Swiss Agency for Development and Cooperation SDC
Swiss Agency for the Environment, Forests and Landscape SAEFL

International POPs Elimination Project

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

---

Assessment of Contamination of Chicken Eggs by Some POPs in Different Regions of Russia

Boris Revich
Environment – Risk - Health

Russian Federation
March 2006

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, the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM), Mitchell Kapor Foundation, Sigrid Rausing Trust, New York Community Trust and others.

The views expressed in this report are those of the authors and not necessarily the views of the institutions providing management and/or financial support.

This report is available in the following languages: English

Special Terms, Abbreviations and Acronyms:

EPA	Environmental Protection Agency (USA)
I-TEQ	International Toxicity Equivalent
IUPAC	International Union of Pure and Applied Chemistry
TEQ_{xx}	Toxicity Equivalent (dioxin equivalent, DE). The subscript indicates a system of measurement
UNEP	United Nation Environmental Program
WHO	World Health Organization
GLC	Gas-liquid chromatography
SSS	Standard state samples
HCB	Hexachlorobenzene
HCCH	Hexachlorocyclohexane
o,p'-DDE	or 2,4'-DDE - 1,1-dichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethylene
p,p'-DE	or 4,4' DDE - 1,1-dichloro-2,2-bis(p-chlorophelyl) ethylene
o,p'- DDT	or 2,4'-DDT - 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)-ethane
p,p'-DDT	or 4,4'-DDT - 1,1,1-trichloro-2,2-bis-(p-chlorophenyl)-ethane
TEF	Toxic equivalency factor
TEQ	Toxic equivalent
MS	Mass spectrometry
WIP	Waste incineration plant
TSIL	Tentatively safe impact level
TSC	Tentatively safe concentration
PAH	Polycyclic aromatic hydrocarbons
PVC	Polyvinylchloride
MAC	Maximal allowed concentration
PCB	Polychlorinated biphenyls
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
POPs	Persistent organic pollutants
CMS	Chromatography with mass spectroscopic detection
mg	milligram ($1mg = 10^{-3}$ g)
µg	microgram ($1\ \mu g = 10^{-6}$ g)
ng	nanogram ($1ng = 10^{-9}$ g)
pg	picogram ($1pg = 10^{-12}$ g)

Prefixes, specifying numbers of chlorine atoms in PCDD, PCDF and PCB molecules.

T	tetra-
Pe	penta-
Hx	hexa-
Hp	hepta-
O	octa-

Assessment of Contamination of Chicken Eggs by Some POPs in Different Regions of Russia

Introduction

Persistent polychlorinated organic chemicals, such as DDT, Lindane, hexachlorobenzene and polychlorinated biphenyls (PCBs) were produced and used in Russia for a long time. These chemicals mainly enter a human body with food products, particularly with fat-containing ones (eggs, butter, fatty meat or fish). Particularly heavily exposed population groups incorporate local residents in areas nearby pollution sources, who consume local food produced at contaminated land areas. For example, Novomoskovskiy Chemical Plant in Tula Oblast (Chapaevsk) produced PCB-based liquids (Sovol, Sovtol) for more than 30 years in addition to different organochlorine pesticides (hexachlorocyclohexane, hexachlorobenzene), The State Environmental Assessment categorised the city as an environmentally affected area in terms of POPs contamination. At the agricultural South in Saratov Oblast, pesticides were intensively applied, including DDT. Until recently, most toxic pesticides were broadly applied by state-run agricultural facilities and by private gardeners as well. Official statistical reports suggest illusory safety, as no pollution hot spots have been identified where local residents are the most heavily exposed. In small settlements, local residents consume locally produced food, including chicken eggs.

There is almost no information on levels of different PCB congeners and Lindane in food products, including eggs of free range chickens.

In the framework of this project, we measured polychlorinated biphenyls (dioxin-like and indicative ones), DDT and its metabolites, as well as hexachlorocyclohexane and hexachlorobenzene (in the majority of samples) in eggs. In terms of health impacts, PCBs may be considered as the most significant pollutants of the above group.

Polychlorinated biphenyls belong to the group of aromatic compounds. They consist of two benzene rings, connected by a single C-C bond and may contain from one to ten chlorine atoms. Overall, there are 209 individual PCB congeners. For easy identification, every individual congener has its individual IUPAC code. PCBs have some unique physical and chemical properties: high thermophysical and electric insulation parameters, high heat resistance, resistance to acids and alkalis, fire resistance, high solubility in oil and organic solvents, high solubility in resins and high adhesive capacity [Zanaveskin, Averianov, 1998]. Such properties determined their broad application as dielectric liquids in transformers and capacitors, as hydraulic liquids, coolants and cutting oils, components of paints and glues, plasticizers and fillers in plastics, fire retardants, and solvents.

Unique technical properties, a large scale production, substantial volatility, solubility and extreme chemical persistence resulted in global-scale PCB pollution. As it often happens, the hazards of PCBs were underestimated for a long time. Their real hazardous properties were realised only after introduction of bans on their production in many countries. Similarly to other polychlorinated aromatic compounds, the synthesis of PCBs is associated with generation of polychlorinated dibenzo-p-dioxins and dibenzofurans - the most toxic chemicals known. As if it were not enough, in 1997, the World Health Organisation classified 12 PCB congeners as dioxin-like compounds in terms of their health impacts. The scale of the potential health threat may be illustrated by a simple example. According to estimates of EPA experts, 1 kg of Arochlor 1254 (the most commonly used PCBs mixture) has the toxic equivalency of 150 mg TEQ. If we account for the overall global production of PCBs (1-2 million tons), their overall toxicity will reach tens of tons TEQ. For comparison, in the course of the Vietnam War, 50 - 150 kg of dioxins were sprayed over the jungle as micro-contaminants in defoliants. Industrialised countries spend millions of dollars to reduce annual emissions of PCDDs/PCDFs in the range of kilograms of TEQ while global PCB production yields TEQ levels orders of magnitude higher.

Due to the diverse and large scale applications of PCBs, in practice, the contribution of dioxin-like PCBs to summary toxic equivalents of products often is similar to the contribution of PCDDs/PCDFs or event exceeds it. PCBs are detected everywhere. In addition to DDT and its metabolites they belong to most often detected substances from the "dirty dozen" of the Stockholm Convention.

PCBs are rated as the fifth in the ranking of the most dangerous chemicals for health of the US residents, after arsenic, lead, mercury and vinyl chloride. The most hazardous substance from the group of PCDDs/PCDFs is ranked only 73rd in the range (http://www.atsdr.cdc.gov/clist.html). Such toxicity ratings are based on assessment of toxicity of chemicals and probability of population exposure. Nevertheless, now there are no official standards for tolerable limits of dioxin-like PCBs in food, and that hinders development of measures to control and reduce human PCBs intake.

High environmental persistence of PCBs and lack of efficient detoxication mechanisms makes food quality control one of the main instruments for protection of human health. Accounting for the fact, that fish and fish-oil may contain the highest levels of PCBs, they may be present in fish-meal and poultry feedstuffs. Such feeding mixtures could hardly cause acute poisoning, as it happened in Belgium, but contaminated chicken meat and eggs may become a substantial source of human intake of dioxin-like substances.

When PCBs enter biological food chains, shares of low-chlorine content components gradually decrease due to their lower resistance to biotransformation. As a result, the relative shares of high-chlorine content PCBs increase.

The range of project objectives incorporates:

- to estimate levels of PCBs, DDT and HCCH (Lindane) in chicken eggs in different regions of Russia,
- to inform local residents, authorities and managers of different facilities on contamination of local food products by the above chemicals,
- to enhance public roles in addressing problems of identification, storage and elimination of POPs stockpiles and mitigation of their health impacts

The project meets IPEP aims and objectives, pertaining to identification of pollution hot spots.

