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**Persistent organochlorine compounds in human milk collected in Croatia over two decades**

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**Abstract**

Distribution and time trend of organochlorine pesticides (OCP), polychlorinated biphenyls (PCB) and polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDD/PCDF) concentrations in human milk samples from Croatia collected in 1981-2003 are presented. Between 1981/82 and 1987/89, the concentrations of HCB,  $\beta$ -HCH, DDE and total PCBs decreased about 50% while for the last decade, the concentrations have been decreasing very slowly. In 2002/03 range of PCB congeners and OCPs was between below limit of determination and 332 ng g<sup>-1</sup> milk fat. PCDD/PCDFs in human milk samples collected in 1981-2000 concentrations ranged between 5.2 and 26.7 pg I-TEQ g<sup>-1</sup> milk fat and show decreasing trend.

**Keywords:** PCB, pesticides, PCDD, PCDF, breast milk

## **Introduction**

The most widely found organochlorines as pollutants in biotic and abiotic parts of the environment are polychlorinated biphenyls (PCB), organochlorine pesticides (OCP), polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). PCBs and OCPs have intensively been used while PCDDs/PCDFs have never been produced intentionally.

PCBs, OCPs and PCDDs/PCDFs belong to a group of Persistent Organic Pollutants (POPs). Because of world-wide public concern about adverse outcomes in wildlife and the presence and persistence of organochlorines in the environment, the use of PCBs and OCPs was banned or restricted in many countries in the 1970s and 1980s.

Due to persistence and lipophilic properties, these pollutants enter the food-chain and consequently accumulate in human and animal adipose tissues and other tissues which contain fat. It is known that these compounds are excreted via human milk. Their concentrations in human milk are therefore indicators of human exposure and reflect their concentrations in adipose tissue as well. Organochlorines are transferred from the mother to the child via the placenta and primarily via breast milk. Breastfeeding bears well-known benefits for developing infants and WHO recommended that breastfeeding should be promoted and encouraged in spite of the content of unwanted POPs, considering the short breastfeeding period in comparison with the whole life (WHO, 1996).

Over the last decades, the concentrations, distribution, biochemical and toxic effects of organochlorine compounds in humans have been intensively researched. In Croatia, research of organochlorine distribution in human milk samples started in the early 1970s. The first investigation included DDE (1,1-dichloro-2,2-di(4-chlorophenyl)ethene) and DDT (1,1,1-trichloro-2,2-di(4-chlorophenyl)ethane), followed by PCBs. These early studies analysed total PCBs, while recent work include total PCBs and PCB congener-specific analysis.

The aim of this study was to present the distribution and time trend of OCP, PCB and PCDD/PCDF concentrations in human milk samples from Croatia over more than two decades, 1981-2003. This paper includes previously reported data and unpublished results.

### **Materials and methods**

Human milk samples were collected from healthy mothers living in urban or semi urban places in Croatia. No mother was accidentally or occupationally exposed to organochlorine compounds. All mothers were volunteers and they did not receive any payment. The milk was manually expressed into pre-cleaned glass bottles and stored at -20 °C until analysis. In 2002/2003 milk was collected from 20 mothers living in Zagreb. Zagreb is the northwestern Croatian capital with about 1,000,000 inhabitants. Samples were collected from mothers aged 18-41; nine mothers were multiparae, while the others were primiparae. In 1994 milk was collected from 18 (age 20-35; nine mothers were multiparae, while the others were primiparae) and in 1997 from 20 mothers (age 23-43; six were primiparae while the others were multiparae) living in Osijek (town in eastern Croatia). In 1992 milk was collected from 18 mothers (age 19-35; eight were primiparae while the others were multiparae) living in Jastrebarsko (town near Zagreb). Results from samples collected in Osijek and Jastrebarsko between 1992 and 1997 have so far not been published. The following compounds were analyzed: six indicator PCB congeners (PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, PCB-180 numbered according to IUPAC), total PCBs, which were determined by comparison to Aroclor 1260, and organochlorine pesticides DDE, DDD (1,1-dichloro-2,2-di(4-chlorophenyl)ethane, DDT,  $\alpha$ -,  $\beta$ - and  $\gamma$ -HCH (alpha-, beta-, gamma-hexachlorocyclohexane) and HCB (hexachlorobenzene).

