# LEVELS OF ORGANOHALOGENATED POLLUTANTS IN HUMAN SERUM FROM IASSY, ROMANIA

Dirtu AC[1,2], Hanganu E[3], Dragan D[1], Mocanu R[1], Van Grieken R[2], Neels H[4], Covaci A[4]

[1]Department of Inorganic and Analytical Chemistry, University "Al.I. Cuza" of Iassy, R-700506, Romania; [2]Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium; [3]Department of Hematology, University of Medicine and Pharmacy "Gr.T. Popa" of Iassy, Romania; [4]Toxicological Centre, University of Antwerp, Universiteitsplein 1, B-2610 Antwerp, Belgium

## Introduction

Persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are highly lipophilic substances that persist in the environment, bioaccumulate through the food chain and pose a risk of causing adverse human health effects. In order to assess the risk of human exposure to POPs, their measurement in body tissues and fluids (biological monitoring) is generally recognized as a convenient procedure.[1]

Less knowledge on POPs has been built for human populations from Central and Eastern Europe. Most of the data available from Romania are limited to OCPs.[2,3] Although products based on DDT and technical mixtures of hexachlorocyclohexane (HCH) isomers were banned in Romania since 1985, important contamination sources are the illegal use of HCHs and DDT and the large stockpiles of these obsolete compounds. Such contamination sources are probably the cause of high levels observed in several Romanian human serum samples collected in 2001.[4] The scarcity of data available in the literature on the levels of OCPs and PCBs in human serum from Romania makes further interpretations impossible.

The present study aimed to measure the levels of OCPs, PCBs and polybrominated diphenyl ethers (PBDEs) in serum samples from the general population of Iassy County, Eastern Romania. Secondly, relationships between age, gender, place of main residence and concentrations of various pollutants were also investigated. A comparison between the levels of these pollutants in samples from Romania with levels found in samples from other Central and East European countries has been done showing that an extensive and rigorous program for the monitoring of OCPs and PCBs in Romanian population is highly needed in the light of possible adverse health effects acknowledged for these pollutants.

## Materials and Methods

Human serum samples were obtained from 142 persons during their visit at the Clinical Hospital of Pneumology of Iassy, Romania. Information from each volunteer regarding age, gender, place of main residence (rural or urban) and diagnosis, together with the concentrations of triglycerides (TG) and cholesterol (CHOL) of each sample were also known. Total lipids (TL) calculated using the formula TL = 1.33*TG + 1.12*CHOL + 1.48 (g/L) were found in the range of 3 to 10 with a mean value of 5.3 g/L and concentrations of OCPs and PCBs were expressed per lipid weight (lw).[5] Each individual sample was analyzed for PCBs and OCPs, while one pooled sample (4 ml serum) was prepared for PBDEs analysis. The OCPs under investigation were α-, β-, γ- and δ-HCH (expressed as HCHs), *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDD and *p,p'*-DDT (expressed here as DDTs), hexachlorobenzene (HCB), oxychlordane (OxC), *trans*-nonachlor (TN), *trans*-chlordane (TC) and *cis*-chlordane (CC). The following PCB congeners (IUPAC numbers) were targeted: 28, 52, 99, 101, 118, 138, 153, 156, 170, 180, 183, 187, 194, and 199. Internal standards used were PCB 46, PCB 143 and ε-HCH. In the pooled sample, the following BDE congeners (47, 99, 100, 153, 154 and 183) were analyzed. The procedure for extraction and clean-up of OCPs and PCBs from serum was described by Covaci and Schepens[6] and was used with minor modifications.

For samples with concentrations below LOQ, which were minor in number, zero was used for calculations. All statistical analyses were performed using SPSS 11.0.0 for Windows. Concentrations of POPs in serum were summarized using medians, 1st and 3rd quartiles (25 and 75 percentiles) together with minimum and maximum values. Gender differences in concentrations of pollutants, as well as differences in concentrations of pollutants related to the place of residence, were tested using one-way ANOVA with Scheffe's post-hoc test.

