MINISTRY OF EDUCATION AND SCIENCE OF UKRAINE
VINNYTSIA MYKHAILO KOTSIUBYNSKYI STATE PEDAGOGICAL UNIVERSITY

PERSONALITY AND ENVIRONMENTAL ISSUES

2 (4)

Vinnytsia
2023

UDC 502/504:159.9:37(06)
P 47

ISSN 2786-6033 (print)
ISSN 2786-6041 (online)
DOI: 10.31652/2786-6033-2023-2(4)-1-42

Recommended by the Academic Council of Vinnytsia
Mykhailo Kotsiubynskyi State Pedagogical University
(Protocol No.11 dated June 21, 2023).

Personality and environmental issues. Vinnytsia: VSPU, 2023. 2, № 4. 43 p.

The journal presents modern scientific research on ecology, environmental psychology, theoretical and methodological aspects of the development of environmental awareness and environmental protection, improving the quality of environmental education and highlighting the experience of best environmental and environmental psychological practices, creating conditions for public discussion and testing of theoretical and scientific-practical research in the field of human-environment interaction.

Frequency of publication: 4 times a year. Year of foundation: 2021.
Founder: Vinnytsia Mykhailo Kotsiubynskyi State Pedagogical University
Certificate of state registration of the print media:
Series КВ № 24839-14779Р from 30.04.2021.

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PROBLEMS OF ENVIRONMENTAL PROTECTION AND BALANCED NATURE MANAGEMENT

UDC 5. 504 **DOI: 10.31652/2786-6033-2023-2(4)-26-32**

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PERSISTENT ORGANIC POLLUTANTS OF ECOSYSTEMS

Abstract. The development of synthetic organic chemistry is always determined by creating of new compounds and application in medicine (pharmaceutics), production of cleaning, cosmetic remedies and nutrient additives. The production and application of such compounds are of minimum harm for people and environment regarding to special toxicological and sanitary requirements are concerned. However, multi-tonnage production of lacquers, dyes, rubber, pesticides, disinfectors, plastics, mineral and synthetic lubricants and their stabilizers, industrial surfactants and detergents, fluorocarbons, organometallic compounds make a great harm to environment. In this article the physico-chemical and toxicological characteristics of the most important persistent organic pollutants (POP) have been described. The possible approaches and technologies of POP disposal have been considered in the framework of Stockholm Convention.

Research show that when determining the most appropriate method of POPs detoxification, it is necessary to take into account, in addition to technological, some more economic and social factors, pay attention to ensuring human health.

Keywords: persistent organic pollutants, chlorine-containing pesticides, ecotoxicants, detoxification, waste disposal

Introduction. The development of synthetic organic chemistry is always determined by creating of new compounds and application in medicine (pharmaceutics), production of cleaning, cosmetic remedies and nutrient additives. The production and application of such compounds are of minimum harm for people and environment regarding to special toxicological and sanitary requirements are concerned. However, multi-tonnage production of lacquers, dyes, rubber, pesticides, disinfectors, plastics, mineral and synthetic lubricants and their stabilizers, industrial surfactants and detergents, fluorocarbons, organometallic compounds make a great harm to environment. The main part of such negative influence is determined by existing in Ukraine residues of liquid rocket fuels (so-called "heptyl" – 5000 tons, "amyle", "melange" - 18000 tons), unused pesticides (~14000 tons), chlorine-containing wastes contain 1,2-dichloretane and vinyl chloride (at "Lukor", Kalush (Ukraine) only in 2004 was burned 6000 tons of such wastes), hexachlorobenzene (HCB) residues (at «Oriana», Kalush (Ukraine) there are ~ 11000 tons of HCB stored on the polygon of toxic wastes), acid oil tar from petrochemistry (only in 2002-2003 years it was brought ~20000 tons of such wastes into the territory of Lviv Region, Ukraine), millions m^3 of wastes from the uranium ore enrichment (Taromske, Dnipropetrovsk Region, Ukraine), multi-tonnage wastes of Ukrainian petroleum industry etc. The most toxic and dangerous are the chlorine-contained organic substances of so-called "dirty dozen" among the above mentioned chemical substances which pollute the environment.

