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Structural - chemical studies of the destruction of organochlorine compounds

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Abstract: Polychlorinated biphenyls (PCB) are persistent organic pollutants used worldwide up 1990s. Although their use has been heavily restricted, PCB can be found in contaminated soils and sediments. Conducted structural-chemical studies of the destruction of polychlorinated biphenyl salts of amino acids in the soil. The effect of concentrated solutions of sodium salts of amino acids on soil particles has been investigated using FTIR spectroscopy as a means of identifying PCBs in the soil, controlling the interactions of PCBs with amino acid salts. The reaction products —C—substituted biphenyl polyamino polyacetic acids and their salts are soluble in water and extracted from particles on the surface of which polychlorinated biphenyls are adsorbed.

Polychlorinated biphenyls (PCBs) belong to the group of persistent organic pollutants (POPs), have toxic properties, are persistent and bioaccumulative, and are capable of long-distance transport in various environments. PCBs are biologically one of the most terrible carcinogenic (Pencikova et al., 2018) poisons, and, most importantly, having got into the soil or water bodies, accumulate in fats, for example, in breast milk (Rawn et al., 2017). PCBs were included in the 2002 Stockholm Convention on Persistent Organic Pollutants.

PCBs are used industrially as combustible oils (heat carriers) in capacitors and transformers, in addition to ballast resistances, fluorescent lamps, hydraulic and dielectric fluids, insulation of electrical wires, cables, plasticizers in adhesives, protective compositions of metals, wood, concrete, as a component in varnishes, paints, plastic fillers, paper impregnations, coolant during metalworking, as a flame retardant, insecticides and bacterial preparations (Schlatter C., 1994).

Currently, there are industrial and the surrounding area, where soil polluted with PCBs. They have a significant ecotoxic effect (Needham & Ghosh, 2019), primarily on the microflora. An example is the territory located in the zone of the factory in Serpukhov, which previously used PCBs in its manufacturing (Khakimov et al., 2003). Due to the ban on the use of PCBs and toxicity, the negative impact of the affected areas should be stopped. To do this, the contaminated soil must either be removed and placed in a special repository, or detoxified by transforming the chemical conversion of PCBs into less toxic substances, preferably biodegradable. Chemical detoxification in all respects is preferable to excavation and burial. However, to date there have been no effective reagents for these purposes (Gomes et al., 2013).

It is known that organochlorine compounds interact with derivatives of primary and secondary amines, including simple and complex amino acids. Currently, there is information about the possibilities of chemical detoxification and the disposal of highly toxic organochlorine compounds using NaL (Fridman



et al., 2005). An example is the process of transformation of 2,2' - dichlorodiethylsulfide (mustard gas) and other halogen-containing molecules in building structures. It is very likely that similar processes can be carried out for polychlorinated biphenyls to produce products of the type of complex aromatic amino acids that are soluble in water and are capable to biotransformation.

Concentrated solutions of α -amino acid salts consist of liquid solvatocomplexes (liquid hydrates), which form with the halogen-organic compounds molecules sufficiently strong molecular associates capable of hydration. In such molecular associates intramolecular transformations with the elimination of halide – ion and the formation of salts of complex amino acids are possible. The latter are soluble in water and do not form associates with liquid hydrates of α -amino acid salts. Typically, in an associate, react as many solvates complexes as halogen atoms exist in an organohalogen compound. At the same time, the associates include a larger number of solvates complexes. The process will continue until all of these molecules are converted into salts of the corresponding complex amino acids. The rate of reactions of intramolecular transformations in associates is catalyzed by alkali metal hydroxides, which bind hydrogen ions, which are cleaved from the amino groups of the salts of amino acids simultaneously with the removal of halide ions from the organohalogen molecules. Reactions can be catalyzed by aluminosilicate carriers that form the basis of soil particles.

