



**Perfluorinated Carboxylic Acids (PFCAs)
and Precursors:
A Proposed Action Plan for
Assessment and Management**

Perfluorinated Carboxylic Acids (PFCAs) and Precursors: A Proposed Action Plan for Assessment and Management

Purpose of Action Plan

Environment Canada (EC) and Health Canada (HC) have developed a proposed Action Plan to provide a broad perspective on the Departments' approach to PFCAs and their precursors.

This proposed Action Plan intends to address:

- substances currently prohibited under the New Substances provisions of the *Canadian Environmental Protection Act, 1999* (CEPA 1999),
- the approach by the New Substances Program in addressing such substances in the future
- members of this class already in commerce, and
- engagement of the research community and international regulators in contributing to assessment and management issues.

Introduction

In 2004, the New Substances Program of EC and HC assessed four new substances which are considered sources of PFCAs. These substances are all fluorotelomer based polymers. Fluorotelomers are used to add fluorinated carbon chains to more complex materials. Various reactive functional groups are used to attach these moieties, e.g. alcohols, epoxides, olefins. These fluorotelomer substances can be released from these complex materials. Fluorotelomer alcohols have been shown to form PFCAs in the environment, and a similar fate is expected for the olefins and epoxides.

Empirical evidence has demonstrated that some PFCAs are bioaccumulative, persistent, subject to long-range transport (via a precursor), widespread in Arctic wildlife and associated with adverse effects in laboratory animals. Evidence shows a trend of increasing concentrations of long chain PFCAs in wildlife based on tissue samples archived over the last 30 years.

Following the assessments of these four substances, the Ministers of Health and Environment imposed a temporary prohibition using the New Substances provisions of CEPA 1999.

Prohibitions under the New Substances provisions of CEPA 1999 expire after two years unless the Ministers propose a regulation to control the substances. The first prohibition was signed on June 23, 2004; consequently a proposed regulatory amendment would need to be published in the Canada Gazette Part 1 by June 23, 2006 in order to continue the prohibitions.

Substances similar to these four new substances are present on the Domestic Substances List (DSL) and in Canadian commerce.

The knowledge base on polyfluorinated substances is increasing rapidly, with involvement by industry, academia and government. There is considerable international activity underway.

Terminology

Perfluorinated carboxylic acids (PFCAs) and their salts are a series of substances whose anion has the general structure of $\text{CF}_3(\text{CF}_2)_n\text{COO}^-$.

Certain members of this class, including the PFCA with 8 carbons, called perfluorooctanoic acid (PFOA or C8), are manufactured as a processing aid to produce fluoropolymers¹.

Fluorotelomer alcohol (FTOH) is a general term which describes a class of alcohols of the general structure $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CH}_2\text{OH}$.

Fluorotelomer epoxide is a general term which describes a class of epoxides of the general structure $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}_2\text{CHCH}_2\text{O}$.

Fluorotelomer olefin is a general term which describes a class of alkenes of the general structure $\text{F}(\text{CF}_2\text{CF}_2)_n\text{CH}=\text{CH}_2$.

These fluorotelomer substances can be used to append fluorinated carbon chains to substances such as acrylates, isocyanates etc. These can add fluorinated character to phosphates, polyesters, polyamides or polyurethanes and may be present as (unintended) unreacted "residuals" in fluorotelomer based substances.

Commercially, these fluorotelomer substances are manufactured and used as mixtures, with fluorinated chain lengths typically ranging from C4 to C18 (<C8 (~2 wt %), C8 (~30 wt %), >C8 (~68 wt %) ².

Fluorotelomer alcohols have been shown to form PFCAs in the environment, and a similar fate is expected for the olefins and epoxides. Because the commercial substances contain a range of fluorinated carbon chain lengths, the resulting acids also contain a range of fluorinated carbon chain lengths. The focus of this Action Plan is on the longer chain PFCAs (C>8).

¹ Fluoropolymer is a general term used to describe a polymer which has fluorine attached to the majority of carbon atoms which comprise the polymer chain backbone, e.g. polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF); these are typically high molecular weight polymers used in high performance applications

² http://www.dupont.com/fluorointermediates/products/alcohols_ba.html

Current PFCA Activities under CEPA 1999

New Substances

The New Substances program assessed four new fluorotelomer based polymers in 2004 and concluded they are sources of perfluorinated carboxylic acids (PFCAs) with a range of carbon chain lengths. These substances are considered to meet the criteria set out in paragraphs 64 (a) and 64(c) of CEPA 1999.

