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ORIGINAL PAPER

Carcinogenic and teratogenic status of human population and polychlorinated biphenyls contaminations of soils and biota (European pied flycatcher) in a Perm (Western Ural, Russia)

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Abstract Polychlorinated biphenyls (PCBs) are included in the persistent organic pollutants designated by the Stockholm Convention and are hazardous compounds both for the environment and public health. The aim of this study was to determine the level of environmental pollution of PCBs in the Perm, in soil and biota (European pied flycatcher), and to analyze whether its presence was the cause of cancer and congenital malformations in the population. Soils in the study area had PCB concentrations of 101.87 μg/kg in the Industrialniy District and 27.81 μg/kg in the Leninskiy District of the Perm in 2005. The chemical composition of the individual PCBs and PCB groups were the same in the soils of both regions. The blood of nestlings of the European pied flycatcher raised in the Industrialniy District contained 9.61 ng PCB/ml, while those in the Leninskiy District had 5.64 ng PCB/ml in 2005. A linear correlation was established between the PCB contamination of soils and PCB contamination of pied flycatcher nestling's blood, and inverse linear correlation was established between the content of PCB in the blood of nestlings and the success of breeding of the pied flycatcher in Perm. An epidemiological analysis revealed a high incidence of cancer among the human population of the Industrialniy and Leninskiy districts (371.7 and 376.85 cases per 100,000 population, mean for the 2003–2018, respectively), which exceeded the figure for the whole of Perm (350.77 cases per 100,000 population, mean for the 2003–2018). The incidence rate of congenital malformations in Perm for the study period was 48.51 per 1000 human births. However, a decrease in the concentration of PCBs in soil and biota over a 15-year period (2005–2019) to the less than the detection limit did not lead to a decrease in the incidence of these diseases. Probably, PCB contamination was not the main cause of oncological diseases and congenital malformations in the population of the study area.

Keywords PCB · Contamination · Soil · Blood · Malignant neoplasm morbidity rate · Congenital malformations

Introduction

One of the global environmental problems is persistent organic pollutants (POPs). POPs, including polychlorinated biphenyls (PCBs), are superecotoxicants, which even in small doses can have a negative effect on animals (http://chm.pops.int).

PCBs are a group of 209 synthetic organic compounds, each of which carries 1–10 chlorine atoms attached to a polyaromatic biphenyl structure. Due to their unique chemical and physical properties,

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PCBs have been widely used in the manufacture of pesticides, plasticizers, lubricants, paints, varnishes, adhesives, and also as a component of dielectrics used in electrical apparatus, in particular transformers. Despite the ban on their production and use (Polychlorinated biphenyls 2018), the level of environmental pollution by these substances remains high due to their resistance to abiotic and biotic decomposition, as well as their leaching from industrial waste storage sites and accidents at transformer stations (Markowitz and Rosner 2018; Weber et al. 2018).

In the 1970s, it was found that PCBs were toxic compounds that had carcinogenic and teratogenic effects on animals and humans. Subacute and chronic PCB exposures were most dangerous. It is precisely this type of exposure that affects populations of birds and mammals living in large industrial areas (Kania-Korwel and Lehmler 2016). Due to its high lipophilicity, PCBs accumulate in biological trophic chains, with a tendency to accumulate at higher levels (Muir et al. 2003; Zhao et al. 2006; Polder et al. 2008; Mahmood et al. 2014; Mamontova et al. 2017). In the bodies of birds, PCBs penetrate the skin, lungs and gastrointestinal tract (Kania-Korwel and Lehmler 2016). As a result of absorption, PCBs accumulates in the blood and is then distributed between the organs of the body. At the same time, the accumulation of PCBs in birds leads to progressive weight loss, bone marrow suppression, immunosuppression, thinning of egg shells and, as a result, death of offspring before hatching, reduction of reproductive functions, as well as alterations of behavior and care for offspring (Neigh et al. 2007; Kania-Korwel and Lehmler 2016). In this regard, environmental pollution with PCBs is a serious problem for the conservation of numbers and diversity of bird species. It is known that a large proportion of avifauna of large industrial centers is composed of insectivorous birds, representatives of the order *Passeriformes*. This group of birds is most intensely exposed to the chemical pollution that is present in their habitat. However, information on the content of PCBs in passerine bodies is extremely scarce (Neigh et al. 2007; Yu et al. 2014; Mo et al. 2018). One of the indicator species of insectivorous birds living in large cities is the European pied flycatcher (*Ficedula hypoleuca* Pallas, 1764) (Berglund et al. 2007; Salvador et al. 2017; Mo et al. 2018).

The pied flycatcher is the dominant species among double nesting birds inhabiting artificial nesting sites in the city. This species inhabits nest houses in forest parks and urban gardens equally well and is resistant to many stressors, such as frequent nest visits, temporary nesting and blood sampling. This species of bird is used as a bioindicator when conducting research on environmental pollution by heavy metals (Nyholm 1998; Berglund et al. 2007). We proposed that in order to study the level of PCB contamination of the food chain in a large industrial center, the pied flycatcher could also be used as an indicator species. It is known that the pied flycatcher is tied to a habitat for the period of feeding its chicks. In this regard, the content of PCBs in the blood of chicks would reflect the overall picture of contamination by these compounds in the studied area (Neigh et al. 2007; Yu et al. 2014; Mo et al. 2018).

Studies have shown that the long-term presence of PCBs in the environment can cause the development of cancer in the population and also increase the incidence of congenital anomalies in children (ATSDR 2000; Orlinskii et al. 2001; Robertson and Hansen 2001; Liu et al. 2010; Lauby-Secretan et al. 2016; Polychlorinated biphenyls 2018). An epidemiological analysis of the incidence of oncological pathologies in the population of large industrial centers, as well as an analysis of the development of congenital anomalies in children in these areas, combined with quantitation of PCB in the environment, makes it possible to draw correlations and assess the danger of PCB pollution in the urban environment.

Perm is one of the largest industrial centers of the Western Urals in Russia. Chemical and machine-building enterprises are located in Perm (https://www.gorodperm.ru). There were no PCB production plants in this area; however, PCBs produced under brand names Sovol and Sovtol were actively used both as parts for transformers and capacitors and in the manufacture of products at industrial enterprises in the city (http://geum.ru/next/art-68284.leaf-2.php). The main enterprises that used the Sovol PCB mixture in Perm were the Nefteorgsintez plant and the Lubricant and cutting fluids plant. However, there is no data on the volumes of used Sovol at these enterprises, as well as on the conditions of its storage. When studies were conducted to assess the level of contamination of the urban environment with hazardous substances, PCBs were not taken into account.

The purpose of this study was to determine the level of environmental pollution of PCBs in the Perm, in soil and biota (European pied flycatcher), and to analyze whether its presence was the cause of cancer and congenital malformations in the population.