1. Methods and the project implementation locations

1.1. Methods

In regions of Russia with already identified or potential presence of POPs pollution, almost no information is available on contamination of local food products in the most problem-prone territories. Compared to information on other environmental media, only minimal information is available on contamination of food products. At the same time, the latter source of human intake of highly toxic POPs is the easiest one for regulation, provided sufficient public awareness of health hazards of POPs. As an example we may refer to the results of Serpukhov project, where adverse health impacts of PCBs had been proven and measures were taken to reduce human intake of these substances (meetings of local residents, meetings in schools and kindergartens, publication in local media, TV and radio programs, etc.).

Prior to implementation of the project activities, we conducted meetings with all participants of the project and developed methodological recommendations for future work. (See the information letter on methods of sampling, storage and transportation of egg samples in Annex 1). Samples were taken in small private holdings. In order to select private holdings in the most heavily POPs-contaminated territories, we analysed available information on environmental contamination levels, proximity to pollution sources and reclamation activities conducted (see Annex 2). In the course of sampling, a special form was completed, specifying locality parameters and numbers of eggs in a daily diet (see Annex 3). Every sampled egg was marked by territorial codes.

Accounting for the rather high costs of analytical measurements and limited budget of the project we decided to identify dioxin-like PCB congeners (WHO-PCBs), as well as DDT and DDE isomers in every individual sample. Dioxin-like PCBs are present in all technical PCBs mixtures, however, they are considered as comparatively new study objects. However, even according to comparatively limited published data in foreign periodicals and information of a few Russian research studies [Chernyak Y et al., 2004, Shelepchikov A. et al., 2004], in many cases, the health hazards of these substances may exceed health hazards of dioxins (polychlorinated dibenzo-p-dioxins and dibenzofurans). In addition to WHO-PCBs and DDT/DDE, we registered territory-specific substances - Lindane, hexachlorobenzene and several indicative PCBs. Based on results of this study, we plan to analyse PCDDs/PCDFs in several egg samples, if funding will be available for additional sources.

Analytical measurements were made with application of high resolution chromatography and mass spectrometry. The method provides high sensitivity and maximal reliability of analytical data. See a brief description of the analytical methods in Annex 4.

1.2. Study locations

1.2.1. Novomoskovsk (Tula Oblast, 134,000 residents).

In Novomoskovsk, "Orgsintez" plant produced large amounts of PCBs from 1939 to late 1995. Results of the inventory of PCBs in Russia, conducted by "Sintez" Association, suggest that, overall, in Russia, at two plants in Novomoskovsk and Dzerzhinsk, about 180 thousand tons of PCBs have been produced (see Table 1).

Table 1 PCBs production (thousand tons) by "Orgsteklo" plant in Dzerzhinsk and "Orgsintez" plant in Novomoskovsk

PCBs	Dzerzhinsk		Novomoskovsk		Total
	Production	Period of time	Production	Period of time	
Sovol	43	1939-1990	10	1972-1993	53
Sovtol	32	1939-1987	25	1972-1990	57
Trichlorobiphenyl	70	1968-1990	-	-	70
Total	145		35		180

A mixture of tetra- and pentachlorobiphenyls was produced under brand name "Sovol". Another product - "Sovtol" - was a mixture of "Sovol" and 10% of trichlorobenzene. Trichlorobiphenyl (TCB) was produced as an individual product. "Sovol" was used as an additive for paints and grease that were sold to different consumers and have been already used. "Sovtol" and TCB were used as dielectric liquids in transformers and capacitors, respectively.

In 1972, the Production Association "Orgsintez" started to produce "Sovol Plasticizer" and "Sovtol-10". The rated capacity of the production line reached 1800 tons/year (including 300 tons/year of "Sovol"). By January 1, 1983, the production output was raised to 2000 tons/year (including 500 tons/year of "Sovol"). The output was increased by 200 tons/year due to process adjustments and production intensification measures. "Sovol Plasticizer" was produced by chlorination of biphenyl to pentachlorobiphenyl and subsequent purification. To produce "Sovtol-10", purified "Sovol" was mixed with trichlorobenzene (9 - 7.5 to 1).

"Sovol Plasticizer" (C12H5Cl5) and "Sovtol-10" are highly soluble in organic solvents and almost insoluble in water. "Sovol Plasticizer" was used as a plasticizer in PVC and nitro-cellulose lacquers (inflammable films), to improve thermal resistance and dielectric parameters of insulating materials, and as antiwear and antigalling additive for lubricating oil. "Sovol Plasticizer" was also used as a component of dielectric liquids for electric installations (e.g. "Sovtol-10").

In 1990, only 2.4 tons of "Sovtol-10" was produced, while in 1991-92, "Sovtol" was not produced due to termination of manufacture of relevant transformers in the country. In 1991-92, only small batches of "Sovol" were produced, while since 1992, its production was cancelled due to lack of market demand.

Chlorine compounds were emitted to air in the course of different technological operations.

Table 2 Sources of releases of chlorine compounds at "Orgsteklo" production facilities

Release sources	Height of the release point (m)	Pollutants	Frequency	Emissions (kg/hour)
Chlorinators	8	Hydrogen chloride	permanent	0.0004
Sovol collectors	16	Hydrogen chloride	permanent	0.0004
Rectification stills	16	Hydrogen chloride	permanent	0.0001
Local ventilation outlets (Sovol and Sovtol discharge points)	15	Sovol	5 hours/day	0.2640
General ventilation outlets	16	Sovol	permanent	

Industrial wastewater with Sovol levels in the range of 1500-3000 mg/l was generated only in the course of equipment washing operations. Until 1986, 0.1 - 0.8 m3/day of the wastewater was discharged without treatment 1-4 times in a month to Shakhtskoye Water Reservoir. Since 1986, the wastewater has been transferred to a facility for pumping to deep geological formations. Information on production waste is shown in Table 3.

Table 3 Waste generation at "Orgsteklo" facility (tons/year)

Waste	1987	1988	1989	1990	1991
Rectification residues of raw Sovol rectification	50.3	135.3	153.2	52.8	25.8
Filtration bentonite, contaminated by Sovol	16.9	-	-	5.3	2.6

Production waste was disposed to an unauthorised industrial waste dump. The dump did not meet sanitary requirements, in 1999 it was closed and now the dump is idle. There is no information on emergency releases to air and the scale of environmental contamination.

The sanitary protection zone of "Orgsteklo" facility covers a distance of 1000 m from the facility site. In 1987, the zone improvement works were completed and local residents were resettled from the zone. Part of Knyaginino village is located in close proximity to the production facility (within the facility's sanitary zone) and some village residents were resettled. In the early 1990s, the sanitary zone of the synthetic surfactants production facility of "Novomoskovskbytkhim" Production Association was established - it covered another part of the village and some other residents of Knyaginino village were also resettled. The remaining villagers found themselves abandoned. The former Ministry of Chemical Industry planned to resettle all residents of the village but these plans have not been implemented. In Knyaginino village, a local shop and a kindergarten were closed; only 50 houses are still used by a few permanent residents and city residents who use them as summer houses. There are no other settlements in close proximity to "Orgsintez" Production Association under impacts of the facility's emissions.

We took six samples of chicken eggs in Knyaginino village and Novomoskowsk-2 town (Zavodskoi district). Novomoskovsk-2 is located at the distance of 1500 - 2500 m from "Orgsteklo" facility's site. There are both residential blocks and small private houses in the town.

The majority of local residents, who provided samples of chicken eggs, regularly consume them. About half of them eat eggs four - six times a week.

