Studies of the effectiveness of the chemical decomposition of polychlorinated biphenyls in alluvial meadow soils in situ under the influence of special physicochemical active 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. The interaction of polychlorobiphenyls (PCBs) in soils with an alkaline amino acid reagent (NaL) and humic acids was studied. According to IR spectroscopy, intermolecular interaction of PCBs with NaL reagent was revealed. Chromatography and IR spectroscopy revealed the transformation and removal of chlorine in the aromatic ring of PCB macromolecules under the influence of an amino acid reagent. In the experiment, from 32 to 77% of PCBs undergo soil degradation, depending on the concentration of the reagent and the frequency of its introduction into soil samples.

1. Introduction
Among POPs, PCBs are among the most common. They were mass produced and used. PCBs belong to the class of aromatic compounds consisting of two benzene rings connected via the C — C internuclear bond and substituted by one to ten chlorine atoms in the ortho, meta, or para positions. There are 209 individual PCB congeners that differ in the number and position of chlorine atoms in the molecule, having the general formula C12H10-nCln, where n = 1-10. MPCs for PCBs, including the total toxic effect of all 209 congeners, in the soils are 0.06 mg / kg. Currently, about a third of PCBs produced have been released into the environment. The remaining two thirds are in a bound state in old electrical equipment and waste. PCBs are formed in the process of burning waste and all industrial processes using chlorine. PCBs are present in all components of the environment, and have been found in the tissues of animals living in untouched wild landscapes. [1,2,3,4,5] Removal of these xenobiotics is a global problem [6]. Cleaning soils contaminated with PCBs has been a challenge for decades [7]. The most common technologies used in the remediation of PCB-contaminated soils and technogenic formations are their burning or disposal in landfills, but these solutions are destructive and unstable. The chemical inertness of polyhalogenated dioxins and resistance to high temperatures only add to the problems when searching for approaches to their destruction.

Most technologies are still in their infancy and further research is needed on this issue. Field pilot experiments are important for evaluating the effectiveness of developed technologies. There is still no technology that is applicable for soil remediation from PCBs in situ [8]. Each technology is a unique case influenced by a number of physicochemical and biological factors and soil properties.

Of the physical factors, the most natural and economical way of degradation is solar radiation. However, most PCB congeners do not absorb electromagnetic waves with wavelengths of more than 300 nm, and therefore direct solar degradation is not very effective. In true solutions, especially in organic solvents, PCBs are relatively easily dechlorinated under UV irradiation. The efficiency of photodegradation depends on the level of chlorination of the congeners, the position of substituents in the PCB molecule (ortho> meta> vapor)
and on the phase (liquid or gas) in which the PCBs are located [9]. Thermal irreversible degradation of PCBs occurs only in fairly harsh conditions - over 1200°C and at least 2 seconds [10]. Various methods of chemical destruction of PCBs have also been proposed, for example, by alkoxylation of technical mixtures of PCBs with sodium alcohohates, which leads to a decrease in the chlorine content and, thus, a decrease in their toxicity [11]. However, as a result of such a reaction, complex mixtures of products are formed containing dozens of compounds whose toxicity has not been studied [12]. The results of laboratory experiments on the treatment of PCB contaminated soil with NaBH₄ reagent, with an exposure time of 3.5 to 30 hours, showed a decrease in the level of contamination from 2600 mg/kg to <0.2 mg/kg [13]. The final products of the interaction of PCBs and the reagent in this case were biphenyl, NaCl and boric acid. All of the above methods require the removal of contaminated soils, the availability of special equipment for further chemical treatment, which is quite time-consuming and dramatically increases the cost of work. Recently, biological methods of destruction of PCBs, based on the use of special strains — fungi and microorganisms [13, 14] have been of great interest. The biological destruction of PCBs occurs with the participation of enzyme systems of various types of microorganisms and can take place in two ways - aerobic (oxidative decomposition), and anaerobic (reductive dechlorination). These two processes proceed in different environmental conditions with the formation of specific metabolites. At the same time, bacterial dechlorination and degradation are not effective for PCB congeners with more than six chlorine atoms [15]. Microbiological methods have low efficiency and high cost, and the problem of controlling the possible mutation of microorganisms becomes very urgent, which makes the expediency of introducing them into natural environments very problematic. The use of the combined method of biological destruction is based on the introduction of sorbents (activated carbon, peat or other sorbents) into the soil that can absorb excess xenobiotics and a bacterial preparation of microorganisms-destructors. The sorbent provides a gradual release of the toxicant into the soil solution at concentrations non-toxic to the bacteria-destructors, which allows them to almost completely decompose the xenobiotic [16]. This method requires constant maintenance of the sorbent in a state of optimal moisture and aeration.

Therefore, all the above methods of detoxification of PCBs have one or another disadvantage. Successful soil restoration depends on the proper selection, design and regulation of remediation technology. Recent studies show that the use of a combined approach using the basics of biological and chemical destruction for soil remediation from PCBs is promising. In this regard, the search for cost-effective recovery technologies to remove these persistent organic pollutants from the environment is an urgent and sought-after problem for the whole world. The solution to this fundamental scientific problem can lead to the creation of a cost-effective technology. Therefore, the search for new effective methods for the rehabilitation of soils contaminated with organochlorine compounds is an urgent task. A promising area is a combination of chemical and biological methods.