**Results and Discussion**

With few exceptions (*trans*-chlordane, *cis*-chlordane, and *p,p'*-DDD), the investigated OCPs had a detection frequency higher than 80% with α-HCH, β-HCH and *p,p'*-DDE being measured in all samples. The distribution of the 13 OCPs under investigation in serum samples in presented in Figure 1. The OCPs measured in higher concentrations were β-HCH (the most persistent HCH isomer), *p,p'*-DDE (principal metabolite of *p,p'*-DDT) and γ-HCH.

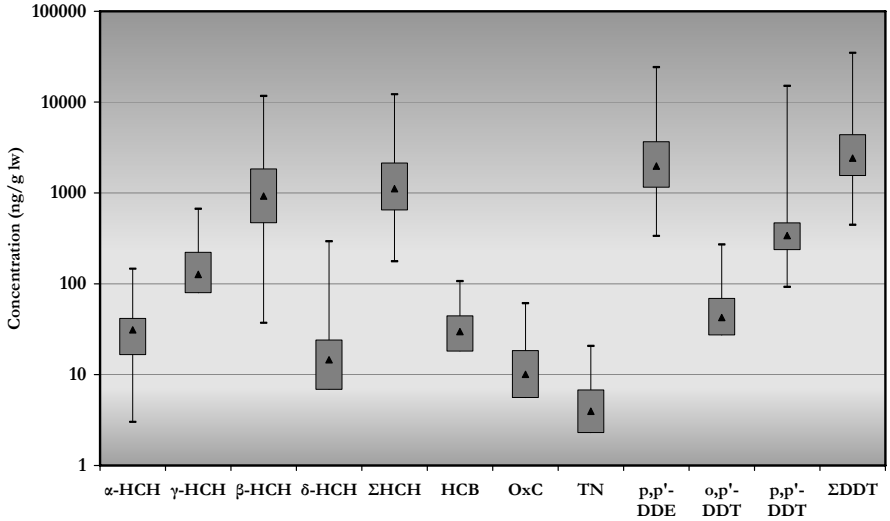


Figure 1. Distribution of OCPs (ng/g lipid weight) in human serum samples (n=142)

Two HCH formulations were used in Romania in the past: lindane, containing only the γ-HCH isomer and technical lindane which consisted in a mixture of HCH isomers in following proportions: 60-70% α-HCH, 5-12% β-HCH and 10-12% γ-HCH[7]. In the present study, HCHs were found in more than 98% of the investigated samples and β-HCH was the predominant HCH isomer with a median value of 923 ng/g lw. The presence of the α-HCH isomer in measurable amounts and the high levels found in all samples for the β-HCH isomer suggest an exposure of the general population to the technical lindane. Also, occasional high values for the γ-HCH isomer combined with its high detection frequency (98%) indicate the parallel use of the pure lindane formulation.

