



Contamination of River Kymijoki sediments with polychlorinated dibenzo-*p*-dioxins, dibenzofurans and mercury and their transport to the Gulf of Finland in the Baltic Sea

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ARTICLE INFO

Article history:

Received 1 February 2008

Received in revised form 16 June 2008

Accepted 24 July 2008

Available online 20 September 2008

Keywords:

Polychlorinated dibenzo-*p*-dioxins

Polychlorinated dibenzofurans

Chlorophenol production

River sediments

Transport

Gulf of Finland

ABSTRACT

Kymijoki, the fourth largest river in Finland, has been heavily polluted by pulp mill effluents as well as the chemical industry. Up to 24000 ton of wood preservative, chlorophenol known as Ky-5, was manufactured in the upper reaches of the river, an unknown amount of which was discharged into the river between 1940 and 1984. Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) occurred as impurities in the final Ky-5 product. The PCDD/F concentrations and burden in the river sediments were studied and the transport of PCDD/Fs from contaminated sites downstream and into the Gulf of Finland in the Baltic Sea was estimated. More than 190 sediment cores were sampled to estimate the volume of contaminated sediments and the total PCDD/F burden. The transport of PCDD/Fs was estimated using sediment traps placed at several sites. The survey revealed that sediments in the river were heavily polluted by PCDD/Fs, the main toxic congener being 1,2,3,4,6,7,8-heptachlorodibenzofuran, a major contaminant in the Ky-5 product. The mean total concentration at the most polluted river site downstream from the main source was 42000 $\mu\text{g kg}^{-1}$ d.w. (106 $\mu\text{g I-TEQ kg}^{-1}$). The elevated concentrations in the coastal region and the present estimated transport from the River Kymijoki confirm earlier assessments that the river is a major source of PCDD/F for the Gulf of Finland.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are formed unintentionally in numerous chemical manufacturing processes and in thermal and pulp bleaching processes in which sources of chlorine, organic matter and sufficient energy are incorporated. A significant source of PCDD/Fs in the environment is the former use and manufacture of chlorophenols, which were used, e.g., as fungicides, herbicides, insecticides and as a precursor in the synthesis of other pesticides (Hutzinger et al., 1985; Czuczwa and Hites, 1986; Koistinen et al., 1995; Götz et al., 1998; Bright et al., 1999). PCDD/Fs are poorly water soluble and when discharged to surface waters they are largely sediment bound, a tendency which increases with increasing chlorination level (e.g. Govers and Krop, 1998).

In the Baltic region several historical point sources and major river sources of PCDD/Fs have been identified such as pulp bleaching (Rappe et al., 1989; Koistinen et al., 1995; Sundqvist et al., 2006), vinyl chloride production (Isosaari et al., 2000), and the metal industry (Sundqvist et al., 2006). Surveys of PCDD/F concentrations in the Baltic Sea sediments and especially in Finnish territory have shown that chlorophenol production along the River Kymijoki and subsequent transport to the sea is a significant source of chlorinated dibenzofurans (PCDFs) and a major contributor to the total toxicity (I-TEQ) of sediments in the Gulf of Finland (Isosaari et al., 2002; Verta et al., 2007). However, it is evident that atmospheric deposition is the dominant source of PCDD/Fs to other offshore areas in the Baltic Sea. A major uncertainty for the total budget of PCDD/Fs in the Baltic is the input from rivers (e.g. Assmuth and Jalonen, 2005).

The concentrations of PCDD/Fs in many Baltic Sea fish and fish products exceed the safety limits for foodstuffs set by the EU (EC 1881/2006) and have led to recommendations to restrict the use of contaminated fish for human consumption. The findings by Verta et al. (2007) did not support suggestions that Kymijoki or any of

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the known point sources significantly influence the congeners that are most abundant in Baltic herring and salmon (2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD). Instead, the regional distributions of sediments in the Baltic Sea indicated that atmospheric deposition may act as a major source of these congeners (Verta et al., 2007).

Kymijoki is the fourth largest river in Finland and is located in the south-eastern corner of the country. The area has a long tradition of paper manufacturing and related industry and the river has been heavily polluted by effluents from pulp mills and the chemical industry. Up to 24 000 ton of wood preservative, known as Ky-5, was manufactured in the upper reaches of Kymijoki, in Kuusankoski, between 1940 and 1984. An unknown amount of the product and its impurities ended up in the river and was subsequently transported to the Gulf of Finland. The modelling of river hydraulics and sediment transport using a one-dimensional unsteady river flow model with 19 sections between the pollution source and the Gulf of Finland did not suggest a notable decrease in the PCDD/F concentration in surface sediment for many decades (Malve et al., 2003). In the Gulf of Finland sediments the present background concentration has reached some 75 km from the river estuary (Isosaari et al., 2002). These findings called for continuous estimation of contaminant transport to the Gulf of Finland.

