

TORONTO WORKSHOP MATERIALS

September 13-14, 2004

Fluorotelomer Alcohol and Fluorotelomer-Based Polymer (Bio)degradation

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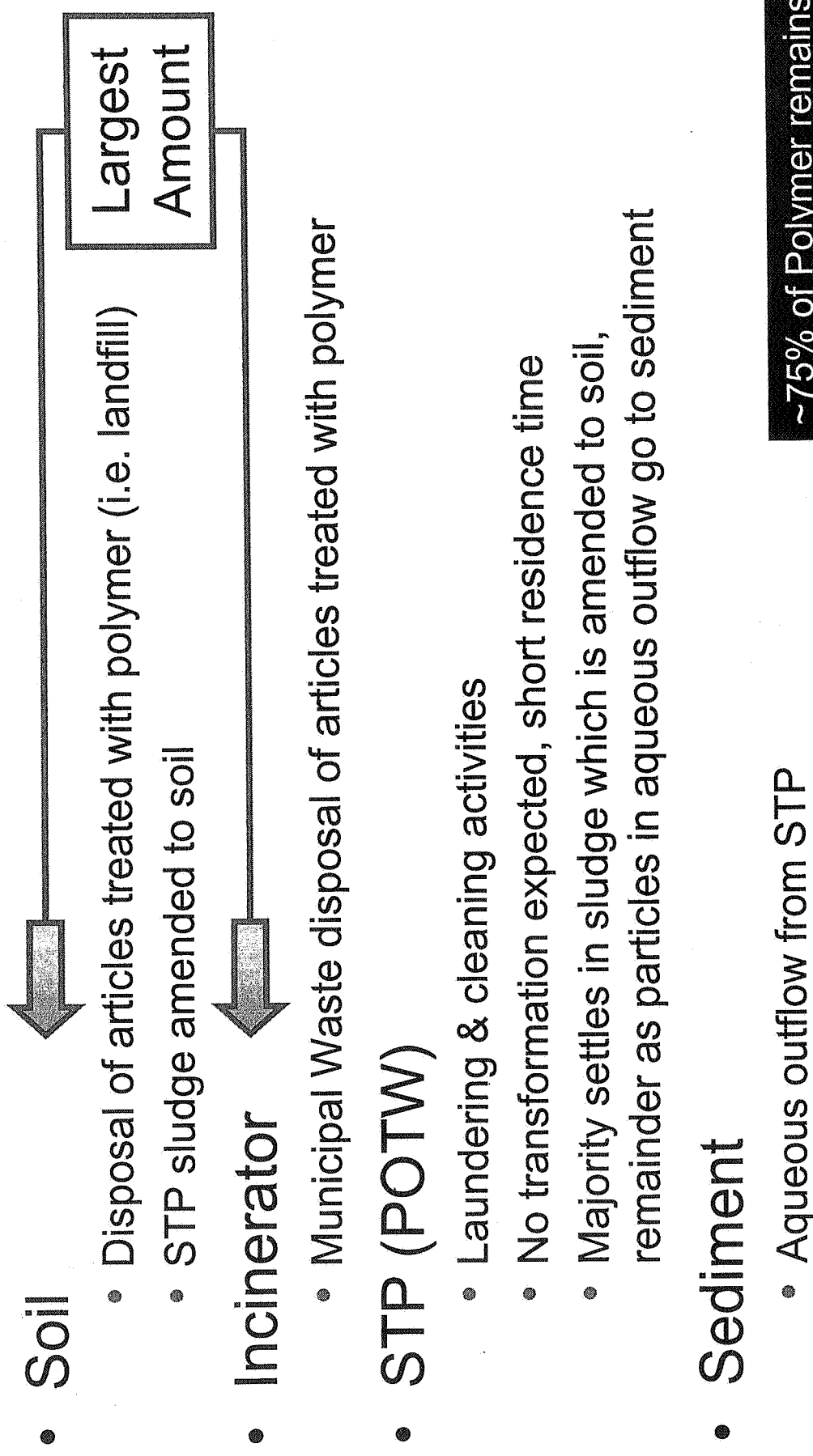
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Fluorotelomer-based Polymers

Do polymers “degrade” to form
fluorotelomer species that can
transform, partition, migrate?



