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Actual Conditions and Alternative Materials for the Pesticides containing Persistent Organic Pollutants in South Korea

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ABSTRACT: A global binding agreement was adopted with the leading of United Nations Environment Program (UNEP) on May 22, 2001 in Stockholm to regulate the production and distribution on persistent organic pollutants (POPs). The agreement took effectuation with the ratification of 59 countries from the approval of 151 countries on May 17, 2004. After the approval on October 4, 2001, South Korea performed systematical investigation on POP-related substances such as chlordane, dichloro diphenyl trichloroethane (DDT), hexachlorobenzenes (HCB), heptachlor, polychlorinated biphenyls (PCBs) to get ready for the ratification of the convention with country-specific exemption. The domestic distributions of those chemical substances have been officially prohibited since the late 1960s to the early 1980s. Although there were occasional reports for the detection of some of those chemical substances, those performed minute signification in their existence in the environment. A series of investigation with documentary examination and fact-finding survey showed the possibility for the ratification on the convention without country-specific exemption.

Key Words: persistent organic pollutants, Stockholm convention, pesticide

INTRODUCTION

Persistent organic pollutants (POPs) are the toxic chemical substances which are not readily decomposed with common biological or chemical methods in the environment but can be accumulated in living organisms within food web. POPs have the attributes of intense remaining and wide-geographical distribution with long half-life period[1)]. These chemical substances have been reported to cause cancer in breast and prostate, impede generating function and brain activity, reduce immunity, and induce malformed children[2)]. For that reason, global community proposed that a binding agreement should be established against POP distribution. The United Nations Environment Program (UNEP) adopted a global binding agreement on persistent organic pollutants on May 22, 2001 to regulate the distribution of the 12 most offensive chemical substances[3)].

The chemical substances are classified into three groups as organochlorinates, industrial chemicals, and incineration by-products according to their applications. Organochlorinates are aldrin, chlordane, dichloro diphenyl trichloroethane (DDT), dieldrin, endrin, heptachlor, hexachlorobenzenes (HCB), perchlordecone (mirex), and chlorinated camphechlor (toxaphene). Industrial chemical includes polychlorinated biphenyls (PCBs) and incineration by-products are polychlorinated dipenzo-p-dioxin

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(PCDD) and polychlorinated dibenzofurans (PCDF)[4].

In May 17, 2004, the global binding agreement took effectuation with the ratification of 59 countries from the approval of 151 countries. The approving countries can ratify the treaty after the certification in proper controlling the chemical substances. The controlling methods are listed in 3 Annexes in the convention. Annex A listed the chemical substances which should be exterminated afterward such as aldrin, chlordane, dieldrin, endrin, heptachlor, HCB, mirex, PCBs, and toxaphene. Annex B included the substance which should be restricted except agricultural purpose such as DDT. Annex C had the chemical substances which should be produced with improved manufacturing techniques such as PCDD, PCDF, HCB, and PCBs[3].

Meanwhile, UNEP granted grace periods to the ratifying countries as country-specific exemption which was in Article 4 of the convention. The country with specific exemption can postpone the fulfillment of the agreement at least 5 years[5]. After the approval of the binding agreement on October 4, 2001, South Korea ratified the convention with 137 countries on January 25, 2007 with the systematic investigation of country-specific exemption for the 5 chemical substances such as chlordane, DDT, HCB, heptachlor, and PCBs[1].

Although all the chemical substances listed in the convention as organochlorinates have been officially prohibited in domestic distribution since the late 1960s to the early 1980s[6], the National Institute of Environmental Research has monitored the distribution of the organochlorinates in the atmosphere, the hydrosphere, soil, and the bottom land[4]. Additionally, the Korea Food and Drug Administration (KFDA) and Rural Development Administration (RDA) have examined the organochlorinate residues on daily foods[7-12].

This case study was conducted for the systematic investigation for the domestic distribution of the 9 POP-related organochlorinates through documentary examination and fact-finding survey for providing detailed information to the ratification of Stockholm convention. Additionally, some alternate materials were surveyed for the fulfillment of the binding agreement after the ratification.

MATERIALS AND METHODS

A series of investigations with documentary examination and fact-finding survey were conducted for the 9 POP-related organochlorinates such as aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCB, mirex, and toxaphene.

Actual conditions for the chemical substances

Research institutes and academic societies provided the monitoring information for the chemical substances. The research institutes were the National Institute of Environmental Research (NIER), the Korea Environment Institute (KEI), the Korea Food and Drug Administration (KFDA), the Rural Development Administration (RDA), and the Korea Crop Protection Association (KCPA). The academic societies included the Conservation Study, the Korean Environment Science Society, the Korean Society of Agriculture and Environment, the Korean Society of Environmental Engineers, the Korea Society of Environmental Toxicology, the Korean Society of Food Preservation, and the Korean Society of Horticultural Science.

