Results and Discussion

The draft ecological screening assessment of perfluorooctane sulfonate (PFOS)¹³ found PFOS to be persistent (P), bioaccumulative (B) and inherently toxic (iT), and to meet the criteria under Section 64 of CEPA 1999. The public comments received covered a range of topics including exposure, effects, and level of caution applied in the risk assessment. Of particular note were comments concerning the bioaccumulation properties of PFOS. The assessment raised interesting questions regarding the relationship between Canada's bioaccumulation criteria as stated in Canada's *Persistence and Bioaccumulation Regulations*¹¹, previously developed for and primarily applied to lipid-partitioning organic substances, and perfluorinated substances, which preferentially bind to proteins. Environment Canada (ESD) convened a workshop in August 2005 and summarized the discussion on these issues¹⁴ and has continued to collect information.

<u>Use of BCF, BAF, BMF as indicators of Bioaccumulation:</u> Notably, unlike many other persistent organic pollutants in biota, certain perfluorinated substances, such as PFOS and PFOA, preferentially partition to proteins in tissues such as liver, blood and kidney, rather than lipids ^{7,8, 14, 15-18}. Therefore bioaccumulation criteria based on log K_{ow} values are not appropriate for this class of substances. A number of studies indicate that PFOS and some other perfluoroalkyl substances biomagnify in aquatic food webs ^{7,8, 15, 16, 19, 20}. In this case, biomagnification is taken to be the ratio of the concentration of a substance in predator relative to its prey thereby involving a food relationship and having one trophic level transfer. By contrast a Trophic Magnification Factor considers the average increase in concentration across multiple trophic levels¹⁴. Table 2 summarizes published information on the BCF, BAF and BMF values for PFOS in wildlife. In addition to the tissue specific data presented in Table 2, BMFs and TMFs recently calculated based on whole body burden in bottlenose dolphin food web ranged from <1 to 18 and 1.4 to 6.3, respectively²⁰. BMFs and TMFs calculated based on plasma and liver concentrations were found to overestimate the BMF and TMF ²⁰.

Table 2. Range of BCF, BAF and BMF data for PFOS in whole body, specific tissues and organs in wildlife

	Whole Body	Tissue Specific (blood or liver)
BCF	690-2796 ^(14, 21)	2900-5400 (14)
BAF	None available	274-125000 (6,5)
BMF	0.3-3.7 ⁽¹⁵⁾	0.4-20 ^(9, 15, 16, 19)

<u>Whole Body versus Tissue Specific Calculations:</u> Whole body aquatic BCFs or BAFs are below 5000. However, the weight of evidence from both laboratory and field-based BCFs and BAFs (based upon specific tissues e.g. liver and plasma) in conjunction with the field-based BMFs (avian and aquatic) indicates that PFOS is a bioaccumulative substance. This raises an interesting question of how to interpret bioaccumulation data for perfluorinated substances against numeric criteria, particularly if BMF criteria are not also included. The application of the numeric criteria for bioaccumulation may require discretion in regulatory decision-making when determining whether substances such as perfluorinated chemicals can be described as bioaccumulative. Furthermore, the weight of evidence for bioaccumulation may consider other factors such as biomagnification. There is a growing body of evidence indicating perfluorinated substances such as PFOS, PFOA, and certain long chain perfluorocarboxylic acids (PFCAs) biomagnify in certain biota, such as mammals at or near the top of the food chain (e.g. Arctic polar bear, bottlenose dolphins)^{15, 16, 9, 20}. This may warrant the need to consider a precautionary approach to these substances, to account for demonstrated biomagnification.

<u>Bioaccumulation Considerations for Other Perfluorinated Substances:</u> Most recently, Environment Canada has evaluated bioaccumulation data on PFOA²². The draft ecological review noted that PFOA was persistent, with moderate to low aquatic toxicity. However, the bioaccumulation data was ambiguous. Most of the available information at the time indicated that PFOA does not bioaccumulate to the same extent as PFOS in either marine or freshwater food webs^{15,16,19}. However, new data has emerged indicating PFOA may biomagnify in certain species,

such as marine mammals (e.g. bottlenose dolphins)²⁰. PFOA has been detected in saltwater and studies suggest PFOA may alter biomarkers of health in loggerhead sea turtles and bottlenose dolphins ^{23, 24}.

