Fluorotelomer Products in the Environment – An Update

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E. I. duPont de Nemours & Co., Inc.

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Reference Forums

- Fluorinated surfactants in AFFF products discussed and debated in numerous journal articles and highlighted in each of the three Reebok Meetings:
  - Meeting 1, August 2002
    - Focused on general information about FFFC, TRP, Testing Approaches and Plans in Toxicology and EF&E
    - Presented initial physical property and Environmental Effects data
  - Meeting 2, December 2004, *"Foam Under Fire!"*
    - AFFF Surfactant Beliefs - Fact or Fiction
    - Toxicology and Ecotoxicology Updates and Plans
  - Meeting 3, September 2007
    - Key Questions, Comparative Chemistry, Sources of PFCAs
    - Trends, Toxicology, Biopersistence and Bioaccumulation
    - EF&E and Industry Efforts

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Central Questions

- Where are PFOA and higher homologues (PFCAs) and related polyfluorinated materials found in the environment?
- Where did/do the PFCAs come from?
- Are consumers exposed? Are there any hazards?
- What is being done? Emission Reduction Efforts?
- How will we know exposure is getting lower?
- Are my products safe?

Highlighted Results

- PFHxA, C6 acid, toxicology in rats
  - NOAEL for **subchronic toxicity** is 20 mg/kg/day; No effects on **reproductive** parameters, NOAEL = 500 mg/kg/day; NOAEL in **development toxicity** test is 100 mg/kg/day. **Neither a selective developmental nor reproductive toxicant**
  - **NOAEL for Neurotoxicological behavior was 500 mg/kg/day**
  - **Not Genotoxic**
- Biopersistence screening in rats
  - PFHxA, 6-2 FTS, and Fluorotelomer-based AFFF surfactants showed very low uptake and rapid clearance overall and versus PFOS
- Environmental Fate and Effects Studies on 6-2 FTS
  - Rainbow Trout Early Life Stage (ELS) 90-day Study gave NOEC values of low concern for chronic toxicity
  - Rainbow Trout Bioconcentration and Bioaccumulation Study showed rapid depuration and gave BCF/BAF values of low concern (BCF <50)

6-2 FTS = 6-2 Fluorotelomer sulfonate; PFHxA = Perfluorohexanoic Acid

Fluorotelomer and ECF Products : *Different Chemistry*

Fluorotelomers (Fluorotelomers)

$CF_2=CF_2$ (TFE)

↓

$F(CF_2)_nI$ Perfluoroalkyl Iodide

↓ n = 6,8,10,12, even

$F(CF_2)_nCH_2CH_2I$ Fluorotelomer Iodide

→ $F(CF_2)_nCH_2CH_2SO_3X$: FT Sulfonate

→ AFFF Surfactants

↓

$F(CF_2)_nCH_2CH_2OH$ Fluorotelomer Alcohol

↓

Sales Products

Even number, straight chains, No Branching
Polymers n≥ 8 ; Surfactants n=6 primarily

ECF (ElectroChemical Fluorination)

$H(CH_2)_nSH$

↓

$F(CF_2)_nSO_2F$ → $F(CF_2)_nSO_3X$
PFOS n = 8;
PFH_xS n = 6
PFBS n = 4

↓

$F(CF_2)_nSO_2N(R)CH_2CH_2OH$

↓ Perfluoroalkyl sulfonamido ethanol

Sales Products

ECF produced materials have up to 30% branched isomers at the fluorinated chain end and contain odd and even carbon chain lengths

Sources, Fate and Transport of Perfluorocarboxylates (PFCAs)

-Trends in the Environment

PFOA = Perfluorooctanoic Acid = $C_7F_{15}CO_2H$ = $CF_3(CF_2)_nCO_2H$, where n =6