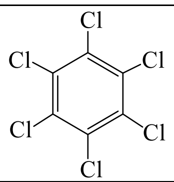
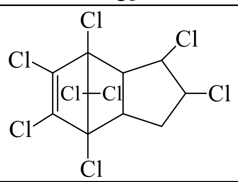
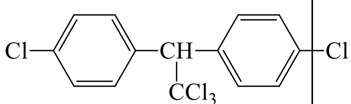
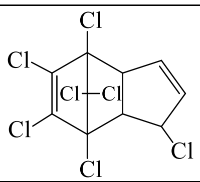
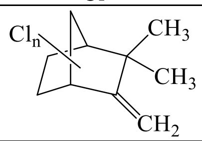
The aim of the work. In this work the authors tried to pick out and generalize the main physico-chemical and toxicological characteristics of POP in order to establish the safety conditions or treatment and possible ways of the extermination of such ecotoxicants. This work was carried out in accordance which has been adopted by 127 countries all over the world. Ukraine has adopted the Stockholm Convention for POP at 23.05.2001. Nowadays the project of Ukrainian Law concerning the Stockholm Convention ratification about POP in the Ministry Cabinet of Ukraine and later will be in Supreme Council for the ratification. In case of Stockholm Convention ratification Ukraine will accept finances including the finances of Global economic fond for the solution of the problems related to POP chemical substances extermination for preventing release to the environment such highly toxic compounds due to modernization of the technologies of key industry branches.

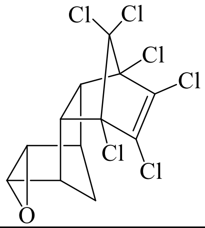
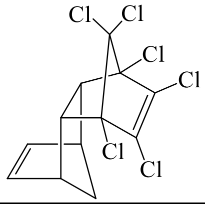
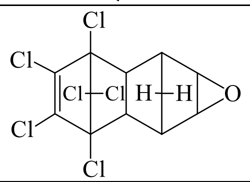
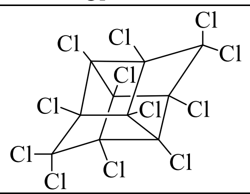
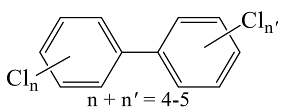
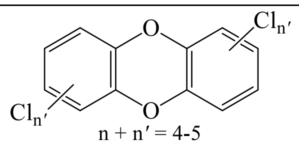
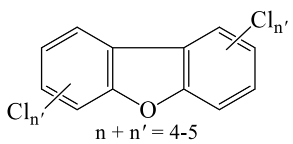
Objects of the investigation. According to the Stockholm Convention (17.05.2004) the POP (table 1) are divided into 3 groups. The POP of 1st group contains highly toxic pesticides (DDT, Dieldrin, Aldrin, Heptachlor, Mirex, Toxaphene, Endrin, Chlordane, HCB). The POP of 2nd group contains the industrial polychlorinated biphenyls (PCB). The POP of 3rd group are not industrial produced, but high temperature processed on dust-burning factories and form waste which contains the chlorine. This group of over-toxic substances called «dioxins»: polychlorinated dibenzo-para-dioxins (PCDD), polychlorinated dibenzofurans (PCDF).

The physico-chemical properties of considered POP are listed in table 1. As a rule these substances are the polychlorinated compounds with large molecular weight and large chlorine content (50–78 %), large solubility in fat tissues of animals and human [8, 9]. Such compounds possess the cumulative properties and thermal stability, they are inert for the influence of the environment. That is why such POP can migrate in under-soil waters, crust, atmosphere during a long time. The POP of the II and Ill group are the most stable. These substances have aromatic structure with developed substituents (the dependence "structure-properties") [l0]. The attractive idea of studying fundamental dependence "structure-pesticide activity" by mathematical methods [11, 12] and making the total screening [13] is great stimulus for many investigations and publications in this field. It has been established the common requirements of "structure-activity" not only for polychlorinated aromatic systems [14], but also for iminoderivatives of sulfur [15], quaternary ammonium salts [16, 17], substituted ureas [18, 19], N-benzylacetamides [20], other chemical substances [21]. However, such investigations are auxiliary during the application and introducing the biological active compounds to the industry.

