

## Mussel incubation in the monitoring of PCDDs, PCDFs, PCBs, PBDEs and PCNs in two Finnish watercourses

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### Introduction

The concentrations of chlorinated compounds in Finnish watercourses have been monitored by mussel incubation since 1980's <sup>1</sup>. Mussels are widely used test organisms in watercourse investigations providing information on the spreading and levels of pollutants in the aquatic environment. They bioaccumulate pollutants without metabolising them and can survive even in unfavourable conditions.

The levels of chlorophenols that mainly have originated from pulp and paper industry have decreased, but for example the levels of polychlorinated biphenyls (PCB) have remained unchanged. The manufacture of a chlorophenol-based wood preservative named Ky-5 nearby the River Kymijoki in the southern part of Finland from 1940's until 1980's has been reflected as high concentrations of dioxins (polychlorinated dibenzo-*p*-dioxins and dibenzofurans, PCDD/PCDF) in mussels incubated in this river <sup>2</sup>. The concentrations of dioxins have not been measured in the mussels incubated in the River Vuoksi near the border of Finland and Russia, but PCBs have occurred at elevated levels in this watercourse compared to some other watercourses.

The main aim of this study was to investigate the contamination of the River Vuoksi by dioxins and by other less studied contaminants, polybrominated diphenyl ethers (PBDE) and polychlorinated naphthalenes (PCN). PBDEs have had wide use as flame retardants and industrial applications of PCNs have been similar to those of PCBs. The levels in mussels incubated in the River Vuoksi were compared to those in mussels incubated in the River Kymijoki.

## Methods and Materials

Fifteen caged freshwater mussels (*Anodonta piscinalis*) were incubated both in one site of the River Vuoksi and in one site of the River Kymijoki for four weeks in August 1999. The incubation was performed by Central Finland Environment Centre as presented previously<sup>1,3</sup>. The storage and extraction of mussels was performed similarly as described earlier<sup>4</sup>. Briefly, each mussel was measured and weighed and the soft part was freeze-dried. The tissues of five mussels were combined to one analysis sample for extraction. The mussels were extracted in a Soxhlet-apparatus with toluene. The lipid content was determined gravimetrically and the extract was purified by column chromatography as previously described<sup>5</sup>. Briefly, the extract was purified using three columns: silica gel impregnated with sulphuric acid (fat removal), carbon-Celite (separation of PCDD/PCDFs from PCBs) and alumina (final purification). For the analyses of PCNs, an aliquot was taken from the sample after the silica column, and the aliquot was purified on an alumina column.

The extracts were analysed for 17 PCDD/PCDFs, 16 PCNs, 14 PBDEs and 33 PCBs. Of dioxins toxic congeners were studied and the analysed PCBs included mono- and non-*ortho*-PCBs. All analyses were performed using high-resolution gas chromatography-high-resolution mass spectrometry (HRGC-HRMS). Analyses were performed with VG 70-250 SE or Micromass Ultima in electron impact ionisation mode using selected ion monitoring mode with a 10,000 resolution. PCDD/PCDFs and PCBs were separated on a DB-Dioxin column (60 m x 0.25 mm i.d. x 0.15 µm), and PBDEs and PCNs on a DP-5 column (60 m x 0.25 mm i.d. x 0.15 µm). The limits of determination of PCDD/PCDFs, PCBs, PBDEs and PCNs varied between 2 and 650 pg/g lw, between 1 and 750 pg/g lw, between 50 and 7100 pg/g lw, and between 6 and 460 pg/g lw, respectively.

## Results and Discussion

The sum concentrations of all the measured analyte groups were higher in the mussels incubated in the River Kymijoki than in the mussels from the River Vuoksi (Figure 1). In both watercourses, the highest level was measured for PCBs and the lowest for PCNs. The contamination by dioxins was clearly higher in the River Kymijoki compared to the River Vuoksi, whereas the levels of PBDEs were quite similar in both watercourses.

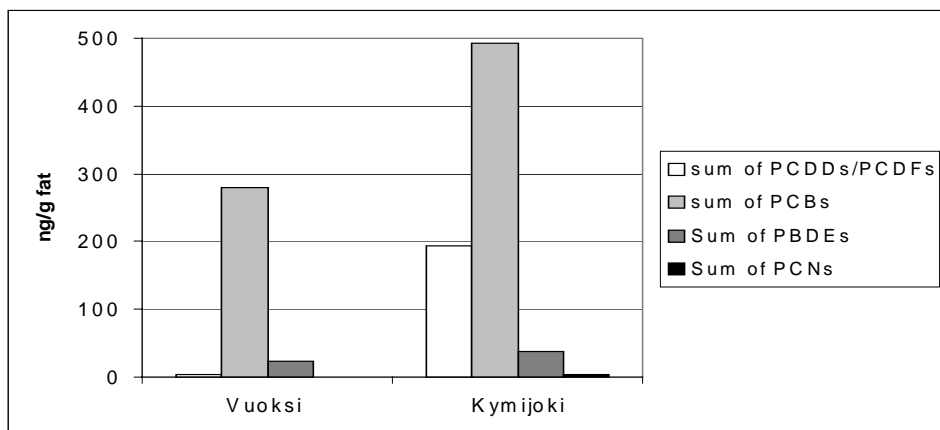


Figure 1: The sum concentrations of dioxins, PCBs, PBDEs and PCNs in mussels incubated in the Rivers Kymijoki and Vuoksi.

