ANNEX 2
(HUMAN TISSUES)

GLOBAL MONITORING PLAN
FOR PERSISTENT ORGANIC POLLUTANTS

UNDER THE STOCKHOLM CONVENTION ARTICLE 16 ON EFFECTIVENESS EVALUATION

FIRST REGIONAL MONITORING REPORT

WESTERN EUROPE AND OTHER STATES GROUP (WEOG) REGION

JANUARY 6 2009

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A2. POPs in Human Tissues: Programme Summaries

The following compilation of programme summaries for international and national monitoring efforts for persistent organic pollutants (POPs) is the basis for Chapter 5 of the WEOG region report. The programme summaries were prepared according to a template provided by the regional organizational group (ROG). The summaries were submitted by program leads/managers and have not been edited by the ROG. For further information, please contact the program managers/leads or refer to the appropriate contact information provided in each summary.

A2.1 International Monitoring Programmes for POPs in Human Tissues

A2.1.1 AMAP: Arctic Monitoring of Human Media for Persistent Organic Pollutants in the Regions of the Central and Eastern Europe and the Western European and Others Groups

Key Message

The Arctic Monitoring and Assessment Programme (AMAP) has collected information of human levels of POPs since the early 90thies. The program has focused mainly on pregnant women and children. Baseline data on blood levels and, partly, breast milk levels, are now available for both temporal and spatial trends. The highest Arctic exposures to several POPs are faced by Inuit populations in Greenland and Canada. The exposures are linked mainly to consumption of marine species as part of the traditional diets. Fragmentary temporal trends seem to demonstrate a decline in levels of the POPs presently subject to the Stockholm Convention related to long range transport. Exposure related to local exposure of may be increasing from some POPs in some areas, (e.g., the DDT-group), as well as emerging contaminants (e.g., brominated flame retardants and polychlorinated naphtalenes - PCN). Dietary intake of PCBs exceeds national guidelines in a number of Arctic communities; especially in the Russian Arctic, Canada and Greenland.

AMAP anticipates continuing participation in the global monitoring of human exposure under the Stockholm Convention on POPs. More specific trend data will be available through ongoing studies organized by AMAP during 2009.

Background

The AMAP is one of five Working Groups of the Arctic Council The primary function of AMAP is to advise the governments of the eight Arctic countries (Canada, Denmark/Greenland, Finland, Iceland, Norway, Russia, Sweden and the United States) on matters relating to threats to the Arctic region from pollution, and associated issues. The human data on levels and trends of contaminants listed in the Stockholm convention are available, basically from three reports (AMAP 1998; AMAP 2002; AMAP 2004), supplemented by a number of scientific publications

(e.g., Odland et al 2005; Anda et al 2007; Polder et al 2008; Hansen et al 2008). This creates opportunities to assess reliable data on human contaminant levels from the early 1990s. AMAP anticipates future trend monitoring, basically in 5 years periods.

Sampling

The AMAP HHAG Sampling Program is based on a strict protocol with guidelines for sampling, transportation and storage, as well as analytical performance criteria including a ring test program. Basic prerequisites include competence of personnel, adequacy of infrastructure and equipment, documentation of procedures, traceability of measurements, and calibration. Legislative bodies and international standardization organizations have promoted guidelines addressing these requirements; e.g., ISO guide 17025 "General Requirements for the Competence of Calibration and Testing Laboratories" (ISO 1999) is generally accepted as an appropriate basis for laboratory quality systems. The protocols for inclusion of the mother/child pairs include the relevant inclusion variables, such as age, parity, duration of breast feeding.

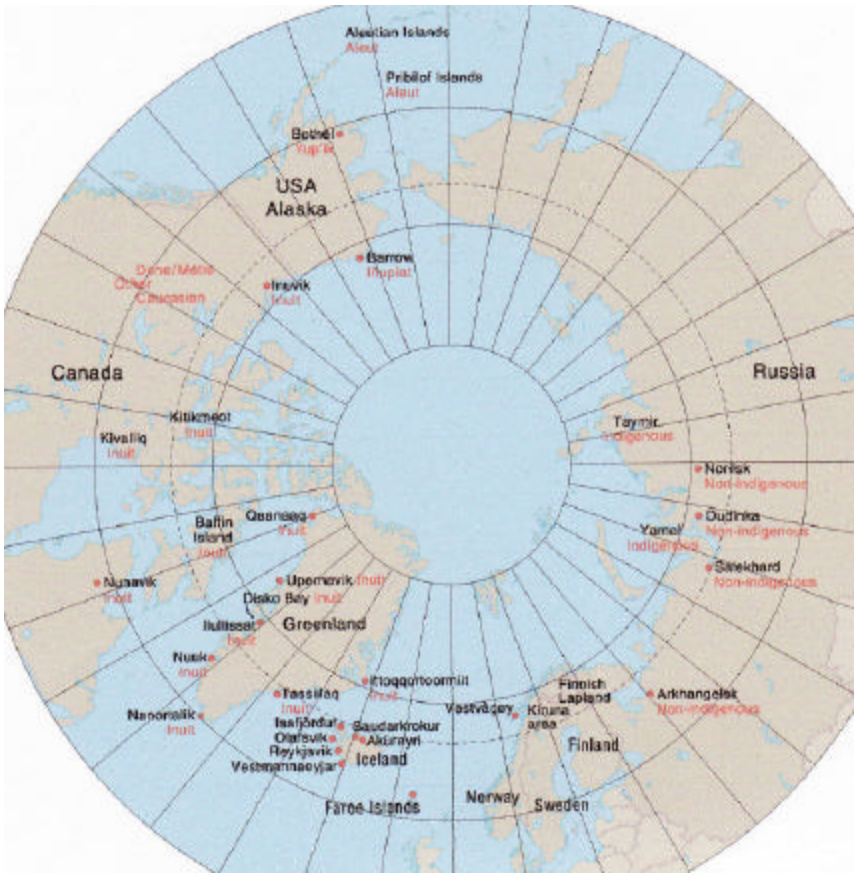

Figure 1: Sampling locations in the AMAP Phase II circumpolar blood monitoring study.

Sample analytical procedures and data comparability
The standard protocol has been developed under the leadership and supervision of the Centre de Toxicologie of the Institute Nationale de Sante Publiques du Quebec (CTQ website). A key issue is QC, which incorporates a range of activities such as the establishment and implementation of appropriate in-house QA routines, the use of relevant reference materials, and participation in inter-laboratory compariuson programmes. The AMAP Human Health QA/QC system has been established to accomplish this. Main activities include intercomparison programmes on relevant reference samples based on human material. This includes preparation and distribution of test samples, collection and interpretation of data, and the communication of results. All laboratories producing data for the AMAP are required to participate in this interc omparison programme and to achieve acceptable results (for details, see AMAP 2003; CTQ website).

Data storage
A process to integrate and store in a common database all human data related to the AMAP has been in operation since the establishment of the activities. Since all national protocols on human scientific studies are controlled and recognized by the national and regional ethical committees, it has been impossible to store individual data from participants in a common international database. This question has so far been solved by close cooperation on reporting of data not traceable to individual participants. The databases are built on compatible software for national and international comparisons.

Results
Sampling locations and levels of different POPs in the blood of mothers and women of childbearing age, stratified by regions are shown in figures 5.1 to 5.8 ((figures from AMAP (2003) are reproduced at the end of this summary)); Chlordane (Fig.5.2); DDE (Fig.5.3); HCH (Fig.5.4); PCB (Fig.5.5, as Arochlor 1260); HCB (Fig.5.6); Toxaphene (Fig.5.7);. Detailed levels by region are available in AMAP 2003, AMAP Assessment 2002 "Human Health in the Arctic".

The AMAP studies demonstrate that the levels of environmental contaminants in blood samples from humans living in the Arctic regions of the eight circumpolar countries are generally higher in the Arctic people who consume certain (mainly marine based) traditional/country foods (e.g., the Inuit of Greenland and Arctic Canada). For Greenland Inuit in particular, the levels of polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), total chlordanes, found in maternal blood samples are higher than those found in samples from other circumpolar countries, and are likely to reflect the higher consumption of marine mammals by this group.
Other key findings include higher levels of total DDT in a non-indigenous population from Arkhangelsk (Russia) than in any other region, indicating possible local sources of this pesticide or in Russian agricultural regions from which food is transported to the Arkhangelsk region. For HCH, the highest levels were also seen in Arctic Russia among non-indigenous groups, but elevated levels were also observed in Iceland and among the 'Others' group (i.e., non-Caucasian, non-Dene/Métis, non-Inuit) in the Canadian Arctic. Recent data for the Faroe Islands indicate that, due to public health advice for mothers to restrict their consumption of pilot whales, there has been a significant decrease in maternal Hg levels, although very little change in PCB levels. The differences with these two contaminants are probably due to the short half-life of Hg in the body compared to that of PCBs. It is difficult to determine time trends in environmental contaminants of concern in other Arctic human populations since only one or two sequential

datasets exist. Most monitoring of human contaminant levels in the Arctic has taken place over only the last five to ten years, and although this has permitted a reasonably good assessment of the spatial variation in contaminant levels in humans, it is too short a period (at the time of preparation of this summary) to reliably determine temporal trends.

The Russian Persistent Toxic Substances (PTS) Study (AMAP 2004) is the first assessment of the environmental status of these substances in the Russian Arctic, with emphasize on the indigenous populations. Both the AMAP blood study protocol for 250 mother/child pairs, 60 breast milk samples following the WHO protocol as well as blood from close to 1500 persons of different age and gender in the general population were included in the study in the period 2002-2003. In this study all toxic metals and new contaminants (e.g., brominated flame retardants) were included. Main levels of contaminants in blood and breast milk are shown in the Figures 7.1 – 7.21b (figures from AMAP (2003) are reproduced at the end of this summary). The main conclusions were:

1. As the occurrence of PTS in human blood in the Russian North is explained to a large extent by the intake of contaminated fish (marine and freshwater), marine mammals, sea birds, and reindeer meat, it follows that PTS concentrations in the blood of women giving birth, and of their children, are also affected by the traditional diet of indigenous people. The highest concentrations of PTS in maternal and umbilical cord blood were detected in Chukotsky District of the Chukchi REGION. These high levels of PTS in blood in this particular area may be associated with high levels of consumption of species occupying the upper trophic levels in marine food webs, as part of the traditional diet.
2. Among the DDT group of compounds, DDE is the most prevalent POP in human blood, the ratio of DDE/DDT concentrations in blood in the various regions ranging from 3-8, although a ratio of 30 was found in the Aral control area.
3. A comparison with results obtained during the 2002 AMAP circumpolar maternal blood survey shows that levels of organochlorine pesticides in human blood samples from the Russian Arctic are similar to those found in coastal areas of Greenland and northern Canada, although for some POPs, such as toxaphene and mirex, the levels found in the Russian Arctic are much lower.
4. Geometric mean concentrations of dioxins in blood samples from adults of both sexes and for all regions, are within the range 0.3–9.4 pg/g TEQ of lipids. The highest concentrations in individual samples were 18.7 and 18.1 pg/g TEQ of lipids (in the Chukchi and Taymir Regions, respectively). The highest concentration of PCDD/PCDFs in human blood from the northern areas of Russia (18.7 pg/g TEQ of lipid) is close to the lowest concentrations found in residents of industrial regions.
5. Among the samples of breast milk from the Chukchi Region, the highest levels of nearly all POPs were found in breast milk from Chukotsky District. Levels here, exceed those found in other areas of the Chukchi Region by 3-6 times for HCB, 10-80 times for oxychlordane, 10 times for mirex, trans- and cis nonachlor, and toxaphene, and 4-5 times for the sum of 15 congeners of PCBs. Concentrations of DDT and its metabolites in breast milk did not differ significantly in samples from different areas of the Chukchi Region.
6. With respect to levels of PCBs, oxychlordane, DDT, DDE and trans-nonachlor, Chukotsky District is similar to Nunavik in northern Canada. However, concentrations of b-HCH and HCB in breast milk from Chukotsky District are 30 and 5 times higher, respectively, than values found in Canada. Concentrations of PCBs, HCBs, b-HCH, and oxychlordane in breast milk from other

areas of the Chukchi Region are comparable to those occurring in the breast milk of women from Kargopol, Severodvinsk, Arkhangelsk, and Naryan-Mar.
7. Maximum levels of breast milk contamination, like human blood samples, for all PTS determined, including PCDD/Fs and PBDEs, were found to be in the Chukotsky District, which is situated in the coastal area of the Chukotka peninsula.
8. Average concentrations of dioxin and furans detected in breast milk of women from Chukotka are the same as levels detected in breast milk of women from Norway and Ireland, and are lower than levels found in Northern Canada (northern and southern Quebec).
9.Comparison of concentrations of PBDE and PCDD/F in blood samples of the adult population reveals a marked difference in the distribution of these PTS in the Russian North, with low levels of PCDD/Fs coinciding with high levels of PBDEs, and vice versa. The difference is most obvious in the Taymir Region, the Nenets Region (Nelmin-Nos), and the Kola Peninsula (Krasnoshchelie). There is not yet sufficient data to ascertain the reasons for the difference in dioxin and PBDE distribution, but it is clear that the sources of pollution and contamination pathways for these groups of substances differ from each other. PBDEs occur at higher levels in areas close to the industrialized source regions of Europe and North America.
10.Maximum PBDE concentrations (of 934 pg/g lipids) in blood samples of populations from the Russian Arctic regions were found on the Kola Peninsula (Krasnoshchelie), and correspond to those observed in sampled populations in Norway in 1981.
11.PBDE concentrations in breast milk samples of women from the Chukchi Region (0.1-0.3 ng/g of lipids) are an order of magnitude lower than concentrations measured in Germany. Control samples of breast milk from St. Petersburg contained PBDE in amounts (1.06 ng/g of lipids) comparable with those from Germany. The predominant congener in all samples was BDE-47.

One important aspect of this study was the possibility to perform an assessment of the different media for levels and trend assessments. Anda et al (2007) concluded, based on the analytical and statistical comparison of breast milk, maternal blood, and cord blood, that both maternal blood and breast milk are reliable media for population assessment regarding contaminant levels over time. This indicates that the WHO protocol for breast milk and the AMAP protocol for blood studies can be complementary for parallel project design in the future.

Odland et al (2005) did a comparative study of new contaminants in North Norway and the Russian Arctic as a follow up to the Russian PTS Study (AMAP 2004). The study concluded that brominated flame retardants of the type polybrominated diphenyl ethers (PBDE) were discovered in all women participating in the study. The levels were low, but the results indicate that the substances can be found in humans living far away from the sources. The levels of PBDE were higher in the Norwegian blood samples compared to the Russian. This indicates that urban Norwegian locations might be more exposed to brominated flame retardants than remote areas in Siberia.

As for the fluorinated compounds the most common PFAS, the perfluoroktylsulfonat (PFOS), was found in 70 % of the blood samples of both groups.. The levels were higher in the Norwegian blood samples. The blood levels of this important contaminant group seem generally higher than more well known pollutants, such as the PCBs.

The first comprehensive trend study of breast milk data in the Arctic has been published by Polder et al (2008) and deserves some detailed comments. This study presents for the first time temporal changes of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in Russian human breast milk samples. Concentrations of OCPs and PCBs in samples from three locations in the North West of Russia in 2000-2002 (n=42), were compared to corresponding levels measured in 1993-1996 (n=58). In addition brominated flame retardants (BFRs), consisting of polybrominated diphenylethers (PBDEs) (including BDE-209) and hexabromocyclododecane (HBCD) were analysed in samples from 2000-2002 (n=37). The present levels of SigmaDDTs and SigmaHCHs were 5 and 10 times higher than corresponding levels in the neighbouring country Norway. Median concentrations of SigmaHCHs (196 microg/kg lw), SigmaCHBs (19.7 microg/kg lw) and SigmaPCBs(16) (316 microg/kg lw) were highest in Murmansk. The percentage of p,p'-DDT to SigmaDDTs and ratio DDE/DDT suggest possible ongoing use of DDT in Russia. Levels of PBDE were low and dominated by the congeners BDE-47 and BDE-153. The deca brominated BDE-209 was detected in all analysed samples (median concentration 0.19 microg/kg lipid). Levels of SigmaOCPs and SigmaPCBs decreased 56 and 30% in Murmansk and 36 and 43% in Arkhangelsk during the study period. The decline of SigmaOCPs was significant at both locations ($p<0.05$-$p<0.0001$). For SigmaPCBs, the decreasing trend was only significant in Arkhangelsk ($p<0.0001$). In addition, a decline of Sigmatotal TEQs (SigmaTEQs of PCDDs/PCDFs, non-ortho- and mono-ortho PCBs) was observed in Murmansk and Arkhangelsk during the study period. The exposure of infants by PCDDs/PCDFs and dioxin-like PCBs is still exceeding the daily tolerable intake (TDI) in North West Russia. However, the concentrations of PCDDs/PCDFs and dioxin-like PCBs seem to have declined very rapidly. Another observation seems to emerge from the follow up of the Russian PTS Study; that the global source contaminants are declining, while the local sources lead to a continuous increase in human levels.

Citations

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AMAP, 2003. AMAP Assessment 2002: Human Health in the Arctic. Arctic Monitoring and Assessment Programme (AMAP), Oslo, Norway. Eds. Hansen JC, Gilman A, Klopov V, Odland JO. xiv + 137 pp. Main author of chapter 6, co-author of three other chapters.

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Hansen JC, Deutch B, Odland JO. Dietary transition and contaminants in the Arctic: emphasis on Greenland. Int J Circumpolar Health Suppl 2, 2008.
Odland JO, Sandanger T, Heimstad E. Kartlegging av miljøgifter i humane blodprøver fra Taimyr, Russland og Bodø, Norge – en pilotstudie av "nye" miljøgifter. SFT 2005. SPFO-rapport: 930/2005.
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The following figures are taken from the AMAP Assessment Report (2003)

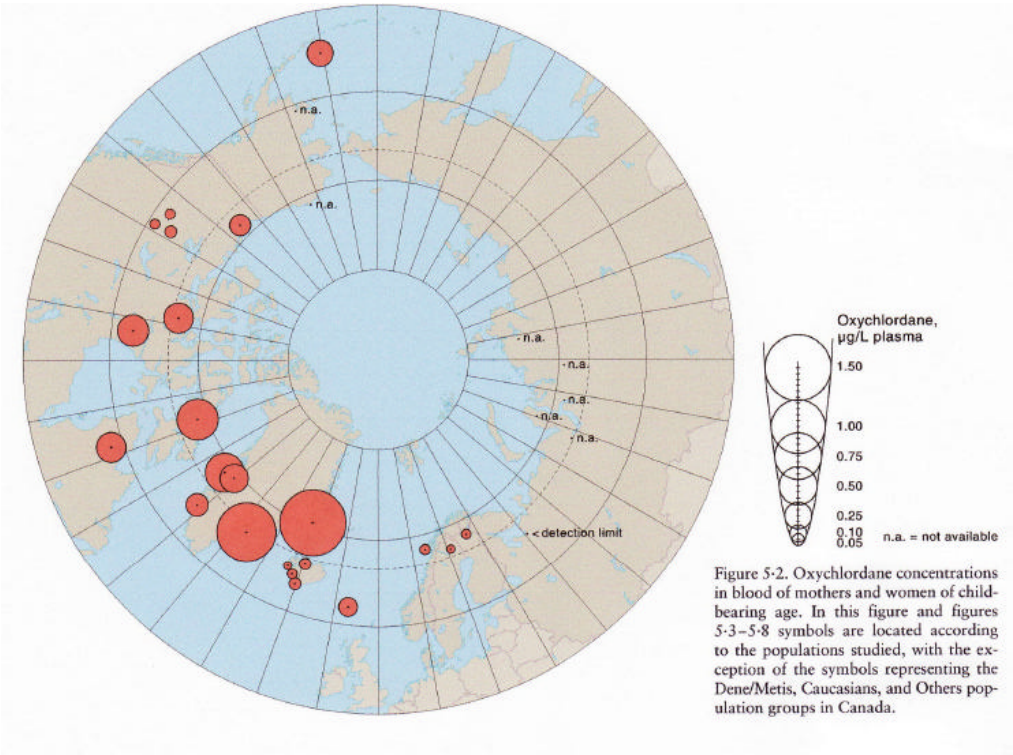


Figure 5·2. Oxychlordane concentrations in blood of mothers and women of childbearing age. In this figure and figures 5·3–5·8 symbols are located according to the populations studied, with the exception of the symbols representing the Dene/Metis, Caucasians, and Others population groups in Canada.