The analytical procedure for determination of OCPs and PCBs (Krauthacker et al. 1986; Herceg Romanić and Krauthacker 2006) has not changed over the two decades, but gas

chromatographs and conditions have. The first analyses were done on a gas chromatograph equipped with packed columns and later on, PCB and OCP concentrations were measured using a high resolution gas chromatograph (HRGC/ECD) with capillary columns. Milk (2.5 g) was extracted twice with a mixture of chloroform and methanol (1:1). Chloroform extracts were separated and dried under nitrogen flow. Milk fat was weighed and dissolved in *n*-hexane and cleaned up with sulphuric acid. Purified hexane extracts were evaporated to dryness.

Recent analyses were conducted using two capillary columns used simultaneously (Herceg Romanić and Krauthacker 2006): 1) 60 m × 0.25 mm, SPB-5 film thickness 0.25 µm, temp. programme 100 °C, then 4 °C min<sup>-1</sup> to 240 °C, 50 min isothermally. 2) 30 m × 0.25 mm, SPB-1701 film thickness 0.25 µm, temp. programme 110 °C, then 4 °C min<sup>-1</sup> to 240 °C, 50 min isothermally. The carrier gas was nitrogen. The injector and the detector temperatures were 250 °C and 270 °C, respectively. Qualitative and quantitative analyses were done by comparison with the external standard, and each sample was analyzed on both columns. Only compounds identified on both columns were evaluated. At present method determination limits are 1.64 ng g<sup>-1</sup> milk fat for PCBs congeners, β-HCH, DDE, DDD and DDT and 0.98 ng g<sup>-1</sup> milk fat for HCB, α-HCH and γ-HCH.

Quality control was periodically carried out using certified reference materials CRM 450 (powdered natural cow's milk), CRM 187 (powdered natural cow's milk), and CRM 188 (powdered cow's milk spiked with OCPs) (Herceg Romanić and Krauthacker 2006).

## **Results and discussion**

### *1. Organochlorine pesticides and PCB levels in human milk samples*

Table 1 shows the ranges and medians of organochlorine pesticides and six indicator PCBs in human milk samples collected in Jastrebarsko, Osijek and Zagreb between 1992 and 2002/03.

The range of PCB congeners and OCPs in human milk samples was between zero (below limit of determination) and 1879 ng g<sup>-1</sup> milk fat. In all samples the most prominent OCP was DDE, and the least prominent  $\alpha$ -HCH and DDD. Ratios DDE/DDT and  $\alpha$ -HCH/ $\gamma$ -HCH are often used to indicate a recent input of DDT or  $\gamma$ -HCH in the environment. The range of DDE/DDT ratios was between 1.7 and 28, except for one sample where DDE/DDT ratio was 0.2. The DDE/DDT ratios were mostly greater than unity, which means that there was no recent input of DDT. We have no explanation for the low ratio in one sample as DDT had not been used in Croatia for decades. The range of  $\alpha$ -HCH/ $\gamma$ -HCH ratios were between 0 and 0.8, which implies that general population was recently exposed to lindane. However, lindane concentrations in human milk were low, which implies relatively fast elimination from the body and/or low lindane exposure. The presence of HCB in human milk could be explained by continuous input of HCB in the environment and humans. HCB is detected in industrial emissions and is still generated as a by-product or impurity in several chemical processes. PCB-138 and PCB-153 were found in all analysed samples, while concentration median for PCB-101 was below determination limit in all groups, except Osijek in 1994 when it was 1 ng<sup>-1</sup> milk fat. The concentration range of PCBs was between the determination limit and 289 ng g<sup>-1</sup> of milk fat.

Insert Table 1

The highest concentration was measured for PCB-153, PCB-138 and PCB-180 which are higher chlorinated congeners differing from PCB-28, PCB-52 and PCB-101. Their higher presence in comparison to others implies persistence to the metabolic breakdown. A concentration median of total PCBs was between 121 and 215 ng<sup>-1</sup> milk fat.

