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EMISSIONS OF PERSISTENT ORGANIC POLLUTANTS (POPs) AND THEIR INFLUENCE OVER HUMAN HEALTH AND ENVIRONMENT

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Abstract. Assessment of the emissions as a quantity and quality of different industrial, municipal, transport and agricultural sources is reported in the framework of Stockholm convention. Polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF), polychlorinated biphenyls (PCBs), influence over human health and environment is a subject of discussion. Different possibilities for reducing the emitted quantities of POPs are discussed and effective measures proposed. On the basis of the results obtained, prognosis is made about future losses, and needed action recommended.

Keywords: persistent organic pollutants (POPs), emissions, human health risk, reduction.

AIMS AND BACKGROUND

Polychlorinated dibenzodioxins and dibenzofurans (PCDD/PCDF) as by-products and polychlorinated biphenyls (PCBs) as industrial chemicals together with nine specific pesticides belong to the chlorinated aromatic hydrocarbons and are covered by the Stockholm Convention under name Persistent Organic Pollutants (POPs)[1]. These organic compounds are extremely resistant, regarding photolytic, chemical and biological degradation[2]. POPs have abilities to bioacumulate in fatty tissues of living organisms, thereby posing a risk of adverse effects to human health and the environment. With the evidence of long-range transport of these substances to regions where they have never been used or produced and the consequent threats they pose to the global environment, the international community has on several occasions called for urgent global actions to reduce and eliminate releases of these chemicals[1].

The Stockholm Convention on Persistent Organic Pollutants (POPs), adopted in May 2001, banned selected persistent organic pollutants. During the Stockholm Convention negotiations, UNEP Chemicals initiated a project funded by the Global Environment Facility (GEF) aiming to assist 12 countries with the development of their National Implementation Plans (NIPs) and to strengthen national capacities for managing POPs and meeting their obligations under the

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Stockholm Convention[3]. Bulgaria is one of these 12 countries, which have to develop NIP.

The aim of recent study is to assess the POPs emission data collected from different industrial sectors in Bulgaria, to relate them with human health and environment risks and to give some proposals and measures to be taken for reducing the quantities of emissions, regarding Bulgarian National Implementation Plan.

HUMAN HEALTH AND ENVIRONMENT RISK CAUSED BY POPs

Great number of published papers is dedicated to this topic. The most important characteristics relevant to this study are summarised and briefly presented. In general, POPs are extremely stable in environment in wide range of temperatures and pH conditions, as well they are very resistant to photolytic, chemical and biological treatments. Due to their low biodegradation and water solubility, and fact that solubility in fatty acids helps them to accumulate in tissues of animals and humans, POPs are concentrated in fatty tissues of living organisms and different environmental components. POPs are also semi-volatile, therefore, they are distributed via water and air ecosystems and pollute distant areas[4].

Both humans and environmental organisms are exposed to POPs around the world, in many cases for extended period of time. Over the past several years, the risk posed by POPs has become of increasing concern in many countries, resulting in actions to protect human health and the environment being taken or proposed at the national, regional and international levels[2]. People are generally exposed to POPs through their food supply although workers and residents of communities near POPs sources can also be exposed through inhalation and dermal contact. Other pathway is by accidents. Contamination of food can occur through environmental pollution of air, water and soil. POPs exposures are often highly pronounced in peoples whose diets include large amounts of wild food and especially big fish, marine animals and other aquatic resources. Some of the best documented, highly exposed populations are aboriginal people living in vary cold climates far distant from most POPs sources. Ordinary domesticated meat and milk products, however, generally are also significantly contaminated by POPs in most regions[5].

POPs are toxic for living organisms, especially for man, in very low concentrations. Depending on interaction with other pollutants they possess different acute toxicity. Speaking generally, these toxic effects can be summarised as follows:

- Cancers and tumors at multiple sites;
- Neurobehavioural impairment including learning disorders, reduced performance on standard tests and changes in temperament;

- Immune system disfunction;
- Reproductive deficits and sex-linked disorders;
- A shortened period of lactation in nursing mothers;
- Diseases such as endometriosis, increased incidence of diabetes, and others[5].

Regarding PCBs, their toxic effects and environmental behaviour strongly depend on degree of chlorination as well as position of chlorine atoms of biphenyl. Great number of toxicological research has been performed in order to assess toxic effects in man and the health impact of PCB mixtures.

