AMOUNTS AND SOURCES OF PCDD/FS IN THE GULF OF FINLAND

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Introduction

One of the industrial processes where polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are formed as byproducts, is the synthesis of chlorophenols. In Finland, chlorophenols were manufactured in 1939–1984, and used as a wood preservative Ky 5 (mainly 2,3,4,6-tetrachlorophenol). The chemical plant was situated next to the Kymijoki River, which discharges into the Gulf of Finland, a subbasin of the Baltic Sea. Recent analyses have shown that the sediments of the Kymijoki River still contain high levels of PCDD/Fs, up to 350 000 ng TEQ/kg dry weight (d.w.)[1,2]. It seems that the river has transported pollutants into the Gulf of Finland for many years.

Methods and Materials

Sediment cores were collected from areas with a known accumulation of recent sediments. The suitability of the sampling sites for monitoring purposes was verified by echosounding the sea bottom. The sediment cores were sliced into 1–2 cm sections, and dated on the basis of the activities of Cs-137, Pu-239,240 and Pb-210 radionuclides[3,4]. Eleven sediment cores were selected for PCDD/F analyses (Fig. 1). The representative time coverage of the sediment cores varied from approximately ten to hundred years, depending on the time resolution and length of the period of active, constant accumulation conditions at the site. In addition to the surface sections of the dated sediment cores, surface sediments (0–2 cm or 0–5 cm) were analyzed from nine coastal and three offshore sampling sites.

For the PCDD/F analyses, 1.5-g samples of lyophilized and homogenized sediment were Soxhlet-extracted with toluene for 20 h. The extracts were fractionated and purified by eluting them through three columns consisting of (1) sodium sulfate and silica gel, (2) activated carbon and Celite, and (3) aluminum oxide. Sulfur was precipitated from the sediments with activated copper powder. The quantification of PCDD/Fs from the concentrated samples was achieved by measuring the native compounds and ^{13}C-labeled internal standards by high-resolution gas chromatography-mass spectrometry[5,6].

Results and Discussion

PCDD/F levels in the Gulf of Finland started to increase rapidly in the 1940–1950s, and the concentration maximum was typically located in sediment layers that had been deposited during the 1960–70s. The highest concentrations were analyzed from the sediment core closest to the inlet of the eastern branch of the Kymijoki River (sampling station K15), 12 km away from the coast (Fig. 2). At

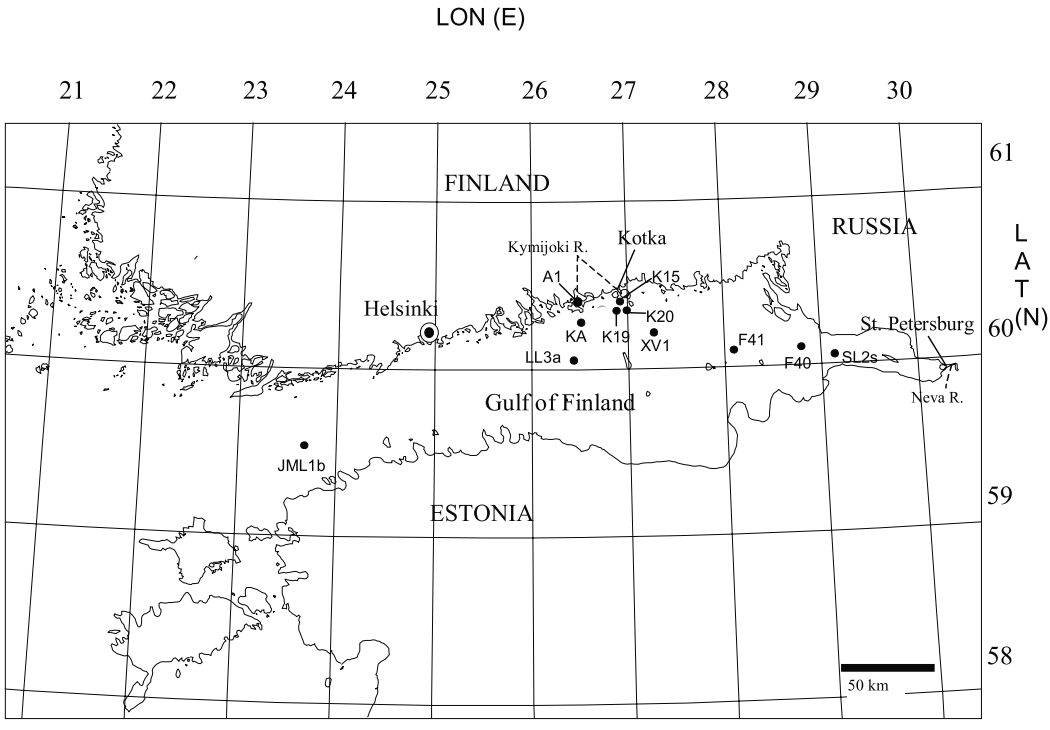

Figure 1. A map of the study area with the sites where sediment cores were sampled.