In 1994, the EcoToxicology Laboratory of A.N. Severtsov Institute and "Taifun" R&D Association measured PCDDs/Fs and PCBs in soil and breast milk samples in areas nearby "Orgsteklo" facilities. Average levels of dioxins and furans in soil samples varied between 3.0 and 7.0 ng TEQ/kg (i.e. close to the official Russian MAC of 10 ng/kg). In other countries, similar limits for agricultural land are recommended.

Levels of dioxins and furans in cow milk reached 6.3 ng TEQ/kg fat or much higher than in other regions of the country (0.3 - 0.6 ng I-TEQ/kg fat) [Dioxins in Russia, 2001, pp. 74-76]. Limits for dioxin levels in milk and dairy products in Russia are set as 5.2 ng TEQ/kg. According to [Soboleva et al., 1995] PCDDs/PCDFs levels in butter samples taken in the town varied in the range of 4.9 - 53.6 ng I-TEQ/kg fat.

In breast milk samples, the aggregate level of PCDDs/PCDFs reached 9.1 ng I-TEQ/kg fat, or lower than in such cities with chlorine industry facilities as Chapaevsk, Ufa and Usolie-Sibirskoe and close to dioxin levels registered in Volgograd [Dioxins in Russia, 2001, pp. 182-184].

Previous studies of POPs in Novomoskovsk focused predominantly on measurements of dioxins and furans in environmental media, food and breast milk, while PCBs - key pollutants - were ignored. Therefore, in this project we focused on measurements of PCBs.

1.2.2. Chapaevsk (Samara Oblast)

Studies of health impacts of environmental pollution in Chapaevsk (71,000 residents) have been conducted since 1994. From 1967 to 1987, a local chemical plant produced organochlorine pesticides, including hexachlorocyclohexane (HCCH, Lindane), later the plant started production of liquid chlorine, synthetic hydrochloric acid, sodium hypochlorite and other chlorine compounds. These technological processes caused environmental releases of dioxins and HCCH. However, dioxin releases were observed even after decommissioning of the plant in 1987. Now, the plant is almost idle, but its installations, contaminated plant site and industrial waste continue to release pollutants.

Similarly to other smaller cities of Russia, residents of Chapaevsk consume locally-produced food. Owners of private houses (about 18,000 people) cultivate almost all their fruits and vegetables and consume chicken eggs and animal meat, produced by small individual holdings. Besides that, fishing in local ponds near the chemical plant is popular among local residents. Results of a survey of families of boys in Chapaevsk revealed that the majority of them consumed locally produced food: local dairy products (more than 70%), chicken meat/eggs (more than 50%), and fish from local surface water bodies (more than 80%) [Sergeev et al., 2002].

Dioxins were measured in the milk of cows from small holdings. Now, in this study, levels of dioxins in chicken eggs were measured in the city.

Dioxin levels in environmental media varied in the range of 0.001 - 1.13 pg I-TEQ/m3 (0.00001 - 1.76 pg WHO-TEQ/m3). According to measurements conducted in 1994, excess levels of dioxins (relative to the limit of 0.5 pg/m3); in some cases were two - three times higher within 1.5 km of the chlorine plant. In 1998, dioxin levels in air samples, taken at the plant site, reached 16 pg/m3.

According to estimates of "Taifun" R&D Association, as of 1994, in the case of the regularly operating plant, excess levels of dioxins in air could reach 2 MACs or more, within the range of 3 - 4 km from the plant, 7 - 10 days/year. In the period of Hexachlorane[1] production (1962 - 1987) excess dioxin levels could reach 2 - 3 MACs over the whole town area [Revich B. et al. 2001].

Dioxin levels in environmental media

Dioxin contamination of soils in the town developed for more than 30 years. Average dioxin levels in soil samples near the plant reach 141 ng TEQ/kg, decrease to 37 ng/kg at distances of 2-7 km, and further decrease to 4 ng/kg at distances of 7-10 km. In addition to dioxins, soils in all areas of the town are contaminated by organochlorine pesticides. HCCH levels are under limits, while levels of DDT metabolites exceed applicable MACs by 1.4 - 13.4-fold. Accounting for the relatively short half-life of Lindane, we may assume that in the period of HCCH production (1969 - 1987), Lindane levels in soil were much higher.

The chemical plant started production of hexachlorane in 1962. Until 1974, the plant discharged its wastewater after a partial treatment to the Chapaevka River. Now, the river is heavily polluted by HCCH and its metabolites. In the plant waste, specialists of "Taifun" R&D Association identified dioxins (56.3 ng/kg); more than 200 isomers of chlorinated biphenyls with different numbers of chlorine atoms per molecule (tri- to octa-PCBs, up to 3 g/kg); chlorinated naphthalene and its derivatives (up to 20 g/kg); as well as herbicides, banned for application in Russia (1 - 10 g/kg).

Huge amounts of wastes were accumulated in the waste pond of the plant, including chlorophenols, HCCH, chlorobenzenes, dioxins, furans and other toxic chemicals that pose a major threat of groundwater and river contamination in the case of rupture of the pond's bottom.

Dioxins were found in all samples of cow milk, concentrations reached: 2,3,7,8-TCDD - 17.32 pg TEQ/g fat; and 1,2,3,7,8-PeCDD - 61 pg TEQ/g fat. In the majority of milk samples, the following dioxins and furans were identified: 1,2,3,4,7,8-, 1,2,3,6,7,8- and 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HxCDD; 1,2,3,4,6,7,8-, 1,2,3,6,7,8,- 1,2,3,7,8,9 -HxCDF. Levels of other compounds of the group were close to the detection limit.

Concentrations of dioxins and furans in cow milk substantially exceeded applicable limits (5.2 pg TEQ/g fat). Unfortunately, we have no information on dioxin levels in beef, pork, chicken meat and eggs, and local fish in the town (Chapaevsk Environment, 1999). Fruits and vegetables were found to contain 0.002 - 10.6 pg TEQ/kg of polychlorinated dioxins and furans). Cabbages, tomatoes and carrots, cultivated in small holdings within the town area, were most heavily polluted (10.6, 0.48 and 2.0 pg/g, respectively).

[1] Brand name of HCCH

Breast milk

Compared to other Russian cities and other countries, breast milk samples in Chapaevsk (7 composite samples made from 40 individual ones) contain much higher concentrations of the most toxic dioxin congeners: 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HeCDD and octa-CDD. The average level of dioxins was found to reach 42.26 pg WHO-TEQ /g fat. [Revich et al., 2001]. Compared to other Russian cities and other countries, breast milk samples in Chapaevsk contained much higher concentrations of dioxins.

1.2.3 Saratov Oblast

The oblast was selected as a territory with high pesticide loads. In 1982-1987, 2.4 tons of DDT was applied to 5.4 thousand hectares of agricultural land. Samples of chicken eggs were taken in settlements in different parts of the oblast (Velskiy, Marksovskiy and Engelsovskiy districts).

2.0 Levels of DDT, HCCH, HCB and PCBs in chicken eggs

POPs levels are presented in pg/g and pg/g lipids. Codes of PCBs congeners follow the IUPAC system. Toxic equivalency was estimated with use of the system of toxic equivalency factors, proposed by WHO [Van den Berg M., Birnbaum L., Bosveld A.T.C., Brunström B., Cook P., Feeley M., Giesy J.P., Hanberg A., Hasegawa R., Kennedy S.W., Kubiak T., Larsen J.C., Rolaf van Leeuwen F.X., Liem A.K.D., Nolt C., Peterson R.E, Poellinger L., Safe S., Schrenk D., Tillitt D., Tysklind M., Younes M., Wærn F., Zacharewski T. (1998) Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. Environ. Health Perspect. 106, 775-792]. In recent years, the WHO system has been predominantly applied in biological studies (see Table 4).