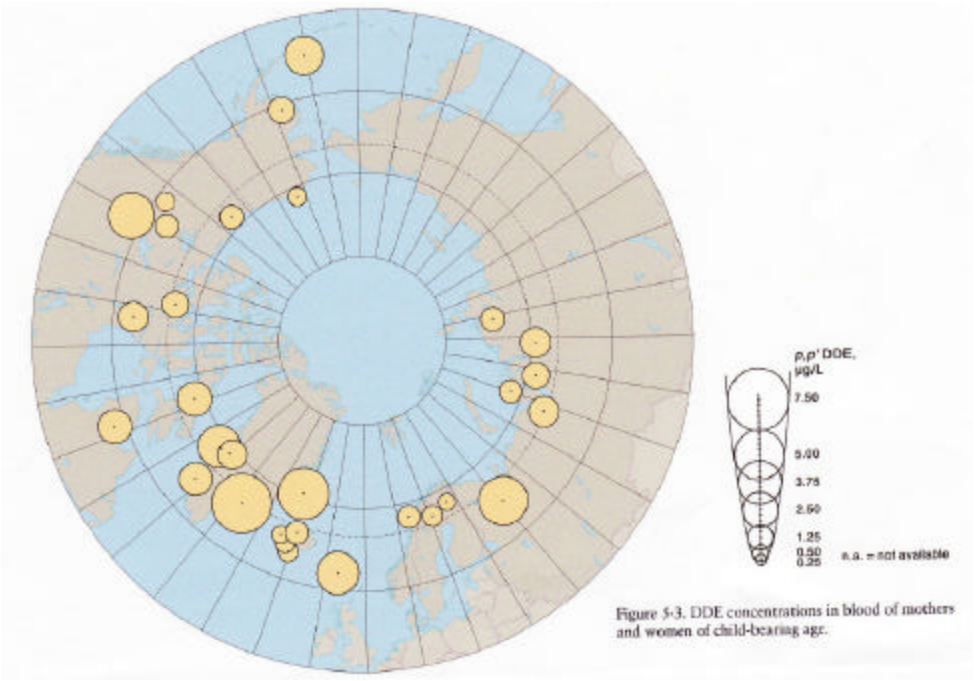


Figure 5-3. DDE concentrations in blood of mothers and women of child-bearing age.

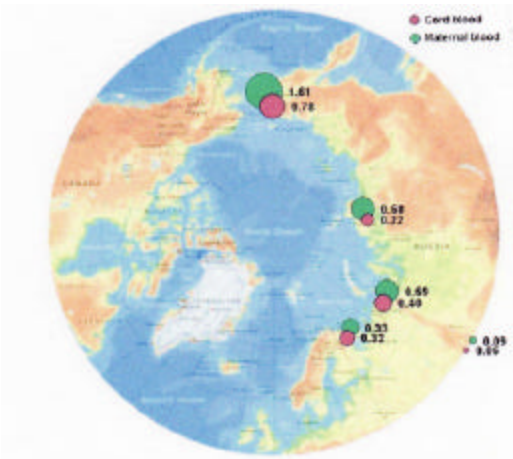


Figure 7.1. Levels of HCB in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

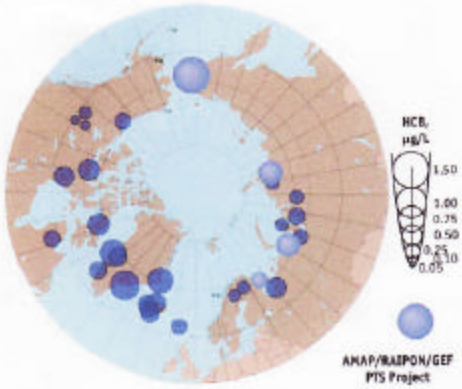


Figure 7.2. Comparison of the results obtained in this project for HCB in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

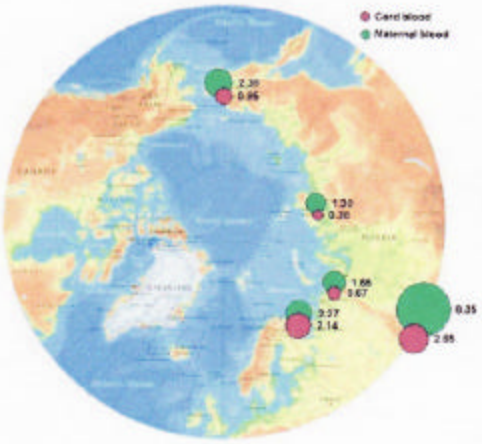


Figure 7.3. Levels of DDE in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

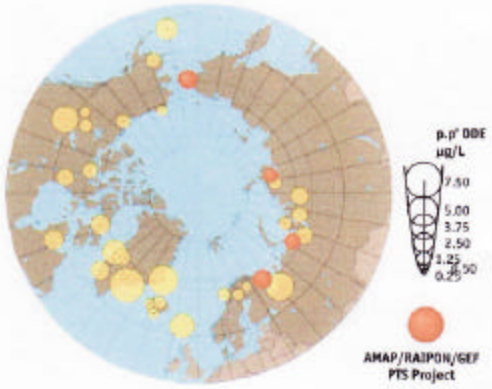


Figure 7.4. Comparison of the results obtained in this project for DDE in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

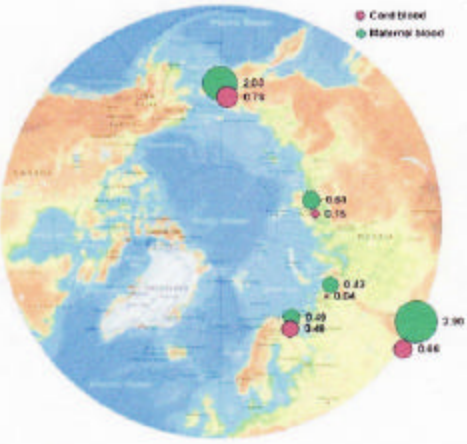


Figure 7.5. Levels of β-HCH in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

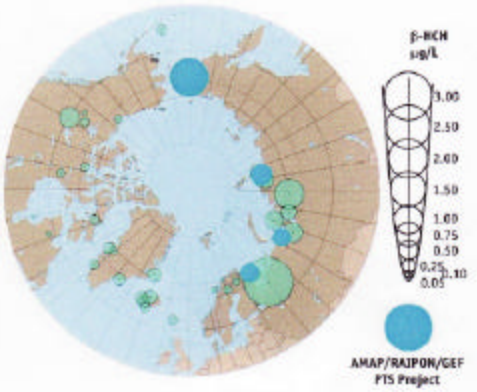


Figure 7.6. Comparison of the results obtained in this project for β-HCH in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

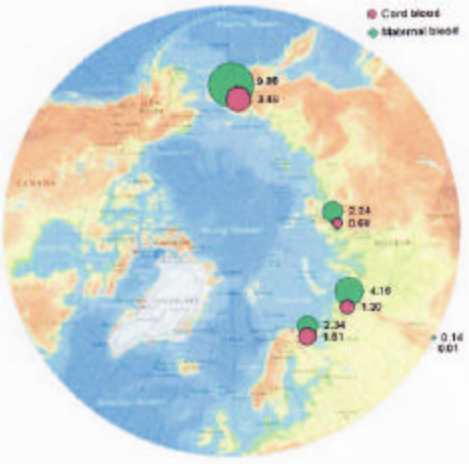


Figure 7.7. Levels of sum of PCBs (shown as Aroclor 1260 equivalents) in maternal and cord blood in Russian Arctic (geometric means, µg/L, plasma).

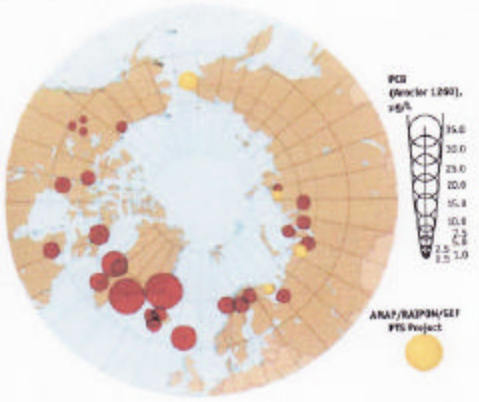


Figure 7.8. Comparison of the results obtained in this project for sum of PCBs (as Aroclor 1260 equivalents) in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

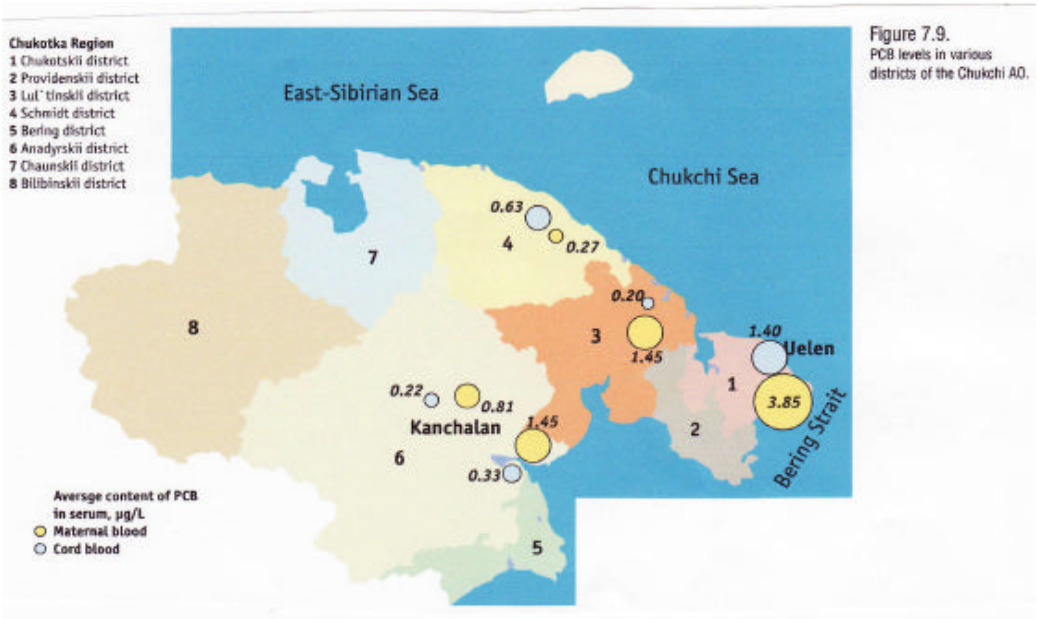


Figure 7.9.
PCB levels in various districts of the Chukchi AO.

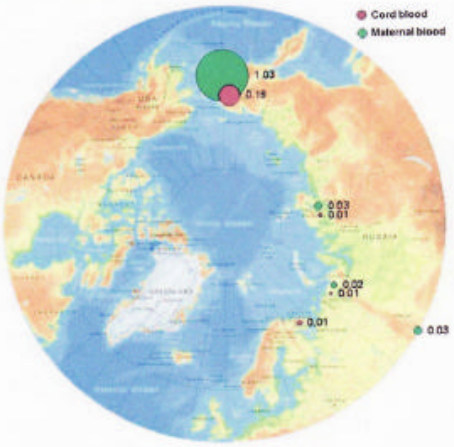


Figure 7.10. Levels of oxychlordane in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

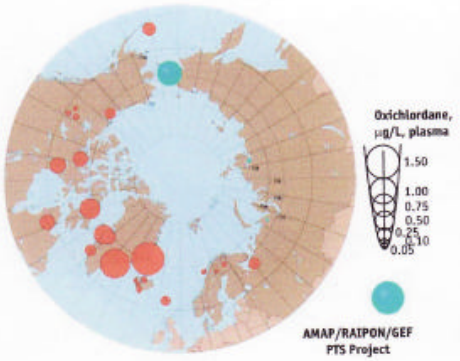


Figure 7.11. Comparison of the results obtained in this project for oxychlordane in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

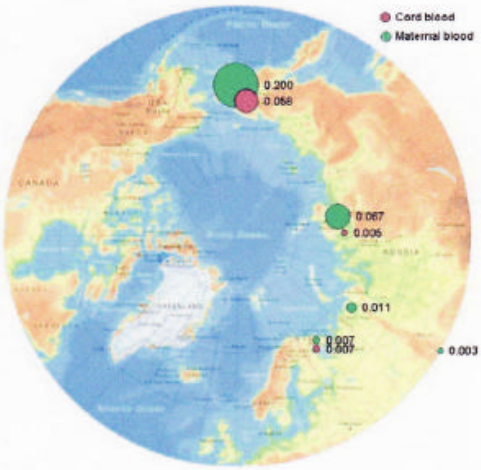


Figure 7.12. Levels of total toxaphenes in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

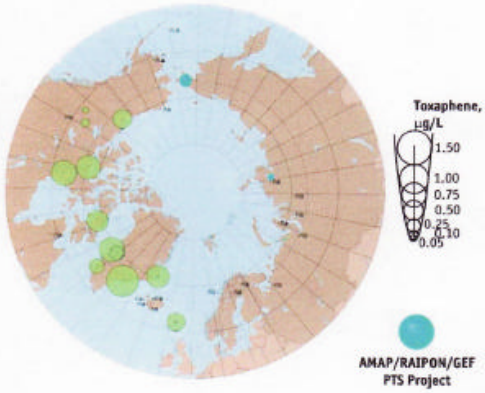


Figure 7.13. Comparison of the results obtained in this project for toxaphene in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

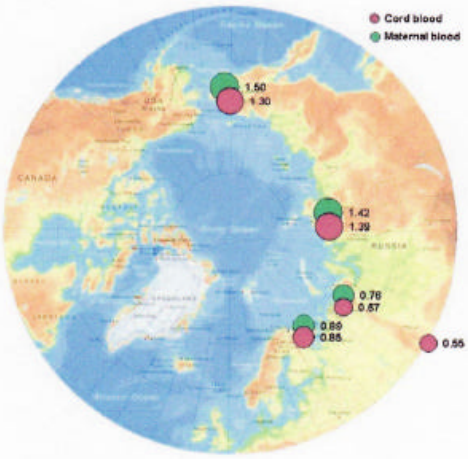


Figure 7.14. Levels of mercury in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

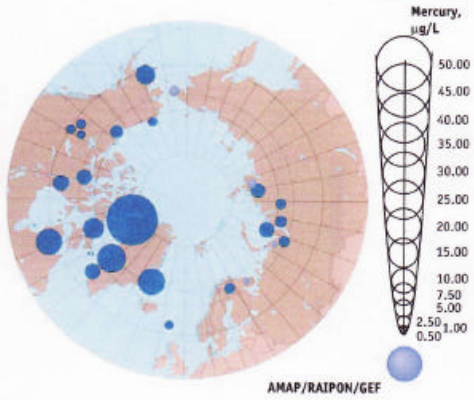


Figure 7.15. Comparison of the results obtained in this project for mercury in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

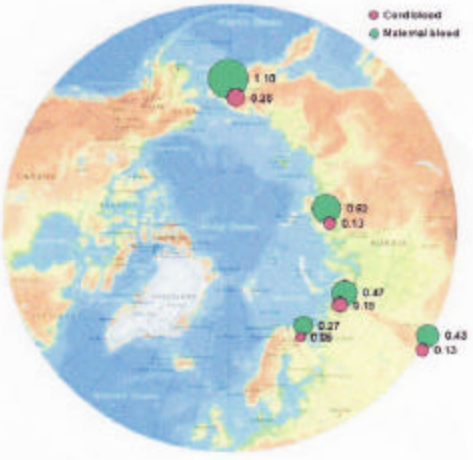


Figure 7.17. Levels of cadmium in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

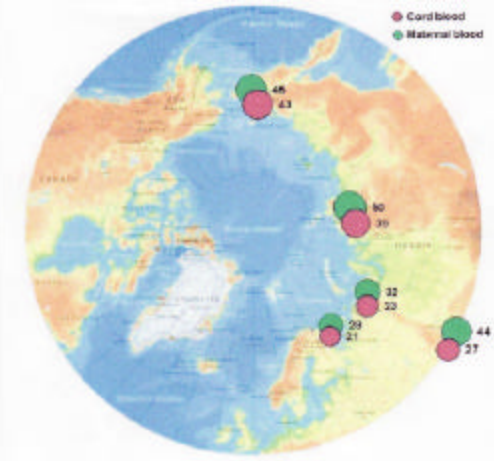


Figure 7.16. Levels of lead in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

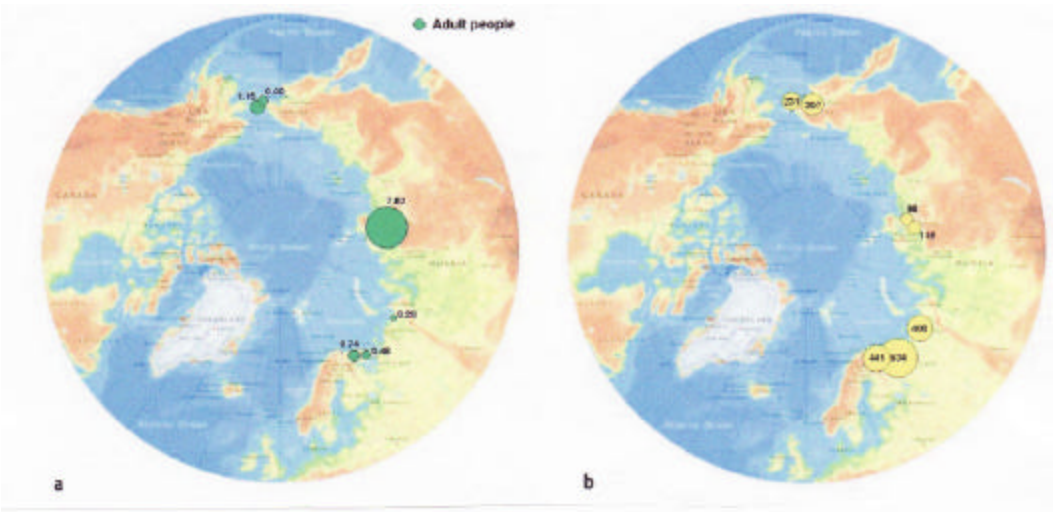


Figure 7.18. Levels of (a) PCDD/F (geometric means; pg/g TEQ of lipids), and (b) PBDE (geometric means; pg/g of lipids) in plasma of adults in Russian Arctic.

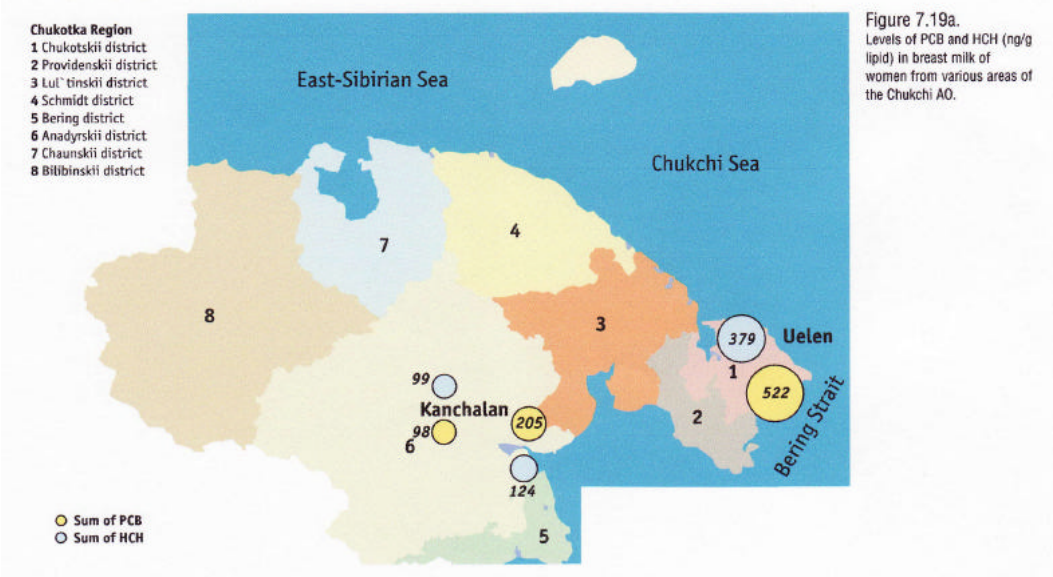


Figure 7.19a.
Levels of PCB and HCH (ng/g lipid) in breast milk of women from various areas of the Chukchi AO.

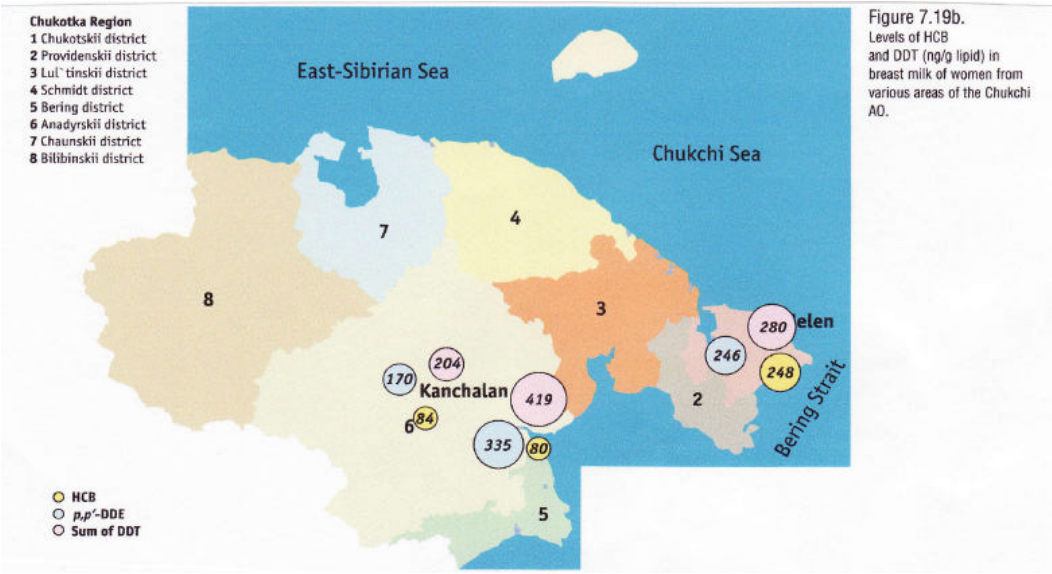


Figure 7.19b.
Levels of HCB and DDT (ng/g lipid) in breast milk of women from various areas of the Chukchi AO.

