

Ministry of
Environment
and Water



INVENTORY

OF

POLYCHLORINATED DIBENZODIOXINS

POLYCHLORINATED DIBENZOFURANS

POLYCHLORINATED BIPHENYLS

HEXACHLOROBENZENE RELEASES

in the Republic of Bulgaria



Sofia, December 2004,
Updated, June 2006

Title: **National Inventory of Polychlorinated Dibenzo-p-dioxins, Polychlorinated Dibenzofurans, Polychlorinated Biphenyls and Hexachlorbenzene Releases in the Republic of Bulgaria**
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LIST OF ABBREVIATIONS

BSS	Bulgarian State Standard
SG	State Gazette
ADD	Admissible Daily Dozes
ET	Ecological threshold
EA BAS	Executive Agency “Bulgarian Accreditation Service”
EEPA	Executive Environment Protection Agency
MARC	Maximum Admissible Residual Content
MoH	Ministry of Health
MoAF	Ministry of Agriculture and Forestry.
MoEW	Ministry of Environment and Water.
NGO	Non-Governmental Organization
NIS	National Institute of Statistics
ALV	Admissible limit values
AVL	Admissible Limit Values
PT	Pollution threshold
DCM	Decree of the Council of Ministers
PCB	Polychlorinated biphenyls
PCDD/F	Polychlorinated Dibenzodioxins/Furans
RIEW	Regional Inspectorate of Environment and Water.
TPP	Thermal Power Plant
POPs	Persistent Organic Pollutants
HCB	Hexachlorbenzene
b.m.	Body Mass
EF	Emission factor
GC	Gas chromatograph
IARC	International Agency for Research of Cancer
ISO	International Standards Organisation
LC	Lethal Concentration
LD	Lethal Dose
MDL	Minimum Detection Level
TEF	Toxic Equivalency Factor
TEQ	Toxic Equivalency Quotient
WHO	World Health Organisation

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Sofia, December 2004,
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1. BASIC CHARACTERISTICS OF PERSISTENT ORGANIC POLLUTANTS (POPS) IN EMISSIONS

Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs), Polychlorinated biphenyls (PCBs) and Hexachlorbenzene (HCB) are persistent organic pollutants (POP), which:

- ❖ exhibit toxic properties;
- ❖ persist for a long time;
- ❖ bioaccumulate (accumulate into the biosphere);
- ❖ are capable of transboundary long-range atmospheric transfer and deposition; and
- ❖ even far from their source may have unfavourable consequences for human health and the environment.

According to the Stockholm Convention, effective since 17 May 2004 and ratified by an act of law by the 39th National Assembly of the Republic of Bulgaria on 30.09.2004, our country must take measures to reduce the overall releases from anthropogenic sources of

- ✚ Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF);
- ✚ Polychlorinated biphenyls (PCBs);
- ✚ Hexachlorbenzene (HCB);

aiming at their lasting reduction and removal from unintentional use.

1.1. POLYCHLORINATED DIBENZODIOXINS (DIOXINS, PCDD) AND POLYCHLORINATED DIBENZOFURANS (FURANS, PCDF)

1.1.1. Introduction

According to the Stockholm Convention, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are unintentionally formed persistent organic pollutants. Dioxins and furans are substances released by thermal processes that involve chlorine and organic matter, resulting from incomplete combustion and chemical reactions.

1.1.2. Basic characteristics of Dioxins (PCDD) and Furans (PCDF) *

Chemical name: Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). Dioxins and furans have, respectively, 75 and 135 isomers*.

CAS No.: different for different isomers:

2,3,7,8-tetraHDD - 1746-01-6

2,3,7,8-tetraHDF - 51207-31-9

Empirical formula: PCDD - $C_{12}N_{(8-n)}Cl_nO_2$; PCDF - $C_{12}H_{(8-n)}Cl_nO$, $n = 1$ to 8

Structural formula: Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have similar structure and on practice they are 210 different compounds, comprising of 75 PCDD congeners and 135 PCDF congeners. (fig. 1).

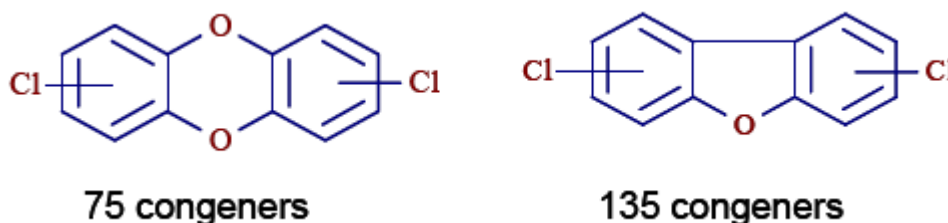


Figure 1 Structure of 75 PCDD and 135 PCDF

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) represent tricyclic aromatic compounds formed by two benzene rings connected by two oxygen atoms (PCDD) (Figure 1) or by one oxygen atom (PCDFs) (Figure 2), and their hydrogen atoms may be replaced by 1 - 8 chlorine atoms.

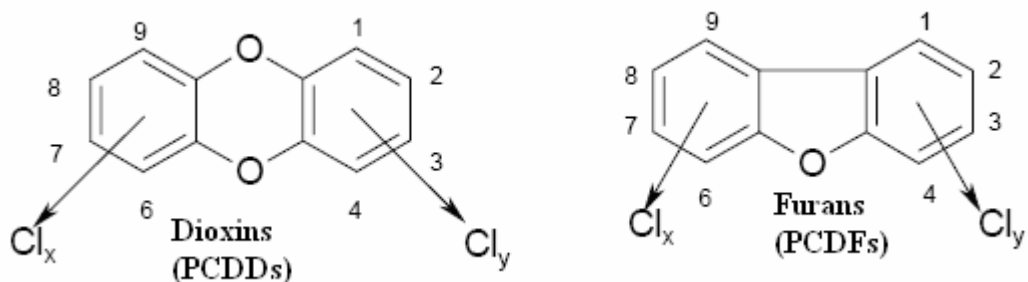


Figure 2 Structural Formula of Dioxins and Furans

All 210 congeners are different compounds and exhibit different chemical, physical and toxicological properties. All PCDD/PCDF are persistent, but only 2,3,7,8 chloro -substituted congeners are toxic and bioaccumulate in living organisms (fig.3).

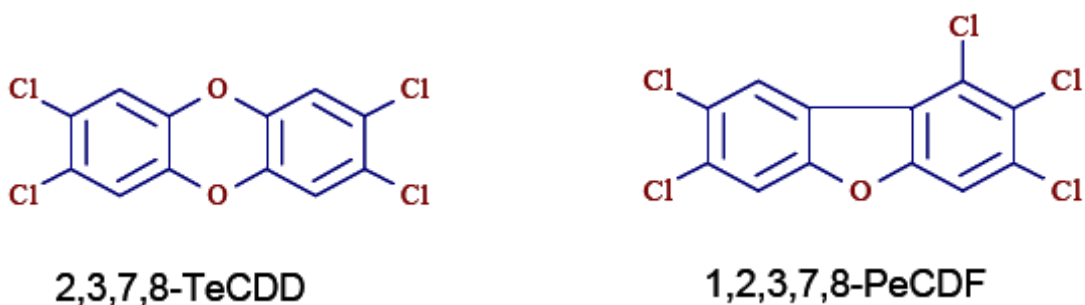


Figure 3 Structural formula of 2, 3, 7, 8-TeCDD and 2, 3, 7, 8-PeCDF

Spatial Structure:

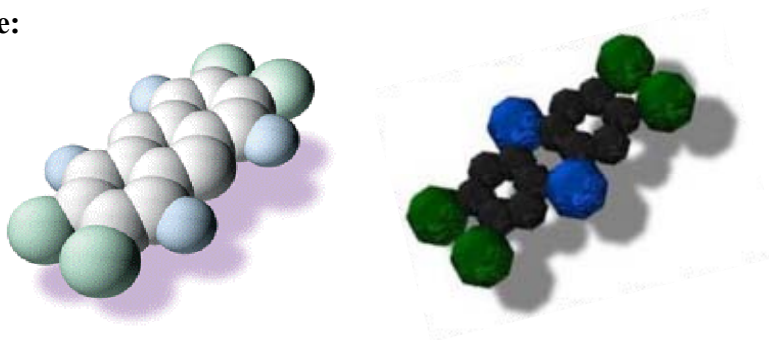


Figure 4 Spatial structural formula of Dioxins/Furans

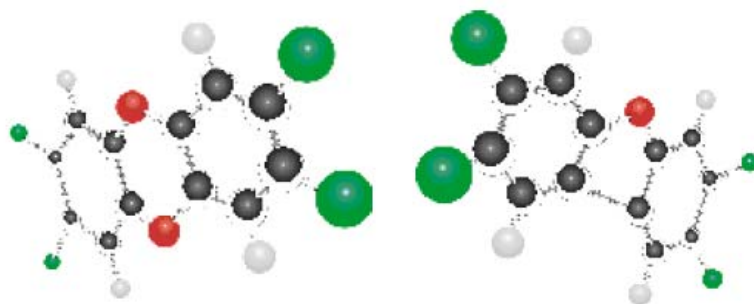


Figure 5 Spatial structural formula of Dioxins/Furans

Physical and chemical properties: Dioxins are colourless while furans are non-odorous white needle-shaped crystals. They exhibit similar physical and chemical properties: The molecular mass of PCDD varies between 188 and 499. Dioxins feature high melting and boiling temperatures, and very low relative velocity of evaporation which increases slightly with increasing temperature. They are non-flammable. For example, 2,3,7,8-THDD is colourless, with a melting temperature of 305-306°C; thermal disintegration 700°C; vapour pressure of 64.10^{-11} mm Hg at 20°C and 14.10^{-10} mm Hg at 25°C.

The other representatives have different properties that depend on the number and on the position of the chlorine atoms in the molecules. For example, the tetra to octa-substituted congeners are: soluble in water - 0,43 – 0,0002 ng.l⁻¹ at 25°C; vapour pressure: 2 – 0,007 x 10⁻⁶ mm Hg at 20°C; log KOW: in the range 6,60 – 8,20.

Table 1 Physical and chemical properties of Dioxins

Congener Groups	Molecular weight	Vapour pressure (Pa X 10 ⁻³)	Water solubility (mg/m ³)	Log K _{ow}
M1CDD	218.5	73-75	295-417	4.75-5.00
D2CDD	253.0	2.47-9.24	3.75-16.7	5.60-5.75
T3CDD	287.5	1.07	8.41	6.35
T4CDD	322.0	0.00284-0.275	0.0193-0.55	6.60-7.10
P5CDD	356.4	0.00423	0.118	7.40
H6CDD	391.0	0.00145	0.00442	7.80
H7CDD	425.2	0.000177	0.0024	8.00
O8CDD	460.0	0.000953	0.000074	8.20

Persistence/Fate: PCDD and PCDF exhibit lipophilic properties, semi-volatility, persistence (the half-life of tetraHDD in soil is 10 – 12 years; and that of 3,3,7,8-tetraHDD and PHD is 2.6 years), and capacity for long-range transferring. Also, they are known for their capacity for bioconcentration and bioaccumulation under common environmental conditions.

* *Regionally Based Assessment of Persistent Toxic Substances, Global Report 2003, Annex I. Basic chemical definitions. Stockholm POP Pesticides, pp 192 – 195, UNEP Chemicals, Switzerland.*

Toxicity: The studied toxic impact applies mainly to 2,3,7,8-substituted isomers (Table 2).

Table 2 Toxic Equivalence Factors of 17 isomers (congeners), applied to 2,3,7,8- TCDD
(Regulation 11, SG 152/22.12.1998, Regulation 31, SG 88 /08.10.2004)

Congener	Congener	TEF values in food	TEF value in waste gases and waste water
Dibenzo-p-dioxins (PCDDs):	2, 3, 7, 8-TCDD	1	1
	1, 2, 3, 7, 8-PeCDD	1	0.5
	1, 2, 3, 4, 7, 8-HxCDD	0.1	0.1
	1, 2, 3, 6, 7, 8-HxCDD	0.1	0.1
	1, 2, 3, 7, 8, 9-HxCDD	0.1	0.1
	1, 2, 3, 4, 6, 7, 8-HpCDD	0.01	0.01
	OCDD	0.0001	0.001
Dibenzofurans (PCDFs):	2, 3, 7, 8-TCDF	0.1	0.1
	1, 2, 3, 7, 8-PeCDF	0.05	0.05
	2, 3, 4, 7, 8-PeCDF	0.5	0.5
	1, 2, 3, 4, 7, 8-HxCDF	0.1	0.1
	1, 2, 3, 6, 7, 8-HxCDF	0.1	0.1
	1, 2, 3, 7, 8, 9-HxCDF	0.1	0.1
	2, 3, 4, 6, 7, 8-HxCDF	0.1	0.1
	1, 2, 3, 4, 6, 7, 8-HpCDF	0.01	0.01
	1, 2, 3, 4, 7, 8, 9-HpCDF	0.01	0.01
	OCDF	0.0001	0.001

Abbreviations: T = tetra; Pe = penta; Hx = hexa; Hp = hepta; O = octa; CDD = chlorodibenzodioxin; CDF = chlorodibenzofuran.

All 2,3,7,8 - substituted PCDD and PCDF and the coplanar PCB (without ortho substitution with chlorine) exhibit the same type of biological and toxic response. The possible negative impacts include: dermal toxicity, immune toxicity, reproduction toxicity, and teratogenic toxicity, damage of the endocrine system and carcinogenic property. According to the IARC classification, 2,3,7,8-THDD belongs to group 1 – a proven carcinogen – while the remaining representatives are not classified as carcinogens for humans (Group 3). Presently, the only effect related to exposure to dioxins in chlorine is chloracne. The groups most sensitive to the impacts of dioxins and furans are foetuses in the mother's organisms and newborns.

Impacts on the immune system of mice were established at doses of $10 \text{ ng. kg}^{-1} \text{ bw.day}^{-1}$ while the reproductive toxicity in monkeys was $1\text{-}2 \text{ ng.kg}^{-1} \text{ bw.day}^{-1}$. Biochemical effects have been observed in rats at doses of $0,1 \text{ ng. kg}^{-1} \text{ bw.day}^{-1}$. The WHO recommends the daily admissible level for dioxins and furans (and for planar PCBs) $1\text{-}4 \text{ TEQ pg.kg}^{-1} \text{ b.m.}$, although the recent monthly admissible dose is $1\text{-}70 \text{ TEQ pg.kg}^{-1} \text{ b.m.}$

1.2. POLYCHLORINATED BIPHENYLS (PCBs)

1.2.1. Introduction

According to the Stockholm Convention, polychlorinated biphenyls (PCB) form unintentionally and are released by thermal processes that include organic substances and chlorine as a result of incomplete combustion or chemical reactions.

1.2.2. Basic characteristics of PCBs*

Chemical name: Polychlorinated biphenyls

Empirical formula: $\text{C}_{12}\text{H}_{(10-n)}\text{Cl}_n$, $n = 1$ to 10 .

Structural formula: PCBs are aromatic compounds, whose hydrogen atoms can be replaced with up to ten chlorine atoms. There are 209 possible PCB congeners. They can be divided into groups according to the number of their chlorine atoms.

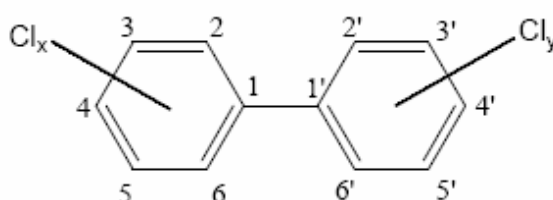


Figure 6 Structural formula of PCBs

Spatial structural formula:

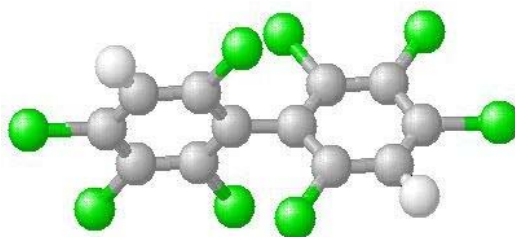


Figure 7 Spatial structural formula of PCBs

Physical and chemical properties: PCBs are liquids or resins depending on the degree of substitution, colourless or yellow, with specific odour. Their molecular mass varies between 188 and 499. They are insoluble in water but are easily dissolved in fats, hydrocarbons and others organic compounds. Solubility in water – 0,01 – 0,0001 $\mu\text{g.L}^{-1}$ at 25°C (decreasing with the increasing number of chlorine atoms). PCBs are lightly volatile but in time, their evaporation capacity increases, and their vapour pressure is $1,6-0,003 \times 10^{-6}$ mm Hg at 20°C; log K_{OW} : 4,3-8,26.