All PFCAs are considered environmentally persistent, and those from fluorotelomer sources are subject to long range transport via volatile precursors. Some members of the PFCA family are bioaccumulative. Bioaccumulation potential appears to be proportional to the length of the fluorinated carbon chain. Measured bioconcentration factors in fish are higher for longer chain PFCAs, and monitoring data show widespread low concentrations of PFCAs (C8 to C15) throughout Arctic biota. Increased concentrations were measured in wildlife feeding at higher trophic levels (e.g. polar bears, seals), suggesting biomagnification. There is evidence that for C9 and C10 PFCAs, the concentrations found in polar bear liver have been doubling every 5 to 8 years, indicating increasing exposure in the environment.

Most toxicological studies on laboratory animals have been on PFOA. While information on potential risks resulting from the use of PFOA as an Existing Substance are being considered in a separate assessment, data on the hazard of this compound are reviewed here in the context of their possible implications for the hazards of higher chain PFCAs.

Based on available data, PFOA and its salts are not genotoxic, but are tumourigenic in rats and immunotoxic in mice, and display reproductive and developmental toxicity in rodents and moderate to high subchronic oral toxicity in rodents and monkeys. An assumption of the new substances assessment is that despite the absence of robust toxicity datasets for longer chain PFCAs (>C8), these substances are reasonably expected to display even greater adverse human health impacts than PFOA as a result of their known slower clearance rates and higher bioaccumulation potential. Toxicological data on these substances would reduce the uncertainty surrounding this assumption. It is suggested that longer chain PFCAs exhibit properties of persistent organic pollutants (POPs) as there is evidence they are persistent, bioaccumulative, widespread throughout Arctic biota and based on data for PFOA, associated with adverse effects in laboratory animals.

Existing Substances

The Existing Substances Program is presently conducting a Screening Assessment of PFOA, the 8 carbon containing PFCA. This was prompted by the emergence of many new studies on the persistence and potential impacts of PFOA on the environment and human health, its continued importance as a

commercial chemical, regulatory activities in other jurisdictions, and increasing public concern.

The PFOA assessment by Health Canada and Environment Canada has not yet reached a conclusion.

The Existing Substances Branch (ESB) has also initiated some data collection and data generation on other PFCAs.

Future Activities

New Substances

Management under CEPA 1999

As a consequence of the conclusions of the new substances assessments, the Ministers of Environment and Health have subjected the four substances to prohibitions under paragraph 84(1)(b) of CEPA 1999. These prohibitions expire after two years (first expiration date would be June 23, 2006) unless the Ministers propose a regulation to control these substances, in which case the prohibitions expire on the day the regulation comes into force.

There has not been any assessment of new substances containing long chain perfluorinated moieties (>C8) since the publication of the last prohibition in February, 2005. Many potential notifiers are aware of the position taken by the New Substances Program, and notifications of substances containing longer chain perfluorinated moieties are considered unlikely at this time.

Efforts are being undertaken by some companies to design alternative substances to those prohibited by the New Substances Program.

Proposed Management for New Substances

Environment Canada and Health Canada propose to:

1. list the four substances already subject to prohibition on Schedule 1 of CEPA 1999, and
2. maintain the prohibitions via a proposed regulation.

The assessment reports prepared for these 4 substances have been made available to the public and for scientific review in November, 2005. External science reviewers have been invited to comment on the adequacy of the science appearing in the assessment reports, and to identify relevant information which may not have been taken into account. In addition, Health Canada and Environment Canada are preparing a report on scientific information which has become available since the assessment reports were completed. This will ensure the consultations are informed by a current view of the science.

The New Substances Program at Health Canada and Environment Canada will maintain its current approach, with similar recommendations foreseen for substances containing long chain perfluorinated moieties. This would be a precautionary measure to limit the introduction of new substances into Canada which would contribute to the observed environmental load of long chain PFCAs. This measure will continue to provide incentive for industry to develop alternative substances with a favourable environmental profile.

Existing Substances

While the current prohibitions apply only to the four new substances, there are additional substances on the DSL which may be sources of PFCAs. Preliminary data from the January, 2005 Perfluoroalkyl and Fluoroalkyl Substances Notice to Canadian industry indicates there is import of substances which are believed to be precursors to PFCAs with chain lengths >C8. Further analysis and verification is underway, and data refinement may entail contacting respondents with further questions.

Prohibiting all existing long chain PFCA precursors is not considered a viable strategy at this time. Further information gathering and assessment activities are required to determine whether this should be considered as a viable management strategy in the long term.

