International POPs Elimination Project

Hotspot Report

International POPs Elimination Project

Promotion of Active and Efficient Civil Society Participation in Preparation for Implementation of the Stockholm Convention

---

The Spolchemie chlor-alkali and chlorine based chemical production plant in Usti nad Labem (Czech Republic) - a case study for unintentional production of hexachlorobenzene

Jindrich Petrlik
Arnika Association - Toxics and Waste Programme

Czech Republic
January 2006

Arnika Association - Toxics and Waste Programme
Chlumova 17
CZ-130 00 Prague 3, Czech Republic
http://english.arnika.org, e-mail: toxic@arnika.org

About the International POPs Elimination Project

On May 1, 2004, the International POPs Elimination Network (IPEN http://www.ipen.org) began a global NGO project called the International POPs Elimination Project (IPEP) in partnership with the United Nations Industrial Development Organization (UNIDO) and the United Nations Environment Program (UNEP). The Global Environment Facility (GEF) provided core funding for the project.

IPEP has three principal objectives:

- Encourage and enable NGOs in 40 developing and transitional countries to engage in activities that provide concrete and immediate contributions to country efforts in preparing for the implementation of the Stockholm Convention;

- Enhance the skills and knowledge of NGOs to help build their capacity as effective stakeholders in the Convention implementation process;

- Help establish regional and national NGO coordination and capacity in all regions of the world in support of longer term efforts to achieve chemical safety.

IPEP will support preparation of reports on country situation, hotspots, policy briefs, and regional activities. Three principal types of activities will be supported by IPEP: participation in the National Implementation Plan, training and awareness workshops, and public information and awareness campaigns.

For more information, please see http://www.ipen.org

IPEN gratefully acknowledges the financial support of the Global Environment Facility, Swiss Agency for Development and Cooperation, Swiss Agency for the Environment Forests and Landscape, the Canada POPs Fund, and the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM).

This report is available in the following languages: English

The Spolchemie chlor-alkali and chlorine based chemical production plant in Usti nad Labem (Czech Republic) - a case study for unintentional production of hexachlorobenzene

Hexachlorobenzene

Hexachlorobenzene (HCB) was originally introduced in 1940's as a seed-dressing for cereal crops to prevent fungal disease. HCB is used as fungicide, disinfectant, and as a starting or intermediate raw material during the production of certain chemicals (e.g. pentachlorophenol, and some chlorinated aromatic compounds). As an industrial chemical, it was used, for example, in production of pyrotechnic products, synthetic rubber and aluminum. HCB is also produced as an unintentional by-product of combustion processes involving chlorinated compounds (for example, during waste incineration or in metallurgy) and as a by-product in the manufacture of certain chlorinated pesticides (such as lindane) and industrial chemicals (for example, in chlorine chemistry or during chlorine bleaching of pulp). In this latter group are chlorinated solvents, such as carbon tetrachloride, perchloroethylene, trichloroethylene and chlorinated benzenes.[a]

Barber, J. L. et al. 20051 focused on HCB's fate in the environment:

"Hexachlorobenzene (HCB) is considered here as a 'model persistent organic pollutant.' Data on its sources, emissions, environmental levels and distributions and trends are compiled and used to assess its fate and behaviour in the global environment. Consideration is given as to the extent to which it has undergone repeated air-surface exchange or 'hopping' to become globally dispersed, the balance between primary and secondary sources in maintaining ambient levels, and its ultimate sinks in the environment. Global production exceeded 100,000 tonnes and primary emissions to atmosphere probably peaked in the 1970s. There has been a consistent downward trend in the environment over the past 20 years. Temporal trends of HCB in the environment vary, dependent on time period measured, media studied and study location, but the average half-life from all the studies is approximately 9 years. Estimates are made of the contemporary burden in the environment; these range between 10,000 and 26,000 tonnes and are dominated by the loadings in treated and background soils, sediments and oceans. Estimates of the trends of HCB emissions from treated soils are derived. At its peak, the amount of HCB emitted from soil to air may have been in the hundreds to thousands of tonnes per year, which would have made it a significant source of HCB to the environment. Whilst the amount of HCB being emitted from contemporary soil is much lower, only a small amount of re-emission of HCB from soil to air is required to maintain contemporary air concentrations under the current primary emission scenario."

[a] "The waste streams from the production of pentachloronitrobenzene (PCNB), chlorothalonil and dacthal are expected to contribute the bulk of HCB released from the pesticide industry (Brooks & Hunt, 1984), although HCB can also be generated as a waste by-product from the production of pentachlorophenol, atrazine, simazine, propazine and maleic hydrazide (Quinlivan et al., 1975; Mumma & Lawless, 1975). These pesticides are also known to contain HCB as an impurity in the final product, usually at levels of less than 1% HCB when appropriate procedures are used for the synthesis and purification stages (Tobin, 1986). When such procedures are not met, the level of HCB could be much higher (e.g., pentachloronitrobenzene has been reported to contain 1.8-11% HCB (Tobin, 1986)). However, owing to many voluntary and regulatory pressures, it is unlikely that such high levels of HCB are present in today's pesticide formulations, but no information is available to substantiate this point." [EHC 195, WHO 1997.]