PFCAs = Perfluorocarboxylic Acids, where n = 3-12

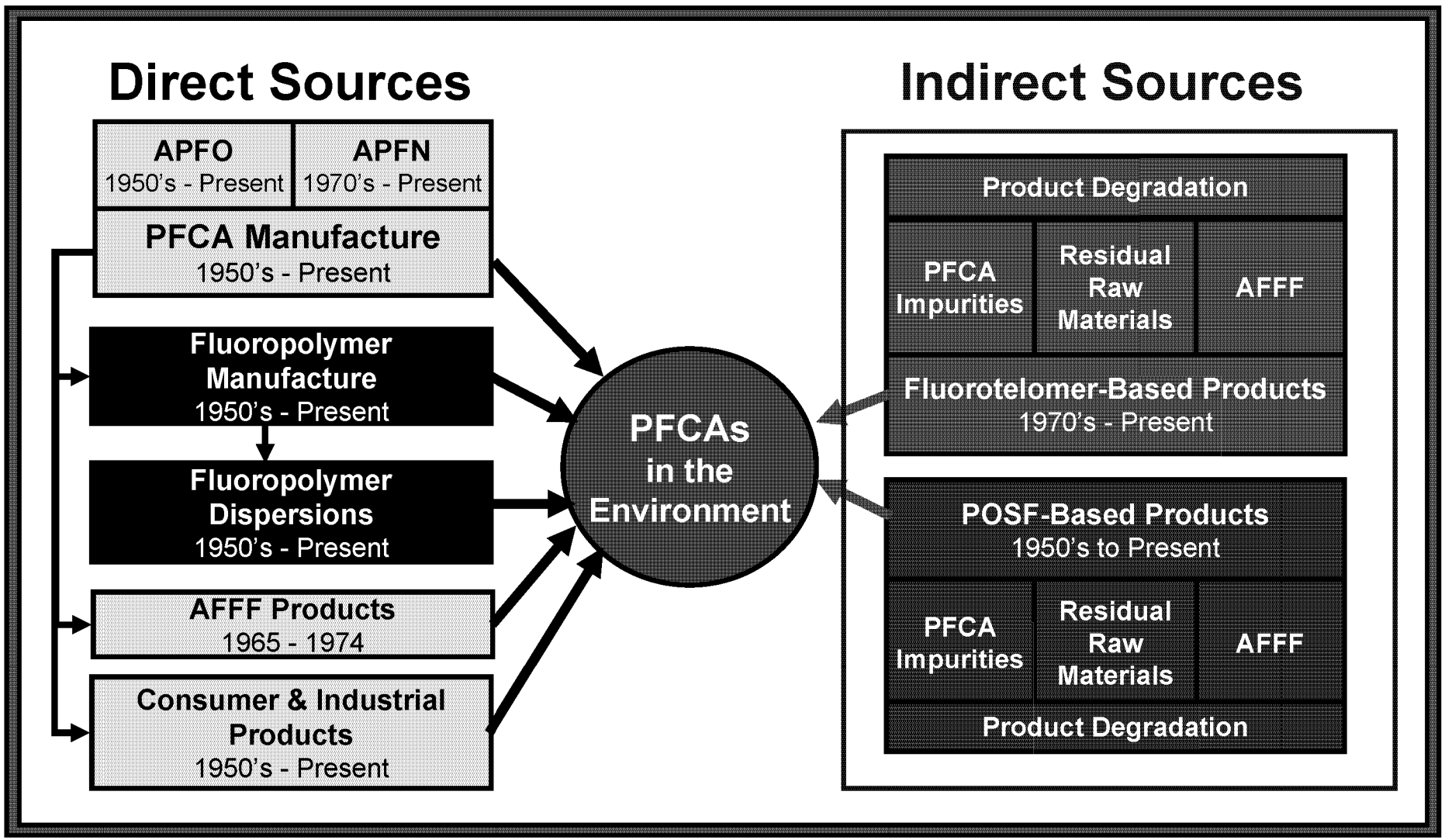
Precursors – can transform to PFCAs by abiotic and/or biotic means

What is Perfluorooctanoic Acid (PFOA)?

- PFOA is a surfactant used as a processing aid to produce fluoropolymer high-performance materials
- PFOA and other PFCAs are unintended byproducts of other fluorochemical manufacturing and the previous manufacture of POSF-based products
- PFOA and other PFCAs are <u>not</u> used to make a different family of compounds, called fluorotelomers.
  - However, they are found at very low trace levels in some fluorotelomer products as a byproduct of their synthesis and as a result of residuals/precursors breaking down to PFCAs
- PFOS and its derivatives are not used to make fluorotelomer-based products and are not formed during manufacture and processing

Other PFCAs = Other Perfluorocarboxylic Acid chain lengths such as $C_8F_{17}CO_2H$, also called C9 and PFNA

Sources of Perfluorocarboxylic Acids (PFCAs) in the Environment : A COMPLETE Picture



Prevedouros, et al. *Environ. Sci. Technol.* **2006** *40(1)*, 32.

Sources, Fate & Transport Summary

- The sources of PFCAs:

  Largest historical sources = **direct emissions**

  Small historical sources = **indirect emissions** (fluorotelomers, fluorotelomer-based AFFF, POSF derivatives, residuals, degradation, etc.)

- How PFCAs move in the environment:

  Multiple mechanisms in air and water result in long-range transport of PFCAs

  Surface waters are the environmental sink compartment for PFCAs

- We believe we understand how to minimize future exposure:

