Chapter 7

PTS levels in humans

7.1. Sampling strategy

Sampling of human blood was undertaken in parallel with the dietary and lifestyle surveys, with two sets of respondents involved: pregnant women, from whom blood (and cord blood) were sampled at maternity departments of local hospitals, and representatives of the general adult indigenous population in selected indigenous settlements within the areas chosen for project implementation. Additional control samples, from urban populations in Norilsk and the Aral Sea areas, were analyzed to compare their PTS levels with those found in northern indigenous populations. The Aral Sea area is generally acknowledged to be an environmental disaster area, characterized by high usage of a range of pesticides in previous years, whilst Norilsk is a heavily industrialized area, with a wide range of pollutant sources. Information on the numbers and geographical distribution of samples for each area is presented in Table 7.1.

Project area	Pregnant women			General adult indigenous population	
	No. interviewed	No. of maternal blood samples	No. of cord blood samples	No. interviewed	No. of blood samples
Murmansk Oblast	17	16	14	264	52
Nenets AO	39	25	25	347	44
Taymir AO	80	67	68	354	52
Chukchi AO	101	100	71	611	92
Norilsk (control area 1)	17	17	16	-	-
Aral (control area 2)	30	30	28	-	-
Total	**284**	**255**	**222**	**1576**	**240**

Table 7.1. Numbers of persons interviewed, and blood samples taken.

The World Health Organization (WHO) recommends the use of breast milk as an indicator of the human body load of dioxins, PCBs, and other contaminants of this type. Despite this, AMAP human health assessments are usually based on PTS levels in human blood. This approach was selected after a thorough analysis of all factors, which included the ethical principles of undertaking studies among indigenous peoples, and the population groups to be covered by surveys. In order to ensure that project data would be comparable with both circumpolar and global data, breast milk samples were taken and analyzed in parallel with blood samples from a group of women in the Chukotka peninsula, one of the project areas.

A total of 60 samples of breast milk were analyzed for POPs. The samples were collected from different districts of the Chukchi AO: Chukotsky (27 samples), Anadyrsky (21 samples), and the town of Anadyr (7 samples). Five samples were also collected and analyzed from St. Petersburg, which was chosen as a control area.

Blood sampling was undertaken using vacutainers, fiberglass plungerless vacuum test-tubes with a needle screwed on a holder for dosed intravenous blood sampling. Blood was collected first from the mother's *vena ulnaris* and then from the umbilical cord of the fetus. For further blood treatment, special pipettes and vials, pre-tested to ensure the absence of pollutants that might confuse blood analysis findings, were used. Samples were processed in a 3000 rpm centrifuge and stored in a freezer at –20°C. Special thermally insulated containers were used for the transport of frozen blood samples.

Blood was collected from mothers on the first to the third day after delivery. Cord blood was sampled immediately after the tying and cutting of the umbilical cord. Methods used for blood sampling and blood treatment techniques were identical for maternal and cord blood. Mothers were also interviewed on the third to the fifth day after delivery.

7.2. Analytical methods and quality control

7.2.1. Analysis of POPs

Analysis of blood serum for persistent organic pollutants (POPs) was carried out in the Center for Environmental Chemistry (CEC) of SPA 'Typhoon', and the laboratory of the Regional Center 'Monitoring of the Arctic' (RCMA). Analyses at CEC were based on GC/MS, and those conducted at the RCMA laboratory involved chromatographic separation with electron capture detection. Quantitative calculations were based on external calibration using standard solutions.

Extraction of POPs from blood serum

Prior to extraction, blood serum samples were defrosted at room temperature. Each serum sample was weighed to an accuracy of 0.01 g and placed in an Erlenmeer flask. The isotope-labeled surrogate standards solution was then added and mixed for 30 minutes, after which methanol (MeOH) was added (in a volume equal to that of the sample) and the solution mixed for a further minute.

