

Perfluorinated Compounds in San Francisco Bay Harbor Seals

As part of a three-year project examining the effects of contaminants on the health of harbor seals, twenty-one seals were captured from San Francisco Bay and a reference location (Tomales Bay). The animals were weighed, sexed, tagged and tissue samples were collected before the animals were released. Blood serum was analyzed for perfluorinated compounds among other analytes. The dominant perfluorinated compound was perfluorooctanesulfonate (PFOS). The average PFOS concentration in San Francisco Bay seals was approximately an order of magnitude higher than the average for the reference site (322 ng/mL vs 29 ng/mL). San Francisco Bay seals contain some of the highest PFOS concentrations observed in seals worldwide. This study will continue in 2008 with additional samples collected from San Francisco Bay and the reference location.

Introduction

Due to their stability and their hydrophobic and hydrophilic properties, perfluorinated compounds have been widely used for the last 50 years in a variety of applications including insecticides, refrigerants, surfactants, coatings for food-packaging, stain repellants for textiles and furniture, and fire-fighting foams. They encompass a large class of compounds including perfluoroalkyl sulfonates, perfluoroalkyl carboxylates, and fluorotelomer alcohols which are intermediates in the production of fluorinated polymers and surfactants. Because of the stability of the carbonfluorine bond, many of these compounds are resistant to biological and chemical degradation.

San Francisco Bay has a resident population of Pacific harbor seals (*Phoca vitulina richardii*). In contrast to the growing harbor seal population along the California coast, the San Francisco Bay population has remained constant at an estimated of 500 seals. The possible causes for this static population are unclear and could include loss of habitat, decline in prey, and contaminants.

In 2007, the Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) began a pilot study in collaboration with the Marine Mammal Center to examine bioaccumulative contaminants in harbor seals in the San Francisco Bay (e.g., polybrominated diphenyl ethers, perfluorinated compounds, etc.). This pilot study is part of a larger three-year study that the Marine Mammal Center is undertaking to evaluate and track the health of harbor seals. To date, most of the studies of pinnipeds have been on dead and stranded animals. This study is focused on evaluating the effect of contaminant levels and infectious diseases in live seals (trapped and released). This poster presents preliminary results of analyses that were conducted in the first year.

Materials and Methods

Fourteen seals were captured using seines and tangle nets in the fall of 2006 and spring of 2007 from an urbanized area of the San Francisco Bay (Castro Rocks beneath the Richmond Bridge, Figure 1). This is the largest of three haul-out sites in San Francisco Bay. Another seven seals were collected from the reference site, Tomales Bay, adjacent to the Point Reyes National Seashore (Figure 1). The animals were weighed, length-measured, sexed, flipper-tagged, and a tracking device (hat or radio) attached. Animals were classified into age categories: weaner (1 to 12 months); yearling (approximately one year old); subadult (older than yearling but not an adult); and adult. Blood, blubber, and hair samples were collected for contaminant analyses and basic blood chemistry and diagnostics (e.g., blood cell count, exposure to infectious diseases, presence of pathogenic bacteria, etc).

Serum was sent to AXYS Analytical (Sidney, BC, Canada) for analysis of perfluorinated compounds using SPE cartridges for extraction and high performance liquid chromatography – mass spectrometry (HPLC-MS/MS) for analysis. Blood serum was analyzed for the following 12 perfluorinated compounds: perfluorobutanoate (PFBA); pefluoropentanoate (PFPeA); perfluorohexanoate (PFHxA); perfluoroheptanoate (PFHpA); pefluorooctanoate (PFOA); perfluorononanoate (PFNA); perfluorodecanoate (PFDA); perfluoroundecanoate (PFUnA); perfluorododecanoate (PFDoA); perfluorobutanesulfonate (PFBS); perfluorohexanesulfonate (PFHxS) and perfluoroocatanesulfonate (PFOS).

