RISKS OF CONTAMINATED SEDIMENTS BY RIVER KYMIJOKI

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Introduction

The sediments of the river Kymijoki draining to the Gulf of Finland are heavily polluted from pulp and paper and chemical industries (chlor-alkali and chlorophenol production) established in the 1940s. Wood preservative, called Ky-5, was manufactured at the upper reaches of Kymijoki in the City of Kuusankoski from 1940 to 1984, from which an unknown amount of the product and impurities ended up in the river and finally to the Gulf of Finland. The product consisted mainly of polychlorinated phenols (PCP), main components 2,3,4,6-tetrachlorophenol (83%), pentachlorophenol (8%) and 2,4,6,-trichlorophenol (6%). Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), especially higher chlorinated dibenzofurans occurred as impurities in the PCP product.[1] In a preliminary study sediments of the Kymijoki were observed to contain high levels of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) with a maximum concentration of over 400 000 ng g^{-1} (3-6 cm, site 3).[2,3] Hepta- and octachlorinated dibenzofurans, typical impurities of the tetrachlorphenol produced, represent from 79 to 95 % of the total PCDD/Fs in sediments. The sediments are polluted also by mercury (Hg) from chlor-alkali production and the use as slimicide with a maximum concentration of 33 µg g^{-1} in sediments (125-150 cm, site 3).

From 1996 research has been carried out in the Kymijoki region as well as in the estuary and in the Gulf of Finland to:

- Examine the spatial extent of the contamination
- Elucidate and model the transport of the sediment and pollutants
- Predict future changes
- Investigate ecotoxicological effects and assess risks on aquatic biota
- Assess human health risks
- Find out restoration needs and preconditions

These studies form the basis of the risk management strategy and possible remediation of contaminated sediments currently under consideration in the Southeast Finland Regional Environment Centre (Fig. 1).

Spatial extent and and burden of contaminated sediments

The study area is a 130-km long river stretch with two main branches between Lake Pyhäjärvi and the Gulf of Finland. The location of soft sediments in the river was estimated by echo and acoustic-seismic surveys. Sediment cores were collected during 1997-2003 through the soft sediment until the hard river bottom or glacial clay layer was reached. Sediment cores from 220 sites were sliced to 25 cm sub samples. Mercury concentration was analysed from each sub sample of 130 cores and PCDD/F concentration from sub samples of 10 sediment cores and additionally from 35 surface (0-3 cm) sediment samples from 15 locations in the river (Fig 2).[4] The emission histories of Hg and PCDD/F in the river were spatially and temporally nearly identical starting during 1940s and having maximum during early 1960s. The linear regression equations between Hg and PCDD/F concentrations were used to calculate overall PCDD/F burden. Additional surveys were conducted in the Gulf of Finland.[5]

