INVENTORY AND STATUS OF PERSISTENT ORGANIC POLLUTANTS – PESTICIDES IN CROATIA

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Abstract. Persistent organic pollutants (POPs) which include some pesticides are very important environment polluters. Their harmful impact is mainly consisted of their air transmission, resistance to chemical-, photo- and bio-degradation and possibility of their accumulation in fat tissue of all living organisms. As they can be transported by air on long distances, they were found in samples on locations where they were not used. This group of pollutants includes pesticides (such as aldrin, chlordane, dieldrin, endrin, heptachlor, lindane, alpha-hexachlorocyclohexane, beta-hexachlorocyclohexane, hexachlorobenzene, mirex, toxaphene, DDT), industrial chemicals (such as polychlorinated biphenyls, PCBs) and unintentional by-products of industrial processes (such as dioxins, furans etc.). Because of their high efficacy in agriculture through the middle of 20th century their consumption was very high. In the meantime their negative impacts appeared and their harmfulness became well known threat to the environment and to human health all over the globe. In this work an overview of inventory and status of POPs in Croatia is given. The emphasis is given on POPs pesticides. In accord with global tendencies to reduce and eliminate production, use and releases of harmful substances a gradual prohibition of pesticides (aldrin, dieldrin, hexachlorocyclohexane, DDT) usage started in Croatia 1972 and ended in 2001 with proscription of lindane and dicofol usage. Up to date all of them are banned from production and application, and no stockpiles are detected. In the period of their common usage, production of POP's pesticides in Croatia was mainly based as supplement to some fertilizers (aldrin). Today there is no need for their production, since all preparations based on POPs are now substituted with

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numerous toxicologically and environmentally friendlier active ingredients. Also there is no import and export of POPs through Croatian border, with exception for some institutions which have permission for import of small quantities used as laboratory standards for determination of residual POPs pesticides. Residues of POP's pesticides are monitored now days only in water. There is still pronounced need for adequately equipped laboratories and trained stuff for their monitoring in vegetables, animals, water, soil and human biomaterial.

Keywords: inventory, pesticides, persistent organic pollutants, Croatia,

1. Introduction

Persistent Organic Pollutants (POPs) are chemical compounds which persist in the environment. All of them are to some level resistant to photo-, chemical- and bio-degradation processes. They tend to be highly soluble in fat but not in water. Since they bio-accumulate in the fat of living organisms they represent a high risk to human health (WFPHA, 2000; MEPPPC, 2009). Exposure to individual POPs has been associated with cancer, neurotoxic, behavioral, and reproductive changes. Due to their accumulation in fats they are likely to be passed to the next generations in uterus and through breast milk. They have also been found far away from places where they have been produced or used. They are able to evaporate in warm climates and can be absorbed and transported by atmospheric particles. POPs have been linked to population declines in fish and other wildlife, and also to specific disorders such as reproductive and hormone system dysfunction, eggshell thinning, metabolic changes, deformities and birth defects, cancers, behavioral changes, etc. (WFPHA, 2000). In order to eliminate and reduce production, use and releases of POPs joined action of international community resulted in two important agreements: (i) The Protocol to the Regional UNECE Convention on Long-Range Trans boundary Air Pollution (CLRTAP) on POPs opened for signatures in June 1988 and comes into force on 23rd October 2003 and (ii) The global Stockholm Convention on POPs, opened for signatures in May 2001 and comes into force on 17th May 2004. These documents establish strict international regimes for initial lists of POPs (16 in the UNECE Protocol and 12 in the Stockholm Convention). Both documents also contain provisions for including additional chemicals into lists of prohibited compounds. Croatia has signed implemented international documents on POPs as well as thirty international conventions and agreements

having similar implications. Illustration of POP's pesticides status in the Republic of Croatia is given in Table 1.

TABLE 1. List of active ingredients classified as POPs under the Stockholm Convention and the time of their prohibition in the Republic of Croatia.