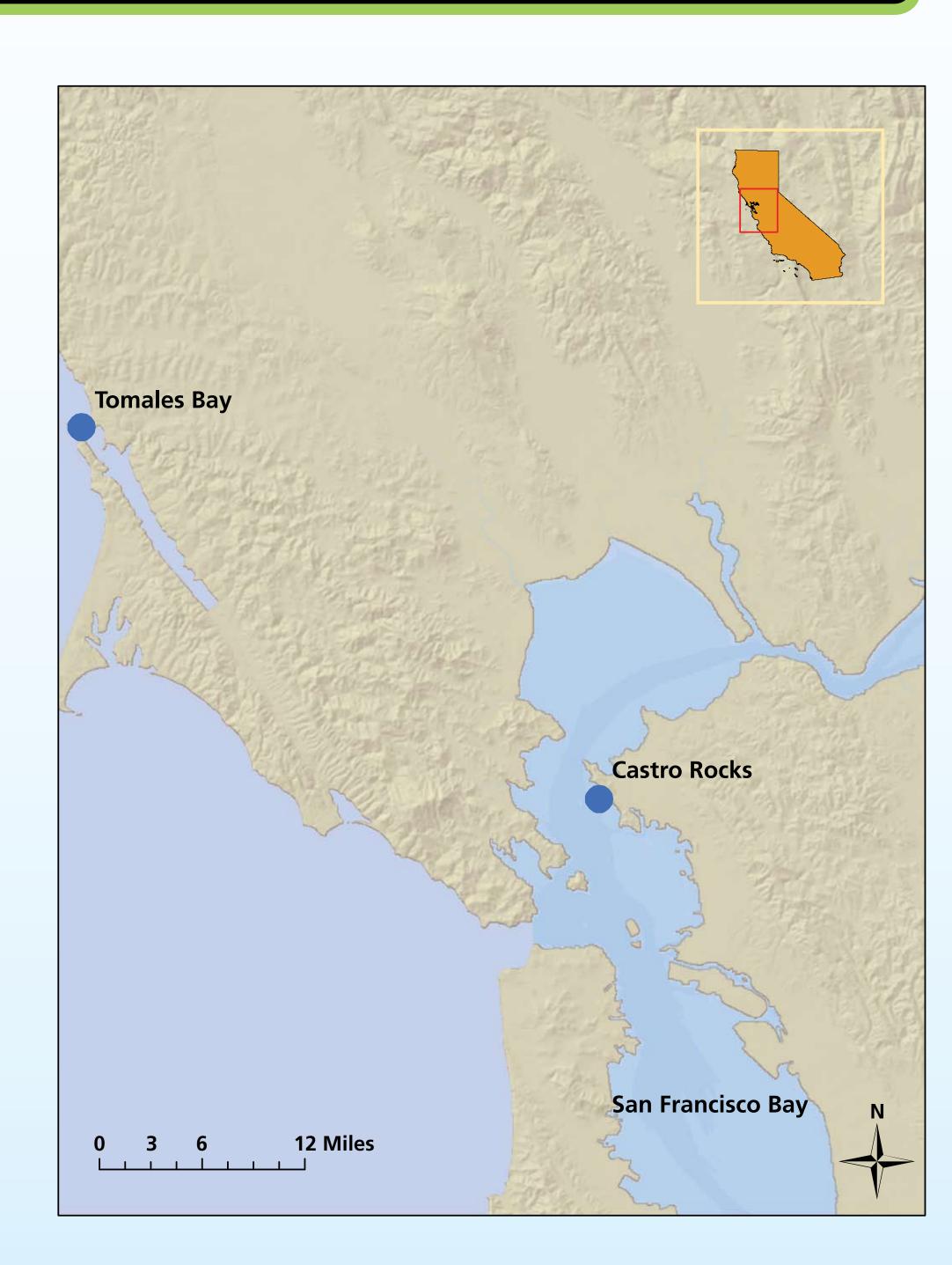
