

## PCDD/PCDF in sediments of arctic rivers in the European part of Russia

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### Introduction

Highly developed timber and pulp and paper industries on the territory of the arctic rivers catchment area in European North presumes the presence of PCDD/PCDF in its ecosystems. PCDD/PCDF belong to POPs category of "unintended production" and result from bleached pulp production and application of chlorophenolic biocides in timber industry<sup>1</sup>.

The data on the levels, space distribution and congeners profiles of PCDD/PCDF in the sediments of the river the Northern Dvina in hydrodynamical conditions of the tidal estuary were reported earlier<sup>2</sup>. This paper is concerned with the results of the study of the sediments of the flat river Vycheгда - the largest tributary of the Northern Dvina river.

Syctyvcар pulp and paper mill that is situated in the middle stream of the Vycheгда has been producing bleached pulp for 35 years. Nowadays, following the world practice, the mill, on its own initiative, carries out the monitoring of PCDD/PCDF in bleach plant wastewaters. This allows to estimate PCDD/PCDF emission with the mill effluents, to find out their congeners profile. The production of bleached hardwood pulp is performed according to the ECF technology, and the concentrations of 2,3,7,8-TCDD/TCDF in the waste waters are below the minimum detection levels of BAT effluent limitations of US EPA<sup>3</sup>. The load on the river depends on PCDD/PCDF in the wastewaters of bleach plant of soft pulp production that is now on the transition to ECF technology.

### Materials and methods

The sampling was carried out in 2003 at the end of the summer low river discharge when the fine particles deposition reaches its highest level. 23 samples of surface sediments were collected on the part of the river 147 km long including the sites upstream and downstream from the mill effluents discharge point. 10 samples, analyzed for the PCDD/PCDF concentrations, were selected on the basis of the levels of EOX, polychlorinated phenols, guaiacols and catechols, organic carbon ( $C_{org}$ ) and taking into the account grain-size composition of the sediments and the distance of the sites from the pulp and paper mill and the large settlements.

$C_{org}$  was analyzed by the method of dry combustion on CHN-analyzer. Grain-size composition was determined by sieving followed by sedimentation. Fractions < 0,01 mm were estimated by measuring the rate of sedimentation based on Stokå's law. The PCDD/PCDF analyses were performed in the laboratory of analytical ecotoxicology of the Institute of evolution and ecology problems of RAS by GC/MS<sup>4</sup>. EOX was determined on AOX-analyzer (IDC). Chlorophenols were analyzed in the form of their acetyl derivatives on GC with ECD detector.

### Results and discussion

PCDD/PCDF were found in all analyzed samples both upstream and downstream from the pulp and paper plant effluent discharge point. Concentrations ranged from 164.88 to 2442.39 pg/g of air-dried sediment. Toxicity of the sediments comprised the values from 6.269 to 118.491 pg/l-TEQ/g. Based on the organic carbon of the sediments PCDD/PCDF, concentrations ranged 8750-58712 pg/g  $C_{org}$  or 346-2850 pg l-TEQ/g  $C_{org}$ . These data fall into the interval of benchmark values for estimation of total PCDD/PCDF or some selected dioxin congeners in sediments<sup>5</sup>.

The contribution of PCDD comprises 76.7-96.9% of the total concentrations PCDD/PCDF and 85.2-97.1% to the toxicity of the sediments, that allows to rule out incineration and combustion processes as an important source of the sediment contamination in the region. OCDD is the dominating congener on all investigated sites of the river.

As shown in the figure 1, the influence of pulp bleaching on sediment contamination is observed on a narrow site of the river, 0.1-0.5 km downstream from the mill effluent discharge, where the highest EOX levels are recorded and 3,4,5-trichloroguaiacol – the indicator of pulp bleaching with molecular chlorine - is found. Levels of PCDD/PCDF

here are not elevated, but the association of pollution with pulp bleaching is supported by their congener profile: OCDD prevails and the toxicity of the sediments is 86% caused by 2,3,7,8-TCDD and 2,3,7,8-TCDF. This agrees with PCDD/PCDF profile, found in bleach plant waste waters of the mill: OCDD prevails, 2,3,7,8-TCDD and 2,3,7,8-TCDF, that are specific for pulp bleaching, are present in equal concentrations and their contribution into total toxicity reaches 91.0-99.0%.

