Drains → Sanitary System → WWTP

Improbable E

2. Plugged, totally segregated storm sewer

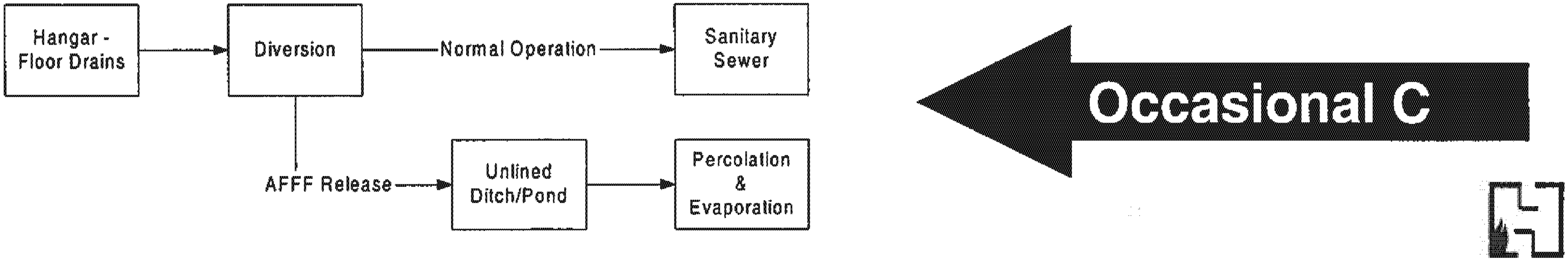


Hangar - Floor Drains → Diversion —Normal Operation→ Sanitary Sewer

Diversion — AFFF Release → Plugged Storm Sewer → Pump & treat off-site

Probable B

3. Pond, Percolate (drains into soil)



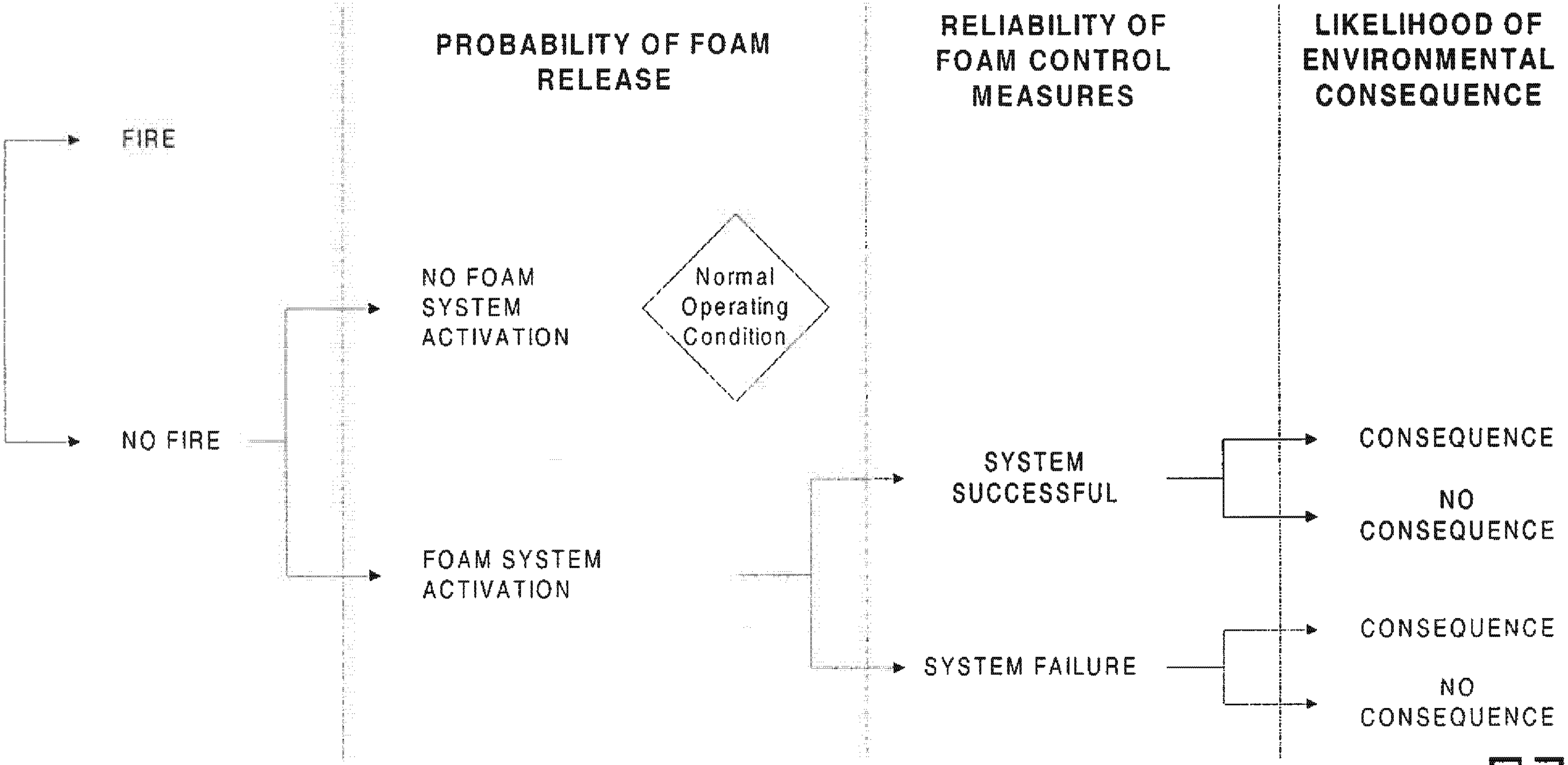
Hangar - Floor Drains → Diversion —Normal Operation→ Sanitary Sewer