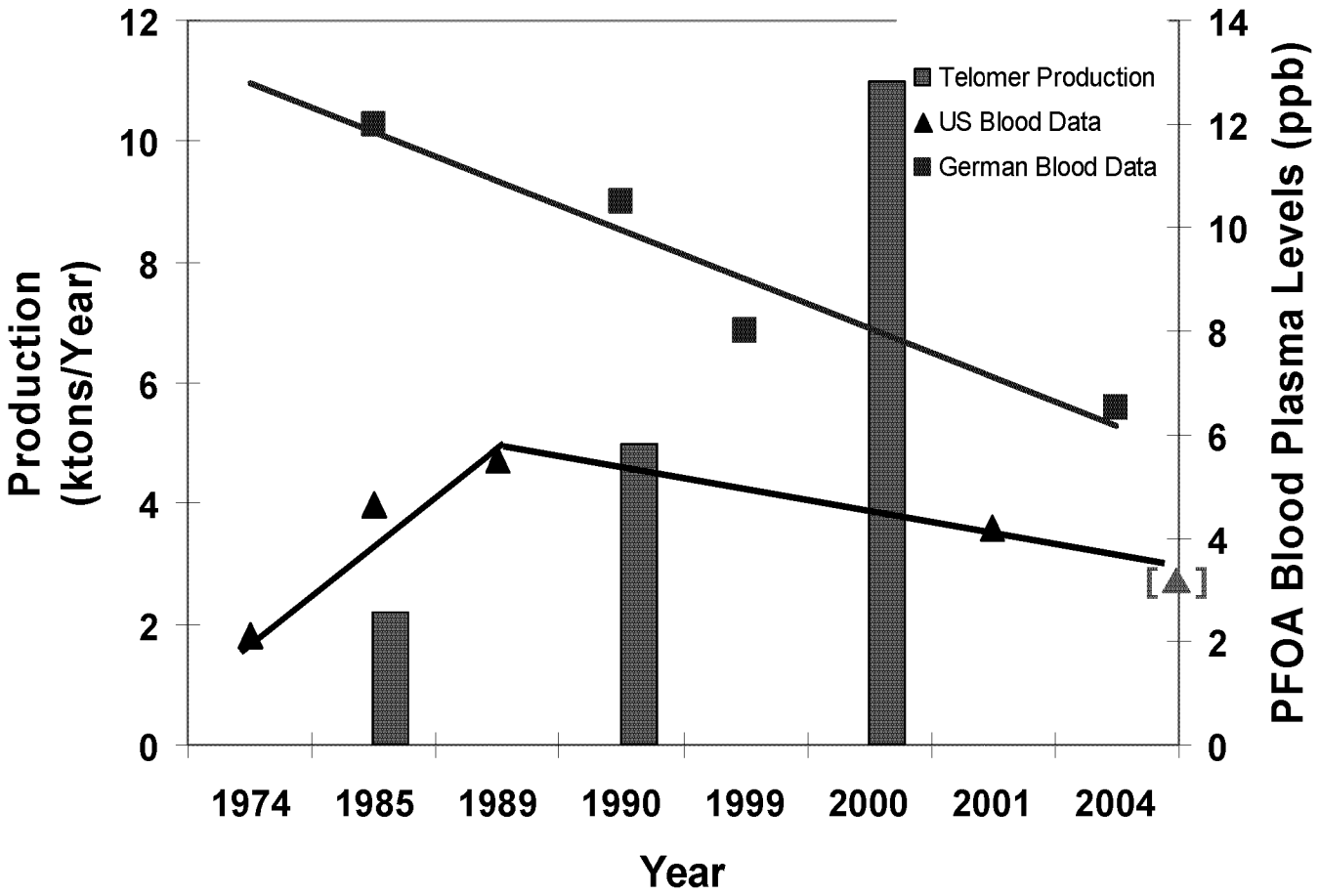
  Global action is needed by all manufacturers and users

  Significant PFCA emission **reductions have already occurred**

  US EPA 2010/15 **Stewardship Program** – commitment to dramatically reduce future manufacturing emissions and product content

Prevedouros, *et al*. *Environ. Sci. Technol.* **2006**, *40*, 32.
Armitage, *et al*. *Environ. Sci. Technol.* **2006**, *40*, 6969
Wania, F., *Environ. Sci. Technol.* **2007**, *41*, 4529

Global Fluorotelomer Industry Manufacturing Volumes and PFOA Blood Levels over Time



CDC Data published in 2007 for NHANES study confirms trend in US

- US data from Olsen et al, Environmental Health Perspectives, Feb 2005; 2005 3M 8(e) filing AR 226-3575/3576 - this mean data point for PFOA is 3.0 ppb for 2004 sampling: ([▲])
- German data from German Federal Environmental Agency UBA report 2004.

Trend Data

- Human Data
  - Statistical correlations observed between PFOA and PFOS in human blood
  - Results do not correlate with fluoropolymer or fluorotelomer historic production and are inconsistent with biodegradation of fluorotelomer products
- Arctic Wildlife
  - Limited data suggest decreasing concentrations in Arctic biota of PFOS and PFCAs over the past few years (Butt et al.; Kannan et al.; Tomy et al.)
  - PFOA and PFCAs < 8 have negligible bioaccumulation potential in wildlife
  - Water is proposed to be an important exposure medium
  - No statistical correlation between PFCAs and any fluorotelomer-based substance
- Research Needs
  - Additional longitudinal studies of human blood
  - More spatially and temporally integrated monitoring data

-Mammalia

-Biopersiste

-Environme

- **Fluorotelomers**
- **Perfluorohexanoic Acid, Sodium Salt**
- **AFFF Surfactants**

n Toxicology

ence: Relevant Comparisons

ental Fate and Effects

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Fluorotelomer-based Raw Materials & Products

- **More than 125 DuPont fluorotelomer-based raw materials and products have been studied:**
- Test substances are commercial products as they are made and sold
- Extensive repeated-dose studies have been completed
  - Oral, dermal, inhalation; reproduction, developmental
- Toxicity testing has been conducted over the past 30+ years