The sample solutions were initially extracted using a mixture of 1 : 1 hexane-MTBE (methyl-tri-butyl ether), the extraction process repeated twice, using 20–35 ml of an extracting agent. After separation of organic and aqueous layers, the extract was transferred to an Erlenmeer flask using a pipette. The extracts were combined, and the remaining water removed using anhydrous sodium sulfate, for a period of 30 minutes. The extract was then put through a fiberglass filter and concentrated to a volume of 10 mL, using a rotor evaporator. An extract aliquot of 2 mL was used to determine the level of lipids in blood serum. The remaining extract was then further concentrated to a volume of 1 mL, cleaned of lipids using gel-filtration on a Bio-Bead SX-3 column, and impurities were separated out using activated aluminum oxide and column chromatography with columns of silica gel, Florisil, and carbon AX-21.

Determination of the lipid content in blood serum
Lipids in blood serum were determined in the 2 mL aliquot of primary extract that had been prepared for POP analysis, using the gravimetric method.

Determination of polychlorinated biphenyls (PCBs)
PCBs determined in blood serum included the compounds identified by IUPAC nomenclature as: PCB-28/31, PCB-52, PCB-99, PCB-101, PCB-105, PCB-118, PCB-128, PCB-138, PCB-153, PCB-156, PCB-183, PCB-187, PCB-170 and PCB-180. A surrogate standard, consisting of a mixture of PCBs that were isotope-marked with ^{13}C (#28-$^{13}C_{12}$; #52-$^{13}C_{12}$; #101-$^{13}C_{12}$; #118-$^{13}C_{12}$; #138-$^{13}C_{12}$; #153-$^{13}C_{12}$; and #180-$^{13}C_{12}$, manufactured by Wellington Laboratories) was added to samples prior to extraction to control the efficiency of extraction and quantification, using PCB-166 as the recovery standard.

After preparation, sample extracts were analyzed using a Varian SATURN-2200T GC/MS, by operating in electron impact ionization mode. Analytes were identified by comparison of the resulting mass-spectra with chromatographic retention times characteristic of different PCB congeners. The detection limit of individual PCB congeners ranged from 0.002 to 0.2 µg/L.

Determination of organochlorine pesticides (OCP)
Organochlorine pesticides determined in blood serum included the following compounds: HCB, α-HCH, β-HCH, γ-HCH, *p,p'*-DDD, *p,p'*-DDT, *o,p*-DDE, *o,p*-DDD, *o,p*-DDT, heptachlor, *cis*-chlordane, *trans*-chlordane, oxychlordane, *cis*- and *trans*-nonachlor, dieldrin, and mirex.

Analytical determination of OCPs was performed using a Varian SATURN-2200T GC/MS, with identification of components by their characteristic mass-spectra, recorded in the range m/z = 80-420 amu. Control of the efficiency of extraction and quantification was achieved by adding analogues of analytes marked with ^{13}C ($^{13}C_{12}$-*p,p'*-DDE, $^{13}C_{12}$-*p,p'*-DDT, $^{13}C_6$-γ-HCH, and $^{13}C_6$–HCB; supplied by Cambridge Isotope Laboratories) to samples prior to extraction. The internal standard used was PCB #166.

The detection limit for organochlorine pesticides ranged from 0.003 to 0.16 µg/L for the various compounds.

Toxaphene
Analysis of toxaphene In blood serum samples was undertaken for those compounds known to be the most persistent and frequently occurring in the environment; namely, the *octa*- and *nona*- chlorinated toxaphenes that are conventionally referred to as Parlar-26, Parlar-50 and Parlar-62.

Extraction of toxaphenes was carried out in conjunction with other OCPs, as described above. After preparation, extracts were analyzed by GC/MS operating in chemical ionization mode, with detection of negative ions (NCI) characteristic of toxaphene compounds, i.e, selective ion monitoring (SIM). Analyses were performed on a SATURN-1200 MS/MS.

Analytes were identified by the presence of characteristic ions and the coincidence of chromatographic retention times. Due to the lack of available isotope-labeled compounds, calculations were carried out using external calibration based on the analysis of standard solutions of a mixture of individual toxaphene congeners, TOX-482, manufactured by Promochem.

The detection limit for individual congeners of toxaphene ranged from 0.01 to 0.03 µg/L.

