Fluorotelomer Products in the Environment – An Update and Future Direction

"Foam – Fit for Purpose"
6-7 July 2009
Bolton, UK

Dr. Stephen Korzeniowski
E. I. duPont de Nemours & Co., Inc.

"Safety & Protection – Be Sure"

The Vision of DuPont

To be the world's most dynamic science company,

creating sustainable solutions essential

to a better, safer, healthier life for people everywhere.

DuPont Mission – Sustainable Growth

The creation of shareholder and societal value while we reduce the environmental *footprint* along the value chains in which we operate.

DuPont defines "*footprint*" as all injuries, illnesses, incidents, waste, emissions, use of water and depletable forms of raw materials and energy.

Reference Forums

- Fluorinated surfactants in AFFF products discussed and debated in numerous journal articles and highlighted in each of the three Reebok Meetings as well as in the present 4th Reebok forum:
  - Meeting 1, 12-13 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, 20-21 December 2004, *"Foam Under Fire!"*
    - AFFF Surfactant Beliefs - Fact or Fiction
    - Toxicology and Ecotoxicology Updates and Plans
  - Meeting 3, 3-4 September 2007, *"Foam Attack?"*
    - Key Questions, Comparative Chemistry, Sources of PFCAs
    - Trends, EF&E, Toxicology, Biopersistence and Bioaccumulation
  - Meeting 4, 6-7 July 2009, "*Foam – Fit for Purpose*"
    - Fluorine vs Non-fluorine – the debate continues

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Key Messages (1)

- Fire fighting foams that contain telomer-based AFFF agents are the most effective agents and available technology currently available to fight flammable liquid fires to save lives and protect plant and equipment as they have over the past 35 years
- The AFFF Industry continues to develop new fluorosurfactants (C6 telomer-based) that provide the same fire protection characteristics but with reduced environmental impacts
- Optimal choice is an agent that provides the best combination of performance, reliability and life safety balanced with minimal toxicological and environmental impact

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Key Messages (2)

- Fluorotelomer-based surfactants for AFFF and both 6-2 FTS and PFHxA exhibit a low biopersistence tendency
- Aerobic biodegradation studies on 6-2 FTS indicate nearly 70% remains unchanged, 20% is absorbed on soil and ~10% is converted to recoverable short-chain metabolites
- Initial environmental fate and effects studies do indicate that 6-2 FTS and PFHxA have:
  - low aquatic toxicity and are not bioaccumulative
- Significant progress has been made toward meeting the EPA VSP 2010/15 goals and timelines

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6-2 FTS is 6-2 fluorotelomer sulfonate and PFHxA is perfluorohexanoic acid

Why Fluorinated Surfactants in AFFF?

- **Telomer-based AFFF are used for life safety and the protection of high value property:**
  - ARFF, Refineries, Marine, Military, Municipal, Industrial
- **Fluorosurfactants are essential components of AFFF:**
  - To our knowledge, no other class of surfactants can provide the required low surface tension (15 to 17 dynes/cm vs. water: 72 dynes/cm)
  - Only the combination of fluorinated surfactants and hydrocarbon surfactants provides positive spreading coefficient and enables film formation on top of polar solvents

→ Most AFFF fire fighting agents currently on the market contain fluorosurfactants. AFFF typically have rapid extinguishing time and excellent burnback resistance

Fluorotelomer-based AFFF Products and Fluorine-free Agents

- Fluorotelomer-based AFFF agents do not contain or degrade to PFOS and are not made with PFOA
- They are effective at 30-60% less fluorine than PFOS-based AFFF
- The predominant breakdown product from the six-perfluorinated carbon (C6) based fluorotelomer surfactants is 6-2 fluorotelomer sulfonate (6-2 FTS). Traces of PFHxA may also be present
- Fluorine-free foams are limited in their ability to avoid burnback and fuel pickup when applied directly
- A study of commercially available fluorine-free foams indicated that they are an order of magnitude higher in aquatic toxicity[1] than telomer-based AFFF agents

[1]Fire Fighting Foam Coalition Newsletter – Aquatic Toxcity of Fire Fighting Foams, October, 2006

Fluorotelomer and ECF Products : *Different Chemistry*

Fluorotelomers (Telomerization)

$CF_2=CF_2$ (TFE)

↓

$F(CF_2)_nI$ Perfluoroalkyl Iodide

n = 4,6,8,10,12, 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
By YE 2010 n ≤ 6 primarily

ECF (ElectroChemical Fluorination)