Diversion — AFFF Release → Unlined Ditch/Pond → Percolation & Evaporation

Occasional C

Probability Estimation

Environmental Consequence



PROBABILITY OF FOAM RELEASE

RELIABILITY OF FOAM CONTROL MEASURES

LIKELIHOOD OF ENVIRONMENTAL CONSEQUENCE

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NO FOAM SYSTEM ACTIVATION

Normal Operating Condition

FOAM SYSTEM ACTIVATION

SYSTEM SUCCESSFUL

SYSTEM FAILURE

CONSEQUENCE

NO CONSEQUENCE

CONSEQUENCE

NO CONSEQUENCE

Probability Estimation

Environmental Consequence

Successful Foam Control (Risk By Media)

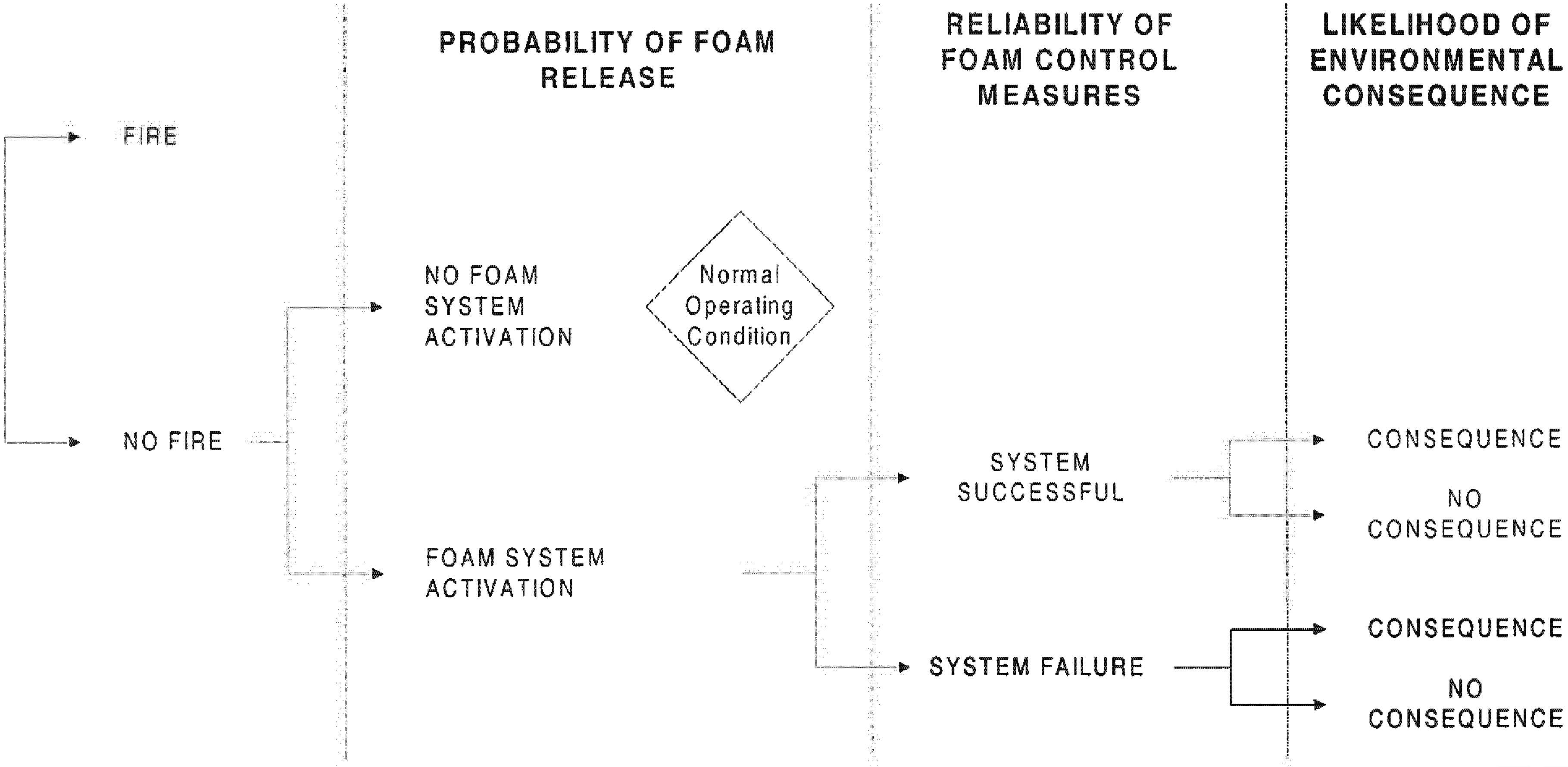
	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP	Remote	Frequent	Improbable	Frequent
2. Plugged, Storm Sewer	Remote	Improbable	Improbable	Improbable
3. Unlined Pond, Percolates	Remote	Remote	Remote	Improbable

Unsuccessful Foam Control (Risk By Media)

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP	Remote	Frequent	Remote	Frequent
2. Plugged, Storm Sewer	Remote	Occasional	Remote	Occasional
3. Unlined Pond, Percolates	Remote	Occasional	Occasional	Occasional

