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Biomonitoring of 89 POPs in blood serum samples of Czech city policemen

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ABSTRACT

In this biomonitoring study, we evaluated the concentrations of 8 polychlorinated biphenyls (PCBs), 11 organochlorinated pesticides (OCPs), 33 brominated flame retardants (BFRs), 7 novel brominated and chlorinated flame retardants (novel FRs) and 30 per- and polyfluoroalkylated substances (PFAS) in human serum samples (n = 274). A total of 89 persistent organic pollutants (POPs) were measured in blood serum samples of city policemen living in three large cities and their adjacent areas (Ostrava, Prague, and Ceske Budejovice) in the Czech Republic. All samples were collected during the year 2019 in two sampling periods (spring and autumn). The identification/quantification of PCBs, OCPs, BFRs, novel FRs and PFAS was performed by means of gas chromatography coupled to (tandem) mass spectrometry (GC–MS/(MS)) and ultra-high performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry (UHPLC–MS/MS). The most frequently detected pollutants were perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluorooctanesulfonate (PFOS), perfluorohexanesulfonate (PFHxS), 2,2′,3,4,4′,5′-hexachlorobiphenyl (CB 138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (CB 153), 2,2′,3,3′,4,4′,5-heptachlorobiphenyl (CB 170), 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (CB 180), hexachlorobenzene (HCB), and *p,p'*-dichlorodiphenyldichloroethylene (*p,p'*-DDE) quantified in 100% of serum samples. In the serum samples, the concentrations of determined POPs were in the range of 0.108–900 ng g^{-1} lipid weight (lw) for PCBs, 0.106–1016 ng g^{-1} lw for OCPs, <0.1–618 ng g^{-1} lw for FRs and <0.01–18.3 ng mL^{-1} for PFAS, respectively. Locality, sampling season, and age were significantly associated with several POP concentrations. One of the important conclusions was that within the spring sampling period, statistically significant higher concentrations of CB 170 and CB 180 were observed in the samples from Ostrava (industrial area) compared to Prague and Ceske Budejovice. Older policemen had higher concentrations of five PCBs and two OCPs in blood serum.

1. Introduction

Blood (including plasma, serum and specific blood components – e.g., lymphocytes) represents one of the most important and commonly used biological material for determining the levels of various biomarkers including the persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), brominated flame retardants (BFRs), novel brominated and chlorinated flame retardants (novel FRs), and per- and polyfluoroalkylated substances (PFAS) (Alves et al., 2014; Angerer et al., 2007; Luque et al., 2012). Biomonitoring studies require accurate and sensitive quantitative measurements of POPs in blood in order to study the relationship between an individual's exposure to these pollutants and their effects on health (Hao et al., 2020).

POPs are listed in the Stockholm Convention for their persistence, potential toxic properties, bioaccumulation, and long-range atmospheric transport ability ("Listing of POPs in the Stockholm Convention," n.d.). However, the main problem is their tendency to accumulate in

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the environment for a long time, and despite the ban or restriction on their use, they are still detected in various environmental compartments including living organisms (Alves et al., 2014). Overall, POPs may be hazardous to human health; as an increasing number of epidemiological studies have demonstrated, POP exposure is associated with a number of negative effects such as neurotoxicity, disruption of thyroid function and male reproductive hormones, and declining sperm quality (in terms of concentration, viability, morphology and motility) (Chen et al., 2011; Foster Warren G. et al., 2010; Y. Yu et al., 2020; Zheng et al., 2017). Contrary to the classic POPs, PFAS do not tend to accumulate in lipids, but rather create a strong bond to protein fractions in blood (Jian et al., 2018; Sochorová et al., 2017). Nowadays, PFAS are a constantly emerging issue, mainly because of their bioaccumulation, potential to expand into almost all parts in the ecosystem and the possible negative effects on human health (e.g., allergic disease, endocrine dysfunction, hepatotoxicity, cardiovascular and kidney diseases, low birth weight of newborns and decreased enzyme activity) (Geiger et al., 2014; Lee et al., 2018; Motas Guzmàn et al., 2016; Verner Marc-André et al., 2015). A number of human epidemiological studies provides strong support for the causal associations between exposure to perfluorooctanesulfonate (PFOS)/perfluorooctanoic acid (PFOA) and increased serum cholesterol in adults (Knutsen et al., 2018). In general, human exposure to PFAS is primarily through food intake (fish, seafood, crops, and food packaging), environmental sources, and drinking water. PFAS can easily accumulate in the human body, which is caused by a slow elimination rate and biodegradability of long-chained PFAS (Cui et al., 2020).

Human biomonitoring focuses on the analysis and distribution of pollutants and their metabolites in the human body and related diseases. Regarding human biological samples, studies have monitored a number of POPs in maternal serum, umbilical cord serum, urine, amniotic fluid, seminal fluid, cerebrospinal fluid, and breast milk (Cabrera-Rodríguez et al., 2019; Cui et al., 2020; Kubwabo et al., 2013; Luzardo et al., 2009; McComb et al., 2019; Raymer et al., 2012; Zhang et al., 2018). In addition, POP concentrations in serum may represent an indicator of their circulation through all organs in the human body, and samples can be collected from the entire population, unlike, e.g. breast milk (only from pregnant women). It needs to be emphasized that serum collection is limited by the required volume, especially if infants are studied. Moreover, classic POPs are detected at trace levels in serum compared to adipose tissue. Therefore, a high throughput extraction method using a small volume of serum sample is needed in a combination with a method of instrumental analysis that detects trace amounts of POPs with high accuracy (Artacho-Cordón et al., 2015b; Lee et al., 2020a; Ploteau et al., 2016).

The presented research was conducted within the frame of a project "Healthy Aging in Industrial Environment" (HAIE), which evaluates the effects of selected environmental and lifestyle risk factors on the health and aging of the population in the industrial region. Currently, there is no published study in Europe which has focused on the investigation of such a wide range of POP in blood serum samples obtained from an not yet described population group of city policemen. The main objectives of this study were to evaluate the concentrations of 89 POPs in the serum samples collected in 2019 from 142 city policemen residing in three cities of the Czech Republic (Prague, Ostrava, and Ceske Budejovice) and to evaluate how the POP concentrations were related to locality and age.

2. Materials and methods

2.1. Sample collection

A total of 274 human serum samples were provided within the HAIE research programme (2018–2022). The samples were collected from the same city policemen in two rounds in 2019, spring (February/March; n = 142) and autumn (September/October; n = 132; 10 serum donors did not participate in the second period), living in three cities and their adjacent areas in the Czech Republic (Prague, Ostrava and Ceske Budejovice). The collection of human samples was approved by the Ethics Committee of the Institute of Experimental Medicine of the Czech Academy of Sciences before the start of the HAIE project. All participants of these surveys signed an informed consent.

Table 1
Characteristics of the city policemen in the study.