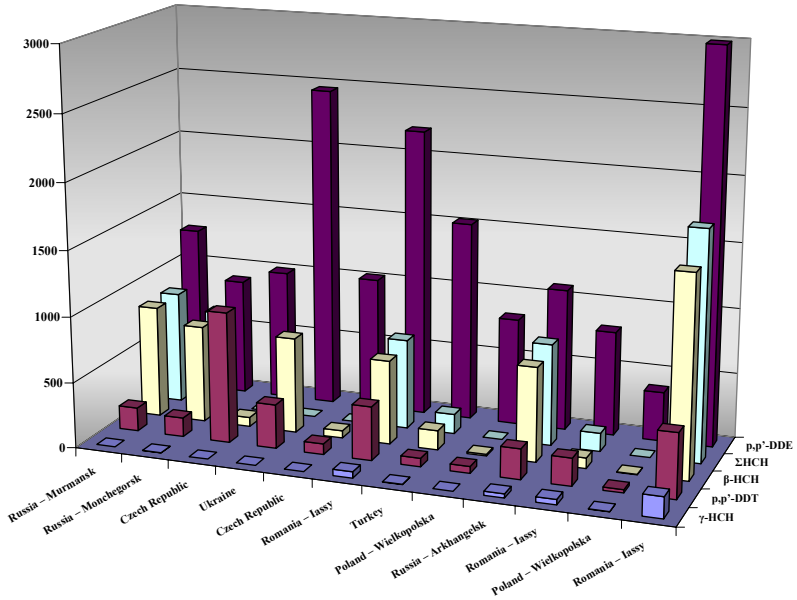


Figure 2. Levels of OCPs from different Central and East European countries

With exception of *p,p'*-DDD, all other DDT analogues (*p,p'*-DDE, *o,p'*-DDT and *p,p'*-DDT) were measured in all samples. The major contributor (>70%) to the ΣDDT was *p,p'*-DDE which was found at a median value of 1 975 ng/g lw with a range between 340 and 24 280 ng/g lw. The median values found for *p,p'*-DDD and *o,p'*-DDT were 6 and 42 ng/g lw, respectively. The technical mixture of DDT used in Romania contains 65-80% *p,p'*-DDT, but also 15-21% *o,p'*-DDT and up to 4% *p,p'*-DDD[7]. Although the profile of DDTs was dominated by *p,p'*-DDE, the large variation of the ratio *p,p'*-DDT/*p,p'*-DDE (range between 0.02 and 0.80) suggests various degree of exposure to DDT, including recent exposure, at least to some subgroups.

HCB was detected at low levels (median value of 30 ng/g lw) in all samples, while chlordane isomers were in most cases close to the LOQ. OxC and TN were detected in most samples (detection frequency >87%) with median values of 10 and 4 ng/g lw respectively, while TC and CC were found in most of the cases at concentrations <2 ng/g lw. These low concentrations indicate a low usage of chlordane in the studied area.

Except for *p,p'*-DDD, all analyzed OCPs were found at higher levels (up to 7 times higher for β-HCH) in 2005 compared to the sampling campaign from 2001, taking into account the same gender and age category in both studies[4]. This indicates that the exposure to OCPs has not decreased in the last years. Moreover, the levels of OCPs found in the studied Romanian population are in general higher than the corresponding levels in human samples collected from Central and Eastern European countries (Figure 2).

PCBs were present in all serum samples at sometimes considerable levels, indicating a higher exposure of the population from Iassy than previously reported. The total PCB values ranged from 45 to 4 970 ng/g lw, with a median value of 383 and the 25$^{th}$ and 75$^{th}$ percentiles of 243 and 588 ng/g lw, respectively.

The PCB profile was dominated of persistent congeners such as CB 138, 153, 170 and 180 which contributed to 75% to the ΣPCBs. PCB 101, a non-bioaccumulative congener, was above LOQ (6 ng/g lw) only in 6 samples (4.2%). The distribution of the PCBs under investigation in serum samples in presented in Figure 3.

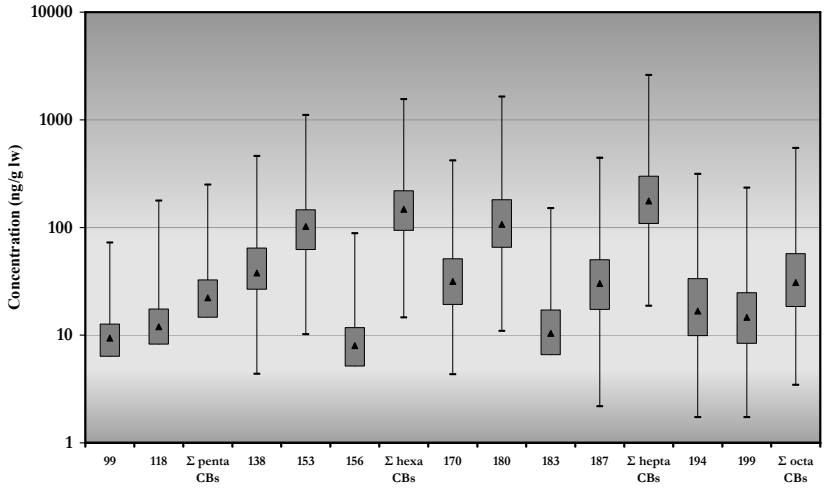


Figure 3. Distribution of PCBs (ng/g lipid weight) in human serum samples (n=142) (median values, 25 and 75 percentile and range)

All PCBs measured in 2005 were found at higher levels compared to the sampling campaign from 2001 (up to 5 times higher for PCB 138 and 16 times higher for PCB 170) indicating an on-going exposure to these pollutants. However, the present concentrations of PCBs in individuals from Iassy were lower compared to concentrations found in 2001 in individuals from the Western Romania[4]. Only CB congeners 170 and 180 were found at higher levels in samples from Iassy compared to other Central and East European countries (except Czech Republic) (Figure 4).