Polymers: Route(s) to the Environment



~75% of Polymer remains on the article at disposal

Polymer "Degradation" - Where to Investigate ?

- Abiotic Transformation : Hydrolysis, Photolysis
 - Industrial Use : Product Dispersion
 - Consumer Use : Cleaning, washing, sunlight ($h\nu$), etc.
 - Disposal : Incineration
- Biotic Transformation : Sludge, Soil, Sediment
 - Disposal
 - Down-the-drain => POTW
 - Municipal waste => landfill or incineration

Polymer Hydrolytic Stability : OECD 111 - DuPont

- Fluorotelomer-based Acrylate and Urethane Polymers studied
- Reactions in water are one of the most common means of non-biological degradation of substances in the environment.
- Aqueous stability tests at environmentally and biologically relevant pH's and temperatures.
 - pH 4, 7, 9 at 50°C ; pH 1.2 at 37°C
- Four replicates : Analysis at 0 and 5 Days
- Study Conclusion
 - No change , Polymers are hydrolytically stable

Incineration - DuPont

- Experimental Approach
 - Typical municipal waste incineration condition
 - >1000°C, 2 seconds
 - University of Dayton Research Institute, Advanced Thermal Reactor System
 - Article treated with Polymer and Polymer itself Studied
- Study Complete
 - Manuscripts in preparation, To be presented at SETAC N.A. Nov. 2004
- Study Conclusion
 - The polymer is destroyed under typical municipal waste incineration conditions
 - Municipal incineration is not a source of perfluorocarboxylic acids

Polymer Biodegradation Studies - DuPont

Acrylate and Urethane Polymers

- Sludge
 - Ready Biodegradation (OECD 301 B/D)
 - Inherent Biodegradation (OECD 302 B)
 - Work complete, Analysis and reports in-progress
 - *Preliminary evaluation indicates no evidence that polymer is degrading*
- Screening Studies (commenced September 2004)
 - Soil : Aerobic; Sediment : Anaerobic
 - For method development
 - Then, commence longer-term studies