- **Fluorotelomer-based products are not generally regarded as hazardous chemicals:**
  - As a class of compounds, Fluorotelomer products are not genotoxins i.e. not mutagenic materials
  - Fluorotelomer products are not viewed as significant environmental toxins
  - Fluorotelomer products that have been tested are neither selective developmental nor selective reproductive toxins
  - Fluorotelomer products must be used as directed on their respective MSDS

NaPFHxA* Toxicity Data

- Subchronic toxicity study in rats
  - Crl:CD(SD) Rats (male and female) dosed with either 0, 20, 100, or 500 mg/kg/day via gavage for 90-days
  - **NOAEL for Subchronic Toxicity was 20 mg/kg/day**
- Reproductive toxicity study in rats
  - No effects observed on reproductive parameters. Not a selective reproductive toxicant
  - **NOAEL for Reproductive Toxicity was 500 mg/kg/day**
- Neurobehavioral toxicity study in rats
  - No effects seen on neurobehavioral parameters
  - **NOAEL for Neurobehavioral Toxicity was 500 mg/kg/day**

*Perfluorohexanoic Acid, C6 acid sodium salt

NaPFHxA Toxicity Data (Cont.)

- Developmental Toxicity Study in Rats
  - Crl:CD(SD) Rats (time-mated female) Dose groups: 0, 20, 100, or 500 mg/kg/day via gavage during pregnancy
  - **NOAEL = 100 mg/kg/day. Not a selective developmental toxicant**
- Genotoxicity Studies (*in vitro*)
  - No evidence of mutations in the Bacterial Reverse Mutation Assay (OECD 471)
  - No evidence of chromosome aberrations in human lymphocytes (OECD 473)

  Conclusion: Not genotoxic

Forafac® 1157 AFFF Surfactant Toxicity

Test Description	Results	Comment
28-day Subchronic Oral Toxicity in Rats	NOEL for M/F rats is 200 mg/kg/day	Doses were 0, 10, 40, 200, and 1000 mg/kg/day. No mortality seen
Developmental Toxicity	NOAEL 1000 mg/kg/day	**Not a selective developmental toxicant**
Bioconcentration in Carp, *Cyprinus carpio*, via OECD 305	5 ug/L, BCF = < 5.1 50 ug/L, BCF = < 51	Whole fish test Very low bioaccumulation potential **By all criteria, not bioaccumulative**

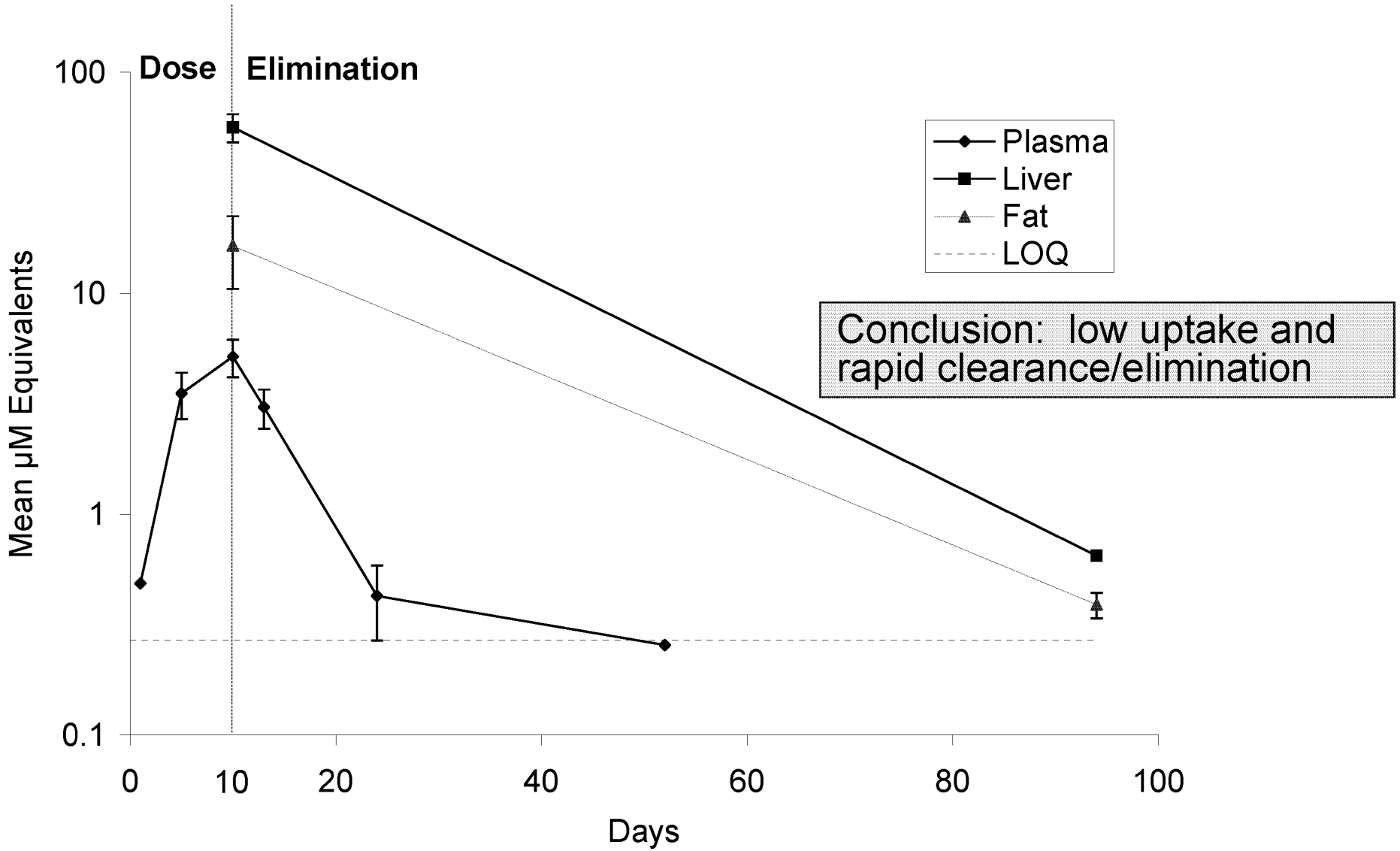
Ecotoxicity: **low-moderate toxicity** in acute fish, invertebrates, and bacterial toxicity tests. Conclusion: of low concern