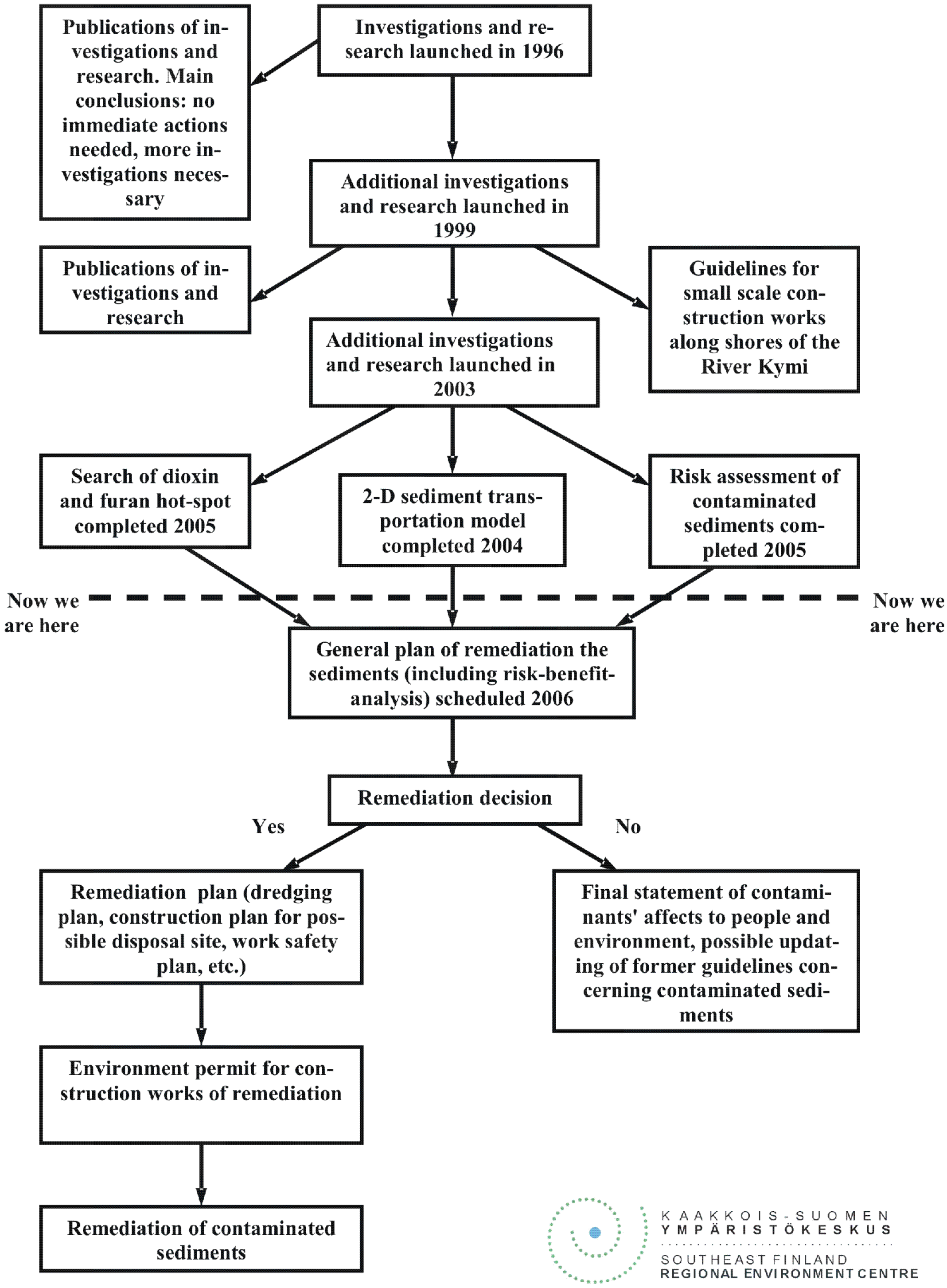

Figure 1. A schematic diagram of river Kymijoki risk assessment and remediation project.

The total burden of Ky-5 derived PCDD/Fs was estimated as ca 5960 kg (17.3 kg as I-TEQ) in the river and 1770 kg (12.4 kg as WHO-TEQ) in the Gulf if Finland. The total volume of contaminated sediment (exceeding the level of 500 pg I-TEQ g^{-1} dw) in studied river course was $5 \cdot 10^6$ m^3, the majority of which located in the lake Tammijärvi (Fig. 2). The most contaminated area immediately downstream the pollution source with extremely high concentrations (max 292 000 ng g^{-1} or 1 060 ng I-TEQ g^{-1} dw at 0-25 cm, site 3) contained some 23% from total PCDD/F burden in the river.[6]

