LEVELS OF PERSISTENT ORGANIC COMPOUNDS IN THE SEDIMENTS OF GULF OF BOTHNIA, THE BALTIC SEA

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Introduction
The Baltic Sea is a semi enclosed shallow basin consisting of series of basins. Bothnian Bay and Bothnian Sea constitute the northernmost part of the Baltic Sea, the Gulf of Bothnia. The surroundings of Gulf of Bothnia are quite sparsely inhabited, but several industrialized cities both on Finnish and Swedish site surround the area. Also, a number of rivers run into the Gulf of Bothnia.

The Baltic Sea has been a focus of several researches due to its vulnerable ecosystem. However, there are only few studies on organochlorine contaminants in the area of the Gulf of Bothnia, whereas most of the literature has been focused on the Gulf of Finland and the Baltic Proper, the eastern and southern parts of the Baltic Sea.

A temporal distribution in sediments from the Baltic Proper reveals the highest levels for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/PCDFs) and polychlorinated biphenyls (PCBs) in the 1960's-1970's [1,2]. One sediment profile from the Baltic Proper shows an increasing concentration of polybrominated diphenyl ethers (PBDEs) from the 1970s up to year 1988 when the sediment sample was taken [3]. Sediment samples from the Western Baltic Sea revealed significant contribution of river discharges to the PCDD/PCDF contamination of sediments [4].

In the Gulf of Bothnia, PCB concentrations have been studied in the surface sediments from the year 1991 along the Swedish coast of the gulf by van Bavel et al. [5] and Strandberg et al. [6] Some offshore stations have also been studied for PCB concentrations in surface sediments [7]. Only one study has been published from the Finnish coast of the Gulf of Bothnia [8]. PCDD/PCDF concentrations in the sediments in the vicinity of pulp mill in Finnish coast [8] were higher compared to the concentrations measured in the sediment from Gulf of Finland and near Gotland [9].

The aim of this study was to study the levels and sources of PCDD/PCDFs, PCBs and PBDEs in the sediments of Gulf of Bothnia, and concentrate on the previously unexplored Finnish coast in particular. We also wanted to evaluate the trends in the accumulation of these substances in sediment layers in the course of time.

In order to do this, we analysed five sediment samples in front of five towns along the Finnish coast of the Gulf of Bothnia, and three sediment samples from offshore stations in Gulf of Bothnia. All the sediments were analysed for the surface and the deepest sediment slices.

Materials and Methods
Sediment samples from the offshore sampling sites and near the coast were collected during the years 2002-2003. The sediment cores were collected with a pistonless corer with an inner diameter of 9-13 cm and divided into 2 cm slices. The surface samples (0-2 and 2-4 cm) and deep samples (26-48 cm) were analyzed for PCDD/PCDFs, PCBs and PBDEs.

5 g sample of lyophilized and homogenised sediment was Soxhlet-extracted with toluene for 20 h. Sulphur was precipitated from the samples with activated copper powder. The samples were then purified and fractionated with three columns consisting of sodium sulphate and sulphuric acid impregnated silica gel, activated carbon and celite and aluminium oxide. 13C-labelled internal standards were used to quantitate the amount of analytes. The quantification was performed by HRGC/HRMS with a resolution of 10 000. 17 toxic PCDD/PCDFs and the total sum of tetra- to octa PCDDs and PCDFs and 37 PCBs were analysed from the samples, including seven indicator PCBs and all the 12 dioxin-like PCBs. 15 PBDEs (BDE 28, 47, 66 ,71,75, 85, 99, 100, 119, 138, 153, 154, 183 and 190) were included in the analysis. The Laboratory of Chemistry is an accredited testing laboratory T077 in Finland, and the scope of accreditation covers analysis of PCDD/PCDFs, PCBs and PBDEs from soil and sediment samples.

Results and Discussion

The sampling locations for the sediment samples can be seen in Figure 1. Offshore sampling was performed from sites BO3, US5b and SR5, whereas coastal sampling stations were situated in front of the towns Oulu, Kokkola, Vaasa, Kaskinen and Pori.