Materials and methods

Site characterization

The study area was located in the city of Perm, Russia (Fig. 1). Perm was located in the east of the European part of Russia. The population of the city was 1,051,583. Perm was one of the largest industrial centers of Russia. The Industrialniy District of Perm was characterized by a significant accumulation of factories and industrial plants, including oil refining and the production of chemical compounds. The Leninskiy District consisted of office and shopping centers. The largest part of the total industrial production of Perm was in the Industrialniy District. Emissions to the atmosphere were distributed in the following order: Industrialniy (∼ 50%), Ordzonikidzevskiy (∼ 20%), Sverdlovskiy and Kirovskiy (∼ 10% each), Dzerginskiy and Motovilihinskiy (∼ 4%) and Leninskiy (1%).

According to an inventory of PCB-containing equipment from 2000 to 2009, 32,28 tons of PCBs are contained in Perm Krai (www.unido-russia.ru). Industrial plants and oil refineries that used PCBs in the technological cycle are located in the Industrialniy (Nefteorgsintez plant) and Sverdlovskiy (Lubricant and cutting fluids plant) districts of Perm. The sampling areas for this study are located in the direction of the prevailing winds relative to these plants. Currently, PCBs are not used at these plants, and PCB-containing equipment is decommissioned in accordance with the ratification of the Stockholm Convention.

The samples for the study were collected in 2005 and 2019 at four sites established in 2000–2001 and located in forest parks and urban gardens of

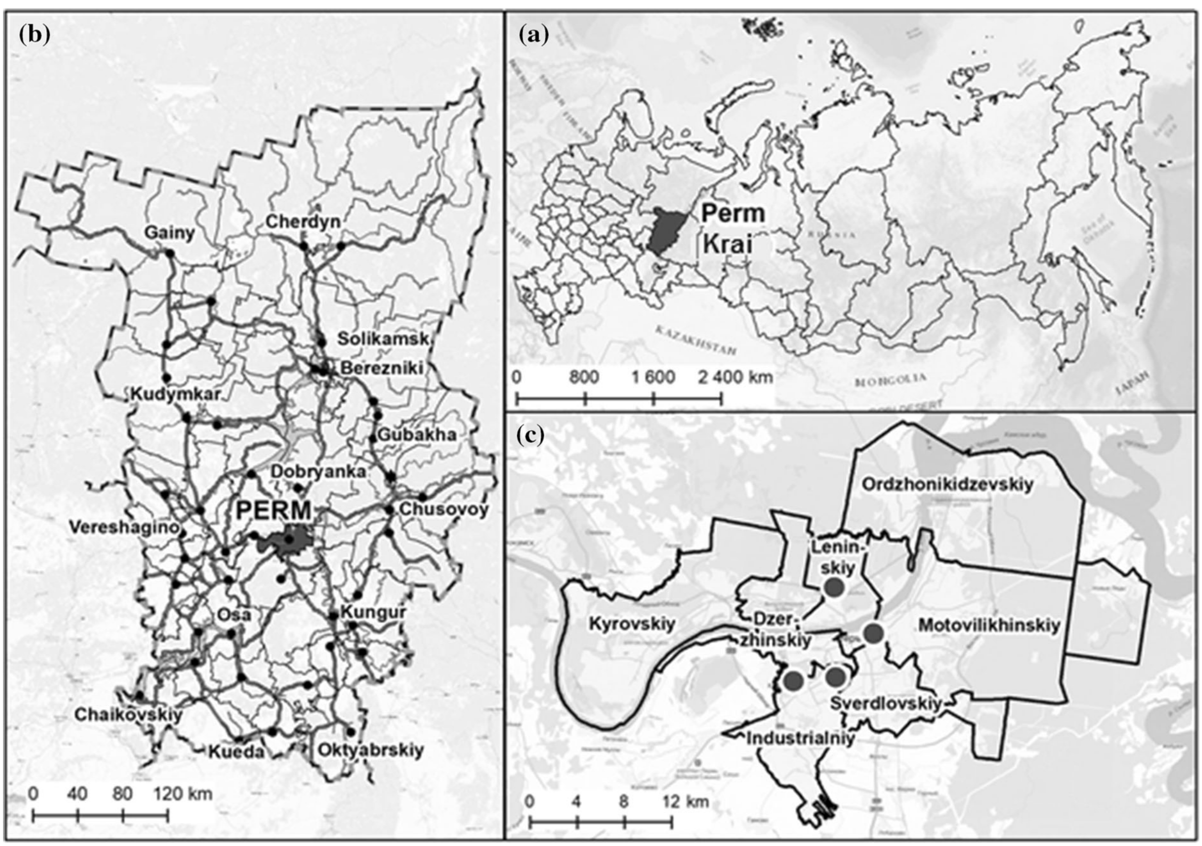

Fig. 1 Maps of Russia (**a**), Perm Krai (**b**) and Perm (**c**) and sampling locations (filled circle) in the Industrialniy and Leninskiy districts of Perm

Industrialniy (total size of sites 6.47 km^2) and Leninskiy (total size of sites 1.4 km^2) districts. Soil sampling points were located in the fodder area for birds within the forest parks and urban gardens, where there were artificial nests. The nest boxes (50 sets in a line) were located about 4.5–5.0 m above the ground with a distance of approximately 15–20 m between them. Of the nest boxes in Perm, 43% were occupied by pied flycatchers.

Soil sampling

The soils were sampled in forests and park areas in the two districts of Perm (Fig. 1). Twenty-seven soil samples were collected from Industrialniy District, and twenty-one soil samples were collected from Leninskiy District from the surface layer (0–30 cm) of podzol soils of different texture (IUSS Working Group WRB 2015; Soil Science Division Staff 2017). Control soil samples (20 pcs.) were taken in the protected natural area "Preduralie." Each sample was a composite of about five subsamples collected from an area of 1 m^2. The envelope method was used, where subsamples were collected from each corner and the center of a sampling square. Soil materials were homogenized and transported to a laboratory, air-dried at 25 ± 1 °C, and stored in the dark at a temperature of 15 ± 1 °C.