Polybrominated diphenyl ethers (PBDE)
Polybrominated diphenyl ethers are widely used in industry as flame retardants. These are lipophilic compounds of low-volatility. The compounds determined in blood serum were those PBDE congeners most frequently used in products, namely:

2,4,4'- tribromodiphenyl ether (BDE-28)
2,2',4,4'- tetrabromodiphenyl ether (BDE-47)
2,2',4,4',5- pentabromodiphenyl ether (BDE-99)
2,2',4,4',6- pentabromodiphenyl ether (BDE-100)
2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153)
2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154)
2,2',3, 4,4',5',6-heptabromodiphenyl ether (BDE-183)

Analysis was performed by GC/MS using a SATURN 1200 MS/MS operating in chemical ionization mode, with detection of negative ions (NCI) and selective ion monitoring (SIM). Identification of analytes was based on the presence of characteristic ions and coincidence of chromatographic retention times. For calculations, data from PBDE calibration solutions based on the mixture of EO-4149 standards, manufactured by Cambridge Isotope Laboratories, and containing all determined compounds, was used. The detection limit of individual PBDE congeners ranged from 0.1 to 0.4 ng/L.

Polychlorinated dibenzo-n-dioxins/dibenzofurans (PCDD/PCDFs)
Quality control of the efficiency of extraction, and quantitative calculations was achieved by adding a surrogate standard prior to extraction. This solution (EPA-23 ISS, manufactured by Wellington Laboratories) contains a mixture of PCDD/Fs, isotope-marked with ^{13}C, including:

$^{13}C_{12}$ –2,3,7,8-TCDD
$^{13}C_{12}$ –1,2,3,7,8-PeCDD
$^{13}C_{12}$ –1,2,3,6,7,8-HxCDD
$^{13}C_{12}$ –1,2,3,4,6,7,8-HpCDD
$^{13}C_{12}$ –OCDD
$^{13}C_{12}$ –2,3,7,8-TCDF
$^{13}C_{12}$ –1,2,3,7,8-PeCDF
$^{13}C_{12}$ –1,2,3,6,7,8-HxCDF
$^{13}C_{12}$ –1,2,3,4,7,8-HpCDF

The recovery standard was the mixture NK-IS-A, containing $^{13}C_{12}$ –1,2,3,4-TCDD and $^{13}C_{12}$ –1,2,3,7,8,9-HxCDD.

Analyses we performed on a GC/MS SATURN 1200MS/MS, using chemical ionization with detection of negative ions (NCI) and selective ion monitoring (SIM). Identification of analytes was based on characteristic ions and coincidence of chromatographic retention times. The detection limit for individual congeners of PCDD/Fs ranged from 0.02 to 1.4 ng/kg.

7.2.2. Quality Assurance/Quality Control of POPs analysis

Quality control procedures involved a set of measures to check the accuracy of measurements and to estimate the size of any errors arising during sample preparation for analysis and measurement.

Analysis of samples was performed in series batches. Each batch included no more than 12 samples, a procedural blank, and a sample of a certified reference material or a control sample prepared in the laboratory, which contained known amounts of the analyte being determined. As the weight of individual blood samples delivered to the laboratory was less than 10 g, no duplicate analyses were performed.

The validity and accuracy of measurements was tested using (^{13}C) isotope-labeled surrogate standards introduced to the samples prior to extraction. The surrogate standards used for analysis of each type of compound are described in preceding sections.

Acceptance criteria for analyses were as follows:

- *Content in a blank:* lower than the method detection limit (MDL) for each analyte according to the maximum weight of the sub-sample used for a given type of analysis.
- *Extraction of analytes in a control sample:* within a range of 70–120% for 90% of compounds introduced to the sample.
- *Recovery range for surrogate standards:* 40–120%.

The performance of analytical instruments was checked on a daily basis, and included a check of instrument sensitivity and chromatographic and spectral resolution.

Linearity of instrument calibration was determined by analysis of 5 standard solutions of analytes with concentrations within the range of measured concentrations in samples. The standard deviation of the estimated relative response factor (RRF) in linearity checks had to be less than 15%.

Instrument performance was tested before and after the analysis of each batch of samples, by undertaking an analysis of a calibration solution of medium concentration.

The quality criterion used was that the difference in values of the relative response factor (RRF) calculated before and after the analysis of each series of samples should not exceed ±15%.

Instrument contamination by analytes was checked after each analysis of the calibration standard solution by injecting a clean solvent. The value of background errors due to the instrument had to be no more than 1% of the mean value of determined concentrations.