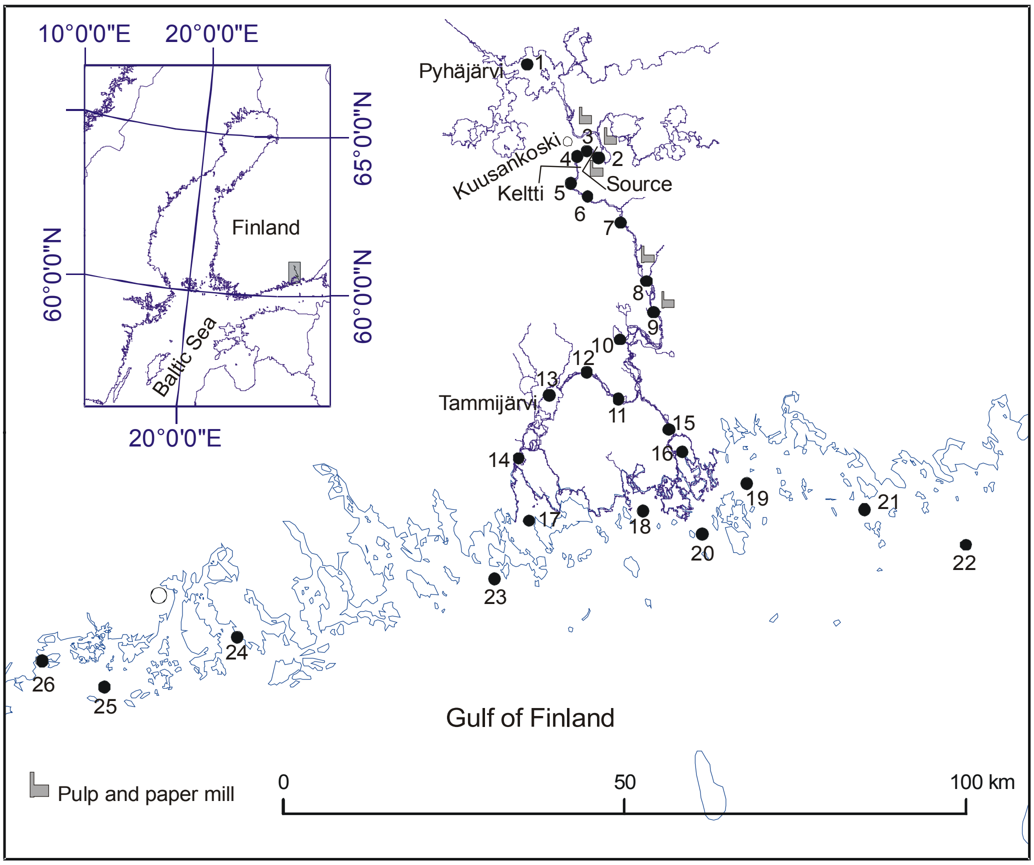

Figure 2. The study area and the map showing the major sites for sediment sampling (offshore sites in the Gulf of Finland not included[5]).

Transport modeling and future trends

Most of the PCDD/Fs entering from the hot spot accumulate at the lower course of the river. The total PCDD/F flux to the Gulf of Finland was estimated as 13 kg (44 g I-TEQ) in 2001 (Fig.3).[4] Earlier studies have shown that Kymijoki is the major source of PCDD/Fs in the sediments of the gulf representing more than 90% of the total load of PCDD/Fs since 1940s.[5] One dimensional flow and transport model was used to simulate the transport of PCDD/F compounds and to assess the impact of a possible restoration dredging of the most contaminated sediments.[7] Using the estimated trend in PCDD/F loading downstream concentrations were calculated until 2020. If contaminated sediments are removed by dredging, the temporary increase of PCDD/F concentrations in downstream water and surface sediments will be within acceptable limits. Long term predictions indicated only minor decrease in surface sediment concentrations with no remediation but a major decrease if the most contaminated sediments close to the emission source were removed.

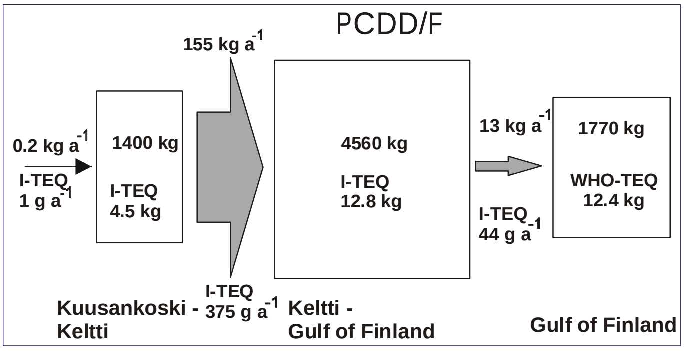

Figure 3. A schematic diagram showing the burden of PCDD/Fs in different river regions and transport between the pools and to the Gulf of Finland in 2001.[4]

A more detailed assessment of the effects was made using a two dimensional sediment erosion and transport model based on SMS (Surface-water Modeling System) for hydrodynamic modeling (U.S. Army Corps of Engineers TABS-MD). This indicated that with no remediation 25-50% of the dioxins and 20-40% of Hg sedimented in the immediate sedimentary basins would be transported downstream within the next 30 years. The major sites of erosion were identified. Removing and/or capping these sites (36 000 m^3, 40% of contaminated sediments between the source and Keltti) would significantly reduce the PCDD/F transport downstream. The major fraction (70-80%) of Hg at Keltti station, however, is originated from other than the identified sites (and 30-40% from upstream, Fig 3.). Consequently, the residual contaminants for PCDD/Fs and Hg has to be considered when evaluating management strategies.

Ecotoxicological effects

High toxicity of sediment to exposed micro-organisms and high frequencies of mentum deformities in midge (*Chironomus* spp) larval populations were measured in areas with high pollutant concentrations in sediments but in some occasions at the lower river Kymijoki as well. Sediments did not clearly affect the survival of midge larvae, but growth and development tended to be slower in the most contaminated sediments.[2] Sediment contamination seems to cause changes in benthic assemblages, but any direct effects on measured benthic parameters were masked by many factors.[8]

The fish muscle showed highly elevated levels of polychlorinated diphenyl ethers (PCDE) that were also impurities of Ky-5 product, but only slightly elevated PCDD/F levels compared with the levels in the same species in Finnish freshwater and in the Baltic Sea. Ky-5 impurity congeners could be observed in fish in Kymijoki river, but only occasionally in the estuary. Baltic salmon and herring showed an order of magnitude higher level of PCDD/Fs than river Kymijoki fish. Concentrations in liver were orders of magnitude higher than in muscle for most of the contaminants.[9]

Comparison of the contaminant concentrations in the benthic invertebrates with the concentrations in fish indicated that the contaminant bioavailability and bioaccumulation were not directly proportional to concentrations of the contaminants in sediments or at lower trophic level. The PCDD/F congener composition in fish was different to that in benthic invertebrates. For certain 2,3,7,8-substituted PCDD/Fs biomagnification was observed.[10]