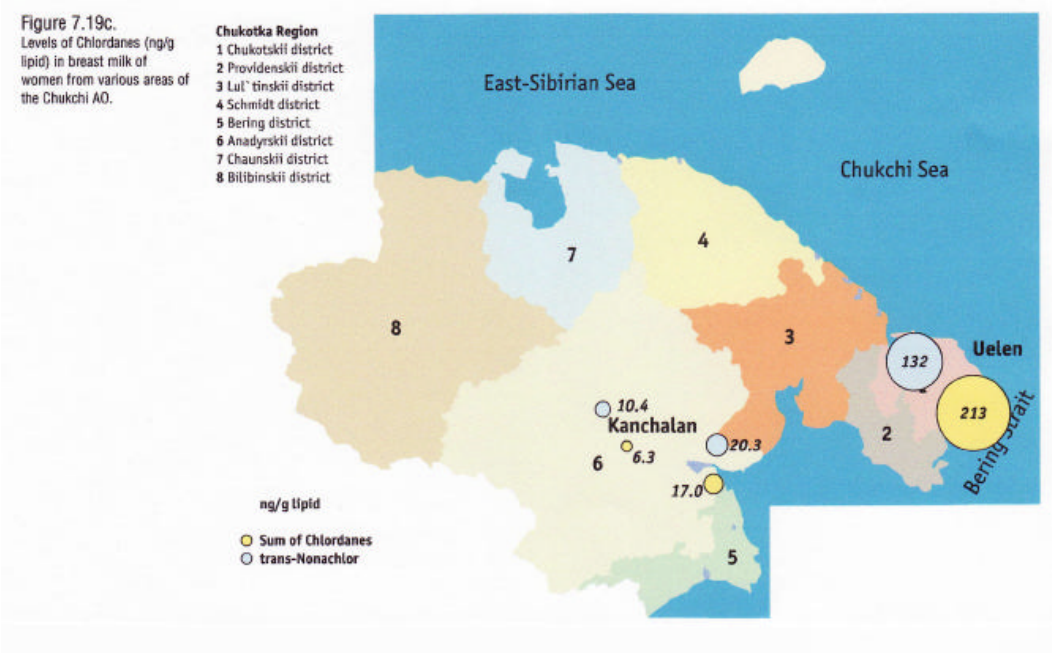


Figure 7.19c.
Levels of Chlordanes (ng/g lipid) in breast milk of women from various areas of the Chukchi AO.

Figure 7.19d.
Levels of Mirex and toxaphene (ng/g lipid) in breast milk of women from various areas of the Chukchi AO.

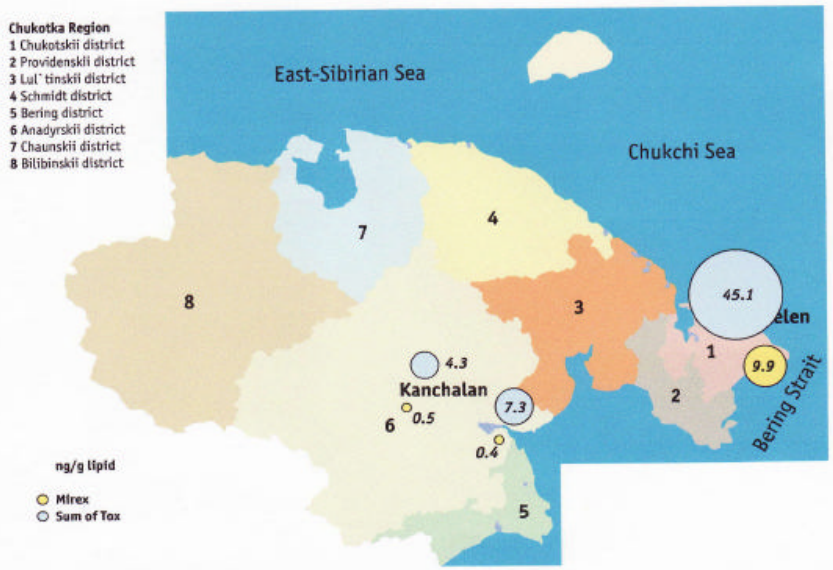


Figure 7.21a.
Levels (ng/g lipid) of PCDD/F in breast milk of women from various areas of the Chukchi AO.

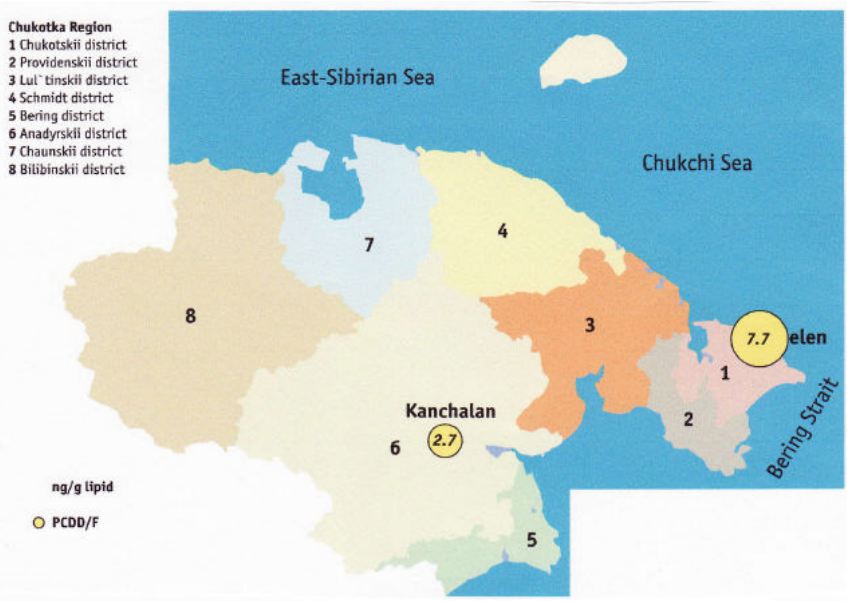
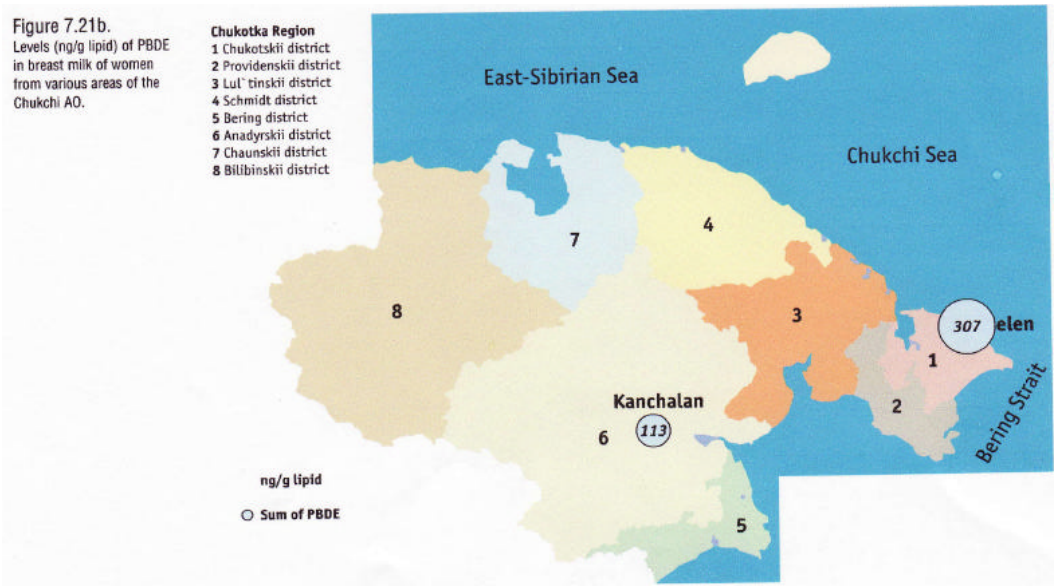


Figure 7.21b.
Levels (ng/g lipid) of PBDE in breast milk of women from various areas of the Chukchi AO.



A1.1.2 WHO- Coordinated Survey of Human Milk for Persistent Organic Pollutants in Cooperation with UNEP. Results from the WEOG region.

Key Message

In the Western European and Others Group (WEOG), the overall results of the monitoring coordinated by WHO indicates that trends in the levels of the most Stockholm POPs in human milk continue to decline. For PCDDs, PCDFs, data from over the past two decades suggest that the levels of these POPs have fallen steadily in human milk from their earlier rather high levels. For dioxin-like PCBs, the picture is less clear for some countries, but in general, declining levels are observed. For marker PCBs, levels are also declining, but the distribution PCB profiles observed among countries suggest that the sources of PCBs are different. Levels for the other POPs are low with levels for aldrin, endrin and mirex below the limit of determination. Most organochlorine pesticides have been banned for many years, which is reflected in the ratio of parent compound to degradation product, e.g., DDT to DDE. Declining trends in these POPs indicate a continuing decline of exposure of the general population as a result of emission reduction and other control measures that have been taken in the past.

Background

Since the mid-seventies, WHO in collaboration with UNEP has implemented the food component of the Global Environment Monitoring System (GMES/Food), which collects, collates and evaluates data on the levels and trends of contaminants in food and human milk. These contaminants include the organochlorine pesticide POPs, which were the initial focus of attention. Beginning in the mid-eighties, WHO coordinated several surveys of the levels of dioxin-like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These surveys were carried out in collaboration with other international organisations and national institutions, and concentrated particularly on the health risk of infants, due to exposure through contaminated human-milk, and aiming to prevent and control exposure to these chemicals through food.

More recently, the WHO protocol for these surveys has been revised to include the objective of providing accessible, reliable and comparable data on levels of POPs in human milk for purposes of the Stockholm Convention. The latest protocol (used for the ongoing 4th survey) is different from the early protocol because it: a.) emphasizes the protection, promotion and support of breastfeeding; b.) specifies a minimum of 50 donors for one pooled sample, and; c.) includes the analysis of all 12 POPs currently covered by the Convention. The latest version of WHO Guideline(1 October 2007) is currently available at: http://www.who.int/foodsafety/chem/POPprotocol.pdf

Participation by WEOG countries in the WHO surveys has varied with some countries participating in all of the surveys while some have not participated in any of the surveys. Nonetheless, the geographical and temporal coverage for WEOG is the best of any of the UNEP regions. As additional WEOG countries continue to enrol in the WHO fourth round survey, coverage is expected to improve in the future.

Sampling

In order to promote reliability and comparability, participating countries are encouraged to adhere as closely to WHO protocol as possible. However, it is also recognized that the situations in countries vary considerably so that some flexibility is required. However, guidance is provide to assist countries in developing their national protocols, including:

Number of donors: A minimum of 50 individual donors should each provide 50 ml of human milk for preparing the pooled sample. Note that one additional participants per million population over 50 million is recommended for large countries and in some cases, more than one pooled sample may need to be prepared. On the other hand, a lower number samples may be necessary for small countries.

Strategies for selecting donors: Interviewing of potential donors can take place pre- or post-natal or well-baby clinics. The stratification of donors should represent the presumed national exposure profile of each country. This would include consideration of diet, occupational exposure, rural and urban residence and proximity to potential POPs releasing activities such as industries and waste sites.

Biosafety: In general, the handling with any milk sample should comply with biosafety rules to protect workers who will handle samples.. The National Coordinators should decide whether HIV-positive donors can participate in the survey.

Consequently, the sampling protocol will vary among countries and therefore, comparison of results between countries should be approached with caution. However, once the national protocol is established, it should be applied in subsequent rounds so that changes/trends can be followed. In these cases, observation of temporal trends should be scientifically valid provided information on the distribution of levels in individual samples is available.

Sample analytical procedures

PCDDs, PCDFs and PCBs

After freeze-drying of the whole sample, fat and contaminants of interest are extracted in a hot extraction device ("Twisselmann extractor") with cyclohexane/toluene (50/50) for 8 hrs. After evaporation of the solvent, an aliquot of fat is spiked with 13C-labeled internal standards (17 PCDD/Fs, 5 non-ortho PCBs [37, 77, 81, 126, 169], 6 mono-ortho PCBs

[28, 60, 105, 118, 156,189] and 7 di-ortho PCBs [52, 101, 153, 138, 180, 194 and 209]). Gel permeation chromatography on Bio Beads S-X3 removes fat. A silica column impregnated with sulfuric acid removes remaining oxidizable substances. A florisil column separates PCDD/F from PCBs. The PCDD/F-fraction is purified on a Carbopack C-column. After addition of 1,2,3,4-13C12-TCDD, determination is performed by HRGC/HRMS (Fisons Autospec; resolution 10,000; DB5-MS). The PCBs are separated on a Carbopack B-column into three fractions of first di-ortho PCBs (elution with hexane), then mono-ortho PCBs (elution with hexane/toluene; 92.5/7.5) and finally non-ortho PCBs (reversed elution with toluene). After addition of 13C12-PCB 80, the different PCB groups are determined by HRGC/HRMS (Fisons Autospec; resolution 10,000; DB5-MS) in three separate runs. Marker PCBs are PCB 28, 52, 101, 138, 153 and 180.

Data comparability

To ensure reliability of exposure data and to improve comparability of analytical results from different laboratories, WHO has coordinated a number of inter-laboratory quality assessment studies. A study on levels of PCBs, PCDDs and PCDFs in human milk was conducted between February 1996 and April 1997, with the objective of identifying laboratories, whose results could be accepted by WHO for exposure assessment studies (Malisch et al., 2000; WHO, 2000). Only the State Institute for Chemical and Veterinary Analysis of Food Freiburg met all the pre-set criteria for analyses of PCDDs, PCDFs, dioxin-like PCBs, marker PCBs and fat in human milk and was thus selected as the WHO Reference Laboratory for the third and fourth round of the WHO human milk studies.

As noted above, the protocol for collection of samples may vary from country to country and therefore, data comparability between countries is not advised without a review of the national protocols. However, temporal trends should be possible based on the use of a consistent protocol for collection and handling of samples and on stringent criteria to assure that analytical quality assurance and control over long periods of time.

It should also be noted that the calculation of levels of PCDDs, PCDFs and dioxin-like PCBs may be slight different for earlier surveys, which use international toxic equivalence factors (I-TEQs) in comparison to the more recent surveys, which use WHO toxic equivalence factors (WHO-TEQs). However, the levels reported for the earlier surveys should only be considered indicative of exposures because of the limited sampling plan and therefore, the differences between I-TEQs and WHO-TEQs are not considered to be minor.

Data storage.

Data are stored at the GEMS/Food database located at WHO in Geneva, Switzerland and is password-accessible through the WHO Summary Information and Global Health Trends (http://SIGHT) portal.

Results.

PCDDs, PCDFs and dioxin-like PCBs

Four WHO-coordinated human milk surveys have taken place since 1987. A summary of the results are present in Tables 1-3. The current levels of dioxin-like PCBs were in the range of 5 to 11 WHO-TEQ (pg/g fat). The current levels of PCDDs/PCDFs were in the range of 4 to 10 WHO-TEQ (pg/g fat). The levels of marker PCBs were in the range of 40 to 80 ng/g fat. The number of participating countries has varied over the years. For PCDDs and PCDFs, some countries have participated in 3 or more of the survey and data for these countries suggest a continuing decline in levels of these POPs (see Figure 1). For dioxin-like PCBs, levels, reported levels from a few countries have remained flat while declining in others (see Figure 2). Note, however, because of the differences in protocols and in the toxic equivalence factors used to calculate these levels, no general statement on trends can be made. In regard to marker PCBs indicates a decline in levels for all countries reporting (see Figure 3).

The overall results for PCDDs, PCDFs and marker PCBs suggest declining levels of these POPs in human milk. Preliminary analyses of the results reveal varying profiles of the individual congeners of PCBs suggesting different sources of contamination. Further analysis of the pattern of the various congeners and the demographic data collected in the different countries will provide a clarification of these differences. From the results of countries participating in the current as well as in one of the previous WHO exposure studies, it can be concluded that the declining trend for these POPs , as observed before, is continuing. The declining trends indicate a continuing decline of exposure of the general population, to these POPs, which in turn is the result of emission reduction measures that have been taken place as well as regulatory limits for these POPs in food.

Table 1 Levels of PCDDs and PCDFs in Human Milk in the WEOG region

PCDDs/PCDFs (pg/g lipid)				
	1987/88 Data as Nordic-TEQ[1] Range	1992/93 Data as I-TEQ[2] Range	2001/2002 Data as WHO-TEQ[3] Range	2007 Data as WHO-TEQ Mean
Australia			5.5 – 5.79	
Austria	17.1 – 18.6	10.7 – 10.9		
Belgium	33.7 – 40.2	20.8 – 27.1	16.92	10.30
Canada	15.6 – 23.0	10.8 – 18.1		
Denmark	17.8	15.2		
Finland	15.5 – 18.0	12.0 – 21.5	9.35 – 9.52	6
Germany	27.6 – 36.8	16.5	12.53	

Ireland			6.19 – 8.54	
Italy			9.40 – 14.83	
Luxemburg			14.97	10.80
Netherlands	37.4 – 39.6	22.4	17.09 – 21.29	
New Zealand	5.8		6.08 – 7.00	
Norway	15.0 – 19.4	9.3 – 12.5	7.16 – 7.43	5.5
Spain		19.4 – 25.5	10.41 – 18.32	
Sweden	20.2 – 22.8		9.58	6.0
United Kingdom	16.6 – 37.0	15.2 – 17.9		
USA	16.7		7.17	

1) Environmental Health Series No 34 (1989)
2) Environmental Health in Europe No 3 (1996)
3) Van Leeuwen, R. and Malisch, R. (2002)

Table 2 Levels of Dioxin-like PCBs in Human Milk in the WEOG region

Dioxin-like PCBs (pg/g lipid)			
	1992/93 (I–TEQ pg/g lipid) Range	2001/2002 (WHO-TEQ pg/g lipid) Range	2007 (WHO-TEQ pg/g lipid) Mean
Australia		2.48 – 3.69	
Austria	11.7 – 19		
Belgium	4.7 – 7.8	12.6	7.02
Canada	3.0 – 6.8		
Denmark	4.5		
Finland		5.66 – 6.03	3.8
Germany	11.7	13.67	
Ireland		2.72 – 5.19	
Italy		11.02 – 19.33	
Luxemburg		13.67	10.3
Netherlands	11.0	10.90 – 13.08	
New Zealand		3.50 – 4.71	
Norway	9.5 – 19.5	6.56 – 9.61	5.6
Spain	8.2 – 10.6	9.96 – 16.97	
Sweden		9.71	6.8
United Kingdom	4.0 – 4.3		
USA		4.61	

Table 3 Levels of marker PCBs in Human Milk in the WEOG region

Marker PCBs (ng/g lipid)				
	1987/88 Range	1992/93 Range	2001/2002 Range	2007 Mean
Australia			25 – 35	
Austria		303 – 381		
Belgium	525 – 734	260 – 306	191	80.5
Canada		58 – 137		

Denmark	530 – 1320	209		
Finland Germany	150 – 203 762	133 – 189 375	84 - 98 220	41.3
Ireland			41 - 64	
Italy			195 - 323	
Luxemburg			217	115
Netherlands	392 – 419	253	178 - 210	
New Zealand			30 - 41	
Norway	255 – 947	273 – 302	106 - 132	65.7
Spain		452 – 461	278 - 469	
Sweden United Kingdom	600 - 1900	129 – 131	146	84.5
USA	202 – 220		54	

The sum of PCB 28, 52, 101, 138, 153 and 180 were used as marker PCB.

