**Perfluorococanucleate and Related Fluorinated Hydrocarbons in Marine Mammals, Fishes, and Birds from Coasts of the Baltic and the Mediterranean Seas**

KURUNTHACHALAM KANNAH, SIMONETTA COROSOLINI, JERZY FALANDYSZ, GUNTER OEHME, SILVANO FOCARDI, AND JOHN P. GIESY

National Food Safety and Toxicology Center, Department of Zoology, Institute for Environmental Toxicology, Michigan State University, East Lansing, Michigan, and Department of Science Ambient, Universita di Siena, I-53100 Siena, Italy.

Introduction

Perfluorinated sulfonates have been commercially produced by an electrochemical fluorination process for over 40 years (1). A major fluorocarbon produced by this process is perfluorooctanate sulfonamide [(OSF: CF$_3$SO$_2$N)]. Using this fluorinated compound as a building block, further reactions produce several other fluorinated compounds, including perfluorococanucleate (PFOS) (1, 2). These compounds repel water and oil, reduce surface tension, catalyze oligomerization and polymerization, and maintain their properties under extreme conditions. Depending upon the specific functional derivatization or the degree of polymerization, PFOS-based compounds may degrade or metabolize to PFOS (2, 3). PFOS is stable, chemically inert, and nonreactive and thus has the potential to bioaccumulate (4–6).

PFOS has been identified in serum samples from both occupationally and nonoccupationally exposed human populations and in various species of wildlife (2, 5–7). PFOS, PFOA, and PFNA have been detected in human blood (7). Studies describing the occurrence of PFOS, PFOA, and PFNA in wildlife are scarce (6, 11, 12).

The mechanisms and pathways leading to the presence of perfluorinated compounds in wildlife and humans are not well characterized, but it is likely that there are multiple sources of the compound. To understand the spatial distribution of perfluorinated compounds, exposure concentrations were measured in a range of species with different natural histories from various parts of the world. In this study, concentrations of PFOS, PFOA, PFHxS, and PFNA were measured in marine mammals including bottlenose dolphins (Tursiops truncatus), striped dolphins (Stenella coeruleoalba), common dolphins (Delphinus delphis), fin whales (Balaenoptera physalus), and long-finned pilot whales (Globicephala melas) from the Italian coast of the Mediterranean Sea and in livers of ringed seals (Phoca hispida), gray seals (Halichoerus grypus), white-tailed sea eagle (Haliaeetus albicilla), and Atlantic salmon (Salmo salar) from coastal areas of the Baltic Sea. PFOS was detected in all of the wildlife species analyzed. Concentrations of PFOS in blood decreased in order of bottlenose dolphins > bluefin tuna > swordfish. Mean PFOS concentrations (61 ng/g, wet wt) in cormorant livers collected from Sardinia Island in the Mediterranean Sea were less than the concentrations of PFOA (65 ng/g, wet wt). PFOS concentrations in cormorant livers were significantly correlated with those of PFOA. PFOS was found in 14 of 19 livers or blood samples of marine mammals from the Mediterranean Sea. The highest concentration of 578 ng PFOS/g, wet wt, was found in the liver of a common dolphin. Livers of ringed and gray seals from the Bothnian Bay in the Baltic Sea contained PFOS concentrations ranging from 130 to 1100 ng/g, wet wt. No relationships between PFOS concentrations and ages of ringed or gray seals were observed. Concentrations of PFOS in livers of seals were 27-fold greater than those in corresponding blood. A significant positive correlation existed between the PFOS concentrations in liver and blood, which indicates that blood can be used for noninvasive monitoring of PFOS.

**Trend analysis of PFOS concentrations in livers of white-tailed sea eagles collected from eastern Germany and Poland since 1979 indicated an increase in concentrations during the 1990s. Livers of Atlantic salmon did not contain quantifiable concentrations of any of the fluorocarbons monitored. PFOS is a widespread contaminant in wildlife from the Baltic and the Mediterranean Seas, whereas FGS and PFNA were detected only in certain locations indicating their sporadic spatial distribution.**

**Perfluorooctanoic acid (PFOA: CF$_3$CO$_2$H), perfluorooctanesulfonamide (PFSA: CF$_3$SO$_2$NH), perfluorooctanesulfonate (PFOS: CF$_3$SO$_2$O), and perfluorooctanoate (PFOA: CF$_3$CO$_2$O) were detected in 175 samples of liver and blood of bluefin tuna (Thunnus thynnus), swordfish (Xiphias gladius), common bottlenose dolphins (Tursiops truncatus), striped dolphins (Stenella coeruleoalba), common dolphins (Delphinus delphis), fin whales (Balaenoptera physalus), and long-finned pilot whales (Globicephala melas) from the Italian coast of the Mediterranean Sea and in livers of ringed seals (Phoca hispida), gray seals (Halichoerus grypus), white-tailed sea eagle (Haliaeetus albicilla), and Atlantic salmon (Salmo salar) from coastal areas of the Baltic Sea. PFOS was detected in all of the wildlife species analyzed. Concentrations of PFOS in blood decreased in order of bottlenose dolphins > bluefin tuna > swordfish. Mean PFOS concentrations (61 ng/g, wet wt) in cormorant livers collected from Sardinia Island in the Mediterranean Sea were less than the concentrations of PFOA (65 ng/g, wet wt). PFOS concentrations in cormorant livers were significantly correlated with those of PFOA. PFOS was found in 14 of 19 livers or blood samples of marine mammals from the Mediterranean Sea. The highest concentration of 578 ng PFOS/g, wet wt, was found in the liver of a common dolphin. Livers of ringed and gray seals from the Bothnian Bay in the Baltic Sea contained PFOS concentrations ranging from 130 to 1100 ng/g, wet wt. No relationships between PFOS concentrations and ages of ringed or gray seals were observed. Concentrations of PFOS in livers of seals were 27-fold greater than those in corresponding blood. A significant positive correlation existed between the PFOS concentrations in liver and blood, which indicates that blood can be used for noninvasive monitoring of PFOS. Trend analysis of PFOS concentrations in livers of white-tailed sea eagles collected from eastern Germany and Poland since 1979 indicated an increase in concentrations during the 1990s. Livers of Atlantic salmon did not contain quantifiable concentrations of any of the fluorocarbons monitored. PFOS is a widespread contaminant in wildlife from the Baltic and the Mediterranean Seas, whereas FGS and PFNA were detected only in certain locations indicating their sporadic spatial distribution.**