Levels of persistent fluorinated, chlorinated and brominated compounds in human blood collected in Sweden in 1997-2000

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Introduction

Levels of persistent fluorinated, chlorinated and brominated compounds in blood collected from the Swedish population have been determined in connection with several exposure and monitoring studies at the MTM Research Centre. A data base with 631 individual congener specific measurements on halogenated POPs such as dioxins, PCBs, HCB, DDE, chlordanes, PBDEs and PFAs including information on residency, age, BMI, diet, occupation, number of children, smoking habits, immunological status etc. has been compiled from samples collected between 1994 and 2004. A brief overview focusing on levels of some persistent chlorinated, brominated and fluorinated, compounds in blood collected in a background population group (n=83) in 1997-2000 is given here.

Materials and methods

In the frame work of the Swedish Environmental Protection Agency's program Health and Environmental Monitoring (HÄMI) the levels of five perfluoroalkylated (PFA) compounds, PFOS, PFOA, PFHxS, PFOSA and PFNA were determined in 66 whole blood samples and 17 plasma samples collected in 1997-2000 from 47 males and 36 females in Sweden. The samples represent background exposure of Swedish adults of all ages.[i]

Historically the analysis of PFAs have been limited to mainly PFOS and PFOA, but recently a number of other, potentially bioaccumulating, perfluorinated acids were reported in wildlife and in human blood[ii]. They have been shown to be associated with proteins in blood and plasma[iii]. Since possible degradation pathways, distribution and exposure routes for this group of compounds are poorly understood the information of exposure to a larger number of PFAs is necessary. The exposure of these compounds to the Swedish population had not been studied before this project was performed, except for 11 samples from Swedish blood banks analysed by 3M Company in 1998[iv] . Only PFOS was reported in the 3M study.

Our analytical method validated and used for determining the PFAs in the blood samples included solid-phase extraction and liquid chromatography electrospray mass spectrometry[v]. In the same

samples, which consist of a control group in a testicular cancer study, determination of some chlorinated and brominated halogenated persistent organic pollutants; PCBs, chlordanes, DDE, HCB and PBDE were done by high performing gas chromatography and mass spectrometry. More detailed data on these analysis have been reported elsewhere[vi, vii].

Results and discussion

Of the five PFA compounds analysed PFOS (perfluorooctanesulfonate) was the one found at the highest concentration in whole blood (n=66) (mean 18.2 pg/µl, range 1.7-37.0 pg/µl) followed by PFOSA (perfluorooctanesulfonamide) (mean 4.1 pg/µl, range 0.4-22.9 pg/µl), PFOA (perfluorooctanoic acid) (mean 2.7 pg/µl, 0.5-12.4 pg/µl), PFHxS (perfluorohexane sulfonic acid) (mean 2.3 pg/µl, range 0.4-28.4 pg/µl) and PFNA (perfluorononanoic acid) (mean, 0.3 pg/µl, range <0.1-1.9 pg/µl).

Besides the five compounds determined, we detected PFHxA (perfluorocaproic acid), PFDA (perfluorodecanoic acid), PFDS (perfluoro-1-decansulfonate), PFUnDA (perfluoroundecanoic acid), PFDoDA (perfluorododecanoic acid) and PFTDA (perfluorotetradecanoic acid) in some of the samples at low ppb concentrations. The only compound included in this study that we did not detect was PFBuS (perfluorobutanesulfonate) (the level of detection was 2pg/µl for this compound). Levels in the plasma samples were more or less comparable to whole blood levels when adjusted for volume. However, the distribution of the different PFAs between whole blood and plasma is not fully understood today, and a compound specific levels' comparison between these two matrixes should be done with some caution.

Our study shows that the Swedish population is exposed to a number of PFAs which are present in blood at ppb (ng/g whole blood) level. The concentrations of PFOS and PFOA are at the same order of magnitude as those reported to be found in other countries, such as US, Japan, Italy and India[viii].

A comparison of levels of all analysed persistent compounds in blood of 40 and 61 males respectively 18, 26, 41 and 45 females are reported in table 1. Since the PFA compounds are not lipophilic their levels are reported in ppb on whole blood basis whereas the other POPs are reported in ppb on lipid weight basis. The males (age 19-46) and females (age 46-75) represent different age groups, which also makes it possible to draw some conclusions concerning the effect of age on the different compound groups.

Concerning PFOS and PFOA blood levels and ranges there is no evident difference in the two age groups (men and women). A tendency can be seen towards higher levels in the younger male group. For the sum of PCBs, HCB, DDE and Chlordanes mean levels and maximum levels are significantly higher for the older group, which also is expected from the bioaccumulation and historical use that is characteristic for this class of POPs. For PBDE the exposure pattern is somewhat different from the 'older' POPs, the reason is not fully known today. It is also generally understood that there are no significant differences between levels of POPs in males and females of the same age in Sweden.

Table 1. Comparison of some persistent fluorinated (ppb in whole blood), chlorinated (ppb in lipids) and brominated (ppb in lipids) compounds in blood collected in 1997-2000 from Swedish males (average age 32) and females (average age 57).

Compound	Males	Females
PFOS	18.4 (1.7-37)[a]	17.8 (4.6-33)[b]
PFOA	2.9 (0.5-12.4)[a]	2.3 (0.8-4.1)[b]
PCB sum	394 (110-1,083)[c]	592 (141-1,193)[d]
HCB	24 (8.8-47)[c]	34 (8.9-81)[e]
DDE	140 (99-601)[c]	428 (51-1,431)[e]
Chlordanes	22 (8.2-70)[c]	32 (5.8-76)[e]
PBDE sum	8.1 (1.5-28)[f]	5.6 (1.9-11)[g]

a n=40, b n=26, c n=61, d n=41, e n=45, f n=38, g n=18

Perfluoroalkylated (PFA) compounds possess unique properties like thermal, chemical and biological stability due to a short C-F bound (1.38 Å), the small size of fluorine and fluorines electronegativity, and they have a potential for bioaccumulation[ix]. PFAs have been shown to be distributed on a global scale in biota including wildlife and humans[x] and the human exposure seems to be possible through the diet. The next question then to be answered is, why do not PFOS and PFOA show age related increase (or decrease if exposure would follow the pattern of PBDE) in blood levels?

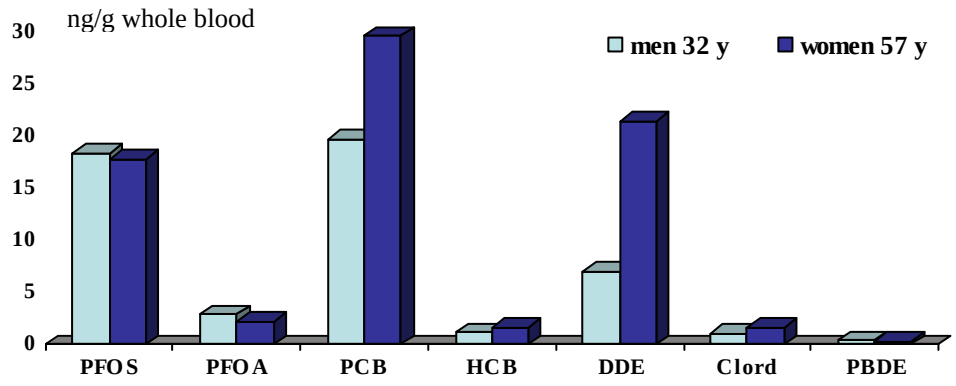

Figure 1. Comparison of levels (ng/g whole blood) of some fluorinated, chlorinated and brominated persistent compounds in human blood collected in Sweden in 1997-2000.

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