Probability Estimation

Environmental Consequence



PROBABILITY OF FOAM RELEASE

RELIABILITY OF FOAM CONTROL MEASURES

LIKELIHOOD OF ENVIRONMENTAL CONSEQUENCE

FIRE

NO FIRE

NO FOAM SYSTEM ACTIVATION

Normal Operating Condition

FOAM SYSTEM ACTIVATION

SYSTEM SUCCESSFUL

SYSTEM FAILURE

CONSEQUENCE

NO CONSEQUENCE

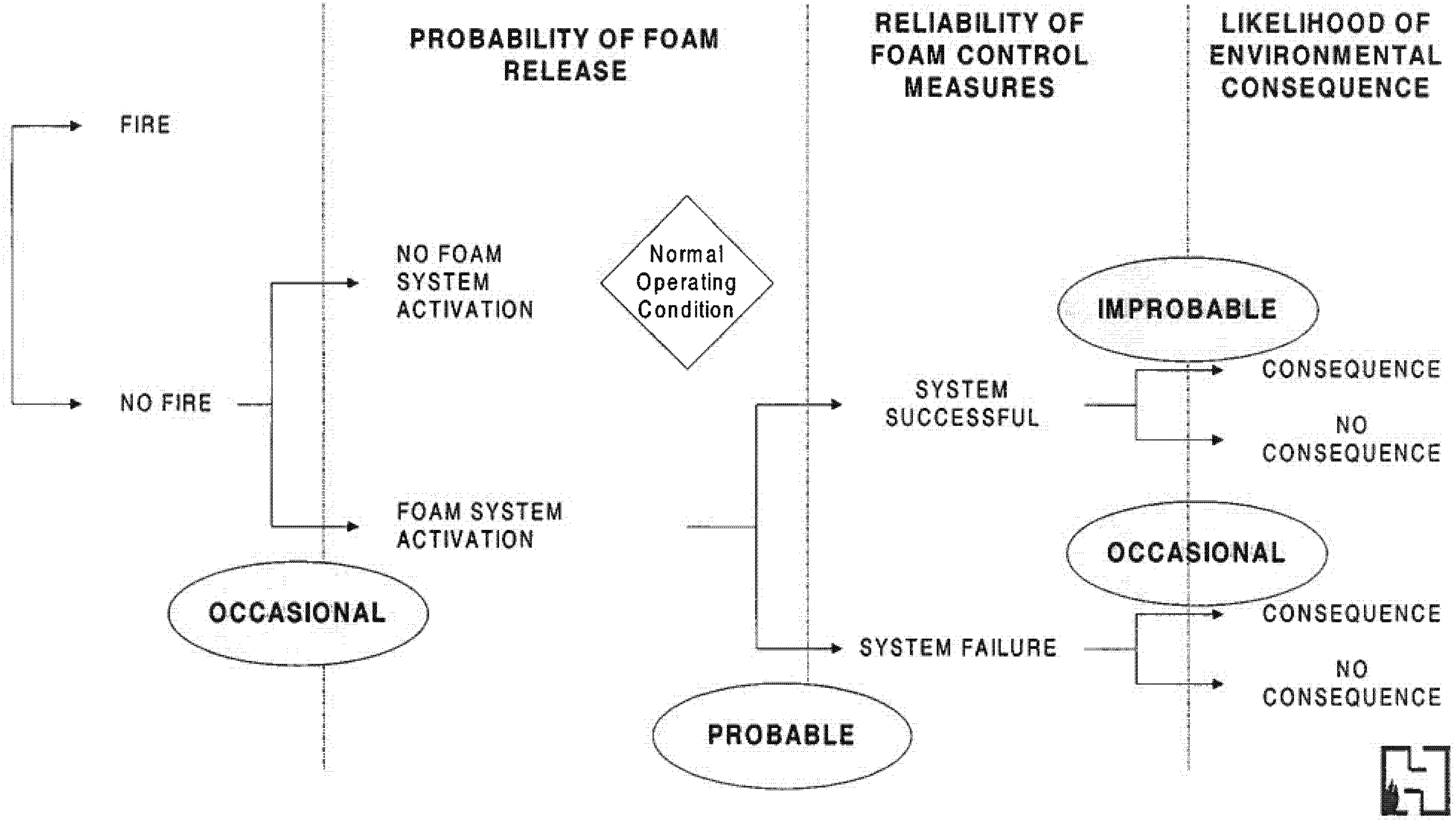
CONSEQUENCE

NO CONSEQUENCE

Probability Estimation

Environmental Consequences

Option 2: Plugged storm sewer Sensitive body of water



Probability Estimation

Frequency Estimation		Suggested Range
A	FREQUENT	$X > 10^{-1}$
B	PROBABLE	$10^{-1} > X > 10^{-2}$
C	OCCASIONAL	$10^{-2} > X > 10^{-3}$
D	REMOTE	$10^{-3} > X > 10^{-6}$
E	IMPROBABLE	$10^{-6} > X$

Probability Estimation
Environmental Consequence

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP	E	C	E	C
2. Plugged, Storm Sewer	E	D	E	D
3. Unlined Pond, Percolates	E	E	E	E

Consequence Estimation
Severity of Environmental Impact

Air	Negligible/Marginal*
Sensitive Body of Water	Marginal
Soil Ground Water	Marginal
WWTP	Critical

*Air becomes marginal if foam in WWTP

Risk Assessment & Acceptance

CATEGORY FREQUENCY	1 CATASTROPHIC	2 CRITICAL	3 MARGINAL	4 NEGLIGIBLE
A – FREQUENT	1A	2A	3A	
B – PROBABLE	1B	2B	3B	
C – OCCASIONAL	1C	2C	3C	4C
D – REMOTE	1D	2D		4D
E - IMPROBABLE				4E

UNACCEPTABLE:	1A, 1B, 1C, 2A, 2B, 3A
UNDESIRABLE:	1D, 2C, 2D, 3B, 3C
ACCEPTABLE WITH REVIEW:	
ACCEPTABLE WITHOUT REVIEW:	4C, 4D, 4E