Persistence/Fate: A significant part of the PCB isomers (congeners), particularly those with non-replaced neighbouring positions of biphenyl rings (for example, 2,4,5-, 2,3,5- or 2,3,6-substituted for the two rings), are highly stable in the environment. The half-life of these representatives in air is three weeks to two years, except for mono and dichlorobiphenyls, and more than 6 years in aerobic soil and sludge. Also, PCBs in the organisms of adult fish degrade very slowly, and it has been established in an eight-year study that the half-life of chlorobiphenyl 153 in eels is longer than ten years.

Toxicity: Experimental and epidemiological studies have shown that PCBs possess a high toxicity potential. The acute LC_{50} for rainbow trout larvae is $0,32 \mu\text{g/l}^{-1}$, and the inactive concentration is $0,01 \mu\text{g/l}^{-1}$. PCBs are severely toxic for mammals – the acute oral LD_{50} in rats is 1 g/kg^{-1} b.m. The negative health effects in humans and/or animals include: liver and thyroid gland damage, skin and eye changes, immunitoxicity, neurobehavioral deviations, reduced body mass of the newly born, reprotoxicity and carcinogenicity. PCBs can damage the ductless glands. IARC has classified PCBs as carcinogenic for laboratory animals and as a probable carcinogen for humans (Group 2B).

Table 3 Toxic Equivalence Factors (TEFs)

(Regulation 31,SG 88/0 8.10.2004)

Congener	Congener	TEF values in food
Dioxin-like PCBs	PCB 77	0.0001
	PCB 81	0.0001
	PCB 126	0.1
	PCB 169	0.01
Mono-ortho PCBs	PCB 105	0.0001
	PCB 114	0.0005
	PCB 118	0.0001
	PCB 123	0.0001
	PCB 156	0.0005
	PCB 157	0.0005
	PCB 167	0.00001
	PCB 189	0.0001

* Regionally Based Assessment of Persistent Toxic Substances, Global Report 2003, Annex I. Basic chemical definitions. Stockholm POP Pesticides, pp 192 – 195, UNEP Chemicals, Switzerland.

1.3. HEXACHLORBENZENE (HCB)

1.3.1. Introduction

Hexachlorobenzene belongs to the group of industrial persistent organic pollutants as a pesticide and to the group of unintentionally formed pollutants released by thermal processes, in result of incomplete combustion for chemical reactions. Hexachlorobenzene reaches the atmosphere along with the flue gases generated by waste incinerators and by metallurgical companies.

1.3.2. Characteristics of Hexachlorbenzene (HCB)*

Chemical name: Hexachlorobenzene*

CAS No.: 118-74-1

Empirical formula: C₆Cl₆

Structural formula:

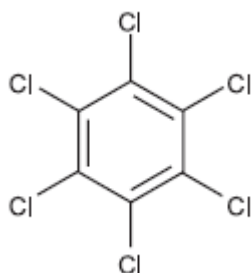


Figure 8 Structural formula of HCB

Appearance/Description: HCB is white monoclinic crystals or crystalline solid.

Hexachlorobenzene (HCB) is a chlorinated monocyclic aromatic compound in which the benzene ring is fully substituted by chlorine. HCB is a white crystalline solid (melting point 231°C) that is virtually insoluble in water, but is soluble in ether, benzene and chloroform (NTP, 1994). It has a high octanol/water partition coefficient, low vapour pressure and low flammability. HCB is found almost exclusively in the gas phase (as is predicted by its vapour pressure), with less than 5% associated with particles in all seasons except winter, where levels are still less than 10% particle-bound (Cortes *et al*, 1998).

Physical and chemical properties: Molecular weight: 284.78; State of aggregation: crystals; Colour: white; Melting temperature: 231°C; Boiling temperature: 325°C; Relative density at 23°C: 2.044; Solubility in water: 50 µg/L at 20°C, practically insoluble; in organic solvents – lightly soluble in ethanol, soluble in ethyl ether and highly soluble in benzene; Vapour pressure: 1.09 x 10⁻⁵ mm Hg at 20°C; log K_{OW}: 3.93-5.73.

Use: Historically, the major use of HCB has been as a fungicide, first introduced in 1945. It was used worldwide as an agricultural fungicide from early in the twentieth century, particularly as a seed dressing to prevent fungal diseases of grain and other field crops. HCB was used extensively as a fungicide to control Bunt in wheat, representing a major breakthrough for this disease. HCB was applied as a dust. It is a known impurity in several pesticide formulations, including pentachlorophenol and dicloram and may be present as an impurity in others.

Industrial uses, including as a chemical intermediate, represent a relatively small proportion of cumulative global production. The relatively small remaining production is probably mostly for non-pesticide use, particularly as a chemical intermediate.

Historically there were a number of potentially dispersive non-pesticide end-uses for HCB. It has been used as a wood preservative, for impregnating paper, as a means of controlling porosity in the manufacture of graphite electrodes for electrolytic processes, as a fluxing agent in the manufacture of aluminum and in the formulation of military pyrotechnic products and tracer bullets. (ATSDR, 1996).

HCB is a byproduct of the manufacture of industrial chemicals including carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorobenzene. Also, it is used in the manufacturing of fireworks, ammunitions and synthetic rubber. Presently, it is a by-product of a large number of chlorine containing substances, in particular low-content chlorbenzenes, solvents and some pesticides.

It is quite volatile and can be expected to partition into the atmosphere as a result. Hexachlorbenzene reaches the atmosphere along with the flue gases generated by waste incinerators and by metallurgical companies.

Persistence/Fate: The half-life of hexachlorobenzene in soils ranges between 2,7 and 5,7 years, and between 0,5 and 4,2 years in air. It has a comparatively high bioaccumulation potential and a long half-life in the biota.

It is very resistant to breakdown and has a high partition coefficient ($K_{OW} = 3.03-6.42$), and is known to bioconcentrate in the fat of living organisms as a result. HCB is ubiquitous in the environment, and has been measured in foods of all types.

Toxicity: The acute LC_{50} of hexachlorobenzene varies between 50 and 200 $\mu\text{g/l}$ for various fish species. The acute toxicity of HCB to laboratory animals is quite low, with acute oral LD_{50} values in the range of more than 2,6 mg/kg body mass in rabbits and 4,0 mg/kg in mice. The acute oral LD_{50} for rats is 3,5 mg/kg b.m. Porphyria, skin lesions, hyperexcitability and changes in weight, enzyme activities and morphology of the liver have been reported in association with subchronic toxicity of HCB. HCB has also been reported to stimulate the immune system in rats, and suppress the immune system of mice. HCB may also produce adverse effects on reproduction and reproductive tissue.

HCB is unlikely to cause direct toxicological effects in aquatic animals at or below saturation concentrations (approximately 5 $\mu\text{g/L}$) in water. LC_{50} of hexachlorobenzene varies between 50 and 200 $\mu\text{g/l}$ for various fish species. Some insignificant liver problems have been observed in rats at daily exposure of 0, 25 mg/g b.m. It is a fact that hexachlorobenzene causes liver diseases in humans too (porphyria cutanea tarda). IARC has classified hexachlorobenzene as belonging to Group 2B, as a probable carcinogen for humans.

* *Regionally Based Assessment of Persistent Toxic Substances, Global Report 2003, Annex I. Basic chemical definitions. Stockholm POP Pesticides, pp 192 – 195, UNEP Chemicals, Switzerland.*

2. SOURCES OF POPS EMISSIONS INTO THE ATMOSPHERE

Polychlorinated dibenzodioxins (PCDD) and Polychlorinated dibenzofurans (PCDF), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) belong to the persistent organic pollutants formed and released unintentionally from anthropogenic sources.

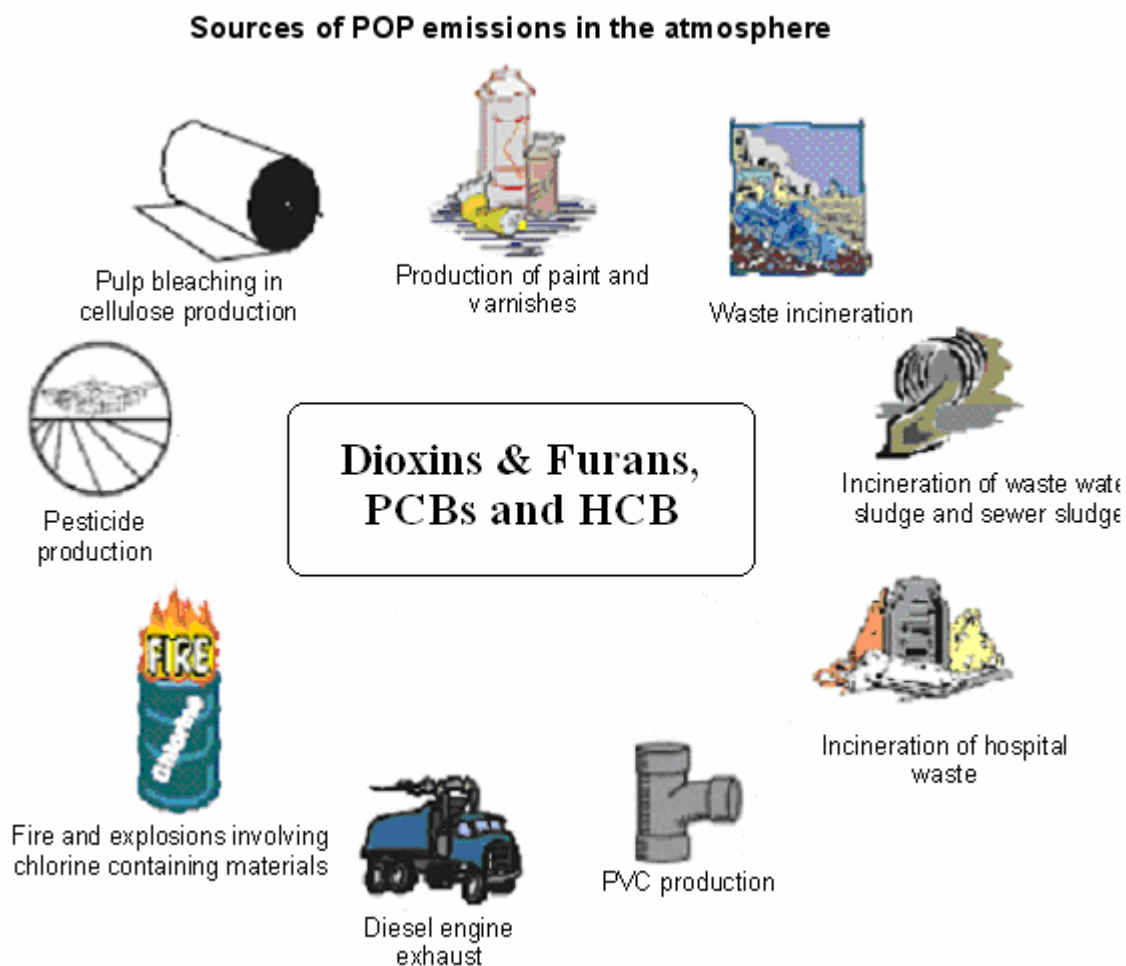
They are formed and released by thermal processes that include organic substances and chlorine in result of incomplete combustion or chemical reactions. The categories of industrial sources with potential for formation in comparatively large quantities and for releasing of POPs into the environment are:

- (a) waste incinerators, including co-incinerators for household, hazardous or medicinal waste or sewerage waste;
- (b) cement kilns incinerating hazardous waste;
- (c) production of cellulose which releases unbound chlorine or chemical substances forming unbound chlorine for bleaching;
- (d) thermal metallurgical processes.

The polychlorinated dibenzodioxins (PCDD) and Polychlorinated dibenzofurans (PCDF), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCB) may form and be released unintentionally from the following source categories:

- (a) open-air incineration of waste, incl. Incineration in landfills;
- (b) thermal metallurgical processes.
- (c) combustion in residential buildings;
- (d) fossil fuel combustion plants and industrial boilers;
- (e) wood and other biomass fuel combustion plants;
- (f) specific industrial chemical processes, releasing unintentionally formed persistent organic pollutants, particularly during production of chlorophenol and chloroanil;
- (g) crematoriums;
- (h) motor vehicles, particularly those utilizing leaded petrol;

- (i) incineration of animal carcasses;
- (j) dyeing of textile and leather goods (using chloroanil) and finishing (by alkaline extraction);
- (k) installations for cutting and processing of decommissioned motor vehicles;
- (l) burning of copper cables;
- (m) used oil refineries.



The emissions of PCDD/F, PCB and HCB are released into the environment by means of direct emission and/or transfer by air, water, soil and waste (Figure 9 & Figure 10).

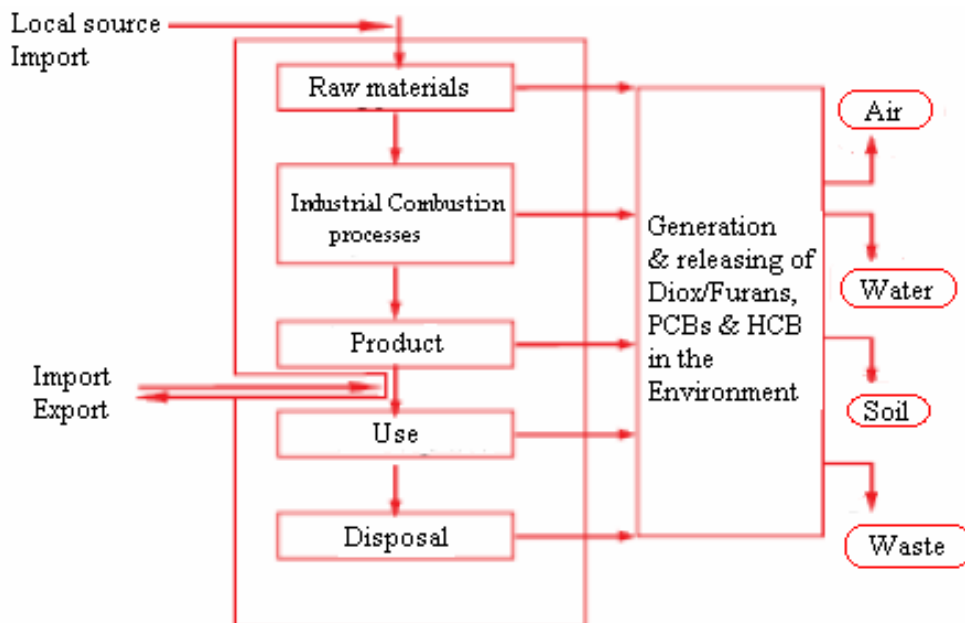


Figure 10 Unintentional production and routes of entry of PCDD/Fs, PCBs and HCB into the environment (air, water, soil and waste).

Distribution of POPs source categories in Bulgaria

Table 4 Number of facilities by source categories of unintentional POPs releases

Source categories	Number of facilities
Incinerators	
Municipal solid waste;	-
Hazardous waste;	25
Medical waste;	52
Cement kilns	3
Metallurgy	
Thermal processes in metallurgy;	16
Secondary copper production;	-
Sinter plants in the iron and steel industry;	5
Industrial combustion processes	427
Combustion processes in energy generation and transformation	34
Combustion processes in trading, administrative and household sectors	644
Firing installations for wood	1
Waste oil refineries	2

3. INSTITUTIONAL AND REGULATORY FRAMEWORK FOR THE MANAGEMENT OF POPs IN BULGARIA

3.1. INSTITUTIONAL RESPONSIBILITIES

The Ministry of Environment and Water (MoEW) is responsible for the state policy on protection of the atmospheric air. The municipal authorities and the regional environmental inspectorates control and manage the activities aimed to ensure clean air in their territory. The atmospheric air quality is monitored through the National System for Monitoring, Control and Information.

The control and monitoring of transboundary transfer of polluting substances, of the background quality of atmospheric air, and of the impact of atmospheric air pollution on the global processes are conducted by the Ministry of Environment and Water and by the National Institute of Metrology and Hydrology at the Bulgarian Academy of Sciences.

The assessment of health and environmental risks related to the atmospheric air quality is conducted by the **Ministry of Health (MoH) and the Ministry of Environment and Water (MoEW)**.

The direct control of the state and the operation of the sites that are sources of emissions into the atmospheric air and on the emissions of various sources are performed by:

- + The Minister of Environment and Water, the Regional Inspectorates of Environment and Water and the municipal authorities;
- + The authorities of the Ministry of Internal Affairs and of the Ministry of Transport – for motor vehicles.

The ministries, the agencies and the municipal authorities conduct activities to protect water and soil from pollution:

- + **The Minister of Environment and Water (MoEW)** controls the protection of soil against pollution.
- + **The Minister of Health (MoH)** carries out sanitary control of the condition of water and soil, and in agreement with the Minister of Environment and Water, issues compulsory sanitary norms and rules.
- + **The Minister of Agriculture and Forestry (MoAF)** in cooperation with the Academy of Agriculture issues mandatory standards and rules for protection of animals and agricultural crops and supervises their enforcement.