PCB extraction from soil

A soil sample of 10 g was wrapped in a white ribbon filter and placed in a Soxhlet apparatus and extracted with a mixture of hexane/acetone in a ratio of 50:70 for 3 h. After extraction, the extract flask was cooled to room temperature. The cooled extract was then poured into a separatory funnel, and about 150 ml distilled water was added, and it was shaken two times for 2 min. After separation of the phases, the aqueous solution of acetone was removed, and the hexane extract was dried over anhydrous sodium sulfate for 15–20 min. The dried extract was then placed in a pear-shaped flask, and distillation of hexane was carried out on a rotary evaporator under vacuum created by a water-jet pump. The extract was concentrated to a volume of 3 ml and poured into a 25-ml separatory funnel. Two ml of hexane was added to the flask, with the remaining solution being washed off and added to the extract. The volume of the extract was now 5 ml. Two ml concentrated sulfuric acid was added to the funnel, shaken, and then allowed to separate. After separation of the phases, the acid layer was removed and the hexane layer was washed with 10 ml distilled water. After further separation of the phases, the hexane extract was removed and dried for 10 min over anhydrous sodium sulfate. The extract was then evaporated to dryness in a water bath, 0.2 ml of acetone was added, and gas chromatography–mass spectrometry (GC–MS) analysis of the solution was performed (USEPA 1668A with modifications).

Blood sampling

A volume of 0.02 ml blood was extracted from the brachial vein of 14-day-old pied flycatcher nestlings with a sterile disposable syringe and transferred to appropriate tubes containing heparin. Blood was collected from three nestlings in each nest, and then, the birds were returned to the nest. Two hundred and forty samples in 2005 (123 blood samples were collected from Industrialniy District and 117 blood samples were collected from Leninskiy District) and two hundred and two samples in 2019 (103 blood samples were collected from Industrialniy District and 99 blood samples were collected from Leninskiy District) were transported to the laboratory and stored at − 20 °C until analyzed.

PCB extraction from blood serum

Blood samples were centrifuged for 3 min at 12,000 rpm (MiniSpin centrifuge, Eppendorf) to completely precipitate cellular element. The serum was used for further analysis. PCBs were extracted from the blood serum with hexane/ethyl ether (1:1), with 1 min vortex mixing, 10 min sonication and 2 min mechanical shaking. This procedure was performed in triplicate. The extracts from each sample were centrifuged (5 min, 4500 rpm; MiniSpin centrifuge, Eppendorf), and then, the supernatant was removed. The supernatants from the replicates were combined, concentrated and cleaned by column chromatography using a 1 cm glass column, containing 1 g silica, 2 g alumina and 1 g Na_2SO_4. The column was eluted with 40 ml hexane/ethyl ether (1:1, 40), and the entire eluate for each sample was finally evaporated. The samples were then capped, mixed by vortex and analyzed by GC–MS (USEPA 1668A with modifications). Decachlorobiphenyl (PCB 209) was used as an internal standard.

Standards

Standards PCB 28, 52, 101, 118, 138, 153 and 180, belonging to the group known as indicator PCBs, and PCB 209 (named in terms of their PCB IUPAC numbers) were obtained from Sigma-Aldrich Laborchemikalien GmbH (Seelze, Germany).

Chromatographic conditions

The PCBs were identified by GC/MS on an Agilent Technology GC6890N MSD5973N gas chromatograph mass spectrometer (Agilent Technologies, USA) with a HP-5MS SN US15189741-1 quartz capillary column (30 m × 0.25 mm, film thickness 0.25 µm), as well as a quadrupole mass spectrometric detector. Helium carrier gas was used, and samples were introduction into the column by dividing the flow (split 1:50 mode). The initial temperature of the column was 40 °C (isotherm 3 min); the temperature rise was 10 °C/min to a final temperature of 290 °C (isotherm 40 min). The evaporator temperature was 250 °C, the transition chamber was at 280 °C, the mass spectrometric source was at 230 °C, and the quadrupole was at 250 °C. Scanning was performed using the total ion current in the mass range of 20–1000 Da in the electron ionization mode (70 eV). Extraction and analysis of samples for PCBs was performed according to ISO 10,382:2002 (Soil quality, 2008). Analytical quality control was applied to ensure the analysis of PCB, such as a continuous monitoring of laboratory contamination based on the determination of a blank sample covering the whole analytical procedure, including extraction, cleanup and quantification. Recoveries of samples (soils, blood) with the calibration mixture were in the range of 98–99%. Standard reference material (PCB 28, 52, 101, 118, 138, 153, 180, 209) was analyzed, and the reliable results were obtained by comparison of the data from our study with those from material reference values. The minimum detection limit for each individual PCB, analyzed in this study, is provided at Table 1.

Quantification of PCBs was performed using PCB209 as an internal standard. Compounds were positively identified if their mass-spectrum profile was identical to that of an indicator PCB.

Epidemiologic data collection

Epidemiological data on the incidence of cancer and other pathologies were obtained from official medical documents. For the analysis, we used the statistical indicators of cancer care reflected in the register of the GBUZ PC «Perm Regional Oncology Dispensary» for 2003–2018. The data presented in the annual Report "On the State and Environmental Protection of the Perm Territory" were also taken into account. Data on cancer incidence and congenital malformations in Russia were obtained from the statistical registers of the Central Research Institute of Organization and Informatization of Health Care of the Ministry of Health and Social Development of the Russian Federation. We took into account official statistics of cancers detected in the period 2003–2018, as well as the number of congenital malformations among children for the period 2003–2007. Data for adults were assessed in the city as a whole, as well as by areas. The number of pathologies among the pediatric population was estimated for the whole city. Oncological morbidity rate of the population over the years was calculated per 100 thousand of the population. The level of congenital malformations was calculated per 1000 births.

Statistics

Statistical analysis was carried out using the standard software packages, Microsoft Excel and STATISTICA 7.0 (Statsoft Statistica 2017, http://statsoft.ru). Basic statistical parameters such as mean, geometric mean, standard error, median, standard deviation, range (min, max), level of reliability and correlation dependencies were determined. Differences in datasets were analyzed through one-way analysis of variance (ANOVA) using STATISTICA 7.0 with the determination of the sum of squares (*SS*), the number of degrees of freedom (*df*), the average square (*MS*), the calculated value of the Fisher criterion (F), the significance level of the calculated F (*P* val.) and the tabular value of the Fisher criterion (*F crit.*). Significance levels were set at $P < 0.05$.

Table 1 Values of the minimum detection limit for individual PCB, studied in this study

PCB	Minimum detection limit, pg/ml	PCB	Minimum detection limit, pg/ml
28	2.0 ± 0.2	138	0.5 ± 0.1
52	1.5 ± 0.1	153	0.5 ± 0.1
101	2.0 ± 0.1	180	1.0 ± 0.2
118	0.5 ± 0.1		

Results

PCB contamination status of the soils

All seven PCBs analyzed were detected in soil samples of 2005, but PCBs were not detected in soil samples of 2019 and in soil samples from protected natural area "Preduralie" (Fig. 2). The total concentration of PCBs was estimated at 178.11 ± 0.02 μg/kg dry weight (dw) soil for Perm. Mean total PCB concentration for soils from Industrialniy District was 101.87 ± 0.03 μg/kg dw soil, with individual congener mean concentrations varying from 0.57 ± 0.01 μg/kg dw soil (PCB 138) to 62.51 ± 0.02 μg/kg dw soil (PCB 118). For the Leninskiy District, mean total PCB concentration was 27.81 ± 0.02 μg/kg dw with congeners varying from 0.61 ± 0.03 μg/kg dw soil (PCB 180) to 16.42 ± 0.01 μg/kg dw soil (PCB118). Congeners PCB 28 and PCB 118 predominated in the soil samples of both districts (Fig. 2). Statistical comparison of congener levels between districts indicated significant differences for all detected PCBs (Table 2).

