
Proceedings of a Workshop on the Environmental Fate of Fluorotelomer-Based Polymers

**Toronto, Canada
September 12 – 14, 2004**

**Sponsored by:
Canadian Environmental Modelling Network
Environment Canada
DuPont Canada**

CEMN Report No. 200401

**Prepared by:
Canadian Environmental Modelling Network**



STATEMENT FROM THE SPONSORS

Canadian Environmental Modelling Network

The Canadian Environmental Modelling Network (CEMN) has been pleased to contribute to this workshop and has done so with no financial support from the other sponsors. The workshop has served as an example of the role that the CEMN can play to bring together academic, industry and government scientists in a neutral forum to discuss the science behind the environmental behaviour of chemicals of commerce. We appreciate the constructive, frank and considerate attitude of all participants. It is hoped that it may serve as a template for similar future initiatives. We were particularly pleased that students were able to participate. We also gratefully acknowledge the efforts of scientists from Europe and Asia to attend and contribute and the presence of U.S. EPA scientists who attended as observers.

Environment Canada and DuPont Canada

While it is recognized that the findings and report of the workshop will have value for a variety of purposes, the intent of the workshop was not to establish commitments. Accordingly, scientific testing programs discussed or implied at this workshop, narrow or expansive, are not obligations for testing. Similarly, there is no agreement by the Canadian government that addressing any suggested or identified data gaps is a necessary step prior to regulatory decision making on substances which are members of this class. The contributions of all attendees are greatly appreciated, both through their presentations and their active involvement in the discussion groups. Special recognition is due to the CEMN, and Don Mackay and Jon Arnot in particular, for their efforts in organizing the workshop and producing this account of the proceedings.

AUTHORSHIP

This report is published by the Canadian Environmental Modelling Network as CEMN Report 04-01. The report is primarily authored by Jon Arnot and Don Mackay of the CEMN. A draft was supplied to the other sponsors and to a number of contributors to confirm that their contributions are accurately recorded. We are grateful to those who provided comments, but the responsibility for the content is entirely that of the CEMN.

EXECUTIVE SUMMARY

These proceedings are of a workshop held near Toronto in September 2004 to discuss the scientific aspects regarding the environmental fate of fluorotelomer-based polymers and their degradation products. The workshop was sponsored by the Canadian Environmental Modelling Network, DuPont Canada and Environment Canada and was attended by 45 individuals from academic, industrial and government institutions.

The workshop addressed aspects of a “working hypothesis” that commercially available fluorotelomer-based polymers release volatile fluorotelomer alcohols (FTOHs), from residual unpolymerized sources and/or from degradation processes. These polymers consist of a hydrocarbon backbone to which a fluorinated carbon chain (“telomer”) is appended typically by an ester, ether or urethane linkage. Once released, the FTOHs undergo atmospheric reactions ultimately to form perfluorocarboxylic acids (PFCAs) which are very water soluble and are deposited into terrestrial, aquatic and marine systems. The PFCAs then bioaccumulate in organisms and may biomagnify in food webs, especially in Arctic mammals such as seals and polar bears. Monitoring data have demonstrated concentrations in liver samples of these and other species.

The workshop focussed on the science of fluorotelomer-based substances and did not address their toxicology, nor did it consider regulatory or policy issues. A central theme was the discussion of the working hypothesis, alternative environmental pathways, and what data gaps and uncertainties were evident. The general aim is to establish a better understanding of the environmental fate of fluorotelomer-based polymers and their degradation products.

In a plenary session, reviews were presented by 11 experts in the field covering topics such as basic chemistry, synthesis and manufacture, analytical methods, sources, degradation mechanisms, pathways and kinetics, partitioning, environmental fate and transport, monitoring results (especially in the Arctic), bioaccumulation phenomena and modelling as a means of obtaining a more complete quantitative understanding of environmental fate. An outline of the content of these reviews is presented.

The meeting then divided into work groups addressing specific aspects of environmental fate and documenting data gaps and research needs which would further the understanding of these substances. These were considered in a final plenary session.

There is available scientific information supporting the “working hypothesis”. There remains, however, a lack of full understanding of certain aspects of the broad and complex environmental behaviour of fluorotelomer-based substances.

Key research areas were identified to improve our understanding of the environmental fate of these substances. These and other topics were raised by attendees as areas for research, as well as citing the benefits of improved cooperation internationally and between academia, industry and government. It is hoped that key developments surrounding perfluorinated chemicals in general, including opinions and suggested directions for scientific opportunity from this workshop, will be forthcoming.

TABLE OF CONTENTS

STATEMENT FROM THE SPONSORS	ii
AUTHORSHIP	ii
EXECUTIVE SUMMARY	iii
TABLE OF CONTENTS	iv
INTRODUCTION	1
SUMMARY OF PLENARY SESSIONS	2
SUMMARY OF WORKSHOP GROUP SESSIONS	8
GENERAL COMMENTS	13
APPENDIX 1 - LIST OF ATTENDEES AND CONTACT INFORMATION	14
APPENDIX 2 - OBJECTIVES AND WORKSHOP PROGRAM	15
APPENDIX 3 - TERMS AND DEFINITIONS	17
APPENDIX 4 - DETAILS OF FLUOROS 2005	19
APPENDIX 5 - DETAILS OF WORKGROUP DISCUSSIONS	20

INTRODUCTION

In recent years, observations of the presence of perfluoroalkyl substances in wildlife and human tissue has resulted in these substances being identified as emerging chemicals of concern. Perfluoroalkyl substances include a broad range of charged and neutral compounds that contain a perfluorinated alkyl group. A specific group called “Telomers” are used in commerce as surface active agents particularly in the carpet, textile and paper industries. Their utility is largely the result of their unique physico-chemical properties.

In consideration of increasing academic, industrial and regulatory interest in perfluoroalkyl substances, including fluorotelomer-based substances, it was decided that this was an appropriate time to review the current state of the emerging science concerning fluorotelomer-based polymers. A workshop was organized and focused on the environmental fate of fluorotelomer-based polymers and their degradation products. It was held at The Eaton Hall Inn and Conference Centre, north of Toronto, Canada from September 12 – 14, 2004. The intention of this workshop was to:

- facilitate an understanding among industry, researchers and regulators the current scientific work and knowledge of fluorotelomer compounds, particularly FTOHs and their relationship to PFCAs;
- discuss and inventory gaps in the scientific knowledge related to the objectives;
- discuss and list projects which could assist in addressing the identified gaps; and,
- identify areas of research which will further our scientific understanding of the fate and transport of fluorotelomer compounds, particularly FTOHs and PFCAs.

The format of the workshop included an initial plenary session to provide a scientific foundation for the workshop discussions. A series of selected speakers provided the attendees a current view of what is known about telomer-based polymers and their environmental fate, what is known about fluorotelomer alcohols, fluorotelomer aldehydes and PFCAs, and what has been observed from environmental monitoring. This assembly was followed by workshop breakout sessions consisting of 10-12 participants in four predetermined workgroups. The members of each group included a range of stakeholders and each group was assigned a facilitator and a “scribe”. Each group discussed four subject areas for one hour each followed by assembly and dissemination of the discussions to all members of the workshop. A final session highlighted key points for each subject area and participants gathered for a final review of these issues.