Active ingredient	Permitted since	Usage prohibited since
Hexachlorobenzene (HCB)	1962	11/07/1980
Toxaphene	1957	27/04/1982
Endrin	1957 (since 1971. used as rodenticide)	29/05/1989
Aldrin	1958	1972
Dieldrin	1958	1972
Heptachlor	1956	July 1973
Hexachlorocyclohexane (HCH)*	1944	1972
DDT	1944	1972 (in agriculture)
Lindane	1944	July 2001.
Chlordane	Data before 1995. not known	1971 (in agriculture)
Mirex	Never allowed in the Croatian plant protection	

* Alpha-hexachlorocyclohexane, beta-hexachlorocyclohexane are on the list since 2009

2. POPs Inventory in the Republic of Croatia

The most up to date and comprehensive overview of POPs levels and their sources in Croatia is the 2009 National Implementation Plan for the implementation of Stockholm Convention on POPs (NIP) (MEPPPC, 2009). The NIP contains a good overview of the work which has been done so far on POPs in Croatia. Unfortunately it shows that much of the data available is rather old or that sampling has often taken place on a one-off basis rather than consistently over time. A comprehensive monitoring of POPs in samples taken from the environment, food or people does not exist. Today, in Croatia, organochlorine pesticides (OCPs) are regularly monitored in the frame of national monitoring program only in rivers and accumulation waters. Data on POPs pesticide residues in food, sediments, soil and vegetables can be found in various projects and inspectional supervisions.

2.1. POPs IN SURFACE, GROUND AND DRINKING WATERS

The studies of organochlorine pesticides and polychlorinated biphenyls (PCBs) in the surface and drinking water started in late 1970's. Concentration of OCP in ground water from eastern Slavonia was examined from 1980 to 1983, because of potential grounder water using as drink water. Data obtained during twenty years period are presented in Table 2.

TABLE 2. Concentration of PCBs in river, drinking water (ng L^{-1}), river sediments (mg kg^{-1} dry sample) and potable water (ng L^{-1})

Sample (N^{*})	Sampling period	The range of concentration / weight ratios
	River water	ng L^{-1}
Sava (7)	1992/95.	<1 - 25
Kupa (22)	1985.	<1 - 52
Kupa (6)	1985/86.	2 - 16
Kupa (24)	1988/89.	<1 - 8
Drava (8)	1981/82.	<1 - 7
Cetina (7)	1993/94.	2 - 8
Jadro (7)	1993/94.	3 - 13
	River sediments	mg kg^{-1} (dry sample)
Kupa (6)	1985/86.	1 - 39
Jadro 8)	1993/94.	2 - 507
Cetina (18)	1993/94.	<1 - 7
	Potable water (karst springs before treatment)	ng L^{-1}
Labin	1980/90.	2 - 48
Pula	1980/90.	4 - 176
Buzet	1980/90.	4 - 50
	Drinking water (after treatment)	ng L^{-1}
Zagreb (10)	1988.	<1 - 5
Sisak (16)	1988/89.	<1 - 5
Labin (10)	1989.	<1 - 3
Drava (8)	1981/82.	<1 - 7

According to data from the annual reports of the Institute of Public Health of Istria in the period from 1980 to 1984, the highest concentrations of DDT-type compounds (500 and even 8800 ng L^{-1}) were reached in the regional rivers of Istria (Boljunčica, Mirna, Raša, Pazinčica). Values detected in the later period

of time (from 1986 to 1994) were significantly reduced (<100 or even <50 ng L^{-1}) as a result of limiting 4, 4'-DDT application. During the same period of time γ-HCH concentrations were also reduced in three Istria rivers (Boljunčica and Raša (ca. 50 ng L^{-1}), Mirna (ca. 30 ng L^{-1}) and Pazinčica (200 ng L^{-1})). The values are less than 10 ng L^{-1}, and in Pazinčica from 200 to 100 ng L^{-1}.

According the annual reports of the Institute of Public Health of the Split-Dalmatia county measurements performed in Croatian coastal region has shown that the highest concentrations of DDT-type compounds in Dalmatian rivers from 1988 to 1993 were in the range from 20 ng L^{-1} (river Jadro 1993) to 195 ng L^{-1} (Krka 1988/89). The highest concentration of γ-HCH (ca. 56 ng L^{-1}) was detected in the river Čikola 1988/1989. However, in samples of river water Jadro, Cetina, Žrnovnica and Pantano collected during 1993/1994, concentrations of HCB, α-and γ-HCH, and DDT-type compounds were reduced to 2 ng L^{-1}.