Therefore, emerging data poses new questions about understanding the bioaccumulative potential for PFOA and possible risk to the marine environment. Where emerging data indicates concern for the persistence and bioaccumulation of a substance, industry can be engaged to take appropriate early risk management action. This is the case for addressing residuals in existing substances which may break down to long chain PFCAs. Such actions may also capture PFOA, which, while not concluded on by Canada, has been the subject of early risk management in jurisdictions such as the US²⁵.

Data Collection on Other PFAs of Interest

Categorization on additional PFAs determined that, in addition to PFOS and PFOA, an estimated 63 substances meet Environment Canada criteria of Persistent, Bioaccumulative, and inherently Toxic (PBiT); Bioaccumulative and inherently Toxic (BiT); or, Persistent and inherently Toxic (PiT) (see Table 3)²⁶. These PFAs will require further scoping to decide on the need for or nature of further data gathering or assessment.

Table 3. Perfluorinated Substances on Canada's Domestic Substances List which meet the Categorization Criteria (as of April 2006)²⁶

		Organics	Polymers	UVCBs*	Organo-metallics	
Meet EC Criteria for		25 (8)	0	3	0	
Categorization as PBiT						
Meet EC Criteria for		11 (1)	31 (5)	0	5 (1)	
Categorization as PiT						
Meet EC Criteria for		4	0	0	0	
Categorization as BiT						
Т	Fotal	40	31	3	5	

Notes: UVCBs = Unknown or Variable Composition and Biologicals; () = Number in brackets is the number of substances in that category covered under the assessment of PFOS, its salts and its precursors

To support a long term management strategy, a number of key issues require further work, including:

- Toxicological data on short chain acids to help address questions concerning potential replacements
- Long term environmental fate data on polymers to evaluate their importance as a source of persistent and potentially bioaccumulative perfluorinated acids.
- Environmental monitoring of concentrations in the environment and in biota
- International co-operation and developing partnerships to complement Canadian domestic assessment and management activities.

Further information on ecological risk assessment activities on perfluorinated substances can be obtained through the Existing Substances Division, Environment Canada website at <u>www.ec.gc.ca/substances/ese/</u> or at the Environment Canada Homepage (The Green Lane) at <u>www.ec.gc.ca</u>. CDs containing P, B, iT data and preliminary decisions are available upon request.

References

- 1- Kissa E. 2001. Fluorinated surfactants and repellents. 2nd ed. Marcel Dekker: New York, 2001.
- 2- Hansen KJ, Clemen LA, Ellefson ME, Johnson HO. Environ. Sci Technol. 2001, 35, 766-770.
- 3- Geisy JP, Kannan K. Environ. Sci. Technol. 2001, 35, 1339-1342.
- 4- Kannan K, Koistinen J, Beckman K, Evans T, Gorzelany JF, Hansen KJ, Jones PD, Helle E, Nyman M, Giesy JP. *Environ. Sci. Technol.* 2001, 35, 1593-1598.