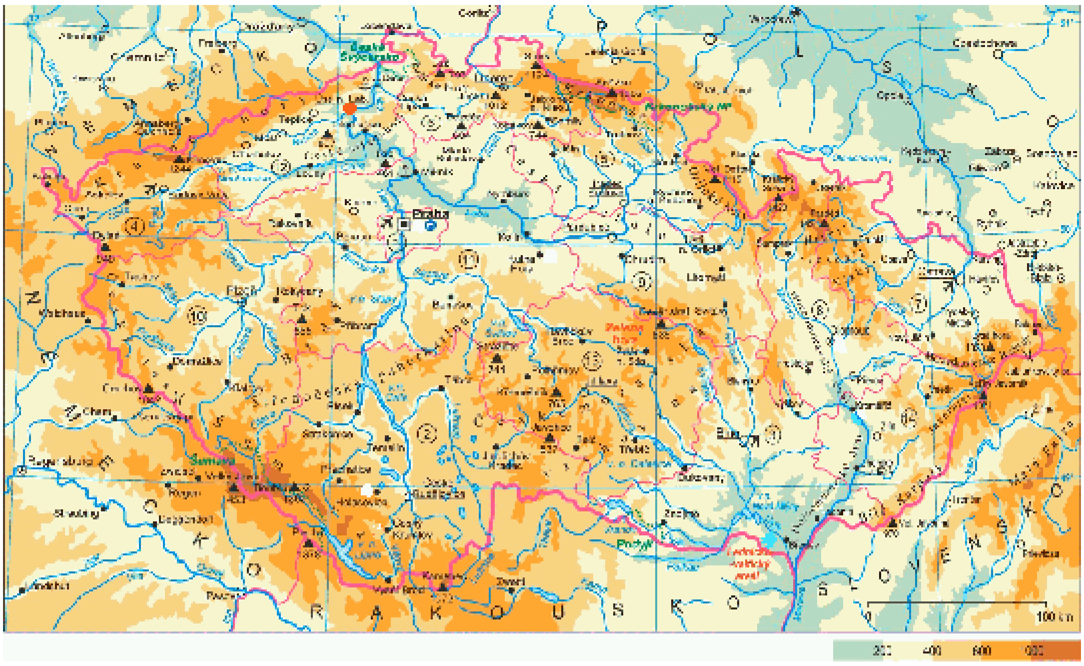
HCB is generated as unintentional by-product also in the Spolchemie Ústí nad Labem chemical plant in the Czech Republic. This plant is focused on the production of synthetic resins, sodium and potassium hydroxide, chlorine, HCl, epichlorohydrin, allylchloride, tetrachloroethylene and other halogenated products.

Basic information about Spolchemie and the city of Ústí nad Labem

The city of Ústí nad Labem, the centre of the region called "Ústecký kraj", has approximately 100 000 inhabitants including the surrounding villages. The city is situated in North Bohemia on the both shores of the rivers Labe and Bílina (see maps at Pictures 1 and 2).

Spolek pro chemickou a hutní výrobu, a.s. Ústí nad Labem, founded in 1856, is situated approximately 500 meters from Ústí nad Labem centre closed to the Bílina river and to the largest Czech river – the Labe (Elbe) (Picture 2). Spolchemie is focused on: production of inorganic compounds, inorganic specialties production, resin production, and organic dye-stuff production.

Picture 1: Ústí nad Labem location in the Czech Republic (red mark)



Spolchemie´s area is placed in the eastern industrial zone between the Bílina river, railway line Ústí nad Labem – Teplice v Čechách (from the south) and the Ovčí vrh ridge (from the north). This industrial area covers aproximatelly 54 hectares. It was always and is still used for production of the chemical substances and chemical products. The plot is between 145 and 160 meters above the sea level and the land falls from the north to the south.

The nearest residential accomodation can be found approximately 150 m to the north from the facility border in Klíšská street.

