

## CONTAMINATION OF NATURAL MATRIXES WITH PERSISTENT ORGANIC POLLUTANTS AS A RESULT OF WOOD TREATMENT IN THE NORTHERN REGIONS OF RUSSIA

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### Introduction

Discovery and assessment of the sources of biosphere contamination with persistent organic pollutants (POPs) is an actual problem up to now to take measures to remove them out of the environment to provide its steady development<sup>1</sup>. Application of chlorophenolic biocides in the past remains to be the significant source of ecosystems contamination with polychlorinated phenols and polychlorinated dioxins and furans (PCDD/PCDF) even nowadays<sup>2</sup>.

Extensive application of sodium pentachlorophenolate (PCP-Na) technical grade preparates in Russia for treatment of wood designed for export proceeded in our country for nearly 30 years up to 1987. In this paper the results of the analyses of the chemical composition of PCP-Na formulation produced in Russia are presented as well as the pollution levels in the samples of soil and sediments collected in the basins of two northern rivers - the Onega and the North Dvina 5-12 years after ceasing the PCP-Na application in this region.

### Methods and materials

During 1996-2000 four sawmills situated on the territory of Arkhangelsk district and producing wood for export were investigated.

The map-schemes of soil sampling on each sawmill were worked out considering mutual space distribution of the main technological processes - sites of PCP-Na supply, preparation of PCP-Na solution for wood treatment as well as treated wood transportation on the sawmill territory and the relief peculiarities. Map-schemes for surface sediments sampling in coastal zones of the northern rivers in the vicinity of the sawmills were composed according to their morphological and hydrodynamic parameters.

The analyses of the PCP-Na preparate, soil and sediment samples for chlorinated organic compounds, including PCDD/PCDF, collected in different years of monitoring were performed by the laboratory of Severtsov Institute of Ecology and Evolution of Russian Academy of Sciences (Moscow) and by the laboratory of Russian scientific research center of Extreme situations (Moscow). The analyses were performed by GC-HRMS using sample treatment procedure described elsewhere<sup>3</sup>.

The analyses of natural matrixes for pentachlorophenol (PCP) levels were carried out in the form of its acetyl derivative by the authors' laboratory using gas chromatography on fused silica capillary column and electron capture detector<sup>4</sup>.

### Results and discussion

The investigated technical prepate of PCP-NA produced in Russia included, in addition to the main component, some amounts of 2,3,4,5-tetrachlorophenol (3,4 %), 2,3,4,6-tetrachlorophenol (2,2 %), 2,3,5,6-tetrachlorophenol (2,2 %), 2,4,6-trichlorophenol (2,0 %). Among the neutral chlorinated organic compounds (3,6 %) hexachlorobenzene prevailed.

The total congeners concentration of 2,3,7,8-substituted congeners of PCDD/PCDF in the above mentioned PCP-Na prepate comprised 32,2 mg/kg. PCDDs prevailed (83,24 %). The main congeners were 1,2,3,4,6,7,8-HpCDD and 1,2,3,4,7,8-HxCDD - 33,7 % and 21,75 % respectively. The Russian PCP-Na prepate differed from analogous prepatates produced abroad for its significant contribution of 2,3,7,8-TCDD (11,33 %) and 1,2,3,7,8-PeCDD (7,7 %). The contribution of OCDD and OCDF was not large - 5,6 % and 12,0 % respectively.

The concentration of PCDDs/PCDFs expressed in I-TEQ comprised 5938,9 µg I-TEQ/kg. That value may be compared with PCP/PCP-Na formulations produced abroad - PCDDs/PCDFs levels ranging from 45 to 2701,81 µg I-TEQ/kg according to different literature data<sup>5,6</sup>. The main contributors to the total toxicity of the Russian PCP-Na technical prepate were chlorinated dioxins (97,7 %). Among them three most toxic congeners prevailed - 1,2,7,8-TCDD, 1,2,3,7,8-PeCDD and 1,2,3,4,7,8-HxCDD comprising 61,55 %, 20,85 % and 11,8 % of the total I-TEQ of the prepate respectively. The contribution of 2,3,7,8-TCDD comprised 62,9 % of PCDDs in I-TEQ.

From the modern point of view on the TEF values for PCDDs and their risk assessment for fish, human beings and mammals, the ecological danger of the Russian PCP-Na prepate for use as a biocide seems to be especially high<sup>7</sup>.

5-12 years after ceasing the application of PCP-Na at all sawmills high levels of residual PCP in non-ionized form were still detected in the soil samples of the sawmills. The vertical distributions of PCP in soils as well as its horizontal distributions were alike at all investigated sawmills. The largest contamination levels were detected on the PCP-Na supply sites, and the sites of PCP-Na solution preparation and wood treatment using method of dipping. The levels of PCP in the upper layers of the soil (0-25 cm) comprised 140-766 µg/g of dry material. The PCP concentrations decreased with increasing the distance of sampling points from the above-mentioned sites, ranging from 1,4 up to 66,3 µg/g and were associated with PCP solution loads.