Congener group chemical fingerprints, the percentage levels for congener groups with the same number of chlorine atoms in the molecule, were similar in the two districts and in the city as a whole (Fig. 3). Statistical comparison of congener group chemical fingerprints between districts indicated significant differences for all detected groups (Table 3). Pentachlorinated biphenyls predominated in all soils samples. Highly chlorinated biphenyls (hexa- and hepta-CB) in the soils samples of the Industrialniy District was 3.1% of PCBs, while in Leninskiy District they constituted 6.5% of PCBs.

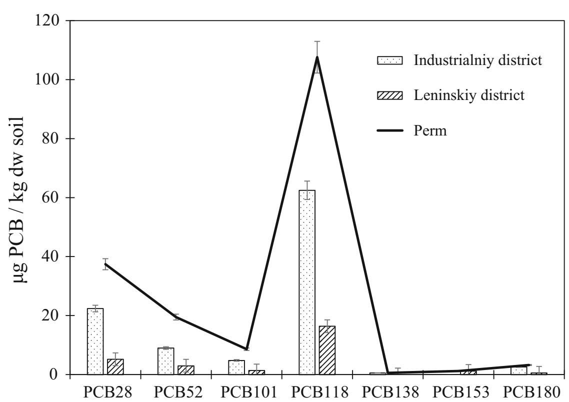

Fig. 2 Concentration of indicator PCBs in soil samples taken in 2005

PCB concentration in pied flycatcher nestlings

In the present study, we found that pied flycatcher nestlings growing up in the Industrialniy District of Perm in 2005 accumulated more of the PCBs ($\sum$PCBs = 9.61 ± 0.01 ng PCB/ml blood serum) than those from the Leninskiy District ($\sum$PCBs = 5.65 ± 0.02 ng PCB/ml blood serum). No PCBs were found in the blood of the pied flycatcher nestlings taken in 2019.

All seven indicator PCBs analyzed were detected in blood serum of pied flycatcher nestlings from the Industrialniy District, but only six PCBs were detected in blood serum of pied flycatcher nestlings from Leninskiy District (Table 4). In blood serum samples of nestlings from the Industrialniy District, the mean concentration of individual congeners varied from 0.11 ± 0.01 ng PCB/ml blood serum (PCB 153) to 1.99 ± 0.02 ng PCB/ml blood serum (PCB101). Notably, blood serum samples from Leninskiy District did not contain PCB153, with mean concentration of individual congeners varying from 0.02 ± 0.001 ng PCB/ml blood serum (PCB 52) to 0.87 ± 0.03 ng PCB/ml blood serum (PCB101). Congener PCB101 predominated in all blood serum samples, with 20.77 and 15.40% of total PCBs in samples from Industrialniy and Leninskiy districts, respectively. One-way analysis of variance showed that the concentration of PCB138 and PCB180 does not significantly differ in the blood serum samples of pied flycatcher nestlings from different districts (Table 5).

Table 2 One-way analysis of variance of indicator PCB congeners in soil samples taken in 2005 in two districts of Perm

	SS	*df*	*MS*	*F*	*P* val	*F crit*
PCB28	11,616.0	2.0	5808.0	562,364.8	6.2E−148	3.1
PCB52	3057.5	2.0	1528.7	1582.5	1.7E−56	3.1
PCB101	573.4	2.0	286.7	15,023.6	1.8E−88	3.1
PCB118	87,427.9	2.0	43,713.9	1,472,715.9	3.7E−154	3.1
PCB138	4.8	2.0	2.4	26,833.0	8.9E−97	3.1
PCB153	21.8	2.0	10.9	692.8	5.1E−45	3.1
PCB180	88.2	2.0	44.1	2728.3	1.3E−68	3.1

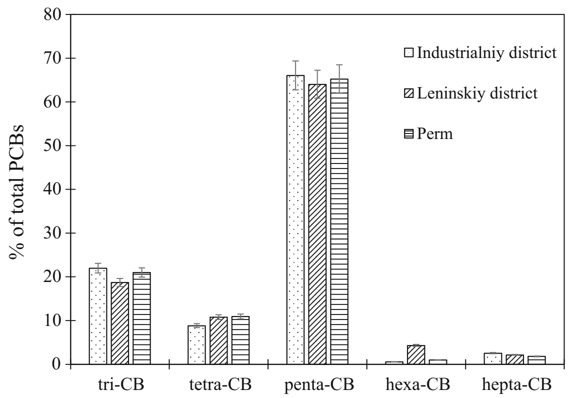

Fig. 3 Percentage level of the PCBs groups in the soil samples taken in 2005

Table 3 One-way analysis of variance of homologous PCB groups in soils samples taken in 2005 in two districts of Perm

	SS	*df*	*MS*	*F*	*P* val	*F crit*
Tri-CB	123.1	2.0	61.5	206.7	2.5E−30	3.1
Tetra-CB	104.7	2.0	52.3	56.1	3.4E−15	3.1
Penta-CB	59.0	2.0	29.5	29.5	5.9E−10	3.1
Hexa-CB	192.9	2.0	96.4	16,817.3	2.3E−92	3.1
Hepta-CB	6.4	2.0	3.2	500.3	2.1E−41	3.1

Congener group chemical fingerprints were not similar in the pied flycatcher blood serum samples from the two districts and significantly differ from each aver (Fig. 4, Table 6). Pentachlorobiphenyls predominated in the samples from Industrialniy District, while heptachlorobiphenyls predominated in the blood serum samples from Leninskiy District. The proportion of highly chlorinated biphenyls in the blood serum of pied flycatcher nestlings (30–31% of total PCB) was an order of magnitude higher than the proportion of highly chlorinated biphenyls in the soil from the two districts in which nestlings were found.

Epidemiological analysis of cancer pathology

During a 15-year period, the malignant neoplasm morbidity rate for the human population in Perm was 350.77 cases per 100,000 (Fig. 5, Table 7). This epidemiological indicator in Perm has been lower than in Russia as a whole. The analysis showed that, on average, the malignant neoplasm morbidity rate in the Leninskiy District was higher than in the Industrialniy District. However, in some years (2004, 2005, 2008, 2010, 2014), the malignant neoplasm morbidity rate in the Industrialniy District exceeded the data for the Leninskiy District.