Variable/Sampling region	Ostrava	Ceske Budejovice	Prague
Number of samples (spring/autumn period)	56/53	18/17	68/62
Personal information			
Age (years) Mean (min-max)	40 (21–61)	38 (22–48)	40 (23–63)
Weight (kg) Mean (min-max)	93 (59–145)	94 (75–130)	93 (67–121)
Height (cm) Mean (min-max)	181 (170–195)	183 (176–190)	181 (168–195)
Body mass index BMI (kg/m^2) Mean (min-max)	28.5 (20.4–44.8)	28.1 (23.1–41.0)	28.5 (19.4–39.1)
Previous smoking (yes/no)	15/41	5/13	20/48
Education level			
Secondary	49	15	52
University	7	3	16

Prague is the capital and the largest city of the Czech Republic and is therefore considered the most densely populated area (1 335 000 inhabitants) in this country, with a high level of traffic. Ostrava, with its 290 000 residents, is the third largest city of the Czech Republic. Thanks to its historical consequences in heavy industry and coal mining (the last coal mining ended in 1994), it is also known as the most industrial area. At present, Nova Hut (known as Liberty Ostrava), which deals with metallurgy and mechanical engineering, is the largest industrial contributor to environmental pollution, but it has undergone a major modernization. The main causes of environmental pollution in this region can be transport, and rather than industrial character, it is a geographical influence, where pollutants may penetrate from neighbouring Poland most often in inverse weather. Ceske Budejovice is an urban residential area with agriculture and 94 000 inhabitants. The industrial burden in this city is the lowest in comparison with Prague and Ostrava.

All participants (age: 21–63) had been residents in the selected localities for at least five years. Each participant filled a detailed questionnaire describing the exposure and lifestyle. More details about the main characteristics of the city policemen are summarized in Table 1.

2.2. Standards, chemicals and other materials

Methanol, dichloromethane, diethylether, *n*-hexane, isooctane, and sulphuric acid (98%) were supplied by Merck (Germany). Acetonitrile and anhydrous magnesium sulphate (98%) were obtained from Sigma-Aldrich (USA); acetone and sodium chloride (99.9%) from Penta (Czech Republic). Polypropylene centrifuge tube filters (nylon, pore size 0.22 μm) were purchased from Sigma-Aldrich. Florisil® for residual analysis (0.15–0.25 mm) supplied by Merck was activated by heating at 600 °C for 4 h, then at 130 °C for 5 h followed by storage in a desiccator.

The characteristics of all target analytes (full name of the compound, abbreviation, concentration, CAS number and other information) and the preparation of calibration/working standards and solutions are described in Tables S1 and S2, respectively, in the Supplementary material. The individual standards of 30 PFAS were obtained from Wellington Laboratories (Guelph, Ontario, Canada). Standards of BFRs, including 16 PBDE congeners, 4 hydroxylated PBDEs (OH-PBDEs), TBBPA, HBCD isomers (α-, β- and γ-), and other BFRs (PBT, PBEB, HBB, BTBPE, OBIND, and DBDPE), were supplied by Wellington Laboratories. The brominated phenols together with seven novel FRs (DBE-DBCH, *syn*-

Table 2
Concentrations of PCBs, OCPs, BFRs, and PFAS in blood serum samples of city policemen (n = 274).[a,b,c]

	1. Round – spring 2019 (n = 142)						2. Round – autumn 2019 (n = 132)					LOQ
	Analyte	Samples > LOQ (%)	Mean	Median	Min-max	5–95% Percentile	Samples > LOQ (%)	Mean	Median	Min-max	5–95% Percentile	
ng mL^{-1}	**PFBA**	89	0.020	0.020	<0.01–0.332	0.005–0.058	88	0.023	0.023	<0.01–0.475	0.005–0.084	0.01
	PFHpA	81	0.017	0.016	<0.01–0.119	0.005–0.061	77	0.016	0.015	<0.01–0.197	0.005–0.058	0.01
	PFOA	100	0.810	0.934	0.081–2.60	0.166–1.93	100	0.871	1.00	0.075–2.90	0.160–2.10	0.01
	PFNA	100	0.323	0.342	0.034–2.07	0.082–0.810	100	0.361	0.383	0.036–3.00	0.079–0.944	0.01
	PFDA	100	0.150	0.162	0.025–0.554	0.054–0.365	100	0.177	0.178	0.031–0.719	0.056–0.525	0.01
	PFUdA	99	0.059	0.064	<0.01–0.184	0.023–0.148	100	0.060	0.057	0.014–0.322	0.021–0.179	0.01
	PFDoA	62	0.012	0.012	<0.01–0.093	0.005–0.047	55	0.011	0.011	<0.01–0.256	0.005–0.049	0.01
	PFTrDA	34			<0.01–0.062	0.005–0.027	31			<0.01–0.094	0.005–0.026	0.01
	PFHxS	100	0.379	0.436	0.043–1.73	0.077–0.915	100	0.398	0.459	0.044–1.79	0.085–0.908	0.01
	PFHpS	94	0.074	0.089	<0.01–0.565	0.005–0.218	92	0.060	0.076	<0.01–0.380	0.005–0.177	0.01
	PFOS	100	2.59	2.66	0.259–16.6	0.551–7.27	100	2.66	2.94	0.237–18.3	0.591–7.06	0.01
ng g^{-1} lw	**CB 28**	58	0.406	0.668	<0.1–7.28	0.050–5.37	61	0.272	0.399	<0.1–7.00	0.050–2.26	0.1
	CB 52	26			<0.1–0.931	0.050–0.508	31			<0.1–3.31	0.050–0.830	0.1
	CB 101	54	0.229	0.331	<0.1–4.09	0.050–1.58	20			<0.1–3.26	0.050–1.27	0.1
	CB 118	93	2.75	3.45	<0.1–18.7	0.050–8.38	97	3.46	3.85	<0.1–17.5	1.31–10.7	0.1
	CB 138	100	28.7	29.9	5.16–219	8.88–99.2	100	45.5	45.9	4.58–280	10.8–144	0.1
	CB 153	100	65.8	64.8	10.1–548	18.0–226	100	77.8	79.3	10.2–567	19.8–257	0.1
	CB 170	100	38.8	37.5	5.60–387	11.1–141	100	30.3	30.8	4.10–227	8.33–94.7	0.5
	CB 180	100	92.2	94.0	10.4–900	28.3–322	100	86.3	91.3	9.29–717	22.9–309	0.5
	HCB	100	17.4	18.1	2.74–63.4	7.45–44.9	100	15.7	15.5	4.54–68.7	6.28–43.4	0.1
	***α*-HCH**	32			<0.1–7.66	0.050–3.28	1			<0.1–0.573	0.050–0.050	0.1
	***β*-HCH**	75	1.57	3.68	<0.1–19.3	0.050–13.5	44			<0.1–31.3	0.050–19.7	0.1
	***γ*-HCH**	32			<0.1–3.74	0.050–1.33	11			<0.1–29.2	0.050–3.81	0.1
	***p,p′*-DDE**	100	103	101	20.7–1016	35.8–326	100	129	123	22.7–997	41.2–416	0.1
	***p,p′*-DDD**	82	0.691	1.01	<0.1–11.9	0.050–3.83	92	1.09	1.34	<0.1–25.9	0.050–4.28	0.1
	***p,p′*-DDT**	51	1.38	2.97	<0.5–90.5	0.250–12.9	27			<0.5–101	0.250–11.4	0.5
	BDE 47	83	1.38	2.09	<0.1–29.8	0.050–18.9	99	1.65	1.67	<0.1–14.1	0.914–3.08	0.1
	BDE 209	44			<1.5–459	0.750–14.3	21			<1.5–618	0.750–230	1.5