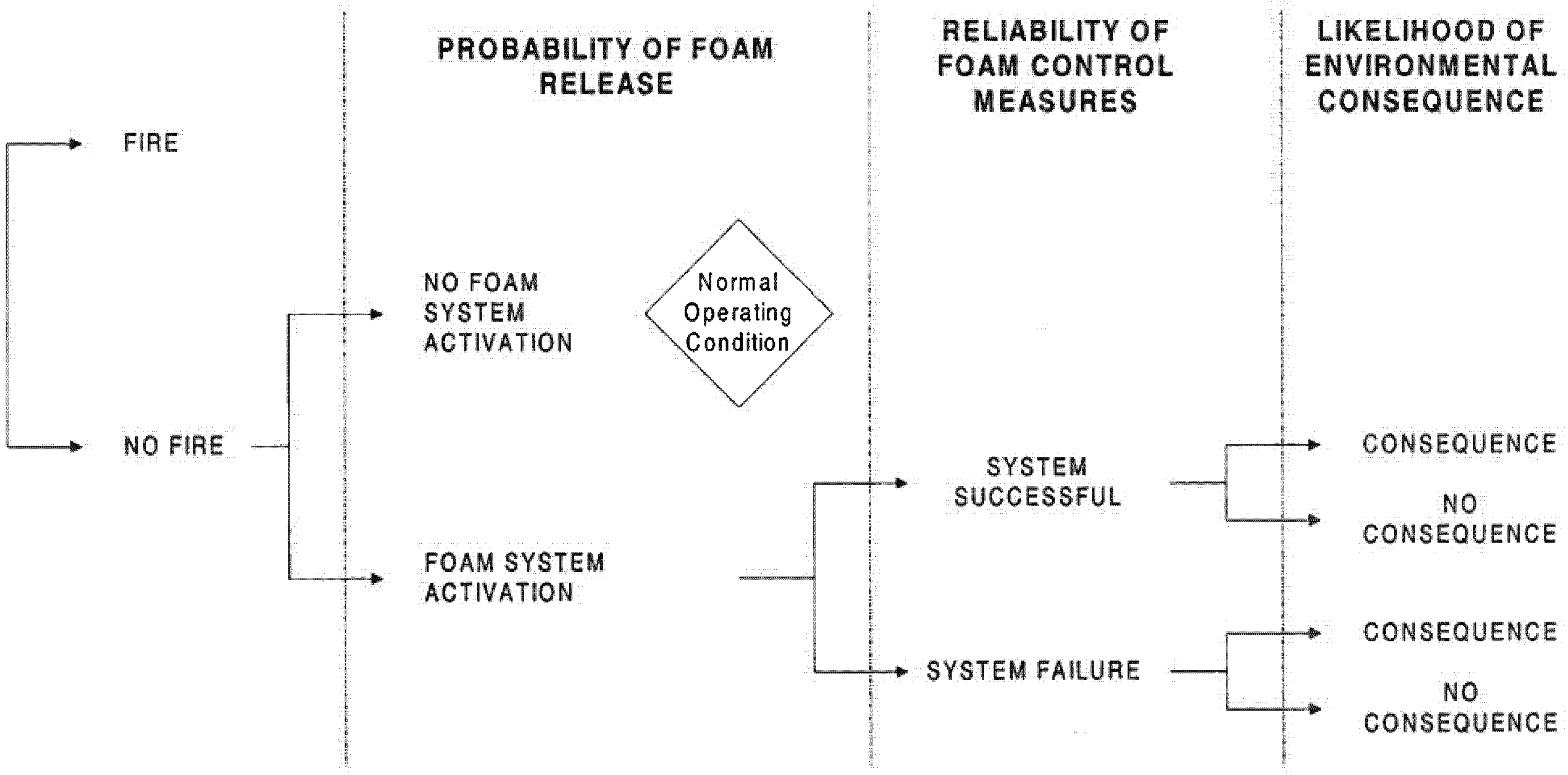
Risk Assessment

Environmental Consequence

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP		3C		2C
2. Plugged, Storm Sewer	4E			2D
3. Unlined Pond, Percolates	4E			