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF), especially higher chlorinated dibenzofurans, occurred as impurities in Ky-5. The main fraction of PCDD/Fs in Ky-5 consisted of chlorinated furans (some 87% of the total concentration of PCDD/Fs and 95% of I-TEQ, Vartiainen et al., 1995). The product impurities consisted mainly octa-, 1,2,3,4,6,8,9-hepta-, 1,2,3,4,6,7,8-hepta-, 1,2,4,6,8,9-, hexa-, and 1,2,3,4,6,8-hexachlorodibenzofurans and the concentration in the product varied from 65 to 200 $\mu\text{g g}^{-1}$ (Kitunen et al., 1985; Vartiainen et al., 1995). The solid impurities that were formed in the process probably contained even more

PCDD/Fs and their disposal into the river during the monthly cleaning operations lasted until the late 1960s. An accidental explosion and resulting fire at the plant in 1960 was a further cause of PCDD/F release.

A chloro-alkali plant and a pulp and paper mill, both potential PCDD/F sources, were also located in the immediate vicinity. The production of chlorine in the chloro-alkali process may have been a source of highly contaminated sludge until the use of graphite electrodes was discontinued (Rappe et al., 1991; Bright et al., 1999). The application of chlorine gas for pulp bleaching before its replacement with less hazardous forms of chlorine is another potential source (e.g. Rappe et al., 1989; Koistinen et al., 1992; MacDonald et al., 1998).

This paper describes the spatial extent of PCDD/F contamination in the River Kymijoki including an estimation of the volume and location of contaminated sediments. The resuspension and transport of PCDD/F contaminated sediments to the Gulf of Finland in the Baltic Sea was also studied and compared with an estimate of other (atmospheric) sources to reveal if the river forms a significant source of PCDD/Fs in the Baltic Sea. This study is a part of a decision framework (alongside ecotoxicological and human risk assessment and epidemiological human studies) that will form the basis for risk management strategy and possible remediation of contaminated sediments in the River Kymijoki.

2. Materials and methods

2.1. Study area

The study area was a 130-km long river stretch with two main branches between Lake Pyhäjärvi and the Gulf of Finland including the coastal region 100 km west and 50 km east from the river estuary.

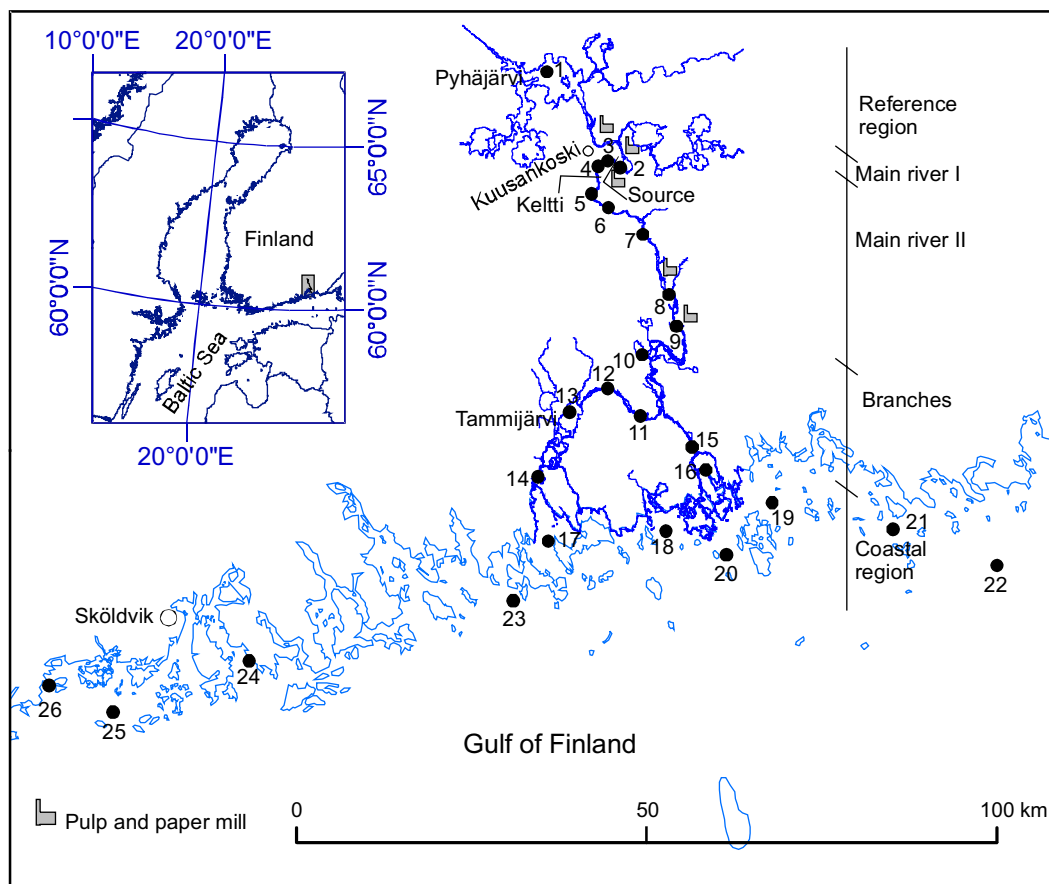


Fig. 1. The study area and the sampling sites numbering for surface sediment samples, sediment cores and sediment traps (for river regions, see the text).

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