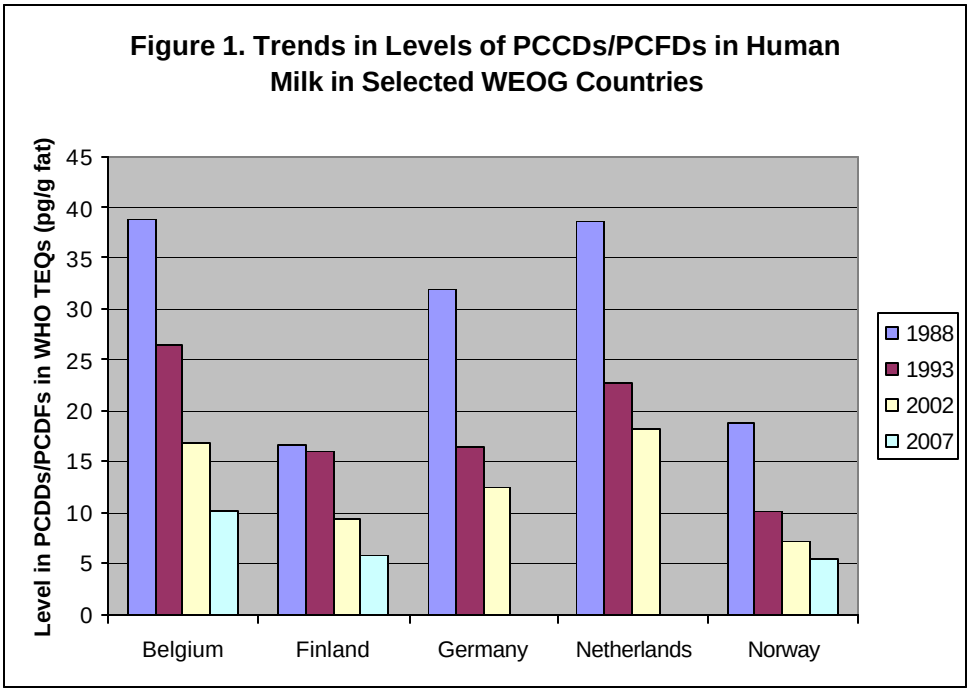


Figure 2. Trends in Levels of Dioxin-like PCBs in Selected WEOG Countries

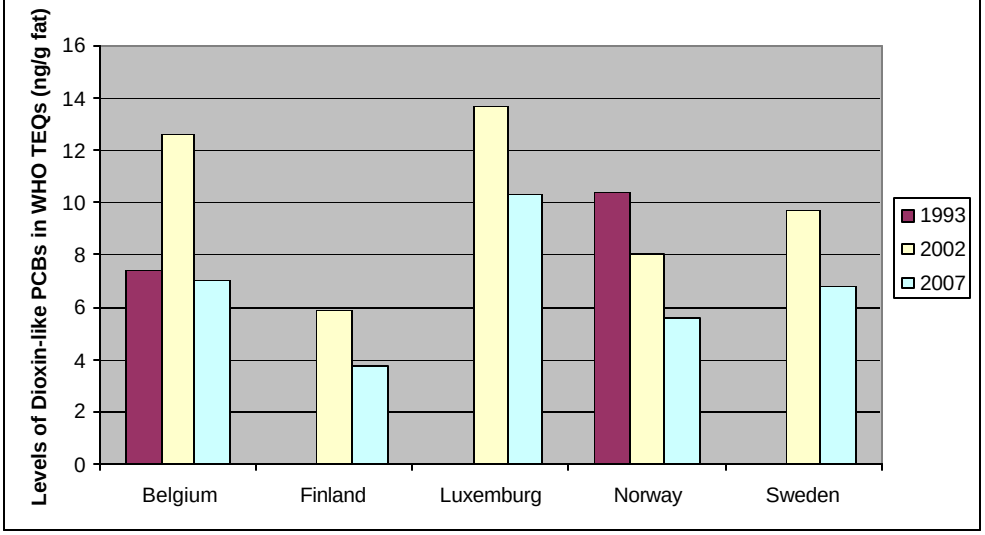
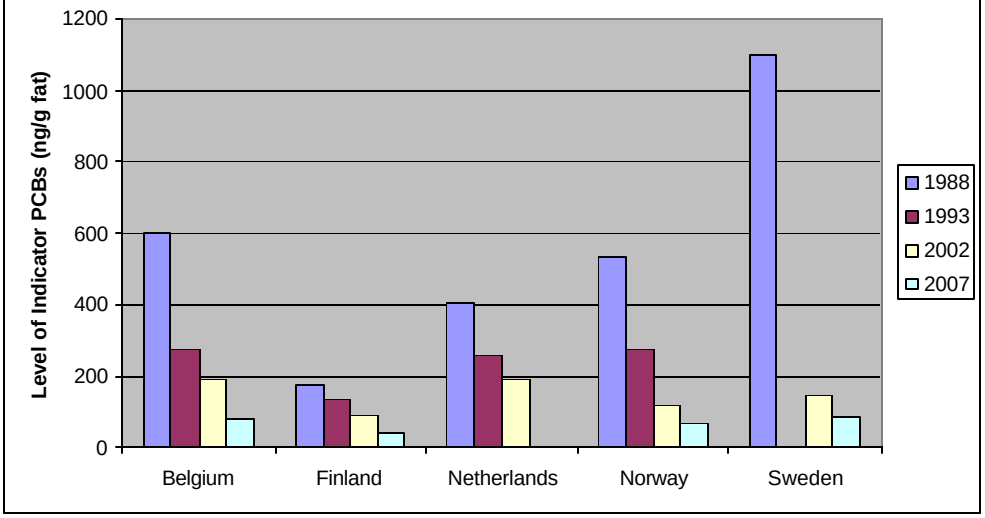


Figure 3. Trends in Levels of Marker PCBs in Human Milk in Selected WEOG Countires



Analytically Simple POPs

With the revision of the WHO protocol to include objectives related to the Stockholm Convention, the analysis of pooled human milk samples was expanded to include all of the analytically simple POPs. Consequently, data on such POPs from pooled samples are available from only Belgium, Finland, Norway and Sweden (see Table 4). Further data collected with the WHO protocol will become available as WEOG countries participate in the 4th WHO survey that is ongoing. While currently not covered by the Stockholm Convention, hexachlorocyclohexane isomers are included in this assessment as they are co-analyzed with the other POPs.

The study of levels of analytically simple POPs goes back to the 1950s in some countries. While the sampling, analytical quality assurance of those studies and presentation of data in the literature are highly variable, the data can be used indicate long-term trends for a number of these analytically simple POPs. WHO prepared a risk assessment of the exposure of infants to certain organochlorine contaminants in human milk and these and other can be used to indicate possible time trends for these POPs in WEOG countries.

Table 4. Levels of Analytically Simple POPs in Human Milk in 4th WHO Survey (2007)

	Belgium	**Finland**	**Norway**	**Sweden**
	Mean (ng/g fat)	Mean (ng/g fat)	Mean (ng/g fat)	Mean (ng/g fat)
Aldrin	**ND**	**ND**	**ND**	**ND**
Chlordane Complex 1)	**7.8**	**3.8**	**3.6**	**2.2**
alpha-Chlordane	ND	ND	ND	ND
gamma-Chlordane	ND	ND	ND	ND
Oxychlordane	8.0	1.0	3.7	2.3
trans-Nonachlor	1.7	2.8	5.7	3.0
Dieldrin	**6.7**	**1.5**	**2.5**	**1.8**
DDT Complex 2)	**156.3**	**33.1**	**69.6**	**81.9**
o,p'-DDD	ND	ND	ND	ND
p,p'-DDD	ND	ND	1.0	ND
o,p'-DDE	ND	ND	ND	ND
p,p'-DDE	132.3	27.8	60.0	70.2
o,p'-DDT	ND	ND	ND	ND
p,p'-DDT	8.8	2.1	1.6	3.6
Endrin Complex 3)	**ND**	**ND**	**ND**	**ND**
Endrin	ND	ND	ND	ND
Endrin ketone	ND	ND	ND	ND
Heptachlor Complex 4)	**5.3**	**0.5**	**0.6**	**0.8**
Heptachlor	ND	ND	ND	ND
Heptachlor-epoxide cis	5.6	0.5	0.6	0.9

Heptachlor-epoxide trans	ND	ND	ND	ND
Hexachlorobenzene	**15.0**	**2.7**	**16.9**	**7.1**
Parlar (Toxaphene) 5)	**2.3**	**1.9**	**3.7**	**2.4**
Parlar 26	0.7	0.5	1.1	0.7
Parlar 50	1.5	1.5	2.6	1.8
Parlar 62	ND	ND	ND	ND
Mirex	**ND**	**ND**	**ND**	**ND**

Notes:

ND=Not Detected (<0.5 ng/g fat)
1) Sum of alpha-chlordane, gamma-chlordane, oxychlordane and trans.nonachlor, expressed as chlordane
2) Sum of o,p'-DDT, p,p'-DDT, p,p'-DDE, o,p'-DDE, p,p'-DDE, o,p'-DDD and p,p'-DDD, expressed as DDT
3) Sum of endrin and endrin ketone, expressed as endrin
4) Sum of heptachlor and heptachlor-epoxide (cis/trans), expressed as heptachlor
5) Simple sum of parlar 26, parlar 50 and parlar 62

Aldrin

Aldrin was not detected in any sample. Having been banned for many years, any aldrin present would have degraded into dieldrin, which is discussed below.

Chlordane Complex

Chlordane was not detect in any sample. However, degradation products oxychlordane and trans-nonachlor were detect in the range of 2.2 to 7.8 ng/g fat. Note that while cis-nonachlor was not included in these analyses, level of cis-nonachlor are usually about 20% of the levels of trans-nonachlor and therefore, would not contribute significantly to the total chlordane comples. Historical data for the chlordanes are very limited. Data from Sweden in 1988 indicates levels of 12 ng/g fat for oxychlodane and 17 ng/g fat for trans-nonachlor, which are about 5 time higher than the levels reported in 2007.

Dieldrin

Levels of dieldrin ranged from 1.5 to 6.7 ng/g fat. Note that this would include any aldrin that wish oxidizes to dieldrin. In Sweden, dieldrin levels have dramatically fallen from about 70 ng/g fat in the late 1960s, to about 10 ng/g fat in the mid-1980s to their current level of 1.8 ng/g fat. Banned for many years in most countries, similar profiles would be expected in other countries.

DDT Complext

The database on DDT in human milk is perhaps the most extensive available. However, DDT has been banned in all WEOG countries for many years. The levels for total DDT complex currently reported in the WHO survey range from 33.1 ng/g fat to 156.3 ng/g fat. This is mainly comprised of p,p'-DDE indicating that these residues are the result of use of DDT in the distant past. Levels of DDT in human milk have fallen significantly. In Belgium for

example, the levels of DDT fell from 4800 ug/g fat in 1969 to 156.3 ug/g fat in 2007. In many countries, further declines in levels of DDT in human milk are expected to be slight. In Finland the current level is 33.1 ng/g fat and is nor likely to decline significantly in the future.

Endrin

The levels of endrin in the four reporting countries was below the limit of determination (0.5 ng/g fat) and therefore, monitoring of endrin in the future is not likely to produce an further useful data.

Heptachlor

Levels of heptachlor complex reported in the WHO survey ranged from 5.3 to 0.8 ng/g fat. As with DDT, the bulk of the residue was in the degradation product heptachlor epoxide- cis and not the parent molecule. This is evidence that there is no current use of heptachlor in the reporting countries. Again the monitoring of heptachlor complex may not result in further useful information.

Hexachlorbenzene

Levels of hexachlorobenzene reported in the WHO survey ranged from 2.7 to 16.9 ng/g fat. The levels reported in various WEOG countries in the 1990s were in the range of 10 - 20 ng/g fat, with the exception of Australia, which reported significantly higher levels of this chemical. Dramatic decreases in levels have been observed for most WEOG countries over the past several decades. In Sweden, levels which exceeded 200 ng/g fat in 1974 were down to 7.1 ng/g fat in 2007.

Parlar (Toxaphene)

The levels of parlar ranged from 1.9 to 3.7 ng/g fat in the current WHO survey. Available historical data are limited, but levels reported in Northern Canada in 1997 suggest that parlar levels can be quite high (aboiut 70 ng/g fat) in areas far remote from its use.

Mirex

Mirex was not detected in the current WHO survey down to the limit of determination of 0.5 ng/g fat. A few studies in Canada and the USA suggest that levels are at very low levels. Therefore, the further monitoring of mirex is unlikely to produce useful data.

Citations

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A2.2 National Programs and 'snap-shot' studies on POPs in Human Tissues

A2.2.1 Australian National Dioxins Program: Levels of dioxin-like compounds in pooled blood serum collected throughout Australia in 2002-2003

Key Message

The results of this study provide a measure of the levels of dioxin-like compounds, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), in pooled blood serum collected throughout Australia in late 2002-2003.

Dioxin-like compounds were detected in all samples. The mean and median levels expressed as upper bound TEQ values for all pooled samples were 10.9 and 8.3 pg TEQ g-1 lipid, respectively.

A direct relationship of increasing dioxin-like compound levels with increasing age was observed and found to hold from approximately 25 years of age until at least the eighth decade.

For males, and females the mean levels were 10.4 and 11.5 pg TEQ g-1 lipid, respectively. No systematic differences were observed in the levels of dioxin-like compounds in samples collected from males and females.

Overall the levels in the Australian population were low by international standards and comparable with, although lower than, those observed in the New Zealand population in the late 1990s (Buckland et al, 2001).

Background

This study aimed to quantify and assess the concentrations and relative chemical compositions of dioxin-like chemicals in blood serum of the Australian population. The study formed a component of the Australian National Dioxins Program, which also included measurement of dioxin-like chemicals in human milk, air, aquatic environments and soils. There are 12 technical reports available at: http://www.environment.gov.au/settlements/chemicals/dioxins/reports.html

Around 9000 blood samples collected in late 2002 to late 2003 were stratified, pooled and analysed for 7 dioxins, 10 furans and 12 PCBs (4 non ortho and 8 mono ortho) classified as dioxin-like by the World Health Organization (WHO).

Sampling

The following stratification criteria were used:

- *Regional Stratification:* 5 regions representing the regional and population distribution of Australians
- *Age Stratification:* 5 age groups (<16 years;16-30 years; 31-45 years; 46-60 years; >60 years)
- Gender Stratification: males and females

The samples used in this study were obtained from de-identified stored sera that had been collected as part of the routine pathology service. Due to the potential for the introduction of bias, a pilot study was carried out in which the levels of dioxin-like compounds in samples collected for routine pathological assessment were compared with those collected for insurance assessments in order to determine whether there was a detectable difference between the two groups. Differences were assessed using the normalised difference. The findings indicated the possibility of greater variation within the same group than between different groups, thus indicating the suitability of use of pathology samples for the main study.

In total 9,090 samples from the 50 strata were collected and pooled to give 96 pools. An additional 204 samples, representing four pools, were also assessed as part of the pilot study. Stored sera were collected within each stratum until a maximum of 200 samples were achieved or the sample list was exhausted, for each stratum. Each stratum was divided randomly into two pools, with 100 samples in each pool.

The project received Medical Research Ethics Committee Approval.

Sample analytical procedures

All pooled samples were sent to ERGO- Forschungsgesellschaft mbH, Hamburg, and ten duplicate samples, representing 10% of the total number of pools, were sent to Health Canada Health Products and Food Branch, for inter-laboratory comparison. Four pools also underwent duplicate analysis within ERGO in order to determine the analytical reproducibility of the results.

Prior to shipping, samples were stored at -30 °C in an alarmed freezer. Samples were air freighted frozen on dry ice to either ERGO in Germany or to Health Canada in Canada. Samples were received by both laboratories frozen and in good condition.

Analysis was conducted for 7 dioxins,10 furans and 12 PCBs (4 non ortho and 8 mono ortho) classified as dioxin-like by the World Health Organization (WHO). Both laboratories were accredited for analytical dioxin analysis. ERGO used high resolution mass spectrometry (HRMS) while Health Canada used gas chromatography (GC)-mass spectrometry (MS).

Data comparability

Identified errors and quality assurance details as part of the sampling design and sample pooling are outlined in the full technical report and accounted for in the results.

Both laboratories were accredited for analytical dioxin analysis.

Health Canada analytical QA/QC measures were as follows:

- regular chemicals and glassware checks (blanks), once a block of 4/6/10 samples

- regular checks of so called instrument blanks (GC/MS)
- regular checks of quality control samples (e.g. blood pools) (GC/MS)
- daily calibration verification tests
- regular GC performance tests (separation, retention windows)
- identification based on definite abundance ratio and retention time criteria, with the use of internal and external standards
- quantification based on the isotope dilution method with the use of internal and external standards
- regular method performance checks by analysing control samples of known PCDD/PCDF concentrations
- daily MS performance checks to control the resolution and sensitivity.

External measures:

- regular participation in inter-laboratory quality control studies
- exchange and control measurements of standards with other qualified laboratories.

Data storage.
The raw analytical data are held by the authors of the report. Electronic copies of the technical reports are held by the Australian Government Department of the Environment, Water, Heritage and the Arts (DEWHA).

Results.

PCDD/PCDFs and PCBs were detectable in all 100 blood samples. The full technical report gives the levels of PCDDs and PCDFs in each sample as upper and lower bound TEQ. For *Upper Bound TEQ*, the TEQ level of the congener was calculated using the detection limit, while for *Lower Bound TEQ*, the TEQ level of the congener was calculated using a zero concentration. The greater the number of non-detectable congeners, the greater the difference in the upper and lower bound TEQ values.

In summary, the mean and median levels expressed as upper bound TEQ for all pooled samples were 10.9 and 8.3 pg TEQ g-1 lipid, respectively. For males and females, the mean levels were 6.5 and 7.2 pg TEQ g-1 lipid, respectively. Figure 3.2 shows the average upper bound for total TEQ for all pooled samples.

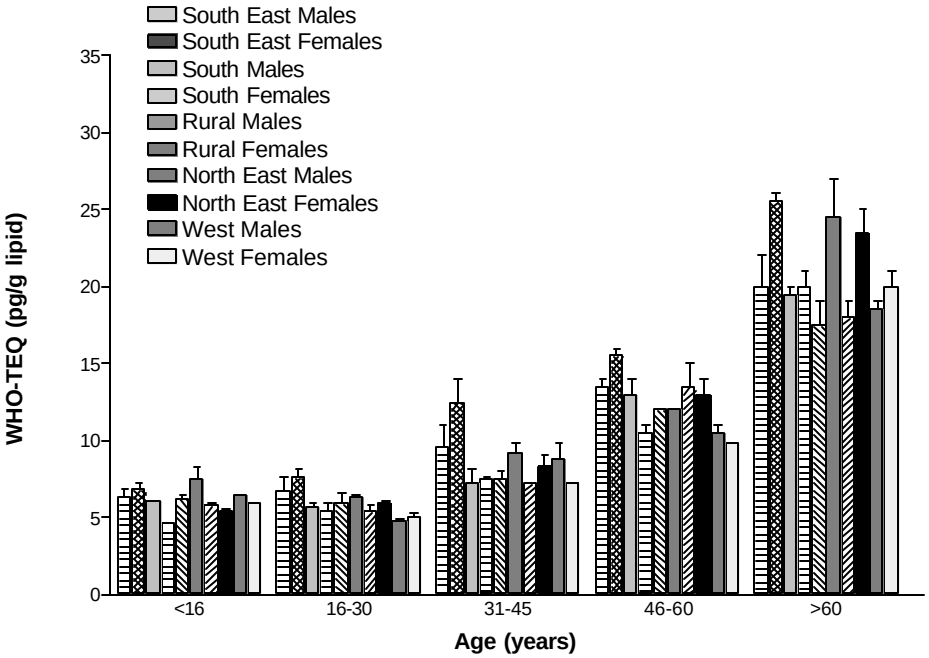

Figure 3.1 Upper bound TEQ in the serum of representative groups of the Australian population.

For PCDD/PCDFs, the levels expressed as TEQ varied by a factor of 5.8 from a minimum value of 2.9 pg TEQ g^{-1} lipid detected in Southeast females <16 years pool II to 17 pg TEQ g^{-1} lipid detected in Southeast females >60 pool II.

For PCBs alone, TEQ based on PCB, varied by a factor 9.2 from a minimum value of 1.3 pg TEQ g^{-1} lipid detected in a pool of South region females 16-30 years pool II to a maximum value of 12 pg TEQ g^{-1} lipid detected in a pool of rural females >60 years pool II.

For PCDD/PCDFs and PCBs the data indicated that on a TEQ basis there was little difference between the upper and lower bound results, indicating negligible impact of non-detected congeners.

Congeners

The full technical report also shows the mean, maximum, minimum concentrations as well as the percent contribution of each congener to the overall TEQ. For dioxins and furans, the higher chlorinated PCDD, OCDD dominated in the overall congener profile. OCDD contributed an average of approximately 80% to the total of all detected congeners. Despite the dominance of OCDD, its low toxic equivalency factor (TEF) of 0.0001 meant that its contribution to the TEQ was minimal (0.2%). In contrast, other compounds that were present in much lower concentrations had much higher TEFs and therefore had much greater contribution to the total TEQ. These included 2,3,7,8-TCDD and 1,2,3,7,8-Penta CDD.

1,2,3,7,8-pentachlorodibenzodioxin and 3,3',4,4',5-pentachlorobiphenyl were the single most relevant components in the congener profile, each contributing approximately 20% to the overall TEQ value. Overall the PCDD/PCDF congener profile was dominated by higher chlorinated PCDDs whereas concentrations of higher chlorinated PCDFs (Cl6 or greater) were almost exclusively below the limit of detection in all samples.

Age effects

For all of the five regions, the TEQ increased with age from the 16-30 year age group onwards. For upper bound TEQ, there was a clear trend of increasing levels of dioxin-like chemicals from the younger strata (6.3 ± 0.4 pg g^{-1} lipid) to the older strata (22.7 ± 0.91 pg g^{-1} lipid) in samples from all regions. This increase in concentration only applied from the second youngest age group onward. No difference was observable between the concentrations in the <16 year old group (6.3 ± 0.4) and the 16-30 year old group (6.1 ± 0.3).

The relationship between the age of an individual and the levels of dioxin-like chemicals (expressed as pg TEQ g^{-1} lipid) in their blood serum can be described using an exponential equation from approximately the middle of the third decade onwards to at least the eighth decade. This equation does not appear to hold for persons below the age of 25. The reason for this is not known but may be due in part to placental transfer during pregnancy and neonatal loading during breastfeeding. As well, a smaller number of samples was analysed in the <16 years age group compared to the 16-30 years age group and this may also have contributed the result.

Figure 3.3 indicates the relationship between age and the level, expressed as TEQ, of dioxin-like chemicals in blood serum in the Australian population.