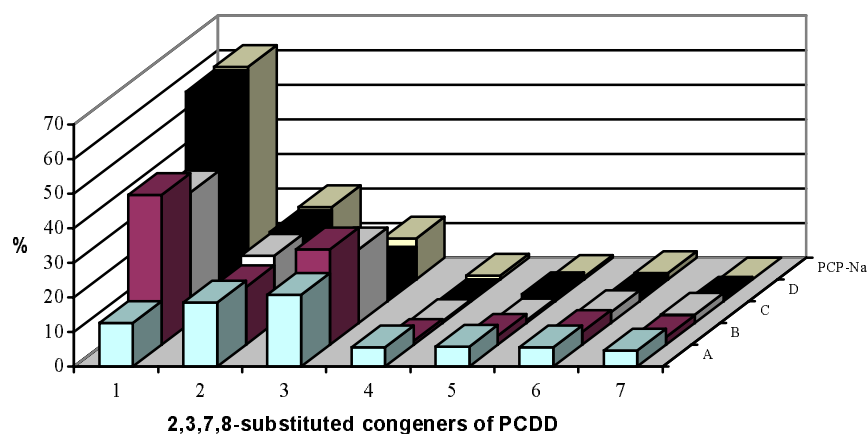
As for the vertical distribution PCP was found, in the non-ionized form in the soil samples of all investigated sawmills on the depth 60-100 cm in the levels 3-5 times and more higher than in the top layers. On the wood treatment sites the maximum concentrations were found on the depth 60 – 80 cm and were equal to 1060 and 1140 µg/g on the territories of two sawmills. The levels of PCDD/PCDF congeners in the top layers of the soil ranged from 0,2 to 224,0 µg I-TEQ/kg of dry material with maximum concentrations on the wood treatment sites. The trends of horizontal distributions of PCDDs/PCDFs as well as PCP were alike for all investigated sawmills. The

vertical migration of PCDDs/PCDFs into lower layers of the soil was demonstrated. The congeners concentrations on the depth of 60-80 cm was found in the range of 211-7910  $\mu\text{g}/\text{kg}$  or in 6,4-117,0  $\mu\text{g}$  I-TEQ /kg.

The results of the analyses showed that on the territories of the investigated sawmills the depositories of residual amounts of PCP and PCDDs/PCDFs formed as the result of long-term pollution input. The comparative analysis of the homologous and isomer-specific profiles of PCDDs/PCDFs in the soil samples of two sawmills and Russian PCP-Na prepate had demonstrated their similarities both for the prevailing PCDDs (comprising 59,8-86,2 % of total congeners concentrations and 70,1-90,0 % in I-TEQ) and the main contribution of 2,3,7,8-TCDD (12,4-60,5%), 1,2,3,6,7,8-PeCDD (11,3-26,5 %) and 1,2,3,4,7,8-HxCDD (17,2-37,1 %) expressed in I-TEQ.

In the surface sediments of the small rivers and the North Dvina and the Onega estuaries 8-12 years after ceasing PCP-Na application the highest levels of PCP comprised 0,790 and 4,920  $\mu\text{g}/\text{g}$ . The background level of PCP in the sediments of the North Dvina varied from 0,001 to 0,008  $\mu\text{g}/\text{g}$ . In the sediments of the river estuaries hexachlorobenzene was also determined in the concentrations ranging from 53 up to 701 ng/g of dry material. The PCDDs/PCDFs levels varied in the interval 126,9-2666 ng/kg (9,0-167,7 ng I-TEQ /kg), the values that are 2-3 orders of magnitude higher than background levels. Tendency of decreasing PCDDs/PCDFs levels in sediments with increasing distance downstream the sawmills was demonstrated during the investigation. As can be seen from fig.1, the similar isomer-specific profiles of PCDDs/PCDFs in the samples of sawmills soils and sediments collected in the rivers near these sawmills give the

Normalized isomer-specific PCDD profiles (in I-TEQ) in Russian technical PCP-Na prepate, sawmill soils and northern rivers sediments



Legends: A, B - soil samples collected at sawmills 1 and 2, respectively; C and D - sediments collected in the estuaries of the Northern Dvina and the Onega, respectively.

strong evidence of the identity of their contamination source as well as the migration of pollutants from the contaminated territories into the waters-streams up to now. In such situations PCP may serve as an indicator of potential presence of PCDDs/PCDFs in the natural matrixes as the result of PCP-Na long-term application for nearly 30 years.

The received results give the possibility to predict the situation with contamination on the territories where the PCP-Na preparate and treated wood had been used.

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