Probability Estimation

Foam System Activation



PROBABILITY OF FOAM RELEASE

RELIABILITY OF FOAM CONTROL MEASURES

LIKELIHOOD OF ENVIRONMENTAL CONSEQUENCE

FIRE

NO FIRE

NO FOAM SYSTEM ACTIVATION

Normal Operating Condition

FOAM SYSTEM ACTIVATION

SYSTEM SUCCESSFUL

SYSTEM FAILURE

CONSEQUENCE

NO CONSEQUENCE

CONSEQUENCE

NO CONSEQUENCE

Probability Estimation

Foam System Testing

- Should foam control systems be used for testing?
- Foam system activation becomes probable
- Reliability improved as testing supervised

Risk Assessment
Environmental Consequence

For Foam Testing

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP		3B		2B
2. Plugged, Storm Sewer	4D			2D
3. Unlined Pond, Percolates	4D			

For Accidental Release

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP		3C		2C
2. Plugged, Storm Sewer	4E			2D
3. Unlined Pond, Percolates	4E			

Risk Assessment
Environmental Consequence

	AIR	Sensitive Body of Water	Soil Ground Water	Wastewater Treatment Plant
1. Sanitary sewer, WWTP		3C		2C
2. Segregated Storm Sewer	4E	3C		
3. Plugged, Storm Sewer	4E			2D
4. Pavement, Plugged Storm Sewer/drains	4E			
5. Pavement, Plugged Combined Sewer/drains	4E			2D
6. Pavement, Combined Sewer WWTP		3C		2C
7. Pavement, Storm Sewer	4E	3C		
8. Unlined Pond, Percolates	4E			
9. Lined Pond, Pump Off-Site	4E			
10 Lined Pond, evaporate	4E			
11. Lined Pond, Meter WWTP				2D
12. Lined Pond, Meter Storm Sewer	4E	3C		2D
13. Lined Pond, Degrade WWTP				2D
14. Lined Pond, Degrade Storm Sewer	4E			2D
15. Tank, Pump Off-Site	4E			
16. Tank, Meter WWTP				2D
17. Tank Meter Storm Sewer	4E	3C		2D
18. Tank, Degrade WWTP				2D
19. Tank, Degrade Storm Sewer	4E			2D

Costs

- Single module, 16 minutes of foam discharge
- Costs options we have identified are in the $0–200K range
- More stringent control criteria can lead to much greater costs
- However risk of an environmental consequence is not reduced

APPENDIX (13)

Presentation: "Summary of Shore Facility AFFF Management Breakout Session"

D. Verdonik
Hughes Associates, Inc.
Baltimore MD

Summary of Shore Facility AFFF Management Break-Out Session

Dan Verdonik

3 August 2000

Facility AFFF Management Working Group

- Decision to 'formalize' a Working Group
  - Develop Facility Policy for AFFF Management
    - Changed name from "Hangar" to "Facility" to reflect broader scope
    - Target for Completion: Approximately 6 months
  - Develop a draft DoDI
    - Staff Through Environmental Side of Services
    - Present to OSD
  - Next Meeting Scheduled for October 12
- Accepted-in-Principle the Risk Based Approach
  - Use as the Basis for the Policy
  - Need to Review Details and Back-up Information
  - Report will be Provided Prior to Next Meeting

Facility AFFF Management Working Group - Membership

Service	**Office**	**Name**
Navy	HQ NAVFAC	Joe Gott
Navy	HQ NAVFAC	Joe Simone
Navy	NAVFAC	Vincent Donnally
Navy	CNO N457C	Ms. Kathy Ellis
Navy	NAVAIR	Larry Wolf
Navy	HQ NAVFAC (Contractor Representative)	Kim DePaul Dawn Roderique
Army	USACE	Bob DiAngelo
Army	USACE	K.C. Kochhar
Army	ACSIM F&H	Bruce Park
Army	USACE/ACE	Billy Ray Scott
USAF	AFCESA	Fred Walker
USAF	HQ USAF ILEV	Jayant Shah
USMC	HQUSMC DCS/I&LFL	Michael Doherty
USMC	HQUSMC DCS/I&LFF	Kevin King

- Additional Members To Be Identified Prior to Next Meeting

APPENDIX (14)

Presentation: Summary of AFFF Environmental Breakout Session"

J. Hoover
Naval Air Warfare Center
China Lake CA

R. Darwin
Hughes Associates, Inc.
Baltimore MD

Summary
Of
AFFF Environmental Impact Breakout Session

Naval Research Laboratory
3 August 2000

Dr. Jim Hoover
Head, Combustion Research Branch
NAWCWD China Lake

Robert Darwin
Senior Engineer
Hughes Associates, Inc.