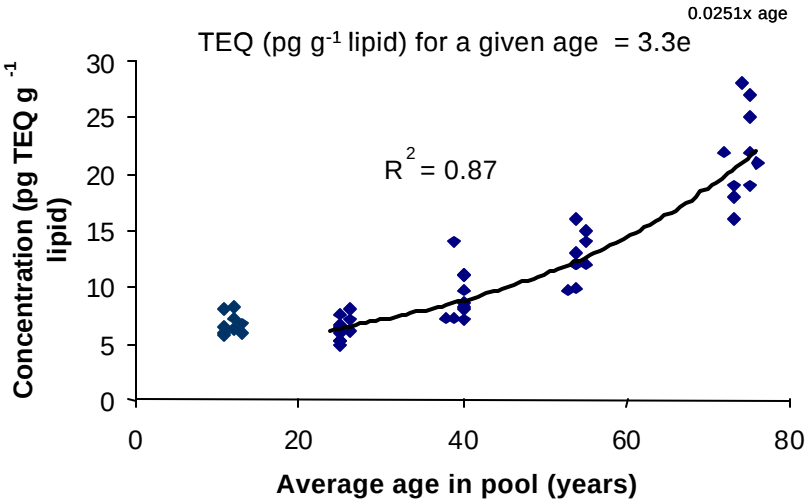

Figure 3.2 Relationship between age and the level of dioxin-like chemicals in the blood.

Other studies have found that with increasing age of an individual there is a corresponding increase in the concentrations of dioxin-like chemicals in the blood serum (Buckland et al. 2001). Reasons for such an increase include but may not be limited to:

- continuous accumulation (i.e. steady state is not attained over a life time)
- decrease in historical contamination (i.e. older people were exposed at much higher levels in the 1950s and 1960s when there were less regulations governing the control of industrial emissions)
- potential differences in metabolism and body fat.

Gender effects

For total TEQ, the data do not show any systematic difference between males and females. For all age groups except the >60 years age group, there are no differences between males and females. For the >60 years age group, the total TEQ appears to be slightly higher for females than males. This difference cannot be explained by differences in the average age, as these were remarkably similar for males and females.

Regional effects

It should be noted that because de-identified samples were used in this study, determination of regional differences was complicated. The use of such samples did not allow any assessment of the length of time an individual had resided in a particular area prior to their sample being collected or recording of either food intake or possible exposure to environmental contaminants in that region.

Conclusion

In summary, the levels of dioxin-like compounds in the Australian population are low by international standards and are very similar across all regions of Australia within each designated age range. The levels of these chemicals were found to increase with age.

Citations

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Glossary/Abbreviations

ADI	Acceptable daily intake.
Congener	Closely related chemicals derived from the same parent compound.
Dioxins/ Dioxin-like Compounds	Common name when referring to all of the following compounds polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls.
Furan	polychlorinated dibenzofuran.
GC/MS	Gas chromatography/mass spectrometry.
Homologue	A group of structurally related chemicals that have the same degree of chlorination.
HRGC/HRMS	High resolution gas chromatography/ high resolution mass spectrometry.
I-TEQ	Toxicity equivalencies using NATO-CCMS (1988) toxicity equivalency factors.
LCS	Laboratory control sample.
LOD	Limit of detection, the lowest level at which a chemical can be measured in a sample by the analytical method used.
Lower bound TEQ	Toxic equivalencies (TEQ) for which concentration of a non-detected congener assumed to be equal zero.
ml	Milliliter.
Middle bound TEQ	Toxic equivalencies (TEQ) for which concentration of a non-detected congener assumed to be equal to half the non detect value.
Mono-*ortho* PCBs	includes PCB congener numbers 105, 114, 118, 123, 156, 157, 167, 189.
nd	Non-detect.
NDP	National Dioxin Program.
Non-*ortho* PCBs	Includes PCB congener numbers 77, 81, 126, 169.
OCDD	Octachlorodibenzo-*p*-dioxin.
OCDF	Octachlorodibenzo-furan.
PCBs	Polychlorinated biphenyls.
PCDDs	Polychlorinated dibenzo-p-dioxins.
PCDFs	Polychlorinated dibenzofurans.

pg g^{-1}	Picogram per gram, 10^{-12} g. Equal to nanogram per kilogram (ng/kg).
Pool	Samples collected within each stratum.
POPs	Persistent organic pollutants.
r^2	Regression coefficient.
Region	Geographical location in Australia.
QC	Quality control.
QA	Quality assurance.
QLD	Queensland.
QHSS	Queensland Health Scientific Services.
SA	South Australia.
SNP	Sullivan and Nicolaides Pathology.
Stratum/strata	Represent samples within defined criteria e.g. age, gender, geographical location.
TEQ	Abbreviate of WHO_{98}-TEQ (this document).
TEF	toxicity equivalency factors.
Upper bound TEQ	Toxic equivalencies (TEQ) for which concentration of a non-detected congener assumed to be equal to the non detect value.
UQ	The University of Queensland.
Vic	Victoria.
WA	Western Australia.
WHO	World Health Organization.
WHO_{98}-TEQ	World Health Organization toxic equivalent: the quantified level of each individual congener multiplied by the corresponding TEF. TEQs of each congener are summed to achieve an overall toxic equivalency for a sample (Van den Berg, 1998). In this document WHO_{98}-TEQ is abbreviated to 'TEQ'.

A2.2.2 Trends for Organic Pollutants in Using Blood samples from the German Environmental Specimen Bank

Key Message

PCB 153 and HCB have been analyzed in blood on a yearly basis starting in 1985. The groups studied are students from different parts of Germany. The data indicate a continuous decreasing trend with 4-5% each year.

Background

The German Environmental Specimen Bank (ESB) was established in 1985 as a permanent institution for the systematic collection, processing, characterisation and storage of environmental samples from marine, freshwater and terrestrial ecosystems as well as human samples. Blood and other human specimens have been collected since 1981 from a group of about 100 unexposed persons in defined peripheral conditions. The subjects have to complete standard questionnaires about family and health status, occupational exposure, nutrition, smoking and drinking habits and the use of medicine.

The German Environmental Specimen Bank (ESB) is a monitoring instrument of the German Federal Ministry for the Environment, Nature Conservation and Nuclear Safety. The ESB is managed by the Federal Environment Agency and operated by contracted research institutes and university groups with special competencies in the particular fields (e.g., sampling of human, biological, and abiotic material, trace analysis of pollutants, cryobank operation).

The human specimens blood, urine, and hair are taken from living persons at selected sites. It was decided to use voluntary students from the Universities of Muenster, Halle, Greifswald, and Ulm as donors. Human specimens are taken every once a year with a sample size of around 100 students at each sampling site. The students come usually from different regions in Germany to the universities and are selected for non-specific exposure. With individuals and groups moving home frequently in a mobile society, it is assumed that almost the entire country is represented.

The objective of the programme is to monitor levels of organic pollutants in blood.

A yearly sampling is expected also in the future.

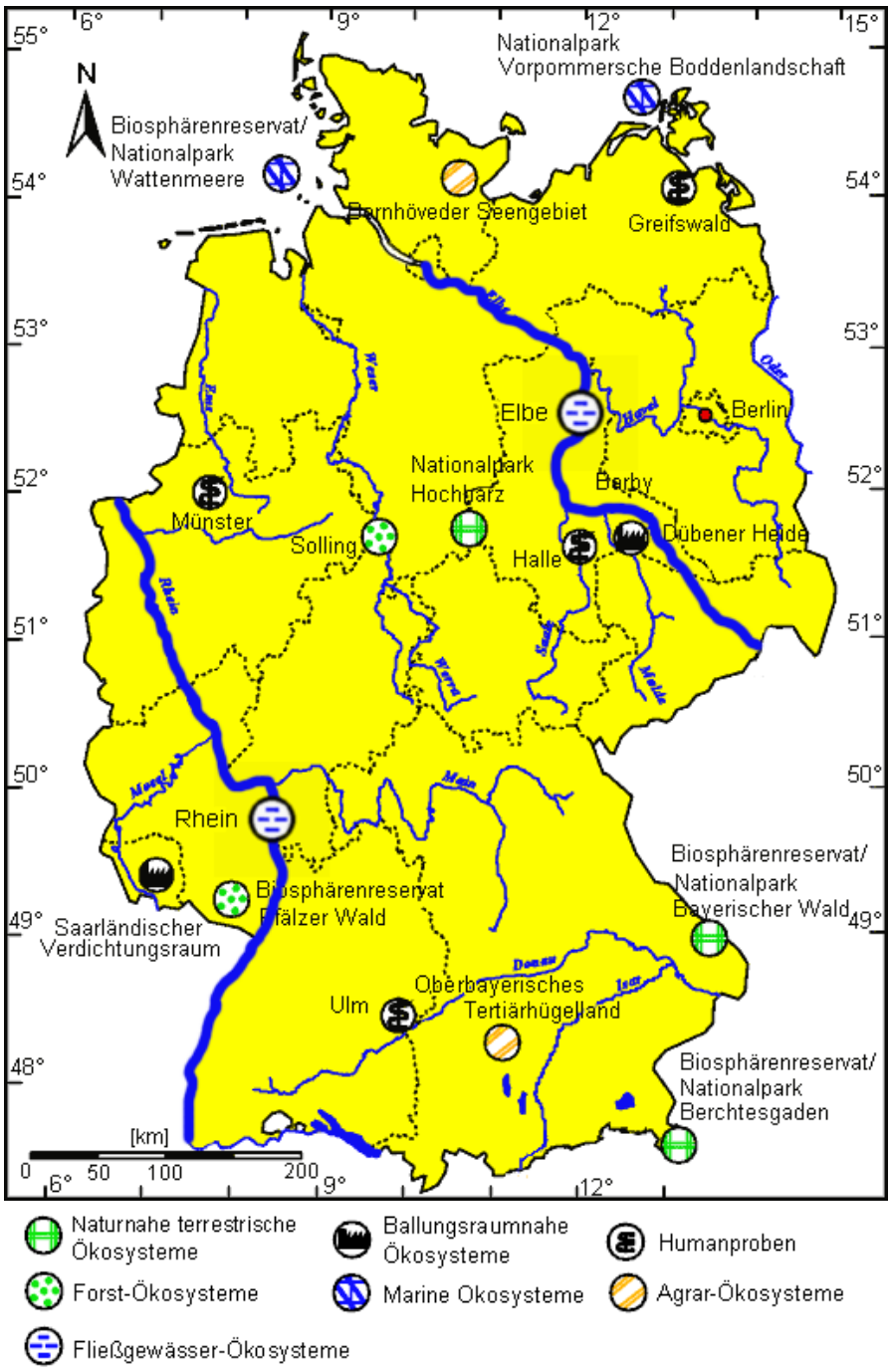

Figure 1: Places where samples were taken. "Humanproben" indicates where human sampling takes place.

Sampling

After pooling and homogenizing, environmental samples are stored at temperatures below -150°C. After two decades of operation the ESB provides now a continuous historical record of the state of the environment in Germany in this period.

Sample analytical procedures

The ESB is founded on a high degree of continuity in all work steps. Therefore, all important work is regulated by ESB-specific standard operating procedures (SOPs). The SOPs describe all main operations in detail and were published by the Federal Environment Agency. Currently all ESB SOPs are in the process of revision. Already revised versions of the SOPs are available via the internet site of the ESB (www.umweltprobenbank.de; in German and English language).

Data storage.

Data can be obtained via internet from the German Environmental Specimen Bank, ie. free of charge.

Results.

PCB 153 and HCB have been analyzed in the samples on a yearly basis. The data indicate a continuous decreasing trend with 4-5% each year.

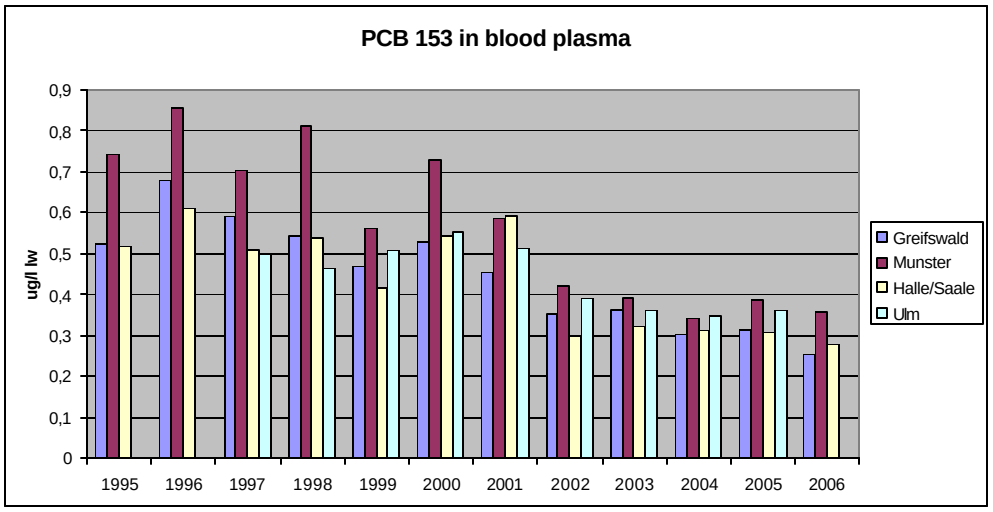

Figure 2

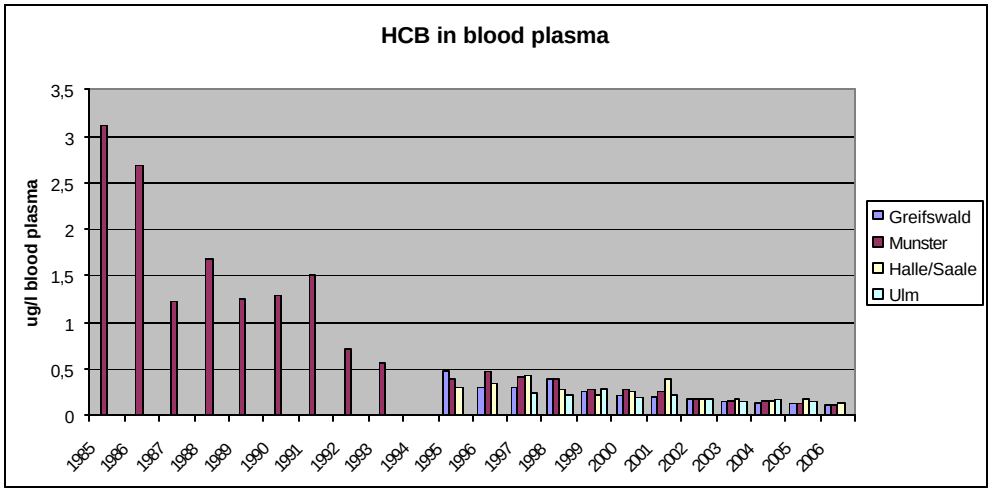

Figure 3

Levels of PCB 153 in blood plasma

		1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
Greifswald	µg/l lw	0,523	0,677	0,590	0,545	0,469	0,522	0,454	0,354	0,362	0,301	0,314	0,252
Munster	µg/l lw	0,742	0,856	0,705	0,8113	0,562	0,729	0,584	0,422	0,393	0,340	0,386	0,352
Halle/Saale	µg/l lw	0,518	0,612	0,510	0,538	0,418	0,543	0,594	0,297	0,324	0,311	0,308	0,272
Ulm	µg/l lw			0,50	0,465	0,507	0,554	0,514	0,390	0,362	0,3474	0,363	

Levels of HCB in blood plasma

		1998	1999	2000	2001	2002	2003	2004	2005	2006
Greifswald	µg/l lw	0,3943	0,2623	0,2225	0,2127	0,1914	0,1528	0,1425	0,1300	0,1144
Munster	µg/l lw	0,3956	0,2833	0,2767	0,2544	0,1822	0,1581	0,1689	0,1322	0,1197
Halle/Saale	µg/l lw	0,2778	0,2304	0,258	0,3941	0,1857	0,1813	0,1657	0,1834	0,1343
Ulm	µg/l lw	0,2282	0,2862	0,1948	0,2343	0,1859	0,1573	0,1724	0,1497	

Citations

Frozen Environmental History: The German En vironmental Specimen Bank.
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http://anubis.uba.de/wwwupb/servlet/upb visited in February 2008.

A2.2.3 German Environmental Survey

Key Message

The data from the third and fourth German Environmental Survey can be seen as a base-line for further monitoring.

The observed levels of persistent organic pollutants are dependent on a number of factors such as gender, age, place of living and length of breast feeding. The available data from Germany that could be used for comparison do however indicate decreasing trends when comparisons are made within the same group at the same location.

Background

The German Environmental Survey (GerES) is a representative population study to determine the exposure of Germany's general population to environmental contaminants. The study has been conducted by the Federal Environment Agency since the mid-1980s.

- The first GerES (GerES I) was conducted in 1985/86. No organic pollutants analyzed.
- A new GerES was conducted in 1990/91 and in 1991/92 extended to the former GDR (GerES II). No organic pollutants analyzed.
- GerES III was performed in 1998.
- GerES IV for children started in May 2003. GerES IV fieldwork was completed in May 2006

Blood specimens from GerES III and GerES IV were analyzed for polychlorinated biphenyls (PCB), dichlorodiphenyldichloroethylene (DDE), hexachlorobenzene (HCB) and a number of other substances not a part of this evaluation. In urine specimens the levels of a number of pollutants also not a part of this evaluation were determined.

Sampling

The number of samples taken have varied. E.g. in GerES II a cross sectional sample of 4822 adults aged 18 to 69 years 120 sampling locations representative of the German population with regard to community size, age and gender were taken.

In GerES IV 1 790 children aged 3 to 14 years and living in 150 different sampling locations was examined.

Sample analytical procedures

The chemical analyses for human biomonitoring were performed at the Federal Environment Agency and a number of contract laboratories. External laboratories commissioned to perform analyses for the substances are listed in Becker et al. (2008). A synoptic view of the analytical methods used and the laboratories involved in the analyses is given in Becker et al. (2008).

Quality control

The analyses had to be conducted at the highest possible level of precision and accuracy. For the placing of orders, it was therefore required to pay particular attention to corresponding measures of quality assurance. The validity of the analytical methods used was ensured by internal and external quality controls and by successful participation in interlaboratory studies, as far as these were available for the respective substance groups examined. The accuracy of measuring results was determined by analysis of controls. In addition, comparability of analytical results with the results of previous surveys was ensured. To this aim, additional samples (ca. 5 % of genuine samples) which had already been analyzed in previous surveys were "mixed in". These specimens were provided by the Federal Environment Agency from the stock of samples from previous GerES (Becker et al, 2008).

Data storage

Data is stored at the Federal Environment Agency.

Results

According to the amounts of organochlorines produced and used, the place of residence in East-Germany in 1988 (before unification) is associated with a higher level of PCBs and HCB and a lower level of DDE. BMI, the body mass index, is positively associated with the level of organochlorine compounds (HCB, DDE). The concentration in blood decreases for PCBs and HCB with gain of weight (Becker et al., 1998)

Although it could be demonstrated in a number of studies that the concentration of organochlorine compounds in breast milk has been largely on the decrease (Schade und Heinzow 1998, Doering et al. 1999), breastfeeding could nevertheless be identified as a significant predictor of HCB and PCB levels in the blood of 9- to 11-year-old children. The levels of lower chlorinated PCB (PCB 28, PCB 52, PCB 101) were mostly below the limit of quantification. PCB levels found in boys were higher than those found in girls (for PCB 138, however, the significance level required was not reached). The mean levels were found to decrease with increasing age. Comparatively higher mean levels were calculated for children from households with a high socioeconomic status and for non-migrants. Children living in West Germany showed higher mean PCB levels than those living in East Germany.

The mean DDE level in the blood of the children was 0.206 µg/L. Also, mean DDE levels were found to decrease with increasing age. Analogous to PCB, the levels found in children with a high socioeconomic status was higher than that in children with a lower

socioeconomic status. However, unlike PCB levels mean DDE levels detected in migrants were higher than those in non-migrants. In East Germany and in large communities, the mean level was higher than in West Germany. The predictors for HCB were the same as for PCB, with the exception of gender, which was of no relevance for HCB levels (Becker et al., 2008).

Levels of pollutants in whole blood of children (7-14 years) in Germany 2003/2006

Substance	***Group***	***Mean estim. level***
PCB (138, 153, 180)	Whole group	0.38 µg/l
PCB (138, 153, 180)	Boys	0.39 µg/l
PCB (138, 153, 180)	Girls	0.36 µg/l
DDE	Whole group	0.30 µg/l
DDE	Boys	0.31 µg/l
DDE	Girls	0.30 µg/l
HCB	Whole group	0.11 µg/l
HCB	Boys	0.11 µg/l
HCB	Girls	0.11 µg/l

Levels of pollutants in whole blood of the general population in Germany 1998

Substance	***Group***	***Mean estim. level***
PCB (138, 153, 180)	Whole country	2.07 µg/l
PCB (138, 153, 180)	West Germany	2.20 µg/l
PCB (138, 153, 180)	East Germany	1.53 µg/l
DDE	Whole country	2.62 µg/l
DDE	West Germany	2.08 µg/l
DDE	East Germany	4.98 µg/l
HCB	Whole country	0.79 µg/l
HCB	West Germany	0.82 µg/l
HCB	East Germany	0.67 µg/l

Discussion of results

For the population not exposed at the workplace, the essential exposure pathway is through food consumption, particularly that of foods rich in fat of animal origin. In children, a history of breastfeeding is an essential exposure pathway, of which evidence can be found also in later years of life (Nawrot et al. 2002, Karmaus et al. 2001). In the process of breastfeeding, substances accumulated in the fatty tissue of the mother are released and passed on to the child with the breast milk (Lackmann et al., 2005). Also, if energy reserves are mobilized during pregnancy, the substances may be transmitted by the transplacental route. Particular attention should be paid to the fact that effects of the intake of pollutants in early stages of development may become evident only after years or decades (Böse-O'Reilly 1999).