## *2. Geographic distribution and time trend of OCP and PCB levels in human milk samples*

Organochlorine pesticides had been measured in human milk samples collected in Croatia for more than two decades. Table 2 shows earlier published concentration medians.

Insert Table 2

As evident from Table 2 and Table 1, human milk samples in late 1980s and early 1990s were collected at sites in Croatia which differ in geographical position and in the level of industrialization (north-western capital of Croatia, Zagreb; towns near Zagreb Jastrebarsko, Karlovac and Sisak; town in eastern Croatia, Osijek; town in the northern part of the Adriatic on the Istrian peninsula, Labin; and on the island of Krk). Concentrations of OCPs in human milk samples collected in the late 1980s and early 1990s at different sites were similar and no marked differences were observed.

A comparison of the concentrations of OCPs between 1981 and 2002/03 (Tables 1 and 2) shows that HCB,  $\beta$ -HCH and DDE are present in larger concentrations in comparison to other compounds. It is also evident that, between 1981/82 and 1987/89, the levels of HCB,  $\beta$ -HCH and DDE decreased about 60% or more, depending on the compound and restriction of use. Over the last decade, the concentrations of HCB,  $\beta$ -HCH and DDE decreased very slowly or not at all. Concentration medians of  $\alpha$ -HCH,  $\gamma$ -HCH, DDD and DDT were higher than determination limit only in some sampling years. This could be due to a marked decrease in their concentrations in the first decade (particularly for DDT). In samples analyzed after 1992, medians above 0 are evident for some compounds (i.e. DDT). As mentioned under Materials and Methods, the analyses before 1992 were done using a gas chromatograph of lower sensitivity and selectivity than the high resolution gas chromatograph with capillary columns we use now and determination limits improved markedly.

Figure 1 shows the time trend for total PCBs over the 20 years.

Insert Figure 1

PCB concentrations in human milk have been monitored since 1981, and the first analysis focused on "total PCBs" in comparison with the commercial mixture Aroclor 1260. In order to illustrate the time trend of PCBs in human milk, total PCBs have continuously been measured since 1981. Similar to organochlorine pesticides, the concentrations of total PCBs in samples from Zagreb decreased continuously between 1981/82 and 1987/89 about 50 % due to restricted use, which is today allowed only in closed systems. A decreasing trend is also obvious in samples from Krk and Osijek. Sampling in Karlovac, Jastrebarsko, Labin and Sisak was done only once. Between 1990 and 2000, PCB concentrations decreased slowly. Comparisons of concentrations obtained in the same year, but in different sites have shown similarity and no marked differences were observed. Exception was in 1992. when concentrations in samples from Krk were two times higher in comparison to Zagreb and Jastrebarsko.

In Table 3 results of PCB congener specific analyses between 1992 and 2000 were presented.

Insert Table 3

Comparison of results presented in Table 1 and Table 3 showed that concentrations of PCB-138, PCB-153 and PCB-180 are higher than lower chlorinated congeners as PCB-28, PCB-52 and PCB-101 in all three populations of human milk samples. In human milk samples from Zagreb and Krk were monitored eight years, concentrations of PCB-138, PCB-153 and PCB-180 dropped about 50%. In human milk collected in Zagreb in 1992 and 1995 and Osijek



between 1994 and 1997 a decreasing trend was not observed (Table 1). A likely explanation is that the period of observation was too short to observe changes in concentrations of specific PCB congeners.