the depth of 29–31 cm in this core, the PCDD/F sum concentration (toxic and nontoxic congeners) reached 101 000 ng/kg d.w., or 440 ng TEQ/kg d.w. In the surface layers of the sediment cores (0–1 cm), the PCDD/F sum concentrations were 24–66% of the maximum concentrations. A part of the observed decline in concentrations was attributed to an increase in the accumulation rate of dry matter that occurred at some sampling stations after the period of the maximum inputs of PCDD/Fs (Fig. 3).

As the distance from the coast increased from 12 to 40–56 km, the maximum and surface concentrations declined to about 1/10 of the initial levels. The lowest surface concentrations measured in the Gulf of Finland were 430–810 ng/kg d.w. (PCDD/F sum). One of these background stations was located in the Neva Bay (SL2s), about 60 km away from St. Petersburg (Russia). Thus, the Neva River was not a major source of PCDD/Fs. The nine surface sediment samples collected from the northern coast of the Gulf of Finland did not reveal any other significant point sources for PCDD/Fs, except for the Kymijoki River. Throughout the gulf, a PCDD/F congener profile typical to the wood preservative Ky 5 predominated, with 1,2,3,4,6,7,8-HpCDF and OCDF as the main congeners. At stations K15 and LL3a, the predominance of these congeners, with <4% of OCDD, was observed starting from the deepest sediment slices, from the 1940-50s.

It was estimated that the impacted sedimentary area stretched a distance of 75 km away out from the coast. Within this distance, the actively accumulating sediments covered an area of 3000 km^2. The

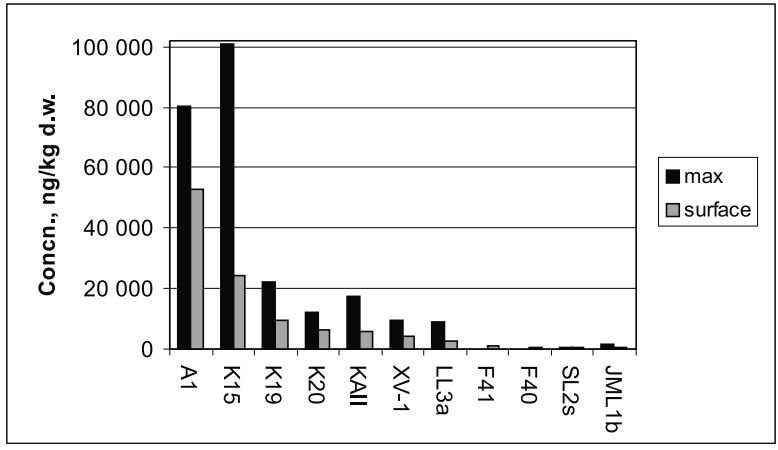

Figure 2. Surface and maximum concentrations at the sampling stations.

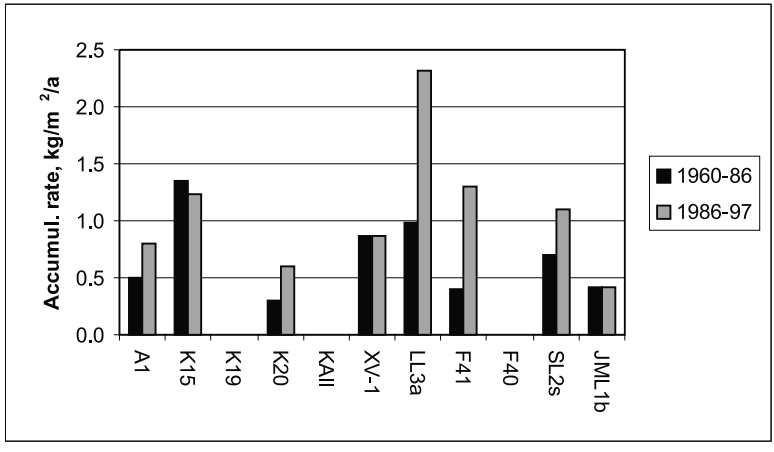

Figure 3. Average annual accumulation rates of dry matter at the sampling stations (K19, KAII, F40: not available).

PCDD/F load attributed to the wood preservative source was 1770 kg, or approximately 12 kg TEQ. The PCDD/F pollution of the sediments may contribute to the high levels measured in some Baltic fish species.

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