[a] Median and geometric mean values were calculated when in >50% of samples analyte was positively detected in a concentration above LOQ.
[b] For results below LOQ, one-half the LOQ value was used.
[c] PFAS: FOSA, N-MeFOSA, N-EtFOSA, PFDS, PFPeA, PFHxA, PFHxDA, PFODA, PFPrS, PFNS, PFDoS, HFPO-DA, NaDONA, 11Cl-PF3OUdS and PFTeDA, PFBS, PFPeS, 9Cl-PF3ONS were quantified in 0–2 and 1–19% of samples, respectively; OCPs: *o,p′*-DDD, *o,p′*-DDT and *δ*-HCH were quantified in 3–8% and in 0% of samples, respectively; BFRs and novel FRs: BDE 49, BDE 66, BDE 85, BDE 100, BDE 154, BDE 183, BDE 196, BDE 197, BDE 203, BDE 207, DBDPE, EH-TBB, syn-DP and BDE 99, BDE 153, anti-DP were detected in 0–7% and 5–33% of samples, respectively; BDE 28, BDE 206, BTBPE, *α*-HBCD, *β*-HBCD, *γ*-HBCD, TBBPA, HBB, OBIND, PBEB, PBT, DPTE, HCDBCO, TBCO, DBE-DBCH, 2,4-DBP, 2,4,6-TBP, PBP, OH-PBDEs were not detected in any sample.

DP, *anti*-DP, DPTE, EH-TBB, HCDBCO and TBCO) were obtained from AccuStandard (New Haven, CT, USA). The individual standards of PCBs (No. 65, 166, 118, and 170, a standard mixture of PCB-MIX 1 with 6 PCB congeners (No. 28, 52, 101, 138, 153, and 180), and 11 OCP standards were supplied by Dr. Ehrenstorfer (Augsburg, Germany). Internal standards of BFRs and isotopically labelled internal standards of PFAS were purchased from Wellington Laboratories. The purity of all standards was at least 97%.

The human blood serum used for the validation experiments was obtained from Sigma-Aldrich. Standard reference material of fortified human blood serum SRM 1958 was supplied by the National Institute of Standards and Technology (NIST, Gaithersburg, Maryland, USA).

2.3. Sample preparation procedure

The sample preparation procedure used for serum analysis was fully described in detail in our earlier study reported by Svarcova et al. (2019) and summarized in the Supplementary material. Briefly, non-polar compounds (PCBs, OCPs, PBDEs, and novel FRs) were isolated from a human blood serum (3 g) using a triple extraction into a mixture of *n*-hexane:diethylether (9:1; *v/v*), followed by purification using solid-phase extraction on a hand-made Florisil® column. For the isolation of more polar and lipophobic (PFASs, OH-PBDEs, HBCDs, TBBPA and brominated phenols) analytes, the remaining fraction was extracted into the acetonitrile with the support of added inorganic salts (sodium chloride and magnesium sulphate).

2.4. Instrumental analysis

The determination of OCPs, PCBs, novel FRs, and BFRs (PBDEs, BTBPE, DBDPE, DBE-DBCH, *anti*-DP, *syn*-DP, DPTE, EH-TBB, HBB, HCDBCO, OBIND, PBEB, PBT, and TBCO) was performed using an Agilent 7890A GC gas chromatograph (Agilent Technologies, USA), coupled to an Agilent 7000C MS triple quadrupole mass spectrometer (Agilent Technologies, USA), operated in the electron ionisation (EI) mode for OCPs and PCBs and negative chemical ionisation (NCI) mode for PBDEs and novel FRs. For the OCPs and PCBs separation, a capillary column DB-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness; Agilent Technologies, USA) was used. In the case of BFR and novel FR analysis, a DB-XLB capillary column (15 m × 0.25 mm i.d. × 0.1 μm film thickness; Agilent Technologies, USA) was applied. For more information about the other parameters of GC-MS analysis, see the studies published by Kalachova et al. (2013a), (2013b) and Svarcova et al. (2019).

The ultra-high performance liquid chromatography coupled to tandem MS (UHPLC-MS/MS) was used for the analysis of PFAS, OH-PBDEs, HBCDs, TBBPA, and brominated phenols. An Agilent 1290 Infinity II LC system interfaced with a mass spectrometer Agilent Triple Quadrupole G6495A (Agilent Technologies, USA), operated in the multiple reaction

Table 3
Overview of current studies (2016–2020) dealing with PFAS, PCB and OCP median concentrations in human serum samples collected worldwide.

A) PFAS median concentrations (ng mL-1) in human blood serum.[a,b,c]

			PFAS (ng mL^{-1})				
Country	Year of sampling	Number of samples	PFOS	PFOA	PFNA	PFHxS	References
Faroe Islands	2007–2008	51	5.59	1.00	0.76	0.50	Hu et al. (2018)
Denmark	2008–2013	1533	8.28	2.02	0.76	0.48	Bjerregaard-Olesen et al. (2016)
Sweden	2007–2010	1616	5.30	1.60	0.52	1.20	Shu et al. (2018)
	2007–2010	1533	5.38	1.61	0.53	1.23	Wikström et al. (2020)
	2011–2014	603	9.4[a]	2.8	1.1	7.5	Stubleski et al. (2016)
Belgium	2008–2009	201	12.6	3.50	0.87	1.61	Colles et al. (2020)
Norway	2007–2008	99	5.52	1.06	0.28	0.25	Papadopoulou et al. (2016)
	2010–2011	495	6.58	1.87	0.47	0.59	Averina et al. (2018)
	2013–2014	61	5.24	1.90	0.94	0.78	Poothong et al. (2020)
Czech Republic	2015	300	2.43	0.756	0.325	0.184	Sochorová et al. (2017)
	2019 (spring)	142	2.66	0.934	0.342	0.436	Presented study
USA	2009–2016	450	3.20	1.07	0.50	0.30	Kim et al. (2020)
	2011–2015	1257	7.07	2.47	0.909	1.58	Hurley et al. (2018)
	2013–2014	458	3.75	1.94	0.700	0.810	Ye et al. (2018)
	2014–2016	123	3.72	1.81	0.61	0.67	Trasande et al. (2017)
	2016	45	23.4[b]	11.7[b]	0.8[b]	7.7[b]	Worley et al. (2017)
	2016–2018	1030	3.04	2.01	0.78	1.22	Yu et al. (2020a)
China	2009	60	16.0	3.00	1.1	2.5	Liu et al. (2020)
	2014	45	20.1	17.0	2.04	0.45	Wu et al. (2017)
	2015	39	9.24	1.96	0.76	0.50	Wang et al. (2018)
	2015–2016	132	4.07	2.21	0.57	0.24	Gao et al. (2019)
	2015–2018	424	4.32	0.99	0.42	0.16	Cai et al. (2020)
	2017	252	14.2	14.8	3.17	0.33	Duan et al. (2020)
	2017	15	13.9[c]	3.59[c]	0.45[c]	10.7[c]	Gao et al. (2018)
	2018	85	4.90	2.80	1.30	0.50	Jin et al. (2020)
South Korea	2009–2010	1874	10.2[b]	2.85[b]	N/A	N/A	Lee et al. (2017)
Japan	2009–2010	339	4.50	2.10	1.80	0.46	Nakayama et al. (2020)
Saudi Arabia	2017–2018	108	5.30	1.03	0.50	1.48	Banjabi et al. (2020)
Australia	2002–2013	29	4.40[c]	2.90[c]	0.55[c]	2.50[c]	Eriksson et al. (2017)
	2016–2017	2400	5.71[c]	1.84[c]	0.47[c]	2.11[c]	Toms et al. (2019)
New Zealand	2011–2013	63	3.40[b]	2.40[b]	0.66[b]	1.0[b]	Coakley et al. (2018)