Salts of amino acids from aqueous solutions are capable of adsorbing onto the surface of silicate particles and aluminosilicates of the soil. In the adsorbed state, they can come into contact with PCB molecules and then react with them in the form of chlorine amines (Demin et al., 2013). The reaction products - carbon - substituted biphenyl polyamine polyacetic acids and their salts may be soluble in water and extracted from particles on the surface of which PCBs have been adsorbed. By structure, they are similar to complex polyaromatic amino acids, which are formed in the metabolic processes of steroids of biosystems, and can be food products of soil microflora and water bodies. In this case, the action of concentrated solutions of sodium salts of amino acids on the soil with adsorbed PCBs can be used as the basis for the methods of detoxification and rehabilitation of the soil in the area of the factory in Serpukhov, previously using PCBs in production.

Soil treatment with reagent can be carried out in different ways - by impregnation with stirring, by injecting liquid reagent into the horizon, by stepwise dredging, suspension, etc. The choice of a particular method of treatment depends on the indicators of the diffusion of the reagent into the soil.

Objective: - To conduct structural and chemical studies of the destruction of organochlorine compounds with salts of amino acids in soils contaminated with polychlorinated biphenyls, including:

- interaction of salts of amino acids with polychlorinated biphenyl molecules sorbed in the soil, structure and solubility of products of transformation
- dynamics of sorption of sodium salts of amino acids in the soil containing polychlorinated biphenyls.

The study of the interaction of amino acid salts sorbed in soil with polychlorinated biphenyl molecules, the structure and solubility of conversion products was performed using FTIR spectroscopy as a means of identifying PCBs in the soil, controlling the interactions of PCBs with amino acid salts to their effects dissolving in water when washing the treated soil.

Studies were carried out on soil samples contaminated with PCBs provided by the Institute of Basic Biological Problems of the Russian Academy of Sciences. For the impregnation of soil contaminated with PCB, the composition of sodium salts of amino acids (composition AK-3E) was used. The concentration of salts of amino acids in the composition is 3.02 mole/l.

Before impregnation, the samples were repeatedly washed with water on the filter in order to remove the components soluble in water.

The water washed soil sample was divided into three parts. One part was used as a sample of soil containing PCBs. Two other parts were placed in a tube and a portion of 3-4 ml of AK-3E composition was added to them. As it is absorbed into the soil, new portions are added until complete saturation. The sample in the bottle was kept for 10 days at room temperature. After that, removed from the bottle and divided into two parts. One piece was used as a sample of the impregnated soil. The other part was washed with water to a pH of less than 8 and used as a sample of washed soil. Before taking the spectra, the samples were dried in air at room temperature to constant mass. The spectra were measured on a

Perkin Elmer – 2000 Fourier spectrometer in the range of 4000-100 cm^{-1} . The diffuse reflection method was modified using a Harrick extension that we modified. The assignment of the bands was performed using reference data (atlas of the IR - spectra of organic and inorganic compounds), and literature data.

Figure 1 shows the IR spectra of soil containing PCB (spectrum 1), soil impregnated with AK-3E (spectrum 2) and washed soil (spectrum 3). Comparing the spectra shows the following. In the spectrum of soil containing PCB, soil impregnated with AK-3E, and washed soil there are a number of identical bands - this is the shoulder at 3697 cm^{-1} , the bands with maxima at 3619, 3406 cm^{-1} ; 2229 and 2134 cm^{-1} , shoulder at 2000 - 1950 cm^{-1} strip with maxima at 1158, 816, 702, 570 cm^{-1} . The shoulder at 3697 cm^{-1} and the band at 3619 refer to OH - stretching vibrations of Si-O-H not associated groups, and the band at 3406 cm^{-1} - to OH- stretching vibrations of Si-O-H associated groups. The bands at 2229 and 2134 cm^{-1} , the shoulder at 2000–1950 cm^{-1} are related to the deformation vibrations of different types of hydrogen bonds, including vibrations in water molecules. The bands at 1158 cm^{-1} to Si-O- stretching vibrations in polysilicic acid anions associated with metal ions (sodium, potassium, calcium) and the bands at 816, 702, 570 cm^{-1} correlate with the oscillation frequencies of the aluminosilicate skeleton.