The most common forms of cancer associated with the presence of PCBs in the environment are those involving the skin, gastrointestinal tract, lungs and breast. Epidemiological studies have shown that in Perm and the studied district, the incidence rate of these forms of cancer is high (Table 8). At the same time, the indicators in 2018 were higher for all these types of cancer in the Industrialniy and Leninskiy districts. On average, in the city of Perm, a slight decrease was noted for cancer of the gastrointestinal tract and lungs.

Epidemiological analysis of congenital malformation

A comparison of the results of an epidemiological study of frequency of congenital malformations (CMFs) in Perm with statistical data for Perm Krai and Russia showed that CMFs were more prevalent in Perm (Fig. 6). The average frequency of CMFs in Perm (2003–2007) was 48.51 per 1000 births, and was higher than for Perm Krai (44.41 per 1000 births) over

Table 4 Levels of indicator PCBs in blood serum samples taken in 2005 of the two populations of *Ficedula hypoleuca* in Perm (ng/ml blood serum, $n = 240$)

	Industrialniy District					Leninskiy District				
	Mean	Geometric mean	Minimum	Maximum	% of total	Mean	Geometric mean	Minimum	Maximum	% of total
PCB 28	0.89	0.74	0.24	1.54	9.26	0.29	0.19	0.05	0.54	5.22
PCB 52	0.14	0.21	0.001	0.27	1.41	0.02	0.01	0.01	0.03	0.35
PCB 101	1.99	2.55	0.21	3.78	20.77	0.87	0.78	0.41	1.33	15.40
PCB 118	0.18	0.29	0.001	0.37	1.93	0.003	0.002	0.001	0.005	0.05
PCB 138	0.13	0.17	0.08	0.19	1.35	0.14	0.09	0.02	0.26	2.48
PCB 153	0.11	0.09	0.02	0.19	1.09	0	0	0	0	0
PCB 180	0.22	0.17	0.1	0.34	2.29	0.22	0.21	0.18	0.25	3.81

Table 5 One-way analysis of variance of indicator PCBs in the pied flycatcher nestlings blood samples taken in 2005 in two districts of Perm

	SS	*df*	*MS*	*F*	*P* val	*F crit*
PCB28	13.1	1.0	13.1	53.6	1.5E−11	3.9
PCB52	0.5	1.0	0.5	57.9	2.3E−12	3.9
PCB101	50.6	1.0	50.6	29.4	2.1E−07	3.9
PCB118	1.3	1.0	1.3	77.3	2.4E−15	3.9
PCB138	0.0	1.0	0.0	0.4	5.2E−01	3.9
PCB153	0.4	1.0	0.4	105.3	1.0E−18	3.9
PCB180	0.0	1.0	0.0	0.1	7.5E−01	3.9

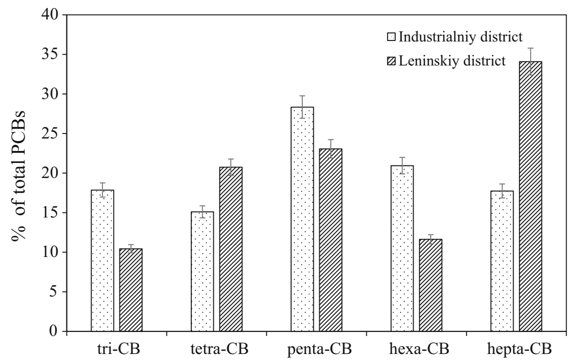

Fig. 4 Percentage level of the PCBs groups in blood serum samples taken in 2005 of two populations of *Ficedula hypoleuca* in Perm

the same period. This value was also higher than for Russia (21.75 per 1000 births). The number of registered congenital malformation for the period 2003–2007 in Perm and Perm Krai increased approximately one and a half times. The dynamics of this indicator was linear. On the contrary, in Russia this indicator fluctuates around 20–21 cases per 1000 births during the same period.

Table 6 One-way analysis of variance of homologous PCB groups in the pied flycatcher nestling's blood samples taken in 2005 in two districts of Perm

	SS	*df*	*MS*	*F*	*P* val	*F crit*
Tri-CB	47.6	1.0	47.6	8241.7	2.9E−152	3.9
Tetra-CB	4.7	1.0	4.7	1509.2	1.9E−89	3.9
Penta-CB	81.8	1.0	81.8	19,394.0	3.2E−185	3.9
Hexa-CB	63.2	1.0	63.2	57,117.1	1.1E−214	3.9
Hepta-CB	0.0	1.0	0.0	27.7	4.2E−07	3.9

Discussion

Polychlorinated biphenyls were found in the environment not only in the areas of their production and use, but also in areas where they were not used (http://chm.pops.int). A ban on the production and use of PCBs, introduced by the Stockholm Convention, was supposed to reduce the level of environmental pollution by these compounds.

In this study, we found that during the use of PCBs in the technical cycle of some industrial concerns in Perm, these pollutants were released into the environment. However, the concentration of PCBs in the soil was significantly lower than in the areas of PCB production (Orlinskii et al. 2001; Zhao et al. 2006;

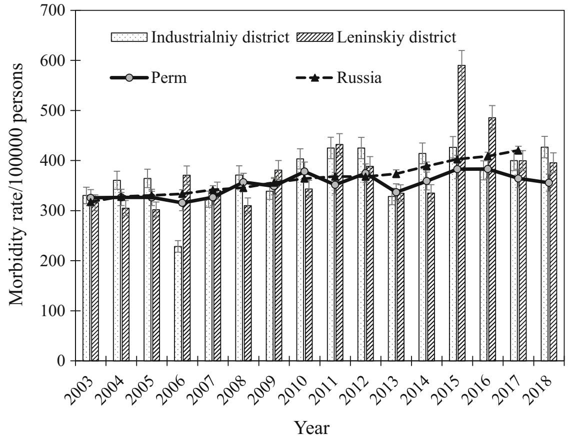

Fig. 5 Cancer morbidity rate in Perm

Ishankulov 2008; Revich and Shelepchikov 2008; Malina and Mazlova 2017). Soils of the Industrialniy District exceeded the maximum permissible level (MPL) of PCBs by 1.7 times, while soils of the Leninskiy District were at 0.5 MPL. The MPL established in Russia was equal to 60 µg PCB/kg (Kryatov et al. 2013). Furthermore, the PCB levels of the current study were lower than Australian and New Zealand ecological investigation levels and Canadian guidelines for soil (1000 µg/kg and 1300 µg/kg) (ANZECC and NHMRS 1992; CCME 2003). Analysis of the congener groups of PCBs found in the Perms, soil showed that their profile is different from the profile of the groups in Sovol, the most common commercial PCB mixture in Russia (Egorova et al. 2013). This could indicate that PCBs entered the Perm soil a few years ago and were subject to transformation by soil microflora and physicochemical processes. As part of the implementation of the Stockholm Convention in Russia, the use of PCBs was stopped at industrial concerns in the Perm. Our studies showed that these measures led to the removal of PCB from the soil of the Industrialniy and Leninskiy districts.