Table 1

Physico-chemical properties of some POP

No	Structure	Trade name / CAS No / chemical name	m.p., °C	Chlorine content, %	Application field [2]
1		Hexachlorobenzene / 118-74-1 / Hexachlorobenzene	231.0	74.69	Fungicide, formerly used in a seed treatment
2		Chlordane / 57-74-9 / 1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene	175.0 (boil.)	69.21	Insecticide, against the thermites, rats
3		DDT / 50-29-3 / 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane	108.5–109.0	50.01	Insecticide, against the various insects, antimalarial and against typhus
4		Heptachlor / 76-44-8 / 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene	95.0–96.0	66.48	Insecticide, used in a combination with seeds
5		Toxaphene / 8001-35-2 / Polychlorocamphene	65.0–90.0	68.54	Insecticide, against the Colorado beetle

No	Structure	Trade name / CAS No / chemical name	m.p., °C	Chlorine content, %	Application field [2]
6		Dieldrin / 60-57-1 / 1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4,5,8-dimethanonaphthalene	175–176	55.84	Insecticide
7		Aldrin / 309-00-2 / 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene	104–105	58.29	Insecticide
8		Endrin / 72-20-8 / 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-endo-1,4-endo-5,8-dimethanonaphthalene	200.0 (decomp.)	55.84	Insecticide, against the pests
9		Mirex / 2385-85-5 / Dodecachloropentacyclo[5,2,1,02,6,03,9,05,8]decane	485.0	77.98	Insecticide, against the thermites. Polymer plasticizer
10		Sovol / Tetra- and pentachlorobiphenyls	325–390 (boil.)	54.30 (n + n′ = 5)	Plasticizer for lacquers and dyes, additive for transformer and condenser oils
11		PCDD / Tetra- and pentachlorodibenzo-*p*-dioxins	> 350.0 (decomp.)	49.73 (n + n′ = 5)	The toxic wastes of the thermal disposal of chlorine-containing organic substances (COS)
12		PCDF / Tetra- and pentachlorodibenzofurans	> 350.0 (decomp.)	52.07 (n + n′ = 5)	

The toxicological properties of POP are listed in table 2. These compounds are xenobiotics. They are introduced to the environment as chemical products and technogenic pollutants. Above mentioned substances possess the carcinogenic, mutagenic, embriotoxic, neurotoxic, immunotoxic properties and kill all living organisms. They change the hormone system, cause the anemia, cancer, diseases of kidneys and human blood.

Table 2

Toxicity, sanitary and hygienic parameters of POP

No	Trade name	Toxicity, sanitary and hygienic parameters				Physiological influence of active substance on living organism
		LD_{50} mg/kg	$MPC_{w.z.}$ mg/m^3	MPC_w mg/l	MPC_{PRQ} mg/kg	
1	Hexachlorobenzene	1700	0.9	–	–	Carcinogenic, teratogenic and immunotoxic

No	Trade name	Toxicity, sanitary and hygienic parameters				Physiological influence of active substance on living organism
		LD_{50} mg/kg	$MPC_{w.z.}$ mg/m^3	MPC_w mg/l	MPC_{PRQ} mg/kg	
						substance. Affects the skin
2	Chlordane	250	0.01	–	–	Carcinogenic, mutagenic, neurotoxic substance. Affects the blood, liver, hormone system
3	DDT	200	0.1	0.2	–	Carcinogenic, mutagenic, embriotoxic, neurotoxic, immunotoxic substance. Affects the hormone system, liver, causes anemia
4	Heptachlor	82	0.01	0.05	0.05	Toxic substance for animals and human. It transforms into the very toxic heptachlor epoxide under the influence of ultraviolet radiation
5	Toxaphene	60	0.2	–	0.5	Strong toxicant for fish and animals. Carcinogenic, neurotoxic substance. Affects the blood, liver and kidneys
6	Dieldrin	24	0.01	–	–	According to the official data, there is no substance on the territory of Ukraine
7	Aldrin	18	0.01	0.02	–	According to the official data, there is no substance on the territory of Ukraine
8	Endrin	5–12	–	–	–	Carcinogenic, neurotoxic substance. Affects the hormone and reproductive system
9	Mirex	–	–	–	–	According to the official data, there is no substance on the territory of Ukraine
10	Sovol	–	1.0	–	–	Causes the Down syndrome. Affects the nervous system of children, increases the toxicity of other substances due to synergetic effect
11	PCDD	At one-moment influence: min: 0.5–1 mcg/kg max: 70 mcg/kg	–	–	EU: 4 pg/kg per day; USA: 1 pg/kg per day; RF: 10 pg/kg per day;	Extremely toxic substance. Carcinogenic for animals and human. Affects the immune system (direct analogues of HIV), causes immunodeficiency similar to AIDS
12	PCDF		–	–		