3.2. EXISTING POLICY

Emission inventory system in Bulgaria

The involved institutions at national and local (sub-national) levels in Emissions inventory are **Ministry of Environment and Water /MoEW/** respectively Executive Environment Agency /EEA/ and Regional Environment Inspectorate /REIWs/, and **National Institute of Statistics /NSI/**.

Two parallel emission inventory programs are conducted in Bulgaria. The first one covers 150 large point sources and it is conducted by REIWs. The second one covers nearly 2000 point sources and it is conducted by National Institute of Statistics. Both are under the guidance of Ministry of Environment and Waters. The data collected are air pollution control facilities and their efficiency, technological and production data, data for fuels used and fines imposed.

The National Institute of Statistics is the responsible organization for assessment of the following air emissions sources:

- Combustion in energy production and energy transformation;
- Combustion in commercial, institutional and residential sectors and agriculture, forestry, fishing;
- Combustion in industry;
- Production processes;
- Extraction and distribution of fossil fuels;
- Agriculture, forestry and land use change;
- Nature.

The Executive Environment Agency is the responsible organization for assessment of the following air emissions sources:

- Road transport;
- Other mobile sources and machinery;
- Waste treatment and disposal.

Data from the emission inventory are stored at local and national level. On a national level the Executive Environment Agency is the responsible organization for final preparation of the National

air emission inventory and data reporting to the UNECE/CLRTAP (Convention on Long-Range Transboundary Air Pollution).

3.3. POPs MANAGEMENT REGULATIONS IN BULGARIA

Regarding environment protection, Bulgaria is party to a number of international conventions and their protocols, used as the basis for the issuance of regulations on the management and control of certain hazardous chemicals and waste, which include to some extent persistent polychlorinated biphenyls and hexachlorobenzene (Table 5).

Table 5 POPs Management Regulatory Framework

No	INTERNATIONAL CONVENTIONS
1	Basel Convention on the Control of Transboundary Movement of Hazardous Waste and their Neutralization SG 8/26.01.1996, in effect since 16.05.1996
2	Geneva Convention on Long-Range Transboundary Air Pollution, ratified in 1981, effective since 16.03.1983.
3	Protocol on persistent organic pollutants under the Geneva Convention on Long-Range Transboundary Air Pollution, SG 102/21.11.2003, in effect since 23.10.2003
4	Convention for the Protection of the Black Sea from Pollution, SG 99/21.04.1992, effective since 15.01.1994.
5	Convention on the Cooperation for Protection and Sustainable Use of the Danube, SG 30/02.04.1999, effective since 6.04.1999, amended and supplemented in the SG 53/28.05.2002.
6	Stockholm Convention on Persistent Organic Pollutants, signed by the Republic of Bulgaria on 23.01.2001 in Stockholm, Sweden. Ratified by the National Assembly with a law on 30.09.2004.
	LAWS
1	Environment Protection Act , promulgated in the SG, 91/25.09.2002, amended in issue 86/30.09.2003, supplemented in issue 70/10.08.2004, effective since 01.01.2005.
2	Clean Air Act , SG 45/28.05.1996, last amendment in SG 112/23.12.2003, in effect since 01.01.2004;
3	Water Act , SG 67/1999, amended SG 91/25.09.2002, amended SG 84/23.09.2003, supplemented SG 107/09.12.2003, supplemented and amended SG 6/23.01.2004, amended SG 70/10.08.2004, effective since 01.01.2005.
4	Protection of Soil against Pollution Act , SG 67/27.07.1999, in effect since 28.01.2000, amended SG 113/28.12.1999.
5	Agricultural Land Protection Act , SG 35/24.04.1996, supplemented and amended SG 28/23.03.2001, supplemented in SG 112/23.12.2003, in effect since 01.01.2004.
6	Protection against the Harmful Impact of Chemical Substances, Preparations and Products Act , SG 10/2000, amended and supplemented in SG 114/30.12.2003, in effect since 31.01.2004;
7	Waste Management Act , SG 86/24.09.2003, amended in issue 70/10.08.2004, in effect since 01.01.2005.
8	Plant Protection Act , SG 91/1997, amended and supplemented in the SG 96/09.11.2001, supplemented in the SG 18/05.03.2004, effective since 05.03.200;
	REGULATIONS
1	Regulation on the Procedures and Manner of Import and Export of Hazardous Substances and Preparations in the Territory of the Republic of Bulgaria, SG 66/09.07.2002, in effect since 01.01.2004, adopted with Decree of the Council of Ministers 161/12.07.2004, amended SG 63/20.07.2004, effective since 01.01.2005.
2	Regulation on the Hazardous Chemicals that are Subject to Prohibition or Restrictions for Trading and Use, Decree of the Council of Ministers 130/01.07.2002, SG, 69/17.07.2002, effective since 01.01.2003, Decree of the Council of Ministers 156/07.07.2004, SG 62/16.07.2004, in effect since 17.10.2004.
3	Regulation 7 on the Requirements for the Sites for Waste Treatment Facilities, SG 81/17.09.2004
4	Regulation 8 on the Terms and Requirements for Construction and Operation of Waste Recycling and Disposal Landfills and Other Facilities, SG 83/24.09.2004.
5	Regulation on the Requirements for Treatment and Transporting of Used Oil and Waste Oil Products, SG 59/21.07.2000, in effect since 01.01.2001;

6	Regulation on the Terms and Procedures for implementation of the Protocol on Environment Protection of the Antarctica Treaty, SG 17/23.02.2001.
7	Regulation on the requirements for treatment and transporting of production and hazardous waste, SG 29/30.03.1999.
8	Regulation on the Procedures and Manner of Importing, Exporting and Transit of Waste and on the Cases Requiring Bank Guarantees or Insurances, SG 102/26.10.2004.
9	Regulation on the Terms and Procedures for Reduction of Pollution from Motor Vehicles, SG 104/26.11.2004.
10	Regulation 2/19.02.1998 on the Admissible Emission Levels (Concentrations in Waste Gases) for Harmful Substances, Released into the Atmospheric Air from Stationary Sources, SG 51/06.05.1998, last supplemented in the SG 93/21.01.2003.
11	Regulation 6/09.11.2000 on the Emission Standards for Admissible Content of Harmful and Hazardous Substances in Waste Water Discharged into Water Bodies, SG 97/28.11.2000, supplemented and amended SG 24/23.03.2004.
12	Regulation 9/16.03.2001 on the Quality of Water Meant for Drinking and Household Use, SG 30/21.05.2001.
13	Regulation 12/18.06.2002 on the Quality Requirements for Surface Water Meant for Drinking Water Supply, SG 63/28.06.2002.
14	Regulation 6/26.03.1999 on the Procedures and Manner of Measuring the Emissions of Harmful Substances, Released into the Atmospheric Air from Facilities with Stationary Sources, SG 31/06.04.1999, amended and supplemented in issue 93/21.10.2003.
15	Regulation 3/1979 on the Admissible Content of Harmful Substances in Soils, SG 36/08.05.1979, amended SG 54/1997, last amendment SG 39/16.04.2002.
16	Regulation 27 on the Import of Goods of Significance for Public Health, SG 75/1995, amended in the SG78/02.09.2003, supplemented in the SG 4/16.01.2004 and SG 25/24.02.2004, in effect since 16.01.2004;
17	Regulation 14 on the Admissible Concentration Standards for Harmful Substances in the Atmospheric Air of Urban Centres SG 14/20.02.2004
18	Regulation 73 on the Approving of New Motor Vehicle Types Regarding Air Pollution from Engines, promulgated in the SG 22/18.03.2004.
19	Regulation 11 dated 6.11.1998 on the Conditions and Requirements for Construction and Operation of Household Waste Disposal Facilities and Plants, SG 152/22.12.1998.
20	Regulation 3 on waste classification, SG 44/25.04.2004.
21	Regulation 1 on the Studying, Use and Protection of Ground Water, SG 57/14.07.2000, in effect since 14.07.2000, amended in the SG 64/04.08.2000;
22	Regulation 24 on the Maximum Admissible Concentrations of Undesired Substances and Products in Fodder, SG 56/20.06.2003.
23	Regulation on the Procedures and Manner of Using of Waste-Water Treatment Sludge in Agriculture, SG 112/23.12.2004
24	Regulation 6 on the Conditions and Requirements for Construction and Operation of Waste Incinerators and Co-Incinerators, promulgated SG 78/07.09.2004.

3.4. STANDARDS FOR PCDD/F, PCB AND HCB IN BULGARIA

Tables 6 – 19 present the approved Bulgarian standards for PCDD/F, PCB and HCB in air, soil, water and food.

Standards for PCDD/F, PCB and HCB in air


-  **Regulation № 1/27.06.2005** on Emission Limit Values of harmful substances (pollutants), released into atmosphere from facilities and activities with stationary point sources, SG 64/05.08.2005, in force from 06.08.2006.

Table 6 Emission limit value (ELV) of PCDD/F released from stationary sources

<i>Nº</i>	Dioxins/Furans (PCDDs/PCDFs)	<i>ELV</i> <i>ng TE/m³</i>
1	Total PCDDs/Fs emissions released into atmosphere from existing and new stationary sources within a single facility or activity, considering their TEQ.	0,1 ng TE/m ³ 0,25 µg/h
2	PCDDs/Fs emissions from sinter plants in the iron and steel industry	0,4 ng TE/m ³
3	Total PCDDs/Fs emissions released into exhaust gases from plants for the production of non-ferrous metals, excluding aluminium and iron-based alloys	0,4 ng TE/m ³
4	PCDDs/Fs emissions released into exhaust gases - in the processes of melting, alloying and refining of non-ferrous metals, excluding aluminium - in the processes of copper melting in shaft furnace	0,1 ng TE/m ³ 0,4 ng TE/m ³

Annex Nº 6 to article 20, item 1

For the determination of the total concentration (TEQ) of dioxins and furans, the mass concentrations of the following dibenzo-p-dioxins and dibenzofurans shall be multiplied by the following equivalence factors before summing:

Table 7 Toxicity Equivalent (TEQ) of Dibenzo-p-dioxins and Dibenzofurans

Chemical		Toxicity equivalent TEQ
2,3,7,8	— Tetrachlorodibenzodioxin (TCDD)	1
1,2,3,7,8	— Pentachlorodibenzodioxin (PeCDD)	0,5
1,2,3,4,7,8	— Hexachlorodibenzodioxin (HxCDD)	0,1
1,2,3,6,7,8	— Hexachlorodibenzodioxin (HxCDD)	0,1
1,2,3,7,8,9	— Hexachlorodibenzodioxin (HxCDD)	0,1
1,2,3,4,6,7,8	— Heptachlorodibenzodioxin (HpCDD)	0,01
	— Octachlorodibenzodioxin (OCDD)	0,001
2,3,7,8	— Tetrachlorodibenzofuran (TCDF)	0,1
2,3,4,7,8	— Pentachlorodibenzofuran (PeCDF)	0,5
1,2,3,7,8	— Pentachlorodibenzofuran (PeCDF)	0,05
1,2,3,4,7,8	— Hexachlorodibenzofuran (HxCDF)	0,1
1,2,3,6,7,8	— Hexachlorodibenzofuran (HxCDF)	0,1
1,2,3,7,8,9	— Hexachlorodibenzofuran (HxCDF)	0,1
2,3,4,6,7,8	— Hexachlorodibenzofuran (HxCDF)	0,1
1,2,3,4,6,7,8	— Heptachlorodibenzofuran (HpCDF)	0,01
1,2,3,4,7,8,9	— Heptachlorodibenzofuran (HpCDF)	0,01
	— Octachlorodibenzofuran (OCDF)	0,001



 **Regulation No. 2** on Emission Limit Values (Concentrations in Waste Gases) for Harmful Substances, Released into the Atmospheric Air from Stationary Sources, SG 51/06.05.1998, last supplemented in the SG 93/21.01.2003.

Table 8 Emission limit value (ELV) of PCDD/F for large stationary sources

No.	Waste incinerators	ELV (applicable to 11% concentration of oxygen in the flue gas), ng TE/m ³
1	Solid household waste (at incinerated waste quantities of more than 3 tonnes per hour)	0,1 ng TE/m ³
2	Solid medical waste (at incinerated waste quantities of more than 1 tonnes per hour)	0,5 ng TE/m ³
3	Hazardous waste (at incinerated waste quantities of more than 1 tonnes per hour)	0,2 ng TE/m ³

 **Regulation 6** on the Conditions and Requirements for Construction and Operation of Waste Incinerators and Co-Incinerators, SG 78/07.09.2004.

Annex № 1 to Article 2

Table 9 Average values for emission limit values of dioxin and furans in air from waste incinerators

Harmful substances	ELV ng /m ³
Dioxins and furans	0,1

The emission limit value refers to the total concentration of dioxins and furans calculated using the concept of toxic equivalence in accordance with Annex № 6. (See table 6 above).


 **Regulation 13** on Workers Protection from Risks, Related to Chemical Agents' Exposure at Work, SG 8/20.01.2004, effective 31.01.2005.

Table 10 Limit values of chemical agents in occupational air

No.	Chemical agent	CAS No.	Limit values		Specific effects
			8 hours	15 minutes	
			mg/m ³	mg/m ³	
361.	Polychlorinated biphenyls (54% chlorine)*	11097-69-1	0,5	1,0	P
362.	Polychlorinated biphenyls (42% chlorine)*	53469-21-9	1,0	2,0	P

P – toxic for reproduction

** - resorption through the skin*

Table 11 Limit values of the harmful substances in the occupational environment of working juveniles (15 – 18 years of age)

Chemical substance	Limit value mg/m ³
Polychlorinated biphenyls	Not allowed

Standards for PCDD/F, PCB and HCB in soil

- ✚ **Regulation** on the Procedures and Manner of Using of Waste-Water Treatment Sludge in Agriculture, SG 112/23.12.2004.

Table 12 Admissible Limit Values for POPs in sludge meant for use in agriculture

Parameter	Value of mg/kg dry substance
Polychlorinated biphenyls	1

- ✚ **Regulation 3** on the Admissible Content of Harmful Substances in Soils, SG 36/08.05.1979, amended SG 54/1997, last amendment SG 39/16.04.2002.

Table 13 Admissible limit values for POPs in soil, in mg/kg of dry soil

Name		1*	2**	3***	4****
Polychlorinated biphenyls	PCB6 (total)	0.005	0.02	0.2	1
	2,4,4' - trichlorobiphenyl PCB-28	0.001	0.001	0.01	-
	2,2,5,5' - tetrachlorobiphenyl PCB-52	0.001	0.001	0.01	-
	2,2,4,5,5' - pentachlorobiphenyl PCB-101	0.001	0.004	0.01	-
	2,2',3,4,4',5' - hexachlorobiphenyl PCB-138	0.001	0.004	0.04	-
	2,2',3,4,4',5,5' - hexachlorobiphenyl PCB-153	0.001	0.004	0.04	-
	2,2',3,4,4',5,5' - hexachlorobiphenyl PCB-180	0.001	0.004	0.04	-
Hexachlorobenzene		-	0.025	0.25	10

* reference background levels:

** levels of concerns and concentrations:

*** admissible limit values:

**** intervention concentration levels

Standards for PCDD/F, PCB and HCB in water

- ✚ **Regulation 1** on the Studying, Use and Protection of Ground Water, SG 57/14.07.2000, in effect since 14.07.2000, amended in the SG 64/04.08.2000.

Table 14 Recommended Parameters for Protection of Ground Water against Pollution

PARAMETER	Unit, international signature	Unit, Bulgarian signature	Ecological threshold	Pollution threshold
Polychlorinated biphenyls (1)	µg/l	mkg/l	0,01	1
Polychlorinated dibenzodioxins	µg/l	mkg/l	10	50
Polychlorinated dibenzofurans	µg/l	mkg/l	10	50
Hexachlorobenzene	µg/l	mkg/l	0,1	5

(1) sum of polychlorinated biphenyls 28, 52, 101, 118, 138, 153 and 180;

Standards for PCDD/F, PCB and HCB in waste

- ✚ **Regulation 8** on the Terms and Requirements for Construction and Operation of Waste Recycling and Disposal Landfills and Other Facilities, SG 83/24.09.2004

Table 15 Limit values for total PCB in waste

Chemical substance	Value, mg/kg
Polychlorinated biphenyls, 7 congeners	1


Standards for PCDD/F, PCB and HCB in fodders

- ✚ **Regulation 24** on the Maximum Admissible Concentrations of Undesired Substances and Products in Fodder, SG 56/20.06.2003.