Distributional status for the chemical substances

The annual report of Ministry of Food, Agriculture, Forestry, and Fisheries (MIFAFF) provided overall status of pesticide distribution as raw material or articles from 1945 up to now. KCPA also supplied the information about the pesticide distribution from 1975 to the present days. The annual reports contained the production and consumption of the chemical substances as raw materials or articles.

Alternative materials for the chemical substances

KEI and RDA provided the detailed information of biotic pesticides as well as other organochlorine pesticides as alternate materials.

RESULTS AND DISCUSSION

Actual conditions for the chemical substances

Stockholm convention listed 12 offensive chemical substances as POPs which were 9 organochlorinates one industrial chemical, and two incineration by-products. The toxicity was surveyed for the 9 organo chlorinates as shown in Table 1.

Within the 9 organochlorinates, documentary examination did not show any distributional records for aldrin, dieldrin, endrin, mirex, and toxaphene. The rest supplied their actual conditions through documentary

Table 1. Information of the organochlorinates containing persistent organic pollutants

Substance	Chemical formula	Toxicity		
Aldrin	$C_{12}H_8Cl_6$	- LD_{50},	rat (oral):	50 mg·kg^{-1}
		- LC_{50},	carp (48 h):	0.056 mg·L^{-1}
			sweet fish (48 h):	0.016 mg·L^{-1}
		- Cancer-causing:		IARC 3
Chlordane	$C_{10}H_6Cl_8$	- LD_{50},	rat (oral):	200 mg·kg^{-1}
		- LC_{50},	rainbow trout (96 h):	0.042 mg·L^{-1}
		- Cancer-causing:		IARC 2B
DDT (dichloro diphenyl trichloroethane)	$C_{33}H_{33}N_3O_7S_2$	- LD_{50},	rat (oral):	250 mg·kg^{-1}
		- LC_{50},	rainbow trout (96 h):	0.042 mg·L^{-1}
		- Cancer-causing:		IARC 2B
Dieldrin	$C_{12}H_8Cl_6O$	- LD_{50},	rat (oral):	60 mg·kg^{-1}
		- LC_{50},	rainbow trout (96 h):	0.0012 mg·L^{-1}
		- Cancer-causing:		IARC 3
Endrin	$C_{10}H_5Cl_7$	- LD_{50},	rat (oral):	7.5-17.5 mg·kg^{-1}
		- LC_{50},	gold fish (96 h):	0.0044 mg·L^{-1}
		- Cancer-causing:		-
Heptachlor	$C_{10}H_5Cl_7$	- LD_{50},	rat (oral):	68 mg·kg^{-1}
		- LC_{50},	rainbow trout (96 h):	13 mg·L^{-1}
			bluegill (96 h):	7.4 mg·L^{-1}
		- Cancer-causing:		IARC 2B
HCB (hexachlorobenzene)	C_6Cl_6	- LD_{50},	rat (oral):	10,000 mg·kg^{-1}
		- LC_{50},	fish (96 h)	0.05-2 mg·L^{-1}
		- Cancer-causing:		IARC 2B
Mirex (perchlordecone)	$C_{10}Cl_{12}$	- LD_{50},	rat (oral):	45 mg·kg^{-1}
		- LC_{50},	-	
		- Cancer-causing:	IARC 2B	
Toxaphene (chlorinated camphechlor)	$C_{10}H_{10}Cl_6$	- LD_{50},	rat (oral):	50 mg·kg^{-1}
		- LC_{50},	-	
		- Cancer-causing:		-

*LD_{50}: median lethal dose.
LC_{50}: median lethal concentration.
*Note for cancer-causing
IARC (International Agency for Research on Cancer):
1=carcinogenic, 2A=probably carcinogenic to humans, 2B=possibly carcinogenic to humans,
3=not classifiable as their carcinogenicity to humans, 4=probably not carcinogenic to humans.

examination and fact-finding survey as shown in Table 2.

1) Chlordane

There was no chlordane in the atmosphere, the hydrosphere, and the bottom land at the present day. While some researches detected chlordane from soil at the level of 120 ng·g^{-1} in the late 1960s[13,14], recent survey found chlordane at the level of from no detect (ND) to 2.60 ng·g^{-1} at the present day. Living organisms held chlordane at the level of ND to 1.52 ng·g^{-1} within their bodies (Table 2).