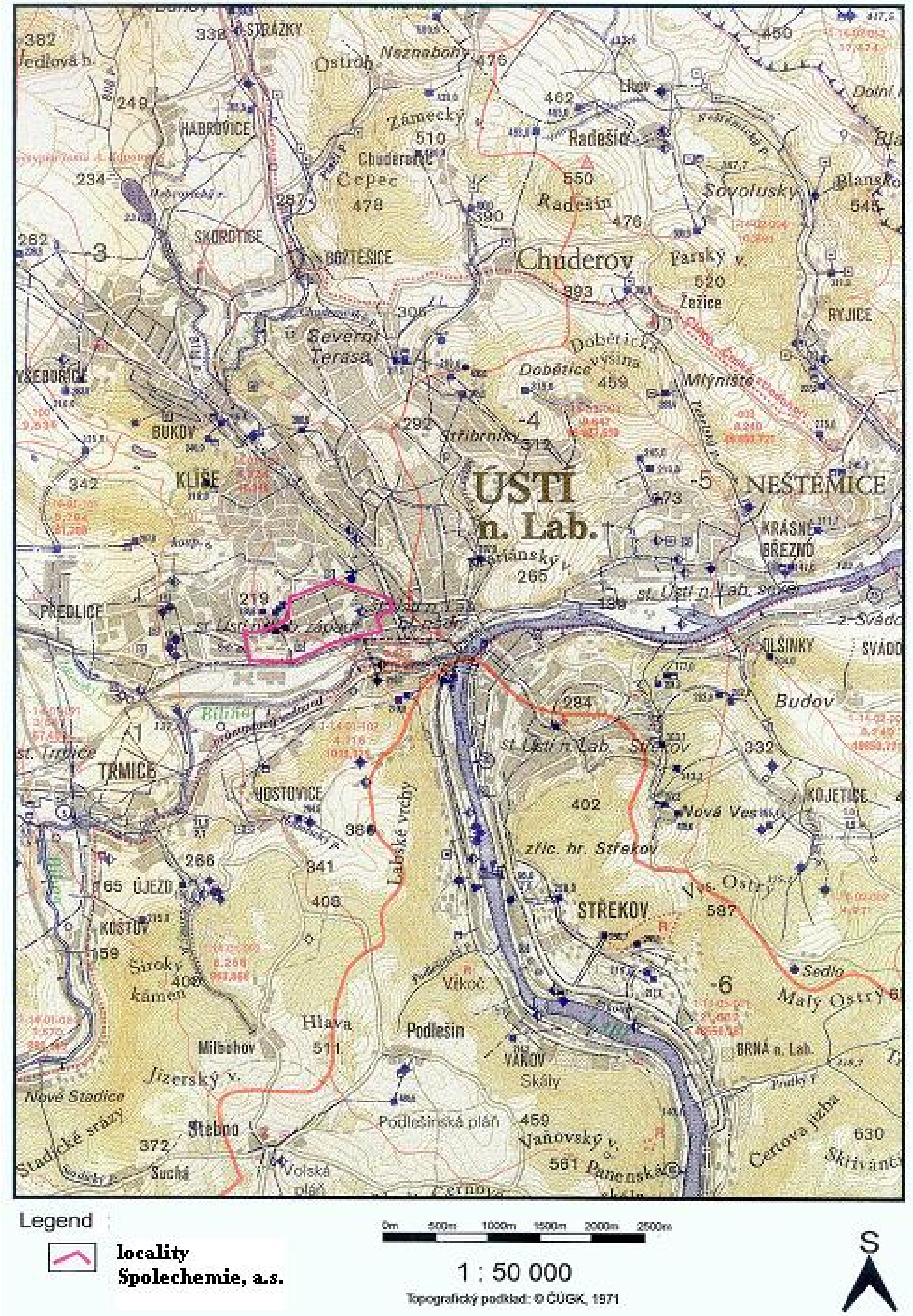
Approximately 500 m south of Spolchemie through the Bílina valley is the boundary of a natural and landscape-protected area called České Středohoří.

The annual chlorine production is shown in Table 1 which gives an indication of the scale of this chemical plant.

Table 1: The Amount of chlorine produced in Spolchemie during years 1999 – 2003 (Source: Czech Ministry of the Environment)

Year	1999	2000	2001	2002	2003
Chlorine produced by Spolchemie (tonnes)	6,982	2,922	1,292	1,293	3,525

Picture 2: Location of Spolchemie (Spolek pro chemickou a hutní výrobu, a.s.) in Ústí nad Labem city (Source: Rýdl J., annex IV_20 Location of Spolek pro chemickou a hutní výrobu, a.s., Application for the Integrated Pollution Prevention and Control permision, 2004)



HCB in wastes produced by Spolchemie

Every year several hundreds tons of HCB are released in wastes as an unintentional by-product. Wastes from the site including HCB were disposed off at an unlined and unmonitored hazardous waste landfill in Chabařovice until 1992. This site is now being monitored and will be capped to reduce the leachate production of the landfill. From 1992 until 1999 HCB was stored in plastic containers with sandy material and covered by layer of mixed ash and cement at Všebořice hazardous waste landfill (see map in Picture 1). Approximately 300 tonnes of HCB was disposed of this way each year. Since 2000, according to National POPs Inventory[2], HCB from Spolchemie has been incinerated in the Megawaste - Ekoterm Prostějov Hazardous Waste Incinerator (HWI). Table 2 shows that this waste incinerator has not met the minimum EU standards for PCDD/Fs emissions to air over that period (0.1 ng I – TEQ/m^3).

Table 2: PCDD/Fs measured in air emissions from Megawaste HWI Prostějov.[3] Data origin from authorized measurements that are done at least two times per year since beginning of 2003 according to Czech legislation requirements.