Measurements performed from 1979 to 1989 in the continental regions revealed that the highest concentrations of DDT-type compounds were below 1 ng L^{-1} (in rivers Sava, Drava, Korana, Dobra, Kupa). However, in several water samples collected near the river Kupa at Sisak area in the period 1988/89 detected concentrations of 4,4 '-DDT and its metabolites were up to 6 ng L^{-1}. The highest concentrations of γ-HCH (1 to 20 ng L^{-1}) were also detected in the same samples. The second most frequently detected OCP in Kupa river was HCB at concentrations up to 3 ng L^{-1}. Examination of OCP in the Sava river, streams, lakes and ground water in the area of Zagreb in the period from 1992 to 1995 confirmed the frequent presence of traces of γ-HCH and the occasional occurrence of very low concentrations of other compounds. From 1980 to 1983 investigations of OCP concentrations were performed in ground water on several locations in eastern Slavonia, including the area of the city Osijek. The highest concentrations of frequently detected compounds were up to 28 ng L^{-1} for γ-HCH, up to 25 ng L^{-1} for DDT and its metabolites and up to 3 ng L^{-1} for HCB. Organochlorine pesticides were detected in drinking water. The frequency of their occurrence in tap water in Sisak was during 1988/89 similar to that of the Kupa River water. Concentrations of γ-HCH ranged from 1 to 59 ng L^{-1}. At the same time examination of OCP in drinking water in Zagreb and Labin revealed regular presence of γ-HCH traces, while other compounds was detected occasionally. In the period from 1981 to 1990 the concentrations of OCP in raw water karst springs from which drinking water is prepared in Labin was 7-574 ng L^{-1}, in Buzet 11-260 ng L^{-1}, and in the area of Pula 1-180 ng L^{-1}.

Data on the levels of OCPs in river sediments in our country are deficient. In accord of high tendency in sorption and bio-concentration in these media one can expect a higher level than in water. Detected traces of HCB, α-and γ-HCH and DDT and its metabolites in sediments of Middle River (Jadro, Cetina,

Pantana and Žrnovnica) may be attributed to global environmental pollution. Sources of pollution of the aquatic environment with PCBs are often results of discharged untreated wastewater and/or improper disposal of waste, primarily waste oil.

2.2. POPs IN THE FOOD CHAIN

Even a small release of POPs can have a significant impact on living organisms due to processes of bio-magnifications. There is little data about POPs pesticides in the food chain and systematic monitoring is not carried out. The Croatian Institute of Public Health has analyzed only the content of some OC compounds in food samples in the period from 1986 to 1989 year and in 1999 given in Table 3. From

TABLE 3. Concentrations (mean, mg kg^{-1} fat, fish mg kg^{-1} wet weight) of OC compounds in food samples. Number of analyzed samples is indicated in parentheses

Source	HCB	α-HCH	Lindane	DDT complexes
Fish and fish products				
1986/89 (153)	5	2	25	127
1999 (46)	0.1	0.1	0.5	4.7
Meat and meat products				
1986/89 (733)	3	2	25	75
1999 (80)	0	1	6	62
Milk and milk products				
1986/89 (438)	7	3	24	83
1999 (52)	1	1	6	35

0- below the limits of determination

Table 3 it is evident that the concentrations of all compounds in all types of food decrease with time. Drastic diminishing of POPs in all food types can be ascribed to positive effects of their prohibition starting 30 years ago.

2.3. POPs IN THE SEDIMENTS AND SOIL

There is little data about POPs pesticides in soil and no systematic monitoring in Croatia is carried out. Studies of OC pesticides and PCBs water starting in early 1980s were expanded to river sediments and it was not until past few

years that soil become included. Levels of total PCBs were measured in samples of surface soils collected in the vicinity of several industrial and power plants, around airports and in urban and rural area that are close to possible sources of contamination. Results of mentioned concentrations of PCBs in soil are presented in Table 4. In most of the samples collected in urban and rural areas, concentrations of PCBs were characteristic of global environmental pollution (<10 μg kg^{-1} dry sample). Higher values were determined in the soil near the substations, especially those destroyed during the war, airports and in industrial areas.