Fluorotelomer Alcohols

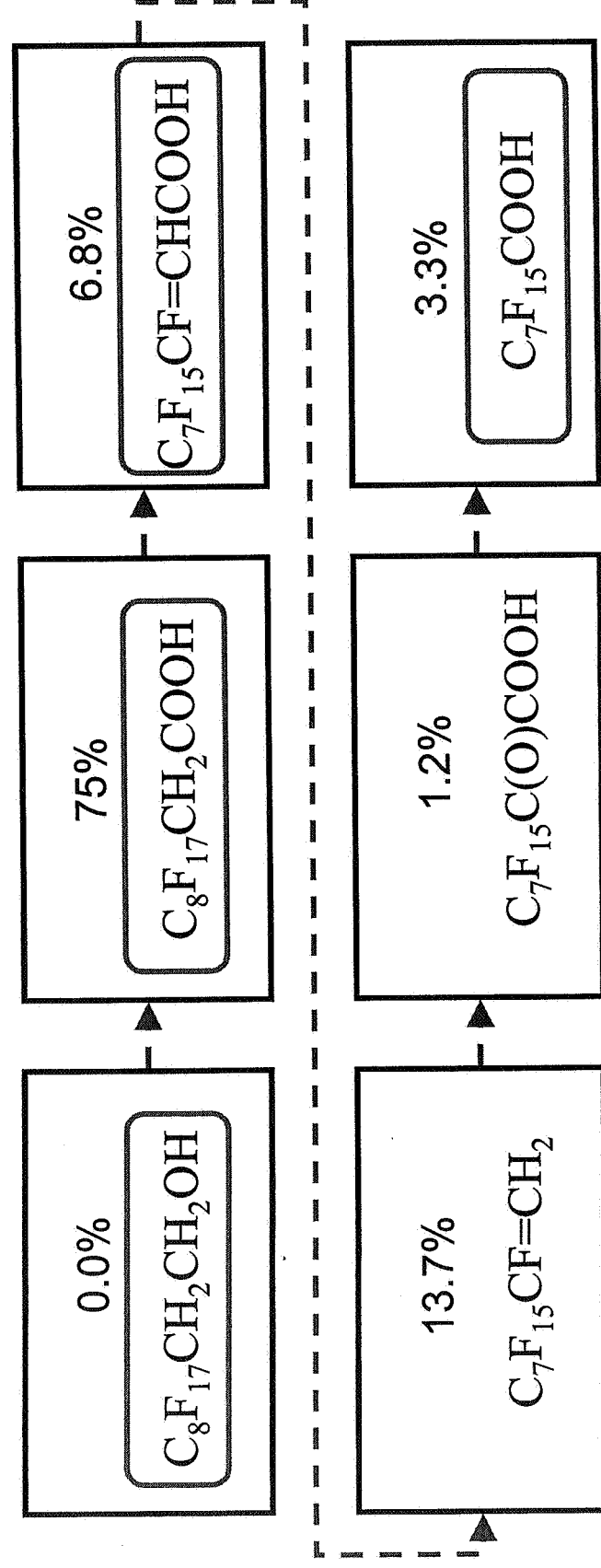


“Telomer B Alcohol”

Telomer B Alcohol : Physical-Chemical Properties

- Water solubility
 - $\sim 150 \text{ mg}\cdot\text{L}^{-1}$ (ppb)
- Vapor Pressure
 - 3 pa at 21°C (measured)
- Hydrolysis
 - hydrolytically stable
 - pH 4, 7, 9 at 50°C, pH 1.2 at 37°C for five days
- Photolysis
 - does not absorb visible light
- Highly Sorptive to soils, sediments, sludge

CATABOL Biodegradation *Prediction*



- The sum of the % values = 100
- The model *predicts* this will be the pathway & distribution of transformation products

Chemical Standards

To achieve unequivocal analytical quantitative accuracy and precision

- **Isotopically - Labeled Standards**

- M+5 : $\text{C}_7\text{F}_{15}^{13}\text{CF}_2\text{CD}_2\text{CD}_2\text{OH}$ (internal standard)
- M+2 : $\text{C}_6\text{F}_{13}^{13}\text{CF}_2^{13}\text{COOH}$
 $\text{C}_8\text{F}_{17}^{13}\text{CH}_2^{13}\text{COOH}$
 $\text{C}_7\text{F}_{15}\text{CF}=\text{CH}^{13}\text{COOH}$

- **“Cold” Standards**

- $\text{C}_8\text{F}_{17}\text{CH}_2\text{COOH}$
- $\text{C}_7\text{F}_{15}\text{CF}=\text{CHCOOH}$
- $\text{C}_5\text{F}_{11}\text{COOH}$
- Others are being synthesized for transformation products observed



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8-2 Telomer B Alcohol : $C_8F_{17}CH_2CH_2OH$

- Biodegradability Screening
 - Ready : emulate a POTW
 - Inherent : favorable, forcing conditions
 - Qualitative Identification & Analysis
 - Enable analytical method development
- Biodegradation Studies
 - ^{14}C Radiolabeled Study Material
 - Quantitative
 - Identify stable transformation product(s)