Table 4 TEFs proposed by the WHO Committee of Experts

Congeners	WHO-TEFs
3,3',4,4'-TCB (77)	0.0001
3,4,4',5-TCB (81)	0.0001
2,3,3',4,4'-PeCB (105)	0.0001
2,3,4,4',5-PeCB (114)	0.0005
2,3',4,4',5-PeCB (118)	0.0001
2',3,4,4',5-PeCB (123)	0.0001
3,3',4,4',5-ReCB (126)	0.1
2,3,3',4,4',5-HxCB (156)	0.0005
2,3,3',4,4',5'-HxCB (157)	0.0005
2,3',4,4',5,5'-HxCB (167)	0.00001
3,3',4,4',5,5'-HxCB (169)	0.01
2,3,3',4,4',5,5'-HpCB (189)	0.0001

2.1 Novomoskovsk.

POPs levels in chicken eggs, sampled in Novomoskovsk and nearby are shown in Table 5 and in Figures 1 and 2. In this case there are substantial differences in level of PCBs and DDT metabolites in close proximity to the former Sovol/Sovtol production facility and relevant POPs levels in chicken eggs, sampled at the distance of 2 km from the plant. The most marked differences (by 5-fold or more) were found for 5 PCB congeners (81, 126, 157, 169 and 189).

Two of these congeners (126 and 169) have high TEFs (0.1 and 0.01, respectively). TEQ levels of PCBs in chicken eggs, collected in close proximity to the plant were almost 5 times higher than those collected 2 km away. Differences in levels of DDT metabolites were less marked, but these levels are also higher in chicken eggs, sampled in close proximity to the plant.

Table 5 Levels of dioxin-like PCBs, DDT and DDE in samples of chicken eggs from Novomoskovsk (Tula Oblast) (pg/g lipids)

Compounds	TEFs	Near the plant n=3	2 km from the plant n=2
PCB-77	0.0001	1 774	4 506
PCB-81	0.0001	674	122
PCB-105	0.0001	389 229	102 004
PCB-114	0.0005	18 355	5 384
PCB-118	0.0001	820 604	219 410
PCB-123	0.0001	15 992	3 551
PCB-126	0.1	899	118
PCB-156	0.0005	116 579	28 523
PCB-157	0.0005	35 338	6 099
PCB-167	0.00001	32 263	9 163
PCB-169	0.01	2 549	460
PCB-189	0.0001	4 913	888.9
WHO-TEQ (PCBs)		324	70
o,p'-DDE		5 837	6 651
p,p'-DDE		2 610 342	2 017 247
o,p'-DDT		680 79	55 567
p,p'-DDT		1 647 497	1 226 308
Sum of DDE and DDT isomers		4 331 756	3 305 773