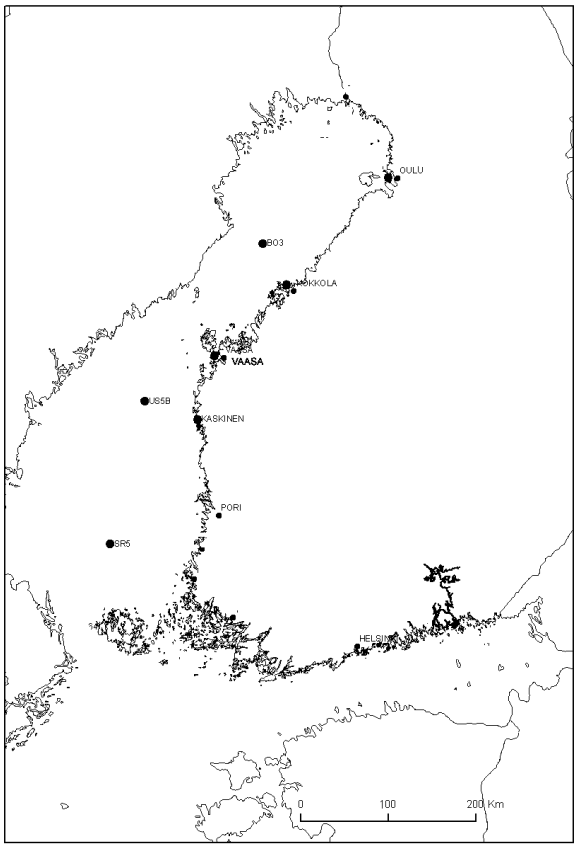

Figure 1: Sediment sampling locations in the offshore and coastal stations

Offshore stations

PCBs were the most abundant studied persistent organic compounds in the sediment samples from the offshore stations (Figure 2). The levels of PCB concentrations were highest in the surface sediment sample from the northernmost sampling point, BO3. However, the deepest sediment slice from BO3, (28-30 cm) showed PCB concentrations of the same magnitude as in other offshore sampling points (US5b and SR5). This points to the fact that even though a declining trend of PCB concentrations can generally be seen in the sea sediments [1,2] there still may exist either on-going point sources or transport from previously contaminated areas which increase the PCB concentrations in the evolving sediment layers. The levels of PCDD/PCDFs [10] and PBDEs were very modest in all the studied offshore sampling points compared to the concentrations in other studies in Baltic sea sediments [2,11], and only slightly increased PCDD/PCDF and PBDE concentrations could be seen in the surface samples. The levels of TOC in the studied sediments varied from 1.6-4.2 %