- 5- Moody CA, Martin JW, Kwan WC, Muir DCG and Mabury SA. Environ. Sci. Technol. 2002, 36, 545-551.
- 6- Taniyasu S, Kannan K, Horii Y, Hanari N and Yamashita N. Environ. Sci. Technol. 2003, 37, 2634–2639.
- 7- Martin JW, Smithwick MM, Braune B, Hoekstra PF, Muir DCG and Mabury SA. Environ. Sci. Technol. 2004, 38, 2, 373–380.
- 8- Martin JW, Whittle DM, Muir DCG, and Mabury SA. Environ. Sci. Technol. 2004, 38, 5379-5385.
- 9- Kannan K, Tao L, Sinclair E, Pastva SD, Jude DJ, and Giesy JP. Arch. Environ. Contam. Toxicol. 2005, 48, 559-566.
- 10- Government of Canada. Canadian Environmental Protection Act, 1999. Statutes of Canada 1999. Chapter 33. Ottawa, Canada. 234 pp.
- 11- Government of Canada. Persistence and Bioaccumulation Regulations. Canada Gazette 2000, Part II Volume 134 (7):607-611. Ottawa, Canada
- 12- Government of Canada. Toxic Substances Management Policy-Persistence and Bioaccumulation Criteria. Final Report of the *ad hoc* Science Group on Criteria. 1995. Minister of Supply and Services Catalogue Number EN 40-499/2-1995E. ISBN 0-662-23524-X. 21pp. Ottawa, Canada.
- 13-Government of Canada. Canada Gazette Notice, Part I (Vol. 138, No. 40 October 2, 2004). Publication after screening assessment of substances Draft screening assessment on perfluorooctane sulfonate (PFOS), its salts and precursors that contain the C₈F₁₇SO₂, C₈F₁₇SO₃ or C₈F₁₇SO₂N group. Ministers of Environment and Health. Ottawa, Canada. 8pp.
- 14- Environment Canada. Bioaccumulation Workshop on Perfluorinated Substance, August 20, 2005, Toronto, Ontario. Workshop Final Notes Prepared November, 2005, Existing Substances Division, Risk Assessment Directorate, Environment Canada, Gatineau, Canada. 16 pp.
- 15-Martin JW, Mabury SA, Solomon KR and Muir DCG. Environ. Toxicol. Chem. 2003, 22: 189–195.
- 16- Martin JW, Mabury SA, Solomon KR and Muir DCG. Environ. Toxicol. Chem. 2003 22: 196–204.
- 17- Smithwick M, Muir DCG, Mabury SA, Soloman K, Martin JW, Sonne C, Born EW, Letcher RJ, and Dietz R. *Environ. Sci. Technol.* 2005, 24,4, 981-986.
- 18- Smithwick M, Mabury SA, Solomon K, Sonne C, Martin JW, Born EW, Dietz R, Derocher AE, Letcher RJ, Evans TJ, Gabrielsen G, Nagy N, Stirling I, Taylor M and Muir DCG. *Environ. Sci. Technol.* 2005.39: 5517-5523.
- 19- Tomy G, Budakowski W, Halldorson T, Helm PA, Stern GA, Friesen K, Pepper K, Tittlemier SA, and Fisk AT. *Environ. Sci. Technol*.2004: 83: 6475-6481.
- 20- Houde M, Bujas TAD, Small J, Wells RS, Fair PA, Bossart GD, Solomon KR and Muir DCG. In Press.
- 21- OECD 2002a. Hazard assessment of perfluorooctane sulfonate (PFOS) and its salts.
- ENV/JM/RD(2002)17/FINAL, November 21, Paris. 362 pp.
- 22- Environment Canada. Draft Ecological risk Assessment of PFOA. 2006. Prepared by Existing Substances Division, Risk Assessment Directorate, Environment Canada. Gatineau, Canada.
- 23- Peden-Adams MM, Romano T, Rice CD, Hesseman L, EuDaly J, Muir D, Houde M, Bossart G, and Fair P. Immune Function and Clinical Blood Parameters Correlate with Perfluorinated Alkyl Acid Concentrations in Bottlenose Dolphins. Poster presentation at SETAC 2004.
- 24- Peden-Adams MM, Kannan K, EuDaly JG, Hessemann LM, Kuckluck JR, Arendt MD, Maier PP, and Segars AL. 2004b. Perfluorinated Alkyl Acids Measured in Sea Turtle Blood Correlate to Modulations in Plasma Chemistry Values and Immune Function Measurements. Poster Presentation at SETAC 2004.
- 25- For details on the US Environmental Protection Agency's global PFOA Stewardship Program addressing PFOA and related chemicals see http://www.epa.gov/oppt/pfoa/
- 26- Environment Canada. Existing Substances Program at Environment Canada. Compact disc April 2006 version. Existing Substances Division, Risk Assessment Directorate, Environment Canada, Gatineau, Canada.