PCDD/Fs	**2000**	**2001**	**2002**	**05/08/2003**	**30/12/2003**
(ng I-TEQ/m^3)	NA	1.31	NA	0.64	0.32

Spolchemie produced 423.39 tonnes of HCB in wastes in 2004 according to data in the Czech Pollutant Release and Transfer Register. All the wastes containing HCB were recovered or disposed of and it is clear, therefore, that waste incineration is not the only current way of handling with HCB wastes produced by Spolchemie.

Water contamination by HCB

From data about HCB levels it appears that a significant direct contamination pathway of this chemical from the plant, at least historically, has been discharges to water. Table 3 shows data about released HCB in waste water from the plant based on its own reporting.

Table 3: HCB Amount in Spolchemie´s waste water.[4,5]

HCB	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**
(kg/year)	51	39	14	2	2	0.06	7.5

High levels of HCB were found in river sediments. Figures from May 2003 range between 20 - 5,300 µg/kg of dry matter (see also Table 4). Significant levels of HCB were also found in fish caught downstream from the plant in the Labe River with levels ranging from 8.7 - 17.6 ng/g of fresh weight in August 2002 with particularly high levels (up to 91 ng/g) measured in August 2000.

Table 4: Bílina river and tributaries – contamination of river sediments by HCB. Sampling date: May, 27 - 2003. Concentration in ng/g of dry matter. Location of sampling sites is shown in Picture 3.

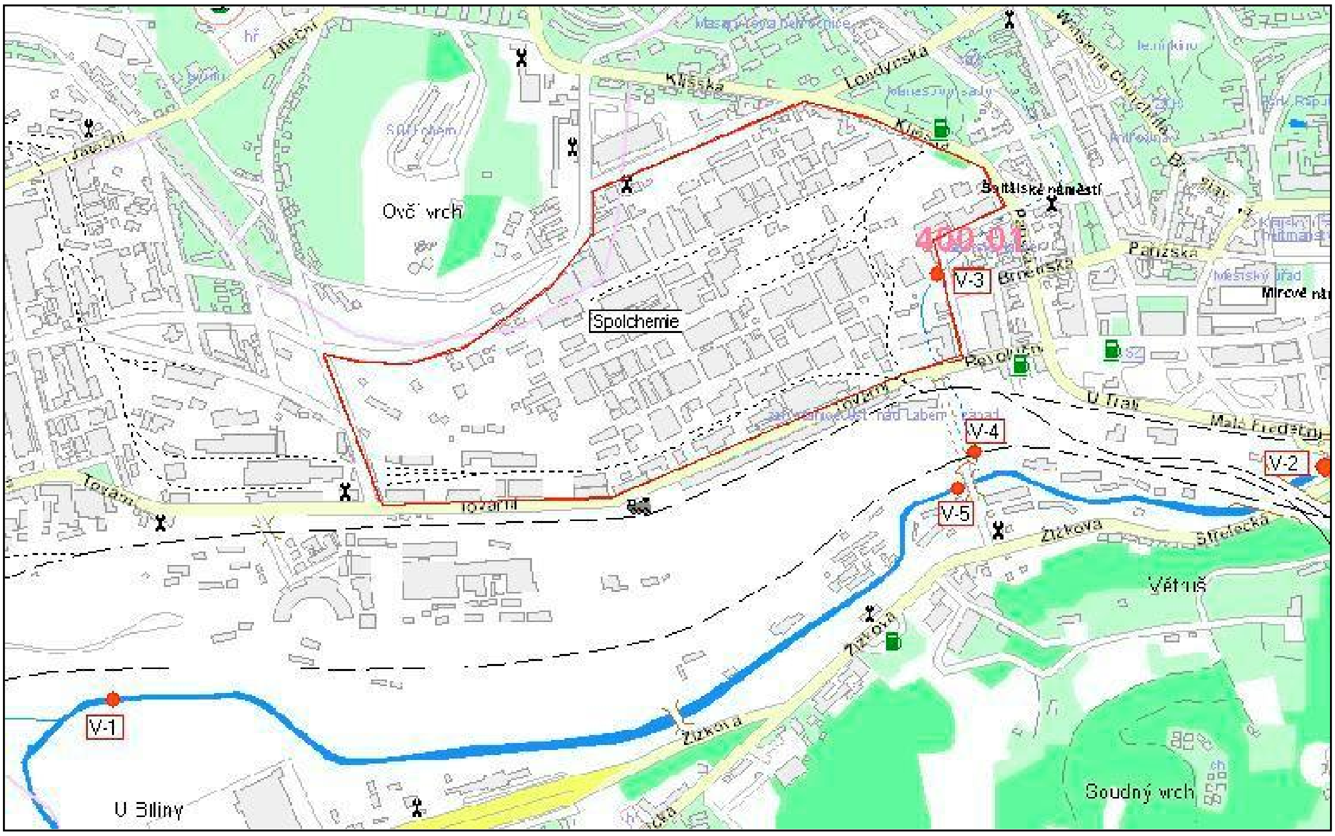
HCB	**V-1**	**V-5**	**V-3**	**V-4**	**V-2**
ng/g of dry matter	20	39.7	50.8	5,300	858

Analysis of river sediments in May 2003 shows clearly that Spolchemie is major source of HCB contamination (see Picture 3 and Table 4). Levels of HCB at sites upstream from the facility (V-1, V-5) both on the river and on the stream (Klíšský potok – V3) along which the contamination enters the river are very much lower than those downstream the facility (V-4 and V-2).