7.2.3. Analysis of samples for lead, cadmium, mercury, selenium and ferritin

Analysis of whole blood samples for lead and cadmium

Analysis for metals was performed in batches, exh batch comprising no more than 12 samples of blood, a procedural blank, a field blank, and a sample of certified reference material. One of the samples was also analyzed twice (replicated).

Prior to analysis, samples of whole blood were mixed, transferred to vials, and after Triton X-100 solution was added. They were then brought up to 4 mL and 2N with nitric acid and centrifuged for 15 minutes at 3000 rpm. Cadmium and lead were measured by flameless atomic-absorption spectrometry using a Perkin Elmer model Z 3030 spectrophotometer with Zeeman effect background correction, using pyro-coated graphite cells, with a Lvov platform. Analysis was performed by the method of standard additions in the presence of ammonium pyrophosphate, as a modifier. The detection limit for cadmium was 0.1 µg/L, and for lead 5.0 µg/L.

Analysis of whole blood samples for mercury

Each batch included 10 samples of whole blood, a procedural blank, a field blank, and a control sample.

For measurements, three 1.0–1.5 mL sub-samples were placed in three conical flasks, to which potassium permanganate solution and a mixture of concentrated nitric and sulfuric acids (in the ratio 1:3) were poured, and 2 g of dry potassium permanganate was added. The flasks were heated for 4 hours in a water bath at 60°C. After cooling, 15 mL of 10% hydroxylamine chloride was added and the samples were transferred to aeration jars.

Mercury was measured by the 'cold vapor' technique using the MHS-15 device with the Perkin Elmer model B 3030 spectrophotometer. Analyses were carried out using the method of standard additions, adding 5, 10, and 15 ng of mercury to sample aliquots prior to measurement. The reducing agent used was a 20% solution of tin chloride, and the carrier gas used was argon.

Analysis of serum samples for selenium

Each batch analyzed included 12 serum samples, a procedural blank, a field blank, a sample of reference material, and a replicate sample. The serum samples

were transferred to conical flasks, to which 0.2 g of ascorbic acid was added, together with sodium molybdate, aqueous solution of potassium permanganate, and a mixture of concentrated nitric and sulfuric acids. Samples were heated for 20 minutes at 120°C. The temperature was then raised to 160°C and the samples heated to complete decomposition. The samples were cooled and transferred to a separating funnel, after which a hydrochloride solution of 1,2 diamino-4 nitrobenzene was added. The resulting 5-nitro-2,1,3-benzoselendiazol was extracted by chloroform.

Selenium was measured by flameless atomic-absorption spectrometry, using a Perkin Elmer model Z 3030 spectrophotometer with Zeeman effect background correction, using pyro-coated graphite cells, with a Lvov platform. For determination of selenium, the modifier used was a mixture of equal volumes of palladium nitrate, at a concentration of 3000 mg/L and manganese nitrate, at a concentration of 2000 mg/L.

Analysis of serum samples for ferritin
Determination of ferritin was undertaken using a DiaSys Diagnostic Systems (Germany) kit for photometric quantification of ferritin in serum, with a 'Specol-11' spectrophotometer. Ferritin concentrations were determined using a calibration curve based on four calibration samples, and a solution of sodium chloride (0.9%) for the determination of the zero value. The lower limit for measurement of ferritin concentration was 16 µg/L.

7.2.4. Quality Assurance/Quality Control of analysis for metals and ferritin

Quality control for lead and cadmium analysis
Analysis of blanks: Procedural blanks were analyzed to detect possible contamination of blood samples during sample preparation. Procedural blanks were included in each batch of samples analyzed.

Analysis of duplicates: For assessing the repeatability of results, replicates were analyzed in each batch. The difference in results of the analysis of replicates varied from 0.4 to 22.1% for lead, whereas for cadmium the difference between the duplicate measurements did not exceed 20%.

Analysis of certified reference material: In order to test the accuracy of the results obtained, a reference material (BCR 195), consisting of a sample of the lyophilized blood of ruminant animals, was analyzed with each batch.. The maximum error detected by the analysis of the certified reference material was 14.2% for lead, and 17% for cadmium.

Quality control for mercury analysis
Procedural blanks were analyzed to detect possible mercury contamination of blood samples during analysis. Procedural blanks were included in each batch of samples.