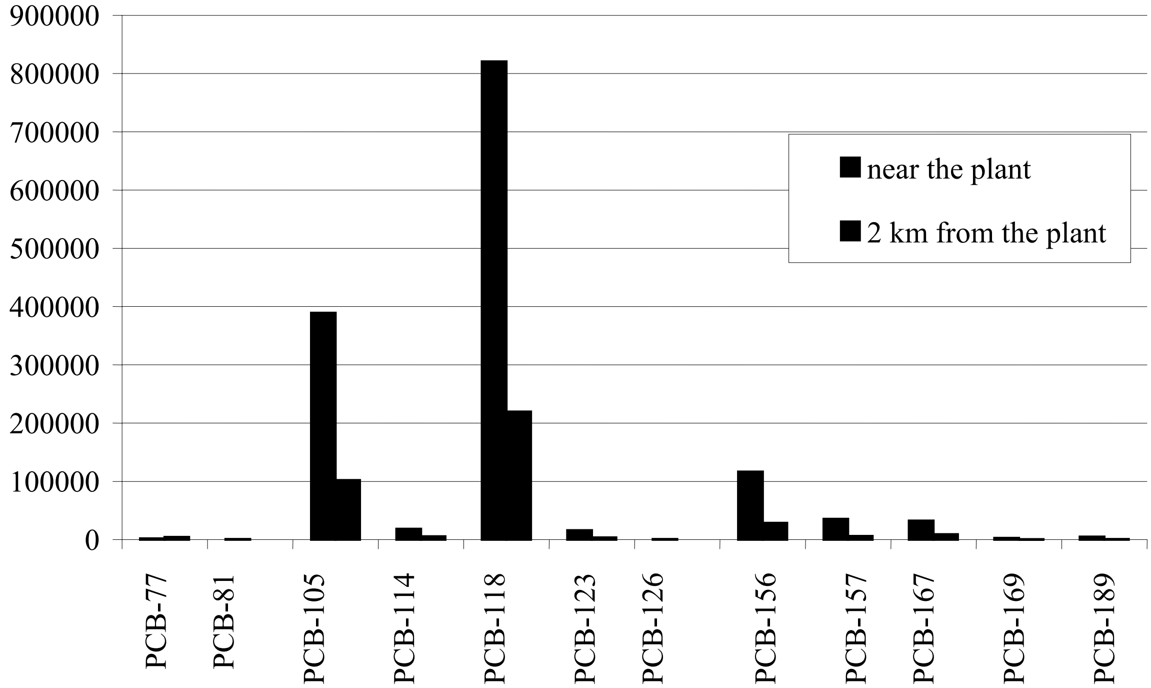

Fig. 1 PCBs levels in chicken eggs (Novomoskovsk), pg/g

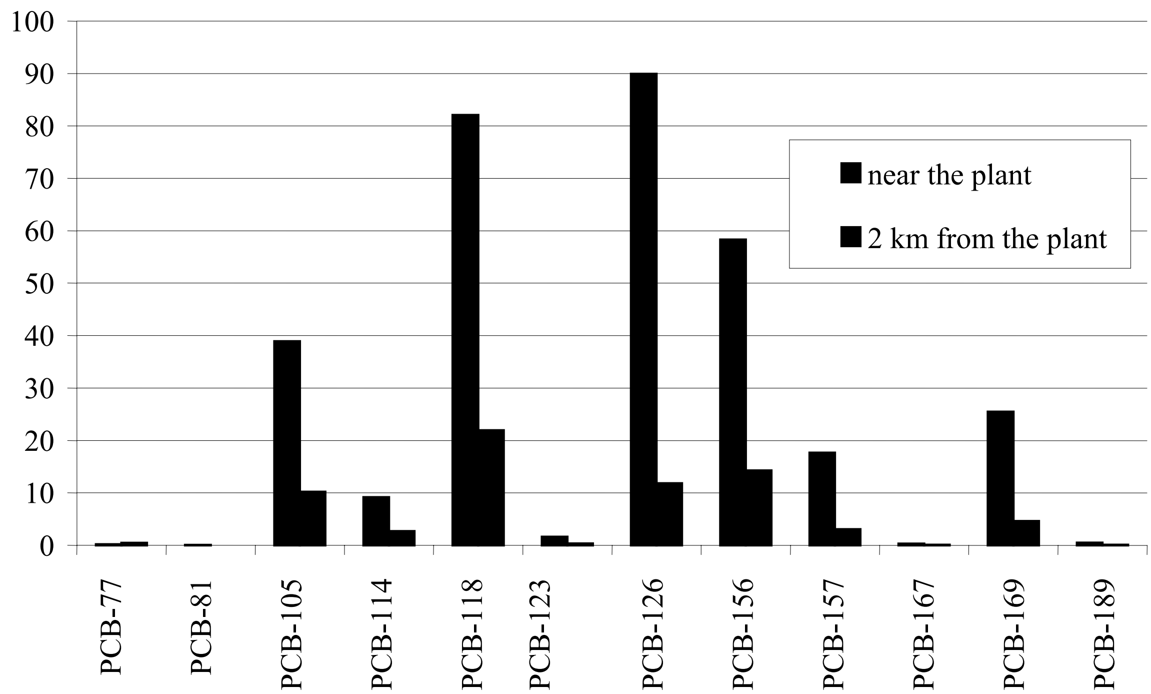

Fig. 2. PCBs levels in chicken eggs (Novomoskovsk), pg WHO-TEQ /g lipids

2.2 Chapaevsk

In the case of Chapaevsk, results of POPs measurements in chicken eggs were grouped to account for different types of chickens (free range vs. poultry facilities) and distances between small holdings and the chemical plant. Levels of almost all POPs in chicken eggs from local small holdings were substantially higher (by 24 – 42-fold for the majority of PCBs) than POPs levels in chicken eggs, bought at local marketplaces - i.e. eggs from poultry facilities from other regions of Russia. Levels of some PCB congeners (81, 126, and 169) were under detection limits. The most substantial differences were found for PCB-189 (177 times higher in small holdings) and PCB-180 (160-fold higher), p,p'-DDE (102-fold higher). Lindane levels in eggs from small holdings in Chapaevsk were 54.2 times higher than eggs from marketplaces and hexachlorobenzene (HCB) levels were 69.6 times higher, (see Table 5, Figures 3 - 6).

Samples of free range chicken eggs from small holdings, located within the city area, may be subdivided into 2 groups depending on distances from the chemical plant - the key source of pollutants (less than 3 km and more than 3 km). Taking into account extremely high POPs levels in one sample from Gubashevo district (the district is located in the centre of the city, at a distance of 7 km from the plant), the data of Table 5 include two data sets for the group of samples, taken in locations at distances over 3 km from the plant. If we exclude the sample with extremely high POPs levels, the summary PCBs toxic equivalents are 3.5 times higher in samples of eggs collected near the plant. In the case of DDT and Lindane, differences between 2 groups are less significant.

It is worth noting that HCB levels were 3.7 times higher in samples of chicken eggs, collected near the plant (earlier, the plant produced HCB).

Families that keep chickens consume chicken eggs 9.9 months/year on an average of 2 - 3 times a week. In other words, every family member of the surveyed families eats approximately 0.4 eggs/day.

Table 5 POPs levels in chicken eggs from Chapaevsk (Samara Oblast), pg/g lipids

Components	Sampling points		Samples from local small holdings		
	Small holdings of Chapaevsk, n=11	Bought at marketplaces in Chapaevsk, n=4	Distances from the plant less than 3 km, n=5	Distances from the plant more than 3 km	
				n=5 [2]	n=1
PCB-77	15 325	362	852	541	161 612
PCB-81	2 432	77	68	9	26 372
PCB-105	67 444	2 311	43 939	14 635	449 024
PCB-114	4 727	196	3 028	1 275	30 488
PCB-118	108 225	4 484.59	86 176	34 253	588 337
PCB-123	4 278	124	1 831	978.2	33 010
PCB-126	649	< d.l. (15)	400	66	4 801
PCB-156	13 023	469	11 184	8151	46 582
PCB-157	2 650	110	2 304	1424	10 509
PCB-167	5 760	170	4766	3 297	23 052
PCB-169	136.9	< d.l. (15)	11	24.17	1 332
PCB-189	1 353	8	740	1700	2 692
WHO-TEQ (PCBs)	96	1	62	18	664
PCB-28/31	939 233	31 746	47 118	11 501	10 038 464
PCB-52	72 502	1 828	6 929	4 564	740 054
PCB-153	93 686	3 122	69 225	97 189	198 472
PCB-138	138 692	3 418	129 758	127 110	241 267
PCB-180	147 595	918.6	118 823	192 529	66 791
HCB	66 417	913	113 615	30 728	8 868
Lindane	252 183	4 651	259 106	268 721	134 886
o,p'-DDE	4 720	383	6 315	3 291	3 890
p,p'-DDE	372 393	3 632	366 527	427 059	128 395
o,p'-DDT	5 098	4 567	8 317	2 064	4 168
p,p'-DDT	120 639	92 225	143 837	72 753	244 076
Sum of DDT and DDE isomers	502 850	100 808	524 996	505 167	380 530

[2] Excluding the sample with extremely high POPs levels (see the right column)

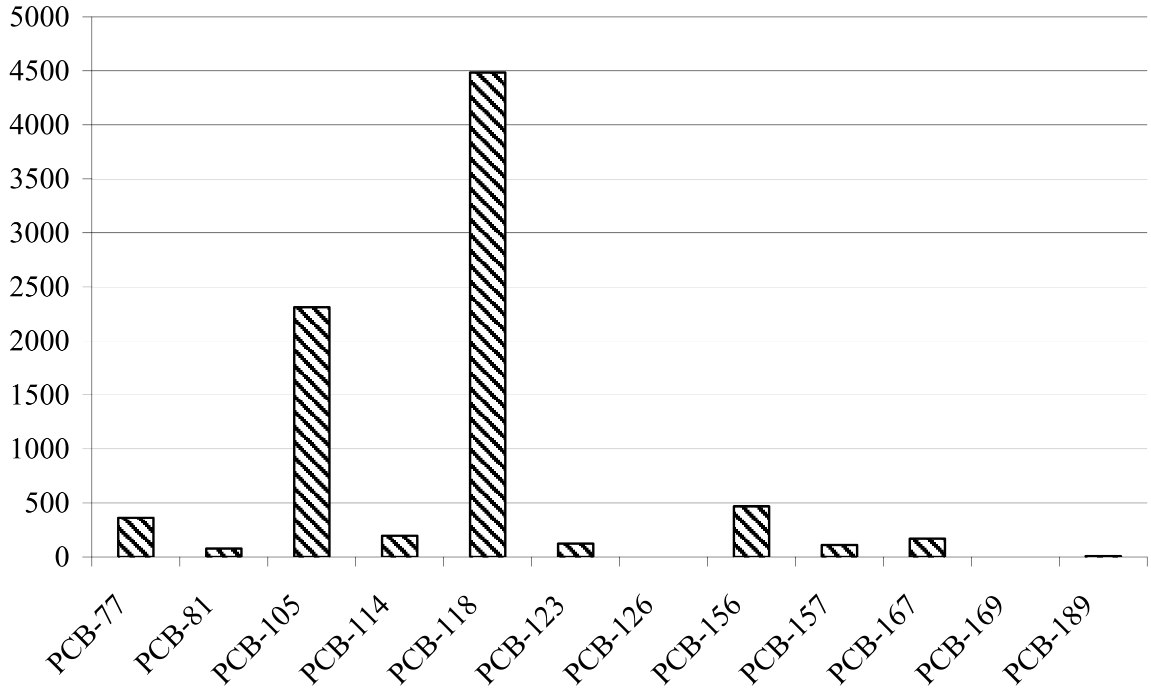

Figure. 3. PCBs levels in chicken eggs, bought at marketplaces in Chapaevsk (pg/g lipids)

