Title: Investigation of the Presence of Perfluorinated Compounds in San Francisco Bay Seals

Estimated Cost: $50,000

Proposed by: SFEI and Marine Mammal Center

PROPOSED DELIVERABLES AND TIME LINE

Deliverable	**Due Date**
Task 1. Sample collection and sample analysis	September 2006/January 2007
Task 2 Preparation of Draft Report	June 2007
Report finalized	August 2007

BACKGROUND

In the last 50 years, fluorinated alkyl substances have been used extensively in a variety of commercially available products including fire-fighting foams, refrigerants, stain repellants in textiles, and coatings for paper used in contact with food products. Their popularity in commercial and industrial applications results from their unique ability to be both hydrophobic and oleophobic, that is able repel both water and oil.

Fluorinated alkyl substances are synthesized from perfluornated sulfonyl fluoride and carbonyl fluoride intermediates by electrochemical fluorination process (ECF) or telomerization fluorination processes. Because these processes are not selective, numerous by-products are produced in the manufacture of these intermediates such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).

As a result of their chemical stability and widespread use, fluorinated alkyl substances such as PFOS and PFOA have been detected in marine mammals and aquatic organisms throughout the world including relatively pristine environments such as the Arctic (Kannan *et al.* 2002). PFOS and related perfluorinated compounds have been associated with a variety of toxic effects including mortality, carcinogenity, and adverse development. Their widespread dispersal throughout the global and their potential toxicity has caused increasing concern among scientists and regulators. In response to this concern, the US Environmental Protection Agency banned the use of PFOS and 3M Corporation initiated a voluntary phase out of the carboxylated and sulfonyl-based perfluorinated chemicals; however, PFOA and perfluorinaed carboxylic acids (PFCAs) continue to be produced in the manufacture of fluoropolymers. It is thought that these compounds degrade to form PFOS.

APPLICABLE RMP OBJECTIVES AND MANAGEMENT QUESTIONS

1. **Describe the distribution and trends of pollutants concentrations in the Estuary.**

- This study will provide some of the first data to determine the distribution of concentrations of perfluorinated compounds in the Estuary and to place these concentrations in context with concentrations observed in other estuaries.

2. Project future contaminant status and trends using current understanding of ecosystem processes and human activities.

4. Measure pollution exposure and effects on selected parts of the Estuary ecosystem (including humans).

- 4.1. Perfluorinated compounds are considered an emerging contaminant. As such, it is important that we determine their concentrations in biota to evaluate whether management actions are needed.
- 4.4 Determining the concentrations of perfluorinated compounds in the upper trophic level is important for assessing both ecological and human health risks.

5. Compare monitoring information to relevant benchmarks, such as TMDL targets, tissue screening levels, water quality objectives, and sediment quality objects

- The concentrations detected in this study would be compared to known threshold effect levels, where possible.

APPROACH

The objective of this study will be to determine concentrations of PFOS and related compounds in Pacific harbor seals (*Phoca vitulina richardsi*). Harbor seals are an ideal indicator species for persistent bioaccumulative contaminants in the Estuary. Seals are apex predators that eat a diet consisting primarily of fish. Long-lived, they tend to forage in areas that are frequently impacted by contamination (e.g., heavy marine traffic, urban and agricultural runoff, etc.). Combined, these factors result in harbor seals being highly exposed to contaminants that can bioaccumlate.

Perfluorinated compounds are of particular concern because they are very stable compounds that are not known to undergo abiotic or biotic degradation (Martin *et al.* 2004). Perfluorinated compounds have been observed in blood collected from seals located in the Arctic and the Mediterranean seas (Kannan *et al*. 2002). FOSA, which is a metabolite of perfluorinated compounds (e.g., insecticides), was also detected in blood at concentrations that were one to five times greater that the PFOS concentrations (Kannan *et al.* 2002).

Researchers have identified contaminants such as PCBs, DDT, and PBDEs in the blood of Bay area seals at significant concentrations (Kopec and Harvey 1995 and Young *et al.,* 1998, Kajiwara *et al.,* 2001). PBDEs were identified in local seal populations at the highest levels reported for the species and at increased concentrations over the past ten years (She *et al.,* 2002).