B) PCB and OCP median concentrations (ng g^{-1} lw) in human blood serum.[a,b,c]

			PCBs (ng g^{-1} lw)			
Country	Year of sampling	Number of samples	CB 138	CB 153	CB 180	References
Spain	2006	322	48.3	122	63.4	Zubero et al. (2017)
	2013	127	4.07	10.7	13.0	Zubero et al. (2017)
Italy (highly polluted area)	2013–2014	816	53.5	93.5	118	Zani et al. (2019)
Belgium	2015	252	ND	53.8	41.1	Pirard et al. (2018)
Czech Republic	2015	38	71	137	158	Svarcova et al. (2019)
	2019 (spring)	142	29.9	64.8	94.0	Presented study
USA	2016–2018	1000	7.45[a]	10.7[b]	7.68[b]	Du et al. (2020)
China	2016–2017	High/low exposure group (n = 38/38)	22.7/6.81	22.5/8.08	19.2/3.92	Yu et al. (2020b)
Korea	1994–2013	151	5.00	10.2	6.95	Moon et al. (2017)
	2011	148	4.67	9.80	ND	Choi et al. (2018)
	2019	25	2.87[c]	4.18[c]	2.72[c]	Lee et al. (2020a, 2020b)
Lebanon	2013–2015	316	8.20	16.4	24.1	Helou et al. (2019)
Iran	2016–2017	300	69.4	159	108	Karimi et al. (2020)

OCPs (ng/g lipid weight)						
Country	**Year of sampling**	**Number of samples**	**HCB**	***p,p′*-DDE**	***p,p′*-DDT**	**References**
Czech Republic	2015	38	29.6	207	13.5	Svarcova et al. (2019)
	2019 (spring)	142	18.1	101	2.97	Presented study
Korea	1994–2013	151	–	101	7.73	Moon et al. (2017)
	2011	147	4.13	63.4	5.31	Choi et al. (2018)
	2019	25	6.10[c]	36.3[c]	3.65[c]	Lee et al. (2020a, 2020b)
China	2014	1923	190	444	11.4	Wang et al. (2017)
Lebanon	2013–2015	316	5.80	15.1	15.6	Helou et al. (2019)
Iran	2016–2017	300	ND	22.4	18.6	Karimi et al. (2020)
Australia	2012–2013	2400	5.60	129	4.30	Thomas et al. (2017)
Russia	2012–2018	152	150	275	–	Abou Ghayda et al. (2020)

NOTES: [a] L-PFOS; [b] Geometric mean; [c] Mean.
NOTES: Not mentioned; ND not detected; [a] CB 138 + CB 158; [b] Geometric mean; [c] Mean.

monitoring mode (MRM) using electrospray ionisation in a negative mode (ESI) was employed. Target analytes were separated on an Acquity UPLC BEH C18 analytical column (100 mm × 2.1 mm i.d., 1.7 μm particle size, Waters, USA). The mobile phase consisted of A) 5 mM ammonium acetate in 20% acetonitrile in deionised water and B) 20% acetonitrile in methanol. Measurement conditions are described in detail in the study (Lankova et al., 2015) and in Table S3 in the Supplementary material.

2.4.1. Quality control and validation

To monitor background contamination, a procedural blank (deionised water was used instead of serum) was prepared together with each batch of 20 samples. When POP concentrations were determined in the procedural blank (the values centred around the limits of quantitation (LOQs)), the procedural blank was subtracted from the detected concentrations in the respective sample batch. LOQs were estimated as the lowest calibration standard with the signal to noise ratio (S/N) > 10 for the quantitative transition (ion), and S/N > 3 for at least one confirmation transition (ion). To compensate the unexpected matrix effects mainly in the GC injector, the standards of PCBs (CB 65 and CB 166) and BFRs (BDE 37, 77 and $^{13}C_{12}$-BDE 209) were used. To monitor the correction of possible matrix effects in the ion source of LC-MS system and the extraction efficiency (recovery of analytes), isotopically labelled surrogates ($^{13}C_{12}$-PFAS, $^{13}C_{12}$-TBBPA, and $^{13}C_{12}$-HBCDs) were applied.

The validation of the analytical method for the analysis of 78 organohalogenated contaminants and newly added 11 PFAS (PFHxDA, PFODA, PFPrS, PFPeS, PFHpS, PFNS, PFDoS, HFPO-DA, NaDONA, 9Cl-PF3ONS, and 11Cl-PF3OUdS) in human blood serum is described in detail in our previous study (Svarcova et al., 2019) and in the Supplementary material.

2.5. Lipid content determination

The resulting concentrations of non-polar POPs (OCPs, PCBs, novel FRs, PBDEs, and other BFRs) are commonly expressed on a lipid weight (lw) basis. Due to the very low lipid content in blood serum, it is not possible to determine its amount gravimetrically, and it is necessary to use a more accurate enzymatic method. The determination of the total lipid content is performed by the measurement of individual lipid classes, such as triacylglycerols and cholesterol in mmol L^{-1}, which are then converted to g l^{-1} according to the equations mentioned in the studies reported by Covaci et al. (2006) and Rugge et al. (2011).

2.6. Statistical analyses

All statistical analyses were performed in Metaboanalyst (metboanalyst.ca) or using custom built R-scripts. Only analytes with concentrations above LOQs in 50% and more samples were used for further statistical evaluation. Analysis of Variance (ANOVA) followed by Tukey's post hoc tests and paired t-tests were used to evaluate different levels of contaminants between localities and sampling time, respectively. For significantly differing analytes (p-value < 0.05), fold changes were calculated using the group's median concentrations. Additionally, Spearman's rank correlation coefficient was calculated to confirm a trend of increasing intensity between age groups. Logarithmic transformation was used prior any univariate statistical test to ensure normal distribution of the data.

3. Results and discussion

3.1. POPs in blood serum samples

The results of 89 POP concentrations (geometric mean, median, minimum and maximum, 5–95% percentile, and the number of positive samples) measured in the serum samples from both sampling periods and three residential areas are summarized in Table 2. The lipid content reached 0.27–1.47% (*w/w*) with a mean value of 0.58%. The most abundant contaminants were PFOA, PFNA, PFDA, PFOS, PFHxS, CB 138, CB 153, CB 170, CB 180, HCB, and *p,p′*-DDE quantified in all samples, followed by PFUdA, PFHpS, PFBA, PFHpA, PFDoA, CB 28, CB 101, CB 118, *β*-HCH, *p,p′*-DDD, and *p,p′*-DDT found in >50% of serum samples. As the values of POP concentrations in both periods are very similar, only the spring period with all participants will be further discussed.

Selected PFAS, PCB, and OCP concentrations in serum samples from the most recent papers (2016–2020) are summarized in Table 3.