2) Heptachlor

An investigation detected heptachlor in paddy field at the level of 1 to 10 ng·g^{-1}, and in orchard soil at the level of 9 to 10 ng·g^{-1} in 1982[14]. Then, there have been few reports detecting heptachlor in the environments up to now. However, a recent detection found heptachlor in soil at the maximum level of 0.05

Table 2. Contamination status by pesticides containing persistent organic pollutants in South Korea

Substance	Atmosphere ($ng \cdot m^{-3}$)	Hydrosphere ($ng \cdot m^{-3}$)	Soil ($ng \cdot g^{-1}$)	Bottom land ($ng \cdot g^{-1}$)	Living organism ($ng \cdot g^{-1}$)
Chlordane	-	ND	ND – 2.60	ND	ND – 1.52
Heptachlor	-	ND	< 0.04	ND	ND
DDT (dichloro diphenyl trichloroethane)	-	ND	ND	ND	ND – 1.40
HCB (hexachlorobenzene)	ND – 3.79	ND	ND – 1.32	ND	ND

ND: no detect.
Source: National Institute of Environmental Research (1999-2004).

$ng \cdot g^{-1}$ in 1999[15]. MEV[4] later confirmed the heptachlor detection in soil at the maximum level of 0.04 $ng \cdot g^{-1}$ but failed the detection from the atmosphere, the hydrosphere, the bottom land, or living organisms (Table 2).

3) DDT

As DDT was appointed as a persistent chemical substance in the environment, its distribution was officially prohibited in South Korea since 1969[16]. After the detection on DDT in paddy fields at the level of 2 to 30 $ng \cdot g^{-1}$ and in orchard soils at the level of 100 to 1,000 $ng \cdot g^{-1}$ in 1982[14], no survey succeeded in detecting DDT in the environments[16]. Besides, Lee and Kang[8] found DDT as isomers such as DDE and DDD in Gwangyang Bay at the level of 0.07 to 0.43 $ng \cdot g^{-1}$ and ND to 0.20 $ng \cdot g^{-1}$, respectively. Jeon et al.[13] also found DDT as *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT in Incheon district at the level of ND to 1,297.2 $ng \cdot g^{-1}$. From that result, Hong et al.[17] presumed that DDT was on the decomposing process. On the other hand, DDT was detected in the conventional provisions at the level of less than 100 $ng \cdot g^{-1}$ after 2000. DDT was also found within human body at the level of 190 $ng \cdot g^{-1}$ lipid in fatty tissue and 500 $ng \cdot g^{-1}$ lipid in bloodstream[15]. MEV[4] confirmed the DDT detection from the living organisms at the level of ND to 1.40 $ng \cdot g^{-1}$ (Table 2).

4) HCB

HCB was hardly found in the environment up to the 1970s, but often detected in the atmosphere, the hydrosphere, soil, and the bottom land from the 1990s[7]. MEV[4] also found HCB in the atmosphere at the level of ND to 3.79 $ng \cdot g^{-1}$ and in soil at the level of ND to 1.32 $ng \cdot g^{-1}$ between 1999 and 2004. Although a certain research detected HCB in the fatty tissue of living organisms at the level of tens of nano grams[18], the chemical substance was hardly detected in the environment (Table 2).

Distributional status of the chemical substances

1) Chlordane

Chlordane was twice imported into South Korea. One was conducted at the raw material with the amount of 1,198 kg in 1964 and the other was done as the emulsifier with the amount of 930 kg in 1967. Chlordane was consumed as emulsifier from 1965 with the amount of 33 kg to 1968 with the amount of 14 kg[1]. The consumption for the other purpose was done until 1995 in certain factories manufacturing containers in which chlordane was applied as glue additive. All the containers were exported without any domestic distribution.

2) Heptachlor

The raw material of heptachlor was steadily imported from 1962 with the amount of 97,968 kg to 1979 with the amount of 63,503 kg. The emulsified heptachlor was once imported in 1963 with the amount of 7,268 kg. The consumption of heptachlor was done as wettable powder from 1963 with the amount of 416,174 kg to 1979 with the amount of 42,397 kg[16].

3) DDT and HCB

After the import of DDT into South Korea from 1946 to 1979 with the total amount of 941 tons, no DDT was imported up to now[16]. There was also no

record of domestic distribution for HCB until the present[18]. Nevertheless, DDT and HCB have been intermittently detected in the environment[14]. As DDT and HCB were inevitably released from the production processes of DDT and HCB as reaction intermediates or impurities[18-20], an interview was performed for the chemical companies dealing with dicofol and chlorothalonil.

