

## Predecessors of dioxins - DDT and PCBs in irrigated agrolandscapes of Russia and Uzbekistan

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### 1. Introduction

DDT insecticide and polychlorobiphenyls (PCBs) are the widespread predecessors of dioxins in the environment. PCBs are of wide using, mainly in the electrotechnical industry in the past, as well as they were utilised as the solvents and carriers of solid organochlorine pesticides. Furthermore, all these compounds form dioxins not only during pyrolysis and incineration, but influence also at various metabolic processes for example, at oxidation process in the presence of hemoproteids. Ecotoxicological situation is getting more dangerous especially under conditions of irrigation agrolandscapes, when the residual quantities of DDT and PCBs can accumulate in bottom sediment of different water sources. In this relation, the given paper is aiming to estimate the distribution of DDT and PCBs compounds in main components (soils and waters) of irrigation agrolandscapes of Russia and Uzbekistan.

### 2. Materials and methods

The irrigated floodplain agrolandscapes of the Moscow region were chosen as the first object for monitoring. These landscapes are intensively used for vegetable production. The biogeochemical approaches which include temporal and spatial assessment of pollutant migration under the influence of biogenic and abiogenic factors allow the samples to be collected in various elemental landscapes of individual soil-geochemical catenas from eluvial through transeluvial and transeluvial-accumulative, up to supraaqualous and subaqualous landscapes. 28 soils were sampled under cabbage, 3 - under carrot and 2 - under fodder beat as well as 6 water bodies and 3 bottom sediments. Kuban low plain (Krasnodar region, Russia), whose floodplain riparian zone of the Kuban river is intensively used for rice growing, was chosen as the second object for monitoring. The same biogeochemical approach was applied for sampling of 21 soils, including 10 under rice, 1 - under winter wheat, 3 - under cabbage, 5 - under vineyards, 2 - under orchards as well as 2 surface water bodies and 19 bottom sediments were chosen for sampling. Four bottom sediments were sampled from rivers and the Krasnodar water reservoir, 5 ones - from irrigated systems, 7 - from the Azov Sea bays, and 3 - from the Black Sea bays. Samarkand oasis, situated in the Zerafshan river valley, was chosen as the third object for monitoring. Samarkand oasis is one of the biggest Uzbekistan region for production of cotton, vegetables and fruits. Using a similar

# TOXA (po)

approach, 71 samples of soils were collected, among them 57 - under cotton, 8 - under tobacco, 5 - under vineyards, and 1 - under orchard as well as 8 samples of waters and 7 samples of bottom sediments were taken from the rivers, the Kattakurgan water reservoir and irrigated systems. The qualitative and quantitative analyses of organochlorinated compounds were carried out using chromatography/mass spectrometry with a Finnigan, model 4000, based on a modified technique of the US EPA (No. 625)<sup>1)</sup>. The pesticides and polychlorobiphenyls were extracted from wetted after drying samples and water samples by a mixture of acetone and hexane in the ratio 1:4 and 1:5, respectively, for soil and water. The extraction efficiency of the standards prepared in soil was  $80 \pm 10\%$  and in water,  $90 \pm 5\%$ . The metrological characteristics of the applied technique were the following: detection limits of organochlorine compounds in soil were 50 ng/kg and in water, 2 ng/L.

## 3. Results and discussion

### 3.1. Moscow region

Five river valleys of the Moscow region used intensively in irrigated vegetable production were monitored: Yachroma, Istra, Klyazma, Moskva and Oka rivers. Considering the content of  $\Sigma$ DDT, the highest mean values of this pesticide in soils of Klyazma river floodplain, which exceeded baseline (100 mkg/kg) as such as 6 times and in some individual samples - 12 times were determined. The minimal values of  $\Sigma$ DDT compounds (pesticide and its metabolites) were determined for soils of Oka river floodplain where both individual and mean contents were lower than that ones of the baselines. The highest contents of  $\Sigma$ PCBs were determined in floodplain soils of the Yachroma river and these mean values exceeded the approximate permissible concentration (APC) of polychlorobiphenyls for soils (60 mkg/kg) by 12 times and in some individual samples - 23 times. In other floodplain soils the  $\Sigma$ PCB content was lower than the APC. Thus, ecotoxicological monitoring of irrigated vegetable agrolandscapes placed in floodplain soils of various rivers of the Moscow region showed that the total content of residues of DDT (78,3%) was higher than that of its metabolites (21,7%), thus attesting to the low selfpurification capacity of these soils. In some cases, the reason could be due to the existence of permanent input sources of DDT, even though its use was prohibited from 1970.