The workshop was sponsored by The Canadian Environmental Modelling Network (CEMN), DuPont Canada and Environment Canada. The focus of the workshop was on the current scientific knowledge of the environmental fate of fluorotelomer-based polymers and not on toxic effects, nor on associated regulatory policies.

This report was generated by CEMN to provide a documented summary of the proceedings of the workshop. A series of five appendices includes: a list of attendees, the workshop program and statement of objectives, a list of relevant terms and definitions, details of FLUOROS 2005 and details of workgroup discussions on key topics.

SUMMARY OF PLENARY SESSIONS

The initial plenary session opened with brief introductions from Jack Soule representing DuPont Canada, Don Mackay representing the CEMN and Greg Hammond representing Environment Canada. The background to the workshop was described and objectives outlined. Attendees introduced themselves including affiliations and statements of any financial or other relationships to the sponsors.

Robert Buck of DuPont gave the first presentation in which he introduced the basic chemistry and nomenclature of the fluorotelomer-based substances which are relatively short chain fluorinated alkanes appended to a polymer backbone by amide, acrylic, ester, ether or urethane linkages. A set of definitions of fluorochemicals was kindly provided and is included here as Appendix 3. Fluorotelomer-based polymers are sold as dispersions in water containing 20-30% active ingredient and 6-10% fluorine. They may contain some residual fluorotelomer alcohol or fluorotelomer olefin at levels of approximately 500 ppm. They are used in many applications such as on carpets, textiles and paper. He described the polymer product trail including production, use and disposal patterns as potential entry points into the environment. Direct and indirect sources of PFCAs in the environment were outlined. Telomer-based substances are an indirect source. He concluded by outlining a hypothesis for the environmental fate of fluorotelomer-based polymers proposed by Scott Mabury as a lead-in to his presentation. He highlighted knowledge gaps in each key step in the hypothesis.

Scott Mabury of the University of Toronto presented a summary of the comprehensive research program from his group and collaborators. The research included physico-chemical properties of telomer alcohols, determination of levels of residual alcohol in products, the potential for cleavage of the polymer-FTOH linkage during consumer use patterns, measurements of concentrations in the atmosphere in various locations, estimates of atmospheric gas-phase reaction half-lives of the alcohol and its corresponding aldehyde oxidation product, the “unzipping” mechanism by which the fluorochain is progressively shortened by loss of COF_2 which can compete with reactions forming PFCAs, levels of perfluorocarboxylic acids in precipitation as measured by Brian Scott of Environment Canada’s National Water Research Institute (NWRI), telomer alcohol biodegradation studies, studies of telomer alcohol metabolism, and perfluorocarboxylic acid bioconcentration studies as well as attempts to reconcile air monitoring levels of telomer alcohols with emission estimates. Figure 1 illustrates this proposed environmental fate pathway of FTOHs to PFCAs. In summary he suggested that a prudent course of action would be to: 1) remove residuals; 2) shorten fluorochain; and, 3) strengthen linkage chemistry. He also noted the upcoming FLUOROS conference in Toronto, August 19-21, 2005 as detailed in Appendix 4.

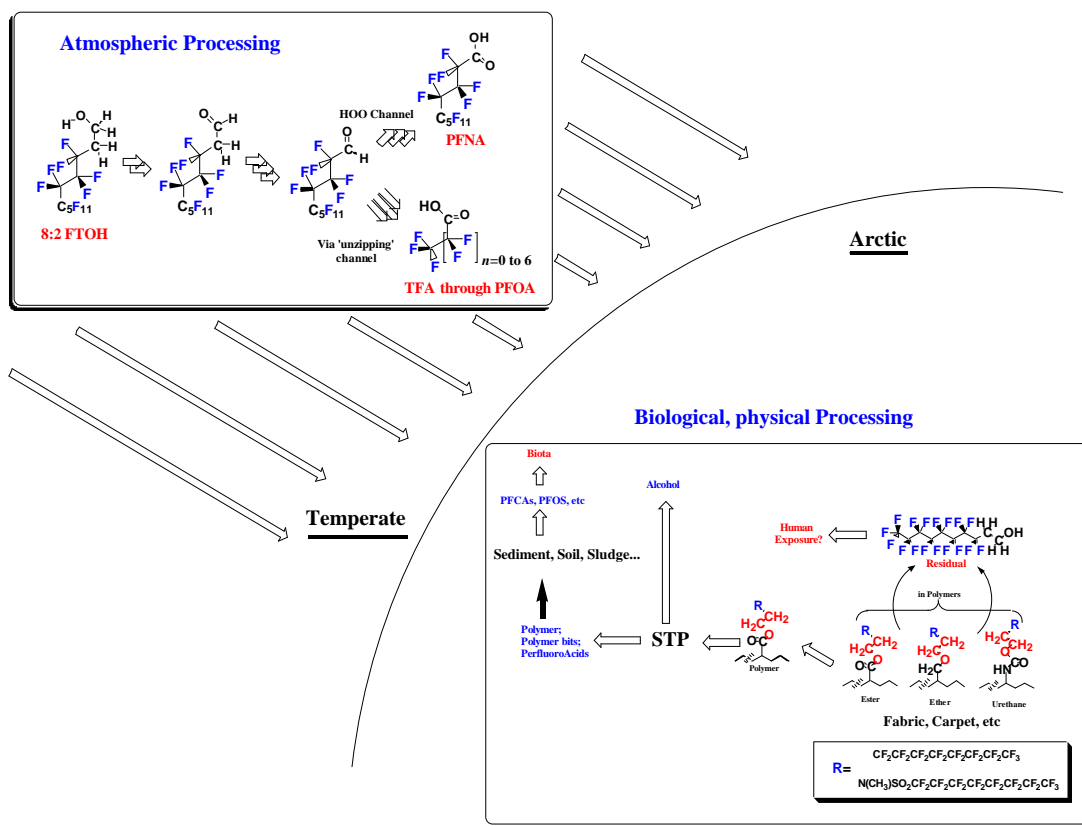


Figure 1. An overview of proposed environmental fate processes for FTOHs to PFCAs as presented at the workshop (used with permission from S. Mabury).

Derek Muir of NWRI surveyed monitoring data in biota in the Arctic, notably of polar bears, ringed seals, beluga whales and seabirds. Figure 2 illustrates monitoring data on PFCA concentrations in polar bear liver from a range of Arctic sampling locations. West to east trends in concentrations of the PFCAs vary depending on the chain length. C9-PFCAs are highest in the Canadian and Alaskan bears while C11 was generally higher in the European arctic. The reasons for these regional trends are not known, but Derek pointed out that previous work on persistent organochlorines in polar bears had demonstrated regional differences, such as higher hexachlorocyclohexane in the western Canadian arctic, that were later explained by differences in use between Asia and Europe. The doubling time for PFCAs appears to be 4 to 10 years in polar bears and ringed seals. Preliminary evidence was presented that perfluorooctane sulfonate (PFOS) levels may now be falling. He also reported on data from bottlenose dolphins off of the U.S. East and Gulf Coasts as well as data on PFCAs in Lake Ontario and Lake Superior (raw, treated water and sewage treatment plant (STP) effluents). He identified knowledge gaps in monitoring geographic trends and temporal trends of C8 - C15 PFCAs in wildlife outside of the Arctic as well as concentrations of precursor chemicals of these compounds.