28-Day Ready Biodegradation Modified OECD 301D

of



Sponsored by the
Telomer Research Program
Asahi Glass, Clariant, Daikin, DuPont

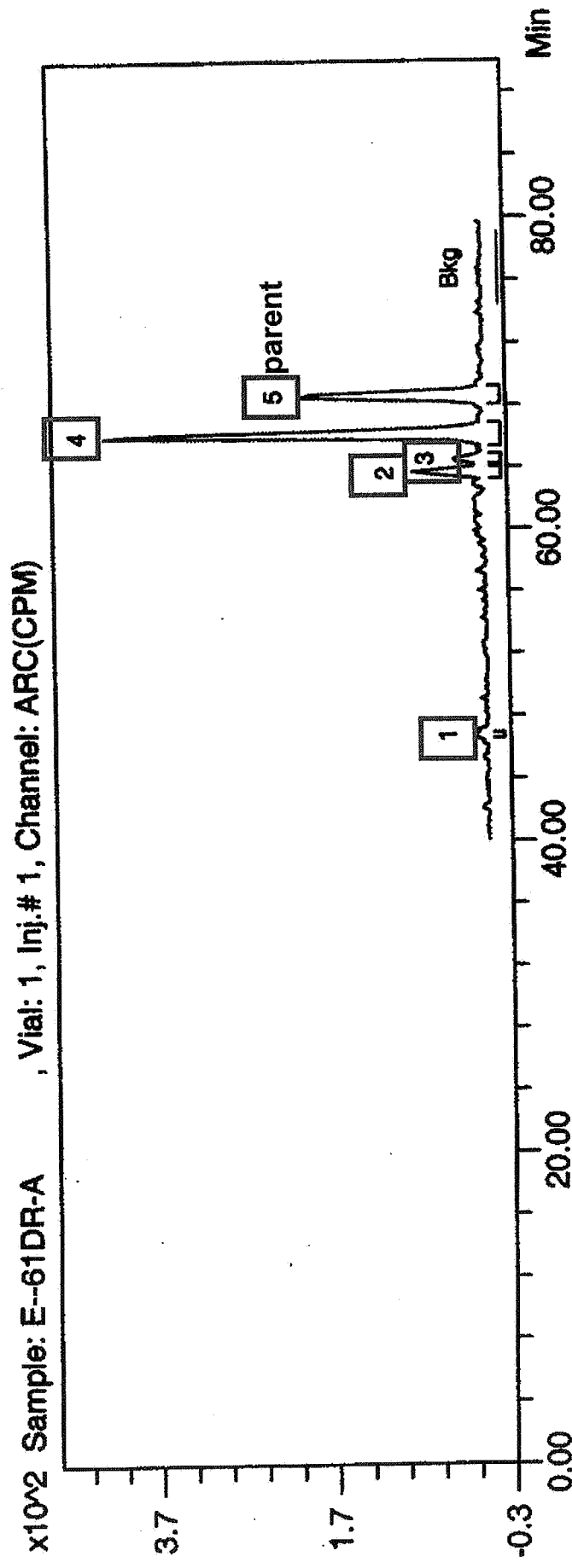
Manuscript submitted to *Environmental Science & Technology*



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Results - Day 28 biodegradation sample