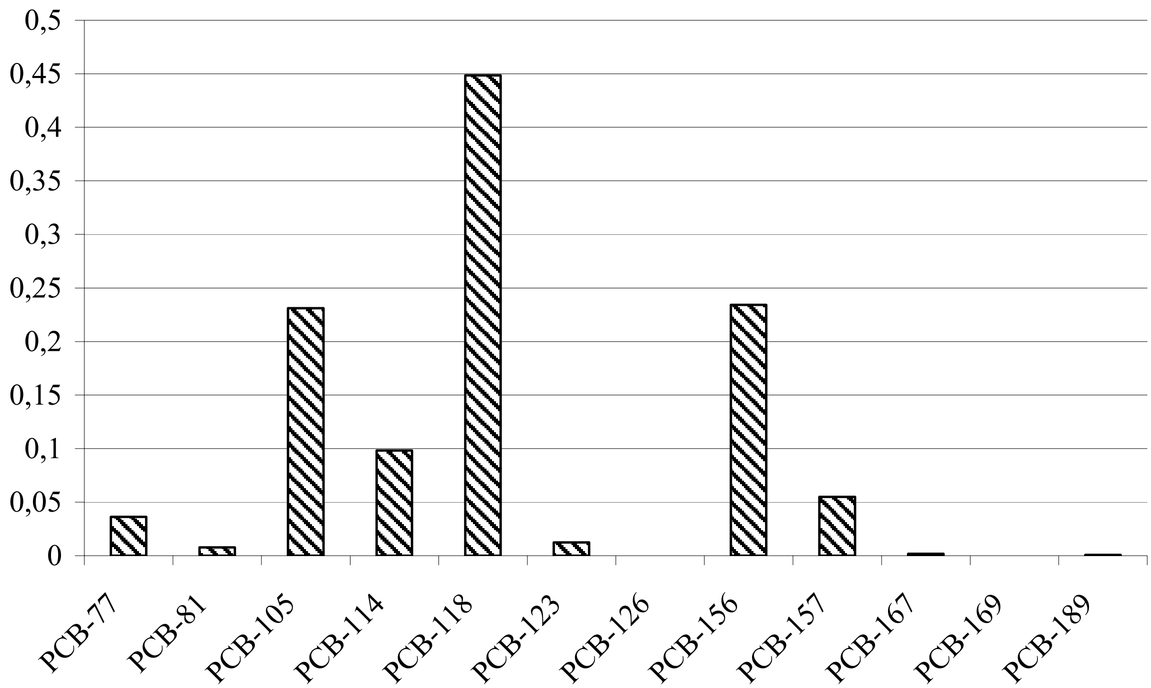

Figure. 4. PCBs levels in chicken eggs, bought at marketplaces in Chapaevsk (pg WHO-TEQ/g lipids)

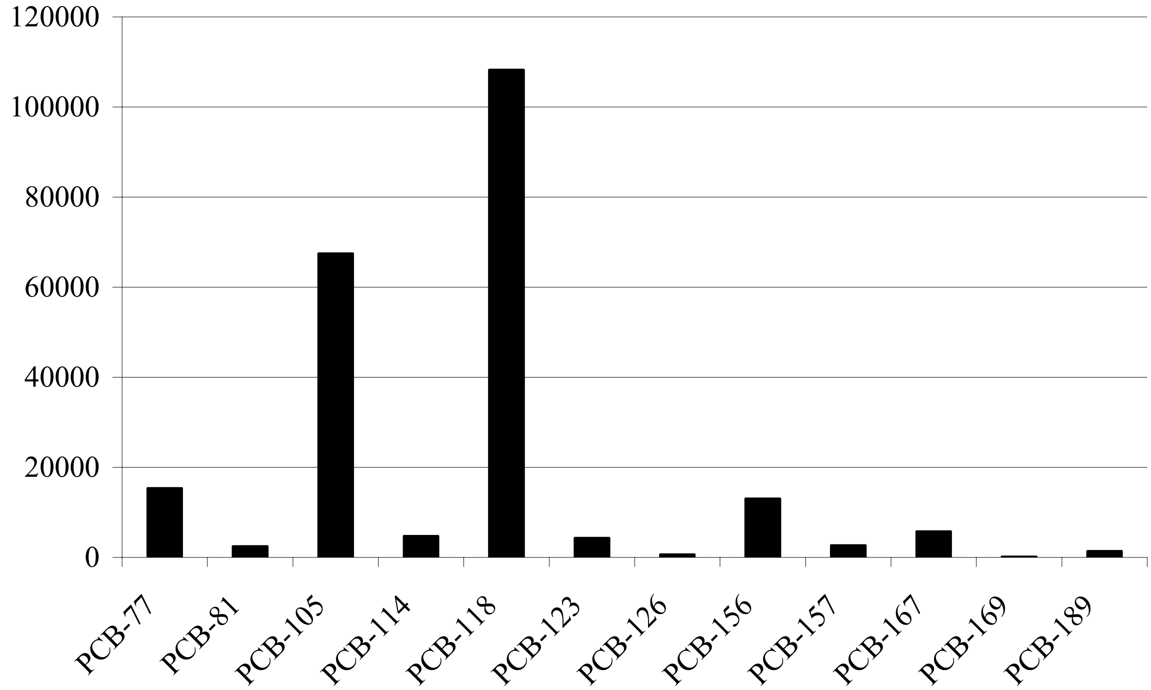

Figure 5. PCBs levels in free range chicken eggs from small holdings in Chapaevsk, pg/g lipids

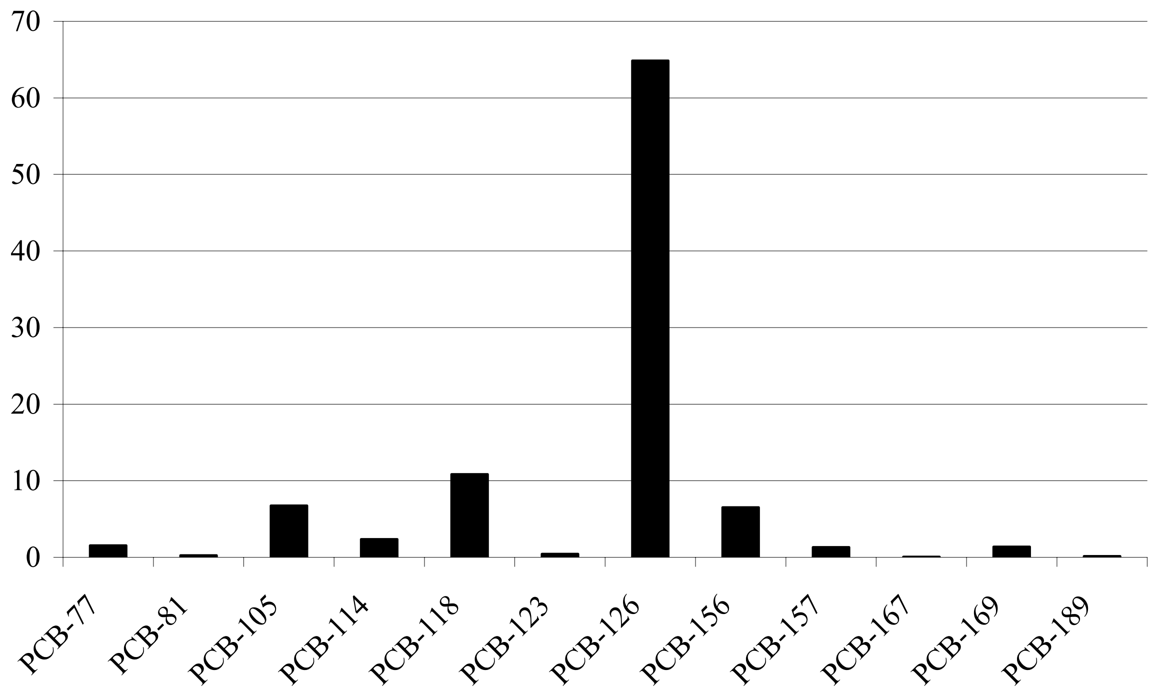

Figure 6. PCBs levels in free range chicken eggs from small holdings in Chapaevsk, pg WHO-TEQ/g lipids

2.3 Saratov

In Saratov Oblast, levels of the majority of POPs in chicken eggs from small holdings in different districts of the oblast do not demonstrate substantial differences. Surveyed families of owners of these small holdings eat chicken eggs 6 times/week and 11 months/year on average (see Table 6, Figures 7 - 8).