Table 8 Incidence of various forms of cancer in Perm and districts

	Industrialniy District	Leninskiy District	Perm
Skin			
2005	56.3	63.7	46.0
2018	89.6	85.3	63.8
Gastrointestinal tract			
2005	84.5	69.0	71.2
2018	87.9	72.7	70.4
Lung			
2005	31.3	18.2	27.4
2018	37.1	34.5	26.7
Breast			
2005	45.1	29.1	41.4
2018	76.0	53.2	74.6

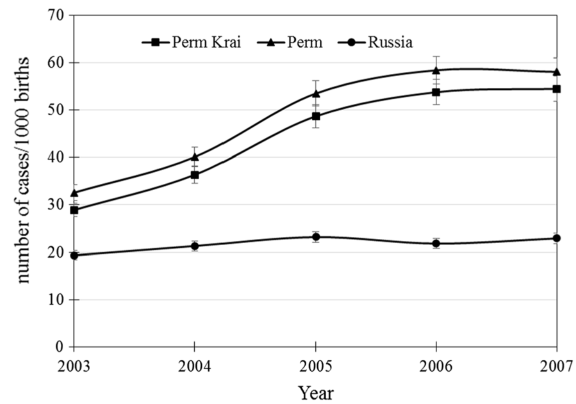

Fig. 6 Congenital malformation rate in 2003–2007, per 1000 births

A similar trend was observed in the analysis of blood contamination of pied flycatcher nestlings with polychlorinated biphenyls. In 2004–2005, the concentration of indicator PCBs in the blood of nestlings decreased from 46 to 289 ng/ml to 5.65–9.6 ng/ml, and PCBs were not detected in blood samples taken in

Table 7 Linear statistics of malignant neoplasm morbidity rate for the period 2003–2018

	Industrialniy District	Leninskiy District	Perm	Russia
Mean	371.7	376.85	350.77	363.11
standard error	13.41	18.97	5.60	8.10
median	375.75	357.1	353.55	364.2
standard deviation	53.65	75.89	22.41	31.38
level of reliability (95.0%)	28.59	40.44	11.94	17.38

2019 (Rybkin and Rybkina 2006). The PCB concentrations in this study were lower than those in passerine bird from Sweden (< 20 ng PCB/g), from different areas in China (23–720 ng/g and 1260–279000 ng/g), from USA (0.011–0.020 ng/g) (Nyholm 1998; Neigh et al. 2007; Yu et al. 2014; Mo et al. 2018). Brink and Bosveld (2001) suggested that the level of PCBs in the blood of birds might be dependent on the initial contamination of the local environment. In the present study, the correlation coefficient between the concentration of PCBs in the soils and in the blood of pied flycatcher nestlings when studying samples of 2005 and 2019, taking into account the data of 2004 (Rybkin and Rybkina 2006), was 0.99. However, we observed that indicator PCB profiles of soil samples were not similar to those of blood from nestlings (Fig. 2, Table 4). In soils samples, PCB118 was the most abundant congener, followed by PCB28 > PCB52 > PCB101 > PCB180 > PCB153 > PCB138 (Fig. 2). By contrast, in the blood of pied flycatcher nestlings, three PCB congener were the most abundant, PCB101 > PCB 28 > PCB153 (Table 4). Notably, PCB118 was the fourth most abundant indicator congener in blood serum of nestlings samples from the Industrialniy District, and only the sixth most prevalent in blood serum from nestlings in the Leninskiy District.

High-chlorinated PCBs were the most abundant components in *Ficedula hypoleuca* nestlings' samples, accounting for 68% of total PCBs (mean for all samples from Perm). A higher proportion of high-chlorinated PCB congeners has also been found in other passerine species (Yu et al. 2014; Mo et al. 2018). Penta- and heptachlorobiphenyls were the most important PCB homologues in nestlings of pied flycatcher, while hexa-chlorobiphenyls were the most abundant in insectivorous passerines in Chine (Mo et al. 2018). It has been suggested that significant accumulation of high-chlorinated PCB congeners occurs in the blood of birds due to bioaccumulation, bioamplification and biotransformation properties of this group of PCB congeners (Brink and Bosveld 2001; Weber et al. 2018).

It should be noted that the amount of PCBs found in blood serum samples from nestlings did not exceed the toxic level previously established for birds (4700 ng/g) (Hoffman et al. 1998; Iseki et al. 2001). Considering this fact, we compared the data on blood contamination with reproductive indicators of the pied flycatcher population in Perm (data on reproductive indicators not shown in this article). An inverse linear correlation was established between the level of PCB in the blood and breeding success (the ratio of the number of nestlings that flew out of the nest to the number of eggs in the clutch) for the two local bird populations. The correlation coefficient was 0.94. Thus, it could be hypothesized that the accumulated PCBs had a toxic effect on the physiological state of the nestlings, leading to their death and, consequently, a decrease in the success of breeding of the pied flycatcher in the study area. However, Neigh et al. (2007) showed that, in addition to PCBs, other factors also influence the reproductive success of passerines.

The long-term presence of polychlorinated biphenyls in the environment has a negative effect on human health (ATSDR 2000; Polychlorinated biphenyls 2018). It is known that PCBs can be the cause of the development of various types of cancer (ATSDR 2000; Liu et al. 2010; Lauby-Secretan et al. 2016). Revich et al. (2001) reported that in Chapaevsk, the malignant neoplasm morbidity rate in 1998 was 480.1 cases per 100,000 males and 350.8 cases per 100,000 females. According to statistical data in Serpukhov, in a district containing PCBs at a concentration of 1200–30,000 μg/kg dw soil, the cancer morbidity rate was 335 cases per 100,000 people; however, in a district with a lower concentration of PCBs, the malignant neoplasm morbidity rate was 165 cases per 100,000 persons (Orlinskii et al. 2001). Medical statistics for Dzerzhinsk showed 462.6 cases of cancer pathology per 100,000 people in 2009 (Dolgova and Denisenko 2010). Epidemiological research in Kazakhstan indicates there are 749.8 cases of malignant neoplasm per 100,000 people in Ablaketka (35,700–1,720,000 μg PCB/kg dw soil) (Ishankulov 2008). The results obtained in this study show that the average number of cancers in Perm and districts is lower than in PCB-contaminated cities.