PFAS belonged to the dominant group of more polar contaminants in human blood serum. The total concentrations of all detected ∑PFAS ranged from 0.516 to 22.2 ng mL^{-1} (mean 5.54 ng mL^{-1}, median 4.93 ng mL^{-1}). The highest concentrations were determined for PFOS (median 2.66 ng mL^{-1}), followed by PFOA (median 0.934 ng mL^{-1}), PFHxS (median 0.436 ng mL^{-1}) and PFNA (median 0.342 ng mL^{-1}). The medians of PFOA, PFNA, PFHxS, and PFOS from our study are comparable with the only data obtained within the similar Czech study (Sochorová et al., 2017). Moreover PFOA concentration in serum samples obtained from men were lower compared to women (Sochorová et al., 2017). Higher concentrations of PFOA in serum were observed in the elderly population (50–65 years of age) and in the population with higher education, however this trend has not been seen in our study (p-value > 0.05). A contributor to higher levels of PFOA may also be the higher intake of dairy products and milk (Sochorová et al., 2017).

In general, as documented in Table 3, the concentrations of PFOA, PFNA, PFHxS, and PFOS in serum of Czech population are the lowest in comparison with the other countries in Europe. The reason may be that these compounds have never been produced in the Czech Republic. Compared to studies from China (Duan et al., 2020; Wu et al., 2017) and USA (Worley et al., 2017), our results are approximately seven times lower for PFOS and sixteen times lower for PFOA. These levels, which are among the highest (median PFOS: 20.1 ng mL^{-1} and PFOA: 17.0 ng mL^{-1}), were detected in serum samples from Shanghai (sampling of 2014), which is one of the most populous and largest cities in China, where these substances are still produced. A polluted environment also contributes to these high levels (Wu et al., 2017). Higher serum PFOS (3–5 times) and PFOA (3–17 times) levels were found within the recent studies from Belgium (Colles et al., 2020), China (Duan et al., 2020; Gao et al., 2018; Liu et al., 2020) and South Korea (Lee et al., 2017). The serum concentration values of PFOS and PFOA detected in the Belgian study were four times higher compared to our results. Nevertheless, within five years Belgium has announced a decrease in PFOS concentrations (median: 7.58 ng mL^{-1}) by about a half, but PFOA levels (median: 2.94 ng mL^{-1}) are almost unchanged (Colles et al., 2020). In the USA, where these substances were produced on a large scale until about 2002 by 3M Company, a declining trend like in Europe is evident. If we compare the values in the studies from 2011 to 2015 and 2016–2018, the decrease in PFOS amounts is approximately two and a half times. This declining trend can be explained by the overall decline in PFOS concentrations in the general U.S. population (Kato et al., 2011) and blood donors (Olsen et al., 2017) due to the termination of PFOS production in the USA since 2000 (Hurley et al., 2018; C. H. Yu et al., 2020). A study reported by Post et al. (2017) indicated, that ongoing exposures to even relatively low drinking water concentrations of long-chain perfluoroalkyl acids (PFAAs) including PFOA, PFOS, PFNA and PFHxS substantially increase human body burdens, which remain elevated for many years after elimination of possible exposure sources.

The concentrations of non-polar POPs found in previous studies performed in the Czech Republic reached higher concentrations in comparison with other EU countries, thus one of the aim of present study was to confirm that the exposure to these contaminants continues to decline gradually. The obtained results confirmed the predominance of highly chlorinated PCB congeners (No. 138, 153, 170, and 180), which were also detected at the highest levels (median CB 138: 29.9 ng g^{-1} lw; CB 153: 64.8 ng g^{-1} lw; CB 170: 37.5 ng g^{-1} lw, and CB 180: 94.0 ng g^{-1} lw). The total concentrations of targeted ∑8PCBs reached the values of 34.1–2075 ng g^{-1} lw (mean 310 ng g^{-1} lw, median 226 ng g^{-1} lw). In general the indicator PCBs (No. 138, 153, and 180) are commonly found in serum at the highest levels worldwide, therefore they were selected as the main PCB representatives and their concentrations are further compared. As shown in Table 3, the current results of selected PCB congeners are twice as low compared to the previous study (Svarcova et al., 2019). It can be claimed that PCB concentrations in the serum of Czech population are rather high compared to other countries. This means that our values of CB 138, CB 153 and CB 180 detected in serum

samples were approximately 2–13 times higher compared to all other studies from Europe (Zubero et al., 2017); (Esposito et al., 2014); (Kalantzi et al., 2011), USA (Du et al., 2020), China (Moon et al., 2017; Y. Yu et al., 2020b), Korea (Choi et al., 2018; Moon et al., 2017), Lebanon (Helou et al., 2019) and Tunisia (Hassine et al., 2014). The lowest findings of these PCB congeners were detected in one of the most recent studies conducted in Korea (Lee et al., 2020a). In contrast, the highest median concentration, especially for CB 153, was determined within the Iranian study (Karimi et al., 2020) – the measured concentration was about 2 times higher compared to our study. It can be concluded that higher levels of selected PCB congeners in blood serum samples from the Czech Republic and Iran reflect the previous production of technical mixtures in these areas and probably inefficient or insufficient disposal of materials containing these substances.

Subsequently, a total of ten substances from the OCP group were detected in at least one sample, and three analytes (HCB, *p,p′*-DDE, *p,p′*-DDD) were quantified in more than 50% of the samples in both rounds (spring and autumn). Only one analyte (*δ*-HCH) was not detected in any sample. The total ∑DDTs (sum of *p,p′*-DDE; *o,p′*-DDE; *p,p′*-DDD; *o,p′*-DDD; *p,p′*-DDT, and *o,p′*-DDT) content in serum varied between 22.7 and 1047 ng g^{-1} lw (mean 143 ng g^{-1} lw, median 103 ng g^{-1} lw). The highest concentrations were determined for *p,p′*-DDE (median 101 ng g^{-1} lw). The most abundant compounds were HCB and *p,p'*-DDE and therefore are further compared with the published data in Table 3. Within the comparison in the Czech Republic, the median values of HCB and *p,p'*-DDE in current study are twice as low compared to the previous study (Svarcova et al., 2019). The targeted *p,p'*-DDE reached the highest levels in all countries and the current median concentration is in a good agreement with Italian, Tunisian, Korean, and Australian studies (Amodio et al., 2012; Hassine et al., 2014; Moon et al., 2017; Thomas et al., 2017). Two times higher median concentrations were observed for *p,p'*-DDE in serum in South Korea (Kang et al., 2008), Greece (Kalantzi et al., 2011) and Russia (Abou Ghayda et al., 2020). Medians of *p,p'*-DDE are 2–7 times lower in Turkey (Ulutaş et al., 2015), Korea (Choi et al., 2018; Lee et al., 2020a), Lebanon (Helou et al., 2019) and Iran (Karimi et al., 2020) compared to results from the Czech Republic. In the case of HCB, higher median concentrations (2–8 times) were published in the Russian (150 ng g^{-1} lw), Spanish (109 ng g^{-1} lw) and Tunisian studies (39.3 ng g^{-1} lw) (Abou Ghayda et al., 2020; Hassine et al., 2014; Porta et al., 2012). Comparable HCB concentrations were found in other studies from Europe (Kalantzi et al., 2011) (Amodio et al., 2012) and South Korea (Kang et al., 2008). The lowest concentrations of HCB were detected in the study from South Korea (Choi et al., 2018). The highest *p,p'*-DDE and HCB levels were found in blood serum samples from China in a study reported by Wang et al. (2017).