$H(CH_2)_nSH$

↓

$F(CF_2)_nSO_2F$ → $F(CF_2)_nSO_3X$

PASF = Perfluoroalkylsulfonates

PFOS n = 8;
PFH_xS n = 6
PFBS n = 4

↓

$F(CF_2)_nSO_2N(R)CH_2CH_2OH$

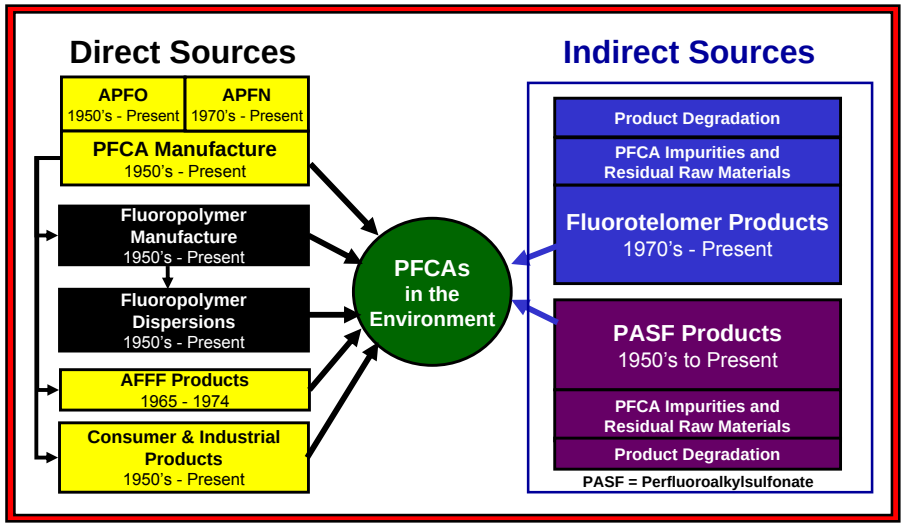
↓

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



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

Key Results: Toxicity and EF&E

- 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, BAF ≤ 2)
- Forafac® 1157 AFFF Surfactant has
  - Low-moderate ecotoxicity in acute fish, invertebrates and bacterial toxicity tests
  - Is not bioaccumulative: BCF <51 ug/L
  - Is not a selective developmental toxicant

6-2 FTS = 6-2 Fluorotelomer sulfonate, 1157 backbone; PFHxA = Perfluorohexanoic Acid

Key Results, Cont.

- 6-2 FTS is not similar to PFOS in either its physical or environmental properties. Recent studies on 6-2 FTS and AFFF-type fluorosurfactants likely to break down to 6-2 FTS show the following:
  - Low in acute and sub-chronic toxicity and aquatic toxicity
  - Negative for both genetic and developmental toxicity
  - Significantly lower than PFOS in biopersistence

Biopersistence Screen Summary

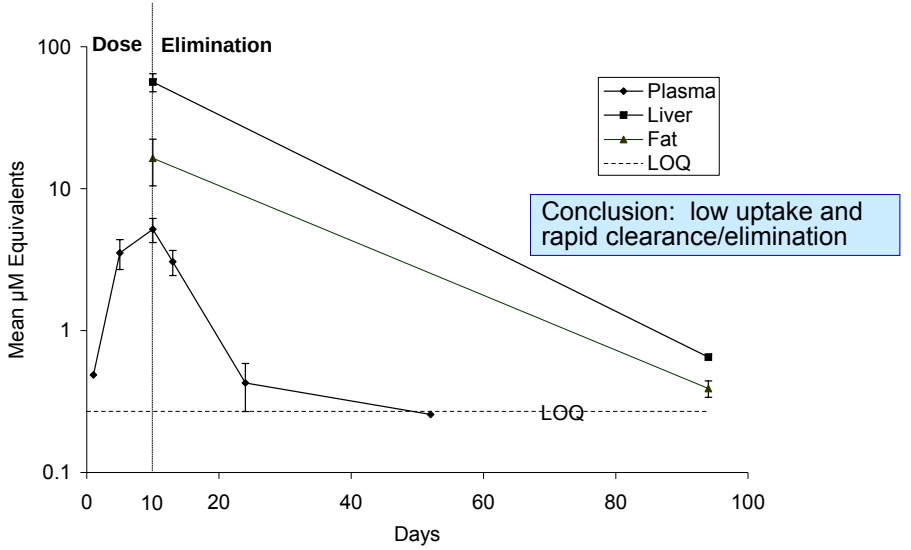
- Fluorine residues can be used to screen test substances for differences in bio-uptake and clearance
- Absorption and distribution is evident
  - AUCINF provides relative integrated measure of absorbed dose
- Elimination is evident based on declining concentrations in blood and tissues
- Relative ranking for blood AUCINF/Dose (in rats) is