### *3. Comparison with other studies*

The range of HCB concentrations is wide and seemed to be influenced by industrial emissions (Murayama et al. 2003). Results from some other countries (United Kingdom, Japan, Indonesia, Sweden) and from Croatia show that DDE, HCB and  $\beta$ -HCH are the most prominent compounds in human milk and are higher than  $\gamma$ -HCH (Aune et al. 1999, Burke et al. 2003). OCP concentrations in human milk from Croatia are similar to those from the United Kingdom, Japan, and Sweden where these pesticides are no longer in use. Furthermore, their concentrations in Croatia could not be considered high, and they reflect global biosphere pollution by persistent organochlorine compounds. High pesticide concentrations such as DDT are found in samples collected in countries where they are still in use. The highest concentration of the sum of DDT and its metabolites of 25259 ng g<sup>-1</sup> milk fat was found in human milk from Zimbabwe collected in 1993-1995 (Chikuni et al. 1997). High DDT concentrations were also found in other African areas such as South Africa where the sum of DDT and its metabolites was 15830 ng g<sup>-1</sup> milk fat. In human milk samples from India, the sum of DDT and its metabolites was 17190 ng g<sup>-1</sup> milk fat (Chikuni et al. 1997). However, in countries where DDT is not in use any more, these concentrations are markedly lower. A comparison of DDT concentrations in human milk between 1967 and 1997 in Sweden showed that 1997 concentrations were about 1 % of the concentrations found in 1967, while DDE concentrations were 5% of the concentrations measured in 1972 (Norén and Meironyté 2000). In Hong-Kong DDT also decreased; in 1982, DDT levels were 2170 ng g<sup>-1</sup> milk fat and in 1999/2000 390 ng g<sup>-1</sup> milk fat (Wong et al. 2002).

The WHO organized exposure studies of PCB, PCDD and PCDF in human milk samples collected from eighteen countries (Croatia, Finland, Italy, The Netherlands, Spain, Slovak Republic, Czech Republic, Brazil, Australia, Bulgaria, Hungary, New Zealand, Ireland, Sweden, Ukraine, Russia, Norway and Egypt) (van Leeuwen and Malisch 2002). The range of the sum of six indicator PCBs was wide; high concentrations were found in samples from Spain, Slovak Republic and Czech Republic (median: 400-500 ng g<sup>-1</sup> milk fat), while low concentrations were found in samples from Brazil, Australia, Bulgaria, Hungary, New Zealand and Ireland (median: 14-37 ng g<sup>-1</sup> milk fat). In Croatia, they were in the lower half of this range (135 ng g<sup>-1</sup> milk fat) and are similar to those in Sweden, Ukraine, Russia, Norway and Egypt. In previously published study PCB congener concentrations in human milk collected in different countries were presented (Zubčić and Krauthacker, 2004). Concentrations in human milk collected in 2002/03 (Table 1, this study) and concentrations in samples between 1992 and 2002 (Table 3) show that as PCB-28, PCB-52 and PCB-101 are higher but concentrations of PCB-138, PCB-153 and PCB-180 are lower compared with concentrations measured in other countries.

#### *4. PCDDs and PCDFs*

Congener-specific analysis of PCDD/Fs requires determination by high resolution gas chromatography with high resolution mass spectrometry (HRGC/HRMS) which has not been available in Croatia so far. PCDD/PCDFs were analyzed in human milk samples in collaboration World Health Organization (WHO) Regional Office for Europe WHO (WHO, 1996; van Leeuwen and Malisch 2002) and with United States Environmental Protection Agency (US EPA) (US EPA Report, 1995-1998). Human milk samples were collected between 1981 and 2000 in the city of Zagreb, towns of Jastrebarsko, Osijek, and Labin, and on the island of Krk. All results are summarized in Table 4. PCDD/F concentrations ranged between 5.2 and 26.7 pg I-TEQ g<sup>-1</sup> milk fat, and showed a decreasing trend.

Insert Table 4

We participated in all three studies conducted by WHO in 1987/88, in 1992/93, and in 2001/02. Results from the 2<sup>nd</sup> round of the WHO study conducted in 1992/93 enabled to assess time trends of PCDDs, PCDFs in human milk. It showed that, in Austria, Belgium, Canada, Croatia, Denmark, Finland, Germany, Hungary, Netherlands, Norway, and the United Kingdom, concentrations of PCDDs and PCDFs did not increase in comparison with the 1<sup>st</sup> study performed in 1987/88. In fact, the annual decrease for all participating countries was estimated to 7.2% with a relative standard deviation of 0.8% (in pg TEQ/g milk fat) (WHO, 1996). On Krk and in Zagreb, PCDD/F concentrations decreased about 50% between 1988 and 2000. In Croatia, the annual decrease in dioxin concentrations was approximately 2% what is slower than in other countries. The levels in Croatian human milk samples were at the lower part of the range. Therefore the decrease in concentrations is lower than in countries where concentrations in human milk were much higher.