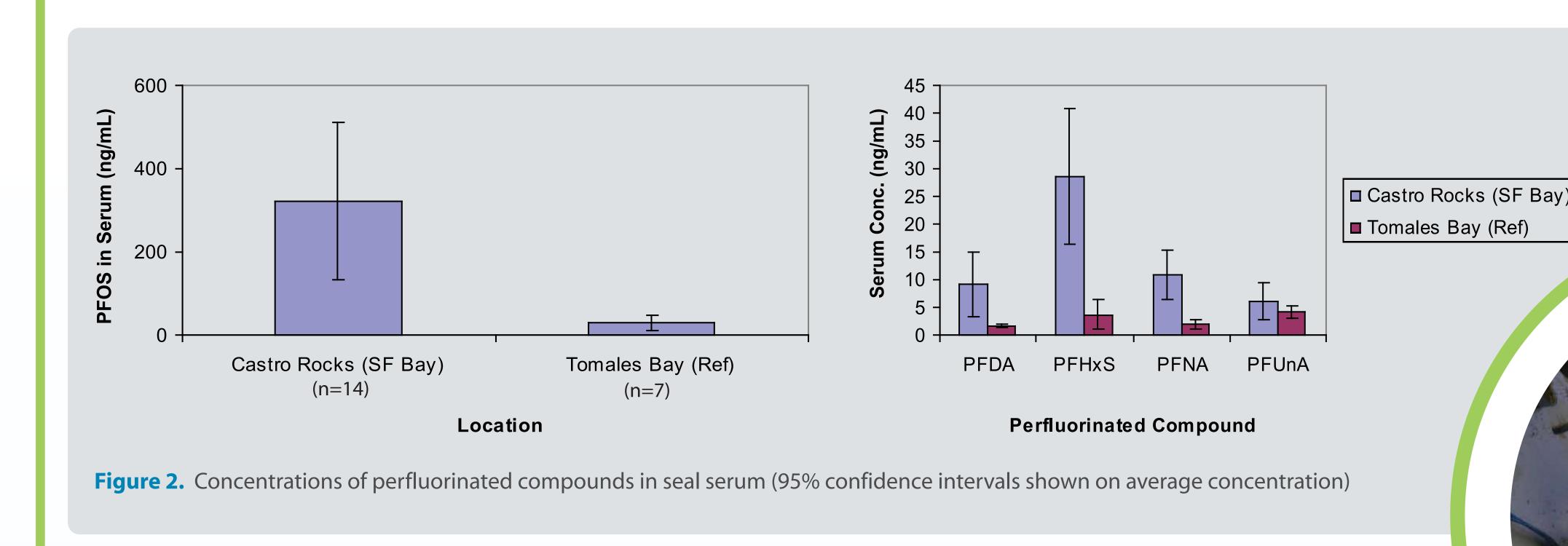