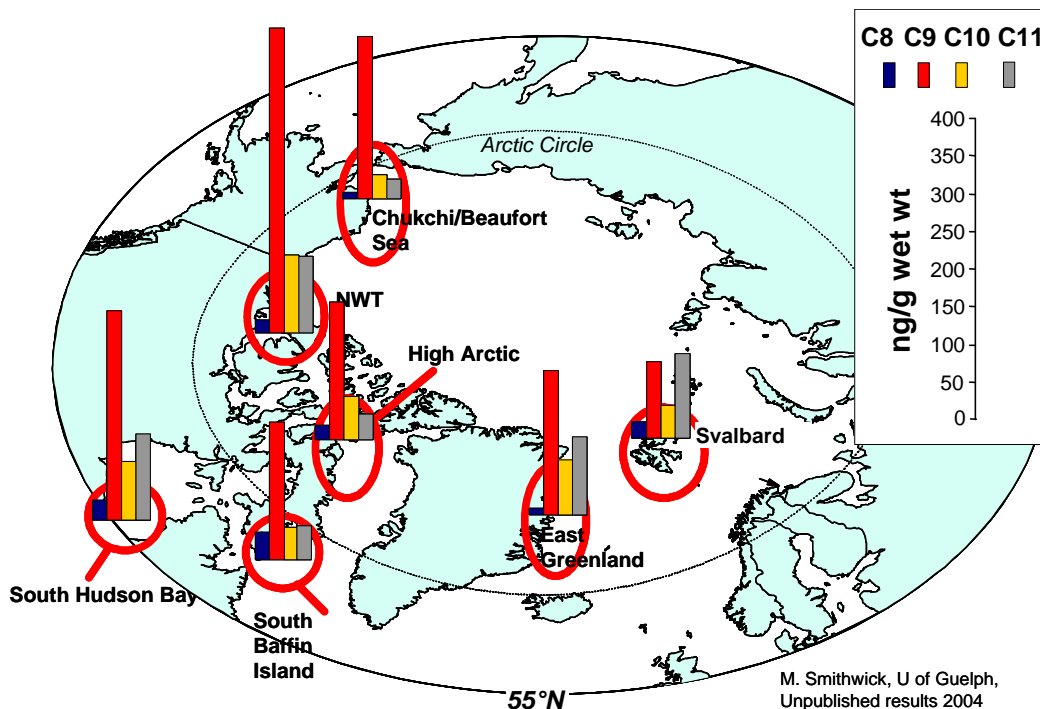


Figure 2. Concentration profiles of major PFCAs in polar bear liver as presented at the workshop (used with permission from D. Muir and M. Smithwick).

Pim de Voogt of the University of Amsterdam described the EU-funded PERFORCE program (approximately 800,000 Euro or 1 million USD) which is now underway and involves several groups from a number of countries working on aspects of this issue including sources, analytical methods, physico-chemical properties, bioassays, monitoring and exposure assessment QA/QC objectives that involve inter-laboratory comparisons as well as integrating industry knowledge. A concluding workshop is planned for summer 2006.

Robert Buck of DuPont discussed biodegradation of fluorotelomer-based polymers and fluorotelomer alcohol in STPs, soil and sediments including mechanisms/routes, kinetics and biotransformation products. He reported that incineration at normal municipal incinerator conditions showed complete destruction of telomer-based polymer rendering fluoride (not presented in the slides) and no quantity of perfluorocarboxylic acids. He also presented biodegradation studies on carbon-14 labelled telomer alcohol and work going on to understand microbial degradation pathways. He noted that the alcohol degrades slowly with only small amounts of perfluorocarboxylic acid formed as well as results which may indicate breakdown of the perfluorocarbon chain. In addition, work on the development of both isotopically-labelled and “cold” standards was mentioned and forthcoming pharmacokinetic results from a mammalian model.

David Ellis of Trent University discussed investigations of atmospheric transformation processes conducted in a smog chamber to identify degradation pathways and half-lives of telomer alcohols and aldehydes. He noted that oxidation of fluorotelomer alcohols in the atmosphere by OH leads quantitatively to the production of the corresponding polyfluorinated aldehyde in which there is a CH₂ moiety left intact between the aldehyde functional group and the perfluorinated alkyl chain. This process indicates that the alcohol and the aldehyde have atmospheric lifetimes on the order of 20 days. He reported that wet and dry depositions are expected to be negligible for these species in comparison to their OH chemistry and that the predominant oxidative pathway of the first formed aldehyde with OH is the production of a further aldehyde which is perfluorinated. In the absence of NO_x, this perfluorinated aldehyde undergoes further oxidation by OH to produce the corresponding PFCA via the hydrolysis of a first formed acid fluoride. A second pathway available to the perfluorinated aldehyde is the production of shorter chain PFCAs. He suggested that although the production of PFCAs by this second route is minor in comparison to the production of carbonyl fluoride it is still deemed to be environmentally significant. He summarized that questions still remain to be answered concerning the degree to which wet deposition plays a role in the atmospheric fate of the perfluorinated aldehyde and how significant these pathways are to the environmental burden of PFCAs with varying amounts of NO_x.



Figure 3. The EUPHORE chamber in Valencia as presented at the workshop (used with permission from R. Waterland).

Robert Waterland of DuPont described atmospheric processes in three categories: what is certain (alcohol volatility, initial gas phase kinetics and alcohol photolysis), what there is some information about (roles of NO_x, HO_x, and aldehyde photolysis) and what is not adequately understood (heterogeneous chemistry, hydrate formation of aldehyde, reactions of fluorotelomer olefins and the exact NO_x and HO_x sequential kinetics). There are also questions relating to the sorption (atmospheric partitioning) of FTOHs to aerosols and Telomer B Olefin (TBO) reactions and properties. He suggested that the EUPHORE chamber in Valencia, as depicted in Figure 3, might be a better testing environment for gas-phase reactions since heterogeneous reactions on the surface of the reaction chamber are minimized.

Mary Kaiser of DuPont described aspects of the unique physico-chemical properties of fluorinated compounds and considerations relating to their analytical methods. She emphasized the need for extreme care to establish background and matrix effects and the need for multi-method analyses using analytical standards, validated methods and rigorous analytical measurement quality control. She also informed that there are some physicochemical data gaps (as well as some ancient data) that need to be either reviewed or determined.

Ulf Jarnberg of the University of Stockholm described work at ITM and the Norwegian Institute of Air Research (NILU) which involved screening levels of perfluorooctanoic acid (PFOA) and PFOS in water, sediments, sludges, fish, birds, seals and whales in Scandinavia, Iceland and the Faroe Islands. He reported that PFOA was generally not detected in any wildlife sample at concentrations above 1 ng/g except in seal and whale samples where concentrations were between 1-5 ng/g, however, PFNA was found at concentrations from below 1 ng/g in fish to 35 ng/g in Baltic seal. In surface water and wet deposition PFOA concentrations frequently exceeded those of PFOS. He presented results from a survey on four waste water treatment plants (WWTP) receiving wastewater from textile treatment plants and industrial laundries were presented. Elevated concentrations of perfluoroalkyl carboxylates, and particularly those with longer chain lengths (9-11 carbons) were clearly related to textile manufacturing process water. Furthermore, the concentrations of perfluoroalkyl carboxylates were generally higher in treated (effluent) WWTP water than in the untreated sewage water. He also included the results of studies near fire fighting training locations, in human blood and in landfill effluents.

