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# Fluorotelomer Products in the Environment – An Update

## 3rd Reebok Foam Seminar

3 September 2007

Bolton, United Kingdom

Dr. Stephen Korzeniowski

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

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# Reconnect to Reebok 1 & 2

- Reebok 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
- Reebok Meeting 2, December 2004, *“Foam Under Fire!”*
  - AFFF Surfactant Beliefs - Fact or Fiction, Dr. J. Field Report conclusions
  - Toxicology and Ecotoxicology
  - Degradation Study Plans
- Reebok 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 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?

# DuPont Fluorotelomer-Based Products Product Stewardship Summary

- *We have done extensive work* to understand our products' content, toxicity, environmental fate & effects and exposure.
  - *We have published our results in peer-reviewed scientific journals*
- We continue to have an *open & frequent dialogue* with Regulators, the Scientific Community, Customers, and Employees
- Fluorotelomer products are safe for their intended uses and offer significant and unique benefits to society

# Highlighted New Results

- PFHxA, C6 acid, toxicology in rats
  - NOAEL for **subchronic toxicity** is 20 mg/kg/day; No effects on **reproductive** parameters; NOAEL in **development toxicity** test is 100 mg/kg/day - **not a selective developmental toxicant**
  - **Not a genotoxin**
- 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)



$n = 6, 8, 10, 12, \text{ even}$



AFFF Surfactants

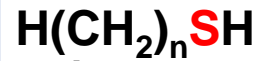


Fluorotelomer Alcohol

**Sales Products**

Even number, straight chains, No Branching  
Polymers  $n \geq 8$  ; Surfactants  $n=6$  primarily

## ECF (ElectroChemical Fluorination)



PFOS  $n = 8$ ;

PFH<sub>x</sub>S  $n = 6$

PFBS  $n = 4$



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

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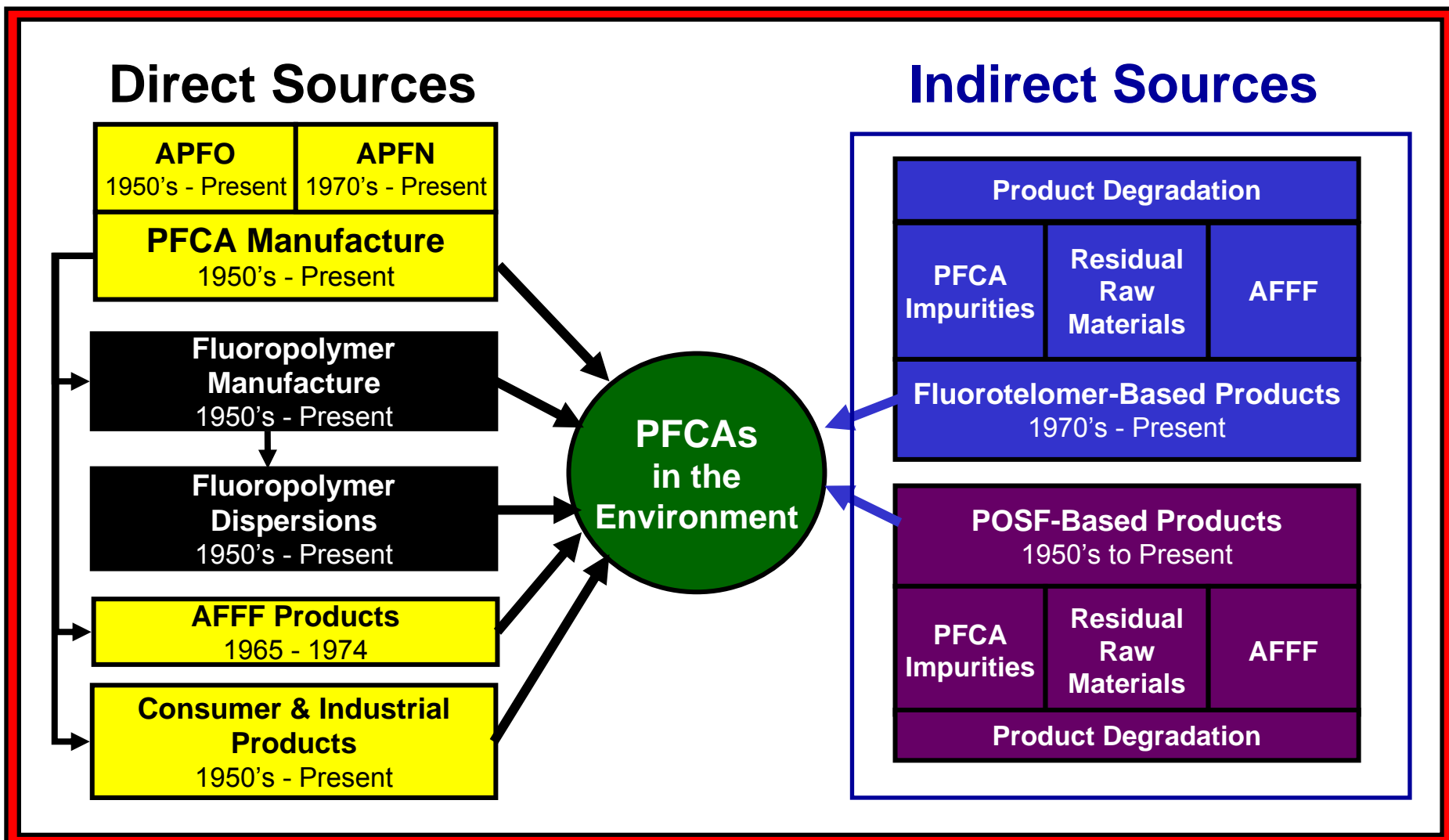
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# What is Perfluorooctanoic Acid (PFOA)?