  PFOS >> PFOA > 6-2FTS ≈ PFHxA > F 1157N ≈ F 1157

AUCINF = area under the curve integrated to infinity

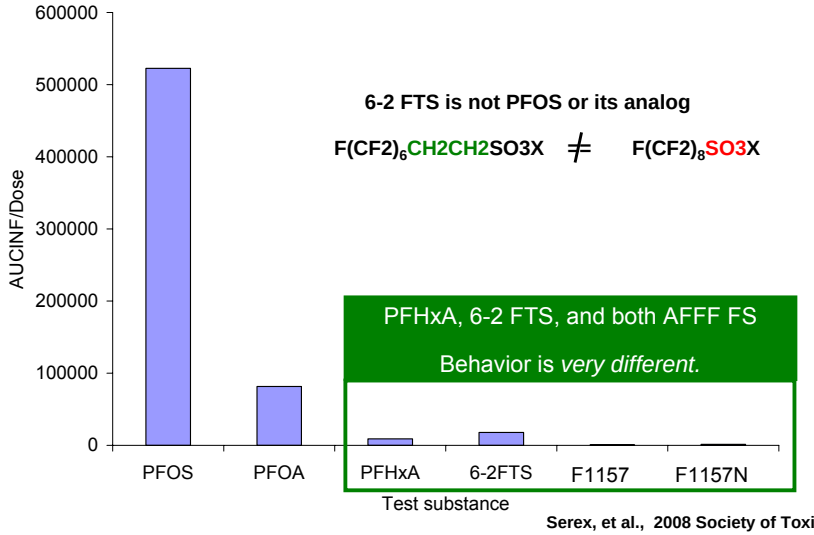
Serex, et al., 2008 Society of Toxicology

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



Conclusion: low uptake and rapid clearance/elimination

Biopersistence Screening Test Results: Internal Dose Comparison using Blood AUCINF/Dose (normalized)



Serex, et al., 2008 Society of Toxicology

Biodegradation Study Rationale and Objectives

- 6-2 Fluorotelomer Sulfonate (6-2 FTS) is a potential degradation product of some AFFF firefighting surfactants
- Study investigated whether or not 6-2 FTS is biodegradable in aerobic activated sewage sludge from three different municipal wastewater treatment (POTW) facilities
  - Test systems were monitored for specific analytes to determine whether 6-2 FTS was transformed
- Experimental system used aerobic activated sewage sludge which has been shown to degrade fluorotelomer alcohols. (Wang et al., ES&T, 2005 and DuPont data to be published)
- Activated sludge was collected from different locations to reflect variation in microbial populations that are able to degrade fluorinated materials

Inherent Biodegradation in Sludge of Forafac® 1176 Fluorosurfactant*

- OECD 302B – Modified Zahn-Wellens/EMPA test
- Main Study Conclusions
  - 6-2 FTS was largely unchanged (70±%) over 90 days, with on average 9% of transformation products being observed in activated sludge (3 municipal WWTP sludges were used)
  - Up to 30% of 6-2 FTS may be absorbed to activated sludge
  - PFPeA and PFHxA accounted for an average of 1% and 0.7%, respectively, of the initial 6-2 FTS after 90 days
    - Approx 7% were C5 fluorinated carbon alcohols and ketones
  - Test substance was not toxic to the microorganisms and the system remained aerobic during the study

*6-2 Fluorotelomer Sulfonate, Potassium Salt

Low Concern for Acute and Chronic Effects on Aquatic Species from 6-2 FTS

- 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)**
  - **PFOS NOEC in a comparable study was 0.3 mg/L**

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

6-2 FTS is Not Bioaccumulative

- Rainbow Trout Bioconcentration and Bioaccumulation Study on Forafac® 1176 (Unaudited draft final analysis)
  - Elimination of compound appears relatively rapid (>95% of uptake phase maximum tissue residue eliminated by end of uptake phase), additional elimination during depuration phase
  - 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**

Norway SFT Fire Training Facilities Study

- PFOS and PFOA were likely contaminants and/or biodegradation products of ECF-based fluorosurfactants in AFFF agents (containing branched and linear chains).
- 6-2 FTS is a likely contaminant and/or biodegradation product of fluorotelomer-based fluorosurfactants in AFFF agents (straight chain).
  - Neither of these compounds (PFOS or 6-2 FTS) was used as is in fire fighting foams
- The bioaccumulation factor (BAF) values for 6-2 FTS in earthworms from the SFT report and in rainbow trout from previous studies are 100-1000 times lower than EU regulatory criteria for bioaccumulation.
  - Therefore 6-2 FTS is not considered bioaccumulative according to EU regulatory criteria