To assess the accuracy of results, a laboratory control sample was analyzed in each sample batch. The laboratory control sample was a matrix spike prepared with whole animal blood spiked with mercury in concentrations from 5.0 to 10.0 µg/L. The recovery of mercury from the control samples varied from 90 to 100%. The detection limit for mercury was 1.0 µg/L of whole blood.

Quality control for selenium analysis
Quality control procedures for selenium analysis involved the determination of the level of contamination of the containers in which the blood samples were delivered, analysis of replicates, and the analysis of a blood reference material (IAEA-A-13).

In the replicated analyses, results did not diverge by more than 20% and the recovery of selenium from reference material varied from 80 to 100%. The detection limit for selenium was 10.0 µg/L of blood serum.

Quality control for ferritin analysis
For ferritin analysis, quality control procedures involved the analysis of wash-offs from containers in which samples were delivered, analysis of procedural blanks, and analysis of acertified reference material prepared using human blood serum with different levels of ferritin (Lot #01143-01146). Errors in ferritin determination in control samples did not exceed 10%. Replicates were analyzed in each batch, in order to assess the repeatability of results. The differences between replicate measurements did not exceed 19%.

7.3. PTS levels in maternal and cord blood

The results of maternal and cord blood sample analysis were grouped according to sampling site and donor type. Sets of analytical results obtained from the different groups underwent statistical analysis. For the calculation of geometric mean concentrations of PTS in blood and serum, where analysis yielded a result for a particular substance below the detection limit, a value of half of the detection limit for the PTS and method concerned was used in the calculation.

The range of PTS concentrations in different blood groups can be very broad, and up to an order of magnitude (Tables 7.2–7.4). Since errors associated with analytical measurement of PTS in blood samples did not exceed 20% (see section 7.2), such differences can largely be attributed to heterogeneity of factors that affect blood concentrations (such as age, diet, number of children, etc). When assessing geometric means of measured results, therefore, differences in PTS concentrations in a certain group are taken to represent general tendencies rather than specific trends.

Hexachlorobenzene (HCB)
The geometric means of HCB concentrations found in maternal and cord blood serum for four project areas within the Russian Arctic are presented in Figure 7.1. The summary tables 7.2–7.4 and Figure 7.1