In the other samples of the sediments, collected upstream and downstream from the pulp and paper mill, the congener profiles differ from the ones taken near the effluents discharge but are close to each other. Highly chlorinated congeners, OCDD and HpCDD, prevail and their contents amount to 80% - 82.7% of PCDD/PCDF. The prevalent congeners, in terms of the total toxicity, are 2,3,7,8-TCDD (54.5%), 1,2,3,7,8-PeCDD (21.7%) and 1,2,3,4,7,8-HxCDD (7.8%). Distribution of the above mentioned congeners suggests sodium pentachlorophenolate (PCPNa) as the main source of PCDD/PCDF contamination of the river sediments. The contribution of sodium pentachlorophenolate into the formation of dioxin pollution is characteristic of the sediments in inner watercourses in Northern Europe and the Baltic<sup>6</sup>. Unlike the widespread biocide Ky-5, containing highly chlorinated OCDF and 1,2,3,4,6,7,8-HpCDF, home biocide predominantly contained 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,7,8-HxCDD, 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD.

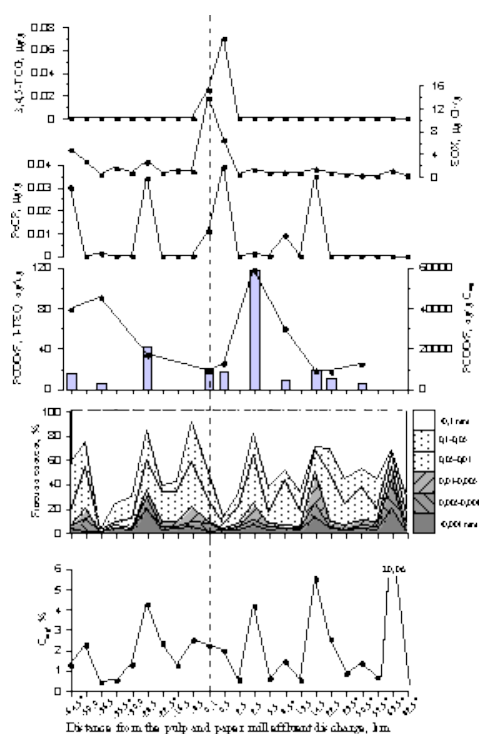


Figure 1. Distribution of chlorinated organic compounds in the sediments of the river Vycheгда

observed, when excluding the sediment samples, collected on the sites of the river 28.5 km upstream and 14.5 km downstream from the pulp and paper mill effluent discharge point. These sediments are characterized by elevated contents of  $C_{org}$  and fractions  $<0.01$  mm.

It can therefore be supposed that PCDD/PCDF levels and their distribution in the river Vycheгда sediments in its middle stream result from the combination of the two main sources: pulp bleaching effluents and PCPNa.

Hydrophobic chlorinated organic compounds, formed during pulp bleaching, are sorbed mainly on fine particles of organic matter from the effluents (mainly chlorolignin) with low sedimentation rates. Based on the above facts, it can be inferred that at the high speed of the flat river Vycheгда with relatively coarse sediments, chlorinated compounds in the sorbed form migrate along the diluted effluent stream. PCDD/PCDF profile of pulp bleaching is observed on the narrow site near the effluents discharge. Farther down the stream it is disguised by PCDD/PCDF of more intensive source of PCPNa origin.

The specific picture of PCP and PCDD/PCDF distribution in the sediments of the investigated area of the river links

It should be noted, pentachlorophenol is present together with 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol and was only found in 8 samples out of 23. Moreover, dioxins are found on the sites of the river where no PCP is detected. The highest concentration of PCDD/PCDF which the profile that is characteristic of PCPNa biocide is discovered on the other side of the river 2.5 km downstream from the pulp and paper mill effluents discharge point.

As it can be seen from the figure 1 the sediments on the investigated sites of the river are mainly coarse (alevrite) with significant admixture of sand. High correlation ( $r = 0.89$ ,  $n = 22$ ) is established between the  $C_{org}$  content and the fraction with particle size less than 0.01 mm.

Pulp and paper mill effluents have a little influence on the formation of the organic matter in the sediments of the river. The sediments with the elevated levels of organic carbon (4.1-5.5%) are characterized by the raised content of finer fraction with particle size less than 0.001 mm, nitrogen content of 0.2-1.18% and are located on the sites of the river upstream and downstream from the pulp and paper mill.

High content of organic matter and elevated content of fine particles in the sediments do not correlate with PCDD/PCDF levels, which can be clearly seen from PCDD/PCDF distribution per  $C_{org}$  unit. The correlation between PCDD/PCDF and  $C_{org}$  ( $r = 0.80$ ), between PCDD/PCDF and

content of the fractions with particle size  $< 0.01$  mm ( $r = 0.87$ ) is observed, when excluding the sediment samples, collected on the sites of the river 28.5 km upstream and 14.5 km downstream from the pulp and paper mill effluent discharge point. These sediments are characterized by elevated contents of  $C_{org}$  and fractions  $<0.01$  mm.

contamination with intensive usage of PCPNa by timber industry in the catchment area of the river in the past years. It is unlikely to be associated with the influence of PCP residual amounts "stored" in "hot spots" type soils and requires further investigation.

## References

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