Figure 1. Location of sampling sites

Results

Compounds found above the detection limits include: PFOS, PFHxS; PFNA; PFUnA; and PFDA (Figure 2). Consistent with observations reported in the literature (Houde et al. 2006; Bossi et al. 2005; van de Vijver et al. 2005), PFOS was the dominant compound by an order of magnitude (Figure 2). In addition, a statistically significant difference was observed between the two sites for PFOS (p = 0.002, using a log normal transformed data set and a general linear model). Elevated concentrations of perfluorinated carboxylic acids were associated with samples that had elevated concentrations of PFOS. Concentrations of PFOA were near the detection limit of 0.5 ng/mL, which is consistent with other seal work (Butt et al. 2007) and the hypothesis that PFOA has a low bioaccumulation potential.



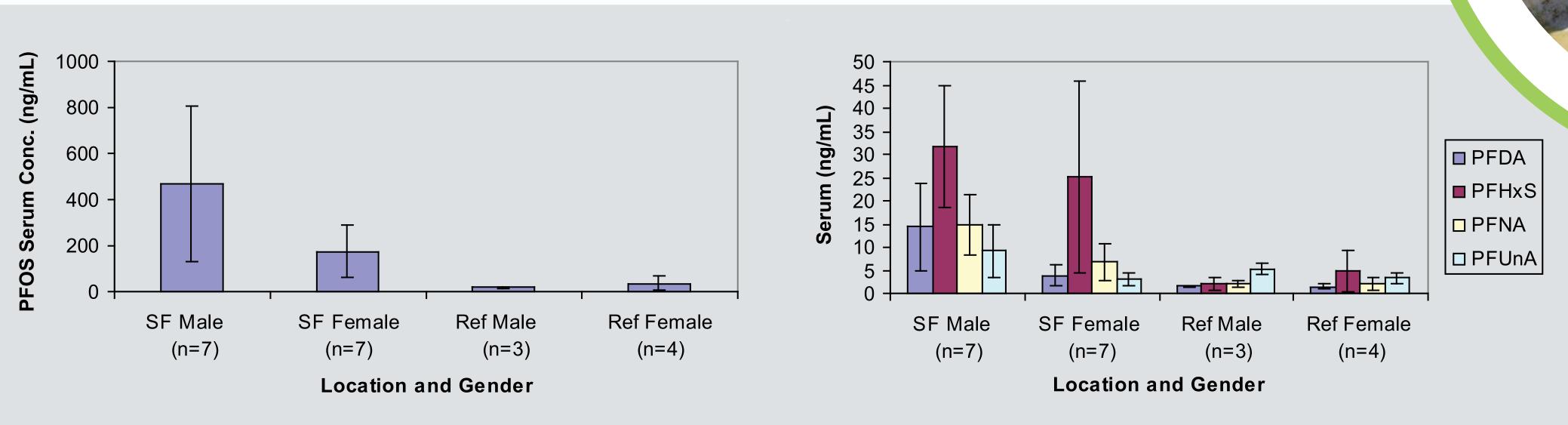
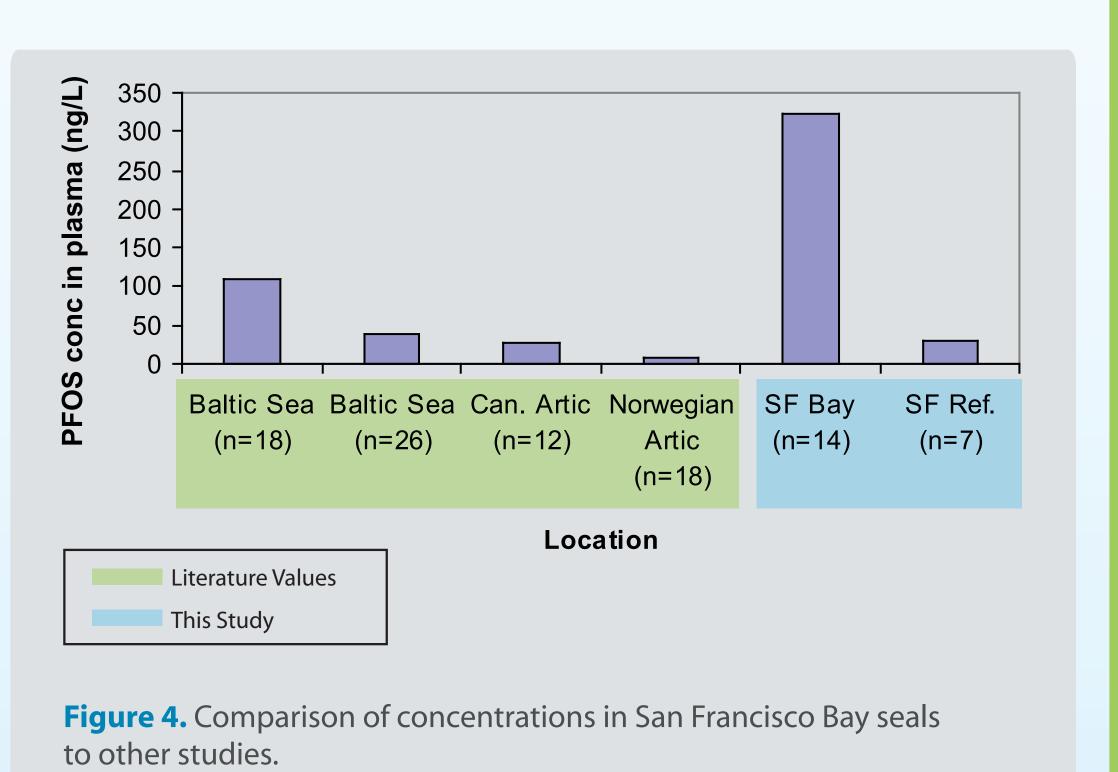