Jennifer Field of Oregon State University described an extensive study of PFCA and PFOS levels in Wastewater Treatment Plants (WWTPs) in various U.S. cities. Bulk reductions and increases in concentrations were observed indicating both removal and possible formation. Her recent analysis includes sets (snapshots) of raw influent and secondary effluents for 12 wastewater treatment plants for analytes including, perfluorohexane sulfonate, perfluorooctane sulfonate, perfluorodecane sulfonates, the C6-10 perfluorocarboxylates, the 6:2 and 8:2 telomer sulfonates, perfluorooctanesulfonamide, 2-(N-ethylperfluorooctanesulfonamido) acetic acid, 2-(N-methylperfluorooctanesulfonamido) acetic acid, N-ethyl perfluorooctanesulfonamide. She reported that more detailed in-plant analyses are underway.

Frank Wania of the University of Toronto at Scarborough described model-based techniques for assessing the potential for long range transport of Persistent Organic Pollutants (POPs) and applied them tentatively to the FTOHs. Based on these simulations, the alcohols can be expected to undergo significant atmospheric transport, the extent of which is determined almost entirely by the degradation kinetics as distinct from the deposition kinetics. He also described the Arctic Contamination Potential concept which combines the potential for atmospheric and oceanic transport with the potential for deposition in cold regions. The extent of the estimated polar accumulation of the FTOHs is strongly dependent on the highly uncertain value of the air-water partition coefficient, whereas the exact value of the equally uncertain volatility (octanol-air partition coefficient or vapour pressure) is of less importance. An improved assessment of the long range transport potential of the FTOHs and their potential degradation products requires (i) physical-chemical property data that are better constrained, (ii) confirmation that the "octanol surrogate" assumption is valid for these substances, and (iii) field measurements for model evaluation. Specifically, measurements of air and precipitation concentrations along a latitudinal transect would allow for the evaluation of simulated changes over a transport range.

John Gannon of DuPont gave the final presentation. He noted that we cannot fully answer questions of why PFCAs are being found in the environment and biota without an understanding of the potential contributions from: 1) emissions from direct PFCa sources; 2) fluorotelomer raw material residuals as an indirect source; and 3) potential degradation of fluorotelomer based polymers as an indirect source. Considering that wind-blown soil particulates and ocean sea-salt sprays account for the bulk of solid mass in the atmosphere and that inverted micelles could potentially account for sorption of PFCAs to soil particulates and ocean spray, he hypothesized that it may be possible for PFCa emissions to be subject to long range transport via a grasshopper-like effect that includes a cycle of deposition and repeated "hoppings" from soil surface via wind-blown soils and/or ocean surface via wind-blown sea-salts/ aerosols to the atmosphere. In regards to FtOH, it was noted that volatility and strong adsorption to soil are competing mechanisms for partitioning and perhaps FtOHs associated with soils may have a stronger tendency to stay bound to soil rather than volatilize to the atmosphere. The question was also raised if FtOHs adsorb to atmospheric particulates (e.g., soot, soil particulates, etc.) would transformation still occur? The presentation concluded by noting that there is a need to: 1) develop a global distribution model to evaluate relationship of 50 yrs. of PFCa emissions with presence in environment and biota; and 2) understand if there is any potential for fluorotelomer based polymers to transform.

Most speakers included a list of data gaps and suggestions for further study. These topics were addressed in more detail in the workshop breakout groups. Workshop group facilitators presented the results of the discussions in the workshop breakout groups during subsequent plenary sessions. Each meeting attendee received a paper copy of each presenter's charts.

SUMMARY OF WORKSHOP GROUP SESSIONS

Four workshop breakout groups were assembled to address each of four subject areas individually. Each breakout group consisted of 10-12 members representing the stakeholders and including a designated facilitator and a “scribe”. The facilitators for each group were: (1) Greg Hammond (Environment Canada), (2) Frank Gobas (Simon Fraser University), (3) Gord Cluett (DuPont – Kingston) and (4) Graham White (Health Canada). Four subject areas were suggested for discussion in the designated workshop groups, namely:

1. **Chemistry, Physical-Chemical Properties and Degradation:** (Abiotic and Biotic): by substance and environmental matrix (air, water, soil, sludge, and sediment) or use condition (light, heat, etc.);
2. **Biota and Environmental Compartment Monitoring:** bioconcentration and bioaccumulation;
3. **Analytical Methods and Tools:** methods (and their validation), data quality criteria and standards;
4. **Environmental Pathways, Partitioning and Transport Mechanisms:** routes to the environment, partitioning, as well as transport mechanisms and processes.

The participants of the workshop groups were asked to address certain issues as they relate to the four subject areas. Basic workshop questions suggested included:

1. In what areas do you feel confident that we have a good understanding with solid supporting data? Briefly detail the key items that are, in your view, well known.
2. In what areas are you uncertain and believe we may need more work or data? What is this work?
3. In what areas do you believe we have no basic understanding? What work needs to be done?

More specific questions that were suggested for consideration in the workshop groups were:

1. Fluorotelomer release from the fluorotelomer polymers:
 - What is the degradation mechanism?
 - Are there alternative mechanisms?
 - What is the rate? Is the rate necessary? Is it obtainable?
 - During which life-cycle stages are most significant losses expected?
2. Fate of the fluorotelomer alcohols:
 - What is the potential for LRT?
 - What are the transformation mechanisms?
 - What is the transformation rate?
 - What should be monitored?
 - What are the degradation products?

3. Transformation to PFCAs:

- What are the available monitoring data? What additional monitoring is needed? Where?
- Is the current analytical methodology appropriate?

The findings of the workshop breakout groups were consolidated in the following summary of the workshop group sessions. The key points identified by the workshop groups for each subject are summarized in Tables 1 to 4. Appendix 5 is a compilation of the notes provided by the workshop “scribes”.

Table 1. A summary of the key points identified by the individual workgroups regarding the chemistry, physical-chemical properties and degradation of fluorotelomer compounds.

Workgroup	Key Research Areas Identified
1	<ul style="list-style-type: none"> • Identify how much of “FTOHs” (including Telomer B Olefins) comes from: <ul style="list-style-type: none"> ○ Residuals ○ Fluorinated polymers (breakdown in use and disposal) • Identify relative importance of abiotic / biotic FTOH → PFCA processes in trophic levels and in geographic regions
2	<ul style="list-style-type: none"> • Develop a strategy to: <ul style="list-style-type: none"> ○ Measure distribution coefficients in the environment ○ Explore relationships with physico-chemical properties • Measuring degradation rate of FT polymers over long periods of time in consumer articles, landfills, STPs, soils and sediments as well as establishing relevant protocols for these measurements
3	<ul style="list-style-type: none"> • Share available information regarding: <ul style="list-style-type: none"> ○ Usage, quantities, mode of entry, precursors, degradation products, chemical identity, etc. • Better understand overall polymer fate regarding degradation
4	<ul style="list-style-type: none"> • Improve interface between industry and academia regarding physico-chemical property testing of these chemicals • Bridge data gaps between government and industry by bringing academic expertise and advice to bear: <ul style="list-style-type: none"> ○ Particularly, Telomer Research Program (TRP) biodegradation studies reporting biodegradation work and iterate in consultation with academia to establish the mechanisms

Table 2. A summary of the key points identified by the individual workgroups regarding the monitoring biota and environmental compartment of fluorotelomer compounds.