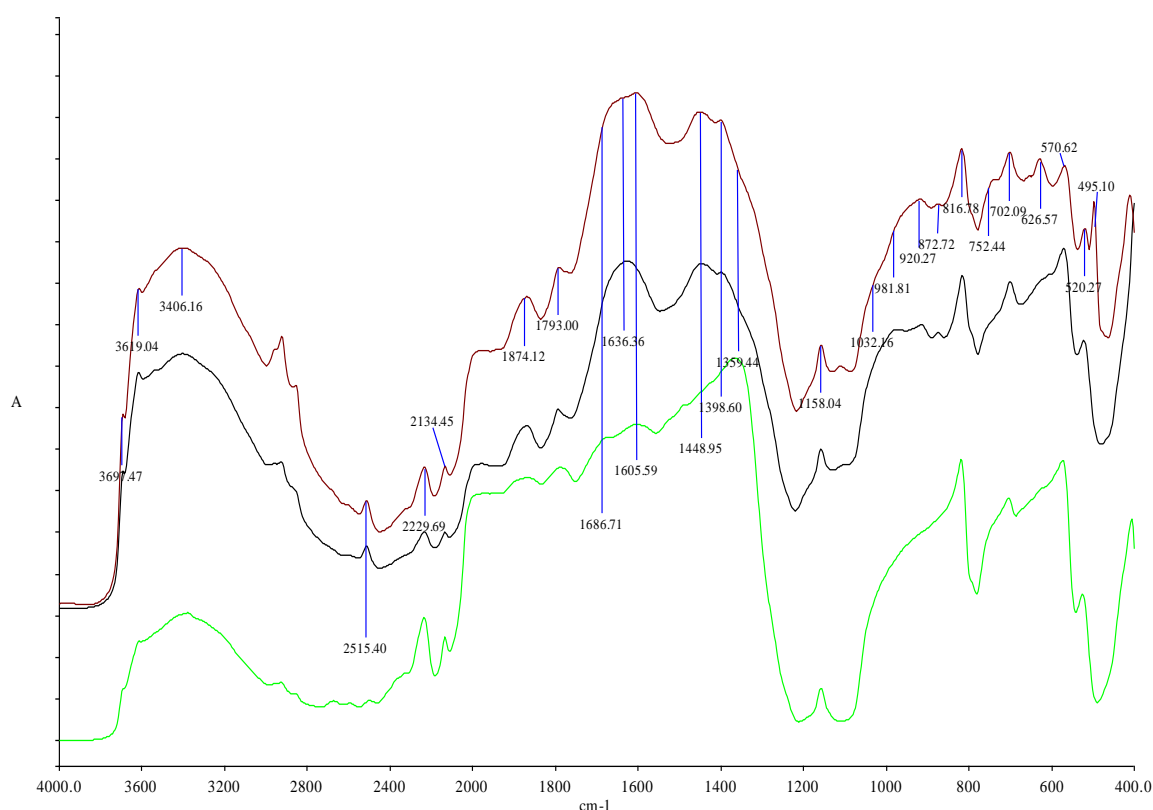


Figure 1. IR - spectra of soil containing PCB (1), soil impregnated with AK-3E composition (2) and washed soil (3).

In the spectrum of soil containing PCB, there is absorption in the region of 2950–2800 cm^{-1} , related to C–H stretching vibrations in biphenyls, there are intense bands at 1625, 1449 and 1359 cm^{-1} , related to vibrations of benzene rings of biphenyls. In addition, it should be noted that absorption in the region of 990–850 cm^{-1} , in which there are Si–O bands, stretching vibrations of Si–O–Si groups of silicate structures (about 985–970 cm^{-1}), deformation and fan vibrations of Si–OH groups (about 870 - 820 cm^{-1}), as well as C–Cl stretching vibrations in PCBs (about 900 - 850 cm^{-1}).