HCB concentrations found in sediments at discharge and downstream from Spolchemie are comparable to River Rhine in 1980-ies. Levels as high as 5100 ng/g dry weight were detected in the Rhine River in Baden-Württemberg, Germany, in 1986. The majority of sediment samples taken from the rivers Rhine and Elbe between 1980 and 1990 contained levels of HCB between 10 and 500 ng/g dry weight, although levels below 1 ng/g dry weight were determined in some other locations.[6]

Higher levels of HCB in sediments were reported in studies conducted near point sources. As much as 280 000 ng HCB/g dry weight was detected in 1985 downstream of the Dow Chemical sewer discharges in the St. Clair River, USA.[7]

Picture 3: Map of Spolchemie area and its surrounding with sites, where sediments for POPs analysis were sampled in May 2003.



Unintentional POPs in the environment of the Ústí nad Labem city and surrounded areas

Data on emissions of dioxins is only available from the waste incinerators in Ústí nad Labem. No data has been published about dioxins releases into the air from the remainder of the chemical plant. The waste incinerator located in the area of Spolchemie released PCDD/Fs into the air from flue gases at levels of 0.011 ng I-TEQ/ m^3 (August 2001) up to 1.42 ng I-TEQ/ m^3 (January 2000) over the 2000 – 2003 time period. Another hazardous waste incinerator located in Trmice (approximately 5 km southwest from the sampling locality) released in flue gases dioxins at concentrations in the range 0.09 - 0.53 ng I-TEQ/m^3.[b]

There is also area of obsolete production buildings highly contaminated by POPs in Spolchemie, that could be a significant source of POPs contamination. This was the amalgam electrolysis area and in 2005 dioxin levels were measured in adjacent soils. Results showed 200 - 700 pg I-TEQ/g of dry matter. Even higher levels, 20 – 3,400 pg I-TEQ /g of dry matter were found in the dust and plasters of the building.

Arnika sampled free range chicken eggs nearby the Spolchemie chemical plant in 2005 for unintentional POPs analysis. The level of HCB observed in eggs from Ústí nad Labem was 35.8 ng/g of fat and was amongst the highest levels observed in free range chicken eggs samples analyzed during IPEN global monitoring project as shown in Table 6 and Picture 4.

Levels of POPs were also measured in the blood serum of Usti nad Labem inhabitants including HCB. Fifty samples taken in 2002 ranged for HCB between 42-1130 ng/g of serum lipids and the median level was 182 ng/g of serum lipids.8

Data for breast milk contamination are shown in Table 5. Maximum observed level of HCB in breast milk in Ústí nad Labem (= 306 ng/g fat) seems to be quite high comparing to other known data (for example from incident in Turkey).[9]

Table 5: Human breast milk contamination by organic compounds in Ústí nad Labem according to sampling and analysis from 2003 (in μg/kg fat).[10]

	HCB	HCH	DDE 44	DDT 44	SDDT	PCB 118	PCB 138	PCB 153	PCB 180	SPCB
A	100	100	100	100	100	100	100	100	100	100
X_a	64	41	321	25	346	15	178	231	180	606
X_g	54	29	304	16	329	8	166	219	170	572
Me	55	36	316	22	343	9	171	228	183	598
$Kv_{0.1}$	28	12	210	1	218	2	104	143	108	372
$Kv_{0.9}$	105	73	452	52	480	34	261	313	244	834
$Kv_{0.95}$	126	87	480	60	516	48	275	352	274	916
H_{max}	306	183	573	110	596	178	375	450	356	1195
H_{min}	14	2	82	1	89	2	43	73	43	180

[b] Dioxin emissions should be measured twice a year according to Czech legislation requirements. Presented data come from these authorised measurements reported to Czech Inspection of the Environment in copies of protocols from authorized laboratory.

Conclusions and Recommendations

This case study shows that HCB is in specific chemical production unintentionally produced in large quantities and that its releases are not fully controlled. It also shows that HCB in wastes is not, in practice, destroyed as required by Article 6 of the Stockholm Convention. This problem was addressed in the Czech National Implementation Plan of the Stockholm Convention approved in December 2005 by saying that it should be solved, but failing to suggest a specific solution.