Table 16 Maximum admissible concentration of PCDDs/Fs and HCB in fodders

Nº	Unacceptable substances or product	Fodders	Maximum admissible concentration of unacceptable substances and products , expressed in mg/kg (ppm), referred to fodders with moisture 12 %
1	Hexachlorobenzene (HCB)	All fodders with exception of : - fats	0,01 0,2
2	Dioxins, expressed by Coefficient of Toxic Equivalent , defined by WHO	All stuff of vegetable origin in fodders, incl. vegetable oils and derivates	0,75 ng WHO-PCDD/F TEQ/kg(1)
		Minerals	1,0 ng WHO-PCDD/F TEQ /kg
		Animal fat, incl. Fats from milk and eggs	2,0 ng WHO-PCDD/F TEQ /kg
		Other products from terrestrial animals, incl. milk and dairy products, eggs and egg products	0,75 ng WHO-PCDD/F TEQ /kg
		Fish oils for human consumption	6 ng WHO-PCDD/F TEQ /kg
		Fish, other aquatic animals, their products and subproducts, excluding fish oil	1,25 ng WHO-PCDD/F TEQ /kg
		Mixed fodders, excluding fodders for animals with valuable fur, pets and fodders for fish	0,75 ng WHO-PCDD/F TEQ /kg
		Fodder for fish, fodder for pets	2,25 ng WHO-PCDD/F TEQ /kg

Standards for PCDD/F, PCB and HCB in food

 **Regulation 6** for the control measures on residues of veterinary medicinal products and environmental pollutants in life animals and foodstuffs of animal origin, SG 32/29.03.2002

Annex Nº 1 to Article 2

Residues groups, subject to control

Group B - veterinary medicinal products and environmental pollutants

3. Other substances and environmental pollutants:
 - a) Chloroorganic compounds, including PCBs;

Annex Nº 2 to Article 4, paragraph 1

Table 17 Groups of substances to be detected by animal species and products of animal origin

Group of Substances	Animal species and foodstuffs of animal origin		
	Bovine, Ovine, Caprine, Swine & Horse meat	Fishery and Aquaculture products	Rabbit meat, meat from wild animals* and farmed game
B (3) a : Chloroorganic compounds, including PCBs	X	X	X

(*) For the wild animals only the chemical elements are subject to control.

Table 18 Limit values for dioxins in some food (pg/g)

Product	Limit value (PCDD+ PCDF) (pg WHO- PCDD/F-TEQ/g fat or product)
Meat and meat products*1 from:	
ruminants (cattle, sheep)	3 pg WHO- PCDD/F-TEQ/g fat*2
farm raised fowl and game	2 pg WHO- PCDD/F-TEQ/g fat*2
pigs	1 pg WHO- PCDD/F-TEQ/g fat*2
Liver and derivative products from terrestrial animals	6 pg WHO- PCDD/F-TEQ/g fat*2
Meat from fish and fish products, and their products	4 pg WHO- PCDD/F-TEQ/g live weight
Milk and dairy products, including butter	3 pg WHO- PCDD/F-TEQ/g live weight*2
Hen eggs and egg products;	3 pg WHO- PCDD/F-TEQ/g live weight*2
Animal fats from:	
ruminants	3 pg WHO- PCDD/F-TEQ/g live weight
farm raised fowl and game	2 pg WHO- PCDD/F-TEQ/g live weight
pigs	1 pg WHO- PCDD/F-TEQ/g live weight
mixed animal fats	2 pg WHO- PCDD/F-TEQ/g live weight
Vegetable oils and animal fats.	0.75 pg WHO- PCDD/F-TEQ/g live weight
Fish oils for human consumption	2 pg WHO- PCDD/F-TEQ/g live weight

*1 Meat for slaughtering and production, proposing of fresh meat on the market.

*2 The dioxin content limit values do not apply to food containing < 1 % fat.

Table 19 Toxic Equivalence Factors (TEFs)

Congener	Congener	TEF values in food
Dioxin-like PCBs	PCB 77	0.0001
	PCB 81	0.0001
	PCB 126	0.1
	PCB 169	0.01
Mono-ortho PCBs	PCB 105	0.0001
	PCB 114	0.0005
	PCB 118	0.0001
	PCB 123	0.0001
	PCB 156	0.0005
	PCB 157	0.0005
	PCB 167	0.00001
	PCB 189	0.0001

3.5. LABORATORY INFRASTRUCTURE

A number of laboratories exist in the Republic of Bulgaria that could become involved in the management of chemical substances, including persistent chlororganic pesticides, at various stages of their “lifecycle”. Some of these laboratories are accredited according to Bulgaria’s current legislation.

Decree of the Council of Ministers 270/30.12.1999 created the Executive Agency of the Bulgarian Accreditation Service (EABAS) as a national authority for accreditation of the Ministry of Economy.

The EABAS has accredited under the Bulgarian State Standard EN ISO/IEC 17025:2001, BSS EN 45000 and ISO/IEC 17000 a number of laboratories working in the field of polychlorinated biphenyls and hexachlorobenzene (Table 19). There is no laboratory infrastructure in Bulgaria for analysis of PCDD/F.

Table 20 presents the laboratories accredited to analyse PCBs and HCB.

Table 20 Laboratories accredited to analyse PCBs and HCB

N	Name/Location	Staff	Available laboratory equipment	Purpose
1	Laboratory for analysis of organic pollutants, Executive Agency Environmental Protection, Ministry of Environment and Water, Sofia	3	2 GC systems "Perkin Elmer", 1 GC/MS system "Hewlett Packard 5890/5972", 1 GC/MS system "Termofinigan DSQ" 2 HPLC systems with DAD, FLD, UV	Water, sediments, soil
2	Regional Laboratory, EA Environmental Protection, Ministry of Environment and Water, Burgas	5	3 GC systems "Hewlett Packard", 1 GC/MS system "Hewlett Packard", LC system "Hewlett Packard"	Water, sediments, soil
3	Regional Laboratory, EA Environmental Protection, Ministry of Environment and Water, Plovdiv	5	1 GC/MS system "Termofinigan DSQ", 1 GC/MS system "Hewlett Packard", 2 GC systems "Perkin Elmer"	Water, sediments, soil
4	Chemistry of Food, National Centre for Hygiene, Medical Ecology, and Nutrition, Sofia	24	2 GC systems, 1 HPLC, 1 UV-VIS Specter Photometer	Food
5	Environmental Chemistry, National Centre for Hygiene, Medical Ecology, and Nutrition, Sofia	35	2 GC systems, 1 GC/MS system 1 HPLC system, IR Specter Photometer, UV-VIS Specter Photometer	Soil, water, air
6	Central Laboratory for Monitoring of Pesticides, Nitrates, and Heavy Metals. National Plant Protection Service, Sofia	10	3 GC systems 2 GC/MS system 1 LC system, 2 HPLC, 1 UV-VIS Specter Photometer	Plant products, soil, sediments

4. INVENTORY OF POPS - DIOXINS AND FURANS, POLYCHLORINATED BIPHENYLS AND HEXACHLOROBENZENE IN EMISSIONS

4.1. INTRODUCTION

The pollution of atmospheric air from stationary and mobile sources has direct negative impact on human health and on the environmental media.

The evaluation of POP emissions into the atmospheric air relied on using the available data from the National System for Monitoring of Atmospheric Air Quality, the National Institute of Statistics, and other agents.

The emissions from all anthropogenic sources of POPs are summarized in 11 main groups:

- ✓ Combustion processes in energy generation and transformation;
- ✓ Combustion processes in the commercial, administrative and household sectors, in agriculture, in forestry and in water supply and sewerage;
- ✓ Industrial combustion processes
- ✓ Industrial processes;
- ✓ Production and distribution of fossil fuels;
- ✓ Use of solvents;
- ✓ Road transport;
- ✓ Other motor vehicles and machines;
- ✓ Waste treatment and disposal;
- ✓ Agriculture and forestry, and changes in land-use;
- ✓ Nature.

Calculations have been made of the emissions of the following POPs: Dioxins and Furans, Polychlorinated biphenyls and Hexachlorbenzene.

4.2. INVENTORY METHOD

The calculation of POP emissions was done using the Methodology for Determination of the Emissions of Harmful Substances in Air approved with an order of the Ministry of Environment and Water. It adapts the EU methodology CORINAIR-94, SNAP-94 on the condition in the Republic of Bulgaria and to account for the national specifics of the activities, technologies, equipment and the current legislation related to the atmospheric air.

This methodology is used for inventorying and for balance determination of the emissions of harmful substances into the air.

The CORINAIR-94, SNAP-94 and the Methodology are using the matrix approach. The rows in the matrix cover the sources of emissions. These are the activities (anthropogenic and natural) that generate emissions of the respective pollutants. The columns of the matrix involve the pollutants of air, i.e. the emitted harmful substances. The CORINAIR-94, SNAP-94 manual puts the pollutants into three groups.

POPs releases belong to the third group – Persistent Organic Pollutants.

Their emissions are calculated using the formula:

$$E = EF \cdot Q$$

where,

E – emission in a certain quantity

EF – emission factor – a relative measure – emission related to a quantitative unit that defines adequately the specific activity.

Q – quantitative characteristic

Depending on the type of the activity, the quantitative characteristic may be: used raw materials, fuel, and energy or manufactured produce. The dimensions use the SI system: g – gram, Nm³ – normal cubic meter, J – joules, Wh – watt hours, cal – calories for Q.

The dimensions for the PCDD/PCDF emissions are: g – gram, µg – microgram (10⁻⁶g), ng – nanogram (10⁻⁹g). The emissions of individual congeners may be also in pg – picograms (10⁻¹²g) – or in fg – femtograms (10⁻¹⁵g).

The emission factor reflects the correlation of quantity emissions of POPs from:

- ✓ used raw materials;
- ✓ the process type;
- ✓ the level of used technology;
- ✓ the availability and type of treatment facilities;

A change of one or more of the four EF determining factors requires recalculation of the quantity of emissions. The emission factor value is not influenced by the geographic location of the activity.

The emission is defined based on the type of activity, as follows:

In combustion processes, the released heat energy or the quantity of burned fuel is multiplied by the EF. In production, the emissions are the product of the manufactured quantities and of the EF. When using solvents, their quantity is multiplied by EF. POP emissions in transport are the product of consumed fuel and EF.

The POP emission quantities in 2002 in Bulgaria have been based on emission factors reflecting the level of technology for the year.

4.3. INVENTORY OF DIOXINS/FURANS – PCDD/PCDF

4.3.1 National annual POPs emissions – Dioxins/Furans, PCBs and HCB

The national annual POPs emissions from unintentional production – dioxins and furans, polychlorinated biphenyls and hexachlorobenzene – in the atmosphere for the period 1990 – 2003 are summarized in Table 21 and figures 11 & 12.



Table 21 National annual emissions of POPs releases in the atmosphere for the period 1990-2003

Year	1990	1995	1996	1997	1998	1999	2000	2001	2002	2003
PCDDs/Fs, g I-TEQ/y	554,2	456	340,9	309,7	288,3	245,2	232,5	200,9	218,5	255
PCB, kg/y	258,5	382,3	261,7	226,9	252,8	234,3	228,5	211,9	250,1	260,7
HCB, kg/y	544	79	87	47	76	46	54	42,5	38	45

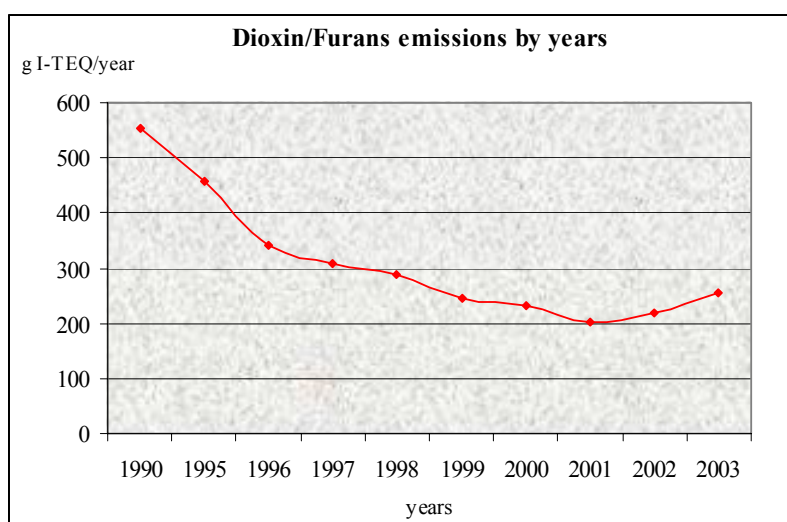


Figure 11 Annual PCDDs/PCDFs releases in the atmosphere by years

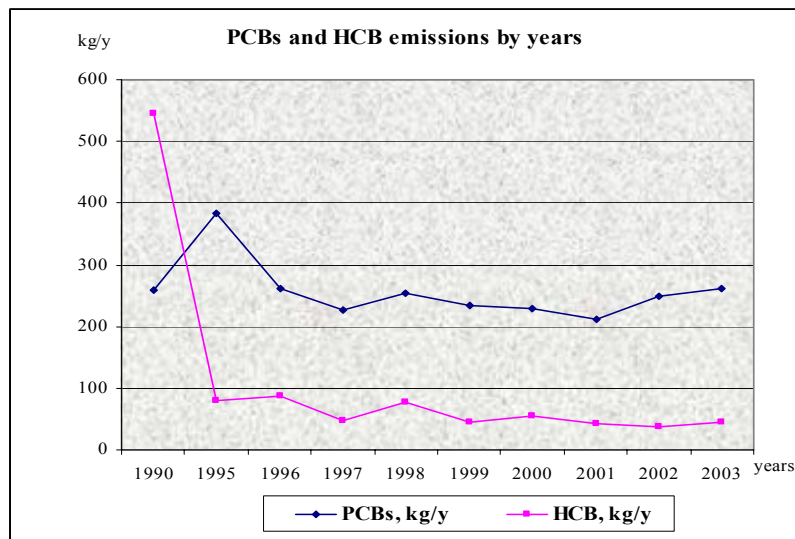


Figure 12 Annual PCBs and HCB releases in the atmosphere by years

An increase of Ds/Fs releases has been observed in 2003 by 16,7% of the 2002 emissions. In comparison to base year 1990, the annual emissions of dioxin/furans for 2003 a downward trend of 53,9% or 2,2 times had been observed, following the European trend. According to official data for PCDDs/PCDF emissions in Europe within the period 1990 ÷ 2003, the decrease is 2,7 times (63%)¹.

The annual PCBs emissions for the period 1990-2003 are almost the same.

For the period 1990-2003, the HCB emissions in the atmosphere show a significant downward trend. Compared to the base year 1990, for the HCB emission in 2003, a sharp decrease with 91,7% or 12,1 times has been registered due to the decline of industrial production.

4.3.2. National annual sector POPs emissions by category sources

The Bulgarian national annual sector POPs emissions – Dioxins/Furans, PCBs and HCB by category sources in air for the period 2000-2003 are presented in Table 22.

¹ Shatalov V. et al., Modelling of POP contamination in European region: Evaluation of the model performance. EMEP/MSC-E Technical Report 7/2005, August 2005, pp 103-117.

Table 22 Annual POPs releases in ambient air by emission categories for year 2000 ÷ 2003 in Bulgaria

Emission categories	PCDDs/PCDFs, g I-TEQ/y				PCBs, kg/y				HCB, kg/y			
	2000	2001	2002	2003	2000	2001	2002	2003	2000	2001	2002	2003
1. Combustion processes in energy generation and transformation;	109,1974	102.049	105.4	122,6	40,6394	37,799	39,341	46,142				
2. Combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing;	58,3389	44.920	59.4	70,9	141,373	124,719	156,7	164,61				
3. Industrial combustion processes;	16,3823	8.325	7,5	9,7	5,151	1,9849	1,755	2,261				
4. Industrial processes;	21,5054	20.464	19,1	23,5					19	18,5	16	21
5. Production and distribution of fossil fuels;												
6. Use of solvents;												
7. Road transport;	7,226	6.241	9,2	10,5	41,236	35,85	41,27	37,055				
8. Other motor vehicles and machines;	9,685	11.494	10,9	10,5	0,076	11,47	10,95	10,514				
9. Waste treatment and disposal;	10,193	7.362	6.978	7,283		0,059	0,056	0,137	35	24	22	24
10. Agriculture and forestry, and changes in land-use												
11. Nature												
Total annual POPs emissions	232,528	200.855	218.592	254,983	228,475	211,882	250,127	260,71	54	42,5	38	45

The lack of substantial restructuring in the industrial sector and the insignificant changes in the quantity, type and quality of fuel used in power and heat generation explain the upward or downward change of the emissions of POPs such as dioxins, furans and polychlorinated biphenyls in the last 4 years of anthropogenic activity.

Power sector is the main source of dioxins/furans and PCBs emissions into the atmosphere. The increase of dioxins/furans releases with 17,2 g (16%) for 2003 versus 2002 is due to the growing up consumption of lignite coal. For instance, the emission factor of Ds/Fs for black(anthracite) coal is 1.6 µg/t, while for lignite coal - 4.37 µg /t. PCBs emissions from combustion processes in energy generation and transformation also has increased with 6,8 kg (17,4%) versus previous year.