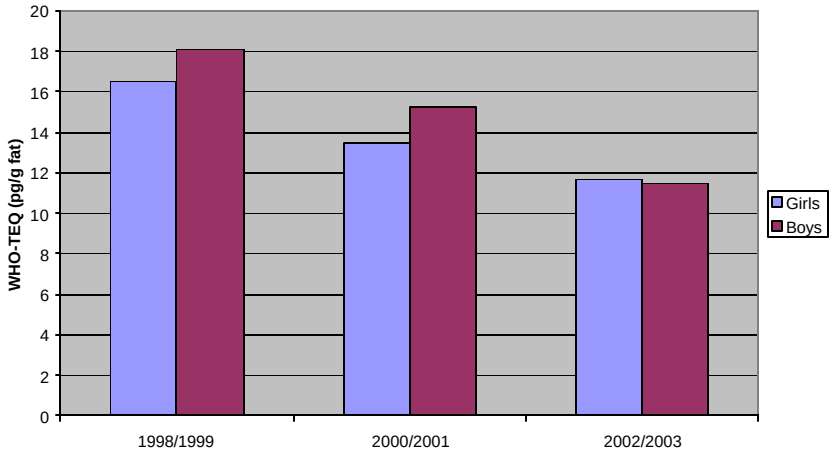
Even if there is not yet any trends to be reported from the German Environmental Survey, comparisons can be made with other German results reported. The data can be compared with e.g. the monitoring of organic pollutants in blood of children from Baden-Württemberg (Link et al., 2005) and data from North Rhine-Westphalia (Wilhelm et al., 2007). These data indicate decreasing trends for the analyzed pollutants PCB, DDE and HCB.

Comparison with data from Baden-Württemberg

Concentration of POPs in the blood samples from children from Baden-Württemberg (Link et.al., 2005).

Year	*Substance*	*Mean estim. level*
1996/1997	PCB (138, 151, 180)	0.55 µg/l
1998/1999	PCB (138, 151, 180)	0.42 µg/l
2000/2001	PCB (138, 151, 180)	0.32 µg/l
2002/2003	PCB (138, 151, 180)	0.30 µg/l
1996/1997	DDE	0.54 µg/l
1998/1999	DDE	0.30 µg/l
2000/2001	DDE	0.29 µg/l
2002/2003	DDE	0.33 µg/l
1996/1997	HCB	0.22 µg/l
1998/1999	HCB	0.15 µg/l
2000/2001	HCB	0.12 µg/l
2002/2003	HCB	0.09 µg/l

Levels of PCDD/PCDF in pooled blood samples from children from Baden-Württemberg (Link et.al., 2005) .



In this study PCB, DDE, HCB as well as PCDD/PCDF levels measured in blood from children from 1996/1997 – 2002/2003. Blood concentrations of the investigated compounds decreased in that time period by a factor 2-4 with an exception of most PCDFs where the changes were less prominent. The concentrations reported in children were significantly lower than those for adults (Link et al., 2005).

Comparison with North Rhine-Westphalia

The areas along the rivers Rhine, Ruhr and Wupper in North Rhine-Westphalia, Germany, represent the largest urban and industrial agglomeration in Europe with about 10 million inhabitants. The average PCDD/F levels decreased from about 40 pg TEQ/g blood fat to about 12 pg TEQ/g blood fat from 1990 to 2002. This is a decrease of more than 60%. A similar decrease was found for PCB, PCDD/PCDF and other POPs in human milk. The levels of POPs in human milk significantly decreased from 1984 until 2003. The authors conclude that the diet represents the main route of exposure to POPs, generally making up more than 90% of the total intake. Since dietary products are usually of widespread origin, there is no distinct difference between urban and rural areas.

Age and total nursing period were used as continuous predictor variables and in a first step the residential locations as a categorical factor, whether the women had ever lived outside Western Europe for more than 3 months or not. Both, PCDD/F- and PCB-TEq levels in human blood as well as in milk increase with age, decrease with the total lactation period and are influenced by the time the women had spent living in different locations/countries (Wilhelm et al., 2007; Wittsiepe et al., 2007).

Levels of I-TEQ, beta-HCH, HCB and DDE in human milk from breast-feeding women living in North Rhine-Westphalia (Wilhelm et al., 2007).

Year	PCB 180 [mg/kg lipid base]	PCB 138 [mg/kg lipid base]	PCB 153 [mg/kg lipid base]	HCB (mg/kg lipid)	DDT (mg/kg lipid)	I-TEQ (pg/p lipid)
2001	0,041	0,055	0,081	0,03	0,124	11,1
2002	0,043	0,05	0,083			11,3
2003	0,036	0,038	0,065			9,5

Conclusions

The observed levels of persistent organic pollutants are dependent on a number of factors such as gender, age, place of living and length of breast feeding (Link et al., 2005, Wilhelm et al., 2007). The available data do however indicate decreasing trends when comparisons are made within the same group at the same location.

The German Environmental Survey provides a basis for further trend monitoring in the future.

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A2.2.4 Organochlorine Contaminants in the Milk of New Zealand Women

Key Message

A study was undertaken of the concentration of UNEP POPs in the milk of New Zealand women from breast milk samples collected between October 1998 and May 1999. (*1*)

The distribution of PCDD/Fs and PCBs was similar across study areas with a tendency for higher concentrations to be found in the milk of women who were older, heavier, and of non-European ethnicity. Mean PCDD/DF concentration was 6.3 pg WHO-TEQ/g fat for all samples combined. The mean sum of 14 PCBs for which toxic equivalent factors have been assigned was 4.2 pg WHO-TEQ/g fat for all samples combined.

The OC pesticides beta-HCH, HCB, dieldrin, heptachlor epoxide, pp-DDT and the metabolite pp-DDE were detected in all the samples. The mean concentrations of these pesticides for all samples combined were 16.3, 10.6, 15.4, 4.7, 25.6 and 626 ng/g fat, respectively. Alpha- HCH was detected in 96 percent of samples at a mean concentration of 0.2 ng/g fat.

The data of this study were compared to data from a similar study undertaken a decade earlier (*2, 3*). This comparison found that levels of each class of POP contaminant, namely PCDD/DFs, PCBs and pesticides, in the milk of New Zealand women had declined by about 70 percent over the ten year period 1988 to 1998. This can be taken as evidence that the exposure of the New Zealand population generally to these substances has substantially declined, and that measures to reduce these contaminants in the New Zealand environment have been effective. The decreases in contaminant concentrations in New Zealand milk are consistent with declining levels in other countries where similar testing has been carried out.

Background

The aim of the study was to investigate whether measures over the period 1988 to1998 to reduce exposure to persistent OC compounds in New Zealand had led to detectable reductions in the levels of these compounds in human milk. This would provide an indication of whether exposure of the New Zealand population to OC contaminants had changed over the same period.

Other objectives included: to generally confirm the findings of a previous study of 1987/88; to establish baseline levels in the milk of New Zealand women of the toxic coplanar (or "dioxin-like") PCBs and to obtain data that can be directly compared with similar data for other countries; and to participate in the third round of the World Health Organization (WHO) co-ordinated study of levels of PCDD/DFs and PCBs in human milk.

Sampling

As far as possible, this study replicated the procedures and selection criteria employed in a study of contaminants in the milk of New Zealand women carried out in 1987/88, and fulfilled the criteria established by WHO including age, parity, health status and residence time. (*5*)

The women who participated in the study were: primiparous; between 20 and 30 years of age (although note that WHO criteria did not require an age restriction); both mother and child were apparently healthy; the pregnancy was normal; and the mother was not supplementing breastfeeding with other liquid or solid food. Each participant provided up to 250 ml of milk. A total of 53 milk samples were collected from October 1998 to May 1999 from two cities and two rural regions, respectively: Auckland (n=20) and Christchurch (n=15); and Northland (n=16), and North Canterbury (n=2).

Sample analytical procedures

Analytical work was undertaken at the IANZ[1] accredited ESR (now AgriQuality Ltd) trace organics laboratory, Gracefield, New Zealand. The fat content of the milk samples was determined by gravimetric analysis. The samples for PCDD/DFs, PCBs and OC pesticides analysis were extracted, purified and detected by high resolution gas chromatography/mass spectrometry (based on USEPA Methods 1613 and 1668A) using a Micromass Ultima High Resolution Mass Spectrometer in selected ion mode, resolution of 10,000. Contaminant concentrations were quantified using the isotope dilution technique.

Data comparability

Aliquots of rural and urban milk from samples collected from Auckland (n =13) and Northland (n = 10) were pooled and analysed by a reference laboratory according to the protocol of the international study co-ordinated by WHO. The results for the pooled and the individual contributing samples were submitted to WHO for inclusion in the third round of exposure studies on the levels of PCBs, PCDDs and PCDFs in human milk.

For analytical quality assurance purposes, three samples of pooled milk were analysed by both the New Zealand analytical laboratory and by Chemisches und veterinäruntersuchungsamt (State Institute for Chemical Analysis of Food), Freiburg, Germany. This laboratory was selected because it was the only one which met the criteria for analyses of PCDD/DFs, PCBs and fat in human milk, in the fourth round of the WHO-ECEH inter-laboratory quality control studies (WHO, 2000). (*4*)

Data storage

Analytical data is available in the scientific report of this study (*1*). Electronic copies are available from the principal author: Dr Michael Bates, School of Public Health, University of California, Berkeley; <m_bates@uclink.berkeley.edu.>

Results

[1] International Accreditation New Zealand (IANZ)

The mean fat content of the sampled human milk for 53 samples was 4.15 percent. Analytical results were obtained for 17 PCDD/DF congeners, 33 PCB congeners and 14 OC pesticides (or pesticide metabolites) comprising HCH (alpha, beta, gamma, aldrin, dieldrin, heptachlor, heptachlor epoxide, HCB, chlordane (alpha, gamma), DDT (pp-DDE, pp-TDE/pp-DDD, op-DDT, pp-DDT):

- The distribution of PCDD/DFs and PCBs was similar across study areas with a tendency for higher concentrations to be found in the milk of women who were older, heavier, and of non- European ethnicity.
- Mean PCDD/DF concentrations were 6.8, 6.4, 5.5, 7.7 pg WHO-TEQ/g fat for Auckland, Northland, Christchurch and North Canterbury, respectively, and 6.3 pg WHO-TEQ/g fat for all samples combined.
- The % >LOD recorded is the proportion (as a percentage) of milk samples in which the individual congeners or analytes were found above the limit of detection. Mean values reported include non detects at half the LOD. Standard deviations (SD)s were not calculated if less than 20% of the values were above the LOD.

New Zealand results for PCDD/Fs in human milk (pg/g fat)

	TEF	NZ 1998 (n= 53) Mean of 4 regions	SD	% > LOD
% fat		4.15	1.23	100
2378 TCDF	0.1	0.20	-	43
2378 TCDD	1	1.22	0.47	100
12378 PeCDF	0.05	0.19	-	21
23478 PeCDF	0.5	2.16	0.95	100
12378 PeCDD	1	2.53	0.82	100
123478 HxCDF	0.1	1.01	-	81
123678 HxCDF	0.1	0.95	-	81
234678 HxCDF	0.1	0.46	-	70
123789 HxCDF	0.1	0.16	-	2
123478 HxCDD	0.1	1.13	-	77
123678 HxCDD	0.1	7.29	2.53	100
123789 HxCDD	0.1	2.28	0.92	100
1234678 HpCDF	0.01	1.20	-	73
1234789 HpCDF	0.01	0.20	-	0
1234678 HpCDD	0.01	13.02	-	81
OCDF	0.0001	0.68	-	21
OCDD	0.0001	67.87	34.96	100
Sum- excl half LOD		97	48	48

Sum- incl half LOD		105	45	45
WHO 1997 TEQ pg/g				
Total TEQ-excl half LOD		6.22	2.07	2.07
Total TEQ-incl half LOD		6.34	2.05	2.05

The mean sum of 14 PCBs for which toxic equivalent factors have been assigned were 4.4, 4.5, 3.7, 4.5 pg WHO-TEQ/g fat for Auckland, Northland, Christchurch and North Canterbury, respectively, and 4.2 pg WHO-TEQ/g fat for all samples combined.

New Zealand results for PCBs in human milk (ng/g fat)

	TEF	NZ 1998 (n= 52) Mean [1] of 4 regions	SD [2]	% > LOD
PCB#77	0.0001	0.01	-	6
PCB#126	0.1	0.02	-	60
PCB#169	0.01	0.02	-	13
PCB#28 + PCB31		2.27	2.59	100
PCB#52		0.16	-	19
PCB#49		0.05	-	10
PCB#44		0.08	-	11
PCB#74		2.25	1.25	100
PCB#70		0.05	-	11
PCB#81	0.0001	0.01	-	6
PCB#101		0.20	-	33
PCB#99		1.44	0.65	100
PCB#110		0.11	-	11
PCB#123	0.0001	0.15	-	8
PCB#118	0.0001	3.22	1.71	100
PCB#114	0.0005	0.16	0.09	100
PCB#105	0.0001	0.78	0.45	100
PCB#153		9.76	5.87	100
PCB#138		9.64	6.12	100
PCB#167	0.00001	0.46	0.26	100
PCB#156	0.0005	1.28	0.90	100
PCB#157	0.0005	0.23	0.16	100
PCB#187		1.84	0.89	100
PCB#183		0.74	0.34	100
PCB#180	0.00001	5.88	2.65	100
PCB#170	0.0001	3.69	1.94	100
PCB#189	0.0001	0.11	-	66
PCB#202		0.10	0.05	100
PCB#196		0.54	0.28	100
PCB#194		0.80	1.62	100
PCB#208		0.02	-	36
PCB#206		0.05	-	40
PCB#209		0.02	-	10

Excl LOD values	45.3	20.4	
Incl half LOD values	46.1	20.1	
WHO 1997 TEQ pg/g			
Excl LOD values	3.13	1.77	
Incl half LOD values	4.23	1.28	

The OC pesticides beta-HCH, HCB, dieldrin, heptachlor epoxide, pp-DDT and the metabolite pp-DDE were detected in all the samples. The mean concentrations of these pesticides for all samples combined were 16.3, 10.6, 15.4, 4.7, 25.6 and 626 ng/g fat, respectively. Alpha- HCH was detected in 96 percent of samples at a mean concentration of 0.2 ng/g fat.

New Zealand results for OC pesticides in human milk (ng/g, fat basis)

	NZ 1998 (n= 52) Mean [1] (of 4 regions)	SD [2]	% > LOD
Alpha-HCH	0.19	0.12	96
Beta-HCH	16.3	15.2	100
Gamma-HCH	0.60	-	38
HCB	10.6	3.39	100
Aldrin	0.00	-	0
Dieldrin	15.4	7.71	100
Heptachlor	0.00	-	0
Heptachlor epoxide	4.69	7.80	100
Alpha-chlordane	0.30	-	4
Gamma-chlordane	0.33	-	4
p,p'-DDE	626	314	100
p,p'-TDE	0.30	-	19
o,p'-DDT	4.36	13.2	100
p,p'-DDT	25.6	68.2	100

Citations

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A2.2.5 Australian National Dioxins Program: Levels of dioxin-like compounds in pooled human milk collected throughout Australia in 2002-2003

Key Message

The results of this study provide a measure of the levels of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/PCDFs) and polychlorinated biphenyls (PCBs) in pooled human milk collected throughout Australia in 2002-2003.

Breast milk samples were collected from primiparae mothers selected according to suitable criteria to allow direct comparison with previous World Health Organization (WHO) studies.

PCDD/PCDFs and PCBs were detected in all pooled samples. For pooled samples collected in 2002 - 2003, the mean and median levels, expressed as TEQ (middle bound), were 9.0 and 8.9 pg TEQ g^{-1} lipid, respectively. No systematic differences were observed in the levels of dioxin-like chemicals in breast milk samples collected from different regions of Australia during 2002-03. In addition to these samples, a further 24 samples collected in 1993 were analysed as three pools of eight samples. For these samples, the mean and median levels, expressed as TEQ (upper bound), were 16 and 16.4 pg TEQ g-1 lipid, respectively.

Overall, the levels of dioxin-like chemicals in the breast milk of Australian women were relatively low in this study when compared to international data reported by WHO.

Background

This study aimed to investigate the levels of dioxin-like compounds in pooled human milk samples collected throughout Australia in 2002-2003. The study formed a component of the Australian National Dioxins Program, which also included measurement of dioxin-like chemicals in human blood serum, air, aquatic environments and soils. There are 12 technical reports available at: http://www.environment.gov.au/settlements/chemicals/dioxins/reports.html

There were 157 samples of human breast milk collected from 12 regions of Australia for 17 pooled samples. These pooled samples were analysed for 7 dioxins, 10 furans and 12 PCBs (4 non ortho and 8 mono ortho) classified as dioxin-like by the World Health Organization (WHO).

Sampling

The emphasis of the study was to distinguish between various geographical regions, including rural, urban and industrial areas. The protocol adopted in this study was identical to that used by the WHO in international studies assessing exposure levels in human breast milk for dioxin-like compounds and PCBs.

In line with the WHO protocol, volunteer mothers were selected using the following criteria:

- A primiparae (first-time) mother with a baby aged two to eight weeks (mothers of IVF babies were included)
- Exclusively breastfeeding
- Willing to provide a minimum of 100 ml (preferably 150 ml) of expressed milk. This volume was to be collected over the six week period (two-eight weeks post-partum)
- Healthy pregnancy, mother and child
- A resident of the area for the past five years.

In total, 173 samples were collected from 12 regions of Australia during the period March 2002 and September 2003. Of these, 16 were excluded because they were later found to have violated the inclusion/exclusion criteria. The remaining 157 samples were analysed as pooled samples and there were 17 pooled samples in total.

A further 24 "historical" samples collected in 1993 were obtained from the Key Centre for Applied and Nutritional Toxicology, Royal Melbourne Institute of Technology, Melbourne, Australia. They were analysed as three pools of eight samples.

The project received Medical Research Ethics Committee Approval from the University of Queensland Medical Research Ethics Committee, as well as from hospital or health services governed by their own ethics committees.

Sample analytical procedures

Samples were stored and shipped frozen to a laboratory at National Research Centre for Environmental Toxicology/Queensland Health Scientific Services (EnTox/QHSS). When collection of a pool was completed, the milk was thawed, thoroughly homogenised and 30 ml from each individual was separately pooled giving approximately 300 ml of sampled milk from each region. The pooled samples were then refrozen and transported on ice to the Australian Government Analytical Laboratories (AGAL), Sydney, Australia and two duplicate samples were sent to the State Laboratory of NRW, Münster, Germany.

Analysis was conducted for 7 dioxins, 10 furans and 12 PCBs (4 non ortho and 8 mono ortho) classified as dioxin-like by the World Health Organization (WHO). Both laboratories were accredited for analytical dioxin analysis. The method for the determination of tetra- through octa-chlorinated PCDD/PCDFs and PCBs in breast milk matrices is through high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS).

Data comparability

Identified errors and quality assurance details as part of the sampling design and sample pooling are outlined in the full technical report and accounted for in the results. Both laboratories were accredited for analytical dioxin analysis.

Analytical QA/QC measures were as follows:

- Batch sizes were typically six to eight samples
- A laboratory blank was analysed with each batch of samples
- A suitable laboratory control sample (LCS) was analysed with each batch of samples as a replicate to assess method precision
- The GCMS resolution, performance and sensitivity was established for each MS run
- The recoveries of all isotopically labelled surrogate standards were calculated and reported
- Ten percent of all samples were analysed by an independent crosscheck QC laboratory.

For the purposes of inter-laboratory comparison, two duplicate samples were analysed by both Australian Government Analytical Laboratories (now known as the National Measurement Institute) and the State Laboratory of North Rhine Westpalia, Germany. These samples were from a rural region in western New South Wales and an urban region from Melbourne, Victoria.

Data storage

The raw analytical data are held by the authors of the report. Electronic copies of the technical reports are held by the Australian Government Department of the Environment, Water, Heritage and the Arts (DEWHA).

Results

PCDD/PCDFs and PCBs were detectable in all 17 pooled breast milk samples. The full technical report gives the levels of PCDD/PCDFs and PCBs in each sample as lower, middle and upper bound TEQ. For *Upper Bound TEQ*, the TEQ level of the congener was calculated using the detection limit, while for *Lower Bound TEQ*, the TEQ level of the congener was calculated using a zero concentration. The greater the number of non-detectable congeners, the greater the difference in the upper and lower bound TEQ values.

In summary, the mean and median levels, expressed as PCDD/PCDF & PCB TEQ, for all pooled samples were 9.0 and 8.9 pg TEQ g^{-1} lipid, respectively. The levels of dioxin-like chemicals expressed as upper bound TEQ varied by a factor of 2.5 from a minimum value of 6.0 pg TEQ g^{-1} lipid detected in the rural Queensland sample, to a maximum value of 15.2 pg TEQ g^{-1} lipid detected in the Brisbane sample. The lowest concentrations were found in samples from rural Queensland, Tasmania, Wollongong and one of the samples from Adelaide.

