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ANALYSIS OF THE PROPERTIES OF CERTAIN STABLE ORGANIC POLLUTANTS

The paper considers the results of the analysis of stable organic pollutants, formed as a result of human activity and accumulated in Ukraine; their toxicologic characteristics have been investigated for further monitoring of these substances in Vinnytsia Region.

Key words: POP, PCDD, PCDF, contamination of territories, toxic substances, Stockholm Convention, toxic factor, dioxins.

Introduction

Problem of persistent organic pollutants (POP) is of great importance for Ukraine and is connected with the developed agricultural production, large share of energy and metallurgic sectors of national economy; problems, dealing with handling of accumulated inapplicable and prohibited pesticides and their real decontamination are of paramount importance.

Ministry of ecology and natural resources of Ukraine and SI Group Consort Ltd with Subcontractor Si Bud System signed the contract in May 2012 regarding services on waste disposal, located on the territory of the region.

In accordance with the given contract “Si Bud System” company began to provide services dealing with provision of ecological security of transporting, storage, handling and decontamination of inapplicable pesticides and their packing materials of Dzhuryn toxin burial ground in Vinnytsia Region. Totally, 1559.253 tons of inapplicable pesticides are planned to be removed from the territory of the region.

Dzhuryn toxin burial ground was built in 1978, it is situated in Shargorod district of Vinnytsia region. On its territory 1023.7 tons of undetermined and unfit for utilization pesticides from neighbouring regions (Zhutomyr, Ivano-Frankivsk, Zakarpatska, Lvivska, Khmelnytska) are buried.

Solid waste of unfit for usage chemical means of plant protection are packed in double polyethylene bags of small volume, stored in large volume package (so-called “Big Bags”) in the quantity of 850 units. Liquid pesticides are packed in plastic barrels, 2706 pieces. Approximate weight of repacked waste is 1030 tons.

Since 14.09.2012 “S.I. Group Consort LTD” began to remove repacked agrochemicals and for the present day 520 packed units of solid and 348 packed units of liquid waste of unfit for usage chemical agents for plant protection, their total weight is 557, 597 tons [1].

Ukraine has powerful industrial and agricultural potential. But, unfortunately, great amount of the applied technologies and productions are outdated and need modernization, that is why, greater part of basic categories of POP emission sources according to classification of SNAP (Selected Nomenclature for sources of air Pollution) – universal system of determination of categories and subcategories of emission sources and kinds of activity, resulting in emissions of pollutants in the atmosphere are valid. It is known [2] that emissions of PCDD/PCDF are formed as a result of thermal processes with participation of organic substances and chlorine as a result of incomplete combustion or chemical reactions. Large stationery sources of PCDD/PCDF may be:

- burning waste, including simultaneous burning;
- thermal metallurgical processes, for instance, production of aluminium and other non-ferrous metals, cast iron, steel;
- power installations of municipal and industrial spheres, burning various kinds of fuel;
- burning processes in household units;
- specific process of chemical production, when intermediate chemical compounds and by products are formed;
- incinerator plants of large cities of Ukraine [3].

Global climatic changes, pollution of agricultural areas with pesticides and other phenomena give rise to serious anxiety regarding the future well-being of the mankind. Within the frame of UNEP programme during the next three decade more attention will be paid to various aspects of the most dangerous group of synthetic chemical toxicants, united by the common term “Persistent organic Pollutants (POP)” [3]. In accordance the Annex 3 of Stockholm Convention polychlorinated dibenzodioxins (PCDD) are defined as tricyclic aromatic compounds with specific chemical properties (Fig. 1a).

Total number of possible isomers for PCDD is 75. These compounds are high toxic and high stable impurities of some industrial chemicals formed as a result of different technological processes of certain productions [3]. They do not exist in nature and never find practical application.

Polychlorinated dibenzofurans (PCDF) in Stockholm Convention are defined as condensed aromatic compounds (Fig. 1b). Total number of possible isomers for PCDF is 135.

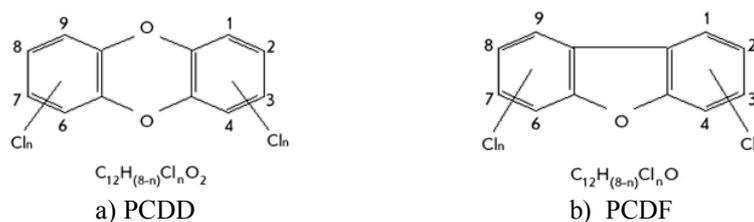


Fig. 1. Polychlorinated dibenzofurans

It turned out, that the most toxic are 17 isomers (congeners) of PCDD and PCDF (further dioxins) where atoms of chlorine must be in 2, 3, 7, 8 – positions of benzene rings. Toxicity of 2, 3, 7, 8 –TCDD exceeds the toxicity of cyanides, strychnine and curare [4]. Toxicity of other dioxine isomers is expressed by means of Toxic Equivalent Factor (TEF) regarding 2, 3, 7, 8 –TCDD, toxic equivalent of which is taken as 1 [5]. For calculation of toxic equivalent factors either LD50 values, characterizing sharp toxicity or parameters, characterizing cancerogenic action are used [6]. Table 1, contains International Toxic Equivalent Factors for dioxins. As it was mentioned above, minimum 7 compounds must be in PCDD group of Stockholm Convention, and to compounds must be in PCDF group.