PCBs that accumulate in various human tissues are the cause of cancerous changes in these organs and tissues. This study and published earlier revealed a high incidence of breast cancer in Perm (Oborin and Gavrilova 2013). These levels exceeded the average values for Perm Krai by 28.2% in 2006 and by 2.3% in 2017. In 2006, breast cancer in Perm ranked first in malignant neoplasm morbidities for women. Statistics for skin cancer in the whole of Russia in 2006 were

5.1% lower than in Perm, while for stomach cancer they were 22.9% higher.

In 2005, the cancer morbidity rate in Industrialniy District was 20.7% and 11.6% higher than in Leninskiy District and the whole of Perm, respectively (Fig. 5). Orlinskii et al. (2001) and Ishankulov (2008) found that malignant neoplasm morbidity rate has positive correlation with PCB contamination of soil. In the present study, the concentration of PCB in the soils of Industrialniy District and in the blood serum of pied flycatcher nestlings growing up in the Industrialniy District was twofold–threefold higher than for comparable samples from Leninskiy District. It has been suggested that PCB contamination could affect the level of cancer morbidity in Perm. However, the study of the long-term dynamics of PCB contaminations in Perm soil and biota and the number of cancer diseases indicate the opposite. The concentration of PCBs in the soil and blood of nestlings over the past 15 years has decreased to zero, while the incidence of cancer has increased. It is likely that environmental pollution with polychlorinated biphenyls is not in this case the main factor in the development of cancer pathologies.

PCBs are known to have a teratogenic effect on animals and humans. The average frequency of CMFs in such PCB-contaminated territory as Chapaevsk and Ablaketka was 11.8 per 1000 births for 1982–1997 and 52.1 per 1000 births for 1999–2003, respectively (Revich et al. 2001; Ishankulov 2008; Demikova and Lapina 2012). The rates of non-syndromic CMFs for European countries for 2000–2009 ranged from 9.3 per 1000 births in Portugal to 31.4 per 1000 births in Germany (Moorthie et al. 2018). In the present study, it was found that the average frequency of CMFs in Russia was at the same level as for the Netherlands and Ukraine; however, the average frequency of CMFs for Perm exceeded the maximum value for European countries by 1.5 times. It is likely that the presence of polychlorinated biphenyls in the spectrum of environmental pollutants of Perm in the period 2003–2007 influenced the occurrence of congenital malformations.

Conclusion

This study assessed the level of PCB contamination of soils and biota (pied flycatcher nestlings), and carcinogenic and teratogenic status of human population in two districts of Perm (Russia). It established that the concentration of PCBs in the soils decreased from 178 μg/kg to concentrations is below the detection limit from 2005 to 2019. In 2005, the concentration of PCBs in soils of the Industrialniy District exceeded that in soils of the Leninskiy District of Perm by four times. At the same time, the profile of contamination by congener group of PCBs in both areas was the same and indicated their long-term presence in the soil. Analysis of the concentration of PCBs in the blood of pied flycatcher nestlings, a typical inhabitant of urban parks and public gardens in Perm, showed that their concentration correlated with PCB contamination of soils and decreases from 5.65 to 9.61 ng/ml to the concentrations is below the detection limit from 2005 to 2019. In 2005, the concentration of PCBs in the blood of pied flycatcher nestlings of the Industrialniy District was higher than that in nestlings from the Leninskiy District. However, the dominant congener in the blood of nestlings was PCB101. An inverse linear correlation was established between the concentration of PCB in the blood of nestlings and success of breeding of the pied flycatcher in the study area. Epidemiological analysis revealed that cancer incidence rates in the Perm were similar to those for the country as a whole and lower than for cities with a high level of PCB contamination. It should be noted that the frequency of CMFs in Perm exceeded that for Perm Krai and for Russia as a whole. It was not possible to establish a relationship between the concentration of PCBs in soil and biota and the frequency of oncological diseases and CMFs in the city population. Nevertheless, the results of this study suggest that during the presence of PCBs in the environment, these compounds were one of the important factors affecting the health of the population and birds of the Perm.

References

ANZECC (Australian and New Zeland Environment and Conservation Council), NHMRC (National Health and Medical Research Council), ANZECC B (invironmental investigation levels) from Australian and New Zealand Guidelines for the Assessment and Management of Contaminated sites (1992).

ATSDR. (2000). *Toxicological profile for polychlorinated biphenyls (PCBs)*. Atlanta: Department of Health and Human Services, Public Health Service.

Berglund, A. M. M., Sturve, J., Förlin, L., & Nyholm, N. E. I. (2007). Oxidative stress in pied flycatcher (*Ficedula hypoleuca)* nestlings from metal contaminated environments in northern Sweden. *Environmental Research, 105,* 330–339.

Brink, N. W., & Bosveld, A. T. C. (2001). PCB concentration and metabolism patterns in common terns (*Sterna hirundo*) from different breeding colonies in the Netherlands. *Marine Pollution Bulletin, 42*(4), 280–285.

CCME (Canadian Council of Ministers of the Environment). (2003). Canadian Environmental quality Guidelines. Summary table.

Demikova, N. S., & Lapina, A. S. (2012). Congenital malformations in the regions of Russian federation: Results of monitoring in 2000–2010. *Epidemiology, 2,* 91–98.

Dolgova, S. V., & Denisenko, A. N. (2010). Structure and level of malignancy incidence in the Nizhni Novgorod region. The cancer service's state and the ways of its improvement. *Volga Cancer Herald, 4,* 10–13. **(In Russ.)**.

Egorova, D. O., Demakov, V. A., & Plotnikova, E. G. (2013). Bioaugmentation of a polychlorobiphenyl contaminated soil with two aerobic bacterial strains. *Journal of Hazardous Materials, 261,* 378–386.

Hoffman, D. J., Melancon, M. J., Klein, P. N., Eissemann, J. D., & Spann, J. W. (1998). Comparative developmental toxicity of planar polychlorinated biphenyls congeners in chickens, american kestrels and common terns. *Environmental Toxicology and Chemistry, 17*(4), 747–757.

Iseki, N., Izuka, T., Hayama, S., Masunaga, S., & Nakanishi, J. (2001). Accumulation profiles and burdens of dioxins, furans and dioxin-like PCBs in common cormorants (*Phalacrocorax carbo*), from Japan. *Organohalogen Compounds, 51,* 336–339.

Ishankulov, M. (2008). PCB-contaminated areas in Kazakhstan and analysis of PCB impact on human health experience. In E. Mehmetli & B. Koumanova (Eds.), *The fate of persistent organic pollutants in the environment* (pp. 387–403). Berlin: Springer.

ISO 10382:2002 Soil quality. Determination of organochlorine pesticides and polychlorinated biphenyls. Gas-chromatographic method with electron capture detection

IUSS Working Group WRB. (2015). World reference base for soil resources 2014, update 2015. International soil classification system for naming soils and creating legends for soil maps. *World Soil Resources Reports* No.106. FAO, Rome.