Forafac® 1157 backbone is $F(CF_2CF_2)_nCH_2CH_2SO_2Y$, where n = 3 predominantly , and Y are various organic functional groups or appendages

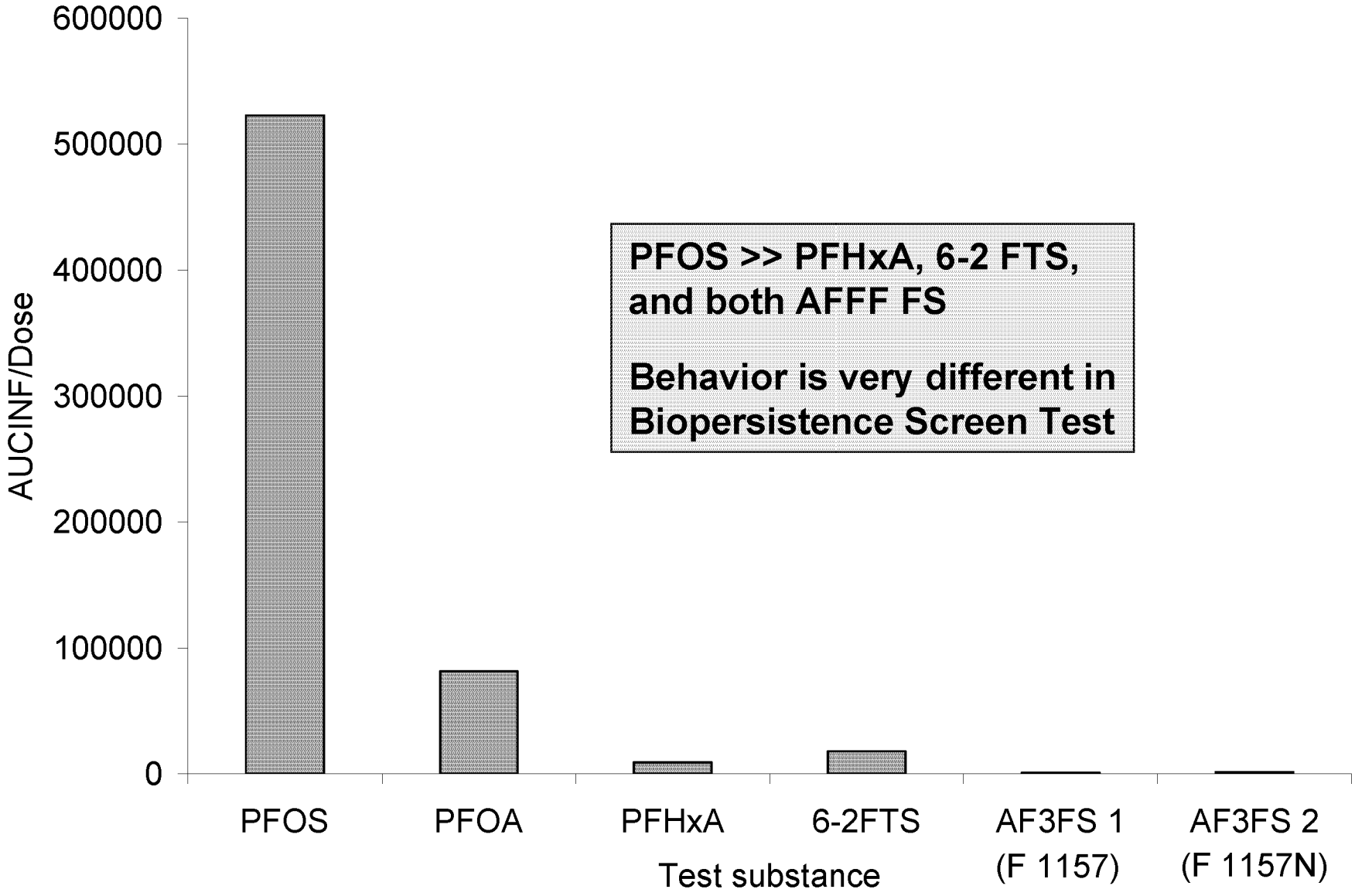
Forafac® 1157 Developmental Toxicity Study (in Rats)