Total PCDD/PCDF and PCB TEQ are presented in Figure 3.1. The highest concentrations of PCDD/PCDFs and PCBs were found in a sample from Brisbane followed by samples from Sydney and Melbourne. The Brisbane sample had a relatively low lipid content (2.8%) and consequently this result is likely an overestimate since it is expressed on a lipid basis.

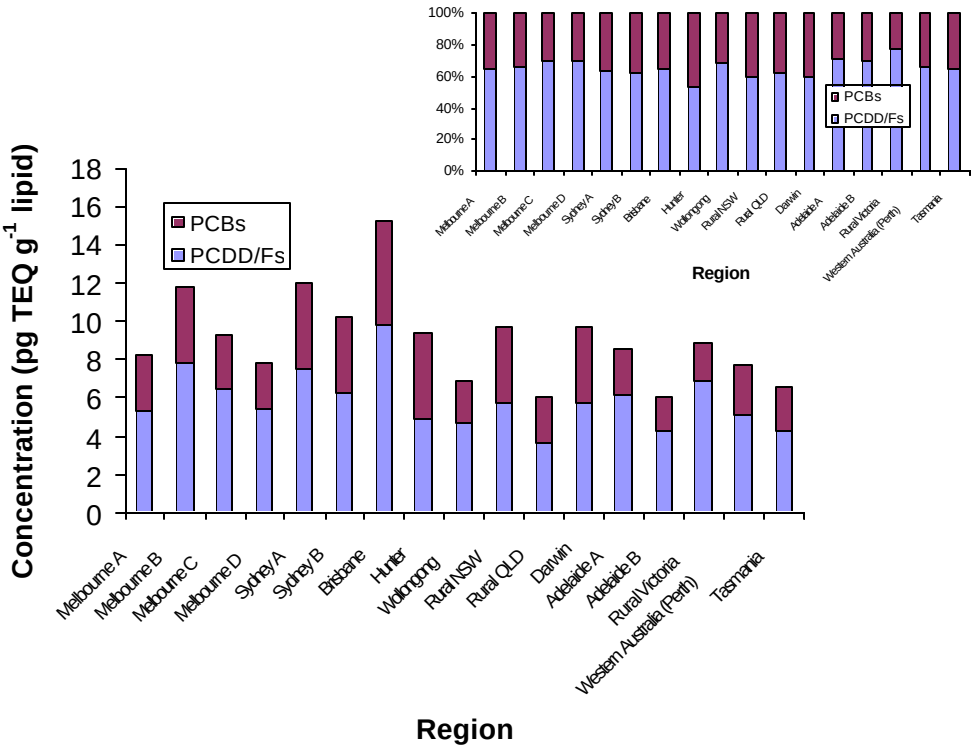

Figure 3.3 Concentration of dioxin-like chemicals in breast milk samples for each sampling region[2].

For PCDD/PCDFs and PCBs the data indicated that on a TEQ basis there was little if any difference between the upper and lower bound results, indicating that the results are not markedly affected by non-detected congeners.

Congeners

The full technical report also shows the mean, maximum, minimum concentrations as well as the percent contribution of each congener to the overall TEQ. For dioxins and furans, the higher chlorinated PCDD, OCDD had the highest concentration in all pooled breast milk samples. Other compounds that were present in much lower concentrations had much higher TEFs and therefore had much greater contribution to the total TEQ.

The average contribution of TCDD to the total TEQ for all pooled samples was 8.7%. 1,2,3,7,8-PeCDD had the highest mean percentage contribution to the mean TEQ, 25.5%, followed by 2,3,4,7,8-PeCDF at 13.8%, then 1,2,3,6,7,8-HxCDD at 9.6%. For the furans,

[2] Presented are the levels expressed as $TEQ_{PCDD/PCDF}$ and TEQ_{PCB} and the inset provides a direct evaluation of the contribution of the PCBs and PCDD/PCDFs to the overall TEQ in each sample pool.

the levels of some congeners were consistently found to be near or below the limit of detection. These were 2,3,7,8-TCDF, 1,2,3,7,8,9-HxCDF and 1,2,3,4,7,8,9-HpCDF.

PCB congeners were detected in all analysed samples. From the non-ortho PCBs, PCB 126 had the highest contribution to the mean total TEQ at 18.9%. From the mono-ortho PCBs, PCB 156 had the highest at 7%. On average, PCBs contributed around 30% to the total TEQ. The inset of Figure 3.1 shows the percentage contribution of PCDD/PCDFs and PCBs to the total TEQ.

It is noteworthy that the percentage contribution of PCB TEQ to total TEQ is consistent. This indicates that the sample base is fairly homogenous and that the exposure of individuals within the pools is similar.

Regional variation

The levels of dioxin-like chemicals observed in all analysed samples from rural, industrial or urban regions were remarkably similar. No consistent trends were observed between pools.

Intra-region variability

Intra-regional variability was assessed by examination of the results from the four Melbourne pools. Dioxin-like chemicals were detected in all pools. The levels expressed as TEQs ranging from 7.9-11 pg g^{-1} lipid with a coefficient of variation of about 15%. Hence, the reproducibility of the sampling/pooling at least for the Melbourne samples was not greater than the typical error of the analytical techniques for the analysis of dioxin-like chemicals.

Levels of dioxin-like chemicals in archived human milk samples from Melbourne

The levels were consistently higher for all congeners in the 1993 samples compared to the levels observed in the 2002/03 samples obtained from the Melbourne pools alone, and data from all pools combined.

The total TEQ levels ranged from 14.6-17 pg g^{-1} lipid (upper bound). The mean TEQ PCB was 5.1 pg g^{-1} which contributed 32% to the mean total TEQ. For two of the historical samples, PCB contributed 25% to the total TEQ and for the other it contributed 44%. As with the 2002/03 samples (Melbourne pools alone and data from all pools combined), the PCB with the highest percentage contribution for the1993 samples was PCB 126. For the mono-ortho PCBs, PCB 156 contributed 9.4%. The mean concentration of TCDD in the 1993 sample was 1.2 pg g^{-1} lipid and this is around 50% higher than in the 2002/03 samples where the mean was 0.8 pg g^{-1} lipid. As with the 2002/03 samples (Melbourne pools alone and data from all pools combined), OCDD was the PCDD/PCDF congener with the highest concentration in all samples.

A comparison of samples collected from Melbourne women (Tables 3.6, Figure 3.3, 3.4, 3.5, 3.6) in 1993 with those collected for the present study shows that the levels of these chemicals have decreased over the ten year time period. However, comparison of the two sample populations is complicated because details of maternal parity and infant age at date of collection were not made available for the older samples. Despite these

limitations, there does appear to be a decrease in the levels of these compounds over time. The concentration decreased by almost a factor of two from 1993 to 2002/03, from 16±1.4 to 9.1±1.3 pg g^{-1} lipid. This decrease likely reflects the world-wide trend over recent decades of declining levels of dioxin-like compounds in the environment and humans.

Conclusion

In summary, the levels of dioxin-like compounds in the Australian population are low by international standards and no systematic difference was observed from different regions of Australia during 2002-03.

Citations

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A2.2.6 Trends for organic pollutants in human breast milk in the Uppsala area in Sweden

Key Message

Temporal trends of levels of PCBs, HCB, ß-HCH, *trans*-nonachlor, oxychlordane, DDT-compounds and dioxins are available from primparae mothers from the Uppsala area in Sweden. The median levels of all POPs decreased significantly during the time period (1996-2006), between 3 and 10% per year. A simple regression model, with sampling year as explanatory variable, in most cases explains only a small fraction of the variation in POP levels in breast milk. It is important to consider lifestyle factors that are associated with POP levels in the analysis of temporal trends.

Background

In order to estimate the body burdens of some organic pollutants among pregnant and nursing women, and to estimate the intake of the compounds by breast-feeding infants, recurrent measurements in human breast milk have been made in the Uppsala area in Sweden. Another aim of this project is to establish if there are temporal trends of levels of some organic pollutants in breast milk.

The study started in 1996 with yearly samplings, and continued from 2000 with sample collections every second year since then. Starting 2007 it is back to a yearly sampling. Temporal trends of PCBs, HCB, ß-HCHs, *trans*-nonachlor, oxychlordane, DDT-compounds and dioxins between 1996 and 2006 are available.

Sampling

The study is designed to meet the requirements for the WHO coordinated survey.

Sample analytical procedures

Lipid adjusted breast milk POP concentrations were used in the statistical analysis since lipid-adjusted concentrations give a better estimate of the body burden than non-adjusted concentrations. Breast milk levels of CB 52, CB 101, CB 114, CB 157, CB 77, CB 81, a-HCH, ?-HCH, *p,p´*-DDD, *o,p´*-DDE and *o,p´*-DDT were low (>50 % of the samples below LOQ), and these substances were therefore omitted from the statistical analysis. The distributions of the organochlorine analytical results closely followed a log-normal distribution, therefore all statistical analysis were performed on logarithmically

transformed data. Multiple linear regression was used to analyse associations between POP concentrations and sampling year. Independent variables (lifestyle factors) that have been shown to influence POP levels in human breast milk were included as explanatory variables in the model. The variables considered were age of the mother, pre-pregnancy BMI (Body Mass Index) and weight changes during pregnancy as well as after delivery. As a consequence of the logarithmic transformation, the associations between sampling year and POP concentrations are presented as percent change of the concentrations per year, and not as change in absolute levels.

Data comparability
The analysis of the breast milks samples have been performed by validated methods at accredited laboratories. The quality control has included analysis of a blank and a control sample in every batch of samples to verify the accuracy and precision of the measurements. The laboratories have successfully participated in several international intercalibration studies organized by e.g. The Norwegian Institute of Public Health, WHO and QUASIMEME.

Data storage
Data are stored at national data hosts. These centers are commissioned by the Swedish Environmental Protection Agency to store data and provide data free of charge to i.e. international organizations.

Results
Multiple linear regression showed that the levels of all analysed POPs decreased significantly during the time period (1996-2006). The adjusted mean decrease in POP concentrations varied between 3 and 10% per year (Table 2). Earlier, it has been shown that a simple regression model, with sampling year as the only explanatory variable, in most cases explained only a small fraction of the variation in POP levels, as shown by low R^2-values. In the multiple regressions, the R^2-values increased considerable, showing that it is important to include lifestyle factors that are associated with POP levels in the analysis of temporal trends.

Since there is a continuous trend of decreasing POP-levels in breast milk, it is difficult to calculate a mean for the Stockholm baseline window of 1998-2008. As a suggestion the levels for 2006 are chosen as baseline values.

Earlier studies have shown that there a no significant geographical trends for the observed levels of these compounds in mother's milk in Sweden. Based on this, it was decided to continue the time series only on one location.

Table 1. Yearly median concentrations of POPs in mother's milk from primiparae mothers in Uppsala, Sweden (ng/g lipid, TEQ as pg/g lipid).

Substance	Year/years	N	Median	Range
Sum PCB[a]	1996-97	87	162	59-402
	1998	90	142	62-323
	1999	26	140	51-293
	2000-2001	29	127	53-261
	2002-2003	31	101	51-219
	2004	32	87	32-165
	2006	30	77	47-197
PCB 153	1996-97	87	69	24-186
	1998	90	56	25-135
	1999	26	61	22-132
	2000-2001	29	55	21-116
	2002-2003	31	43	22-97
	2004	32	35	12-67
	2006	30	31	19-91
HCB	1996-97	87	17	8,0-29
	1998	90	15	7,5-26
	1999	26	14	8,3-25
	2000-2001	29	14	9,4-27
	2002-2003	31	8,8	6,3-21
	2004	32	10	4,0-17
	2006	30	7,6	3,9-11
oxy-chlordane	1996-97	87	4,2	1,7-11
	1998	90	4,1	1,9-9,0
	1999	26	3,7	1,6-7,5
	2000-2001	29	3,6	2,0-8,7
	2002-2003	31	3,1	1,7-8,5
	2004	32	2,9	1,1-9,1
	2006	30	2,3	0,78-5,2
PCDD/F TEQ	1996-97	52	7,5	3,9-16
(based on 2005	1998	29	8,5	3,3-16
WHO TEFs)	1999	17	7,9	4,6-19
	2000-2001	24	6,7	3,5-17
	2002-2003	17	6,0	3,8-12
	2004	15	4,7	3,0-8,1
	2006	30	4,6	2,3-8,9
sum DDT[b]	1996-97	87	128	30-741
	1998	90	109	28-404
	1999	26	108	27-310
	2000-2001	29	83	35-186
	2002-2003	31	65	29-184
	2004	32	71	24-185
	2006	30	67	22-461

[a]including CB 28, 52, 101, 105, 118, 138, 153, 156, 167 and 180
[b]including p,p-DDE, p,p-DDT, p,p-DDD and o,p-DDT

Table 2. Percent change in concentrations of POPs per year in mother's milk from primiparae women living in Uppsala, Sweden, 1996-2006. Adjusted for age, pre-pregnancy BMI, weight gain during pregnancy and weight loss after delivery. TEQ concentrations are based on 2005 WHO TEFs.

Compound	**Change/year (%)**		**R^2 [a]**	**"half- time" [b]**	**P**
	Mean	**SE**	**(%)**	**(years)**	
PCB 28	-4.0	1.4	8	17	0.004
PCB 105	-4.3	1.2	26	16	<0.001
PCB 118	-8.6	0.6	56	8	<0.001
PCB 138	-6.9	0.5	55	10	<0.001
PCB 153	-8.0	0.5	68	8	<0.001
PCB 156	-5.8	0.5	62	12	<0.001
PCB 167	-5.4	0.9	42	12	<0.001
PCB 180	-7.3	0.5	76	9	<0.001
mono-*ortho* TEQ[c]	-7.4	0.5	60	9	<0.001
PCB 126	-7.7	0.7	49	9	<0.001
PCB 169	-3.4	0.7	54	20	<0.001
non-*ortho* TEQ[d]	-7.3	0.6	52	9	<0.001
PCDD TEQ	-6.9	0.5	66	10	<0.001
PCDF TEQ	-5.7	0.6	52	12	<0.001
PCDD/DF TEQ	-6.4	0.5	66	10	<0.001
Total TEQ	-7.0	0.5	64	10	<0.001
HCB	-8.2	0.4	52	8	<0.001
β-HCH	-10	0.5	63	6	<0.001
oxychlordane	-6.9	0.5	58	10	<0.001
trans-nonachlor	-6.3	0.6	53	11	<0.001
p,p'-DDT	-9.4	0.8	32	7	<0.001
p,p'-DDE	-8.5	0.8	41	8	<0.001

[a] coefficient of determination for the regression model
[b] the estimated time it takes for the concentrations to be halved
[c] including CB 105, 118, 156 and 167 TEQs
[d] including CB 77, 126 and 169 TEQs

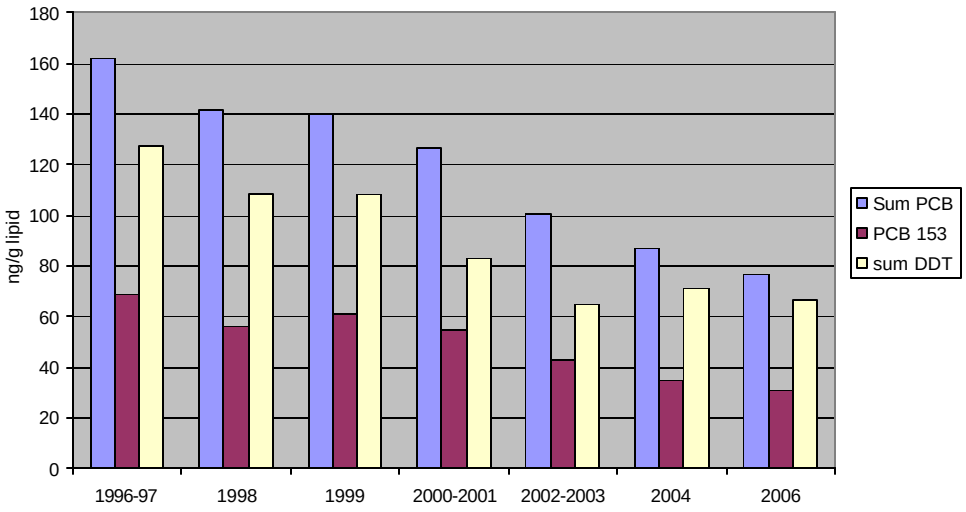


Figure 1. Yearly median concentrations of sum PCB, PCB 153 and sum DDT in mother's milk from primiparae mothers from Uppsala, Sweden.

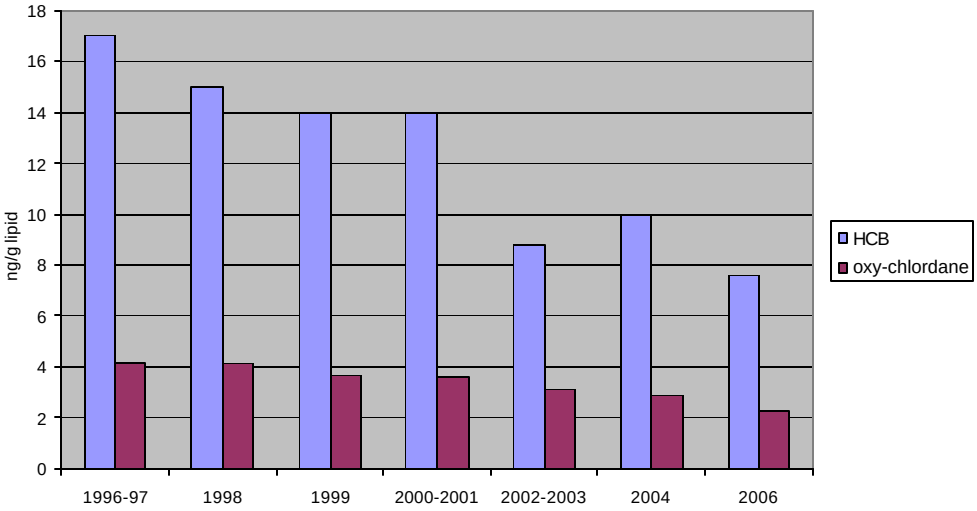


Figure 2. Yearly median concentrations of HCB and oxy-chlordane in mother's milk from primiparae mothers from Uppsala, Sweden.

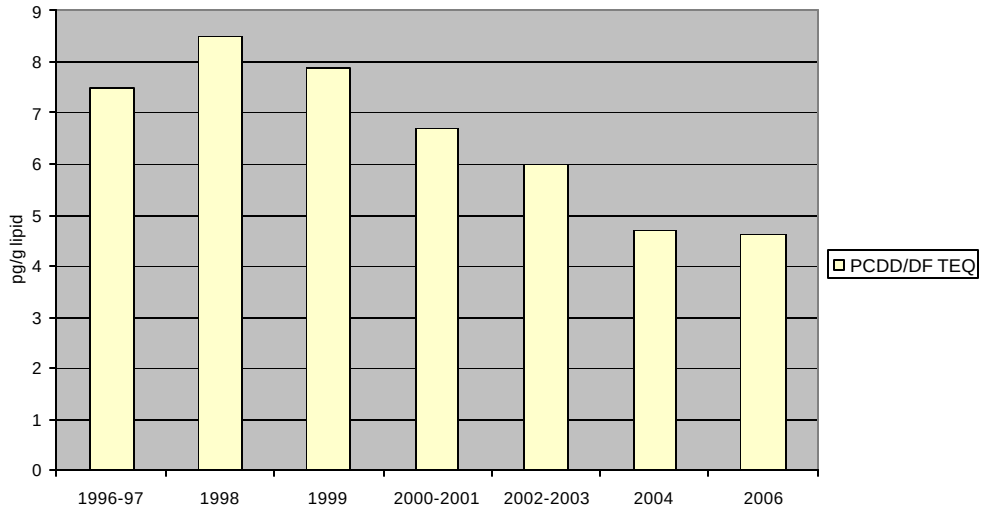


Figure 3. Yearly median concentrations of PCDD/F TEQ in mother's milk from primiparae mothers from Uppsala, Sweden.

Citations

Anders Glynn, Marie Aune, Sanna Lignell, Emma Ankarberg, and Per Ola Darnerud (2007). Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), chlorinated pesticides and brominated flame retardants in mother´s milk from primiparae women in Uppsala County, Sweden – Levels and trends 1996-2006. Report to the Swedish Environmental Protection Agency, 2007-10-31. Contract no. 215 0615.

A2.2.7 Trends for organic pollutants in human breast milk in the Stockholm area in Sweden

Key Message

The investigations of DDTs, PCBs, PCDD/PCDFs, dieldrin, chlordane and HCB in breast milk from women living in the Stockholm region started in 1967. During the course of 20-30 yr the levels of organochlorine compounds in human milk have decreased to various extent. A decrease to the half of the original concentration was attained in the range of 4-17 yr periods.

Background

The objective of the programme is to monitor temporal trends for different organochlorine compounds over time. There is no geographical consideration. Most of the measured substances have been banned for a long time and there is no reason to believe that the exposure differs between different parts of Sweden.

The milk was obtained from healthy native Swedish mothers living in the Stockholm region. The first samples were collected in 1967 but only from 1972 on, milk was banked for coming reanalysis.

Samples are collected on a yearly basis and there is a planned yearly sampling in the future. All recent samples have not been analyzed. The samples are however available and can be analyzed at a later stage.