Table 1

International Toxic Equivalent Factors (TEF) PCDD and PCDF

Congener	Toxic equivalent factor
2,3,7,8–TCDD	1
1,2,3,7,8–PeCDD	0,5
1,2,3,4,7,8–HeCDD	0,1
1,2,3,6,7,8–HeCDD	0,1
1,2,3,7,8,9–HeCDD	0,1
1,2,3,4,6,7,8–HeCDD	0,01
1,2,3,4,6,7,8,9–OCDD	0,001
2,3,7,8–TCDF	0,1
1,2,3,7,8–PeCDF	0,05
2,3,4,7,8–PeCDF	0,5
1,2,3,4,7,8–HeCDF	0,1
1,2,3,6,7,8–HeCDF	0,1
2,3,4,6,7,8–HeCDF	0,1
1,2,3,7,8,9–HeCDF	0,1
1,2,3,4,6,7,8–HeCDF	0,01
1,2,3,4,7,8,9–HeCDF	0,01
1,2,3,4,6,7,8,9–OCDF	0,01

Similar situation is also with PCB. In accordance with the annex C of Stockholm Convention

PCB are defined as aromatic compounds, formed in such a way that the atoms of hydrogen in the molecule of biphenyl are displaced by the atoms of chlorine, number of which totals ten (Fig. 2)

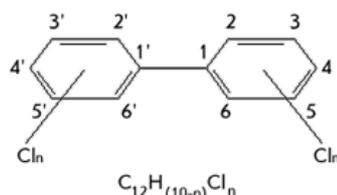


Fig. 2. Polychlorinated biphenyls

It should be noted, that although in literature the term “dioxine” is used, as a rule, to denote tricyclic oxygen – containing aromatic compounds (PCDD), the name “dioxine”, according to the nomenclature of the International Union of Pure and Applied Chemistry (IUPAC) belongs to 1,4-dioxine, instable non-aromatic heterocyclic compound, that easily polymerizes and chlorine derivatives which are not known yet [7].

Theoretically the existence of 209 isomers (congeners) of PCB is possible. However, only 130 compounds are formed in the form of the industrial by products [8]. Congeners of PCB possess the highest toxicity, having no chlorine substituents in orthopositions of benzene rings (the most toxic congener 3,3',4,4',5-PeCB) and some 0-monosubstituted derivatives. Table 2 contains International Toxic Equivalent Factors of 11 most dangerous congeners of PCB relatively 2,3,7,8 – tetrachlordibenzo-para-dioxine (TCDD)[9].

Table 2

International Toxic Equivalent Factors of PCB

Congener	Toxic equivalent factor
3,3',4,4'-TCB	0,0001
3,4,4',5'-TCB	0,0001
3,3',4,4',5'-PeCB	0,1
3,3',4,4',5,5'-HeCB	0,01
2,3,3',4,4'-PeCB	0,0001
2,3,4,4',5'-PeCB	0,0005
2,3',4,4',5'-PeCB	0,0001
2',3,4,4',5'-PeCB	0,0001
2,3,3',4,4',5-HexaCB	0,0005
2,3,3',4,4',5'-HexaCB	0,0005
2,3,3',4,4',5,5'-HeCB	0,0001

Mechanism of POPs impact on a living cell are very complex and represent a number of consecutive events on the molecular level that leads to changes in genes functioning regulation and vital activity of the cells. Persistent Organic Pollutants (POPs) influence, first of all, on endocrine system, destroying it. They possess hormone-like action, but not being real hormones, break normal functioning of endocrine system. Hormone are powerful biological compounds, act as chemical mediators. They regulate wide range of corresponding reactions in the organism: metabolism, reproduction, growth, evolution, behavior and other processes of cells. Mechanism of estrogenic activity of POPs is not studied yet.

PCDD, PCDF and PCB are distinguished as “superecotoxicants”. They can be found almost everywhere: in the air, water, soil, ground, sediments in the tissues of fish, animals, milk, vegetables, etc. The highest concentration of dioxins have been found in soil, ground sediments, biogas. In the air and water the concentration of dioxins is far less because they are insoluble in water and nonvolatile. These compounds are very dangerous for the environment because they are very resistant to chemical and biological decomposition, remain in the environment for decades, and are carried out by nutritive chains (water plants – plankton – fish – human being, soil – plants – herbivorous animals – human being) [10, 11]. Soil contamination by dioxins results in extermination of all living organism and complete loss of its natural qualities. Dioxins are universal poison, acting on cellular level and making harm to all kinds of animals and greater part of plants.

New information regarding the danger of dioxins shows that this danger is outside the frame of carcinogenic effect. Contamination with dioxins and dioxin-like compounds lead to serious negative impacts on human health, which can be transmitted from generation to generation:

- destroy hormonal systems, especially reproductive organs;
- influence embryonic growth and nervous system of the features;
- disturb the evolution of the immune system [12].

Conclusions

1. Definition “dirty dozen” is more emotional than scientific definition, that is why, investigating these compounds it is necessary to use IUPAC nomenclature. Total number of POPs being the subject of the Stockholm Convention contains at least 36 compounds (8 pesticides, 7 PCDD, 10 PCDF and 11 PCB) that constantly change

2. In spite of the fact that Ukraine nowadays is in the situation, already experienced by greater part of developed countries, there exists great probability that as a result of development and realization of the planned national programmes regarding the protection of the environment and population against dioxins and other POPs and measures, aimed at POPs monitoring, the impact of these xenobiotics has considerably reduced.

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