- Results
  - Maternal toxicity No Observed Effect Level (NOEL) is 150 mg/kg/day based on “body weight gain reduction” at 1000 mg/kg/day
  - Fetal developmental toxicity NOEL is 1000 mg/kg/day, the highest dose level tested
- Conclusion
  - Forafac® 1157 is not a developmental toxin

Forafac® 1157 AFFF Surfactant Biouptake and Clearance in Rats: Biopersistence Screen



Internal Dose Comparison using Blood AUCINF/Dose (normalized)



Biopersistence Screen Summary

- Fluorine residues can be used to screen test substances for differences in bio-uptake and clearance
- Absorption and distribution is evident
  - AUCINF provides relative integrated measure of absorbed dose
- Relative ranking for blood AUCINF/Dose is

  PFOS >> PFOA > 6-2FTS ≈ PFHxA > F 1157N ≈ F 1157
- Elimination is evident based on declining concentrations in blood and tissues

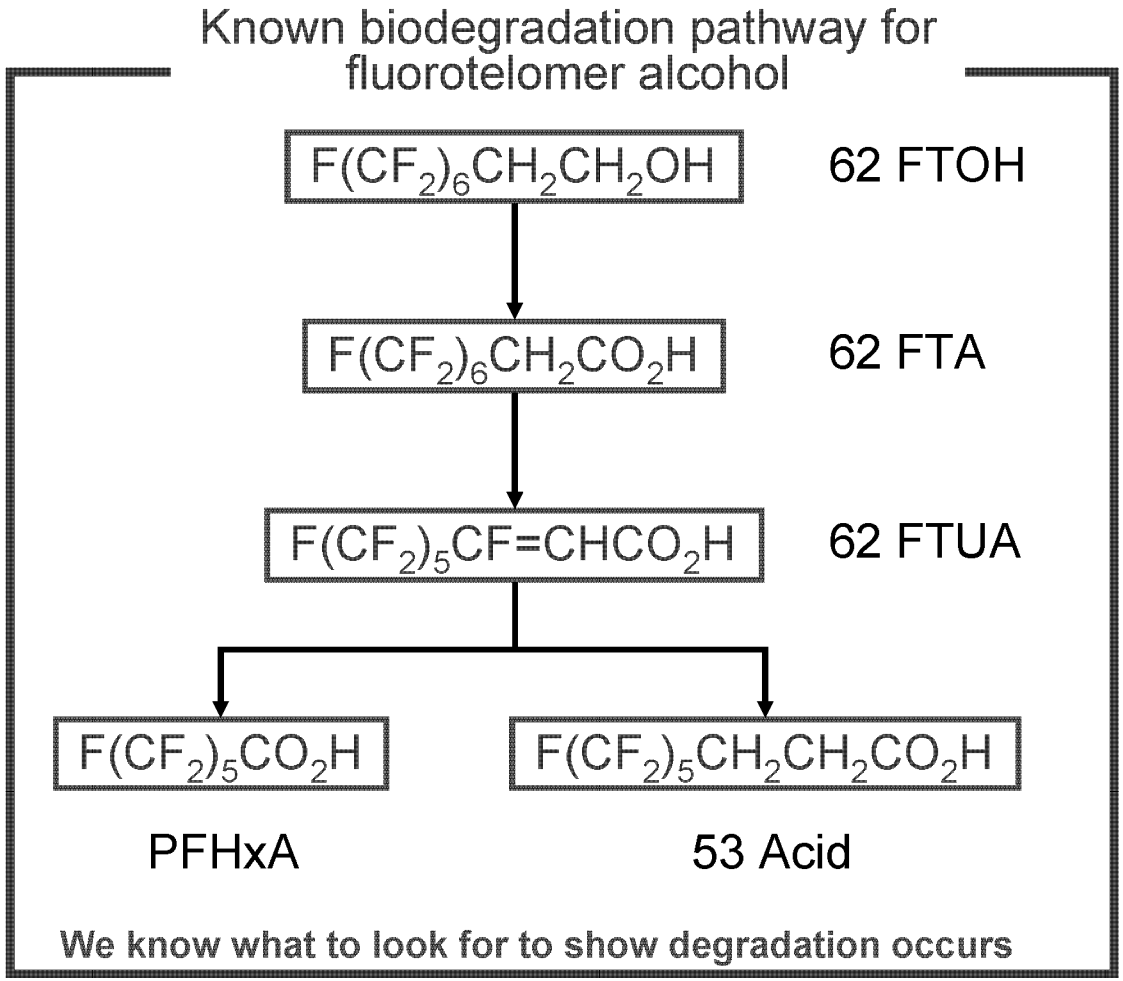
Inherent Biodegradation in Sludge of Forafac® 1157 AFFF Fluorosurfactant