In the past, within the history of organochlorinated substances in Czechoslovakia, the occurrence of PCBs and OCPs was high everywhere in the environment, e.g. PCBs were produced under the name of Delor mixture and their production was stopped in 1984. Moreover, DDTs and HCB, among the other compounds, were produced in the Spolana Neratovice chemical plant. All production of DDTs was terminated between 1978 and 1983. HCB was also formed as an industrial by-product, banned as a pesticide in 1977, the production of which was terminated altogether in 1968. Therefore, these substances still persist in the environment and it is necessary to re-evaluate the exposure of the Czech population after some time. When comparing median concentrations of the most abundant organochlorine analytes (CB 153, HCB, and ∑DDTs) determined by the National Institute of Public Health between 2005 and 2015 in blood serum samples of Czech adults, supplemented by the values from this study (2019), a declining trend can be observed (medians CB 153/∑DDTs/HCB; year 2005: 438/519/97; year 2007: 310/339/63; year 2009: 195/282/48, and year 2019: 64.8/103/18.1 ng g^{-1} lw). Compared to 2005, the quantified levels of selected substances in our study (2019) are approximately 5–6 times lower. The reason is the aforementioned ban on the production and usage of these substances which leads to no further contamination of the environment. Moreover, these compounds are gradually eliminated from the environment, which leads to a reduction in the exposure of the Czech population to these contaminants (Černá et al., 2012, 2008, 2007, The National Institute of Public Health).

Table 4
Fold change of significantly differing (based on ANOVA, p-value < 0.05 followed by Tukey's Post-hoc tests) contaminants between localities (Ostrava, Ceske Budejovice, and Prague).[a]

Season	Group of POPs	Analyte	Fold change (MEDIAN)		
			Ostrava – Ceske Budejovice	Prague – Ceske Budejovice	Prague – Ostrava
Spring (2019)	**PCBs**	CB 28	0.03†	0.65	18.67
		CB 118	1.02	0.84	0.83†
		CB 138	1.29	0.96	0.74#
		CB 153	1.45	0.97	0.67†
		CB 170	1.74†	1.02	0.59‡
		CB 180	1.78†	1.01	0.57‡
	OCPs	*p,p'*-DDD	0.77#	1.03	1.33‡
	BFRs	BDE 47	2.78	0.71	0.26‡
	PFAS	PFHxS	1.44†	1.15	0.80
		PFHpA	1.14	1.36#	1.19
		PFDA	0.55†	0.76	1.36
Autumn (2019)	**PCBs**	CB 118	1.09#	0.93#	0.85
		CB 180	1.55	1.08	0.70#
	PFAS	PFHxS	1.37†	1.12	0.81#
		PFDA	0.41‡	0.68#	1.66‡
		PFUdA	0.46†	0.46†	0.99

[a] Fold changes were calculated using group's median values (#p < 0.05; † p-value < 0.01; ‡ p-value < 0.001 from Tukey's Post-hoc test).

BFRs and novel FRs belong to the minor target analytes in serum. The most frequently detected compounds, present in 83–99% and 21–44% of serum samples, were BDE 47 and BDE 209, respectively. From the novel FRs, anti-DP was quantified in 22–33% of samples. Other FRs, that were quantified in 5–28% of samples, were BDE 99 and BDE 153. Total of 24 of 40 monitored FRs were found below the LOQs in tested samples. In comparison with the former study from the Czech Republic (Sochorová et al., 2017), the detection frequencies of the most common PBDEs (BDE 47, 99, 153, and 209) were much lower than in the presented study. However, the maximum concentration for BDE 209 was higher (<1.5–2693 ng g^{-1} lw) in serum samples collected from 2015 than in samples from 2019 (1.50–459 ng g^{-1} lw). The contribution of individual PBDE congeners is quite variable across different studies and the possible explanation of this phenomenon could be the very different production and consumption rates of BFRs across the countries, e.g. BFRs have been produced in the U.S. and therefore the higher amounts could be expected in human blood serum from the American studies compared to the results from the Czech Republic where those compounds have never been produced. In a recent study from Sweden (Bjermo et al., 2017), congeners BDE 153, BDE 209 and BDE 47 were most commonly found in serum, with a detection frequency (DF) reaching 100%, 74% and 24%, respectively. In similar study, the most abundant PBDEs in blood serum of the Danish population were BDE 47, BDE 99, BDE 153 and BDE 209 reaching DF of 84–98% and 56% (Vorkamp et al., 2014). In an American study BDE 47, BDE 100 and BDE 153 were the ones most frequently found in blood serum, with DF ranging from 78 to 80% (Hurley et al., 2017). Considering the present results, BDE 47 median value is in a good agreement with European, Chinese and New Zealand studies (Antignac et al., 2009; Coakley et al., 2018; Vorkamp et al., 2014; Y. Yu et al., 2020). However, the concentration of this contaminant was approximately seven times lower compared to studies from the USA (Butt et al., 2016; Hurley et al., 2017; Makey et al., 2014). These results support the hypothesis that elevated PBDE concentrations are in human serum samples from country where the technical mixtures of PBDEs have been produced and widely used. The median of BDE 209 measured in the present study was lower compared

Table 5
Fold change of significantly differing (based on paired *t*-test, *p*-value < 0.05) contaminants between serum samples from spring and autumn 2019 (significance in at least one city).[a]

Group of POPs	Analyte	Fold change (MEDIAN) Ostrava (spring-autumn)	Ceske Budejovice (spring-autumn)	Prague (spring-autumn)
PCBs	CB 28	0.08	4.46‡	4.17#
	CB 118	0.91	0.97	0.88†
	CB 138	0.57#	0.61†	0.63‡
	CB 170	1.35†	1.11	1.11
OCPs	*p,p'*-DDE	0.89	0.82	0.68#
	p,p'-DDD	0.60‡	0.64	0.97
BFRs	BDE 47	3.19†	0.89	0.67‡
PFAS	PFBA	0.74#	1.07	1.07
	PFDA	0.98	0.73	0.81†

[a] Fold changes were calculated using group's median values (# p-value <0.05; † p-value < 0.01; ‡ p-value < 0.001 from *t*-test).

to the world, namely nine times lower than in Europe (Antignac et al., 2009; Vorkamp et al., 2014) and thirteen times lower than in serum from China (Qiao et al., 2018; Y. Yu et al., 2020). Nevertheless, compared to blood serum from Sweden (Bjermo et al., 2017; Darnerud et al., 2015), current BDE 47 concentrations were five times higher and for BDE 209 the levels were comparable.

3.2. Differences between sampling localities (Prague, Ostrava and Ceske Budejovice)

As shown in Table 4, within the spring 2019, the median concentrations indicated statistically significant associations between localities for 11 POPs, namely CB 28, CB 118, CB 138, CB 153, CB 170, CB 180, *p,p'*-DDD, BDE 47, PFHxS, PFHpA, and PFDA (ANOVA followed by Tukey's Post-hoc tests). The measured concentrations of five PCBs (CB 118, CB 138, CB 153, CB 170, and CB 180) and BDE 47 were significantly higher (1.2–4 times) in serum samples from the city of Ostrava (an industrial area with a long-term polluted environment) compared to Prague (highly populated area). The highest PCB levels (highly chlorinated PCBs), were also found for the Ostrava region in an earlier Czech study especially in serum samples from men (Černá et al., 2008). However, PFDA and *p,p'*-DDD showed an opposite trend, when their concentrations decreased significantly in serum samples from Ostrava in comparison to Ceske Budejovice. The city of Ceske Budejovice is more focused on agriculture than the other monitored cities, and in the past DDTs were used there, so it can be a historically older burden of the environment. In the case of serum samples collected in autumn 2019 with focus on variability between residential areas, a statistically significant trends were observed for three PFAS (PFDA, PFUdA, and PFHxS) and two PCBs (CB 118 and CB 180). Higher levels of CB 180 and PFHxS in this period were determined again in the city of Ostrava. On the other hand, PFUdA and PFDA concentrations increased significantly in serum samples obtained in Ceske Budejovice, see Table 4 and Fig. S1. In summary, higher findings of PCBs in Ostrava may be caused by the industrial character associated mainly with the past of this city and also by the fact that the only incinerator plant in the Czech Republic with a permit to burn waste containing PCBs is located here. Although, PFAS have never been produced in the Czech Republic, it is possible that some intermediates with PFAS content were processed in Ostrava and therefore, higher amounts of some PFAS in the serum samples from Ostrava were observed. Therefore, more studies with a larger set of samples from different areas of the Czech Republic would be needed.