In 2003 the largest source of **Dioxins and Furans** are the thermal electric power stations (TEPS) with 48,1 % share of the entire releases emitted in Bulgaria from anthropogenic activity, followed by fuel combustion in the household sector – 27,8 %.

Concerning **PCBs** , the largest % share is covered by PCBs emissions from combustion processes in trading, administrative and household sectors – 63,1%, followed by releases from road transport and other motor vehicles and machines - totalling to 18,2% and combustion processes in energy generation and transformation – 17,7%.

The increased consumption of coal and wood in the household sector has resulted in a growth of PCDD/F and PCB emissions. In 2003 the household sector emitted 11,2 g more PCDD/PCDF and 7,9 kg more PCB in air as compared to the previous year. It could be noticed that the increase of PCDDs/Fs and PCBs emissions is less compared to that for 2002 versus 2001 being respectively 14,5 g for PCDD/PCDF and 32 kg for PCB, emitted in the air. Probably this is due to slight decrease in coal and wood consumption and gradual gasification of big cities in Bulgaria.

The main sources of **HCB** emissions in 2003 are the categories “waste treatment and disposal” and “industrial processes” with lasting downward trend as a decrease with 16,6% versus 2000 was registered. The HCB emissions for the period 2000 – 2003 are within the range 38 ÷ 54 kg/year, being for 2003 – 45 kg.

Figures 13 and 14 show the % share of the main category sources emitted PCDDs/PCDFs in air and PCBs for 2003.

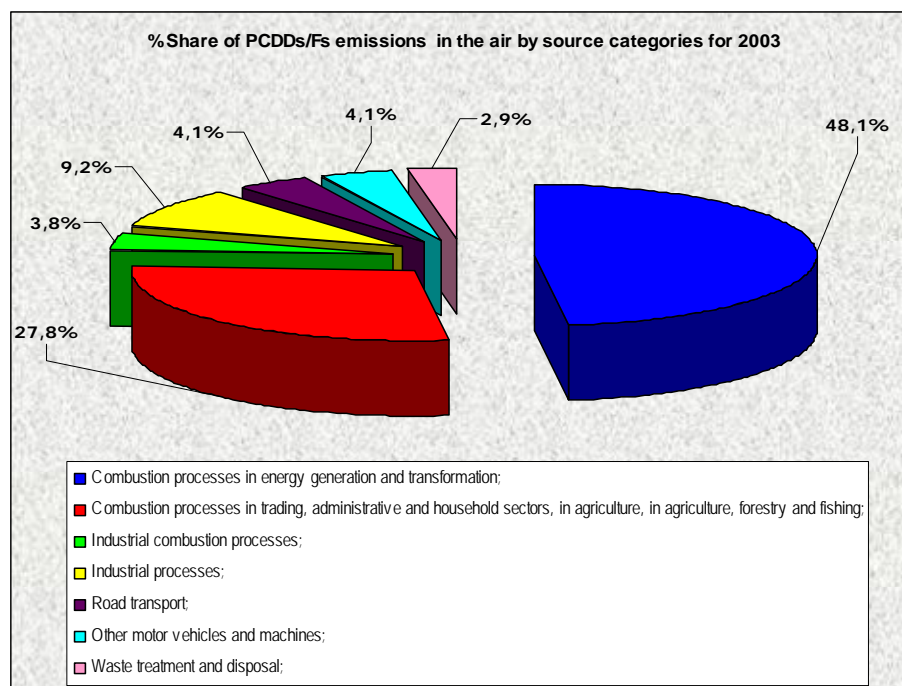


Figure 13 Share in % of the PCDDs/Fs releases by source categories for 2003

The main sources of **PCDDs/Fs emissions** are the large industrial centers, where the big thermal electric power stations and industrial manufacturers are located and the main road and railway routes pass by.

The assessment of data show, that 75,9% of PCDDs/Fs releases are formed by categories “combustion processes in energy generation and transformation” (48,1%) and “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing”(27,8%), followed by “industrial processes” and “road transport”.

The category sources “industrial processes” and “road transport and other motor vehicles and machines” should not be ignored, releasing respectively 9,2% and 8,2” from total national sector PCDDs/PCDFs emissions for 2003. May be it is due to slow restructuring of industry sector and the lack of enough financing. The PCDDs/Fs emissions from industrial processes in 2003 had increased with 18% versus 2002. Road transport marked 4,3% growth of Ds/Fs annual emissions versus previous year, due to an increase of second hand cars import, old automobile park and the slow rate of its renovation.

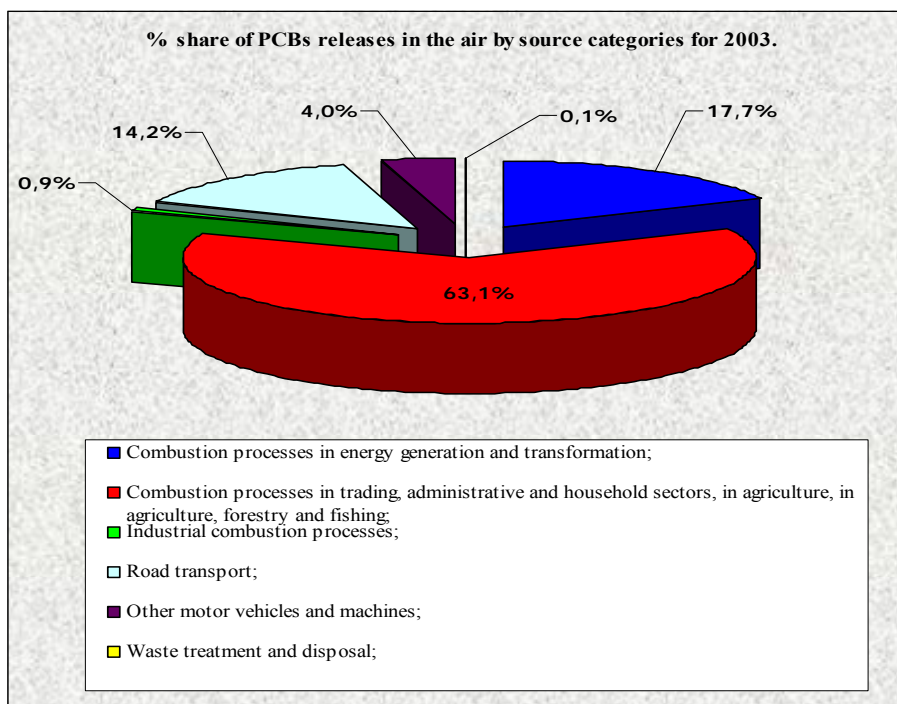


Figure 14 Share in % of PCBs releases in the air by source categories for 2003.

The biggest source of **PCBs emissions** in 2003 are the combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing, representing 63,1% of total PCBs annual sector releases, followed by road transport and other motor vehicles and machines – 18,2% and the combustion processes in energy generation and transformation – 17,7%.

Conclusions:

✚ **POPs releases**, generated in Bulgaria in the past 5 years are within the range as follows:

- ❖ **Dioxins/Furans:** 200 ÷ 255 g I-TEQ/y, and in 2002 have reached 254,9 g I-TEQ/y.
- ❖ **PCBs:** 212 ÷ 261 kg/y, and for 2003 have reached 260,7 kg.
- ❖ **HCB:** 38 ÷ 54 kg/y, and for 2003 being 45 kg.

- ✚ For the period 1990-2003 the **POPs emissions** in the atmosphere show lasting downward trend. Compared to the base year 1990, PCDDs/PCDFs and HCB note a sharp decline, respectively with 53,9% or 2,2 times and with 91,7% or 12,1 times. The annual PCBs emissions for the same period are almost the same, which could be explained with upward or downward change of the PCBs emissions formed by various category sources.
- ✚ The lack of substantial restructuring in the industrial sector and the insignificant changes in the quantity, type and quality of fuel used in power and heat generation explain the upward or downward change of the emissions of POPs such as dioxins, furans and polychlorinated biphenyls in the last 4 years of anthropogenic activity.
- ✚ The registered decline in **PCDDs/Fs emissions** into the atmosphere for 2003 compared to base year 1990 is due mainly to the categories “waste treatment and disposal” – 95%, “combustion processes in industry” – 88%; “industrial processes” - 46% and “road transport and other motor vehicles and machines” – 43%. The lowest decline show category sources “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing” – 25% and “combustion processes in energy generation and transformation” – 23%.
- ✚ The assessment of data show, that 75,9% of PCDDs/Fs releases are formed by categories “combustion processes in energy generation and transformation” (48,1%) and “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing”(27,8%), followed by “industrial processes” and “road transport”.
- ✚ The registered decline in **PCBs emissions** into the atmosphere for 2003 compared to base year 1990 is due mainly to the categories “road transport and other motor vehicles and machines” – 54% and “combustion processes in energy generation and transformation”- 18%. PCBs emissions from categories “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing” have increased considerably with 88,8%, which could be explained mainly with the growth in the consumption of wood and coal in household sector during past 5 years.
- ✚ The main sources of **HCB emissions** in air for 2003 are the categories “waste treatment and disposal” and “industrial processes” with lasting downward trend. Compared to base year 1990 a sharp decline of HCB emissions with 91% or 11 times is registered for the category “waste treatment and disposal”.
- ✚ The combustion processes are the main source of **PCDDs/Fs and PCBs emissions** for 2003.
 - ❖ Thermal electric power stations emit about 48,1% of total annual **Dioxinx/Furans emissions**, followed by combustion processes in household sector – 27,8%, combustion processes in industry – 13% and road transport and other motor vehicles and machines – 8,2%.
 - ❖ The biggest source of **PCBs emissions** in 2003 are the combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing, representing 63,1% of total PCBs annual sector releases, followed by road transport and other motor vehicles and machines – 18,2% and the combustion processes in energy generation and transformation – 17,7%.
- ✚ The main sources of **HCB emissions** in 2003 are the categories “waste treatment and disposal”- 53,4% and “industrial processes” – 46,7%, being for 2003 – 45 kg.

4.3.3. POPs emissions – PCDDs/PCDFs, PCBs and HCB - by source categories for 2002

Tables 23-26 present detailed data about the PCDD/F emissions from various sources in 2002.

Table 23 Data about dioxin and furan emissions in 2002 from the category of Combustion Processes in the Production and Transformation of Energy

Combustion processes in energy generation and transformation	PCDD/F g/year
Thermal power plants	
Thermal power plants = 300 MW	33,7775
Thermal power plants = 100 < 300 MW	55,6776
Thermal power plants = 50 < 300 MW	
Thermal power plants < 50 MW	0,0063
Stationary machines (motor-generators for electricity)	
Heat supply plants	
Heat supply plants = 300 MW	
Heat supply plants = 100 < 300 MW	3,0548
Heat supply plants = 50 < 300 MW	4,7813
Heat supply plants < 50 MW	0,8267
Stationary machines (motor-generators for electricity)	
Petrochemical industry	
Heat generation plants = 300 MW	
Heat generation plants = 100 < 300 MW	6,2991
Heat generation plants = 50 < 300 MW	
Heat generation plants < 50 MW	0,0815
Stationary machines (motor-generators for electricity)	
Heating of raw petroleum	0,9232
Coke ovens (batteries)	
TOTAL	105,428

Table 24 Data about dioxin and furan emissions in 2002 from the category Combustion Processes in the commercial, Administrative and Residential Sectors, and in Agriculture, Forestry and Water Supply and Sewerage

Combustion processes in the commercial, administrative, and residential sectors; in agriculture, forestry and water supply and sewerage	PCDD/F g/year
Heat supply plants in the commercial and administrative sectors	
Heat generation plants < 50 MW	1,8426
Stationary machines (motor-generators for electricity)	0,001
Heat generation plants in the residential sector	
Heat generation plants < 50 MW	
Stationary machines (motor-generators for electricity)	
Heat generation plants in agriculture, forestry and water supply and sewerage	
Heat generation plants < 50 MW	0,1545
Stationary machines (motor-generators for electricity)	0,0024
Household space heaters – EEPA	57,29
TOTAL	59,2905

Tables 23 and 24 show that in the category “combustion processes in energy generation and transformation” 84% of the emissions are generated by thermal power plants (TPP) with capacity higher than 100 MW, and in the category “combustion processes in commerce, administration and household sector, agriculture, forestry, and water supply and sewerage”, 97% of the emissions are from residential space heaters. The increased emissions from these sub-categories cause the total increase of PCDD/F emissions in 2002 as compared to 2001.

Table 25 Data about dioxin and furan emissions in 2002 from the category of Combustion Processes in Industry

Industrial combustion processes	PCDD/F g/year
Combustion processes in steam boilers, gas turbines and stationary machines	
Industrial heat generation plants = 300 MW	0,0021
Industrial heat generation plants = 100 < 300 MW	0,7771
Industrial heat generation plants = 50 < 300 MW	0,15
Industrial heat generation plants < 50 MW	5,4919
Stationary machines (motor-generators for electricity)	0,0075
Heating ovens	
Steel and iron pre-heaters	0,0037
Contact-free furnace processes	
Pre-heaters of open hearth furnaces. Production of iron.	
Contact processes	
Iron ore agglomeration	1,0764
Iron cast foundries	
Lime and dolomite – shaft furnaces, solid fuel	
TOTAL	7,5087

The data in Table 25 show that the main sources of emissions of dioxins and furans in this category are industrial heat generation plants, and that the highest share belongs to the thermal power plants of capacity of < 50 MW, followed by contact processes in iron ore agglomeration.

Table 26 Data about dioxin and furan emissions in 2002 from the category of Production Processes

Production processes	PCDD/F g/year
Petroleum processing	
Catalytic cracking of petrochemicals	
Pouring of iron from open-hearth furnaces	5,3613
Oxygen converters for steel	7,2833
Electric-arc furnaces for steel	3,8833
Drawn steel (rolled profiles)	2,5281
Production of ferric alloys	
Production of spirit and brandy	
Production of bitumen roof shingles	
Asphalt laying	
TOTAL	19,056

Metallurgy is the only source of emissions of dioxins and furans in this category (Table 26).

Tables 27-28 present detailed data about the PCB emissions from various sources in 2002.

Table 27 Data about PCBs in 2002 from the category of Combustion Processes in the Production and Transformation of Energy

Combustion processes in energy generation and transformation	PCB kg/year
Thermal power plants	
Thermal power plants = 300 MW	13,5735
Thermal power plants = 100 < 300 MW	22,8648
Thermal power plants = 50 < 300 MW	
Thermal power plants < 50 MW	
Stationary machines (motor-generators for electricity)	
Heat generation plants	
Heat generation plants = 300 MW	
Heat generation plants = 100 < 300 MW	0,732
Heat generation plants = 50 < 300 MW	1,8922
Heat generation plants < 50 MW	0,0382
Stationary machines (motor-generators for electricity)	
Petrochemical industry	
Heat generation plants = 300 MW	
Heat generation plants = 100 < 300 MW	0,1994
Heat generation plants = 50 < 300 MW	
Heat generation plants < 50 MW	0,0025
Stationary machines (motor-generators for electricity)	
Heating of raw petroleum	0,0291
Coke ovens (batteries)	
TOTAL	39,3317

Table 28 Data about PCBs in 2002 from the category Combustion Processes in the Commercial, Administrative and Residential Sectors, and in Agriculture, Forestry and Water Supply and Sewerage

Combustion processes in the commercial, administrative, and residential sectors; in agriculture, forestry and water supply and sewerage	PCB kg/year
Heat supply plants in the commercial and administrative sectors	
Heat generation plants < 50 MW	0,0542
Stationary machines (motor-generators for electricity)	
Heat supply plants in the residential sector	
Heat generation plants < 50 MW	
Stationary machines (motor-generators for electricity)	
Heat generation plants in agriculture, forestry and water supply and sewerage	
Heat generation plants < 50 MW	0,0051
Stationary machines (motor-generators for electricity)	
Household space heaters – EEPA	156,69
TOTAL	156,7493

Tables 27 and 28 show that the category “Combustion Processes in Power Generation and Transformation”, 92% of the emissions are from thermal and heat generation plants > 100 MW.

In the category “Combustion processes in trading, administrative and household sectors, in agriculture, in forestry and in water supply and sewerage” almost 100% of the emissions are from domestic heating appliances. In 2002 households emitted in air 32 kg more PCBs – the 20% increase as compared with the previous year mainly because of increased use of coal and wood in the domestic sector.

Table 29 Data about PCB emissions in 2002 from the category of Combustion Processes in Industry

Industrial combustion processes	PCBs kg/year
Combustion processes in steam boilers, gas turbines and stationary machines	
Industrial heat generation plants = 300 MW	0,0002
Industrial heat generation plants = 100 < 300 MW	0,0721
Industrial heat generation plants = 50 < 300 MW	0,0132
Industrial heat generation plants < 50 MW	0,2229
Stationary machines (motor-generators for electricity)	0,0002
Heating ovens	
Steel and iron pre-heaters	0,0001
Contact-free furnace processes	
Pre-heaters of open hearth furnaces. Production of iron.	
Contact processes	
Iron ore agglomeration	1,1362
Iron cast foundries	0,1999
Lime and dolomite – shaft furnaces, solid fuel	0,0994
TOTAL	1,7442

The main PCB emissions in the category Processes in Industry are caused by the agglomeration of iron ore – 66% of the total quantity of emissions in 2002 (Tables 29).