Dicofol was intermittently imported without any domestic production whereas chlorothalonil was domestically produced up to 2002 with steady import up to now[21] (Table 3). Dicofol was applied for 4 items with the content of 35% and chlorothalonil for 30 items with the content of 30 to 75%[3]. As these items were made of their active substances, distilled water, and diluents without any chemical reactions, other chemical substances were not released in producing processes.

Alternative materials for the chemical substances

Table 4 listed the alternative materials for the POP-related organochlorinates. The proposed materials were also organochlorine pesticides. In the proposition, chlordane can be replaced with disulfoton, fonofos, chlorpyrifos, propoxur, fenitrothion, diazinon, etc. DDT can be exchanged with diazinon, carbaryl, malathion, trichlorphon, quinalphos, etc. The alternative materials for heptachlor were aldicarb, carbaryl, carbofuran, phorate, fenvalerate, deltamethrin, etc[1].

On the other hand, the alternative materials had the possibility of another contamination. For that reason, RDA has conducted steady research for developing biotic pesticides. Table 5 showed the distributional status of biotic pesticides in the world. The articles of fungicides were 172 as occupying 62% against to the whole amount. Pesticides occupied about 20% of the whole amount as producing 49 articles. The applying

Table 3. Distributional status for pesticides containing persistent organic pollutants

Substance	Domestic production (ton)					Import (ton)				
	2001	2002	2003	2004	2005	2001	2002	2003	2004	2005
Dicofol	-	-	-	-	-	14	10	-	-	3
Chlorothalonil	776	584	-	-	-	131	640	452	531	538
Total	776	584	-	-	-	145	650	452	531	541

Table 4. Substitute materials for the pesticides containing persistent organic pollutants

Substance	Substitute material
Chlordane	disulfoton, fonofos, chlorpyrifos, propoxur, fenitrothion, diazinon, etc.
Heptachlor	aldicarb, carbaryl, carbofuran, phorate, fenvalerate, deltamethrin, etc.
DDT (dichloro diphenyl trichloroethane)	diazinon, carbaryl, malathion, trichlorphon, quinalphos, etc.
HCB (hexachlorobenzene)	-

Table 5. Biotic pesticides in the whole world in 2004

Classification	Pesticide	Fungicide	Nematocide	Herbicide	PGR	Others	Total
Microbe	37	46	3	8	2	-	96
Pheromone	-	53	-	-	-	-	83
Natural enemy	-	53	-	-	-	-	53
Natural substance	12	17	1	2	12	17	61
Gene	-	3	-	6	-	4	13
Total	49	172	4	16	14	21	216

PGR: plant growth regulator

methods were various such as using microbe, pheromone, natural enemy, natural substance, and gene. However, their low efficiency should be improved accompany with their high cost[21].

CONCLUSION

A global binding agreement was adopted with the leading of UNEP in Stockholm on May 22, 2001 to regulate the distribution of the 12 most offensive chemical substances. The binding agreement took effectuation by the ratification of 59 countries from the approval of 151 countries on May 17, 2004. The approving countries can ratify the agreement after certifying the fulfillment of the agreement[4]. At the same time, UNEP gave country-specific exemption to the ratifying countries to admit grace period for at least 5 years. South Korea got the ready of ratification after the approval on October 4, 2001 with country-specific exemption for chlordane, DDT, HCB, heptachlor, PCBs[5].

The 12 offensive chemical substances included 9 organochlorinates, one industrial chemical, and two incineration by-products. South Korea had officially prohibited the distribution of the 12 chemical substances since the late 1960s[1].

Chlordane and heptachlor had their applications in controlling termites. South Korea appointed those substances as residual pesticides to restrict their distribution as the raw material in the 1970s and as the articles in the 1980s[4]. Chlordane and heptachlor were still detected in the environment but their amount was minute. Considering their half-life periods, those substances were expected to be completely exterminated within the grace period.

DDT and HCB were inevitably produced as reaction intermediates in the production process of dicofol and chlorothalonil. Dicofol contained DDT at the maximum concentration of 0.1% and chlorothalonil held HCB at the maximum concentration of 0.05%[19]. There were 4 items with the use of dicofol and 30 items with the use of chlorothalonil from 4,051 items of total agricultural chemicals in South Korea. UNEP appointed the DDT and HCB in dicofol and chloro thalonil as impurities with using the term of "insignificant" and other countries also regarded those substances as unintentional products[5]. For that reason, it possibly seemed for those two substances to be continuously applied without country-specific exemption.

On the other hand, certain alternative materials were surveyed for the prohibition of organochlorine pesticides. Biotic pesticides could be one of the alternative materials. However, the efficiency of those materials should be improved before their actual applications.

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