LC/ARC analysis of ^{14}C -labeled transformation products

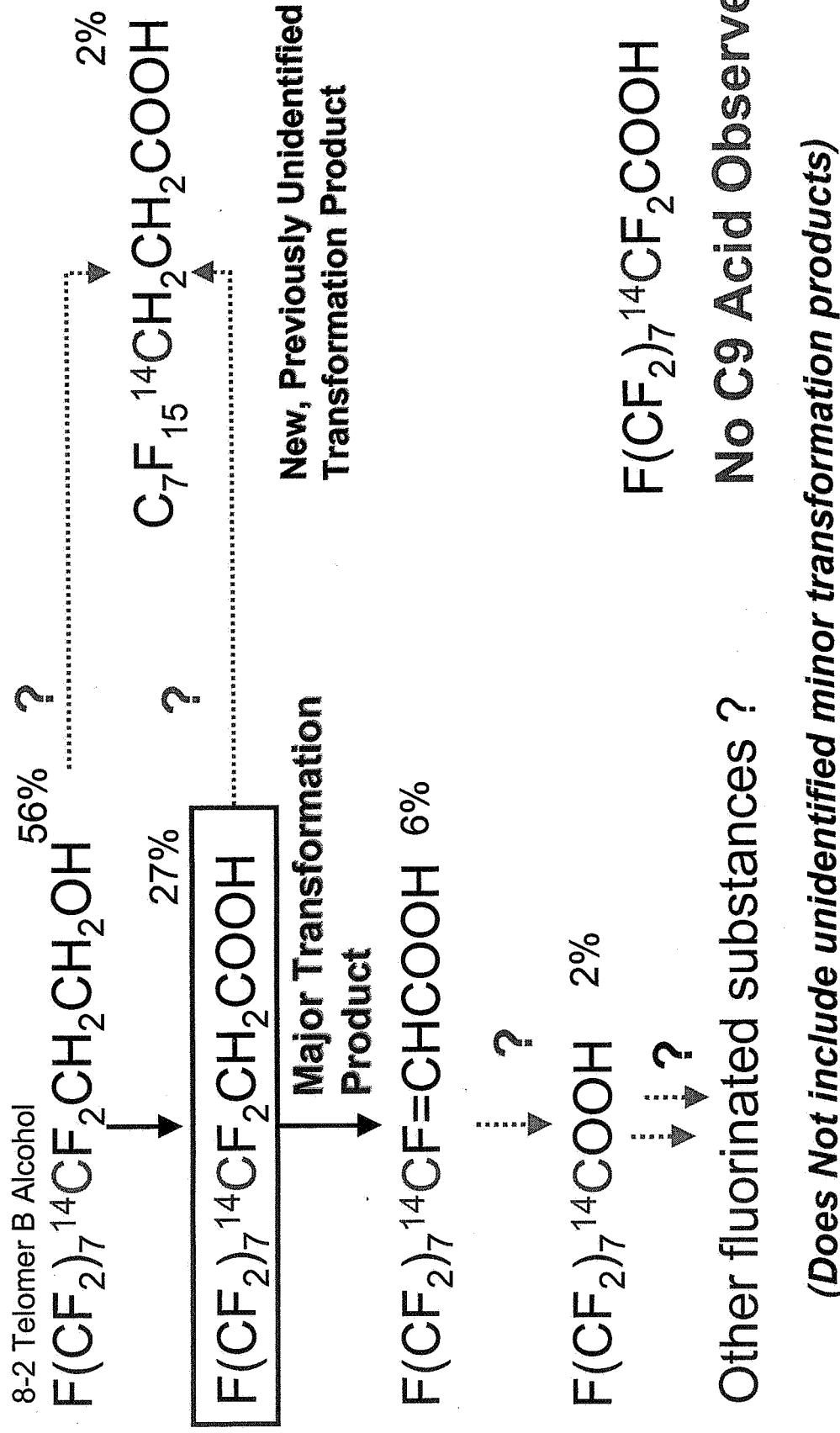


Peaks 1, 2, 3, & 4 are observed transformation products and peak 5 is the parent.



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Ready Biodegradation Potential Biotransformation Route