- OECD 302B – Modified Zahn-Wellens/EMPA test
- Main Study Conclusions
  - No biodegradation products were observed
  - No fluorinated species were observed in the gaseous effluent
  - No additional fluoride was produced (No C-F degradation)
    - Levels measured were at background and did not change
  - Test substance was not toxic to the microorganisms and the system remained aerobic

Aerobic Biodegradation of 6-2 Fluorotelomer Sulfonate Study Rational and Objectives

- Reported that 6-2 FT Sulfonate [$F(CF_2)_6CH_2CH_2SO_3X$] may be converted to 6-2 FTOH [$F(CF_2)_6CH_2CH_2OH$] and 6-2 FTA [$F(CF_2)_6$CH2COOH] (> 15%) and small percentage of PFHxA [$F(CF_2)_5COOH$] (< 4%) in activated sludge when sulfate was depleted (an artificial condition that rarely exists in the environment).
  - Erin Marchington et al., 2007 SETAC NA meeting poster
- The experimental systems using bacterial culture and activated sludge can readily degrade 6-2 FTOH and 8-2 FTOH and thus serve as positive controls
  - Wang et al., ES&T, 2005 and unpublished data.
- The present study investigates whether or not 6-2 FT Sulfonate is biodegradable and can be converted to PFHxA under aerobic conditions.

Study Background :
What do we know? What do we want to know?