In the spectrum of the soil impregnated with a solution of salts of amino acids, compared with the spectrum of the soil containing PCB, in these areas there are the following differences. The maximum of the band related to the vibrations of the benzene ring at 1625 cm^{-1} for soil containing PCBs shifted to the long-wavelength region to 1605 cm^{-1} . In addition, the ratio of the intensity of the vibration bands of the benzene rings of biphenyls has changed. This may be due to a change in the nature of the substituents in the benzene rings of biphenyls to substituents with greater nucleophilicity than the chlorine atom. In the spectrum of soil impregnated with a solution of salts of amino acids, a shoulder appeared at $1660 - 1650\text{ cm}^{-1}$, referring to N-H deformation fluctuations in amino acids and a shoulder at 1636 cm^{-1} , referring to antisymmetric vibrations of the carboxyl group of amino acids. In addition, there are certain changes in the region of $2950 - 2800\text{ cm}^{-1}$ C-H oscillations. Instead of one band, two bands appeared, the intensity of which is greater than the intensity of the band in the spectrum of the soil containing PCB. A number of changes in the region of $990 - 600\text{ cm}^{-1}$ should be noted - a decrease in the intensity of absorption at $920 - 870\text{ cm}^{-1}$ where C-Cl stretching vibrations can be found in the spectrum of the soil containing PCB, as well as the appearance of new bands at 752 and 626 cm^{-1} related to skeletal fluctuations of amino acids. The shift of the band related to the vibrations of the benzene ring at 1625 cm^{-1} for soil containing PCBs to the long wavelength region to 1605 cm^{-1} after impregnation with amino acid salts and changes in the intensity ratio of the vibrational bands of the benzene rings of biphenyls may be due to a change in the nature of substituents in the benzene rings of biphenyls on substituents with greater nucleophilicity than a chlorine atom. A decrease in the intensity of absorption at $920-870\text{ cm}^{-1}$ where C-Cl stretching vibrations in the spectrum of a soil containing PCB can be found can be associated with a decrease in the number of C-Cl bonds in PCBs. This suggests that during the impregnation between PCBs and amino acid salts, interactions occurred, as a result of which part or all of the chlorine atoms in the PCBs were replaced by $-\text{NH}-\text{CHR}-\text{COONa}$ radicals. The composition of the products corresponds to the formula $\text{C}_{12}\text{H}_{12-n}\text{Cl}_{n-m}(\text{NH}-\text{CHR}-\text{COONa})_m$, where n is the number of chlorine atoms in the initial PCB molecule, m is the number of $-\text{NH}-\text{CHR}-\text{COONa}$ radicals in the product.

In the spectrum of washed soil, the absorption significantly decreased in the regions $2950-2800\text{ cm}^{-1}$, $1700-1400\text{ cm}^{-1}$, $980-850\text{ cm}^{-1}$, and $750-850\text{ cm}^{-1}$, which have absorption in the spectra of the soil containing PCB and the soil impregnated with salts of amino acids. At 1449 cm^{-1} , where the absorption maximum of the fluctuation of the benzene rings of PCB is located, there is no absorption characteristic of aromatic compounds. The absorption intensity at 1605 cm^{-1} is significantly lower compared with the intensity of the band in this region in the spectrum of the soil containing PCB. Consequently, there are either no PCBs in the washed soil, or their content has not decreased to trace amounts. PCBs are insoluble in water. Therefore, a decrease in their content in the washed soil is a consequence of the transformations of PCB with the formation of products that are soluble in water. For polyaromatic compounds, solubility in water occurs only when there are several hydrophilic radicals in their structure that can bind a significant number of water molecules in the first solvation shell. Products $\text{C}_{12}\text{H}_{12-n}\text{Cl}_{n-m}(\text{NH}-\text{CHR}-\text{COONa})_m$, as N-substituted aromatic amino acids meet the specified requirements for solvation. It should be noted that they are similar in structure to complex polyaromatic amino acids, formed in the metabolism of steroids of biosystems, and may be food products of soil microflora and water bodies.