Sampling

The milk, obtained from healthy native Swedish mothers living in the Stockholm region, was purchased from the Stockholm Center for Mothers milk. The first samples were collected in 1967 but only from 1972 on, milk was banked for coming reanalysis. From 1986 on, the donors were non-smokers and the milk was collected during the first three months after delivery. Equal amounts of milk from individual mothers were mixed to constitute pooled samples. In order to get comparable samples, the composition of pools was kept as equal to that of the early sampled milk as possible. In the pools 55±75% of the milk was from mothers nursing their first infant. The average age of the mothers was 27-28 yr in the period 1972-1985, 29-30 yr in 1988-1994 and 30-31 yr in 1996-1997.

Sample analytical procedures

The details of the analytical procedures for organochlorine compounds have been described previously (Norén, 1983; Norén et al., 1996). Purification and separation of compounds were made by chromatography on aluminium oxide, silica gel, activated

charcoal and gel permeation chromatography. In the analysis of samples from 1994 to 1997, instead of activated charcoal the separation of planar compounds was performed by HPLC on a Cosmosil 5-PYE column (2-(1-pyrenyl)ethyldimethylsilylated silica gel: 250 ´ 4.6 mm, 0.5 lm particle size) from Nacalai Tesque (Kyoto, Japan) (as described by Weistrand and Norén, 1998). Identifications and quantifications were made by gas chromatography electron capture detection and gas chromatography/mass spectrometry using selected ion recording. Total PCBs refer to determination of the concentrations by comparison to the PCB product Clophen A50 (Bayer, Leverkusen, Germany) using a packed column in the analysis by gas chromatography (Norén, 1983). By the time when capillary columns and standards of individual PCB congeners became available, the concentrations of PCB were determined both as total PCBs using a packed column and as specific PCB congeners using a capillary column and 18 PCB congeners as standards for comparison (Norén et al., 1990; Lundén and Norén, 1998). Congener specific analyses were performed when reanalysing archived samples. The sum of PCB congeners was on an average 68% of the total PCBs. From 1994 on, only capillary columns were used and the total PCBs were calculated from the sum of PCB congeners on the above assumption.

Data comparability

The changes in the levels of organohalogen compounds were examined for adaptation to a first order rate expression:
-dC/dt = k * C; which on integration yields: ln C0/Ct =k * t, where C0 is the concentration at the first investigation, Ct the concentration at the last investigation, k the constant and t is the time range of investigations.
The rate of decrease is given as the time to halve the concentration, decline half-time, the time increase to the double concentration and correlation to the exponential curve as R2.

Data storage

Data are stored at national data hosts. These centers are commissioned by the Swedish Environmental Protection Agency to store data and provide data free of charge to ie. international organizations.

Results

The investigations of organochlorine compounds in breast milk from women living in the Stockholm region started in 1967. During the course of 20-30 yr the levels of organochlorine compounds in human milk have decreased to various extent. A decrease to the half of the original concentration was attained in the range of 4-17 yr periods.

The most consistent decline in the levels is noticed for p, p-DDT and p, p-DDE. The level of p, p- DDT in 1997 was only 1% of the level in 1967 and the halt life was calculated to be 4 yrs. The decrease of its metabolite p, p-DDE was not obvious until after 1972 and the time for decrease to half of the concentration is longer than for DDT, the half life was calculated to be 6 yrs, In Sweden, the use of several organochlorine pesticides (DDT,

aldrin, dieldrin, chlordane) was restricted or prohibited in 1970 (Regulation on certain active substances, 1993).

The levels of dieldrin also declined with a half life of 6 yr. The concentration of dieldrin in 1985 was 13% of that in 1967. The concentrations of a-HCH, b-HCH, oxychlordane, trans-nonachlor and pentachlorophenol also decreased. However, due to the short time range studied (from 1972 to 1985 or 1989) the time for decrease of these pesticides to half of the levels were not calculated.

The concentrations of HCB in breast milk varied during the 1970s but a manifest decline in the average levels is seen from 1974. The average concentration of HCB in 1997 was 5% of that in 1974 and the rate of decline to half of the concentration, t_{dec} 1/2, was calculated to be 6 yrs. HCB has been used as a fungicide and in certain industrial processes, e.g., aluminium melting, graphite electrodes, rubber and dye manufacture. The fungicidal use of HCB was withdrawn in 1980 and also its industrial use has been replaced. HCB is also formed as a by-product
in chemical processes.

The level of total PCBs in 1997 was about 30% of that in 1972. The use of PCBs was restricted in 1972 and only allowed in closed system (capacitors and transformers). The remaining PCBs in closed systems were to be replaced by 1995.

A decline in the levels of PCDDs and PCDFs is seen from 1972. In all samples octachlorodibenzo-p-dioxin (OCDD) is by far the most predominant dioxin congener. Compared to the other dibenzo-p-dioxins this compound is of minor toxic relevance. Among the dibenzofurans 2,3,4,7, 8-PeCDF occurs at the highest levels and this compound is considered of high toxic potency. The sum of PCDDs and of PCDFs in 1997 was 24% and 17%, respectively, of the levels in 1972.
In 1997 the total TEQs was 28% of that in 1972. The half life was calculated to be 15 yrs.

Changes in the levels of organohalogen contaminants in human milk, given as the time to halve the concentration .

Compound	Time range studied	t ½ (years)
p,p´-DDT	1967-	-4
p,p'-DDE	1972-	-6
$MeSO_2$-DDE	1972-1992	-6
HCB	1974-	-6
Dieldrin	1967-1985	-6
PCBs	1972-	-14
CB-118	1972-	-11
CB-138	1972-	-14
CB-153	1972-	-17
$MeSO_2$-PCBs	1972-1992	-9
PCDDs	1972-	-15
PCDFs	1972-	-11
TEQ	1972-	-15

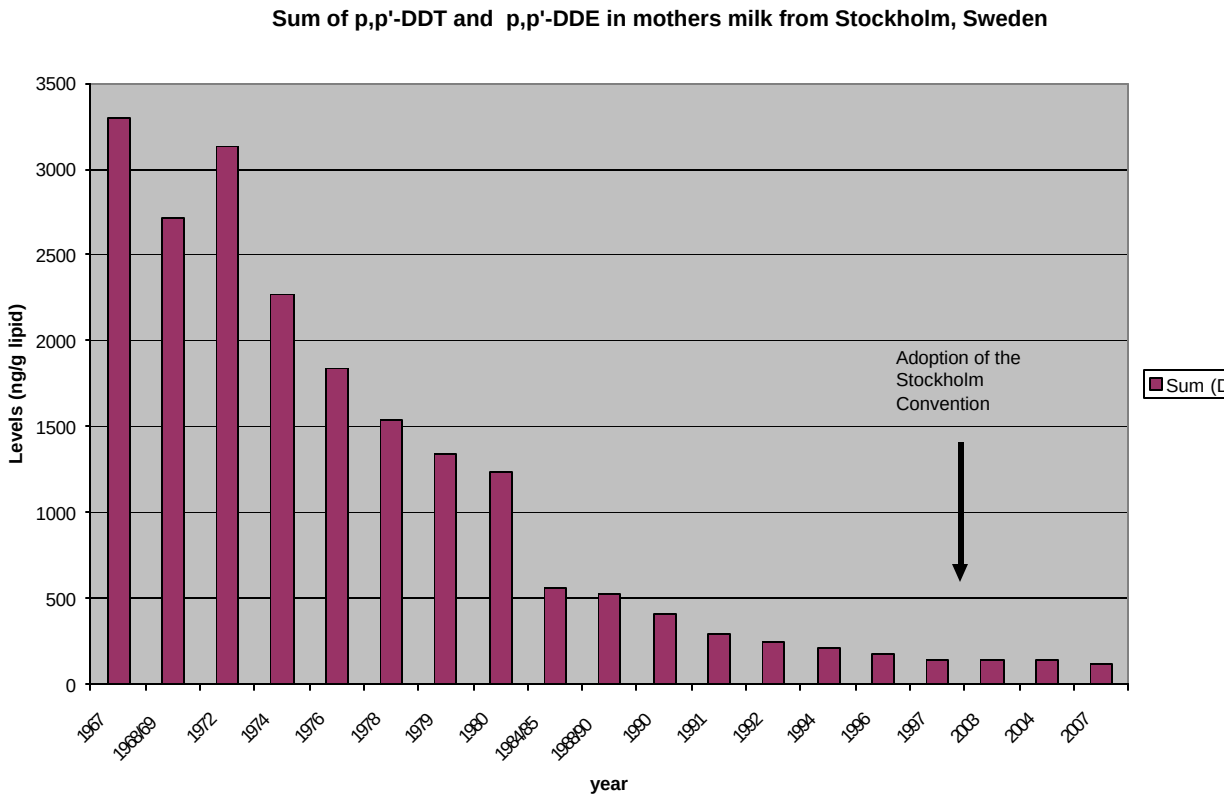
Levels (ng/g lipid)

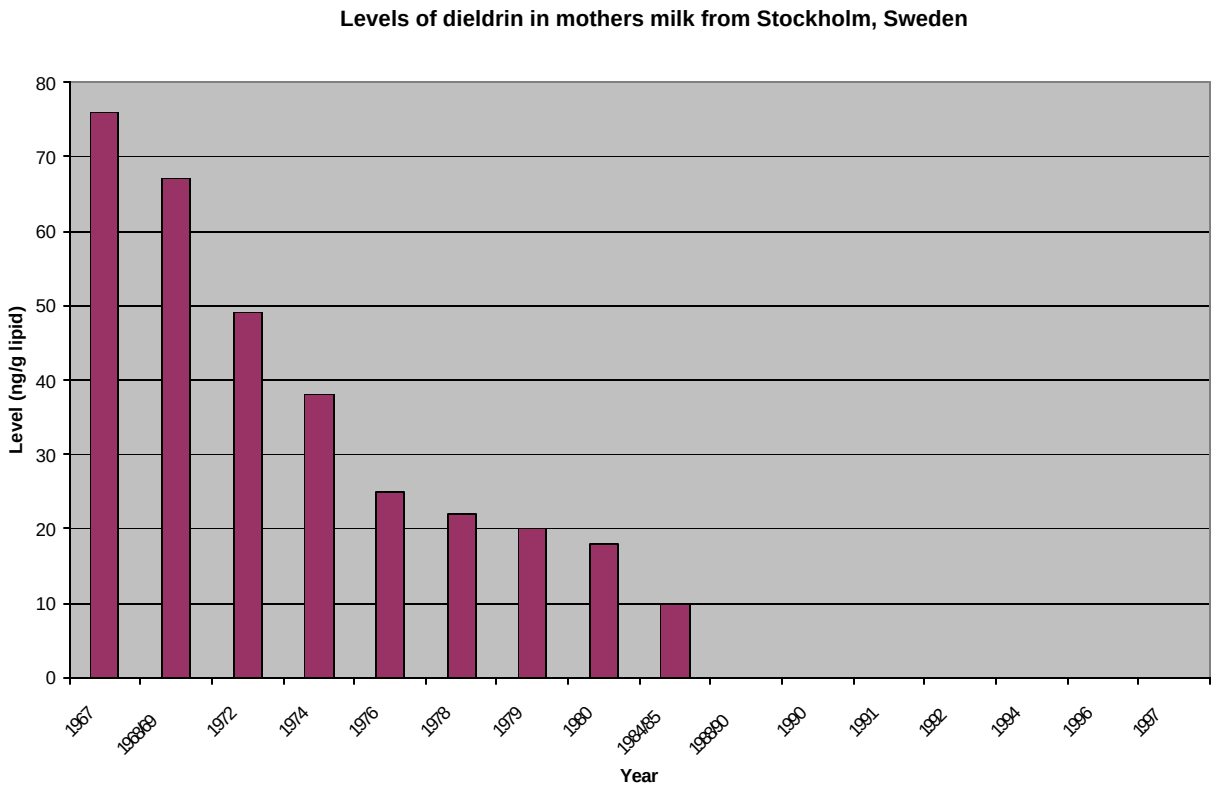
Substance	*1967*	*1968/ 69*	*1972*	*1974*	*1976*	*1978*	*1979*	*1980*	*1984/ 85*	*1988/ 90*	*1990*	*1991*	*1992*	*1994*	*1996*	*1997*
DDE	2000	1700	2420	1800	1500	1270	1130	1055	500	480	369	255	227	199	164	129
DDT	1300	1020	710	470	340	270	210	185	61	47	42	36	22	12	14	14
dieldrin	76	67	49	38	25	22	20	18	10							
oxychlordane			19		16	16	16	14	13	12						
HCB			120	220	110	120	120	125	37	40	33	27	31	15	14	12
CB153			215		197			152	124	146	116	106	96	93	83	73
Tot PCB	500	600	1090	810	910	880	790	780	600	650	510	410	380	416	367	324

Sum TEQ (pg/g lipid)

1972	*1976*	*1980*	*1984/85*	*1988/90*	*1990*	*1991*	*1992*	*1997*
100	77	52	39	44	42	32	40	28

Since there is a continuous decreasing trend the newest value should be taken as baseline value for the Stockholm baseline window of 1998-2008





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A2.2.8 USA: NHANES and Alaska MOMs Study

Key Message
In the U.S., we have two main studies examining human serum concentrations of the 12 UNEP POPs: the continuous, general population (aged 12 years and older) National Health and Examination Survey (NHANES) since 1999 and the Alaska MOMs study (1999- 2004).

In NHANES, we are measuring the 12 UNEP POPs with the exception of toxaphene (toxaphene will be added with the analysis of 05,06 NHANES serum samples) and in the Alaska MOMs (pregnant Native women and cord blood) we are measuring the UNEP POPs with the exceptions of polychlorinated dibenzo-*p*-dioxins and furans.

Background
The study design of NHANES is to include a representative sampling of the civilian, noninstitutionalized U.S. population. The environmental chemical exposure assessment includes measuring serum concentrations of POPs. In time, temporal trend data can be determined. Because of serum volume limitations (hence, a large number of non-detects, starting in 05,06 NHANES dioxins and furans will be measured only in stratified pooled samples. We also measured dioxins and furans in pooled serum samples, selected by demographic groups, in 2001-2002 serum samples. This Survey will continue indefinitely.

In the Alaska MOMs study, we are measuring all 12 UNEP POPs in cord blood and Native pregnant women primarily located in the Y-K river basin in western Alaska although a limited number of samples have been taken in Barrow and the Pribilof Islands. This study will continue.

In both studies, we are also measuring serum concentrations of non-UNEP POPs including polybrominated diphenyl ethers, polyfluoroalkyl compounds, and hexachlorocyclohexanes.

Sampling
In the NHANES the blood sampling is stratified among age range (starting at age 12 years), race/ethnicity, and sex so that the population is representative of general population of the U.S.

In Alaska, the blood sampling involves Native pregnant women and the cord blood from their offspring.

Sample analytical procedures
Although the analytical methods have changed over time, we are currently measuring the polybrominated diphenyl ethers (non-UNEP POPs), polychlorinated biphenyls, and organochlorinated pesticides in 2 mL of serum (this involves 3 gas chromatography injections) by high resolution gas chromatography/high resolution mass spectrometry

with quantification by isotope dilution technique (except for the toxaphene congeners) (*1*).

A separate serum sample is utilized for measuring dioxins and furans, by similar analytical techniques but much more extensive sample preparation (*2,3*).

Data comparability
As previously mentioned, all analytes are quantified using state-of-the-art analytical methods, including high resolution mass spectrometry and isotope dilution quantification except for toxaphene, for which no labeled standards exist.

In house prepared quality control/quality assurance pools have been characterized and are repeatedly analyzed with unknown samples to certify accuracy and precision over time.

We are or have participated satisfactorily in POPs' interlaboratory studies including those from AMAP (Canada), Germany, and WHO-EURO.

Data storage
The final analytical data are stored in Microsoft Excel and/or SAS format and are archived indefinitely. All data files are stored on the CDC Network with daily backups.

Raw data files including chromatograms and electronic log-sheets for sample processing are either stored on the CDC Network or burned to DVDs for archiving. Paper copies of log sheets and other written documentation is further archived as long as storage space allows or at a minimum of 3 years. If in the future written documentation can not be stored the documentation would be scanned in to PDF-files prior to discarding paper copies.

Results
The most recent data from NHANES are from serum samples collected in 2003- 2004. I will summarize the findings for each of the analytes from this Survey and interject other data where appropriate. Toxaphene was not measured in 2003- 2004 but will be measured in 2005- 2006 samples.

Hexachlorobenzene: Hexachlorobenzene was detected in 99.9% of samples . The geometric mean was 15.2 ng/g lipid. Least squares geometric mean (LSGM) showed that sex, age, race (all p=0.006) and sex*age (0.003) are significant. In general, serum concentrations increased with age, with higher increases in females than males, and Mexican Americans higher than nonHispanic blacks and nonHispanic whites.

DDT and its environmental degradate/metabolite DDE: p,p'-DDT was detected in 74% of people, aged 12 years and older. Concentrations increased with age and were significantly higher in Mexican Americans. o,p'-DDT was detected in only 5% of the people.

DDE was detected in 99.7% of the participants. Geometric mean 104.6 ng/g lipid (95% CI= 84.7- 129.0). The LSGM for DDE show that concentrations increase with age, and more so in females and in nonHispanic blacks than in Mexican Americans or nonHispanic whites. However, the LSGM was significantly higher in Mexican Americans was significantly higher than that in nonHispanic blacks/whites, regardless of age.

Chlordane (as evaluated by measuring serum oxychlordane and *trans*-nonachlor): Oxychlordane, a persistent metabolite of chlordane) was detected in 83% of the participants. Geometric mean was 9.4 ng/g lipid (8.7- 10.1).
Trans- nonachlor, a persistent byproduct in technical chlordane, was detected in 93% of the participants. Geometric mean was 14.6 ng/g lipid (13.1- 16.5).

Heptachlor (as evaluated by measuring its persistent metabolite heptachlor epoxide: Detection rate= 60%. The GM in nonHispanic whites (15.8 ng/g lipid; 13.7- 18.2) and nonHispanic blacks (14.4 ng/g lipid; 12.2- 17.0) were significantly higher than that in Mexican Americans (10.2 ng/g lipid; 7.68- 13.2).

Mirex: Mirex was detected in 41% of the participants. Concentrations increased with age. The 95th percentile in nonHispanic blacks was 37.9 ng/g lipid compared to 11.5 and in nonHispanic whites and less than the limit of detection for Mexican Americans, respectively.

Aldrin and **Dieldrin:** Aldrin is rapidly metabolized to dieldrin and hence measurement of dieldrin does not differentiate exposure to aldrin to that of dieldrin. Aldrin was detected in only 0.2% of the participants.
Dieldrin was detected in 87% and increase with age; there were no differences in serum concentrations among males and females or with race/ethnicity. 95th percentile: 18.9 ng/g lipid; 15.8- 24.5).

Endrin: Endrin was detected in only 0.085% of the participants.

Polychlorinated biphenyls: 35 individual congeners were measured and reported separately and by total PCBs. The geometric mean total PCB concentration for all age, sex, and race/ethnicity in the U.S. population for 2003-2004 is 0.820 ng/g whole-weight (95% confidence interval: 0.782-0.863 ng/g whole-weight) and 134.4 ng/g lipid (95% confidence interval: 128.9-140.0 ng/g lipid). The geometric mean and the 50th, 75th, 90th, and 95th percentile levels for total PCBs all increased significantly with age. There was no difference in total PCB levels for males and females. MA had significantly lower geometric mean levels of total PCBs as well as significantly lower 50th, 75th, 90th, and 95th percentile levels than NHW and NHB. There was no difference in the levels for NHW and NHB.

Polychlorinated dibenzo-p-dioxins and furans: The total TEQ for all persons age 12+ years in the U.S. Population is as follows: (1998 TEFs: 90th percentile 39.4 pg/g lipid, 95th percentile 49.1 pg/g lipid; 2005 TEFs: 90th percentile 30.9 pg/g lipid, 95th percentile

37.8 pg/g lipid) and the age 20+ years in the U.S. population (1998 TEFs: 90th percentile 41.1 pg/g lipid, 95th percentile 52.3 pg/g lipid; 2005 TEFs: 90th percentile 32.5 pg/g lipid, 95th percentile 39.9 pg/g lipid). The total TEQ levels are lower using the 2005 TEFs principally due to the much lower TEF values assigned to the mPCBs in 2005. We have evaluated the various TEQs by age groups, and there is a significant increase in total TEQ levels with age at both the 90th and 95th percentiles for all combined race/ethnicity and sex.

In our analyses of the 2001-2002 serum pools for dioxin and dioxin-like chemicals, it is obvious that the total TEQ increased with age in all 3 race/ethnicity groups and with females and males. Also, in all 3 race-ethnicity groups males in the youngest age group (12-19 years) tended to have higher TEQ than females but the converse was true in the oldest age group, 60+ years. The most important take home message for the TEQ, as for most all of the UNEP POPs, is that one cannot give a "universal" geometric mean, for the concentration is so very much age dependent. For example, for the nonHispanic blacks, the total dioxin TEQ was around 7 pg/g lipid for the 12-19 year olds but was about 30 pg/g lipid for the 60+ age group.

AK MOMs Study: These samples through 2004 (all that have been collected) have been measured but the data have not been analyzed. They will be analyzed and reported to the Arctic Monitoring Assessment Program. Again, these analytes will not include dioxins and furans, but will include toxaphene.

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