The first main noticeable symptoms within a few hours high exposure with PCBs are general weakneses, itching and irritation of the eye, skin rash, burning sensations, limbs sensationless, headache, vomiting, etc. These symptoms often appear as long-term chloracne, hair loss and skin hyperpigmentation as well as immune system deficiency, and after a few years contacts – increased level of death cases, due to cancer. On the basis of investigation made during mass poisoning with PCBs and other epidemiological surveys, as well as animal experiments is proved that PCBs destroy humans immune system. Their long-term toxic effect over man and the environment is a result of low biodegradation, as well as high rankage of accumulation in living organisms. That's way PCBs are attached to the so-called cancerogenic substances[6].

Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofuranes (PCDF) are envoronmental contaminants detectable in almost all components in global ecosystem in trace amounts. These compound classes in particular have caused major environmental concern. In contrast with other POPs they are formed as by-product of numerous industrial activities and all combustion processes[7].

Humans can be exposed to PCDD/PCDF through many different ways as diet, or for example, in occupational settings-herbicide production, industrial accidents or chemical fires, and through burning of garbage in dump areas. The main pathways of PCDD/PCDF intake by man are as follows:

- Inhalation of air and intake particles from air;
- Ingestion of contaminated soil;
- Dermal absorbtion;
- Food consumption.

In 1990, a WHO working group concluded that 90% of the daily dioxin intake results from ingestion. Especially, foodstuffs of animal origin are responsible for the daily intake of approximately 2 pg TEQ/(bw d). All other foodstuffs, especially the 'non-fatty' ones, are of minor importance in terms of PCDD/PCDF intake. They are either of plant origin or do not have a high potential for bioaccumulation of lypophilic compounds. Due to many measures to reduce emmisions of PCDD/PCDF into the environment, reduction of PCDD/PCDF

contamination in food was observed. As a conseqence, the daily intake via food decreased.

Dioxin exposures to humans are associated with an increased risk of severe skin lesions (chloracne and hyperpigmentation), altered liver function and lipid metabolism, general weakness associated with drastic weight loss, changes in activity of various liver enzymes, depression of the immune system, and endocrine and nervous system abnormalities[7].

POPs EMISSIONS IN BULGARIA

The main POPs emission sources not only in Bulagria but all over the world are combustions procceses in different industrial sectors. The biggest one is the Thermal Electrical Power Plants followed by domestig heating, where huge amount of fossil fuel is burned. Depending on plant capacity, used furnaces and fuel different quantities are generated. So far in Bulgaria does not exist a monitoring system dedicated to POPs (PCB, PCDD/PCDF, etc.) measurements. Recently, under the National Implementation Plan, regarding POPs inventory procces our team is using a guideline called CORINAIR, based on emission factors. This guideline is adopted in EU and also in Bulgaria. For example emission factor for PCBs emitted from over 300 MW TPP using lignite coals is 1.8 mg/t and emission factor from domestic heating is 183.2 mg/t. Tables 1 and 2 present annual dioxines and PCBs emmisions from different sectors, calculated by CORINAIR.

The presented data and their tendency, regarding generated PCDD emissions show that combustion in energy and transformation industries and waste treatment and disposal are main sources. The tendency illustrates clearly a significant reduction in generated total dioxin emissions from 554.2 g for 1990 to 232.528 g for 2000, which is almost 50% minimisation. PCBs data show that non-industrial combustion plants have major contribution and negative tendency, leading to 141.4 g for 2000.

MEASURES TO BE TAKEN FOR POPs EMISSION REDUCTION

In developed countries combustion technologies and technics, related with waste incineration, are major sources of PCBs, PCDF and PCDD, which are among the most resistant substances. Regarding their reduction, based on the presence of BAT, high efficient cleaning devices and modern systems for ecological and technological control are neaded. In literature sources great number of publications is dedicated to different options for reduction of PCDD/PCDF – plasma treatment of waste gases, purification by sorbtion, filtration, etc. For different systems where PCBs take part wide range of technologies are worked out. For

Table 1. Annual dioxines emissions (in g) from different sectors

Emission categories	1990	1995	1996	1997	1998	1999	2000
Combustion in energy and transformation industries	159.3	141.6	138.1	123	119.8	114.9	109.1974
Non-industrial combustion plants	94.6	201.2	107.1	91.1	68.3	60.2	58.3389
Combustion for manufacturing industries	80.7	17.1	17.8	27.9	39.4	12.5	16.3823
Production processes	43.8	52.3	36.6	40.7	24.1	29.1	21.5054
Extraction and distribution of fossil fuels and geothermal energy	0	0	0	0	0	0	0
Solvent and other product use	0	0	0	0	0	0	0
Road transport	21.8	12.7	13.4	9.8	8.6	6.6	7.226
Other mobile sources and machinery	15.1	7.1	7.5	7.4	10.6	12	9.685
Waste treatment and disposal	138.9	24	20.4	9.8	17.5	9.9	10.193
Agriculture	0	0	0	0	0	0	0
Nature	0	0	0	0	0	0	0
Total annual emissions	554.2	456	340.9	309.7	288.3	245.2	232.528