Figure 3. Perfluorinated compounds detected by site and gender (95% confidence intervals shown on average concentration)

As shown in Figure 3, due to the small sample size, there was no statistically significant age or sex differences although average concentrations of San Francisco Bay adult females were lower than San Francisco adult males (e.g., PFOS concentrations in females was 174 ng/mL vs 470 ng/mL in males). Review of the literature does not show a correlation with concentration for age and gender of animal (Butt et al. 2007; Kannan et al. 2001; Houde et al 2006). As reported on Figure 4, SF Bay concentrations are substantially higher than seal plasma results reported in the literature for other pinnipeds worldwide.



Source: *Giesy, J. and K. Kannan.* 2001. *Global distribution of pefluorooctane sulfonate in wildlife.*

Environ. Sci. Technol. vol 35. 1339-1342.

Conclusions

Results for the first year multi-year study investigating contaminant loads in Pacific harbor seals show:

- A statistically significant difference was observed between the reference location and the San Francisco Bay for PFOS.
- The dominant perfluorinated compound was PFOS and it was an order of magnitude higher than other perflourinated compounds.
- The San Francisco Bay seal population has some of the highest concentrations of perfluorinated compounds observed to date in seals.

Additional sampling and analysis of seals is planned for 2008. The sources of the perfluorinated compounds to these marine mammals remains to be elucidated.



References

Butt, C.; Muir, D.; Stirling, I.; Kwan M and S. Mabury. 2007. Rapid response of Artic ringed seals to changes in perfluoroalkyl production. Environ. Science Tech. Vol. 41. No. 1. p 42 -49.

Bossi, R, Riget, F. and R. Dietz. 2005. Temporal and spatial trends of perfluorinated compounds in ringed seal (phoca hispida) from Greenland. Environ. Sci. Technol. Vol. 39, 7416-7422.

Giesy, J. and K. Kannan. 2001. Global distribution of pefluorooctane sulfonate in wildlife. Environ. Sci. Technol. vol 35. 1339-1342.

Houde, M.; Martin, J. W.; Letcher, R. J.; Solomon, K.; and D. Muir. 2006. Biological monitoring of poly fluoroalkyl substances: A review. Environ. Sci. Technol. 2006. 40. 3463-3473.

Van De Vijver, K., Hoff, P., Das, K., Brasseur, S., van Dongen, W., Esmans, E., Reijnders, P., Blust, R.W. de Coen. 2005. Tissue Distribution of Perfluorinated Chemicals in Harbor Seals (Phoca vitu lina) from the Dutch Wadden Sea. Environ. Sci. Technol. vol. 39. p. 6978-6984.

Acknowledgements

The authors would like to thank the RMP for providing funding for this project and Linda Wancyzk and Joanne Cabling for their artistic talent and support. Staff at Marine Mammal Center, Moss Landing Marine Labs and volunteers generously donated their time, equipment and boats to assist in the collection of biological samples. All samples were collected under NOAA-NMFS permit # 555-1870-00 issued to Moss Landing Marine Laboratory, Moss Landing, California.