Figure 2 compares PCDD/F levels in human milk from Croatia and from other countries. This comparison is made with the results obtained in the 3<sup>rd</sup> WHO study (van Leeuwen and Malisch 2002).

Insert Figure 2

In Europe, the samples from Netherlands, Italy and Spain are characterized with higher concentrations of PCDD/Fs expressed as TEQ. Lower concentrations are found in samples from moderately industrialized countries like Bulgaria, Croatia, Hungary, and Ireland. Very

high concentrations were found in samples from Egypt, while the lowest were found in Brazil and in Australia.

### **Conclusions**

A decreasing trend for all organochlorine compounds in human milk was observed, probably as the result of reduced usage or ban. Median concentration organochlorine pesticides and total PCBs concentrations decreased about 50% between 1981/82 and 1987/89 while between 1990 and 2000 concentrations decreased slowly. PCDD/F concentrations decreased about 50 % between 1988 and 2000.

In samples collected in 2002/03, PCB congeners and OCPs ranged between zero (below limit of determination) and 332 ng g<sup>-1</sup> milk fat. The profile of concentration medians for OCPs was DDE> $\gamma$ -HCH $\approx$  $\beta$ -HCH $\approx$ DDT>HCB> $\alpha$ -HCH>DDD and for PCBs was PCB-153>PCB-138>PCB-180>PCB-28 $\approx$ PCB-52>PCB-101. A comparison with other countries shows that these concentrations are in the lower half of the published data range. The presence of organochlorine compounds in human milk in Croatia could be considered at the level of global environmental pollution.

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**Table 1.** PCB and OCP concentrations ( $\text{ng g}^{-1}$  milk fat) in human milk samples collected in Zagreb (N=20), Osijek (in 1997 N=20; in 1994 N=18) and Jastrebarsko (N=18); number of positive samples are given in parenthesis; total PCBs were determined in comparison to Aroclor 1260

Site		Organochlorine pesticides						
		HCB	$\alpha$ -HCH	$\beta$ -HCH	$\gamma$ -HCH	DDE	DDD	DDT
Zagreb 2002/03	Range	2-23	1-6	0-65	2-35	12-332	0-2	0-70
	Median	5 (20)	2 (20)	12 (16)	14 (20)	104 (20)	0 (8)	13 (17)
Osijek 1997	Range	0-30	0-2	0-224	0-85	171-1157	0-1	7-104
	Median	8 (19)	0 (6)	54 (19)	8 (19)	629 (20)	0 (1)	14 (20)
Osijek 1994	Range	2-60	0-8	16-250	1-237	40-1879	0-1	0-101
	Median	12 (18)	0 (5)	41 (18)	7 (18)	385 (18)	0 (1)	0 (7)
Jastrebarsko 1992	Range	3-27	0	0-103	0	57-896	0	0-500
	Median	13 (18)	0 (0)	24 (13)	0 (0)	285 (18)	0 (0)	170 (12)
Site		Polychlorinated biphenyls						
		PCB-28	PCB-52	PCB-101	PCB-138	PCB-153	PCB-180	total PCB
Zagreb, 2002/03	Range	0-23	0-24	0-7	12-289	6-256	0-41	64-1215
	Median	7 (17)	8 (18)	0 (2)	26 (20)	29 (20)	13 (19)	121 (20)
Osijek, 1997	Range	0-18	0-156	0-7	8-51	13-90	3-26	60-335
	Median	1 (11)	0 (5)	0 (7)	23 (20)	33 (20)	6 (20)	126 (20)
Osijek 1994	Range	0-5	0-50	0-50	0-212	5-282	3-111	12-1987
	Median	0 (7)	0 (5)	1 (9)	21 (17)	36 (18)	17 (18)	215 (18)