- 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 not 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**



# 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**

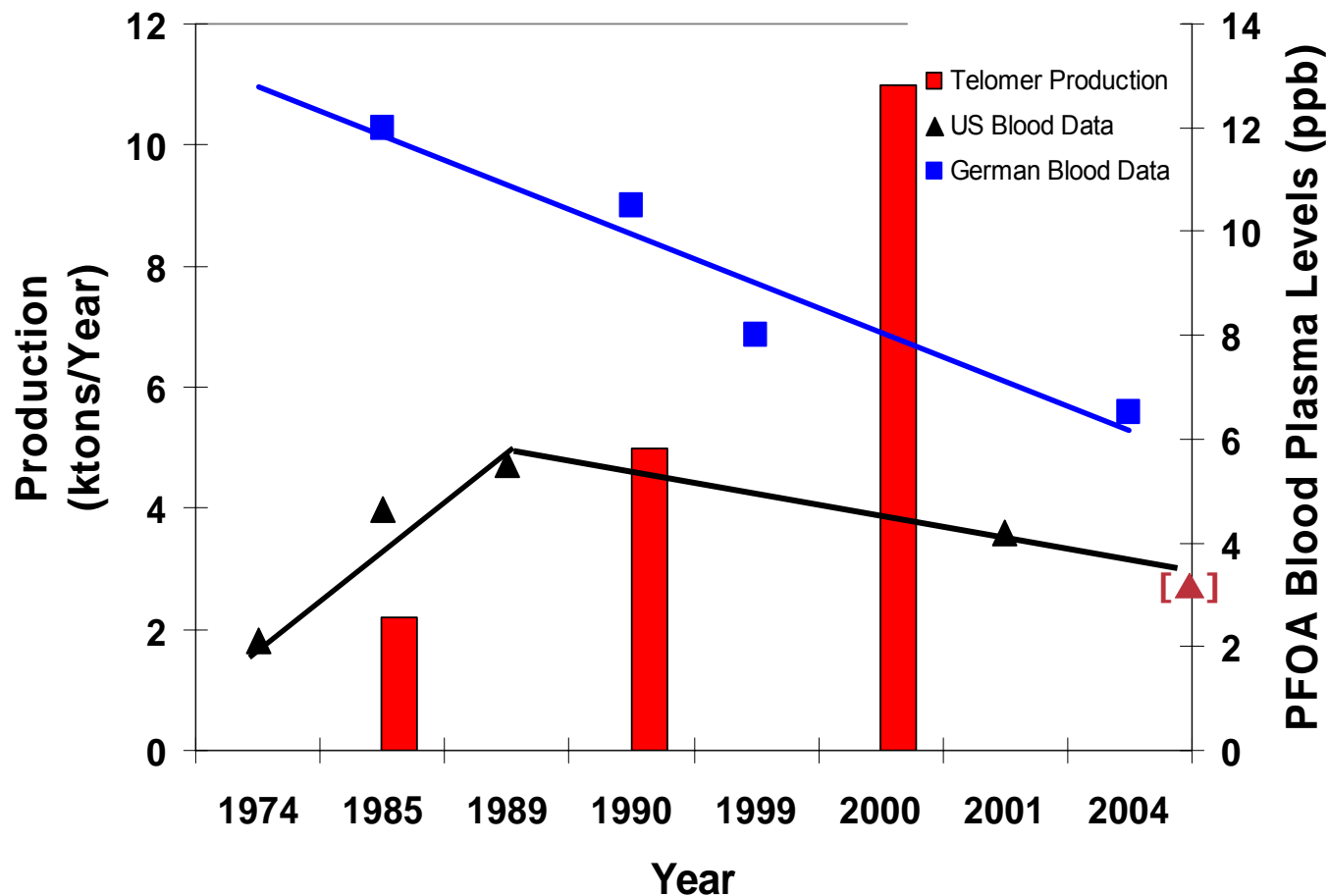
US EPA 2010/15 **Stewardship Program** – commitment to dramatically reduce future manufacturing emissions and product content