Table 6 POPs levels in eggs of free range chicken from different districts of Saratov Oblast, pg/g lipids

Components	Marksovskiy district N=3	Volskiy district N=3	Engelsskiy district N=4
PCB-77	95	71	121
PCB-81	6	7	10
PCB-105	5 509	2 454	6 461
PCB-114	424	164	476
PCB-118	11 910	5 628	14 467
PCB-123	611	234	603
PCB-126	18	22	36
PCB-156	1 399	401	1 885
PCB-157	326	98	473
PCB-167	643	226	937
PCB-169	25	67	38
PCB-189	32	64	56
WHO-TEQ (PCBs)	4	4	7
PCB-28/31	2 733	3 362	2 732
PCB-52	1 907	1 816	1 906
HCB	3 797	4 850	3 797
o,p'-DDE	1 335	747.6	1 335
p,p'-DDE	164 816	126 078	164 816
o,p'-DDT	2 007	566	2 007
p,p'-DDT	25 386	17 383	25 386
Sum of DDT and DDE isomers	193 544	144 774	193 543

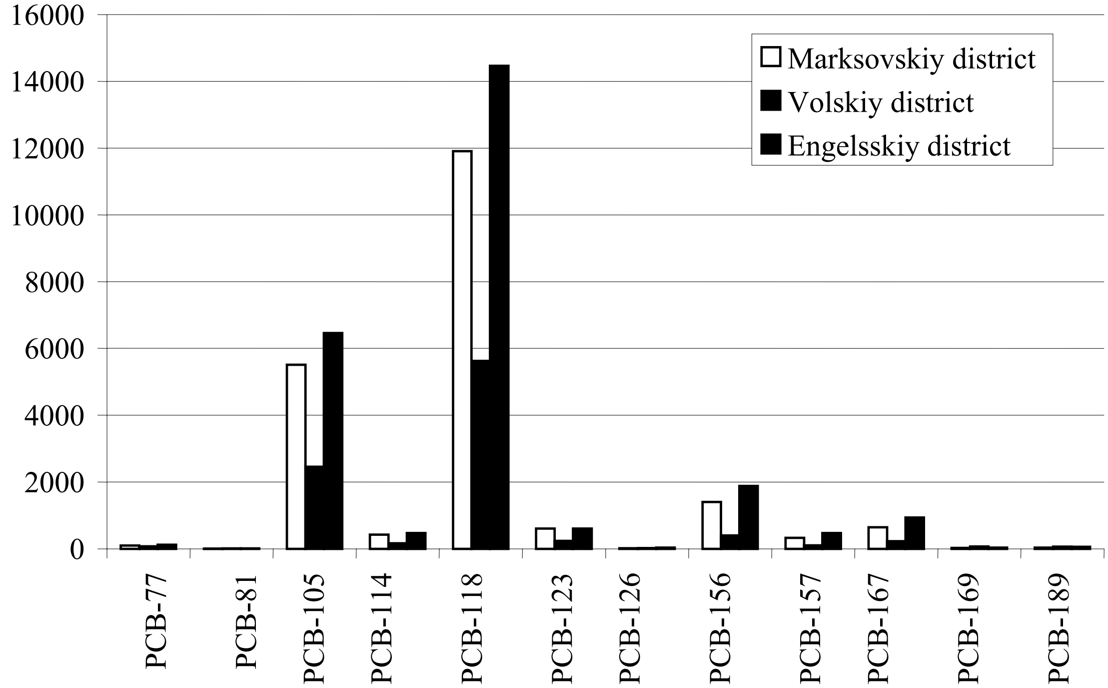

Figure 7. PCBs levels in chicken eggs from Saratov Oblast, pg/g lipids

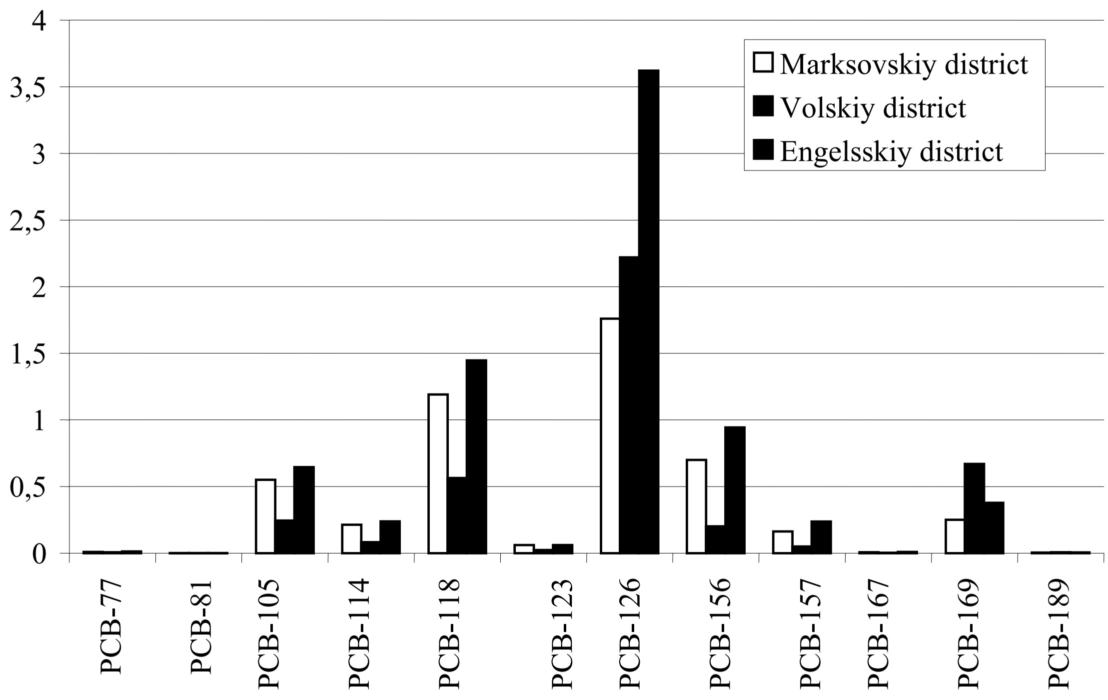

Figure 8. PCBs levels in chicken eggs from Saratov Oblast, pg WHO-TEQ/g lipids

Conclusions

Notwithstanding that production of POPs has ceased at some facilities, their levels in eggs of free range chickens from small holdings near the former PCB-production plant in Novomoskovsk continue to remain rather high (see Figures 9 and 10). The overall levels of 12 PCBs (in TEQs) in samples of eggs of free range chickens collected near the plant is more than 100 times higher than in eggs bought at Chapaevsk marketplaces and 60 times higher than in eggs from Saratov Oblast. These high levels may be attributed to domination of highly toxic PCB congeners (PCB-126. 169, 81, 157 and 189). In addition, high levels of DDT metabolites were also found in egg samples from Novomoskovsk.