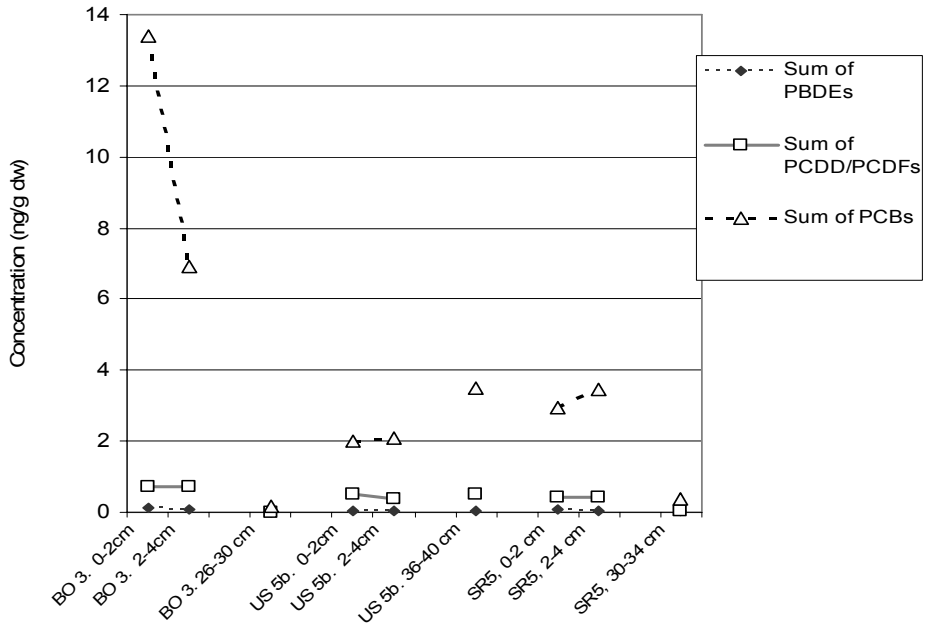

Figure 2. Concentrations of PCBs, PCDD/PCDFs and PBDEs in the sediments of Gulf of Bothnia.

Coastal stations

PCBs were the most abundant studied persistent organic pollutants in the coastal sediment samples as well. There were clear differences in concentrations of PCBs and PBDEs between different coastal sampling sites and between the sediment layers within a sampling point, calculated as concentrations per g dry weight (Figure 3).Even if TOC concentrations in the sediment samples (1.0-4.4 %) are taken into account the trends of the results do not change notably.

In some coastal sediment samples the amount of PCDD/PCDFs and PCB was highest in the deepest sediment slice (Oulu and Pori). This may be due to different sources along the coast in the course of time, or to the fact that sedimentation rates may vary considerably between the sites, and the deepest sediment layers in these samples date back to the period when emissions of PCDD/PCDFs and PCBs have been highest, probably 1960s-1970s [1,2]. Sediment layers between the sampling points are thus not necessarily comparable with each other in this study.

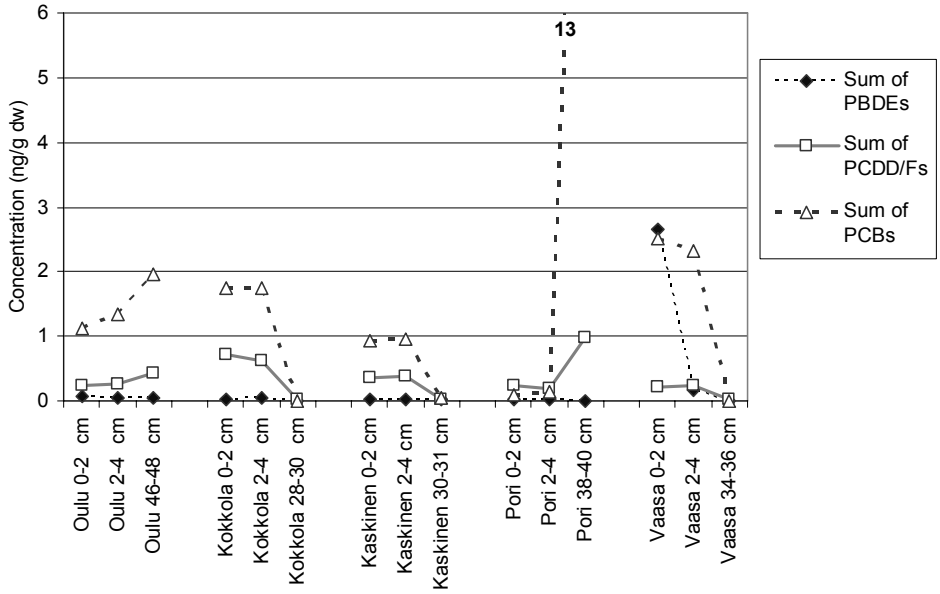

Figure 3. Concentrations of PCBs, PCDD/PCDFs and PBDEs in the sediments along the Finnish coast

At one sampling point (Vaasa), the amount of PBDEs increased notably in the surface sediment sample (0-2 cm) compared to the deeper sediment slices and also compared to the other coastal sediment samples. This may point to an on-going point source in or near the city of Vaasa.

The sum PCB concentrations in the Finnish coastal samples are of the same magnitude, but in general little lower than concentrations measured in the Swedish coast [5,6]. The lower concentrations can be explained at least partly by the fact that the sum of PCBs in the Swedish studies includes 68 congeners instead of the 37 congeners in this study, most of which are included in the Swedish studies.

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