Table 30 presents detailed data about the HCB emissions from the category of Production Processes in 2002.

Table 30 Data about HCB emissions in 2002 from the category of Production Processes

Production processes	HCB kg/year
Petroleum processing	
Catalytic cracking of petrochemicals	
Pouring of iron from open-hearth furnaces	
Oxygen converters for steel	
Electric-arc furnaces for steel	16
Drawn steel (rolled profiles)	
Production of ferric alloys	
Production of spirit and brandy	
Production of bitumen roof shingles	
Asphalt laying	
TOTAL	16

The main sources of HCB emissions are the categories “industrial processes and waste treatment and disposal”. Industrial processes emit HCB only from steel arc furnaces.

4.3.4. POPs emissions – PCDDs/PCDFs, PCBs and HCB- by districts for 2002

The sources of **PCDDs/PCDFs** and **PCBs** emissions in the atmosphere are distributed on the whole territory of the country. 2935 industrial sources generate 0,0001 to 8,29 g of PCDDs/Fs annually. The sources emitting 0,0001 g/year have been excluded from the calculations.

973 industrial sources generate 0,0001 to 3,41 kg of **PCBs** annually. The sources emitting 0,0001 kg/year have been excluded from the calculations.

Table 31 and figure 15 present data about **PCDDs/Fs, PCBs and HCB** emissions from category sources “combustion processes in energy generation and transformation” and “industrial processes” by districts in Bulgaria for 2002.

Table 31 PCDDs/PCDFs, PCBs and HCB emissions by districts for 2002.

№	District	PCDDs/PCDFs, g/y	PCBs, kg/y	HCB, kg/y
1	Blagoevgrad	0,4641	0,1019	
2	Burgas	7,8258	0,9351	
3	Varna	2,2349	0,7329	
4	Veliko Tarnovo	1,0279	0,8058	
5	Vidin	0,0688	0,1499	
6	Vratsa	0,0674	0,8018	
7	Gabrovo	0,1965	0,0078	
8	Dobrich	0,0681	0,0002	
9	Kardzhali	0,1980	0,0065	
10	Kyustendil	10,5287	0,2432	
11	Lovech	0,3032	0,0188	
12	Montana	0,0468	0,0311	
13	Pazardzhik	0,0940	0,0050	
14	Pernik	10,0993	0,0101	11,70
15	Pleven	0,1676	0,0028	
16	Plovdiv	2,0649	0,0301	
17	Razgrad	0,0255	0,0247	
18	Russe	1,1562	0,0628	
19	Silistra	0,2481	0,1806	
20	Sliven	0,6523	0,0474	
21	Smolyan	0,0790	0,5557	
22	Sofia-city	16,1232	12,7108	4,30
23	Sofia-district	0,4461	1,9281	
24	Stara Zagora	77,1736	6,5007	
25	Targovishte	0,0516	1,3828	
26	Haskovo	1,0355	12,6443	
27	Shumen	0,1946	0,5486	
28	Yambol	0,0277	0,0962	
	Total for Bulgaria	132,6694	40,5655	16,00

The largest **PCB** emissions have occurred in Sofia-city at 30% (predominantly from thermal power plants), Haskovo area at 30% (predominantly from the textile industries) and Stara Zagora area at 15% (predominantly from thermal power plants and the food industry).

The industrial **HCB** emission sources are metallurgical enterprises concentrated in the areas around Pernik and Sofia city. Their share is 42,1% from total HCB emitted (38 kg) in 2002 .

Allocated per capita and unit of area, the **PCDD/PCDF**, **PCBs** and **HCB** emission values in base 1990 , 2002 and 2003 are shown in Table 32.

Table 32 POPs emissions per unit area and per capita in Bulgaria by years

POPs emissions	Year	Per unit area, Total country area (110 993 km ²)	Population, number	Per capita
PCDDs/PCDFs				
554,2 g	Base year 1990	0,00499 g/km ²	8487317	0,0000653 g
218,5 g	2002	0,00197 g/km ²	7845841	0,0000278 g
254,9 g	2003	0,00230 g/km ²	7801273	0,0000327 g
PCBs				
258,5 kg	Base year 1990	0,00233 kg /km ²	8487317	0,0000305 kg
250,1 kg	2002	0,00225 kg /km ²	7845841	0,0000319 kg
260,7 kg	2003	0,00234 kg /km ²	7801273	0,0000334 kg
HCB				
544 kg	Base year 1990	0,00490 kg /km ²	8487317	0,0000641 kg
38 kg	2002	0,000342 kg /km ²	7845841	0,0000048 kg
45 kg	2003	0,000405 kg /km ²	7801273	0,0000056 kg

Allocated per capita and unit of area, the PCDDs/PCDFs and HCB emission values versus base year 1990 show a lasting downward trend. The decrease of PCDDs/PCDFs emissions is more the 2 times, while for HCB – 11 times as a result of the decrease in industrial production in Bulgaria after 1990. It is noticed, that allocated per unit area the PCBs emissions are within the same range, while per capita they increase, due probably to the growing consumption of wood and coal in household sector after 1990.

Conclusions

- ✚ The sources of **PCDDs/PCDFs** and **PCBs** emissions in the atmosphere are distributed on the whole territory of the country. 2935 industrial sources generate 0,0001 to 8,29 g of PCDDs/Fs annually. 973 industrial sources generate 0,0001 to 3,41 kg of PCBs annually.
- ✚ The main sources of **PCDDs/Fs** and **PCBs** emissions from category sources “combustion processes in energy generation and transformation” and “industrial processes” for 2002 are thermal electric power stations and industrial manufacturers.
- ✚ The total **PCDDs/PCDFs**, **PCBs** and **HCB** emissions from category sources “combustion processes in energy generation and transformation” and “industrial processes” for 2002 are as follows: **PCDDs/PCDFs** - 132,67 g, representing 60,1% of annual emissions from all category sources (218,48 g); **PCBs** – 40,56 kg or 16,2% of annual emissions (250,06 kg); **HCB** – 16 kg or 42,1% of annual emissions (38 kg).
- ✚ The largest share of **PCDDs/Fs** emissions for 2002 have been registered in Stara Zagora - 58% followed by Sofia-city – 12,2%, Pernik – 7,9% and Burgas – 6 %. The largest **PCB** emissions have occurred in Sofia-city at 30%, Haskovo area at 30% and Stara Zagora area at 15% .
- ✚ The industrial **HCB** emission sources are metallurgical enterprises concentrated in the areas around Pernik and Sofia city, as 73,1% have been registered in Pernik.
- ✚ **PCDDs/PCDFs** and **HCB** emission values, allocated per capita and unit of area, versus base year 1990 show a lasting downward trend in times due the decrease in industrial production in Bulgaria after 1990.

✚ PCBs emissions values, allocated per unit area are almost the same range, while per capita they increase, due probably to the growing consumption of wood and coal in household sector after 1990.

5. ENVIRONMENTAL MONITORING LEVELS AND HUMAN EXPOSURE

The atmosphere pollution from stationary and mobile sources causes direct negative impacts on human health and the environmental media.

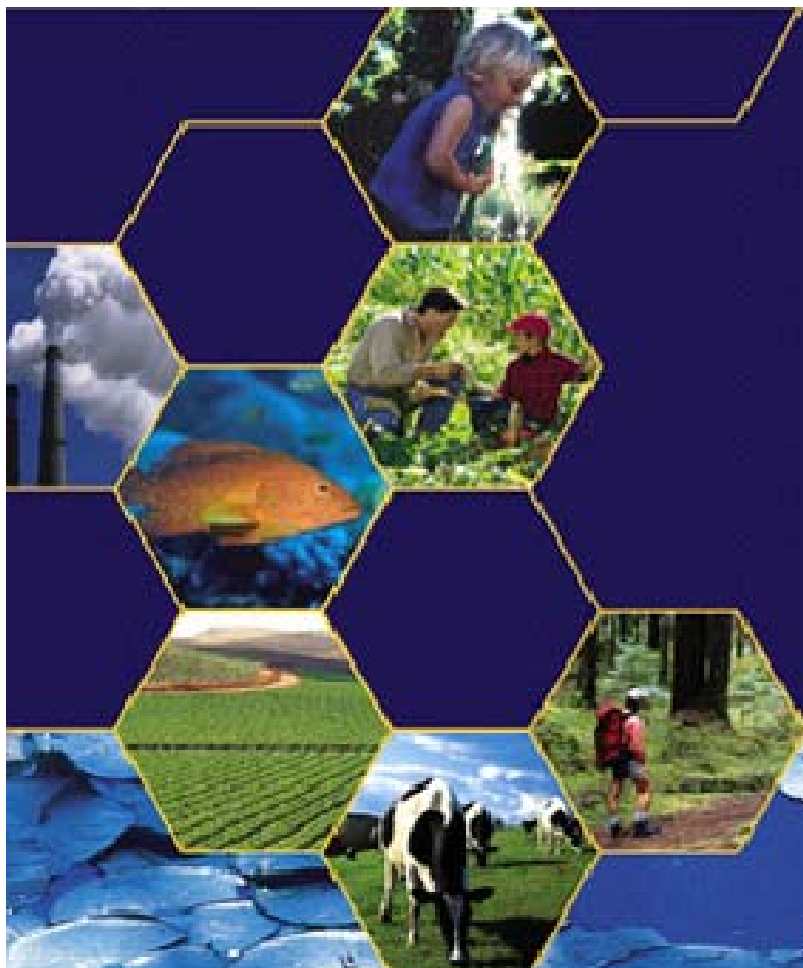


Figure 16 POPs releases impacts on human health and the environment

5.1. ENVIRONMENTAL EXPOSURE ROUTES AND BEHAVIOUR OF POPs RELEASES

The exposure routes and behaviour of dioxins/furans, PCBs and HCB into the environment – air, water and soils are indicated on Tables 33 & 34.

Table 33 Environmental exposure routes of Dioxins/Fs, PCBs and HCB

Environment media	Dioxins/Furans PCDDs/PCDFs	Polychlorinated biphenyls PCBs	Hexachlorobenzene HCB
AIR	Dioxins/ Furans are released into the air from combustion processes in industry; accidental fires; uncontrolled municipal solid waste & tire burning; forest fires and uncontrolled stubble-fields burning; in emissions from industrial incinerators and motor vehicles.	PCBs enter the air during their use and disposal; from accidental spills and leaks; and from leaks or fires in products containing PCBs.	HCB enter the air as by-product during the manufacture of certain chemicals. Small amounts can also be produced during combustion of municipal waste. Under ordinary conditions HCB not much evaporates into the air. Once in air, it can be carried out long distances.
WATER	Dioxins/Furans enter water as a result of deposition after emitted to the atmosphere from combustion sources.	PCBs enter the water during their disposal and from accidental spills and leaks. In water, a small amount of PCBs may remain dissolved, but most stick to organic particles and bottom sediments.	HCB enter the water from contaminated air. Once in water, it binds to sediments and settles to the bottom.
SOIL	Dioxins/Furans enter soil by atmospheric deposition from combustion and manufacturing processes and disposal of contaminated wastes.	PCBs enter soil during their disposal; from accidental spills and leaks. PCBs also bind strongly to soil.	HCB enter the soil from contaminated air and water. It sticks strongly to soil.
WASTE	When released in waste waters, some Dioxins/Furans are broken down by sunlight, some evaporate to air, but most attach to soil and settle to the bottom sediment in water.	PCBs can still be released to the environment from hazardous waste sites; illegal or improper disposal of industrial wastes and consumer products; leaks from old electrical transformers containing PCBs.	HCB can be released to the environment from hazardous waste sites and during combustion of municipal waste.
BIOTA	Dioxins/Furans low levels may build up in the food chain. Low levels of Dioxin/Furans are taken up by eating contaminated food, breathing contaminated air and drinking polluted water.	PCBs are taken up by small organisms and fish in water. They are also taken up by eating contaminated food (fish, meat, and dairy products), breathing air near hazardous waste sites and drinking contaminated well water.	Low levels of HCB are taken up in eating contaminated food (e.g, fish, meat, milk, dairy products), drinking contaminated water, breathing contaminated air and being in contact with contaminated soil.

Table 34 Behaviour of Dioxins/Fs, PCBs and HCB in the environment

Environment media	Dioxins/Furans PCDDs/PCDFs	Polychlorinated biphenyls PCBs	Hexachlorobenzene HCB
AIR	Dioxins and furans are emitted as gas or bound to the particulates dispersed in the waste gases – drops, dust, soot, ash. In the form of gas, they are photo-degradable. However, their low vapour pressure means that usually they are emitted into the atmosphere adsorbed onto various particles and this stops them from disintegrating. This explains their ability to stay in air for long periods of time and to be carried along large distances. The Dioxins life-times in the atmosphere, depending on the rate of chlorination vary from 0,5 to 10 days. The estimated tropospheric lifetimes of furans depending on the rate of chlorination vary from 1.9 to 39 days.	PCBs are heavier than air and can settle in the ground layer. PCB molecules bind to volatile particulates and to fine aerosols of less than 0.05 – 20 µm in size, they spread into the atmosphere, and settle at long distances, mainly in areas of cold climate. PCBs half-times in the atmospheric air vary from 3 weeks to 2 years.	Atmospheric air pollution with HCB bound to particulate matter is a serious threat. Hexachlorobenzene is resistant to ultraviolet radiation. Photodegradation in the atmosphere takes approximately 2 years and the metabolites may cause the formation of greenhouse gases or are greenhouse gases themselves. HCB has an estimated half-life in air of 0.5-4.2 years in air.
WATER	In water, dioxins and furans exhibit extremely low solubility but, also, high capacity for adsorption into sediments and into the biota. Scientists have established that more than 90% of the 2,3,7,8-THDD available in the aquatic environment exist in adsorbed state. The half-life times of dioxins/furans depending on the rate of chlorination in water varies between 2.6 and 4 days.	PCBs evaporate from ground and water surfaces over several days. They accumulate in the sediments on water basin bottoms and may, through infiltration, pollute ground water. Local pollution is possible also in result of emergencies, accidents or illegal activities. The half-life of PCBs in water is more than 6 years.	HCB does not dissolve in water but is carried by it, and in this way pollutes other water basins and, thus, soils. The half-life of HCB in rivers varies between 0.3 and 3 days.
SOIL	Dioxins and furans enter soils by means of wet and dry deposits adsorbed onto solid particles and water drops. The poor waeter solubility of furans and dioxins means that they do not exfiltrate from soils into the ground water and does not wash away from surfaces. The evaporation of these compounds from the soil surface is also a limited process because of their low vapour pressure. The main route for transition of PCDD/F from the soil surface into air is by carrying along into the air stream of suspended particulates onto which these have adsorbed. Estimates of the half-life of TCDD on the soil surface range from 9 to 15 years, whereas the half-life of subsurface in soil may range from 25 to 100 years (Paustenbach et al. 1992).	PCBs enter soils by means of wet and dry deposits adsorbed onto solid particles and water drops. Increasing chlorine atoms increases the adsorption and resistance to biodegradation in soils, and reduces the speed of infiltration. The half-life of PCBs in soil is more than 6 years.	HCB is not heavily absorbed in soil. Its half-life in soil is 2,7 – 5,7 years.
BIOTA	PCDDs/PCDFs have a relatively high bioaccumulation potential and long half-life in biota (log K _{OW} : 6.60 – 8.20).	PCBs have extremely long half-lives in biota as for some species it could reach more than 10 years (log K _{OW} - 4,3-8,26).	HCB has a relatively high bioaccumulation potential and long half-life in biota (log K _{OW} - 3.93-5.73).

5.2. LEVELS IN THE ENVIRONMENT

5.2.1. Levels of Dioxins/Furans, PCBs and HCB in air

POPs releases into the air are calculated by balance determination with adapted to the EU CORINAIR-94 Inventory Manual (Selected Nomenclature for Air Pollution for CORINAIR 94 Inventory (SNAP 94).

There are no international regulatory provisions for implementing of monitoring for Air quality assessment concerning POPs releases.

5.2.2. Levels of Dioxins/Furans, PCBs and HCB in soil

Dioxins/Furans (PCDDs/PCDFs)

There are no international regulatory provisions for monitoring of soil contamination, concerning PCDDs/Fs releases.

Polychlorinated byphenils (PCBs)

In the period 1997-2002, the soil-chemistry monitoring of the MOEW covered 231 soil samples distributed uniformly across Bulgaria's agricultural lands and analysed for content of 8 PCB congeners (Table 35).



Table 36 shows the range of PCBs concentrations for 8 congeners and sum PCB₆ in soils for Bulgaria for the period 1997÷2002.