We would prefer following solutions in accordance with Stockholm Convention requirements:

To avoid unintentional production of HCB as far as possible and, if necessary, substitution of materials and/or technologies that lead to this unintentional production of HCB

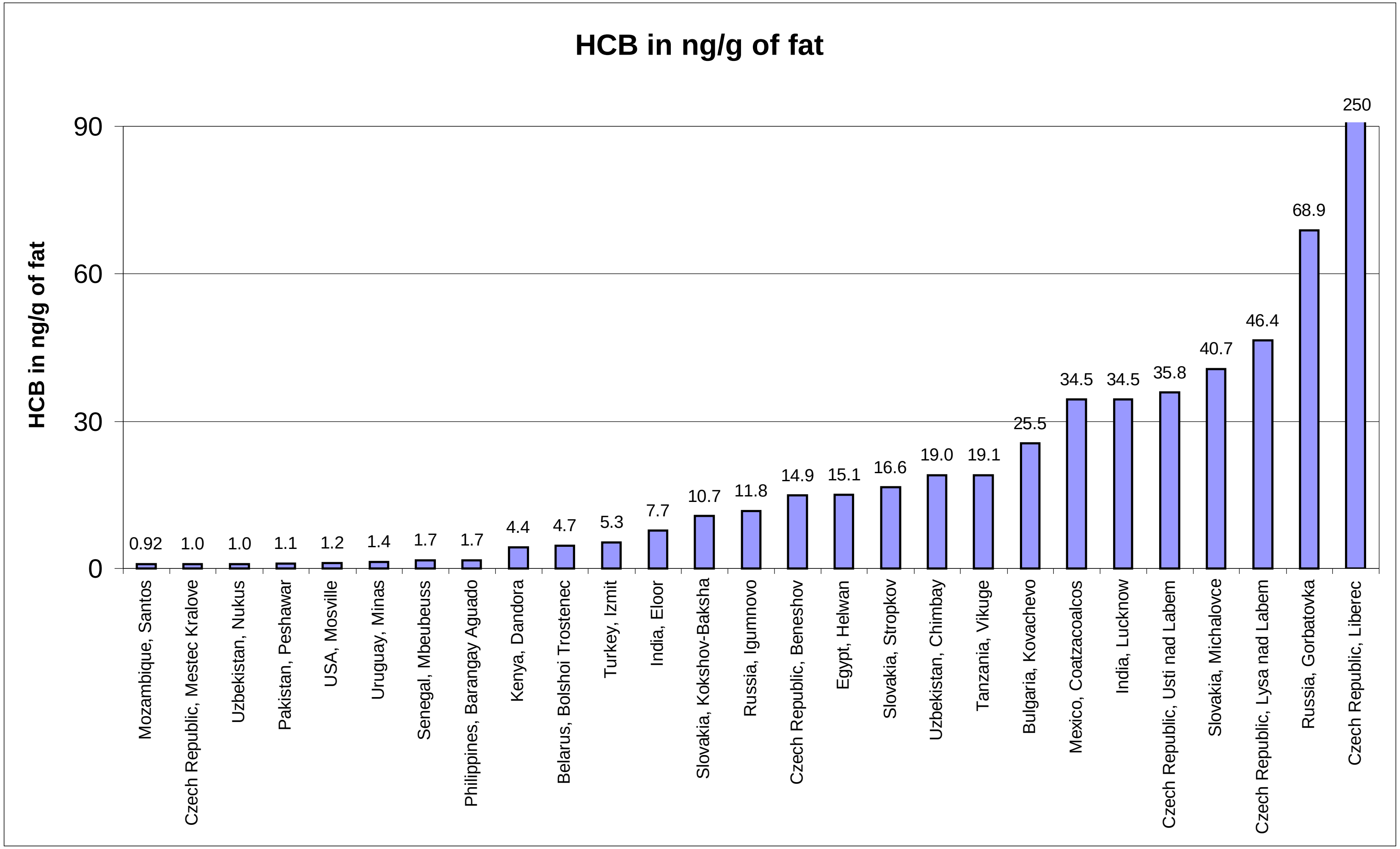
To destroy HCB waste in such way that will not lead to new POPs releases and that will ensure that HCB will be irreversibly destroyed.

Based on the experience with non-combustion technologies this job can be done by some of these technologies that exhibit nearly 100% destruction efficiency for HCB destruction and do not create new unintentional POPs such as dioxins (PCDD/Fs) and/or PCBs.

Table 6: HCB levels found in different free range chicken eggs samples.