Table 7 Average POPs levels in free range chicken eggs from Novomoskovsk, Chapaevsk and Saratov Oblast (pg/g lipids)

Locations	Sum of PCBs TEQs	Sum of DDT and its metabolites	HCB	HCCH (lindane)
Novomoskovsk - Nearby the plant - 2 km from the plant	 324.2 69.6	 4 331 756 3 305 773		
Chapaevsk - Small holdings - Marketplaces (poultry farms from other regions)	 96.4 1.1	 502 850 100 808	 66 416 954	 252 183 4 651
Saratov Oblast	5.5	125 967	15 462	
Galich (Kostroma Oblast), a poultry farm	0.1	20 734	2 133	1 295

The second highest contamination levels were found in eggs from small holdings of Chapaevsk. Compared to Novomoskovsk, PCBs levels in eggs from Chapaevsk are substantially lower, but they are much higher than in eggs from Saratov Oblast. Levels of DDT metabolites are also higher than in Saratov Oblast, where DDT was intensively applied in the past. HCB levels in eggs from Chapaevsk were substantially higher than in Saratov Oblast. Interviews with residents, who provided egg samples, revealed that they eat eggs almost year-round. Members of some families eat eggs at least 4 - 6 times a week.

Results of POPs measurements in eggs from poultry farms in different regions of Russia measured by the Eco-toxicology Laboratory of the Russian Academy of Sciences closely agree with DDT measurements in Marksovskiy district of Saratov Oblast. In eggs from small holdings of 2 other districts of Saratov Oblast, DDT and PCBs levels are higher than in eggs from poultry farms in other regions in Russia.

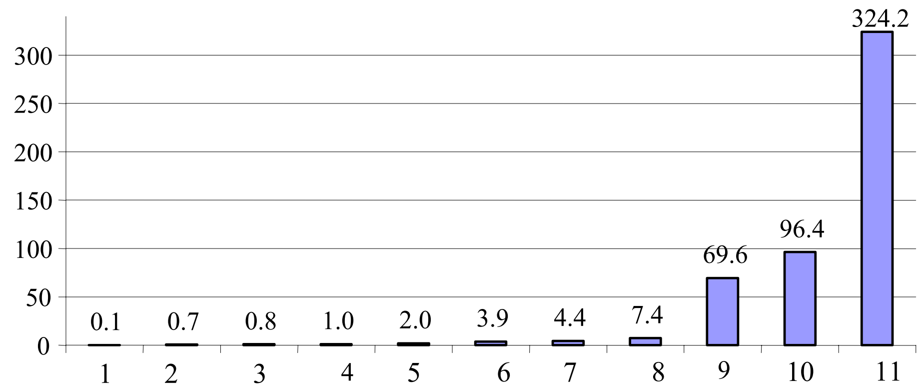

Figure 9. Levels of dioxin-like PCBs in chicken eggs from different regions of Russia (pg WHO-TEQ/g lipids).

1. Galich (Kostroma Oblast), a poultry farm
2. Borovskiy township (Tyumen Oblast), a poultry farm
3. Oktiabrskiy township (Chelyabinsk Oblast), a poultry farm
4. Sorochinsk (Orenburg Oblast), a poultry farm.
5. Ulianovsk Oblast, a poultry farm.
6. Volskiy district of Saratov Oblast.
7. Marksovskiy district of Saratov Oblast.
8. Engelsskiy district of Saratov Oblast.
9. Novomoskovsk, 2 km from the "Orgsintez" plant.
10. Chapaevsk
11.Novomoskovsk, near the "Orgsintez" plant.

In Novomoskovsk, aggregate levels of DDT and its metabolites exceed the applicable limit of 100 ng/g, set in Sanitary Rules and Norms 3.590-96 (clause 6.1.15).

It is necessary to note that food intake of POPs with chicken eggs in the case of children, who live in contaminated areas of Novomoskovsk is aggravated by inadequate diets of these children. Analysis of actual diets and health status of 309 preschoolers and school age children (4 - 5 years, 9 - 10 years and 15-16 years) of Novomoskovsk suggests that the energy value of daily rations of children of all these age groups are lower than relevant physiological needs by 8.5 - 17.4%, depending on age and gender. In addition, the daily diets of all children's age groups are low in protein, particularly in animal protein [Mikhailyuk, 2004].

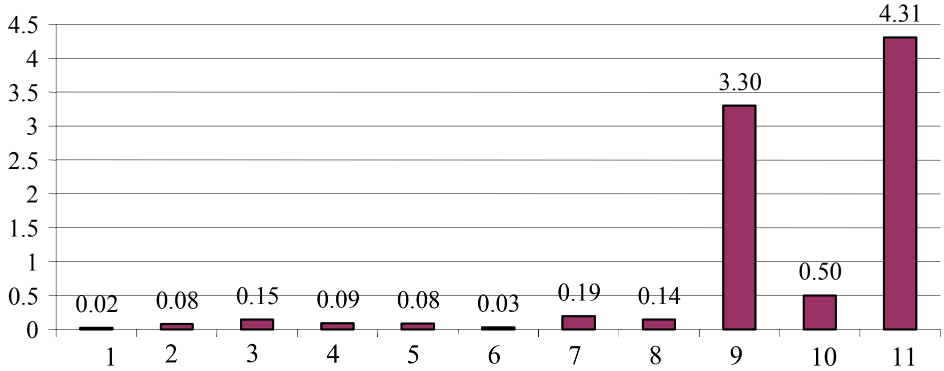

Figure 10. Aggregate levels of DDT and DDE isomers in chicken eggs from different regions of Russia (mg/kg lipids).

1. Galich (Kostroma Oblast), a poultry farm
2. Borovskiy township (Tyumen Oblast), a poultry farm
3. Oktiabrskiy township (Chelyabinsk Oblast), a poultry farm
4. Sorochinsk (Orenburg Oblast), a poultry farm.
5. Ulianovsk Oblast, a poultry farm.
6. Volskiy district of Saratov Oblast.
7. Marksovskiy district of Saratov Oblast.
8. Engelsskiy district of Saratov Oblast.
9. Novomoskovsk, 2 km from the "Orgsintez" plant.
10. Chapaevsk
11.Novomoskovsk, near the "Orgsintez" plant.

If we compare our results with results of the major international study implemented in the framework of IPEN for 17 countries, we may conclude that PCBs levels in chicken eggs from Novomoskovsk and eggs from free range chickens from Chapaevsk, are much higher than relevant levels in such heavily polluted territories as Dzerzhinsk in Russia (PCBs levels of 9.08 - 18.37 pg WHO-TEQ/g lipids), Helwan in Egypt (11.74) , Lucknow in India (9.40), and Bolshoi Trosteknek in Belarus (9.83). [The Egg Report, 2005, P.46] .

HCB levels in eggs of free range chickens from Chapaevsk (66.4 ng/g lipids) are higher, comparatively to Helwan in Egypt (15.1), Bolshoi Trostenek in Belarus (4.7), Kovachevo in Bulgaria (25.5) and comparable to levels in eggs from Gorbatovka settlement in Russia, located at a distance of 2.5 km from the Eastern Industrial Zone of Dzerzhinsk (68.9). In the most heavily contaminated residential district of Chapaevsk (at the distance of 3 km from the chemical plant), HCB levels in eggs are 2 times higher (113.6 ng/g lipids), than in the Gorbatovka district of Dzerzhinsk. The highest HCB levels in Chapaevsk were about half the levels observed in free range chicken eggs collected near a municipal waste incinerator in the city of Liberec in the Czech Republic (250 ng/g lipids).

We can state that a new POPs contamination hot spot has been identified - Novomoskovsk - where no studies of health and environmental impacts of POPs have been conducted. Local authorities and environmental bodies should account for the need to study local areas more closely, to implement reclamation works, and to inform local residents and NGOs on health hazards associated with consumption of contaminated food.

The project implementation allowed improved co-operation on POPs-related problems between the academic community, environmental and health NGOs, supervisory bodies and authorities.