Workgroup	Key Research Areas Identified
1	<ul style="list-style-type: none"> • Identify and quantify point and diffused FTOH sources to be integrated into flux and mass balance • Independent replication of FTOH measurements in atmosphere
2	<ul style="list-style-type: none"> • Include precursors in monitoring studies, namely: <ul style="list-style-type: none"> ○ Homologues for –OHs, =O and COO⁻ • Include temporal scale for monitoring studies
3	<ul style="list-style-type: none"> • Better understand mechanisms of bioaccumulation and bioconcentration of these chemicals • Gradient sampling program that can be archived for telomer alcohols and known degradation products (i.e. analytes of immediate interest) in relevant media • Complement efforts with an independent monitoring agency
4	<ul style="list-style-type: none"> • Industry to provide source information regarding applications (i.e., space / time) and projected use quantities to inform monitoring activity. • Monitor air and precipitation for FTOHs, PFCAs and other fingerprint materials (i.e. FT acids) from sources to remote areas <ul style="list-style-type: none"> ○ Improved understanding of LRT and longitudinal and latitudinal distributions

Table 3. A summary of the key points identified by the individual workgroups regarding the analytical methods and tools used for fluorotelomer compounds.

Workgroup	Key Points Identified
1	<ul style="list-style-type: none"> • Better understanding of environmental partitioning (e.g., air-water, air-particle, water-biota, etc.) rather than pure compound properties • Certified standards: <ul style="list-style-type: none"> ○ “Cold” for FTOHs and PFCAs ○ Isotopically enriched analytical standards for acids (i.e. there are no isotopically labeled FTOHs, just PFOA and 8:2 telomer acids) ○ Analysis to generate ‘round robin’ standards
2	<ul style="list-style-type: none"> • Certified reference materials (i.e., PFCAs) and documentation of results in papers and reports • More detailed reporting of analytical methods including storage, sampling, modifications and work-up in journals or on the internet
3	<ul style="list-style-type: none"> • Guidance document including but not limited to best practises to mitigate significant background, matrix issues including interference and calibration • Inter-laboratory comparisons including standards, perhaps building on or in conjunction with PERFORCE initiatives
4	<ul style="list-style-type: none"> • Develop collaboration including: <ul style="list-style-type: none"> ○ Open exchange of protocols and methods; ○ Inter-laboratory studies; ○ Details from industry regarding structure / composition of test materials (i.e., polymers) • Coordinated inventory of relevant analytical data as an information management tool / repository

Table 4. A summary of the key points identified by the individual workgroups regarding the partitioning behaviour, environmental pathways and transport mechanisms of fluorotelomer compounds.

Workgroup	Key Research Areas Identified
1	<ul style="list-style-type: none"> • More environmental measurements in the Arctic of FTOHs, aldehydes and acids for pathway verification • Better quantify the atmospheric yield of “FTOH” to PFCAs
2	<ul style="list-style-type: none"> • Measure air-particle and air-water partitioning of FTOH and PFCAs in environment including the potential role of sequestration • Explore sources that can explain geographical differences in PFCAs concentrations and C₈ and C₉ [not sure what is meant by this bullet]
3	<ul style="list-style-type: none"> • Empirical partition coefficient and environmental distribution coefficients to improve model inputs and identify mode of entry into the environment • Further understand the relative proportions of telomer degradation pathways (i.e., NO_x vs. HO_x)
4	<ul style="list-style-type: none"> • Ascertain the potential importance of oceanic transport to the Arctic • Establish the relative importance of marine vs. airborne transport

GENERAL COMMENTS

There was generally and frequently expressed sentiment that there is a need to develop improved interactions between academia, industry and government sectors both nationally and internationally. There should be more sharing of available information regarding FTOH usage, quantities, chemical identities, products and physico-chemical properties. The Telomer Research Program and PERFORCE should be active participants in such a dialogue.

APPENDIX 1 - LIST OF ATTENDEES AND CONTACT INFORMATION

Name	Organization	Email
Don Mackay	Trent University	dmackay@trentu.ca
Scott Mabury	University of Toronto	smabury@alchemy.chem.utoronto.ca
Vasile Furdui	University of Toronto	c/o smabury@alchemy.chem.utoronto.ca
Naomi Stock	University of Toronto	c/o smabury@alchemy.chem.utoronto.ca
Amila DeSilva	University of Toronto	c/o smabury@alchemy.chem.utoronto.ca
Craig Butt	University of Toronto	c/o smabury@alchemy.chem.utoronto.ca
Joyce Dinglasan	University of Toronto	c/o smabury@alchemy.chem.utoronto.ca
Derek Muir	Environment Canada NWRI	derek.muir@ec.gc.ca
Marla Smithwick	University of Guelph	c/o derek.muir@ec.gc.ca
Magali Houde	University of Guelph	c/o derek.muir@ec.gc.ca
Brian Scott	Environment Canada NWRI	brian.scott@ec.gc.ca
Jon Arnot	Trent University	jonarnot@trentu.ca
Todd Gouin	Trent University	tgouin@trentu.ca
Linda Lee	Purdue University	lslee@purdue.edu
Jennifer Field	Oregon State University	jennifer.field@orst.edu
Frank Gobas	Simon Fraser University	gobas@sfu.ca
Pim de Voogt	University of Amsterdam	pdevoogt@science.uva.nl
David Ellis	Trent University	Davidellis@trentu.ca
Tom Harner	Meteorological Service, Env. Can.	tom.harner@ec.gc.ca
Mahiba Shoeib	Meteorological Service, Env. Can.	Mahiba.shoeib@ec.gc.ca
Terry Bidleman	Environment Canada	Terry.Bidleman@ec.gc.ca
Ulf Jarnberg	University of Stockholm	ulf.jarnberg@itm.su.se
Frank Wania	University of Toronto	Frank.wania@utoronto.ca
Greg Hammond	Environment Canada NSB	Greg.Hammond@ec.gc.ca
Mark Lewis	Environment Canada NSB	Mark.Lewis@ec.gc.ca
Robert Chenier	Environment Canada ESB	Robert.Chenier@ec.gc.ca
Anita Miettunen	Environment Canada ESB	Anita.Miettunen@ec.gc.ca
Jessy Kurias	Environment Canada ESB	Jessy.Kurias@ec.gc.ca
Roger Sutcliffe	Health Canada ESD	roger_sutcliffe@hc-sc.gc.ca
Graham White	Health Canada NSACB	Graham_White@hc-sc.gc.ca
Al Wiedow	Ciba S.C.	al.wiedow@cibasc.com
Mike Heneghan	Ciba S.C.	Mike.heneghan@cibasc.com
John Erickson	Ciba S.C.	John.erickson@cibasc.com
Keiichi Ohnishi	AGC Chemicals Americas, Inc.	kohnishi@asahiglass.com
Volker Koch	Clariant GmbH	volker.koch@clariant.com
Robert Boethling	U.S. EPA (invited observer)	Boethling.Bob@epamail.epa.gov
David Lynch	U.S. EPA (invited observer)	Lynch.David@epamail.epa.gov
Jack Soule	DuPont - Kingston	Jack.soule@can.dupont.com
Steve Korzeniowski	DuPont - Wilmington	Stephen.H.Korzeniowski @usa.dupont.com
Bob Buck	DuPont - Wilmington	Robert.c.buck@usa.dupont.com
John Gannon	DuPont - Wilmington	John.gannon@usa.dupont.com
Watze de Wolf	DuPont - Brussels	Watze.de-wolf@bel.dupont.com
Mary Kaiser	DuPont - Wilmington	Mary.a.Kaiser@usa.dupont.com
Rob Waterland	DuPont - Wilmington	Robert.L.Waterland@usa.dupont.com
Gord Cluett	DuPont - Kingston	Gord.cluett@can.dupont.com