Linear regression analysis showed that the following chlorinated compounds: ΣHCH, *p,p'*-DDE, *p,p'*-DDT, ΣDDT and PCB congeners: 118, 138, 153, 170 and 180 correlated significantly with age (range of correlation coefficients r between 0.37-0.58), considering all samples together or with gender differentiation. The slope of

the curves showed that the rate of increasing levels with the age was higher for OCPs (∑DDT and ∑HCH) compared to PCBs, suggesting a higher exposure of the population to OCPs than to PCBs.

Except for *p,p'*-DDT and γ-HCH, the levels of other OCPs were significantly higher in females than in males ($p<0.05$). Except for octa-CBs for which concentrations were significantly higher in males ($p<0.05$), all other PCB homologues did not showed different concentrations between males and females. No particular factors associated with samples could explain the observed differences, especially since we do not expect a difference in exposure between the genders in the general population.

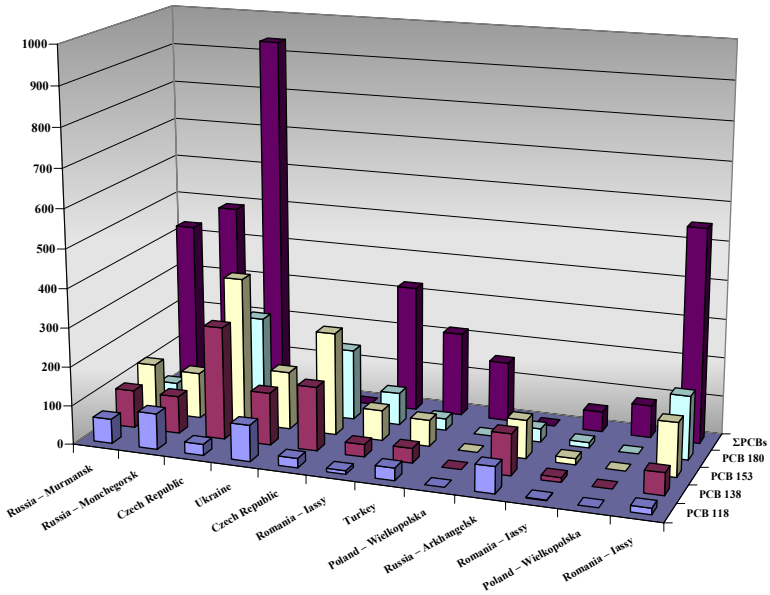


Figure 4. Levels of PCBs from different Central and East European countries

Only *p,p'*-DDE and the penta- to hepta-CB homologues showed significantly higher concentrations in individuals with the main residence in rural area compared to those in urban area. This may, at least partly, be explained by the specific activities and the dietary habits of urban and rural populations from Eastern Romania.

The highest concentrations were found for BDE 47 and 153 (340 and 400 pg/g lw, respectively). BDE 99 and 100 were measured at similar levels (120 and 140 pg/g lw, respectively). A value of 40 pg/g lw was determined for BDE 183, while BDE 154 was below LOQ (< 40 pg/g lw). The total concentration of PBDEs was 1 040 pg/g lw, which is lower that levels usually found in Western European population.[8]

This is the first systematic study applied on a relevant number of human samples from Romania to provide data on the concentrations of OCPs and PCBs. Compared to other Central and Eastern European countries, the Romanian human serum samples contained higher levels of these contaminants in human serum which suggest an on-going exposure to pollutants that officially are banned. This indicates that an extensive monitoring program for PCBs and OCPs in Romanian population is highly needed.

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