Table 2. Annual PCBs emissions (in g) in different sectors

Emission categories	1990	1995	1996	1997	1998	1999	2000
Combustion in energy and transformation industries	56.4	50.8	49.8	48.2	47.5	41.9	40.6394
Non-industrial combustion plants	87.2	244.2	135.1	121.7	138	128	141.3727
Combustion for manufacturing industries	9.6	7.6	7.2	7.9	6.8	5.16	5.151
Production processes	–	–	–	–	–	–	–
Extraction and distribution of fossil fuels and geothermal energy	–	–	–	–	–	–	–
Solvent and other product use	–	–	–	–	–	–	–
Road transport	89.4	72.4	61.9	40.7	49.8	47.1	41.236
Other mobile sources and machinery	15.1	7.1	7.5	7.4	10.6	12	0.076
Waste treatment and disposal	0.8	0.2	0.2	0	0.1	0.1	0
Agriculture	–	–	–	–	–	–	–
Nature	–	–	–	–	–	–	–
Total annual emissions	258.5	382.3	261.7	225.9	252.8	234.26	228.4751

instance, when the PCB is within a closed cycle (transformers and capacitors) a limited number of technologies is available, due to minimum quantities emitted in air. Physico-chemical technologies have been developed, allowing dechlorination of PCB-containing equipment down to a maximum level of 50 ppm PCB by use of alkali reagents (soda) and solvent vapours such as methylene chloride. In these techniques Cl-organic compound bonds are destroyed, leading to formation of chloride and organic substances, which are less toxic. When the system is open (dyes, varnishes, etc.) dry and wet sorbtion technics, shock quenching and other mechanisms are used. For each particular installation and technology used, effective emission minimisation has to be found. In order to improve fuel composition and properties, and used construction devices it is necessary to optimise the basic technological parameters. Of course, in process of technology selection the POPs structures and properties, important facility characteristics, geographic region, local conditions and operation cost have to be taken into consideration.

CONCLUSIONS

On the basis of investigations made and data obtained for annual PCDD/PCDF and PCBs emissions from different industrial sectors in Bulgaria and the serious concerns that they cause to human health and the environment, the following conclusions could be drawn:

- The first main noticeable symptoms within a few hours high exposure with PCBs are general weakneses, itching and irritation of the eye, skin rash, burning sensations, limbs sensationless, headache, vomiting, etc. These symptoms often appear as long-term chloracne, hair loss and skin hyperpigmentation as well as immune system deficiency, and after a few years contacts – increased level of death cases, due to cancer. That's way in order to minimise and avoid such negative effect over human health, the working processes have to be organised in proper way, which ensure no discharges of gases, vapours and particle matters. The workers have to carry equipment, protecting them from possible skin contact.
- Dioxin exposures to humans are associated with an increased risk of severe skin lesions (chloracne and hyperpigmentation), altered liver function and lipid metabolism, general weakness associated with drastic weight loss, changes in activitie of various liver enzymes, depression of the immune system, and endocrine and nervous system abnormalities. In order to decrease dioxin emission levels, fuel composition and properties, used construction devices and basic technological parameters are have to be optimised.
- So far in Bulgaria does not exist a monitoring system dedicated to POPs (PCB, PCDD/PCDF, etc.) measurements. Recently, under the National Imple-

mentation Plan, regarding POPs inventory, our team is using a guideline called CORINAIR, based on emission factors. The tendency illustrates clearly a significant reduction in generated PCDD emissions from 159.3 g for 1990 to 109.2 for 2000. PCBs data show that non-industrial combustion plants have major contribution and negative tendency in the last few years.

• In literature sources many papers are dedicated to different options for reduction of PCDD/PCDF and PCBs – plasma treatment of waste gases, purification by sorption, filtration, etc. In BAT selection process in Bulgarian NIP, regarding PCDD/PCDF and PCBs treatment the comparison between needed investment and gained benefits have to be made. For each particular installation and technology, effective emission minimisation have to be found.

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