Accelerated Biodegradation

90 Days

Acclimated Sludge

$\text{F}(\text{CF}_2)_7^{14}\text{CF}_2\text{CH}_2\text{CH}_2\text{OH}$

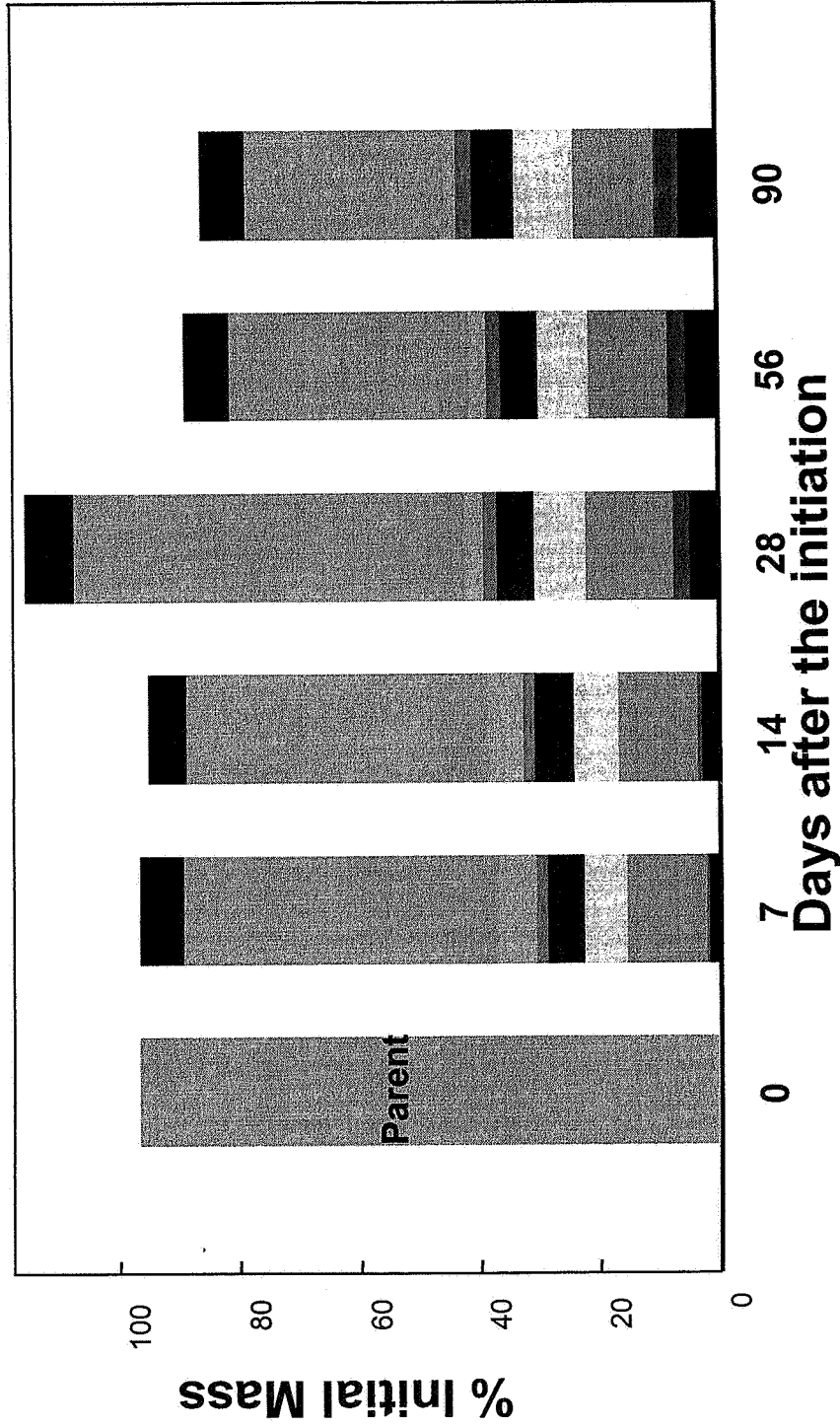
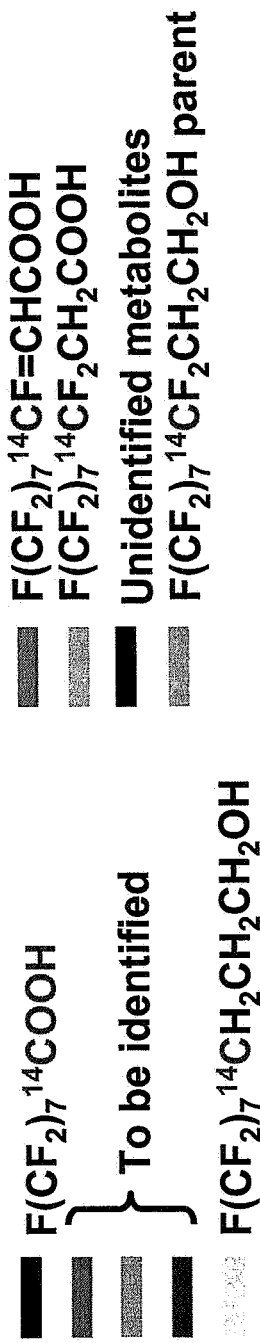
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unpublished results