**Table 2.** Median concentrations (ng g<sup>-1</sup> milk fat) of OCPs in human milk samples collected in the city of Zagreb, towns Labin, Karlovac, Sisak and on the island of Krk between 1981 and 2000 (Krauthacker and Reiner 1994; Krauthacker et al. 1998, Herceg Romanić and Krauthacker 2006). NA-not analysed; 0 – below determination limit; N - number of samples

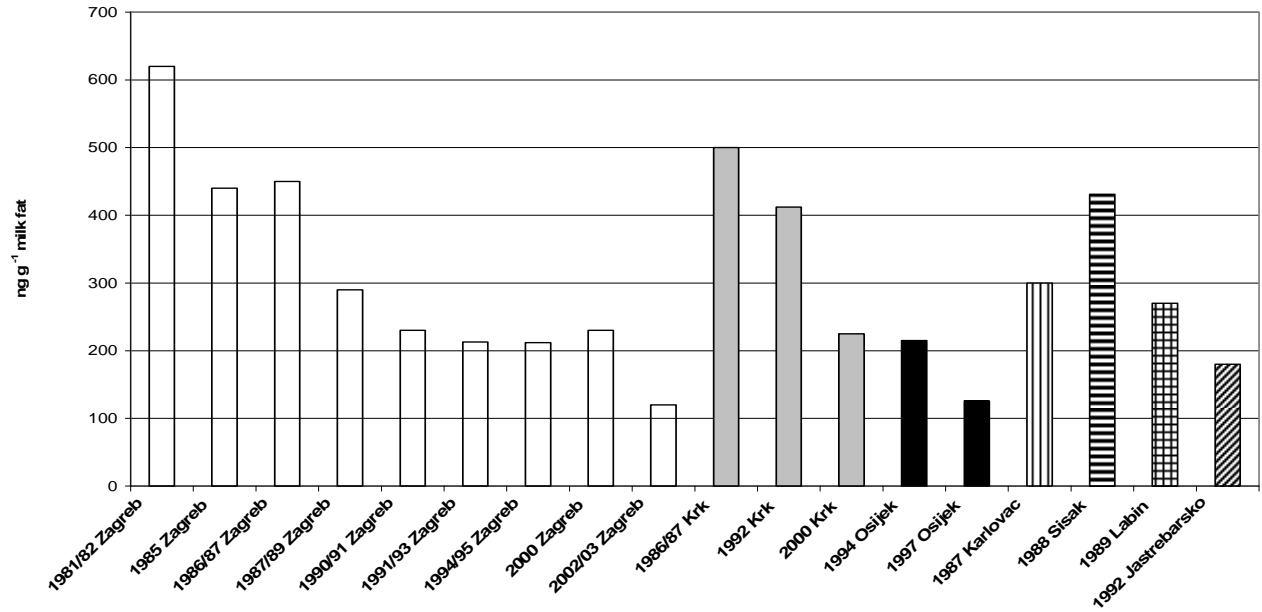
Year	N	HCB	α-HCH	β-HCH	γ-HCH	DDE	DDD	DDT
Zagreb								
1981/82	50	210	NA	280	NA	1900	NA	180
1985	18	210	0	230	0	1060	0	130
1986/87	41	120	0	170	60	1480	0	70
1987/89	22	60	0	40	0	620	0	0
1990/91	30	20	0	40	0	450	0	0
1991/93	54	15	0	24	2	282	0	0
1994/95	45	11	0	35	5	247	0	9
2000	29	13	2	20	19	257	2	19
Krk								
1986/87	33	100	0	100	0	1080	0	160
1992	27	25	8	18	8	104	0	0
2000	23	7	2	19	15	227	5	14
Labin								
1989	20	0	0	50	0	550	0	0
Karlovac								
1987	9	75	0	45	0	600	0	31
Sisak								
1988	9	36	0	59	0	633	0	0

**Table 3.** Concentrations of six indicator PCBs ( $\text{ng g}^{-1}$  milk fat) in human milk between 1992 and 2000 (Zubčić and Krauthacker 2004, Herceg Romanić and Krauthacker 2006). Number of individual samples are given in parenthesis. \*-pooled sample; '-median