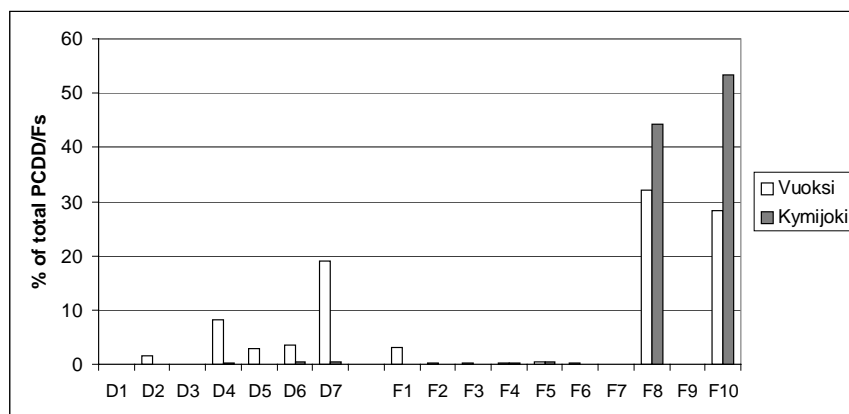


Figure 2: PCDD/PCDF congener distribution in mussels incubated in the Rivers Kymijoki and Vuoksi (D1=2378-TCDD, D2= 12378-PeCDD, D3=123478-HxCDD, D4= 123678-HxCDD, D5=123789-HxCDD, D6= 1234678-HpCDD, D7=OCDD, F1=2378-TCDF, F2=12378-PeCDF, F3=23478-PeCDF, F4= 123478-HxCDF, F5= 123678-HxCDF, F6=234678-HxCDF, F7= 123789-HxCDF, F8= 1234678-HpCDF, F9= 1234789-HpCDF, F10= OCDF)

The concentrations of dioxins were still elevated in the River Kymijoki, as could be expected by previous studies<sup>1,6</sup>. The analyses of sediments have verified that this river is extremely polluted by dioxins<sup>7,8</sup>. The congener profiles of dioxins varied notably between the mussels from the Rivers Vuoksi and Kymijoki (Figure 2) showing different sources for the dioxins. The dioxin profile in the mussels incubated in the River Kymijoki is very typical for contamination by chlorophenol formulation KY-5, with 1,2,3,4,6,7,8-HpCDF and OCDF being the most abundant congeners. In the mussels incubated in the River Vuoksi, the dioxin profile resembled more the background deposition profile, having hexaCDDs and OCDD as dominant congeners in addition to heptaCDFs and OCDF.

The levels and congener profiles of the major PCBs differed slightly between the two sites. The higher prevalence of the less chlorinated PCBs in the mussels incubated in the River Kymijoki (Figure 3) refers to different PCB sources between the Rivers Vuoksi and Kymijoki.

The quite similar levels and congener profiles of PBDEs in the mussels from the River Vuoksi and the River Kymijoki indicate that there are no point sources of PBDEs in these two incubation sites. The same is true for PCNs, although the sum concentration of PCNs was slightly higher in the mussels incubated in the River Kymijoki.

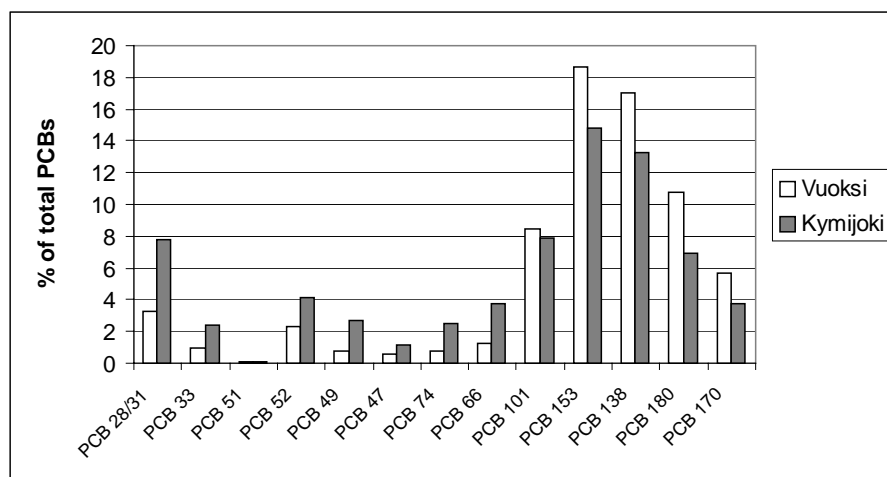


Figure 3: PCB congener distribution (13 congeners) in mussels incubated in the Rivers Kymijoki and Vuoksi

This mussel incubation showed that the River Vuoksi is less contaminated with dioxins, PCBs, PBDEs and PCNs than the River Kymijoki. The results of this study show that mussel incubation can be used for the monitoring of PBDEs and PCNs in watercourses.

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