Screening of polyfluorinated organic compounds at four fire training facilities in Norway (TA-2444/2008) by SFT, Oslo, 2 December 2008

Norway SFT Earthworm Study – 2006

- Study conclusions
  - The reproduction parameters were "far less sensitive to 6-2 FTS than for…" the other PFCs studied
  - Study experiments did show 6-2 FTS was bioavailable providing a BCF of 3.0. The BCF value for PFOA in these experiments was around 1
  - "The BCF values between 2 and 3 are not particularly high, but do indicate a certain concentration of the compound at a low level in the food chain."

Ecotoxicological effects of PFOS, PFOA and 6:2 FTS on the earthworm (*Eisenia fetilda*; TA-2212/2006) by SFT, Oslo, December 2006

Perfluorohexanoate, PFHxA Impurity/Degradation Product

- Low aquatic toxicity
- Low acute oral toxicity
- Not damaging to DNA, not genotoxic or mutagenic
- Not a selective developmental or reproductive toxicant
- Low biopersistence and *not bioaccumulative*
  - Rapidly absorbed and eliminated when dosed orally in rats/mice

Not expected to be harmful to human health or the environment at environmentally relevant concentrations

Slezak, et al., 2008 Society of Toxicology
Loveless, et. al., *Toxicology*, 2009 submitted

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 initial reported results (2007 and 2008) under VSP indicate significant reductions in both product content and plant emissions

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

New York State Newborn Program

Use of Newborn Screening Program Blood Spots for Exposure Assessment: Declining Levels of Perfluorinated Compounds in New York State Infants

HENRY M. SPLIETHOFF,*,† LIN TAO,‡ SHANNON M. SHAVER,† KENNETH M. ALDOUS,†,‡ KENNETH A. PASS,† KURUNTHACHALAM KANNAN,†,‡ AND GEORGE A. EADON†

Wadsworth Center, New York State Department of Health, Empire State Plaza, P.O. Box 509, Albany, New York 12201, and Department of Environmental Health Sciences, School of Public Health, University at Albany, State University of New York, Empire State Plaza, P.O. Box 509, Albany, New York 12201

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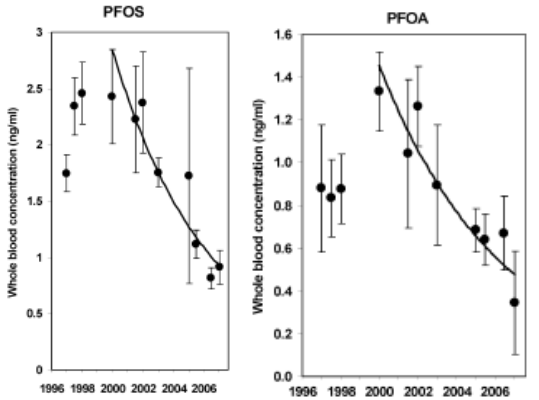

Biomonitoring in Spain – An Example

- Publication by A. Kärrman et al, *Environ Sci Pollut Res*, published online 21 May 2009 titled "Biomonitoring perfluorinated compounds in Catalonia, Spain: concentrations and trends in human liver and milk samples"
  - Samples taken in 2007 and 2008
  - 12 PFCs were analyzed in the milk and liver samples
- In human liver samples neither PFHxA (LOQ = 0.1 ng/g) nor 6-2 FTS (LOQ = 0.01 ng/g) were detected in any sample
- In human milk samples neither PFHxA nor 6-2 FTS were detected at LOQs of 0.02 ng/ml and 0.5 ng/ml, resp.

Conclusions

- Fire fighting foams that contain telomer-based AFFF agents are the most effective agents currently available to fight flammable liquid fires in military, industrial and municipal settings for life safety and property protection
- The AFFF Industry continues to develop new fluorosurfactants (C6 telomer-based) that provide the same fire protection characteristics but with reduced environmental impacts
- Collaborations with government research institutes such as NILU are ongoing to provide understanding on the most efficient and safe use possible

Choose an agent that provides the best combination of performance, reliability and life safety balanced with toxicology and environmental impact

"Safety & Protection – Be Sure"

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Questions & Thank You

Contact Information
Steve Korzeniowski
Tel : 302.695.8672
Email : stephen.h.korzeniowski@usa.dupont.com

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