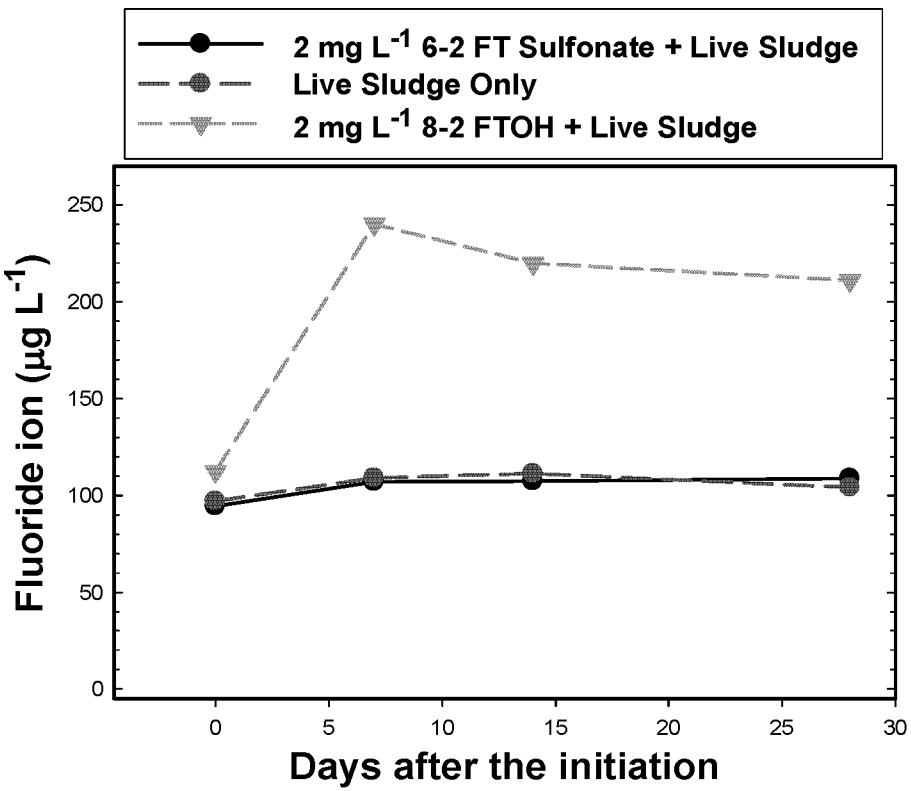
$F(CF_2)_6CH_2CH_2SO_3K$

6-2 FTS

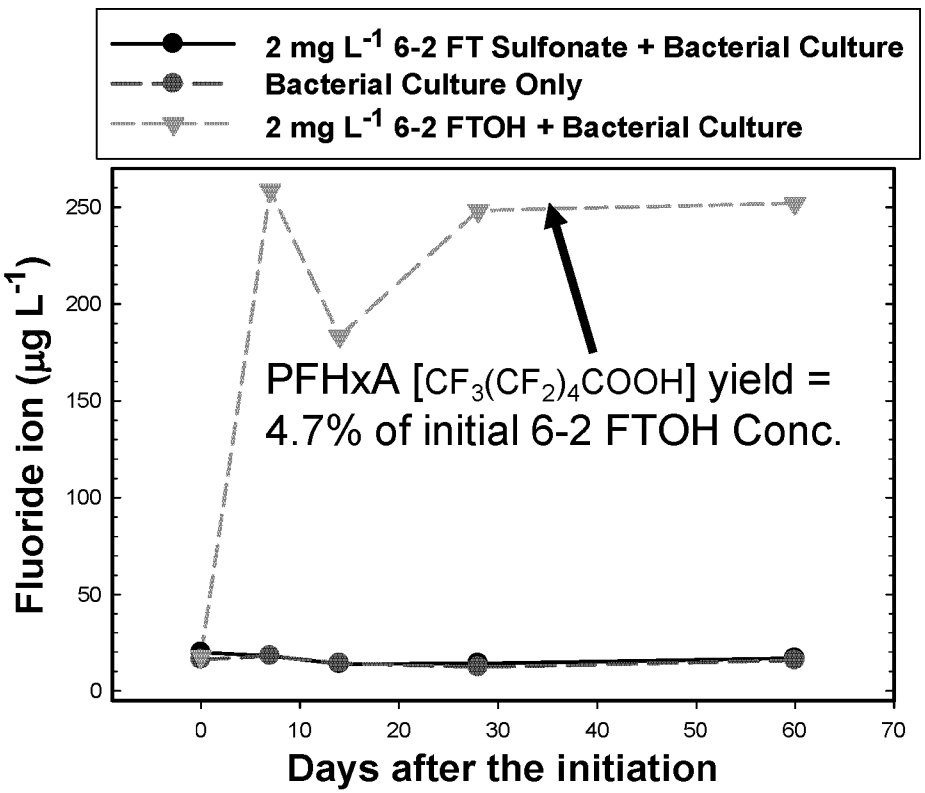
<u>We want to know</u>:

Does 6-2 FTS degrade to form any of the substances in the fluorotelomer alcohol degradation pathway?

No discernible increase of Fluoride (F^-), indicative of degradation, in activated sludge and mixed bacterial culture 28 – 60 days after incubation of 6-2 FTS



82 FTOH Control



62 FTOH Control

Results and Conclusions

- **No PFHxA or other metabolites indicative of biodegradation were observed above background level in any samples from activated sludge or bacterial culture.**
- **62 FTS was not biodegraded in activated sludge under the aerobic study conditions.**

Potential transformation products of 2 mg L^{-1} 6-2 FTS

	6-2 FTOH	6-2 FTA	6-2 FTUA	5-3 Acid	PFHxA
LOD (µg L^{-1})	10	1.6	0.16	0.54	0.32
Activated sludge (Day 0 – 28)	Not detected by LC/MS/MS				
Mixed bacterial culture With sulfate (Day 0 – 60)					
Mixed bacterial culture Without sulfate (Day 0 – 60)					

Environmental Fate & Effects: Key Results

- Rainbow Trout 90-day Early Life-stage Study (ELS) on F1176*
  - Regulatory guideline study (USEPA 850.1400, OECD 210) conducted under GLP
  - Exposure concentrations (mean measured):
    - Control (well water), 0.857, 1.66, 2.62, 4.85, 8.70 mg/L
  - **No Observed Effect Concentrations**
    - NOEC (first day of hatching, first day of swimup) = 2.62 mg/L
    - NOEC (egg hatching) = 4.85 mg/L
    - NOEC (larval survival and abnormalities at thinning, test end; last day of hatching; length and dry weight (i.e., growth) at test end) = 8.7 mg/L (highest test concentration)
  - **These NOEC values are much higher (less concern) than typical values used to screen for chronic toxicity, e.g., NOEC < 0.1 mg/L (Canadian DSL)**

*Forafac® 1176 = 6-2 FTS, Potassium Salt

Environmental Fate & Effects: Key Results

- Rainbow Trout Bioconcentration and Bioaccumulation Study on Forafac® 1176 (Preliminary unaudited analysis)
  - **Elimination of compound appears relatively rapid (95% within 28 days) once exposure is terminated**
  - **BCF/BAF values suggest low concern for bioaccumulation either from water or diet (e.g., CA DSL, EU criteria BCF > 2000, USEPA criterion > 1000)**
    - **Steady state BCF <50; Steady state BAF <2**
- **Not bioaccumulative according to published regulatory criteria**

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Industry

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Action

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EPA 2010/2015 PFOA Stewardship Program

Participation in the stewardship program requires voluntary corporate commitment to two goals:

1) To commit to achieve, no later than 2010, a 95% reduction, measured from a year 2000 baseline, in both:
   - *facility emissions* to all media of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals, and
   - *product content* levels of PFOA, precursor chemicals that can break down to PFOA, and related higher homologue chemicals.

2) To commit to working toward the elimination of PFOA, PFOA precursors, and related higher homologue chemicals from emissions and products by five years thereafter, or no later than 2015.

Results from 1st year reported results under VSP indicate significant reductions in both product content and plant emissions

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- Asahi Glass, Arkema, Ciba Specialty Chemicals, Clariant, Daikin, DuPont, Solvay-Solexis, 3M

Overall Summary Points

- Risk perception regarding PFCs requires a more sophisticated knowledge base and a more refined set of risk communications tools
  - Not all fluorochemicals are the same
- Rely on suppliers that are willing to work toward defining risk-based safe use and exposure levels. Safe is safe. Period.
- The industry needs to consider ways to take action to address the confusion and misleading claims in the marketplace regarding safety and product stewardship
- Fluorotelomer-based products are safe for their intended uses and offer significant and unique benefits to society

Thank You.

Contact Information

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