TABLE 4. Concentrations (mg kg-1 of dry sample) of PCBs in the soil

Locations	Sampling period	Range (N*)
Airports	1994/96	3 - 41 327 (18)
Industrial facilities	1997	21 - 1 207 (7)
Substations destroyed during the war		
Konjsko (Split)	1993	7 - 166 (17)
Komolac (Dubrovnik)	1996	1 640 (2)
Zadar	1996	173 - 204 823 (6)
Šibenik	1996	470320 - 2 094 151 (3)
Delnice	1996	21 (1)
Urban and rural areas	1994/97	2 - 39 (18)

*N denotes samples

It can be clearly seen in Table 4 that the highest level of soil contamination by PCBs occurred in the Croatian karst areas damaged during the war. Risk values, caused by the spread of capacitor oil, also were recorded at several locations in the vicinity of the damaged substation in Zadar. The highest concentrations of PCBs in the soil inside airports were observed in samples collected close to the runway for aircraft. Most probably this is a consequence of some uncontrolled discharge from electrical and hydraulic systems of aircraft. The fact that in the vicinity of airports the level of PBC was regularly at the level of global environmental pollution indicates the existence of local pollution sources within airports. Polychlorinated dibenzodioxins (PCDDs) and Polychlorinated dibenzofuran (PCDFs) in soil were found only in samples taken inside the airport where the mass fraction PCBs was higher than 5000 μg kg^{-1}, and in soils collected near the former plant chloroalcalic electrolysis. The levels of total PCDDs and PCDFs in soil collected inside the airport were within the typical values for urban and rural areas (< 10 ng I-TEQ kg^{-1} dry sample). Much higher values were detected in soil sampled near the former plant chloralkaline electrolysis (Kaštel Sučurac near Split). However, even in these soils, the

calculated values of I-TEQ were far below the value of 10 000 ng I-TEQ kg^{-1} dry sample which is the statutory limit values in Germany over which must be carried out rehabilitation of polluted industrial areas.

3. Status of POPs

Currently, there are no POP compounds productions in Croatia, nor they are planned so far. Today there is no need for their production, since all plant protection products based on POPs are now substituted with numerous toxicologically and environmentally friendly active ingredients. Also there is no import and export of POPs in Croatia, with exception for some institutions which have import permission for small quantities used as laboratory standards for determination of residual POPs pesticides. The NIP (MEPPPC, 2009), gives details about usage of POPs pesticides from 1962 to 1976 and about DDT usage in Forestry Institute until 1986. It must be stressed that all production, circulation and usage of POPs pesticides, whether for agriculture or other purposes, are now forbidden in Croatia (State official gazette, 2005). Additionally, no stockpiles of POPs pesticides have been detected in Croatia.

3.1. FORMER, PRESENT AND FUTURE PRODUCTION OF POPs PESTICIDES

In the period when the POPs pesticides were allowed for application, there were several manufacturers that used to put pesticides of different formulations on the market. It is necessary to emphasize that the amounts produced in Croatia during the former Yugoslavia were meant for use in all Yugoslav republics. INA Kutina produced NPK fertilizers from 1969 to 1972 (12:12:12) with 1% aldrin, which was soon banned. Since 1975 and up to the year 2000 production has been substituted with another type of fertilizer (Florin 3 which didn't contain aldrin). Endrin was used in the beginning of the first applications in 1957. Due to high risk level for the appliers and the environment it was used only in small quantities since 1971 as rodenticide. Numerous products are now days registered that completely replaced the toxicologically unfavorable pesticides, including POPs. Future production of POPs pesticides is neither planned nor possible as their manufacture has been prohibited. Until the ban of POPs pesticides, the quantities used were those indicated in the respective licenses. Their elimination has not caused big problems because of substitution with less toxic, less hazardous and ecologically acceptable compounds. Before the ban, POPs pesticides were used in the control of many pests. With respect to the wide use against the pest and to the target cultures, their quantities were significant.

3.2. EXPORTS AND IMPORTS OF POPS PESTICIDES

In the fact that there is no production of POPs pesticides in Croatia, there is no way of their export in any country of the world. It is permitted to import only the active ingredience from the List of active substances authorized for use in plant protection products in the Republic of Croatia. On the List of existing active ingredients are those allowed in biocidal products or finished pesticide formulations with registered use pursuant with the Register of plant protection products. In the Register of biocidal products that are allowed to be placed on the market and all other are published annually or even more often in the Official Gazette. Each import must be approved by the Ministry of Health (MH) or Ministry of Agriculture (MA) and reported to The Croatian Institute for Toxicology and Antidoping (CITA). The importer is obliged to announce the transfer of such a consignment across the national border at least three days in advance. Importer is also obliged to fill in the prescribed form and submit it to CITA. At listed border crossing there is a competent sanitary inspection for biocidal products or phytosanitary inspection for plant protection products. Inspection based on the permit of the competent ministry and the registry of the permitted products in the Croatia, approves the import of pesticides. Because customs control of import bases itself on the approvals of respective ministries, not many misuses can be expected in this respect. It is not likely that POPs pesticides will be illegally traded because neighboring countries have prohibited most of them, while Croatia has registered corresponding environmentally friendly substitutes. According to the regulations regarding operations of agricultural and veterinary pharmacies, only the pesticides approved by MH or MA can be placed on the market (IPEN, 2006; Official Gazette, 82/12; 90/08; 28/09; 36/10; 31/11; 73/12; 30/12). Small quantities of POPs can be imported if they were used as laboratory standards for determination of residues in food, water and other materials.