Table 35 Number of samples studied for PCBs content in soils in Bulgaria, by year

Number of samples studied for PCBs content in soils in Bulgaria, by congener																								
PCB congener	1997 data			1998 data			1999 data			2000 data			2001 data			2002 data								
	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV
PCB 28	34	21	13	0	107	45	62	0	62	48	14	0	13	13	0	0	12	2	10	0	3	1	2	0
PCB 52	34	25	9	0	107	55	52	0	62	47	15	0	13	13	0	0	12	2	10	0	3	1	2	0
PCB 101	34	27	7	0	107	18	84	0	62	42	20	0	13	13	0	0	12	3	9	0	3	2	1	0
PCB 105	34	34	0	0	107	106	1	0	62	59	3	0	13	13	0	0	12	4	8	0	3	2	1	0
PCB 118	34	32	2	0	107	50	57	0	62	61	1	0	13	13	0	0	12	5	7	0	3	2	1	0
PCB 138	34	17	17	0	107	18	89	0	62	30	32	0	13	13	0	0	12	5	7	0	3	1	2	0
PCB 153	34	14	20	0	107	27	80	0	62	27	35	0	13	13	0	0	12	3	9	0	3	2	1	0
PCB 156	34	34	0	0	107	107	0	0	62	60	2	0	13	13	0	0	12	4	8	0	3	3	0	0
PCB 180	34	9	25	0	107	45	62	0	62	30	32	0	13	13	0	0	12	3	9	0	3	2	1	0
PCB total	34	3	31	0	107	6	101	0	62	21	41	0	13	13	0	0	12	1	11	0	3	1	2	0

Table 36 PCBs concentration ranges in soils in Bulgaria

PCB congener	Range
	µg/kg
PCB 28	0,003 ÷ 4,37
PCB 52	0,007 ÷ 5,76
PCB 101	0,001 ÷ 3,04
PCB 105	0,029 ÷ 0,25
PCB 118	0,004 ÷ 0,71
PCB 138	0,004 ÷ 3,038
PCB 153	0,005 ÷ 2,65
PCB 156	0,031 ÷ 0,41
PCB 180	0,003 ÷ 5,75
PCB total	0,009 ÷ 12,47

- ➡ The analysis of the data shows that no PCB congeners above the ALV have been measured.
- ➡ Measurements in individual local points have shown levels of PCB congeners above the levels of concern.

Conclusion:



✚ The sum PCB content in soil is significantly (by a multiple factor) below the levels of concern which allows the assumption that no potential threat exists for pollution of soil with PCB.

Hexachlorobenzene (HCB)

The soil-chemistry monitoring included 4 years of systematic gathering by the MOEW of 277 soil samples for HCB residues analysis, out of which 124 were collected in the year 2000. The soil sampling points in 1997 had been orientated towards places with assumed soil pollution. The point selection methodology was changed during the period 1998-2000 and the soil samples were equally distributed along the country's agricultural land. The sample analysis was made using gas-chromatograph by means of MS and EC detector, according to ISO/CD 10382.2.

The three levels of reference values – levels of concern, admissible limit values and intervention levels – have been used to evaluate the results, according to Bulgarian legislation.

Table 37 presents data about the number of samples studied for HCB in soils in Bulgaria.

Table 37 Number of samples studied for HCB content in soils in Bulgaria, by area

Area	1997 data				1998 data				1999 data				2000 data			
	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV	Number of samples	Number of samples <MDL	Number of samples below the ALV	Number of samples above the ALV
Blagoevgrad									2	2			3	3		
Burgas									1	1			10	10		
Varna					3	3			2	2			6	6		
Veliko Tarnovo	3	2	1						3	3			10	10		
Vidin									11	10	1		2	2		
Vratsa	5	5							4	1	3		6	6		
Gabrovo									1	1			2	2		
Dobrich					3	3			2	2			5	5		
Kyustendil													1	1		
Lovech									3	3			4	4		
Montana	4	2	2						8	6	2		4	4		
Pazardzhik					4		4		4	1	3		3		3	
Pernik									7	3	4		3	3		
Pleven					4	1	3		1	1			8	8		
Plovdiv					8		8		2		2		9	2	7	
Razgrad									3	3			3	3		
Russe									1	1			5	5		
Silistra									1	1			4	4		
Sliven									1	1			5	1	4	
Sofia-city									11	7	4					
Sofia-district									10	9	1		3	3		
Stara Zagora					14	6	8		3	3			6	3	3	
Targovishte					1	1							6	6		
Haskovo					3		3		2		2		4		4	
Shumen					2	2			3	3			6	6		
Yambol					10	3	7		3	3			6	1	5	
Total for Bulgaria	12	9	3	0	52	19	33	0	89	67	22	0	124	98	26	0

- Of the 277 studied soil samples only 22% exhibit HCB residues, and the remaining soils are below the minimum detection level;
- The registered levels of HCB in soil are $0.02 \div 4,01 \mu\text{g}/\text{kg}$, which is significantly lower than the ALV (0,25 mg/kg, according to the German standard);
- There are no HCB polluted soils in Bulgaria.

5.2.3. Levels of Dioxins/Furans, PCBs and HCB in water

Dioxins/Furans (PCDDs/PCDFs)

There are no international regulatory provisions for monitoring of groundwater contamination, concerning PCDDs/Fs releases.

Polychlorinated byphenils (PCBs)

According to Regulation 1 on the Studying, Use and Protection of Ground Water, SG 57/14.07.2000, amended SG 64 /4.08.2000, the condition of ground water is defined as follows:



1. *Ground water in excellent condition* – the parameters are below the environmental threshold;
2. *Ground water in good condition* – the parameters are between the ecological threshold and the pollution threshold;
3. *Ground water in poor condition* – the parameters are above the pollution threshold;
4. *Ground water in a very bad condition* – water where damages have occurred.

Table 38 presents data from analyses of PCB in ground water from the National Ground Water Monitoring Network.

Table 38 Data about the analyses of PCB in ground water

Year	Area	Municipalities, total	Urban centres number	Nr of samples for PCB 28	Nr of samples for PCB 52	Nr of samples for PCB 101	Nr of samples for PCB 105	Nr of samples for PCB 118	Nr of samples for PCB 138	Nr of samples for PCB 153	Nr of samples for PCB 156	Nr of samples for PCB 180
				$\mu\text{g}/\text{l}$ All samples are below the minimum detection level (< MDL)								
2001	Kardzhali	3	3	4	4	4			4	4		4
2001	Pazardzhik	3	7	8	8	8			8	8		8
2001	Plovdiv	5	6	6	6	6			6	6		6
2001	Haskovo	6	10	8	9	9			10	10		10
TOTAL		17	26	26	27	27			28	28		28

Hexachlorobenzene

In the period 1998-2002 two groups of samples have been taken for analysis of hexachlorobenzene in ground water – at high ground water level in spring time, and low level by the later summer and early fall. The samples taken for HCB in ground water were 287, and in the year 2002 they were 70.

Table 39 presents data from analyses of HCB in ground water in Bulgaria from the National Ground Water Monitoring Network.

Table 39 Number of samples studied for HCB content in ground water in Bulgaria

Area	1998 data				1999 data				2000 data				2001 data				2002 data			
	Number of samples	Number of samples <MDL	Number of samples below the ecological threshold	Number of samples above the ecological threshold	Number of samples	Number of samples <MDL	Number of samples below the ecological threshold	Number of samples above the ecological threshold	Number of samples	Number of samples <MDL	Number of samples below the ecological threshold	Number of samples above the ecological threshold	Number of samples	Number of samples <MDL	Number of samples below the ecological threshold	Number of samples above the ecological threshold	Number of samples	Number of samples <MDL	Number of samples below the ecological threshold	Number of samples above the ecological threshold
Blagoevgrad					2	2			3	3			1	1			1	1		
Burgas					2	2			1	1			9	9			2	2		
Varna	1		1		5	5			4	4			1	1						
Veliko Tarnovo									3	3			2	2						
Vratsa	2	1	1		6	6			7	7			4	4			5	5		
Dobrich	5	2	3		9	5	4		11	11			8	8			3	3		
Kardzhali													4	1	3		4	4		
Montana	4	3	1		4	4			4	4			4	4			6	6		
Pazardzhik	6	4	2		3	3			1	1			8	8			9	9		
Pleven					4	4			5	5							1	1		
Plovdiv	22	17	5						4	3	1		6	6			12	11	1	
Russe					1	1											11	11		
Sliven	1	1			1	1														
Smolyan					2	2			1	1										
Sofia					4	4			3	3			3	3						
Stara Zagora	2	2			1	1							2	2			3	3		
Haskovo	5	4	1		4	4			1	1			11	11			12	11	1	
Shumen					3	3			2	2			1	1						
Yambol	1	1			1	1			1	1			1	1			1	1		
Total for Bulgaria	49	35	14	0	52	48	4	0	51	50	1	0	65	62	3	0	70	68	2	0

- ➡ During the period 1998-2002 no HCB in ground water above the pollution threshold of 5 µg/l and above the ecological threshold of 0,1 µg/l have been registered in Bulgaria.
- ➡ All values were below the minimum detection level in the period 2001 – 2002 and this classifies the ground water as ground water in excellent condition.
- ➡ There is no HCB polluted ground water in Bulgaria.

5.2.4. Levels of PCDD/Fs, PCBs and HCB in food

The National Veterinary Medical Service (NVMS) at the MoAF is the national competent authority responsible for the National Monitoring Program for Control on Residues, including POPs in live animals and animal products intended for human consumption.



The results of control on Residues of PCBs in life animal and animal products - red meat; poultry; hen eggs; raw milk; fish; bee honey; farmed and wild game in 2003, performed by NVMS at MoAF under the National Monitoring Program for Control on Residues (NMPCR) indicate the following:

- ❖ No presence of any residues from B (3)(a) group organochlorine compounds – PCBs in the tested samples of Live Animals, Fresh Meat, Poultry, Fish, Farmed & Wild Game, Raw Milk, Hen Eggs and Bee Honey in Bulgaria for the Year 2003 has been detected.
- ❖ No investigations for PCDDs/PCDFs and HCB in food had been performed.

5.2.5. Levels of PCDD/Fs, PCBs and HCB in animal wild world



The study of PCB in subcutaneous fat of a bear killed in April 2004 in Central Stara Planina, Troyan area, showed 142 ng/g fat of polychlorinated biphenyls (analysis protocol 140 dated 15.06.2004, issued by the Food Chemistry Laboratory at the NCHMEN in the town of Sofia).

5.3. HUMAN EXPOSURE AND HEALTH IMPACT

5.3.1. Human exposure

Human exposure to background contamination with PCDD/PCDF is possible *via* several routes:

- ✚ Inhalation of air and intake of particles from air
- ✚ Ingestion of contaminated soil
- ✚ Dermal absorption
- ✚ Food consumption



Humans occupy a top position in terrestrial and aquatic foodchains and as a result consume a high proportion of food in which persistent lipophilic compounds can be effectively biomagnified. Once ingested, POPs sequester in body lipids, where they equilibrate at roughly similar levels on a fat-weight basis between adipose tissue, serum, and breast milk. Milk monitoring is far more widely practised due to the relatively easy sample collection.

It is possible to document three distinct types of human exposure to POPs compounds:

- ❖ High-dose acute exposure: typically resulting from accidental fires or explosions involving electrical capacitors or other PCB-containing equipment or high dose food contamination.
- ❖ Mid-level chronic exposure: predominantly due to the occupational exposure or high consumption of a POPs –contaminated dietary source such as fish or other marine animals.
- ❖ Chronic, low-dose exposure: characteristic for the general population as a consequence of the existing global background levels of POPs with variations due to diet, geography, and level of industrial pollution. People are exposed to multiple POPs during their lifetime and all individuals today carry detectable levels of a range of POPs in their body lipids.

5.3.2. Levels in human tissue - Human milk

A considerable number of studies have been produced on breast milk mainly aimed to characterise breast-fed infant exposure and the associated risk.

Mothers' age, number of breast-fed infants and dietary habits are in fact crucial parameters in determining POPs body burden and hence milk contamination.

PCBs



The international project conducted in 19 countries (Brasil, Bulgaria, Croatia, the Czech Republic, Egypt, Finland, Hungary, Ireland, Italy, New Zealand, Norway, Romania, Russia, Slovakia, Spain, Sweden, the Netherlands, the Ukraine) by the WHO – “WHO-coordinated Exposure Study on the Levels of PCBs, PCDDs and PCDFs in Human Milk, Organohalogen Compounds, 2003” carried out a study in Bulgaria of PCDD/PCDF content in mother’s milk of 30 healthy women distributed by 10 of three regions in Bulgaria (Bankya – environmentally clean and two (Sofia and Blagoevgrad) polluted in different degrees. The results show the highest content of PCB in human milk from Blagoevgrad, followed by that of Sofia. Lowest levels were found in the milk from mothers from the environmentally clean region of Bankya (Table 40).

Table 40 PCB levels in human milk (pg TEQ/g fat)

	Bankya	Sofia	Blagoevgrad
WHO - PCB	3.74	4.21	4.70
Sum WHO – PCDD/PCDF + PCB	8.82	10.35	11.81

The data from the study of the three PCB representatives -138, 153 and 180 – follow a similar trend (Table 41).

Table 41 Level of the most important PCB markers in human milk (ng/g fat)

PCB	Bankya	Sofia	Blagoevgrad
PCB 138	9.64	14.06	16.33
PCB 153	11.37	17.42	20.29
PCB 180	6.38	9.40	13.20

PCB levels below 5 pg TEQ/g fat and sum content of the three parameters below 40 ng/g fat have been established in human milk in Brasil, Australia, New Zealand, Hungary and Bulgaria. The highest PCB content was registered in the Ukraine, Italy, the Czech Republic and Russia – higher than 15 pg TEQ/g fat. The highest total content of the three PCB representatives 138, 153 and 180 in Spain, Slovakia and the Czech Republic (400 – 500 ng/g fat).

PCDD/PCDFs



WHO carried out periodically monitoring programmes on the levels of PCDD/PCDFs and dioxin-like PCBs in human milk. The results of the third round of the WHO 2001-2002 co-ordinated exposure study show that the lowest levels of PCDDs/Fs have been found in Bulgaria (median value of 6,14 pg WHO-TEQ/g fat) and of dioxin-like PCBs – being one of the lowest (median value of 4,21 pg WHO-TEQ/g fat) after Hungary. (Table 42).

Table 42 Levels of PCDD/PCDFs and dioxin-like PCBs in human milk (2001-2002)
[pg WHO-TEQ/g fat]²

Country	PCDDs/Fs		Dioxin-like PCBs		Number of pools
	median	range	median	range	
Bulgaria	6.14	5.08-7.11	4.21	3.74-4.70	3
Czech Republic	7.78	7.44-10.73	15.24	14.32-28.48	3
Finland	9.44	9.35-9.52	5.85	5.66-6.03	2
Hungary	6.79	5.26-7.46	2.87	2.38-4.24	3
Ireland	6.91	6.19-8.54	4.66	2.72-5.19	3
Norway	7.30	7.16-7.43	8.08	6.56-9.61	2
Romania	8.86	8.37-12.00	8.06	8.05-8.11	3
Russia	8.88	7.46-12.93	15.68	13.38-22.99	4
Slovak Republic	9.07	7.84-9.87	12.60	10.72-19.49	4
The Netherlands	18.27	17.09-21.29	11.57	10.90-13.08	3
Ukraine	10.04	8.38-10.16	19.95	14.10-22.00	3

Industrialised countries like The Netherlands show relatively high levels of PCDD/PCDFs. Elevated levels of dioxin-like PCBs were found in human milk from Ukraine, Russia and the Czech Republic.

5.3.3. Human health effects

Many laboratory experiments have been conducted to test the relationship between POPs exposure and a range of adverse outcomes in animals. Table 42 shows some possible effects that can be produced by some of POPs – dioxins/furans, PCBs and HCB and Category of carcinogenicity by IARC* (Table 43).

Table 43 Potential effects of individual POPs

Types of Effects	PCDDs	PCDFs	PCBs	HCB
Reproduction and/or development	X	X	X	X
Porphyria	X	X	X	X
Immune system	X	X	X	X
Thyroid and retinol effects	X	X	X	X
Skeletal changes	X	X	X	
Endocrine disruptor	X	X	X	
Carcinogenic effects	X*			
Category of carcinogenicity IARC*	Group 1* – carcinogen to humans : Only for 2,3,7,8- Cl₄DD Group 3 – not classifiable as carcinogen to humans: For all other PCDDs	Group 3 - Not classifiable as carcinogen to humans	Group 2A - probable carcinogen to humans	Group 2B – possible carcinogen to humans

* IARC – Classification of agents, mixtures and exposures according to their carcinogenic risk to humans in accordance with the procedures adopted as standard IARC practice:

Group 1 - carcinogenic to humans; **Group 2A** - probably carcinogenic to humans; **Group 2B** - possibly carcinogenic to humans; **Group 3** - not classifiable as to carcinogenicity to humans;

² Regionally based assessment of persistent toxic substances, Global Report 2003, UNEP

Detailed possible effects of POPs on human health are shown on Table 44.