3.3. Differences between seasons (spring and autumn 2019)

According to the paired *t*-test, statistically significant season-dependent differences in at least one city were noted for CB 28, CB 118, CB 138, CB 170, *p,p'*-DDE, *p,p'*-DDD, BDE 47, PFBA, and PFDA (Table 5). The serum concentrations of CB 170 and BDE 47 in Ostrava showed higher levels (up to three times higher) in spring, while results of CB 138 and *p,p'*-DDD were lower during this period. The observed trends were very diverse: the concentrations of CB 28 in serum collected in Ceske Budejovice during the spring had an increasing trend (up to four times) and, conversely, slightly decreased for CB 138. The last monitored city was Prague, where higher values of CB 138, *p,p'*-DDE, and PFDA in the blood serum from the autumn period were mostly observed. The differences were very variable and could probably be related, for example, to a change of daily diet during spring and autumn, as well as to the origin of the food within each period. Although, the minor differences for less abundant contaminants were observed, they were not consistent (no systematic changes has been documented) as well as without trends and therefore could be assumed that within such short period no significant changes in POP concentrations in blood serum occur.

3.4. Differences between age groups

As summarized in Table 6, all these analytes met the criterium of ANOVA (p-value <0.05), that confirmed significantly different concentrations of the targeted POPs between age groups (21–30; 31–40; 41–50, and 51–60 years of age; for Ceske Budejovice only the first three groups were used). As all significant POPs showed a trend of increasing concentration with increasing age, Spearman rank correlation coefficient was calculated to confirm the positive correlation. For all five PCBs (CB 118, CB 153, CB 170, and CB 180), three OCPs (HCB, *p,p'*-DDE, and

Table 6
The correlation between a selected statisticaly significant POP serum levels (ANOVA, *p*-value < 0.05 and Spearman's rank correlation coefficient) with various age groups (21–30, 31–40, 41–50, and 51–63) in Ostrava, Ceske Budejovice and Prague.

Group of POPs	Analyte	Ostrava ANOVA p-value	Ostrava Spearman's rank correlation coefficient	Ceske Budejovice ANOVA p-value	Ceske Budejovice Spearman's rank correlation coefficient	Prague ANOVA p-value	Prague Spearman's rank correlation coefficient
PCBs	CB 118	6.42E-05	0.496	n.s.	–	7.91E-05	0.467
	CB 138	4.56E-08	0.575	n.s.	–	1.22E-15	0.619
	CB 153	2.88E-10	0.622	3.07E-03	0.498	1.10E-18	0.666
	CB 170	4.15E-14	0.679	1.43E-05	0.633	7.86E-22	0.721
	CB 180	1.22E-15	0.700	1.79E-06	0.647	2.36E-21	0.708
OCPs	HCB	1.25E-04	0.442	n.s.	–	1.89E-06	0.398
	p,p'-DDD	n.s.	–	n.s.	–	2.23E-02	0.273
	p,p'-DDE	3.02E-04	0.405	n.s.	–	1.92E-09	0.464
PFAS	PFOS	n.s.	–	n.s.	–	1.76E-02	0.242
	PFHpS	n.s.	–	n.s.	–	2.22E-02	0.292

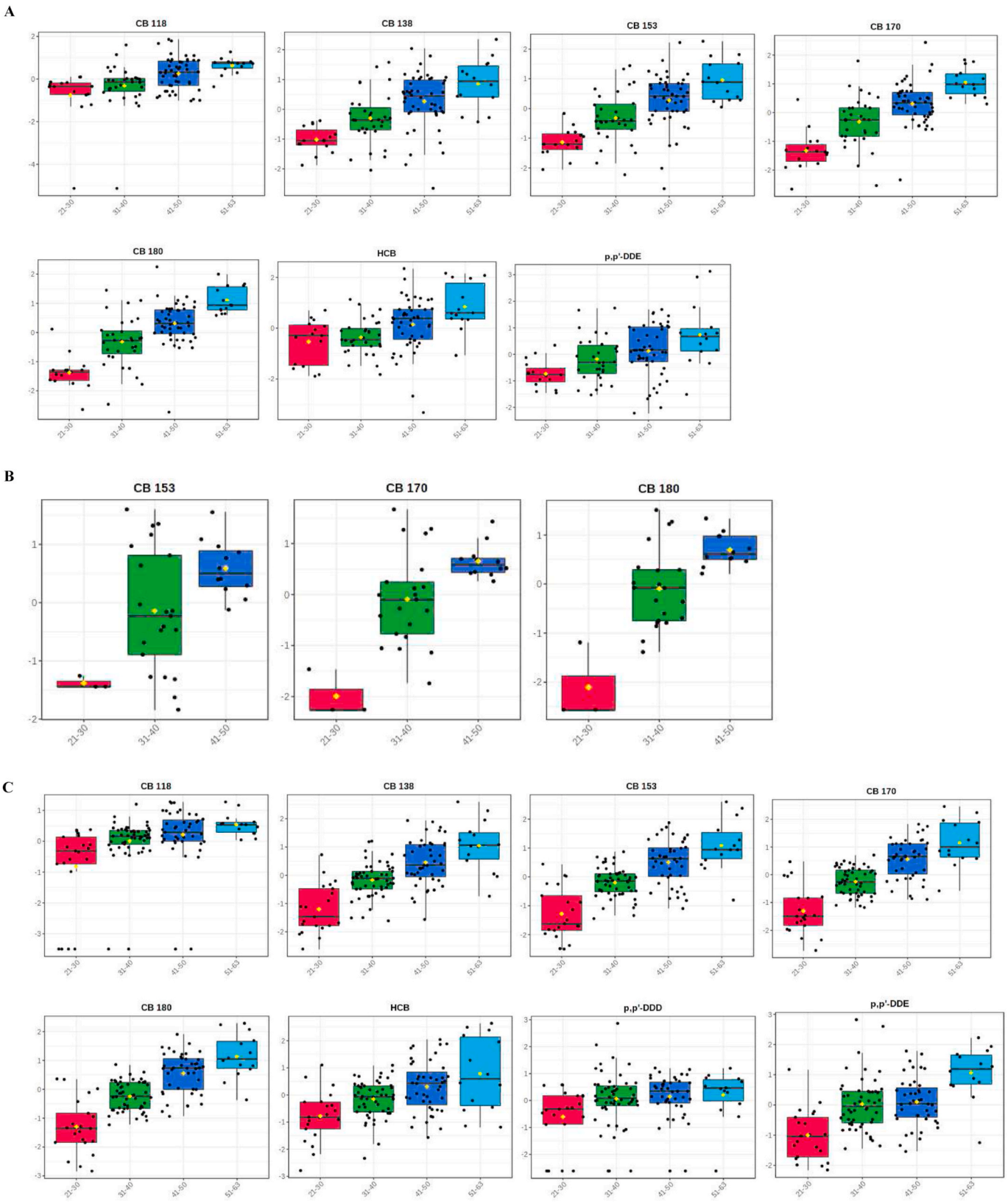

Fig. 1. A Box-plots of human serum concentrations of PCBs and OCPs in Ostrava, divided on the basis of different age groups (21–30, 31–40, 41–50, and 51–63).**B:** Box-plots of human serum concentrations of PCBs in Ceske Budejovice, divided on the basis of different age groups (21–30, 31–40, 41–50).**C:** Box-plots of human serum concentrations of PCBs, OCPs and PFAS in Prague, divided on the basis of different age groups (21–30, 31–40, 41–50, and 51–63).