2. Object and research methods

It is known that organochlorine compounds are able to interact with derivatives of primary and secondary amines, including simple and complex amino acids [17]. In this regard, we developed a method for the destruction of PCBs in soils using special amino acid-based reagents. As a source of amino acids, we used a reagent, which is an alkaline hydrolyzate obtained from waste leather and fur production, the main component of which is the sodium salts of amino acids (NaL).

The destruction of PCBs by an amino acid reagent was assessed on three samples of the surface humus horizons of alluvial soils from the basin of the Borovlyanka stream in Serpukhov. For all samples, some alkalization of the soil solution was noted (pH 7.60, 8.20, and 7.8), which is typical for urban soils. According to the granulometric composition, samples 1 and 3 belong to light loams, and sample 2 to medium loams. The humus content is 3.1, 4.2 and 3.2%, respectively.

A study on the destruction of PCBs in substrates was evaluated by methods: by the content of PCBs by gas-liquid chromatography (GLC) using standards, and the determination of PCB congeners by GLC / LRMS (low resolution mass spectrometry) or GLC / HRMS (high resolution mass spectrometry).

From each moistened to 60-70% of the lowest moisture capacity of the sample, 3 samples of 500 g in terms of absolute dry weight were taken, placed in containers and processed with various doses of NaL. The treatment
was carried out in two dose options: 17 ml of NaL solution (2 mol / L) and 34 ml of NaL solution (4 mol / L). The samples were mixed, left to undergo a reaction between NaL and PCB for 10 days, periodically mixed.

3.Results and discussion
The analyzes performed showed a several-fold decrease in PCB content in soil samples after NaL treatment (Table 1).

| Soil sample no. | The initial amount of PCB, μg / kg | The amount of PCBs after treatment with NaL (85 ml / kg), μg / kg | The amount of PCBs after treatment with NaL (170 ml / kg), μg / kg |
|----------------|----------------------------------|-------------------------------------------------------------|-------------------------------------------------------------|
| 1              | 85.6                             | 20.7                                                        | 21.5                                                        |
| 2              | 107.6                            | 26.2                                                        | 20.4                                                        |
| 3              | 320016                           | 12872                                                      | 5203                                                        |

When treating the soil with a reagent in a dose of 17 ml of NaL solution (2 mol / L), the PCB content in the first and second samples decreased by 4.1 times, and in the third - by 24.9, respectively. When processing a double dose of reagent (170 ml / kg) for the first and second samples, approximately the same data were obtained. The same amount of undestroyed PCB in the first and second samples at two doses of NaL may indicate that the residual PCB is tightly bound to the mineral part or humic substance of the soil. However, in the humus content, these soils vary greatly, therefore, it can be assumed that this amount of PCB is sorbed by the mineral part of the soil, as a result of which it is not accessible for chemical destruction during a single treatment.

In the third sample, PCB at a double dose of the reagent decreases by 61.5 times (by 98.4%). The bulk of PCBs is destroyed, however, in this case, the amount of reagent was not enough, since the soil remains significantly contaminated, and some PCBs are chemically accessible for destruction.

At the next stage, experiments on the destruction of PCBs were carried out in the field in situ in the most polluted area of the river basin Borovlyanka.

To determine the effect of amino acid salts on the destruction of PCBs in soils, experimental sites of 0.25 m2 were laid, to limit the area of which square tin boxes were used, which were driven into the soil to a depth of 20 cm, due to this they were isolated from the secondary side input of PCBs into upper horizon. The sides of the boxes, protruding above the soil, allowed for processing without spreading the reagent. Processing was carried out manually.

In the soils of the first square, which was treated with a minimum dose of 1.9 L of reagent, the PCB content decreased 2.95 times and amounted to 20359.9 μg / kg - 339 MPC. The ratio of congener groups did not change much, the sum of light fractions is 49.83% (Figure 2)
Figure 1. Concentration PCBs before processing by an aminoacidic reactant №1, mkg/kg.

In the soils of the 2nd square, where PCB was initially contained significantly less compared to other studied areas, with the introduction of the minimum dose of the reagent, the decrease in the level of contamination turned out to be the greatest - by 10.2 times, to 332.05 μg / kg, which is 5.5 MPC. The content of light fractions increased to 52% (Figure 2).
Figure 2. Concentration PCBs before processing by an aminoacidic reactant №2, mkg/kg.

In the soils of the third square, where the dose of the reagent was also minimal, the pollution level decreased 2.2 times - 11146 μg / kg (185.8 MPC) (Figure 3).
Figure 3. Concentration PCBs before processing by an aminoacidic reactant №3, mkg/kg.

Thus, after the introduction of various doses of the reagent, the level of PCB pollution decreased relative to the initial one: 1 square - by 75.8%, 2 - by 75.7%, and 3 square - by 98.4%.

4. Conclusions
1. Experiments on the detoxification of PCBs in samples from the upper soil horizons under laboratory conditions showed a several-fold decrease in the content of persistent organic compounds
2. The dose of the amino acid reagent 85 ml / kg (concentration 2 mol / l) leads to the destruction of the entire chemically available amount of PCBs for a given exposure time (10 days)
3. A change in the ratio of homologous groups of congeners in soils indicates the interaction of PCBs with the amino acid composition and the phased replacement of chlorine ions with an amino acid radical.

As a result, it can be emphasized that in experiments with field samples, positive results were obtained on the destruction of PCBs by amino acid salts. However, it is necessary to continue experimental studies to determine the doses of this reagent for soils with an extremely high degree of PCB contamination.

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