Early Risk Management Actions/Assessment of PFCAs and Precursors

It is understood that one source of PFCA contamination is the release of unreacted fluorotelomer reactants which are found within the commercial substances. These can then be transformed to PFCAs. One of the manufacturers of fluorotelomer based substances has reported to Environment Canada that they have developed techniques to reduce fluorotelomer "residuals" in their products. This company has reported they will introduce these techniques in the manufacture of their substances and have indicated their willingness to share these techniques with other manufacturers. A second manufacturer has also reported to Environment Canada that they have processing technology to reduce residuals. Environment Canada and Health Canada propose to seek early reduction of residuals in fluorotelomer based substances. Further characterization of these residuals will be required before regulatory action is considered.

A determination should be made as to the appropriate instrument to reduce "residuals" in existing substances. This could be an Environmental Performance Agreement with manufacturers to create early action. In the longer term, a regulation may be the preferred instrument.

Elimination of "residuals" will not address the potential exposure pathway of emissions of PFCA precursors resulting from the degradation of fluorotelomer

based substances. This pathway is currently not well understood, although research is being undertaken by industry and the US Environmental Protection Agency. As the scientific understanding of this exposure route increases, there may be a need to include additional measures to the risk management approach. However, at the present time, there is insufficient direct scientific evidence to support management measures targeting this potential exposure pathway.

For further assessment of PFCAs and precursor substances, Environment Canada will take into account all available information. Further risk management steps will be proposed if necessary.

To inform Canadians and other stakeholders of this proposed Action Plan, EC and HC will publish a Notice of Intent, following public consultations, which highlight the main steps of this plan.

Research Activities and International Cooperation

Canadian Research

Canada is a leader in research demonstrating that PFCAs occur in Arctic and other environments, and is accumulating in organisms. However, more research needs to be done regarding sources, toxicity and accumulation of these chemicals. Given the data needs, it is critical to continue the engagement of industry, researchers and foreign regulators in filling data gaps on PFCAs and precursors.

Canada can focus in the short term (12-24 months) on research critical to verifying widespread occurrence and accumulation of the substances. This would yield information that would provide further support for Canadian actions as well as provide continued impetus for engagement by the international science and regulatory community.

Primary Canadian Research Institutions

- The National Water Research Institute is undertaking research including precipitation monitoring, glacial snow core analysis, persistence of "precursor" substances and bioaccumulation.
- The Canadian Wildlife Service may undertake analysis from their tissue bank to further establish temporal and geographic trends in PFCA contamination. They may also investigate avian toxicology using ecotoxicogenomics techniques.
- The Meteorological Service of Canada is investigating indoor and outdoor air concentrations and transport mechanisms.
- The University of Toronto is currently a world leader in research on PFCA fate and presence in the environment.

Future research that could be undertaken domestically or internationally should address releases and fate of the substances, which would provide additional information relevant to risk management. Cooperating on research plans with primary institutions will advance the understanding of this class of substance.

Promotion of International Cooperation

There is a long range transport aspect to the environmental distribution of PFCA precursors, consequently PFCAs found in Canada may originate in other countries (e.g., release from manufacturing sites, articles, etc.). International actions may be essential to complement any domestic control actions. As well, international cooperation is needed to address the information gaps. Canada will continue its leadership on this issue by raising the profile of PFCAs and precursors at various international fora.

The United States is interested in acquiring more information on fluorotelomer based substances. The EPA has entered into Enforceable Consent Agreements with Industry to generate certain data, e.g. release of PFCA precursors from aged articles. The EPA is also undertaking studies attempting to quantify PFCA formation from fluorotelomer based polymers.

The European Union is undertaking a research program called PERFORCE. A final European exposure assessment will be based on both field data and modelling. PERFORCE has stated that by gaining new insights into the source and routes for polyfluorinated substances detected in remote areas, and by understanding the behaviour and distribution of polyfluorinated substances, an ecologically sound chemical replacement policy can be developed which could provide a competitive advantage for the European chemical industry.

000031

Summary

The initial Canadian strategy for addressing PFCAs and their precursors in the environment, as outlined in this proposed Action Plan would consist of the following:

1. Maintain the policy of preventing the introduction into Canada of new substances which would contribute to the observed load of PFCAs in the environment:
 - a. continue the prohibitions on the four new fluorotelomer based substances by proposing a regulation.
 - b. following assessment by the New Substances Program, consistent with past actions, recommend Ministerial prohibitions on long chain PFCA precursors
2. Concurrent with the publication of proposed regulation for the four new substances, publish a "Notice of Intent" outlining the broad elements of this proposed Action Plan.
3. Seek early action on residuals from industry.
4. Prioritize and assess existing PFCAs and precursors. Amend the Action Plan as appropriate following assessment conclusions.
5. Continue to encourage research within Environment Canada to further the understanding of the fate and effects of PFCAs and precursors.
6. Engage our international partners in global action which would complement domestic policies.

000032