p,p'-DDD) and two PFAS (PFOS and PFHpS) the correlation coefficients were significant, nevertheless the strongest correlation was observed in case of CB 180 and CB 170 ($r > 0.632$ in all three localities). The obtained results and the associated serum concentrations of selected PCBs, OCPs and PFAS in the various age groups of participants for all three localities are summarized in Fig. 1A–C. The increase in the concentrations of the above-mentioned contaminants is probably caused by the longer exposure to these pollutants during the subjects' lifetimes. In addition, their slow elimination from the body leads to increasing levels of these pollutants in the body as the policemen's age increases as well. Due to the lipophilic properties of these substances, it could be assumed that higher levels of these analytes could be detected in the blood serum of policemen with a higher subcutaneous fat ratio. Other important factor affecting the differences in POP concentrations between the age groups is the period the respective compound has been banned from the usage and subsequent reducing of environmental burden and human exposure (Nøst et al., 2013). The previous human biomonitoring studies also confirmed that higher age was associated with higher PCB and OCP levels (Artacho-Cordón et al., 2015a; Černá et al., 2008; Foster et al., 2012; Ibarluzea et al., 2011; Wittsiepe et al., 2008). Conversely, in the present study, this trend was not confirmed for PFAS, BFRs and novel FRs.

Other aspects such as the correlation between serum samples with lipidomics were assessed. The effect of BMI, cholesterol, education, and former smoking habits on POP levels in serum was further investigated. However, no statistically significant relationships between these examined factors and serum POP concentrations were discovered.

4. Conclusions

The uniqueness of this study lies in the analysis of a wide range of POPs with different physico-chemical properties in a large set of blood serum samples, mapping a sample group of urban policemen. For this population their total body burden to POPs does not depend only on the diet, age, various localities but also the nature of their profession (they move around the city and spend a lot of time outdoors). This is the first study to analyse such a large set of serum pollutants (8 PCBs, 11 OCPs, 33 BFRs, 7 novel FRs, and 30 PFAS) in the unique population group. The total concentrations of ∑PFAS, ∑PCB,s and ∑DDTs in serum samples were in the range of 0.516–22.2 ng mL^{-1}, 34.1–2075 ng g^{-1} lw, and 22.7–1047 ng g^{-1} lw, respectively. In general, the contaminants occurring the most frequently in all serum samples were represented by PFAS (PFOA, PFNA, PFDA, PFOS, and PFHxS); PCBs (No. 138, 153, 170, and 180) and OCPs (HCB and *p,p'*-DDE).

The observed individual groups of serum contaminants can be summarized as follows:

The newly monitored substances (PFHxDA, PFODA, PFPrS, PFPeS, PFHpS, PFNS, PFDoS, HFPO-DA, NaDONA, 9Cl-PF3ONS, 11Cl-PF3OUdS) are included within the monitoring of PFAS in serum. Major PFOS and PFOA serum concentrations are among the lowest compared to population in Europe, China and the USA. Statistically significant differences between localities and seasons were found for PFHxS, PFDA, PFUdA, and PFDA, respectively. However, no significantly different PFAS concentrations associated with various age groups were observed.

Regarding PCBs, the predominance of highly chlorinated PCB congeners (No. 138, 153, 170, and 180) was observed. Higher PCB levels in Czech serum samples were confirmed by the other relevant studies.

The main representatives of OCPs were HCB and *p,p'*-DDE, which were found in all samples with the highest medians (16.3 ng g^{-1} lw and 114 ng g^{-1} lw, respectively). These results were comparable with those concentrations in serum samples from Europe, Australia, Tunisia and Korea (Amodio et al., 2012; Hassine et al., 2014; Kalantzi et al., 2011; Kang et al., 2008; Moon et al., 2017; Thomas et al., 2017).

In general, a declining trend for PCB and OCP content in human blood serum was observed. Based on further statistical evaluation, significantly different concentrations of contaminants between localities and age groups were observed. Specifically, in blood serum samples from spring sampling time, the occurrence of CB 170 and CB 180 was 70% higher in Ostrava compared to Prague and Ceske Budejovice, which could be due to the highly polluted environment of the Ostrava region. When comparing the results from the spring and the autumn sampling times, the minor differences of less abundant contaminants were observed, however no systematic changes as well as trends have been seen. Regarding the age groups, five PCBs (No. 118, 153, 170, and 180), three OCPs (HCB, *p,p'*-DDE, and *p,p'*-DDD) and two PFAS (PFOS and PFHpS) increasing with the increasing age of the policemen was observed. The highest Spearman rank correlation coefficients were noted for CB 170 and CB 180.

Within the minor BFRs and novel FRs in serum, the most abundant representatives were BDE 47, BDE 209, and anti-DP quantified in 83–99%, 21–44% and 22–33% of serum samples, respectively. The congener BDE 209 was commonly detected in highest levels in serum samples, but our levels were lower compared to the European and Chinese studies (Antignac et al., 2009; Qiao et al., 2018; Vorkamp et al., 2014; Y. Yu et al., 2020). In summary, the body burden of these pollutants is very similar to elsewhere in Europe, but there are differences in the contribution of individual PBDEs. Statistically significant associations between concentrations and locality and sampling season were observed only in case of the most abundant BDE 47.

Finally, the obtained results within the project HAIE will partly clarify how long-term stay in differently polluted areas affect the individuals health and also current total body burden of various POPs in population from various localities will be known. The obtained data will be processed within the upcoming epidemiological studies under this project.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.118140.

Credit statement

Andrea Polachova: Writing – original draft preparation, Methodology, Validation, Data Curation. **Tomas Gramblicka:** Methodology, Data Curation. **Kamila Bechynska:** Formal analysis, Software. **Ondrej Parizek:** Investigation, Visualization. **Denisa Turnerova:** Investigation, Visualization. **Darina Dvorakova:** Writing – Reviewing and Editing, Validation. **Katerina Honkova:** Resources. **Andrea Rossnerova:** Data Curation, Conceptualization. **Pavel Rossner, Jr.:** Data Curation, Conceptualization. **Radim J. Sram:** Supervision, Funding acquisition, Project administration. **Jan Topinka:** Supervision, Funding acquisition, Project administration. **Jana Pulkrabova:** Supervision, Conceptualization, Writing – Reviewing and Editing, Funding acquisition.

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