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

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Perfluorooctanesulfonate (PFOS; $C_8F_{17}SO_3^-$), perfluorooctanesulfonamide (FOSA; $C_8F_{17}SO_2NH_2$), perfluorohexanesulfonate (PFHxS; $C_6F_{13}SO_3^-$), and perfluorooctanoate (PFOA; $C_7F_{15}CO_2^-$) were detected in 175 samples of liver and blood of bluefin tuna (*Thunnus thynnus*), swordfish (*Xiphias gladius*), common cormorants (*Phalacrocorax carbo*), bottlenose dolphins (*Tursiops truncatus*), striped dolphins (*Stenella coeruleoalba*), common dolphins (*Delphinus delphi*), fin whales (*Balenoptera 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 eagles (*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 (95 ng/g, wet wt). PFOS concentrations in cormorant livers were significantly correlated with those of PFOA. FOSA was found in 14 of 19 livers or blood samples of marine mammals from the Mediterranean Sea. The highest concentration of 878 ng FOSA/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 2.7-5.5-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 nonlethal 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 salmons did not contain quantifiable concentrations of any of the fluorochemicals monitored. PFOS is a widespread contaminant in wildlife from the Baltic and the Mediterranean Seas, while FOSA and PFOA were detected only in certain locations indicating their sporadic spatial distribution.

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Introduction

Perfluorinated sulfonates have been commercially produced by an electrochemical fluorination process for over 40 years (*1*). A major fluorochemical produced by this process is perfluorooctane sulfonylfluoride (POSF; $C_8F_{17}SO_2F$). Using this fluorinated compound as a building block, further reactions produce several other fluorinated compounds, including perfluorooctanesulfonate (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, POSF-based compounds may degrade or metabolize to PFOS (*2, 3*). PFOS is stable, chemically inert, and nonreactive and 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, 6*−*11*), and PFOS, FOSA, PFHxS, and PFOA have been detected in human blood (*7*). However, studies describing the occurrence of FOSA, PFHxS, and PFOA 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, FOSA, PFHxS, and PFOA were measured in marine mammals including bottlenose dolphins (*Tursiops truncatus*), striped dolphins (*Stenella coeruleoalba*), common dolphins (*Delphinus delphi*), fin whales (*Balenoptera physalus*), long-finned pilot whales (*Globicephala melas*) and fishes such as northern bluefin tuna (*Thunnus thynnus*), swordfish (*Xiphias gladius*), and in common cormorants (*Phalacrocorax carbo*) collected from Italian coast of the Mediterranean Sea. Furthermore, livers of ringed seals (*Phoca hispida*), gray seals (*Halichoerus grypus*), and Atlantic Salmon (*Salmo salar*) were collected from the Bothnian Bay in the northern part of the Baltic Sea. Similarly, concentrations of target compounds were measured in livers of white-tailed sea eagles (*Haliaeetus albicilla*) collected from inland and coastal regions of eastern Germany and Poland since 1979 until 1999. This provided to an opportunity to evaluate temporal trends in concentrations of fluorochemicals during 20 years. The objectives of this study were to determine the current concentrations of target fluorochemicals in biota from the Mediterranean and the Baltic Seas and to determine their accumulation features.

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