<u>Note:</u> *LD_{50} – dose of the product, that causes the death of 50 % of the experimental animals; $MPC_{w.z.}$ – maximum permissible concentration in the air of working zone; MPC_w – maximum permissible concentration in the water; MPC_{PRQ} – maximum permissible concentration (permissible residual quantity) in the nutrients; 1 mcg = 10^{-6} g; 1 pg = 10^{-12} g.*

Such conclusions have been made on the basis of numerous investigations. It has been made the investigations concerned with the influence of physical, chemical and biological factors on the decomposition of pesticides in soil [22, 23], its metabolism in plants and animals [24, 25]. Detailed investigations of the analysis of chlorine-containing pesticides [26], extraction and purification of pesticide metabolites [27] and elaboration of the universal methods of the micro-quantities determination of chlorine-containing pesticides [28] have been made. The key factor is the studying of the mechanism of POP biochemical action [29, 30]. For example, DDT and pyrethroids causes the Na-channel closing in the nervous cell membranes. DDT open and close the channels quickly and cause depolarization, -hexachlorocyclohexane, Dieldrin and other chlorine-containing insecticides increases the concentration of Ca^{2+} due to disturbing the work of Ca-pump regulator or reducing the concentration of Ca^{2+} by endoplasmic reticulum [31].So it may be seen that various disturbings of the biochemical xenobiotics lead to numerous above mentioned diseases.

Technological aspects of POP detoxification. According to the Stockholm Convention the production of compounds No 4-8, 10 (table 1) is prohibited all over the world. The production of compounds No 1-3 (table I) should be allowed only according to the permission for participants which are enumerated in Register. This is explained by comparatively low toxicity values of last substances which is listed in table 2 (LD_{50} = 200-1700 mg/kg). Nowadays, as exception the compounds No 2, 4, 9 can be used against thermites in buildings and compound No 3 can be used in Dicofol production. Other compounds must be exterminated.

The Convention spares the priority attention to the warding off the POP formation and release in the environment. It can be effectively reached by:

- using the low-waste technologies;
- using the less dangerous chemical substances;
- active using of the processes of recuperation and recycling the wastes and substances in framework of single technological process;
- using the principle of "industrial symbiosis" (waste and POP substances from first production can be detoxificated with the aid of POP substances from second production by the method of reagent processing [32, 33];
- reducing of elemental chlorine using or chemicals which generate the elemental chlorine as whitening agents;
- improvement of waste management in order to prevent open and uncontrolled burning of solid household waste, dust, medical and other waste. During the construction of new waste treatment factories it could be advisable to greatly reduce the formation of medical and household waste, use the renewal sources, re-using, recycling, separation of waste and promote the using of products which release less amounts of waste.

Besides the preventive measures there are lots of methods and technologies of the detoxification and extermination of chemical substances [34] including POP substances. The most popular are the methods of thermal [35], high-temperature pyrolysis [36], pyrometallurgical [37], oxidation (or direct burning), biotechnological, electrochemical, radioactive and photochemical dechlorination [6], reagent detoxification [6, 38, 39]. The application of super-high frequency (SHF) micro-wave chemical technologies is also perspective [40].

However, during the determination of the most advisable method of POP detoxification we must take into account, besides the technological, also some economic and social factors, and pay attention to the securing of human health.

Conclusions. The physico-chemical and toxicological characteristics of the most important persistent organic pollutants (POP) have been described.The possible approaches and technologies of POP disposal have been considered in the framework of Stockholm Convention.

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Review received 24.05.2023