Kania-Korwel, I., & Lehmler, H.-J. (2016). Toxicokinetics of chiral polychlorinated biphenyls across different species: a review. *Environmental Science and Pollution Research, 23,* 2058–2080.

Kryatov, I. A., Tonkopiy, N. I., Ushakova, O. V., Vodyanova, M. A., Doneryan, L. G., Evseevs, I. S., et al. (2013). Regulation of safe levels of polychlorinated biphenyls in soil: Russian and international experience. *Hygiene and sanitation, 6,* 52–57.

Lauby-Secretan, B., Loomis, D., Baan, R., Ghissassi, F. E., Bouvard, V., Benbrahim-Tallaa, L., et al. (2016). Use of mechanistic data in the IARC evaluations of the carcinogenicity of polychlorinated biphenyls and related compounds. *Environmental Science and Pollution Research, 23,* 2220–2229.

Liu, S. J., Zhang, S. P., Qu, Ch., Liu, W., & Du, Y. G. (2010). The association between the environmental exposure to polychlorinated biphenyls (PCBs) and breast cancer risk and progression. *Science China. Chemistry, 53*(5), 974–979.

Mahmood, A., Syed, J. H., Malik, R. N., Zheng, Q., Cheng, Z., Li, J., et al. (2014). Polychlorinated biphenyls (PCBs) in air, soil, and cereal crops along the two tributaries of rever Chenab, Pakistan: concentrations, distribution, and screening level risk assessment. *Science of the Total Environment, 481,* 596–604.

Malina, N., & Mazlova, E. A. (2017). Temporal and spatial variation of polychlorinated biphenyls (PCBs) contamination in environmental compartments of highly polluted area in Central Russia. *Chemosphere, 185,* 227–236.

Mamontova, E. A., Tarasova, E. N., & Mamontov, A. A. (2017). PCBs and OCPs in human milk in Eastern Siberia, Russia: Levels, temporal trends and infant exposure assessment. *Chemosphere, 178,* 239–248.

Markowitz, G., & Rosner, D. (2018). Monsanto, PCBs, and the creation of a "world-wide ecological problem". *Journal of Public Health and Pollution, 39,* 463–540.

Mo, L., Zhebg, X., Sun, Y., Yu, L., Luo, X., Xu, X., et al. (2018). Selection of passerine birds as bio-sentiel of persistent organic pollutants in terrestrial environment. *Science of the Total Environment, 633,* 1237–1244.

Moorthie, S., Blencowe, H., Darlison, M. W., Lawn, J., Morris, J. K., & Modell, B. (2018). Estimating the birth prevalence and pregnancy outcomes of congenital malformations worldwide. *Journal of Community Genetics, 9,* 387–396.

Muir, D., Savinova, T., Savinov, V., Alexeeva, L., Potelov, V., & Svetochev, V. (2003). Bioaccumulation of PCBs and chlorinated pesticides in seals, fishes and invertebrates from the White Sea, Russia. *The Science of the Total Environment, 306,* 111–131.

Neigh, A. M., Zwiernik, M. J., Joldersma, C. A., Blankenship, A. L., Strause, K. D., Millsap, S. D., et al. (2007). Reproductive success of passerines exposed to polychlorinated biphenyls through the terrestrial food web of the Kalamazoo River. *Ecotoxicology and Environmental Safety, 66,* 107–118.

Nyholm, N. E. I. (1998). Influence of heavy metal exposure during different phases of the ontogeny on the development of pied flycatcher, *Ficedula hypoleuca*, in natural populations. *Archives of Environmental Contamination and Toxicology, 35,* 632–637.

Oborin, M. S., & Gavrilova, I. N. (2013). Ecological situation region as indicator of the condition of quality of the population (on an example of Perm region). *Bulletin of RUDN. Series Ecology and Safety of Vital Functions, 1,* 22–29.

Orlinskii, D., Priputina, I., Popova, A., Shalanda, A., Tsongas, T., Hinman, G., et al. (2001). Influence of environmental contamination with PCBs on human health. *Environmental Geochemistry and Health, 23,* 317–332.

Polder, A., Gabrielsen, G. W., Odland, J. Ø., Savinova, T. N., Tkachev, A., Løken, K. B., et al. (2008). Spatial and temporal changes of chlorinated pesticides, PCBs, dioxins (PCDDs/PCDFs) and brominated flame retardants in human brest milk from Northern Russia. *Science of the Total Environment, 391,* 41–54.

Polychlorinated biphenyls. (2018). https://monographs.iarc.fr/wp-content/uploads/2018/06/mono107-001.pdf. Accessed 25 Mart 2019.

Revich, B., Aksel, E., Ushakova, T., Ivanova, I., Zhuchenko, N., Kluev, N., et al. (2001). Dioxin exposure and public health in Chapaevsk, Russia. *Chemosphere, 43,* 951–966.

Revich, B., & Shelepchikov, A. (2008). Persistent organic pollutants (POPs) hot spots in Russia. In E. Mehmetli & B. Koumanova (Eds.), *The fate of persistent organic pollutants in the environment* (pp. 113–126). Berlin: Springer.

Robertson, L. W., & Hansen, L. G. (2001). *PCBs: Recent advances in environmental toxicology and health effects* (p. 461). Lexington: University Press of Kentucky.

Rybkin, A. V., & Rybkina, D. O. (2006). Levels of organochlorine contaminants in the blood of *Pied flycatxths* (*Ficedula hypoleuca*) in a big industrial center. *Povolzhskiy Journal of Ecology, 1,* 51–60.

Salvador, R. B., Van der Jeugd, H., & Tomotani, B. M. (2017). Taxonomy of the European Pied Flycatcher Ficedula hypoleuca (Aves: Muscicapidae). *Zootaxa, 4291*(1), 171–182.

Soil Science Division Staff. (2017). Soil survey manual. In C. Ditzler, K. Scheffe, & H. C. Monger (Eds.), *USDA handbook 18*. Washington, D.C.: Government Printing Office.

Weber, R., Herold, C., Hollert, H., Kamphues, J., Blepp, M., & Ballschmiter, K. (2018). Reviewing the relevance of dioxin and PCB sources for food from animal origin and the need for their inventory, control and management. *Environmental Sciences Europe, 30,* 42.

Yu, L.-H., Luo, X.-J., Liu, H.-Y., Zeng, Y.-H., Zheng, X.-B., Wu, J.-P., et al. (2014). Organohalogen contamination in passerine birds from three metropolises in China: Geographical variation and its implication for anthropogenic effects on urban environments. *Environmental Pollution, 188,* 118–123.

Zhao, X., Zheng, M., Zhang, B., Zhang, Q., & Liu, W. (2006). Evidence for the transfer of polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins, and polychlorinated dibenzofurans from soil into biota. *Science of the Total Environment, 368,* 744–752.

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