Purpose of Breakout Session

Share Information on AFFF

- History, performance, chemical composition
- Environmental and human health impacts
- Regulations – current and future
- Replacement activity and status
- Future management strategy

(1) What current and future environmental regulations impact AFFF and why (data and policies)?

Current:

Different regulations affect different components of AFFF

Presentation by Bill Ruppert yesterday provided good summary

Except for UNDS, there are no definitive restrictions at present and no identified directives for change

Future:

Depends on future EPA assessment of AFFF as data is reviewed

(2) What data do we have (or lack) on the environmental impact of AFFF?

Lacking:

Component toxicity/BOD/Persistence (Fate)/Bio-accumulation

Accurate and appropriate dilution factors when AFFF discharged in open bodies of water

Predictive capability/data regarding releases for estimating potential environmental damage. Must consider where the release occurs (shore hangars, runways, unpaved ground, ship bilges, at sea, etc)

(3) What technology or products exist that could help reduce AFFF releases into our environment or mitigate the impact of those releases?

Depends on the type and location of the release

Reducing releases:
- Reduction in system tests, efficiency improvements
- Spill response/advance planning/preparedness

Mitigation:
- ASH (Air-sparged hydrocyclone)
- RO (Reverse osmosis)
- Biological/microbial systems

Education and Planning:
- DOD guidance/standards on prevention, clean-up and disposal, training, intentional discharges

(4) What technology or products could be applied to recycle or reuse AFFF?

Not considered to be feasible or cost effective (reformulation, losses, contamination)

(5) What alternatives to AFFF currently exist and how do they compare in effectiveness, cost, environmental impact, availability, etc ?

None meet performance specification (mil spec)

Development of an AFFF alternative was proposed as project under ONR Future Naval Capability Platform Protection Program

Potential SERDP statement of need

Some UK effort on environmentally friendly foam

(6) What related planning documents exist with other services or agencies?

UK is reportedly working on a standard definition of "biodegradability"

EPA presentation mentioned international dialog on AFFF PFOS issue

USAF needs included in draft NAVAIR ESH-Needs Assessment

(7) What follow-on strategies should be considered ?

Need accurate quantitative definition of the problem
- DOD inventory status
  - How much AFFF in DOD/where used/in-service and reserve stocks/concentrate types
- DOD AFFF discharges
  - How much released/consumed annually (training, system testing and maintenance, accidental discharges, research, fires)
- Review current DOD regs and policy

Need a definition of "environmentally friendly" (need "green" definition—what are acceptable thresholds from an environmental standpoint)
- Biodegradability
- BOD/COD
- Toxicity
- Persistence
- Bio-accumulation

Follow-On Strategies (con't)

Need for future research
- SBIR
- Goals for Universities
- ONR

Need to develop small scale screening tests

Develop "SNAP-equivalent" guidance

Need for "worst case" transition plan (short/mid/long term)

Information distribution to all levels (users, requirers, trainers, regulators, etc)

Develop AFFF detection capability (learn method used by 3M)

Define hazard protocols and appropriateness of AFFF (use and response)

Follow-On strategies (con't)

- Assess commercial state-of-the-art
  - CBD announcement
  - "Turkey shoot" of all available AFFF alternatives
  - Quantify performance, chemical and physical properties
  - Obtain EPA endorsement of screening tests

- Consider future mods to AFFF mil spec
  - Prioritze requirements
  - Consider trade-offs

- Establish formal AFFF working group
  - Info sharing
  - Formal charter
  - DOD primary advocate?
  - Future meetings/host/agenda topics

Summary
Of
AFFF Environmental Impact
Breakout Session

Naval Research Laboratory
3 August 2000

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Biodegradability	Persistence
BOD/COD	Bio-accumulation
Toxicity	

Follow-On Strategies (con't)

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