Human health studies

Plasma concentrations of PCDD/Fs were measured in fishermen from two locations in the Kymijoki area, representing fishermen near the pollution source and the Baltic Sea area. The concentrations of the Baltic Sea area were about twice as high as in the vicinity of the pollution source (170 and 92 pg I-TEQ/g fat, respectively), indicating that the Baltic Sea is more relevant source of PCDD/Fs when compared to river Kymijoki.[11,12]

To examine the prevailing levels of PCDD/Fs in human milk in the Kymijoki area, milk samples from 18 mothers were collected in 1997 (in the Baltic Sea and in the inland river areas). Previous studies have shown the association between high dioxin exposure and demarcated hypomineralization lesions of teeth.[13] Compared to the figures reported earlier in Finland, neither the prevalence of dental lesions nor the levels of PCDD/Fs in human milk were increased in residents of the studied areas compared to general population.[14]

Standardized incidence ratios and relative risks for total cancer and 27 cancer subtypes (diagnosed in 1981-2000) were investigated in the Kymijoki river area by using a geographical information system, which holds register-data from the Population Register Centre, Statistics Finland and Finnish Cancer Registry. Cancer incidence in all people (n=188,884) and in farmers (11,132) living close to the river was at the level expected based on national rates. The relative risk for total cancer was non-significantly but consistently above 1.00 among those living <1.00 km from the river. Despite the limitations of exposure assessment, it cannot be excluded the possibility that residents near the river may have contributed to a small increase in cancer risk, especially among farmers.[15]

Risk asessment

The aim of the ecological and health risks assessment was to disclose the risks that the present situation of the contaminants in Kymijoki sediments incur. No remediation scheme or action and their impacts were calculated or compared to the present risks. This was a conscious choice since a general remediation plan was not available and since the decision of the necessity of remediation actions was still pending.

The risk assessment calculations included human and animal intake calculations of PCDD/F and Hg. Also PCDE was considered as a possible contaminant. Since no tolerable intake levels for PCDEs has been set, the risks could not be calculated. Judged from the TEF-values presented in the literature a preliminary estimate was, however presented that accounted for some 10 % of the risks from PCDD/Fs and PCBs. Different intake route calculations were made by US-EPA procedures and the probability of exceeding the total tolerable daily intake was estimated with a stochastic analysis tool.

The average total daily intake of PCDD/Fs and PCBs for a human living near of the river Kymijoki, swimming regularly in the river, eating only fish from the river, eating some game bird and fish roe from the river was estimated to be 2.6 pg WHO-TEQ kg^{-1} d^{-1} from which PCB accounted for 35%.[16] This hypothetical lifestyle, probably an unrealistic one, was chosen to attain an estimate of a maximum risk, and to find out the significance of different exposure and intake routes. The most significant single intake route was background exposure, 0.98 pg WHO-TEQ kg^{-1} d^{-1} from which PCB accounted for 91%. The probability of exceeding WHO upper limit value of 4 pg WHO-TEQ kg^{-1} d^{-1}, was estimated to be 6%. The total dietary intake of the average Finnish population is 1.5 pg WHO-TEQ kg^{-1} d^{-1}.[17]

The average total daily intake of Hg was estimated to be 0.36 μg kg^{-1} d^{-1}. The most significant single intake route was eating fish (pike), 0.27 μg kg^{-1} d^{-1}. The probability of exceeding WHO limit value 0.23 μg kg^{-1} d^{-1} was estimated to be 62%.[16] The new recommendations for fish eating in Finland released by the Finnish Food Safety Authority in 2005 substantially reduce the risks of exposure; for PCDD/Fs ca 20% and for Hg ca 56%. Consequently, the risks posed by Hg exceed those from PCDD/Fs and can not be ignored when making remediation decisions. The ecotoxicological risks were mainly posed to fish eating predators, especially otter (*Lutra lutra*).[16]

General remediation plan as a decision making tool

Main purpose of the general remediation plan (GRP) is to gather and reveal all facts necessary for the remediation decision. The aim is ambitious, and the scope of research and investigations has been wide and multidisciplinary. At the same time the aim is unavoidable, as a well-founded decision of the remediation must be achieved.

GRP should answer questions what, where, how much, how to and at what price? As sedimentation areas in the river are partly in continuous transition and areas of sedimentation are ranging from few hundred square meters to few square kilometers, the general remediation plan can not answer all details. GRP plan should be finished by the end of 2006. In case that remediation decision is made to certain sedimentation spots, a more detailed plan is to be carried out. Accordingly a pilot remediation project is launched at one site in 2006 where sediments will be encapsulated by building a rock embankment on the riverside.

Acknowledgements

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