Table 44 Possible POPs effects on human health

POPs	Human health effects of POPs
Dioxins/Furans	<p>Dioxins/Furans 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, depression of the immune system, and endocrine and nervous system abnormalities.</p> <p>2,3,7,8-TCDD is a potent teratogenic and fetotoxic chemical in animals and a potent promoter in rat liver carcinogenesis. TCDD also causes cancers of the liver and other organs in animals. The most sensitive groups are fetus and neonatal infants.</p>
PCBs	<p>PCBs may cause: a skin condition called chloracne, which produces pustules, blackheads and cysts; liver and thyroid gland damage, skin and eye changes, immunotoxicity, neurobehavioral deviations, reduced body mass of the newly born, reprotoxicity and carcinogenity. PCBs have also been classified as endocrine disruptors in an intact organism.</p>
HCB	<p>HCB effects on human health are associated with: alterations in liver enzyme activities and liver and thyroid gland damage, neurobehavioral deviations, depression of the immune system, and endocrine and nervous system abnormalities, reduced body mass of the newly born and reprotoxicity and carcinogenity. HCB can produce skin eruptions and colour changes HCB is known to cause liver disease in humans (porphyria cutanea tarda) and cancer of the liver, kidneys and thyroid.</p>

Figure 17 shows the potential effects on human health of dioxins, furans, polychlorinated biphenyls (PCBs) and Hexachlorbenzene (HCB).

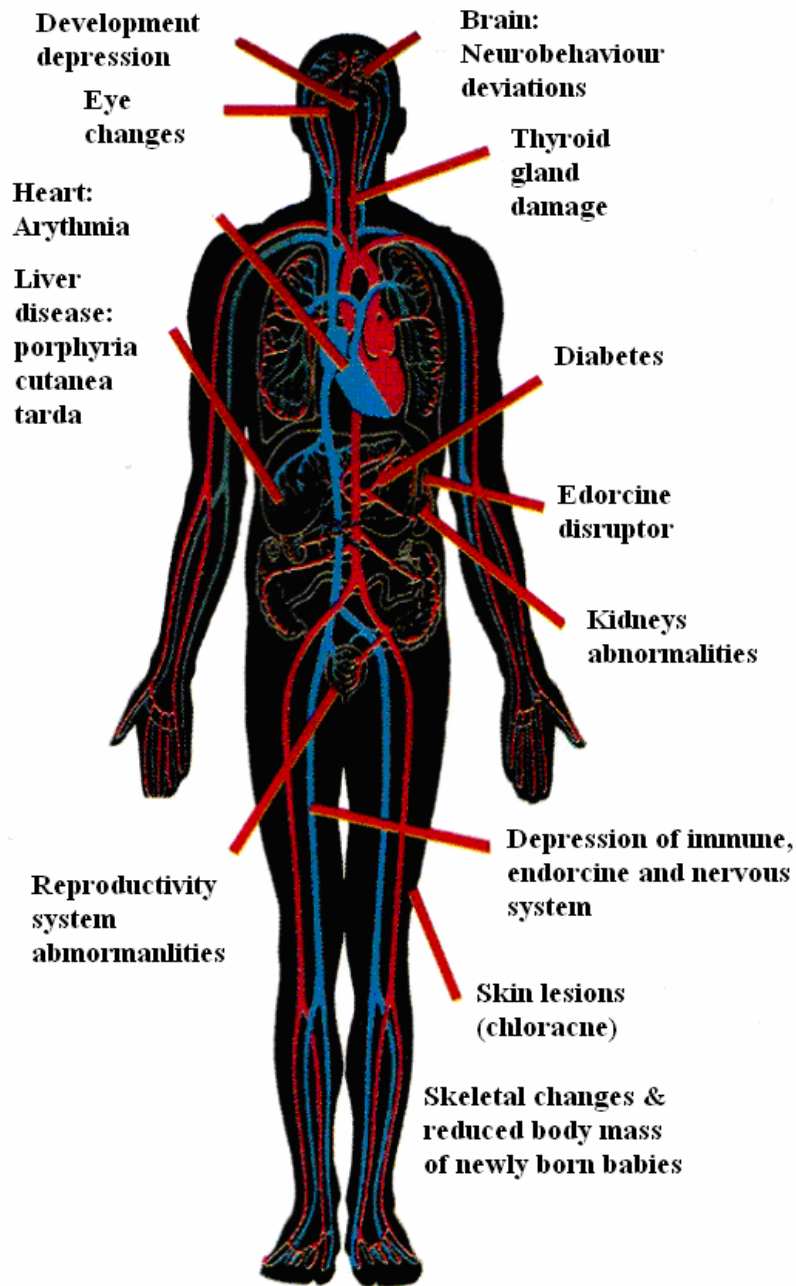


Figure 17 Potential effects on human health of Dioxins, Furans, PCBs and HCB.

- ✓ The PCDDs/PCDFs, PCBs and HCB source category inventory and Environment Pollution assessment give reason to assume that hot spots around industrial and energy generation and transformation sources and landfills for disposal of industrial and municipal waste.
- ✓ No data exists for the level of environment pollution from industrial accidents, forest fires and uncontrolled stubble-fields burning as a source of Dioxin/Furans”
- ✓ No data from health and epidemiological studies of general population exposure to dioxins and furans have been published. No biological monitoring of risk target groups of population had been performed.
- ✓ From the assessment of occupational and environmental pollution with PCBs in Bulgaria it could be suggested that a health risk exists within the regions of thermal electric power stations using coal and mazut, around transformers and capacitors and badly maintained electrical PCBs equipment, near to illegal depot for municipal waste.
- ✓ In Bulgaria no studies has been carried out on the levels of PCBs in human body for target groups of workers and risk groups of general population as well as negative health effects assessment on target organs and systems.
- ✓ No data for acute and chronic intoxications with PCDDs/Fs, PCBs and HCB are available.

Conclusions:

- ❖ One of the lowest levels of PCBs and PCDDs/PCDFs in breast milk has been found in Bulgaria for the period 2001 – 2002 within the European countries.
- ❖ No studies have been carried out in the country for the levels of PCDDs/PCDFs, PCBs and HCB in serum and adipose tissue as well as for HCB levels in breast milk.
- ❖ In Bulgaria no health and epidemiological studies has been carried out on risk groups of general population for negative health effects of PCDDs/Fs, PCBs and HCB on target organs and systems.
- ❖ No data for acute and chronic intoxications with PCDDs/Fs, PCBs and HCB are available.

6. SUMMARY CONCLUSIONS

6.1. ASSESSMENT OF RELEASES FROM UNINTENTIONAL PRODUCTION OF ANNEX C CHEMICALS (PCDD/PCDF, HCB AND PCBs)

The emissions are calculated in relation with National CORINAIR - 94 methodology, approved by the Minister of Environment and Waters. It was developed by adapting the emission inventory Guide - CORINAIR-94, SNAP-94 for the Bulgarian conditions, taking into account the national specificities concerning the respective activity, technologies and equipment.

6.1.1. National annual POPs emissions – PCDDs/Fs, PCBs and HCB

An increase of Ds/Fs releases has been observed in 2003 by 16,7% of the 2002 emissions. In comparison to base year 1990, the annual emissions of dioxin/furans for 2003 a downward trend of 53,9% or 2,2 times had been observed, following the European trend. According to official data for PCDDs/PCDF emissions in Europe within the period 1990 ÷ 2003, the decrease is 2,7 times (63%).

The annual PCBs emissions for the period 1990-2003 are almost the same.

For the period 1990-2003, the HCB emissions in the atmosphere show a significant downward trend. Compared to the base year 1990, for the HCB emission in 2003, a sharp decrease with 91,7% or 12,1 times has been registered due to the decline of industrial production.

6.1.2. National annual sector POPs emissions by category sources

- ✚ **POPs releases**, generated in Bulgaria in the past 5 years are within the range as follows:
 - ❖ **Dioxins/Furans:** 200 ÷ 255 g I-TEQ/y, and in 2002 have reached 254,9 g I-TEQ/y.
 - ❖ **PCBs:** 212 ÷ 261 kg/y, and for 2003 have reached 260,7 kg.
 - ❖ **HCB:** 38 ÷ 54 kg/y, and for 2003 being 45 kg.
- ✚ For the period 1990-2003 the **POPs emissions** in the atmosphere show lasting downward trend. Compared to the base year 1990, PCDDs/PCDFs and HCB note a sharp decline, respectively with 53,9% or 2,2 times and with 91,7% or 12,1 times. The annual PCBs emissions for the same period are almost the same, which could be explained with upward or downward change of the PCBs emissions formed by various category sources.
- ✚ The registered decline in **PCDDs/Fs** emissions into the atmosphere for 2003 compared to base year 1990 is due mainly to the categories “waste treatment and disposal” – 95%, “combustion processes in industry” – 88%; “industrial processes” - 46% and “road transport and other motor vehicles and machines” – 43%. The lowest decline show category sources “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing” – 25% and “combustion processes in energy generation and transformation” – 23%.
- ✚ The assessment of data show, that 75,9% of **PCDDs/Fs** releases are formed by categories “combustion processes in energy generation and transformation” (48,1%) and “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing”(27,8%), followed by “industrial processes” and “road transport”.

- ✚ The registered decline in **PCBs** emissions into the atmosphere for 2003 compared to base year 1990 is due mainly to the categories “road transport and other motor vehicles and machines” – 54% and “combustion processes in energy generation and transformation”- 18%. **PCBs** emissions from categories “combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing” have increased considerably with 88,8%, which could be explained mainly with the growth in the consumption of wood and coal in household sector during past 5 years.
- ✚ The main sources of **HCB** emissions in air for 2003 are the categories “waste treatment and disposal” and “industrial processes” with lasting downward trend. Compared to base year 1990 a sharp decline of **HCB** emissions with 91% or 11 times is registered for the category “waste treatment and disposal”.
- ✚ The combustion processes are the main source of **PCDDs/Fs** and **PCBs** emissions for 2003.
 - ❖ Thermal electric power stations emit about 48,1% of total annual dioxin/furans emissions, followed by combustion processes in household sector – 27,8%, combustion processes in industry – 13% and road transport and other motor vehicles and machines – 8,2%.
 - ❖ The biggest source of **PCBs** emissions in 2003 are the combustion processes in trading, administrative and household sectors, in agriculture, in agriculture, forestry and fishing, representing 63,1% of total **PCBs** annual sector releases, followed by road transport and other motor vehicles and machines – 18,2% and the combustion processes in energy generation and transformation – 17,7%.
- ✚ The main sources of **HCB** emissions in 2003 are the categories “waste treatment and disposal”-53,4% and “industrial processes” – 46,7%, being for 2003 – 45 kg.

6.1.3. POPs emissions – PCDDs/Fs, PCBs and HCB by districts for

2002

- ✚ The sources of **PCDDs/PCDFs** and **PCBs** emissions in the atmosphere are distributed on the whole territory of the country. 2935 industrial sources generate 0,0001 to 8,29 g of **PCDDs/Fs** annually. 973 industrial sources generate 0,0001 to 3,41 kg of **PCBs** annually.
- ✚ The main sources of **PCDDs/Fs** and **PCBs** emissions from category sources “combustion processes in energy generation and transformation” and “industrial processes” for 2002 are thermal electric power stations and industrial manufacturers.
- ✚ The total **PCDDs/PCDFs**, **PCBs** and **HCB** emissions from category sources “combustion processes in energy generation and transformation” and “industrial processes” for 2002 are as follows: **PCDDs/PCDFs** - 132,67 g, representing 60,1% of annual emissions from all category sources (218,48 g); **PCBs** – 40,56 kg or 16,2% of annual emissions (250,06 kg); **HCB** – 16 kg or 42,1% of annual emissions (38 kg).
- ✚ The largest share of **PCDDs/Fs** emissions for 2002 have been registered in Stara Zagora - 58% followed by Sofia-city – 12,2%, Pernik – 7,9% and Burgas – 6 %. The largest **PCB** emissions have occurred in Sofia-city at 30%, Haskovo area at 30% and Stara Zagora area at 15% .
- ✚ The industrial **HCB** emission sources are metallurgical enterprises concentrated in the areas around Pernik and Sofia city, as 73,1% have been registered in Pernik.

- ✚ **PCDDs/PCDFs** and **HCB** emission values, allocated per capita and unit of area, versus base year 1990 show a lasting downward trend in times, due the decrease in industrial production in Bulgaria after 1990.
- ✚ **PCBs** emissions values, allocated per unit area are almost the same range, while per capita they increase, due probably to the growing consumption of wood and coal in household sector after 1990.

6.1.4. Existing policy

The control and monitoring of transboundary transfer of polluting substances, of the background quality of atmospheric air, and of the impact of atmospheric air pollution on the global processes are conducted by the Ministry of Environment and Water and by the National Statistic Institute.

The direct control of the state and the operation of the sites that are sources of emissions into the atmospheric air and on the emissions of various sources are performed by:

- ❖ The Minister of Environment and Water, the Regional Inspectorates of Environment and Water and the municipal authorities;
- ❖ The authorities of the Ministry of Internal Affairs and of the Ministry of Transport – for motor vehicles.

6.1.5. Emission inventory system in Bulgaria

The involved institutions at national and local (sub-national) levels in Emissions inventory are Ministry of Environment and Water /MEW/ respectively Executive Environment Agency /EEA/ and Regional Environment Inspectorate /REIWs/, and National Institute of Statistics /NSI/ .

Two parallel emission inventory programs are conducted in Bulgaria. The first one covers 150 large point sources and it is conducted by REIWs. The second one covers nearly 2000 point sources and it is conducted by National Institute of Statistics. Both are under the guidance of Ministry of Environment and Waters. The data collected are air pollution control facilities and their efficiency, technological and production data, data for fuels used and fines imposed.

Data from the emission inventory are stored at local and national level. On a national level the Executive Environment Agency is the responsible organization for final preparation of the National air emission inventory and data reporting to the UNECE/CLRTAP (Convention on Long-Range Transboundary Air Pollution).

6.1.6. Existing regulatory framework

The observation of existing national legislation in regard with POPs releases from unintentional production management guarantees the reducing of POPs negative impacts on the environment and human health. The country has transposed the main provisions under Stockholm convention in the Environment Protection Act, the Law on protection from harmful impact of dangerous substances and preparations, Clean Air Act, Water Act, the Law on the protection of soil against pollution, the Law of Health, the Law on Foods, Waste Management Act and their sub-legislative acts.

6.2. MONITORING OF POPs RELEASES

6.2.1. Levels of Dioxins/Furans, PCBs and HCB in air

- ✚ There are no international regulatory provisions for implementing of monitoring for Air quality assessment concerning POPs releases.

6.2.2. Levels of Dioxins/Furans, PCBs and HCB in soil

- ✚ There are no international regulatory provisions for monitoring of PCDD/F in soils.
- ✚ The sum PCBs content in soil is significantly (by a multiple factor) below the levels of concern which allows the assumption that no potential threat exists for pollution of soil with PCBs.
- ✚ There are no HCB polluted soils in Bulgaria.

6.2.3. Levels of Dioxins/Furans, PCBs and HCB in water

- ✚ There are no international regulatory provisions for monitoring of PCDD/F in water.
- ✚ In Bulgaria for 2001 there are no ground water polluted with PCBs. All values were below the ecological threshold and this classifies the ground water as ground water in excellent condition.
- ✚ There is no HCB polluted ground water in Bulgaria for the investigated period. All values were below the minimum detection level in the period 1998 – 2002 and this classifies the ground water as ground water in excellent condition.

6.2.4. Levels of PCDD/Fs, PCBs and HCB in food

- ✚ No presence of any residues from B (3)(a) group organochlorine compounds – PCBs in the tested samples of Live Animals, Fresh Meat, Poultry, Fish, Farmed & Wild Game, Raw Milk, Hen Eggs and Bee Honey in Bulgaria for the Year 2003 has been detected.
- ✚ No investigations for PCDDs/PCDFs and HCB in food had been performed.

6.2.5. Levels in human tissue & Human health effects

- ✚ One of the lowest levels of PCBs and PCDDs/PCDFs in breast milk has been found in Bulgaria for the period 2001 – 2002 within the European countries.
- ✚ No studies have been carried out in the country for the levels of PCDDs/PCDFs, PCBs and HCB in serum and adipose tissue as well as for HCB levels in breast milk.
- ✚ In Bulgaria no health and epidemiological studies has been carried out on risk groups of general population for negative health effects of PCDDs/Fs, PCBs and HCB on target organs and systems.
- ✚ No data for acute and chronic intoxications with PCDDs/Fs, PCBs and HCB are available.



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