APPENDIX 2 - STATEMENT OF OBJECTIVES AND WORKSHOP PROGRAM

Statement of Objectives

The aim of this workshop was to develop a better understanding of the environmental fate of fluorotelomer-based polymers, release of FTOHs from these polymers and the fate transport of FTOHs and PFCAs.

It was intended to approach this through consideration of the current scientific evidence and knowledge, research which is underway or pending, and a discussion of what gaps in this knowledge could be further studied.

The workshop addressed only the scientific body of knowledge surrounding the environmental fate and transport of these substances. The workshop did not address toxicology, nor did it address regulatory issues.

Workshop Program

Sunday, September 12, 2004

7:00pm	Cocktails and Dinner
8:30pm	Introductions, background, objectives, final agenda, informal networking

Monday, September 13, 2004

Breakfast individually

8:30am	Plenary Session – Brief Introduction and Background
9:00am	Bob Buck – Chemistry, Sources, Uses, Routes into the Environment
9:15am	Scott Mabury – A Perspective on FTOH's
10:00am	Derek Muir – Monitoring Data
10:35am	BREAK
11:00am	Pim de Voogt – PERFORCE Activities, EU
11:20am	Bob Buck – Biodegradation
11:50am	David Ellis / Rob Waterland – Atmospheric
12:30pm	LUNCH
1:30pm	Mary Kaiser – Physical Chemical Properties / Analytical
2:00pm	Ulf Jarnberg – Monitoring
2:20pm	Jennifer Field – Wastewater
2:45pm	Frank Wania – Global Modeling

3:15pm	John Gannon – An E-Fate Perspective
3:45pm	Plenary Wrap-up and Charge for Breakout Sessions
5:30pm	DINNER
7:00pm	Plenary Session – Workshops report out. Review initial learnings from workshop groups to determine any needs or changes for next day.
9:00pm	ADJOURN

Tuesday, September 14, 2004

Breakfast individually

8:30am	Plenary Session – Any new info for workshops.
8:45am	Breakout workshops resume for each of the four areas of discussion.
11:00am	Plenary Session – Workshops report out.
12:00noon	LUNCH
1:00pm	Breakout workshops review key points
2:00pm	Plenary Session – Review of key points from each workgroup regarding the four areas of discussion.
3:00pm	ADJOURN

APPENDIX 3 - TERMS AND DEFINITIONS

Fluorochemical	a general, non-specific, term used to describe broadly all chemicals containing the element fluorine; Specifically, the term is used most commonly to describe small (1-8 carbon length) fluorinated molecules which are most often used for refrigeration, as fire suppression agents and as specialty solvents.
Fluorinated Chemical	a general, non-specific, term used synonymously with “fluorochemical”.
Fluorotelomer or "Telomer"	a specific term used to describe an oligomer created by reaction of tetrafluoroethylene (TFE) with perfluoroethyl iodide $\text{CF}_3\text{CF}_2\text{I}$ to produce $\text{F}(\text{CF}_2\text{CF}_2)_n\text{I}$ [$n = 3-6$; avg. 4], a linear, even carbon number chain length oligomer; the term "telomer" is often used synonymously with fluorotelomer.
Fluorotelomer Alcohol (FTOH)	a general term which describes a class of alcohols of the general structure $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$ where n is an integer.
Fluoropolymer	a general term used to describe a polymer which has fluorine attached to the majority of carbon atoms which comprise the polymer chain backbone [common fluoropolymers are: polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), fluorinated ethylene-propylene (FEP), etc.]; these are typically high molecular weight polymers used in high performance applications where chemical resistance and thermal stability are essential.
Fluorinated [Organic] Polymer	a general term used to describe a polymer which has a hydrocarbon backbone (polyamide, polyester, polyurethane, etc.) to which is appended a fluorinated carbon chain, also known as a fluorinated alkyl chain; an example would be a polymer such as - $[\text{CH}_2\text{CH}(\text{C}(\text{O})\text{OCH}_2\text{CH}_2(\text{CF}_2)_8\text{F})]_n$. These are not fluoropolymers.
Perfluoro-/ Perfluorinated	describes specifically a substance where all hydrogen atoms attached to carbon atoms are replaced with fluorine atoms - CF_n where $n = 1 - 4$.
Perfluoroalkylated Substance (PFAS)	a general term which describes a substance which bears a perfluorocarbon unit, also known as a perfluoroalkyl, functional group. $\text{F}(\text{CF}_2)_n\text{-R}$ where n is an integer and R is not a halogen, or hydrogen. Examples include $\text{F}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{OH}$, $\text{F}(\text{CF}_2)_6\text{SO}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$, and $p\text{-F}(\text{CF}_2)_6\text{-C}_6\text{H}_4\text{OH}$.
Fluorosurfactant	a non-specific, general term used to describe a surface active, low molecular weight (<1000), substance where carbons bear fluorine in place of hydrogen. Examples would include $\text{CF}_3(\text{CF}_2)_7\text{SO}_3\text{K}^+$, $\text{H}[\text{shouldn't this be F?}](\text{CF}_2)_7\text{COO}^-\text{NH}_4^+$, $\text{F}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{CH}_2\text{SO}_3^-\text{NH}_4^+$, $\text{CH}_3\text{CH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{COO}^-\text{NH}_4^+$, etc.

Fluorinated [Organic] Surfactant

a term to describe a surface active, low molecular weight (<1000), substance which contains fluorinated carbons; the term fluorosurfactant is non-specific but often used synonymously; an example is $F(CF_2)_6CH_2CH_2SO_3^-NH_4^+$.

Perfluorinated Surfactant

a term used to describe a surface active, low molecular weight (<1000), substance where all carbons bear fluorine in place of hydrogen; the term fluorosurfactant is less specific but used synonymously; an example is $F(CF_2)_6SO_3^-NH_4^+$.