Compound	Chukchi AO							
	Chukotsky District		Anadyrsky District		Anadyr town		Iul'tinsky District	
	maternal, n=47	cord, n=41	maternal, n=39	cord, n=19	maternal, n=12	cord, n=6	maternal, n=5	cord, n=4
HCB	1.6 (0.4-6.0)	0.8 (0.01-5.1)	0.6 (0.1-2.7)	0.2 (0.1-0.9)	0.5 (0.2-0.8)	0.2 (0.1-0.7)	0.6 (0.4-2.1)	0.2 (0.1-0.6)
β-HCH	2.0 (0.6-7.6)	0.8 (n.d.-8.0)	0.6 (0.1-2.5)	0.1 (n.d.-0.8)	1.0 (0.4-2.2)	0.2 (0.1-0.5)	0.7 (n.d.-1.0)	0.1 (0.1-0.2)
ΣHCH	2.1 (0.6-7.6)	0.8 (n.d.-8.0)	0.6 (0.1-2.5)	0.1 (n.d.-0.8)	1.0 (0.4-2.3)	0.2 (0.1-0.5)	0.7 (n.d.-1.0)	0.1 (0.1-0.2)
Oxychlordane	1.0 (0.1-7.9)	0.2 (n.d.-3.6)	0.02 (n.d.-0.2)	n.d.	0.02 (n.d.-0.2)	0.01 (n.d.-0.05)	0.2 (0.03-0.6)	0.01 (n.d.-0.13)
p,p` -DDE	2.4 (0.8-7.0)	1.0 (0.3-7.4)	1.2 (0.3-6.3)	0.3 (0.1-1.0)	2.2 (1.3-4.6)	0.7 (0.4-1.5)	1.3 (0.7-2.8)	0.4 (0.2-0.8)
p,p` -DDT	0.2 (n.d.-1.2)	0.1 (n.d.-1.2)	0.2 (n.d.-0.5)	0.04 (n.d.-0.1)	0.4 (0.1-1.0)	0.1 (0.04-0.2)	0.2 (0.1-0.3)	0.06 (0.05-0.09)
ΣDDT	2.7 (0.8-8.0)	1.1 (0.3-8.3)	1.4 (0.3-6.6)	0.4 (0.1-1.0)	2.7 (1.4-5.3)	0.8 (0.5-1.7)	1.5 (0.1-3.2)	0.4 (0.2-0.9)
Mirex	0.1 (n.d.-0.5)	0.03(n.d.-0.5)	0.01 (n.d.-0.03)	n.d.	0.01 (n.d.-0.02)	n.d.	0.03 (0.01-0.05)	0.01 (n.d.-0.02)
ΣPCB	3.8 (0.9 –11)	1.4 (0.01-12)	0.8 (0.2-1.8)	0.2 (0.03-0.7)	1.5 (0.6-6.8)	0.3 (0.05-1.1)	1.5 (1.0-3.2)	0.2 (0.2-0.4)
ΣToxaphenes	0.2 (n.d.-0.8)	0.06(n.d.-0.8)	0.02 (n.d.-0.1)	0.003(n.d.-0.01)	0.02 (n.d.-0.2)	0.003 (n.d.-0.01)	0.04 (0.02-0.1)	0.005(n.d.-0.01)
Cd (blood)	1.1 (0.2-4.7)	0.3 (n.d.-4.0)	0.9 (0.2-2.5)	0.2 (n.d.-0.5)	0.5 (0.1-1.5)	0.2 (n.d.-1.0)	1.0 (0.7-1.5)	0.2 (0.16-0.5)
Pb (blood)	45.0 (18-227)	43.0 (14-210)	34.0 (13-83)	29.0 (14-60)	34.0 (19-92)	34.0 (19-78)	52.0 (36-113)	39.0 (27-100)
Hg (blood)	1.5 (n.d.-6.2)	1.3 (n.d.-3.6)	2.0 (n.d.-7.7)	1.3 (n.d.-4.1)	0.8 (n.d.-3.5)	0.9 (n.d.-3.3)	1.2 (n.d.-2.5)	1.0 (n.d.-2.2)
Se (plasma)	78.0 (22-162)	55.0 (23-132)	59.0 (27-101)	38.0 (16-74)	71.0 (30-136)	43.0 (29-55)	67.0 (55-93)	47.0 (33-69)
Ferritin (plasma)	27.0 (n.d.-343)	87.0 (n.d.-719)	18.0 (n.d.-332)	90.0 (n.d.-305)	11.0 (n.d.-59)	96.0 (29-257)	n.d.	84.0 (58-152)
Lipid %	0.5 (0.8-0.3)	0.2 (0.1-0.8)	0.5 (0.3-0.8)	0.1 (0.05-0.14)	0.4 (0.1-0.6)	0.09 (0.06-0.1)	0.6 (0.5-0.7)	0.1 (0.07-0.1)

Table 7.2. Concentrations (geometric mean and range; µg/L plasma) of PTS in maternal and cord blood from various areas of the Chukchi AO.
n. d. – not detected

show that the highest concentrations of HCBs occur in the Chukchi AO. The highest HCB concentrations of 1.6 µg/L and 0.8 µg/L are found in maternal and cord blood, respectively, from Chukotsky, the most northeasterly, coastal district of the Chukchi AO. Blood samples from other areas of the Chukchi AO (Anadyrsky and Iul'tinsky districts, and the town of Anadyr) contain HCBs at levels 2-3 times lower than in Chukotsky, and more comparable with samples from other regions.

Concentrations of HCB in cord blood are 1.6 to 3 times lower than those in maternal blood. It has therefore been suggested that the placenta may act as a barrier between the mother and fetus and prevents transfer of this toxicant from mother to child, although though this barrier is not fully effective. A similar effect was observed for blood groups of all regions, except the Kola Peninsula, where the difference in maternal and cord blood concentrations was not statistically significant.

In control blood samples, mean HCB concentrations are 6 to 8 times lower than those from other study regions, and 20 times lower than concentrations in maternal blood samples from the Chukotsky district.