Conclusions

1. Conducted structural-chemical studies of the destruction of polychlorinated biphenyl salts of amino acids in the soil.
2. The effect of concentrated solutions of sodium salts of amino acids on soil particles has been investigated (basis - silicates and aluminosilicates with sorbed polychlorinated biphenyls; soil samples in the area of operation of the Serpukhov plant, which previously uses polychlorinated biphenyls in capacitor production). It has been established that salts of amino acids enter with molecules of polychlorinated biphenyls in the reaction of the type of chlorination of amines catalysed on aluminosilicate carriers (parts of the developed surfaces of silicates and aluminosilicates). The reaction products —C— substituted biphenyl polyamino polyacetic acids and their salts are soluble in water and extracted from particles on the surface of which polychlorinated biphenyls are adsorbed. By structure,

they are similar to complex polyaromatic amino acids, formed in the metabolism of steroids of biosystems, and can be food for the microflora of the soil and water bodies.

3. The sorption of concentrated solutions of sodium salts of amino acids on soil particles containing polychlorinated biphenyls was studied. It has been established that salts of amino acids are adsorbed on the surface of silicate particles in the form of solvate complexes from solutions with a deficiency of solvent for ion solvation. The dynamics of the distribution of salts of amino acids in the soil with sorbed polychlorinated biphenyls was studied. It was established that the limiting stage is the wetting of soil particles, including the transfer of solvate complexes from the liquid to the solid phase, and accompanied by a change in the salt concentration in the contact zone. The movement of the fluid front occurs at approximately the same speed regardless of the depth.

References

- [1] Katerina Pencikova, Lucie Svrzkova, Simona Strapacova, Jiri Neca, Iveta Bartonkova, Zdenek Dvorak, Martina Hyzdalova, Jakub Pivnicka, Lenka Palkova, Hans-Joachim Lehmler, Xueshu Li, Jan Vondracek, Miroslav Machala In vitro profiling of toxic effects of prominent environmental lowerchlorinated PCB congeners linked with endocrine disruption and tumor promotion. *Environmental Pollution*, 2018, **v.237**, p. 473-486.
- [2] Dorothea F.K. Rawn, Amy R. Sadler, Valerie A. Casey, François Breton, Wing-Fung Sun, Tye E. Arbuckle, William D. Fraser Dioxins/furans and PCBs in Canadian human milk: 2008–2011. *Science of the Total Environment* 2017, **v.595**, p.269–278
- [3] Schlatter C. Environmental pollution and human health. // *Sci. Total Environment*, 1994, **v.143**, p. 93-101.
- [4] Trevor P. Needham, Upal Ghosh Four decades since the ban, old urban wastewater treatment plant remains a dominant source of PCBs to the environment // *Environmental Pollution*, **Volume 246**, March 2019, Pages 390-397
- [5] Khakimov F.I., Deeva N.F., Ilina A.A. Pollution with polychlorinated biphenyls of the soils of the city of Serpukhov // *Soil Science*, 2003, **№ 4**, p. 493-498.
- [6] Helena I. Gomes, Celia Dias-Ferreira, Alexandra B. Ribeiro Overview of in situ and ex situ remediation technologies for PCB-contaminated soils and sediments and obstacles for full-scale application. *Science of the Total Environment* 2013, **v.445–446**, p.237–260
- [7] Fridman A.Ya., Tsivadze A.Yu., Shemyakina E.V., Khakimov F.I., Sevastyanov S.M., Prokuronov V.G., Sokolova N.P., Gorbunov A.M. Interaction of copper ions with sodium salts of amino acids in organic-mineral substrates capable of biotransformation // *Material Science*. **№ 12**, 2005, p.30-34.
- [8] Demin D.V., Aladin D.Yu., Tatarkin I.V., Sevostyanov S.M., Deeva NF, Il'ina A.A. Study of the destruction of polychlorobiphenyl by sodium salts of amino acids and humic acids in soils. // *Proceedings of the Samara Scientific Center of the Russian Academy of Sciences*, 2013, **vol.15**, №3-4, p.1282-1286.