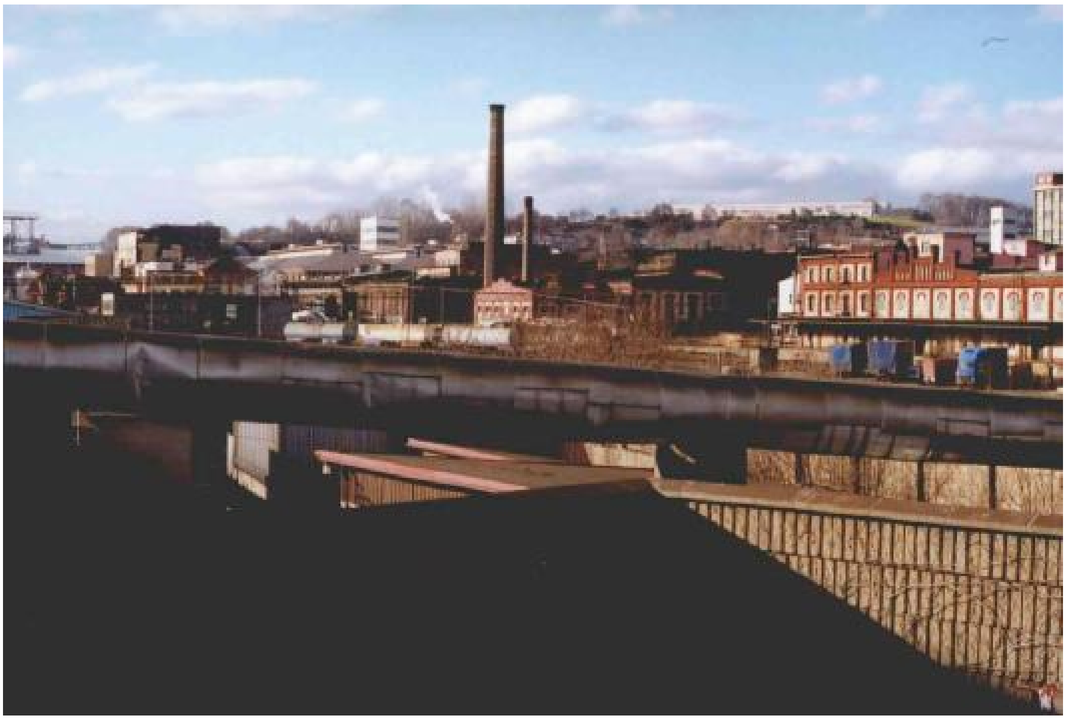
Country	Date/year	Group	Number of measured samples	Measured level in ng/g of fat	Source of information
Mozambique, Santos	2005	free range	6/1 pooled	0.9	Axys Varilab 2005[11]
Czech Republic, Mestec Kralove	2003	free range	3	1.0	SVA CR 2004[12]
Uzbekistan, Nukus	2001	free range	-	1.0	Muntean, N. et al. 2003[13]
Pakistan, Peshawar	2005	free range		1.1	Axys Varilab 2005
USA, Mosville	2005	free range	6/1 pooled	1.2	Axys Varilab 2005
Uruguay, Minas	2005	free range	8/1 pooled	1.4	Axys Varilab 2005
Senegal, Mbeubeuss	2005	free range	6/1 pooled	1.7	Axys Varilab 2005
Philippines, Barangay Aguado	2005	free range		1.7	Axys Varilab 2005
Kenya, Dandora	2004	free range	6/1 pool	4.4	Axys Varilab 2005
Belarus, Bolshoi Trostenec	2005	free range	6/1 pool	4.7	Axys Varilab 2005
Turkey, Izmit	2005	free range	6/1 pooled	5.3	Axys Varilab 2005
India, Eloor	2005	free range	6/1 pooled	7.7	Axys Varilab 2005
Slovakia, Kokshov-Baksha	2005	free range	6/1 pool	10.7	Axys Varilab 2005
Russia, Igumnovo	2005	free range	4/1 pooled	11.8	Axys Varilab 2005
Czech Republic, Beneshov	2004	free range	4/1 pool	14.9	Axys Varilab 2004
Egypt, Helwan	2005	free range	6/1 pooled	15.1	Axys Varilab 2005
Slovakia, Stropkov	before 1999	free range	1	16.6	Kocan, A. et al. 1999[14]
Uzbekistan, Chimbay	2001	free range	-	19.0	Muntean, N. et al. 2003
Tanzania, Vikuge	2005	free range	6/1 pool	19.1	Axys Varilab 2005
Bulgaria, Kovachevo	2005	free range	6/1 pooled	25.5	Axys Varilab 2005
Mexico, Coatzacoalcos	2005	free range	6/1 pooled	34.5	Axys Varilab 2005
India, Lucknow	2005	free range	4/1 pooled	34.5	Axys Varilab 2005
Czech Republic, Usti nad Labem	2005	free range	6/1 pool	35.8	Axys Varilab 2005
Slovakia, Michalovce	before 1999	free range	1	40.7	Kocan, A. et al. 1999
Czech Republic, Lysa nad Labem	2004	free range	1	46.4	Axys Varilab 2005
Russia, Gorbatovka	2005	free range	4/1 pooled	68.9	Axys Varilab 2005
Czech Republic, Liberec	2005	free range	3/1 pool	250.0	Axys Varilab 2005

Picture 4: Graph compars levels of HCB in different free range chicken eggs samples according to data in Table 6.



Annex 1: Photos

General view at Spolchemie chemical plant. Photo by: Hana Kuncova.



Another general view at Spolchemie chemical plant. Photo by: Hana Kuncova.