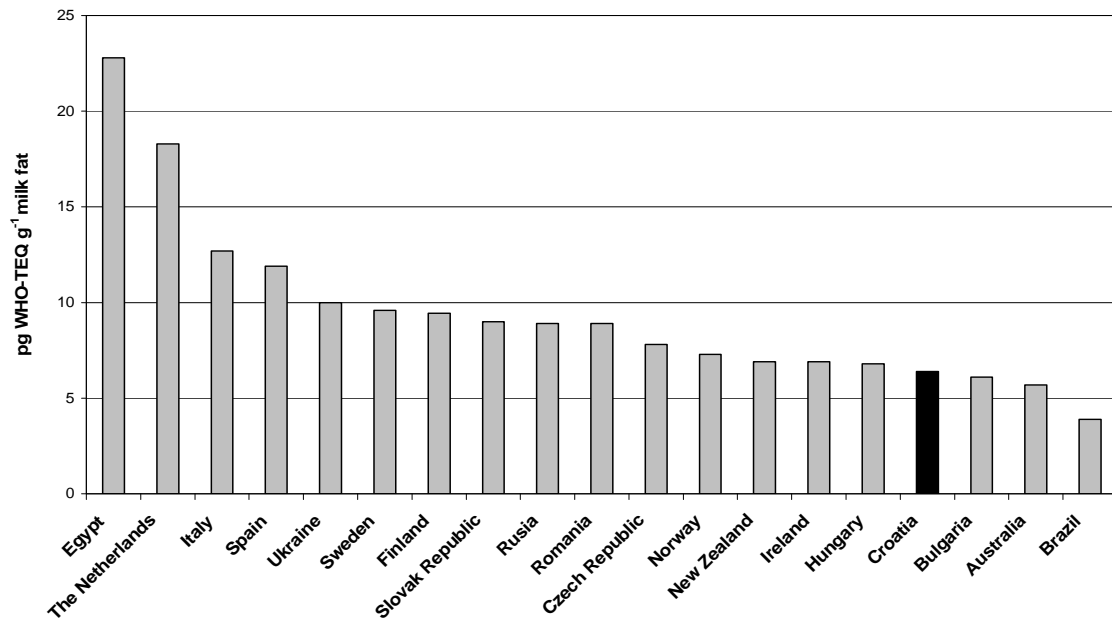
Site	Year	PCB-28	PCB-52	PCB-101	PCB-138	PCB-153	PCB-180
Zagreb	1992 (10)*	4.2	1.2	1.5	67.8	99.8	45.0
	1995 (10)'	2.8	20.3	16.9	83.5	92.9	45.1
	2000 (29)	8.3	12.5	3.0	33.1	41.5	13.2
Krk	1992 (13)*	3.5	0	1.5	62.9	103.0	47.4
	2000 (23)'	10.5	10.4	2.9	32.6	38.8	19.4

**Table 4.** PCDD/F concentrations in human milk collected in Croatia. Number of samples in the pool is given in parenthesis (Report on sources, distribution and effects of POPs on the environment and human health, 2003)

<b>Sampling year</b>	<b>pg I-TEQ g<sup>-1</sup> milk fat</b>
Zagreb	
1981-82 (50)	24.2
1985 (17)	20.7
1987-89 (10)	26.7
1987 (41)	11.8
1990-92 (13)	13.5
1993-95 (61)	13.2
2000 (12)	5.9
island Krk	
1986-87 (14)	12.0
1992 (10)	8.4
2000 (10)	5.2
Labin	
1988-89 (10)	19.4
Jastrebarsko	
1992 (18)	8.4
Osijek	
1994 (18)	11.8
1997 (20)	15.8



**Figure 1.** Median concentrations of total PCB (ng g<sup>-1</sup> milk fat; determined in comparison to Aroclor 1260) in human milk samples between 1981 and 2003 (Krauthacker and Reiner 1994; Krauthacker 2000; Herceg Romanić 2006; this study).



**Figure 2.** Comparison of PCDD/F concentrations in human milk collected in 2001/02, and expressed as WHO-TEQ pg g<sup>-1</sup> milk fat. (Based on data taken from Van Leeuwen and Malisch 2002..)