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Time Course of Biotransformation



Inherent Biodegradation

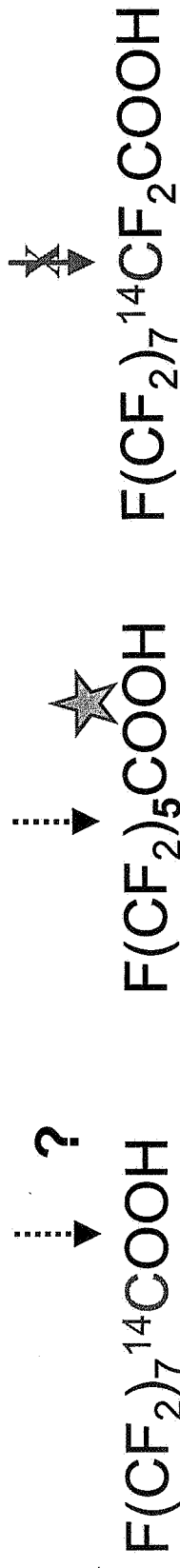
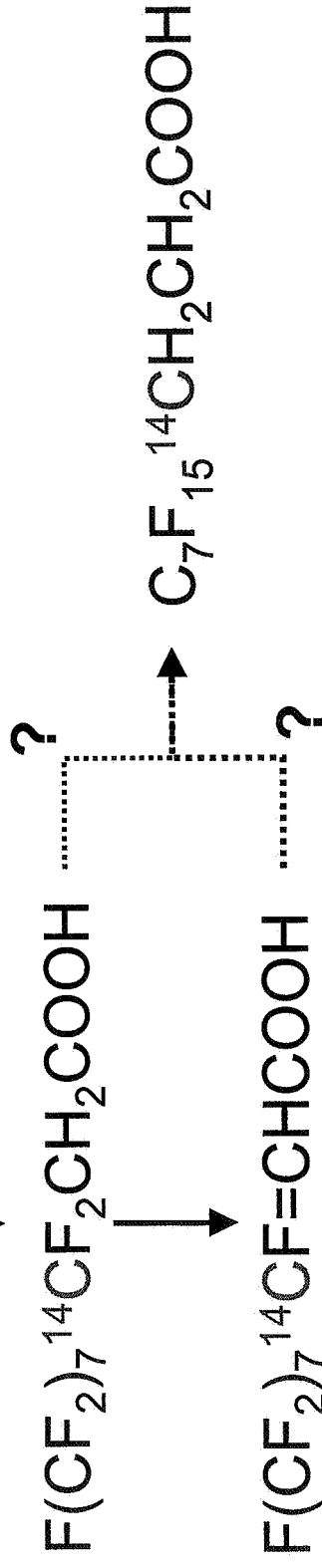
Potential Biotransformation Route