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



- 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

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-Mammalian Toxicology

-Biopersistence: Relevant Comparisons

-Environmental Fate and Effects

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

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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 20 mg/kg/day**
- Reproductive toxicity in rats
  - **NOAEL 100 mg/kg/day**
  - **No Effects observed on reproductive parameters. Not a selective reproductive toxicant**

\*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) and No evidence of chromosome aberrations in human lymphocytes (OECD 473)

**Neither genotoxic nor mutagenic**

# 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	<b>Not a selective developmental toxicant</b>
Bioconcentration in Carp, <i>Cyprinus carpio</i> , via OECD 305	5 ug/L, BCF = < 5.1 50 ug/L, BCF = < 51	Whole fish test Very low bioaccumulation potential <b>By all criteria, not bioaccumulative</b>
<b>Ecotoxicity: low-moderate toxicity</b> 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)

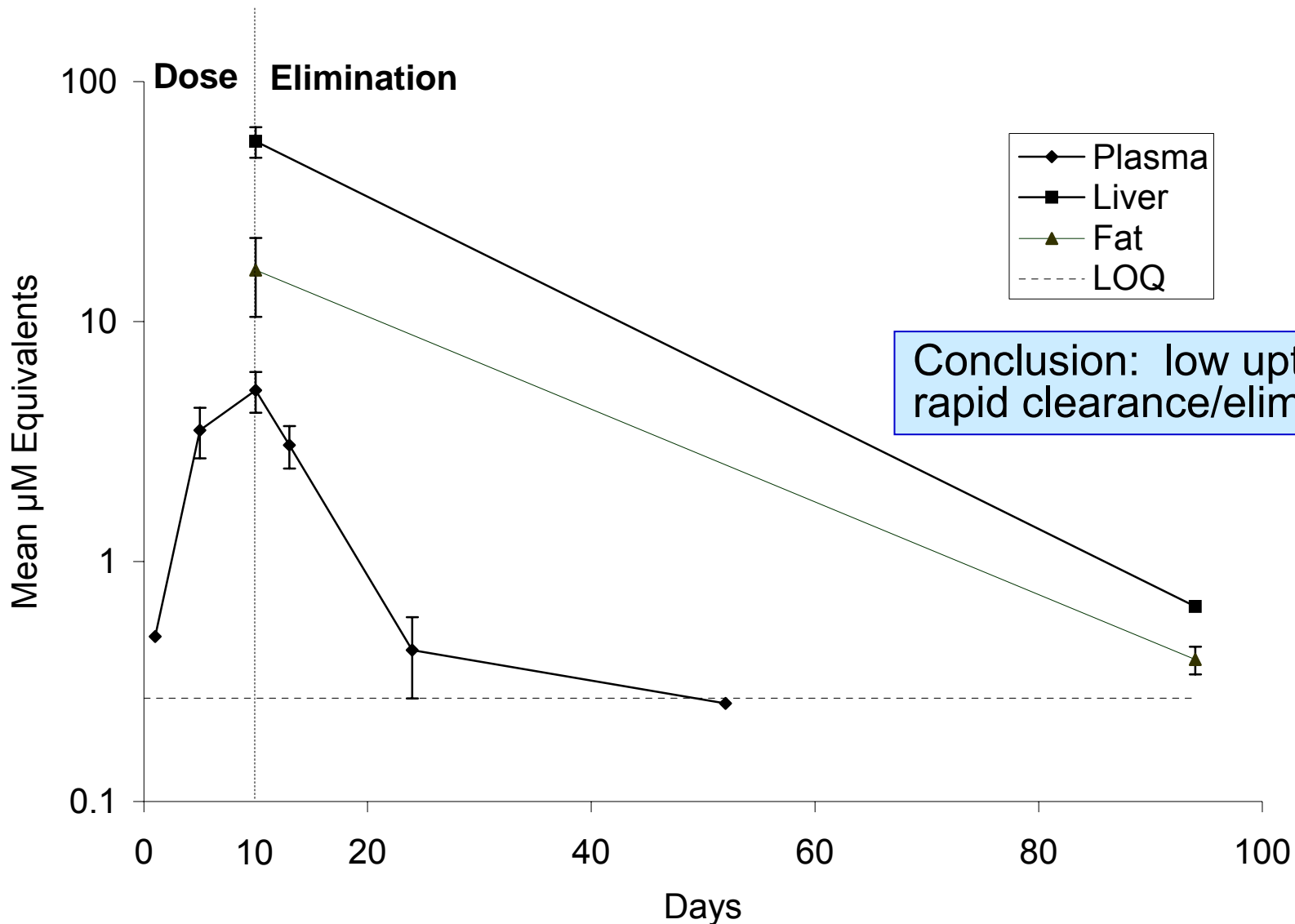
- Results

- 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

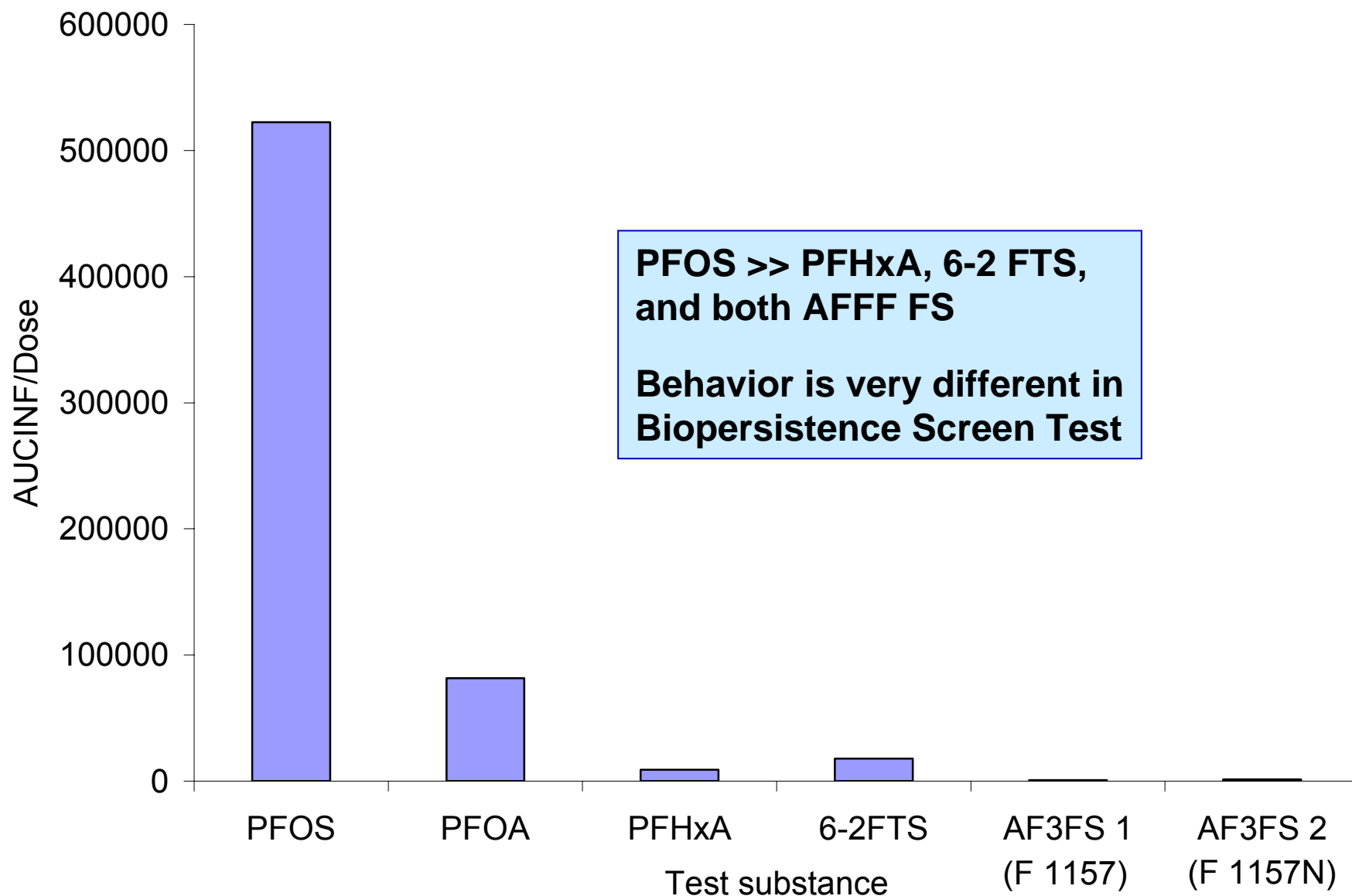
- Conclusion

- 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  $\approx$  PFHxA > F 1157N  $\approx$  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

# 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:
    - Control (well water), 0.857, 1.66, 2.62, 4.85, 8.70 mg/L
  - **Preliminary (unaudited) 90-day 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 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.

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- Our Belief: Industry endorsement of these voluntary goals enhances the public's perception of the industry, puts the issue in an understandable context, and is the right thing to do.
  - 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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