3.3. CURRENT STOCKPILES, WASTE WITH POPs PESTICIDES, DISPOSAL SITES AND SITES, CONTAMINATED WITH POPS PESTICIDES

The inventory of POPs pesticides has not detected any stockpiles (MEPPPC, 2009). The products including currently used pesticides do not contain POPs. Consequently, there is no risk that waste with POPs can be generated. Special disposal sites for such POPs waste do not exist up to now. If there has been any, disposed at municipal waste disposal sites, then it must have been covered by layers and layers of other waste during 40 years, making it difficult to find them. Empty packaging materials for old pesticides could be the exception. So far there has been no site identified for disposal of hazardous waste, i.e. POPs.

However, the association CROCPA (Association of Producers andRepresentatives of Producers of Plant protection products of Republic Croatia) that has 10 members decided to organize collection of empty packages of plant protection products of the companies they represent. The idea is to collect empty packages from the end users, especially small farmers. In front of agricultural pharmacies where plant protection products are sold farmer can dispose the package into the designated box. Collecting of waste is carried out by the CIAK Company that is working on ecological and environmentally friendly disposal of hazardous waste. Considering that there are other types of POPs persistent compounds requiring special disposal sites, in case of their occurrence these landfills should be foreseen for disposal of POPs too.

4. Conclusions

According to the available data in Croatia POPs pesticides are not manufactured, used, exported or imported. Despite the ban or restricted use of PCBs and OCPs, they are still present in the environment. However, POPs inventory has not identified any contaminated sites or stockpiles. Data collected through various projects and from the analysis of inspection samples, although not done permanently and within a national monitoring program clearly revealed significant decrease in POPs concentration with time.

Currently, in accord to legal regulations, environmental levels of POPs pesticides are monitored only in waters, whereas other environmental elements and human are monitored occasionally as part of specific projects. It is, therefore, necessary to promulgate regulations for systematic and permanent monitoring of POPs in all environmental elements and human. Also, it is necessary to establish legal obligated collection of the results and continuous monitoring of their levels at the central registry.

A problem which should be solved in the near future is to provide funding for organization of laboratories, equipment and adequately trained staff. Poorly equipped analytical laboratories and their staff without proper training require the funds that would also enable certification of these laboratories. Despite the falling trend of POPs residue in the analyzed samples of vegetable and animal origin, water, soil and human biomaterial, still reliable information are needed to know their real status.

References

IPEN (International POPs Elimination Network: Croatia - Country Situation Report on POPs), 2006, International POPs Elimination Project Fostering Active and Efficient Civil Society Participation in Preparation for Implementation of the Stockholm Convention.

MEPPPC (Ministry of the environmental protection, physical planning and construction) 2009: National Implementation Plan for the Implementation of Stockholm Convention on Persistent Organic Pollutants, Zagreb, February 2009.

Official Gazette 29/2005: List of Toxins Whose Production, Circulation and Use are Forbidden, Official Gazette 82/2012: List of Active Substances Authorized for Use in Plant Protection Products in the Republic of Croatia.

Official Gazette 94/2012: Register of Plant Protection Products.

Official Gazette 30/2012; 73/2012: Register of Biocidal Products that are allowed to be placed on the Market.

Official Gazette 90/2008, 28/2009, 36/2010, 31/2011: List of Existing Active Substances Allowed in Biocidal Products.

WFPHA (World Federation of Public Health Associations) (2000): International Joint Commission on the Great Lakes: “Seventh Biennial Report on Water Quality, Windsor/Detroit, 1994, “Persistent Organic Pollutants and Human Health”, WFPHA, May, accessed: [http://www.wfpha.org/pg_projects_pops.htm, p.7.], 24.7.2012.