Perfluorocarboxylic Acid (PFCA)

a general term which describes a class of carboxylic acids and their salts of the general structure $F(CF_2)_n-COOX$ ($X = H, NH_4^+, \text{Group I alkali metal, Group II alkaline earth}$). These are generally manufactured by the electrochemical fluorination process or from fluorotelomer-based raw materials. The most common industrially used fluoropolymer polymerization aids are: ammonium perfluorooctanoate (CAS# 3825-26-1) and perfluoro fatty acids, C7-13, ammonium salts (CAS# 72968-3-88).

FLUOROS

... an International Symposium on
Fluorinated Alkyl Organics
in the Environment

August 19th - 20th 2005

The Royal York Hotel



Toronto, Canada



(precedes Dioxin 2005)

- Toxicology •
- Environmental Chemistry •
- Analytical Chemistry and Monitoring •
- Risk Assessment and Policy •

SPONSORS:



Environnement
Canada

Environment
Canada



Ontario



WELLINGTON
LABORATORIES

3M

DUPONT

For more information:

www.chem.utoronto.ca/symposium/fluoros
fluoros@chem.utoronto.ca

APPENDIX 5 - DETAILS OF WORKGROUP DISCUSSIONS ON KEY TOPIC AREAS

1. Chemistry, Physical-Chemical Properties, Degradation

Group 1:

- Water:
 - 1) Solubility for 6:2, 10:2 Telomer B
 - 2) Air-water partitioning (alcohols / olefins as a function of temperature)
 - 3) How (2) relates to modelling / predictions
 - 4) What is the relative importance of olefins?
 - Equal in quantity to alcohol?
 - 5) Telomer acid α / β , rate of loss of HF
 - 6) Reaction of fluorinated aldehyde with water
 - 7) Equilibrium constant
 - 8) What are the polymer residuals?
 - Dry polymer basis
 - Location of breakage
 - Conditions of breakage (temp., pH, biota?)
 - 9) Carpet linkage chemistry
 - 10) Landfill leachate
- Air:
 - 1) Photolysis of longer-chained fluorinated aldehydes
 - 2) NO_x vs. HO_x (reaction rates, temp., pressure, modelling) with information from (1)
 - 3) Measuring FTOH in the Arctic
 - 4) Intermediates (acids) / fluxes in Arctic
 - 5) Independent air sampling methods – better defined and validated
 - 6) Chemistry of telomer B olefins (OH, NO₃, O₃)
- Soil:
 - 1) Degradation in soils
 - 2) Carpets / other consumer products in landfills
 - pH gradient
 - Leachates
 - Deomposition
 - Anaerobic / aerobic – linkage breakage?
 - Identification of landfills with high carpet loading
- STP:
 - 1) Acids produced in STP?
 - 2) Mass balance
 - 3) Can off gassing be measured?

Group 2:

- Assess solubility in water (~critical micelle concentration), air (or vapour pressure), octanol and protein (Z of protein?)
- Lab based partition coefficients (soil-water, soil-air, fish-water)
- Assess “aging” and “sequestration”
- Bioaccumulation indicates an affinity for biota or “organism-philicity”

Group 3:

- Fluorinated organics
 - 1) Source terms
 - 2) Usage
 - 3) Bridging the gap between proprietary information and research scientists with the possibility of 3rd party involvement
- Can residuals be eliminated? To what degree?
- What is the potential influence of degradation to the environment?
- Reduction of chain length versus the quality of the product
- OECD guidelines are only a first step (bound by EPA as a requirement but can go beyond); Need to assess under more ‘realistic use pattern’ conditions
- What are the relevant chemicals contributing to the pathways? Quantities? Applications?
- Need purified chemicals and a better understanding of the ‘mixtures of mixtures’

Group 4:

- Not much satisfaction with currently available physico-chemical data – some exceptions
- Data gaps: Reliable / consistent (agreed upon) values for K_{OW} , K_{AW} , $K_{A-solid}$ for FTOHs and FT olefins; K_{AW} for PFCAs; vapor pressure for PFCAs (anion / APFO)
- Independently verified
- What are the best choices for models?

2. Biota and Environmental Compartment Monitoring

Group 1:

- Biological distribution
- Neutral alcohols not measured in biota
- Snow monitoring (flux air-snow)
- Local arctic sources of FTOHs
- Air monitoring in Asia and the Southern Hemisphere – impacts globally?
- PFCAs do not correlate with PCBs in Inuit blood serum but PFOS correlates – biomonitoring data needed
- Domestic pets as sentinels for indoor exposure measurements – carpet, dust, etc.
- Uptake and clearance rates for various species
- Exposure routes for PFOS and PFOA in humans

Group 2:

- Is octanol an adequate surrogate / predictor for these chemicals?
- Need to K_{OW} of PFCAs
- Need to know air-soil coefficients
- BAFs and BCFs are generally not well known
- PFCAs appear to bioaccumulate – uncertainty in expressing the BMF – normalize concentrations to liver?
- Experiment of food chain accumulation
- Need for pharmacokinetic models to translate concentrations in liver, muscle and plasma
- Are polymers a source to biota?
- Composition of FTOHs / geographical differences
- What are sources of FTOHs to marine environment?
- Run model of bioaccumulation and emissions to investigate bioaccumulation patterns of C_8 and C_9
- Compare ΔH of partition coefficients and ΔH of vaporization

Group 3:

- How do we realistically look at bioaccumulation potential without using K_{OW} ?
 - 1) Albumin-water partitioning? Diffusion through lipid membranes?
 - 2) New model?
 - 3) Problems associated with mixtures
- Are FTOHs surfactants? Do they have surfactant properties?
- Does the current K_{OW} /BCF/BAF model make sense in light of the potential protein binding?
- Need more mechanistic information
- Need source chemical information with regards to the full range of chemicals used (e.g. precursors and intermediates) to effectively monitor
- A mutually agreed upon independent laboratory could be used to conduct / corroborate environmental monitoring (Exygen?)

- Potential for olefins to be a source. If so what is its distribution and compartmentalization.

Group 4:

- General lack of biota monitoring data for telomers / polymers (FTOHs)
- FTOHs in biota? Confirm or invalidate
- Are PFCAs bioconcentrating or FTOHs and then transformed?
- How are FTOHs / PFCAs taken up?
- Look for FTOHs in different levels of food chain as well as in air and sediment
- Monitoring in areas where FTOHs are being applied (air, rain, sediment, biota) and identify “fingerprint” chemicals of telomer chemistry
- Need to determine exposure routes (i.e., is it a food web for polar bears?)
- Monitor in various Arctic compartments and geographical areas (i.e., latitudinal variation)
- Key question – What should we be monitoring for (i.e., alcohols, olefins telomer acids) and where?
- Marine monitoring for acids in Northern regions
- If FTOHs found in different compartments and support provided for hypothesized degradation pathways, still need to evaluate how important this class of compounds is to the overall PFCAs observed in environment
- Landfill flux

3. Analytical Methods and Tools

Group 1:

- Need for ultra-pure standards (e.g., PFCAs, aldehydes)
- Validated and documented methods (i.e. no published methods for FTOH other than air)
 - 1) Research papers
 - 2) Academic of government role to produce these methods
 - 3) Single extraction method for acids / neutrals (all media)
 - 4) Matrix effects – used standard additions (except for PFOA)
- Integrity of biota samples archived for FTOH
- FTOH / 3M sample contamination (blanks can be unacceptably high)
- Surface-volume ratio in smog chambers
- Biodegradation experiments – different protocols / approaches. Recommended to assess polymers in real soil / aquatic systems
- Allow analyte properties to determine the selected methods
- Round-robin comparisons between North America and EU
- Derive GC (analytical) methods to reduce internal contamination for different matrices (e.g., water and soil)

Group 2:

- “Hamburg” paper by Martin *et al* [Environmental Science and Technology 38 (13): 248A-255A, July 2004] covers some of this except more information required for:
 - 1) Documenting QA/QC
 - 2) Description of actual methods
 - 3) Address methods to determine precursors and degradation products
 - 4) Reporting/difficulties of field blanks
 - 5) Access to dual enrichment materials
 - 6) When to use high resolution LCMS, MS/MS, LC-MS/MS
 - 7) Broaden suite of reference standards and standard reference materials
 - 8) Bank extractions for future analysis

Group 3:

- Review / guidance documentation – building from “Hamburg” [Martin *et al* ES&T 2004]:
 - 1) “State of the science / art”
 - 2) Materials, solvents, matrices, stock solutions, standards
 - 3) Various Method detection limits
 - 4) Calibration
 - 5) Blanks / background (e.g., stainless steel)
 - 6) Sampling protocols (collection / storage / accountability of archived data)
 - 7) Protocols for analyzing archived trend data
 - 8) EPA standards or other?
 - 9) Consistent internal standards or surrogates

- 10) Standard reference material (with PERFORCE – inter-lab comparisons?)
- 11) History of trials and errors
- 12) “Co-analyte” interference / matrix effects
- 13) “Non-aqueous” identification methods for interference
- 14) Recovery calculations
- 15) 2 transitions / compound

Group 4:

- Recommendations for appropriate sampling, storage and analytical protocols
- Need reference standards
- Comparison of analytical methods between laboratories and exchange / share information
- Agreed protocols / methods for monitoring sites
- Need to establish QA/QC best practices to analyze for these compounds
- Development of a single method to analyze for telomer alcohols and telomer acids for screening purposes?
- Develop a database for monitoring data, analytical methods towards a coordinated inventory assessing methods
 - 1) For information management – peer review is best, however, some established standards could be developed which could be met prior to including analytical data
 - 2) Allow easy access
 - 3) Reporting sampling locations in monitoring studies (i.e. GIS/GPS)
 - 4) Who would administer? Who would fund?
- Provision of purified chemicals for standards distinguishing between isomer and impurities
- Access to structural information on polymers to “ease” analytical studies
- TRP finished pilot study on 1 of 17 polymers (characterization and degradation)
 - 1) End of 2004 all 17 should be completed
 - 2) Dissemination of this information in a peer-reviewed domain

Possibility for inter-laboratory comparison:

- 1) A solution containing approximately 20 different standard compounds is available from NILU (Norway) and should be analyzed against a lab's own standards
- 2) In 2005 an invitation will be sent out to participate in the PERFORCE inter-lab study; final medium still to be decided. Everyone can participate on a voluntary basis
- 3) Inter-lab study of blood samples will be organized by Orebro University (Sweden) starting 2004/5; G. Lindstrom is contact

As an ‘FYI supplement’: Scott Mabury has informed that stable isotope standards for the fluorotelomer alcohols FTOHs (6:2 through 10:2) fluorotelomer acids, FTCAs (6:2 through 10:2), unsaturated fluorotelomer acids FTUCAs (6:2 through 10:2) as well as PFDA can be purchased from Wellington Labs.

4. Environmental Pathways / Partitioning and Transport Mechanisms

Group 1:

- Does the linkage break? If so, what are the degradation mechanisms?
- High potential of FTOH LRT:
 - 1) Seasonal monitoring of Arctic air for FTOH – observation of acids in precipitation indicates transformation
 - 2) What is the yield of FTOH to PFCAs in the gas phase?
 - 3) FTOH > aldehyde/OH rates are available – need temperature, pressure rates of HOx and NOx with oxidation products
- Assess the role of sea salt in enriched acids for LRT – scepticism
- Ocean transport?
- Transformation to PFCAs:
 - 1) Need independent replication and confirmation with other remote regions, temperate regions and in other matrices (e.g., human food supply)
 - 2) Are current analytical methods appropriate?
 - 3) Relative contribution of biotic / abiotic processes for FTOHs > PFCAs

Group 2:

- Release rate of alcohols unknown
 - 1) Residuals ~20 – 100 tonnes/yr
 - 2) Quantity from polymers – does it degrade?
 - 3) Other sources
- Form / media of release is unknown – this is important for transport and exposure (e.g., bioavailability)
- Potentially important pathways
 - Abrasion > Dust > in-home bioaccumulation
 - Fire fighting and disperse applications
- Measurements needed of distribution coefficients of alcohols
 - Water/soil and particulate (e.g., soot)
 - Air/soil and particulate
 - Ionic strength
 - Potential for marine boundary layer effects
 - Do PFCAs get from water/oceans into atmosphere?
- Pathway leading to relatively high concentration of C₉ in biota is unknown
- Is there another source of C₉ acid resulting from PF - sulfonamido alcohols or PF – alkanes?
- Is biomethylation a possible mechanism for transport of PFCAs into the atmosphere (esterification)?
- Need for simultaneous monitoring of FTOHs, PFAs and PFCAs in air and precipitation both urban and remote

Group 3:

- Need to better understand “emission” of FTOHs from polymers
Residuals – can there be a reduction?
Breakdown of polymer? Cleavage?
- OECD and “real world” tests on specific chemicals or products?
- “source dilemma”: RE: Stock paper (ref) measurements of some 6:2, 8:2 alcohols but very little 10:2, 12:2 alcohols in most cases ∴ how does this account for the theory that FTOHs are the primary source of PFCAs C₈ – C₁₃?
- LRTP to the arctic – could measure Arctic freshwater and marine to see if they are arriving from air or ocean transport
- Reliability of physico-chemical measurements for ionic and neutral forms
- Partitioning using ‘in situ’ studies
- Do FTOHs reduce surface tension?
- Air-soil partitioning – wet vs. dry conditions, various soil types and conditions and application of useful standards
- Photolysis of aldehyde – What is the significance? NO_x vs HO_x?
- Measure a gradient from source to remote area – gas, rain, particle and compare with Tunnel model

Group 4:

- Residuals enter environment from polymers or as degradation / transformation products
- Amount and identification of residual depends on the polymerization process (e.g., PFO for Clariant polymers)
- Applications and consumer use patterns impact releases to environment
- Degradation of other FT chemicals?
- Degradation studies of polymers required – difficult to remove residuals
- How much testing and on what samples is enough to get degradation and rate data?
- Polymers in STP – sorb to sludge? Degrade?
- FTOHs / PFCAs – understand potential oceanic transport mechanisms
- Better understanding of atmospheric pathways (i.e., monitoring data in all compartments)
- Emphasis for collaboration between industry, academia and government
- Emphasis on need for monitoring releases and concentrations in the environment