At present, little information is available regarding the presence of PFOS and perfluorinated compounds in the Estuary. A research group at Stanford University has

recently analyzed South Bay sediment and wastewater sludge for PFOS and its precursors (Higgins *et al.* 2005). PFOS observed in San Francisco Bay sediment is reported to range from 0.124 ng/g to 4.65 ng/g. The range of concentrations in wastewater sludge was approximately two orders of magnitude higher. Of particular interest was the elevated concentrations of PFOS precursors (i.e., 2-(N-methylperfluorooctanesulfonamido) acetate and 2-(N-ethylperfluorooctanesulfonamido) acetate) suggesting that it is important to monitor the precursors which may degrade to PFOS.

To date, no biological samples have been analyzed for perfluorinated compounds in the San Francisco Estuary. The Marine Mammal Center and Moss Landing Marine Laboratories plan to capture harbor seals in the summer of 2006. Seals will be weighed, measured, and tagged; blood samples will be collected for a battery of tests to assess health and fitness (e.g., blood cell count, exposure to infectious diseases, presence of pathogenic bacteria, etc.). Additional blood samples can be collected for chemical analyses. Animals targeted by this study will be young of the year pups that wean in May and feed on fish throughout the summer. Approximately ten young of the year seals will be tagged for a future study assessing health and survival. Although the focus of the Marine Mammal study will be young of the year, it is likely that seals of all ages will be captured and handled. Blood for perfluorinated compounds will be obtained from all age classes to ascertain whether age has an impact on contaminant loads. Previous studies by Kannan *et al.* (2002) did not show a correlation of PFOS concentrations with age.

The results of this study will be summarized in a technical report and a journal manuscript.

TASK DESCRIPTIONS

This project will consist of two tasks:

Task 1: Collection of Samples

The Marine Mammal Center based in Sausalito, California is conducting a study of harbor seal health that will commence in August 2006. In addition to collecting information of the physical aspects of the seals (e.g., weight, condition, etc.), staff will collect blood. The researchers at the Marine Mammal Center have indicated that they could collect approximately 30 grams of blood for analysis of perfluorinated compounds and brominated flame retardants. Unlike neutral compounds such as polychlorinated biphenyls which accumulate in fatty tissues, perfluorinated compounds tend to bind to protein in blood (Kannan *et al.* 2002). Samples will be sent to a commercial laboratory. A list of compounds is included in the Appendix of this proposal. Care will be taken by the staff to avoid the use of Teflon and related PTFE plastics (e.g., vial and tubing). A detailed cost estimate is presented below.

Task 2: Review of Results and Preparation of a Report

Results should be available approximately four months after submission of samples to the laboratory. The results will go through the RMP data validation process (see the 1999

QAPP). These results will be compared to similar studies conducted in the Arctic and elsewhere (e.g., Kannan *et al.* 2002, Giesy and Kannan 2001) and elsewhere to assist in determining whether these compounds present an emerging concern. A draft report and manuscript will be prepared and circulated to the TRC for review. Upon incorporation of comments, the report will be assigned a SFEI contribution number and posted on the SFEI website. The manuscript will be submitted to an environmental journal such as Environmental Science and Technology.

BUDGET

The estimated cost to complete this task is $50,000. A detailed budget is presented below.

Cost for Analyses				
Laboratory Analyses				
	Chemical	Number of Samples*	Cost of Analyses	Subtotal
	Perfluorinated Compounds	10	1000	$10,000
	Methyethyl death	10	1000	$10,000
	PBDEs	10	1000	$10,000
Direct Costs				
	Vials, gloves, misc.			$500
Labor				
	Field coordination and logistics			$2,000
	Data QA/QC			$3,000
	Report Preparation			$9,500
	Final Report			$500
Total				**$50,00**

* Assumes nine samples plus one replicate.

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APPENDIX
List of Perfluorinated Compounds
To be Analyzed

PERFLUORO-OCTANE SULFONATES

Compound	Acronym
Perfluorobutanoate	PFBA
Perfluoropentanoate	PFPeA
Perfluorohexanoate	PFHxA
Perfluoroheptanoate	PFHpA
Perfluorooctanoate	PFOA
Perfluorononanoate	PFNA
Perfluorodecanoate	PFDA
Perfluoroundecanoate	PFUnA
Perfluorododecanoate	PFDoA
Perfluorobutanesulfonate	PFBS
Perfluorohexanesulfonate	PFHxS
Perfluorooctanesulfonate	PFOS
Internal Standards	
13C-Perfluorododecanoate	PFDoA
13-CPerfluorosulfonate	PFOS
13C- Perfluorooctanoate	PFOA