8-2 Telomer B Alcohol



Undefined Pathway
.....→

Defined Pathway
————→



Not Observed

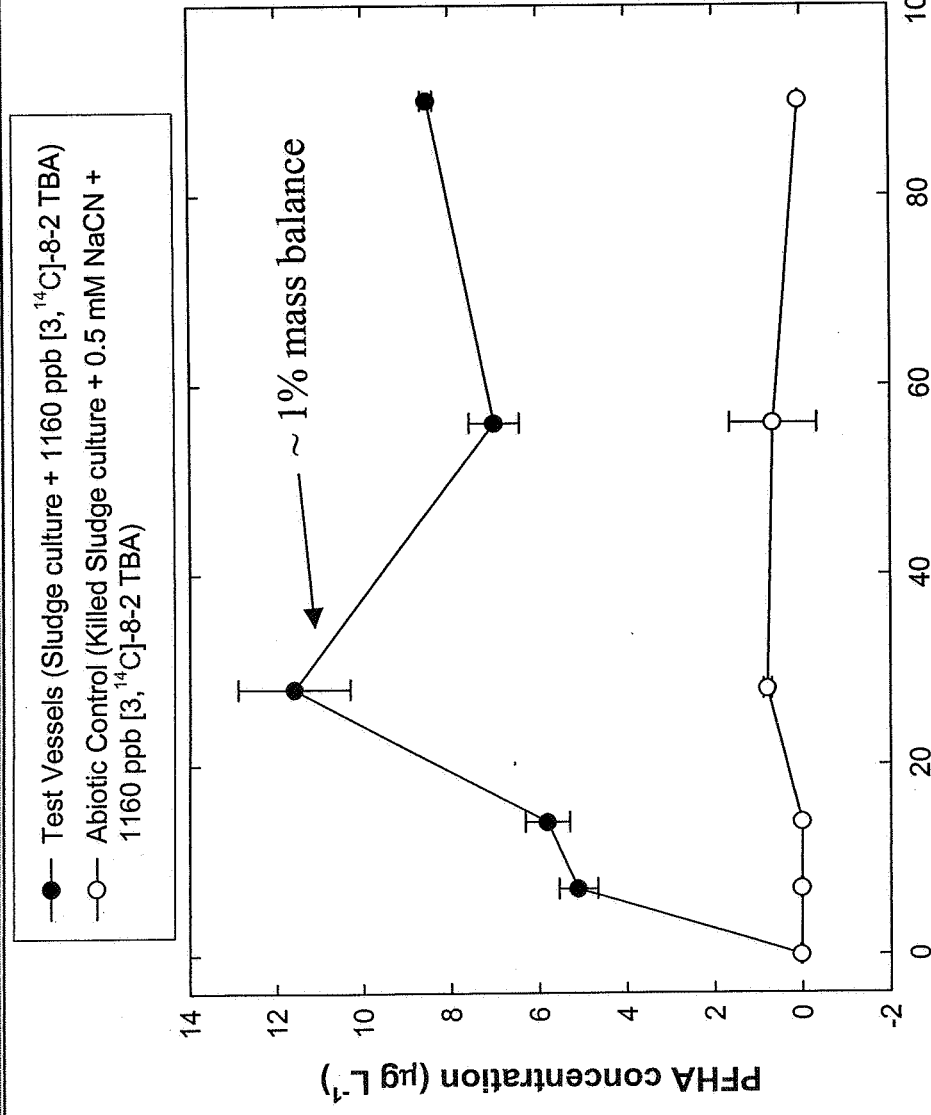
Other fluorinated substances ? unpublished results



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Time Course of $\text{CF}_3(\text{CF}_2)_4\text{COOH}$ Formation

unpublished results



<u>Spike Recovery (%)</u>	
Day 0	113
Day 7	102
Day 14	158
Day 28	134
Day 56	177
Day 90	177

Days after the initiation

- Presence of additional hydrocarbon co-metabolites accelerate formation ?



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Inherent Biodegradation - 90 Day Study



- Many Additional ^{14}C containing transformation products
 - structural identification in-progress
- $^{14}\text{CO}_2$ observed
- $\text{C}_5\text{F}_{11}\text{COO}^-$ is a transformation product
- $\text{C}_7\text{F}_{15}\text{COO}^-$ is not formed rapidly or in great amount nor is it the primary transformation product
- No "C9" $\text{C}_8\text{F}_{17}\text{COO}^-$ observed
- **Results indicate a transformation route or route(s) where more than one $-\text{CF}_2-$ group is "degraded" !**

unpublished results



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Presentation Outline

- Telomer Alcohol Degradation
 - Abiotic
 - Hydrolytic Stability
 - Biotic
 - Catabol
 - Sludge : 3M, UT, TRP, DD studies (9, 6)
 - Soil : DD
 - SO₂ to COOH
- Fluorotelomer-Based Polymer Degradation
 - Abiotic
 - Incineration, Hydrolysis
 - Biotic
 - Zahn-Wellens, Sturm Tests



Release, Fate and Effects Compartments