### 3.2. Kuban low plain

In soils under rice, the mean content of  $\Sigma$ DDT was compared with that of the baseline and in some individual samples it was exceeded 3-4 times. Considering the whole pollution of rice soils by chlororganic compounds, the part of PCB homologies was lower than that of DDT residues. This fact can be explained by intensive application of this pesticide over the first years of rice production in the Kuban low plain. Thus, taking into account that rice and cabbage were predominant crops in the irrigated agrolandscapes of the Kuban low plain, one might conclude that the main pollution of soils was connected with DDT and its metabolites. In some places, various homologies of polychlorobiphenyls, were prevalent pollutants apparently due to the regional air pollution by industrial emissions. The mean load of DDT was lower than the load of its metabolites, testifying to the lack of recent sources of this pesticide input into the soils of the Kuban low plain. Among all monitoring groups of water sources, the highest content of  $\Sigma$ PCB was detected in bottom sediments of the rivers and the Krasnodar water reservoir, on average 1,9-2,3 times higher than in other water sources. Thus, the ecotoxicological assessment of agricultural and marginal areas of the Kuban low plain showed that the load of DDT residues (insecticide itself

and its metabolites DDD and DDE) was compared with the load of industrial pollutants - PCBs. Furthermore, the up-to-date load of DDT on soils is equal or less than that of its metabolites. This can be supported by the absence of significant sources of the input of this insecticide into irrigated agrolandscapes of the Krasnodar region.

### 3.3. Samarkand oasis

In soils under cotton, the mean amount of  $\Sigma$ DDT was 3 times higher compared with the baseline, and in individual samples, this exceedance reached 17 times. The mean content of  $\Sigma$ PCB in soil under cotton was relatively low (27.9 mkg/kg), but in some samples these compounds were determined in amounts that exceeded the APC level up to 7 times. As a whole for cotton soils, part of the  $\Sigma$ PCB was sufficiently lower in comparison with that of  $\Sigma$ DDT. This fact supports a suggestion about predominant agricultural pollutant sources of cotton agrolandscapes. Hence, as a whole for this monitored region, the load on soil by DDT metabolites was a little higher than that one by insecticide itself, and the same is true for the sum of tetra- and pentachlorobiphenyls in comparison with hexachlorobiphenyls. The load of DDT residues was sufficiently higher than that for PCBs. It should be noted that in the flow trend of the Zerafshan river, the total content of PCBs increased from 0 up to 2.5 mkg/L, indicating that local source of input of these persistent chlororganic compounds into water bodies existed. Thus, the assessment of the ecotoxicological situation in agricultural areas of the Samarkand oasis showed that the maximal load on soil cover of the irrigated landscape was due to residual content of DDT (insecticide and its metabolites DDE and DDD) in comparison with industrial pollutants - PCBs (92 and 8%, correspondingly). Generally, the DDT content in soils was less than the content of its metabolites, demonstrating the lack of sufficient sources of its recent inputs into agrolandscapes of this oasis. However, it is necessary to take into account the high level of pollution of soils under cotton by DDT residues that will prevent crop rotation of cotton for fodder and vegetable cultures. In spite of relatively low soil pollution by  $\Sigma$ PCB, this process can be increased due to permanent source of their input on irrigated cotton areas with surface waters enriched by different congeners of polychlorobiphenyls. Hence, the total content of residues of chlororganic pesticides (insecticides and metabolites) in soils was maximal in the Samarkand oasis (275.1 mkg/kg) and it was a little less in the Kuban low plain, while the minimal values were found in the Moscow region (164.8 mg/kg). This reflects the preceding application of the given pesticides, the loads of which were sufficiently higher in cotton and rice agrolandscapes in comparison with vegetable ones. The industrial pollution of soils by PCBs, v.v., was minimal in the Samarkand region and maximal in the Krasnodar region (28.1 and 258.9 mkg/kg, correspondingly). In the Moscow region, significant levels of PCBs in soils were determined, showing the presence of industrial sources of pollution as well as the numerous dumps of municipal wastes. Assessing these values, one can conclude that agricultural land use is closely connected with the content of residual amounts of pesticides and pollution by PCB is related more often to industrial loads. It should be noted that the highest content of PCB in landscapes of the Krasnodar region where industrial development in general is lower than for example, in the Moscow region could be explained by wider usage of modern purification technologies in the Moscow industrial district in comparison with those in Krasnodar.

### 4. Conclusions

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It is necessary to draw the attention of exceedances of the existing baselines (100 mkg/kg) for DDT residues for some areas under study. This is dangerous due to prolonged usage of polluted lands for various crops and perennial plantation as well as due to the necessity to introduce fodder and vegetable crops in rotations instead of rice in the Krasnodar region and cotton in the Samarkand oasis. It is well known that under pollution of soil by DDT levels higher than 100 mkg/kg, the translocation of insecticide in plants can achieve 35-70 percent of substance, found in soils. In accordance with the detection of PCB that occurs everywhere, it should be stressed of the necessity of hygienic control and monitoring of their content in soil, water and air to avoid numerous consequences for the biosphere such as accumulation in ecosystems and biogeochemical trophical chains, poisoning of living organisms, pathological influence on reproductive system etc. Irrigated waters polluted by these compounds as well as atmotechnogenic depositions can be sufficient sources of PCB input in various agrolandscapes. Due to the pollution of bottom sediments by PCBs, there is no way to use these sediments extracted from rivers, lakes, water reservoirs, irrigated channels etc., for melioration of arable lands as well as for recultivation of disturbed areas. Thus, excessive accumulation of the given compounds as the dioxin predecessors could undoubtedly pose dangerous ecotoxicological health risk for animals and human beings.

## 5. Reference

<sup>1)</sup> Lebedev A. and V. Petrosian (1987): Chromathomasspectrometrical analysis of organic substances contaminating environment. Background monitoring of the Environment. Leningrad, Gidrometeoizdat Publ. House (book serial) 5, 184-199.