View at typical quiet urban area, where eggs were sampled. Chimney of hazardous waste incinerator and heat and power plant at Trmice (approx. 5 km far) is visible at picture. Photo by: Hana Kuncova.

References:

[1] Barber, J.L., et al., Hexachlorobenzene in the global environment: emissions, levels, distribution, trends and processes. Sci Total Environ, 2005. 349(1-3): p. 1-44.

[2] Holoubek, I. (koordinátor, projekt manager), Adamec, V., Bartoš, M., Černá, M., Čupr, P., Bláha, K., Demnerová, K., Drápal, J., Hajšlová, J., Holoubková, I., Jech, L., Klánová, J., Kocourek, V., Kohoutek, J., Kužílek, V., Machálek, P., Matějů, V., Matoušek, J., Matoušek, M., Mejstřík, V., Novák, J., Ocelka, T., Pekárek, V., Petira, K. Provazník, O., Punčochář, M., Rieder, M., Ruprich, J., Sáňka, M., Tomaniová, M., Vácha, R., Volka, K., Zbíral, J. 2003/2005: Úvodní národní inventura persistentních organických polutantů v České republice. Projekt GF/CEH/01/003: ENABLING ACTIVITIES TO FACILITATE EARLY ACTION ON THE IMPLEMENTATION OF THE STOCKHOLM CONVENTION ON PERSISTENT ORGANIC POLLUTANTS (POPs) IN THE CZECH REPUBLIC. TOCOEN, s.r.o., Brno. RECETOX - TOCOEN & Associates, TOCOEN REPORT No. 249, Brno, August 2003. Version 2003, upgraded 2005. Chapter 4. Hot spots, dumpsites and contaminated sites.

[3] Protocols about measurments from authorized laboratories obtained from the Czech Inspection for Environment.

[4] Kuncova, H. 2005: Chlor-Alkali Plant Spolek pro chemickou a hutní výrobu, a.s., Ústí nad Labem. International POPs Elimination Project (IPEP) Hot Spot Report. Arnika, Prague 2005.

[5] MoE of the Czech Republic 2005: http://www.irz.cz, data released in PRTR based on companies reports.

[6] BUA 1994: Hexachlorobenzene. Stuttgart, S. Hirzel Wissenschaftliche Verlagsgesellschaft, 257 pp (BUA Report 119). BUA (German Chemical Society-Advisory Committee on Existing Chemicals of Environmental Relevance)

[7] Oliver, B. G., Pugsley, C. W. 1986: Chlorinated contaminants in St. Clair River sediments. Water Pollut Res J Can, 21: 368-379.

[8] Černá, M., Šmíd, J., Malý, M., Brabec, M., Kratěnová, J., Žejglicová, K. 2003: Zpráva o výsledcích studie expozice a zátěže populace v okolí Spolany Neratovice chlorovaným pesticidům, polychlorovaným bifenylům, dioxinům a rtuti. SZÚ, 15. 12. 2003

[9] IPCS 1997: Hexachlorobenzene. ENVIRONMENTAL HEALTH CRITERIA 195. http://www.inchem.org/documents/ehc/ehc/ehc195.htm

[10] SZÚ (State Health Institute) 2005: Data o zdraví ve vztahu k životnímu prostředí - výsledky Systému monitorování zdravotního stavu české populace ve vztahu k životnímu prostředí. Státní zdravotní ústav Praha - Centrum hygieny životního prostředí. Údaje za rok 2003 na http://www.szu.cz/chzp/data_zdravi/. (Czech population monitoring for 2003, data available at http://www.szu.cz/chzp/data_zdravi/).

[11] Axys Varilab CZ 2005: Reports No. 618/1-10 on PCDD/Fs, PCBs and OCPs determinations of samples No. 4443-4450, 5769-5779, 5781-5787, 5783B, 5802 and 5808 issued in March 2005 in Vrané nad Vltavou.

[12] SVA CR (State Veterinary Administration of the Czech Republic) 2004: Chart with results of regular monitoring in Middle Bohemian region. Document reached by Arnika upon request for information.

[13] Muntean, N., Jermini, M., Small, I., Falzon, D., Peter Fuerst, P., Migliorati, G., Scortichini,G., Forti, A. F., Anklam, E., von Holst, C., Niyazmatov, B., Bahkridinov, S., Aertgeerts, R., Bertollini, R., Tirado, C., Kolb, A. 2003: Assessment of Dietary Exposure to Some Persistent Organic Pollutants in the Republic of Karakalpakstan of Uzbekistan. Vol. 111, No 10, August 2003, Environmental Health Perspectives, 1306-1311.

[14] Kočan, A., Jursa, S., Petrík, J., Drobná, B., Chovancová, J., Suchánek, P. 1999: Stav kontaminácie poživatín polychlórovanými bifenylmi v zaťaženej oblasti okresu Michalovce a porovnávacej oblasti okresu Stropkov. In: Cudzorodé látky v poživatinách, 10. - 12. máj 1999, Tatranská Štrba, pp. 31 - 32.