A comparison with results from the AMAP circumpolar blood survey (AMAP, 2003a) is shown in Figure 7.2. This comparison suggests that, on the whole, HCB concentrations measured in maternal blood in the Russian Arctic are close to those detected in coastal areas of Greenland and Canada (where means of 1.5 and 1 µg/L of plasma, respectively, were found). Blood concentrations of HCB reported previously (AMAP, 1997, 1998) for residents of the same territories of Greenland and Canada had geometric mean levels of HCB of 0.9 and 0.7 µg/L of plasma, respectively. In the context of these results, the highest concentrations of HCB found in blood samples from coastal Chukotka are a cause of concern.

DDT

High concentrations of total DDT in maternal blood samples, ranging from 1.4 µg/L (Anadyrsky district,

Compound	Taymir AO					
	Khatanga area		Dudinka area		Norilsk (control area)	
	maternal, n=29	cord, n=29	maternal, n=38	cord, n=39	maternal, n=10	cord, n=10
HCB	0.7 (0.2-2.1)	0.2 (0.1-1.0)	0.5 (0.1-1.9)	0.2 (0.03-0.9)	0.4 (0.2-0.9)	0.1 0.08-0.2)
β-HCH	0.6 (0.1-2.8)	0.2 (n.d.-0.9)	0.7 (n.d.-3.0)	0.1 (n.d.-0.9)	1.3 (0.5-4.5)	0.4 (0.2-0.7)
Σ HCH	0.6 (0.1-2.8)	0.2 (n.d.-1.0)	0.7 (n.d.-3.2)	0.1 (n.d.-0.9)	1.3 (0.5-4.6)	0.4 (0.2-0.7)
Oxychlordane	0.03 (n.d.-0.2)	0.01 (n.d.-0.03)	0.02 (n.d.-0.2)	n.d.	0.01 (n.d.-0.04)	n.d.
p,p` -DDE	1.3 (n.d.-5.0)	0.4 (n.d.-1.5)	1.6 (0.2-7.7)	0.5 (0.1-2.8)	2.9 (1.4-7.2)	0.8 (0.5-1.6)
p,p` -DDT	0,2 (n.d.-0.8)	0.1 (n.d.-0.2)	0.2 (n.d.-0.8)	0.1 (n.d.-0.3)	0.4 (0.2-0.6)	0.1 (n.d.-0.2)
Σ DDT	1.5 (0.3-5.7)	0.4 (n.d.-1.8)	2.0 (n.d.-8.0)	0.6 (0.1-3.0)	3.3 (1.8-7.7)	0.9 (0.5-1.7)
Mirex	0.02 (n.d.-0.1)	0.01 (n.d.-0.02)	0.02 (n.d.-0.1)	n.d.	n.d.	n.d.
Σ PCB	1.2 (0.2-3.0)	0.4 (n.d.-1.0)	2.2 (0.8-5.2)	0.5 (n.d.-4.0)	1.4 (0.8-2.6)	0.8 (n.d.-3.0)
Σ Toxaphenes	0.07 (n.d.-0.3)	0.01 (n.d.-0.07)	0.04 (n.d.-1.3)	0.004 (n.d.- 0.04)	0.02 (0.01-0.05)	0.003 (n.d.-0.01)
Cd (blood)	0.6 (n.d.-1.8)	0.1 (n.d.-0.7)	0.8 (n.d.-2.9)	0.2 (n.d.-0.9)	0.6 (0.2-1.2)	0.1 (n.d.-0.4)
Pb (blood)	50 (14-176)	40 (12-144)	48 (15-224)	35 (14-99)	20 (10-37)	13 (6-34)
Hg (blood)	1.4 (n.d.-4.0)	1.4 (n.d.-3.6)	2.3 (n.d.-20)	1.7 (n.d.-17)	0.8 (n.d.-3.0)	0.8 (n.d.-2.2)
Se (plasma)	81 (44-175)	57 (24-148)	61 (19-144)	61 (18-132)	75 (49-123)	58 (39-86)
Ferritin (plasma)	53 (n.d.-547)	139 (35-269)	59 (n.d.-1095)	159 (46-270)	18 (n.d.-84)	101 (39-405)
Lipid %	0.5 (0.3-0.7)	0.1 (0.04-0.2)	0.5 (0.3-0.8)	0.09 (0.04-0.3)	0.6 (0.5-0.7)	0.2 (0.04-0.8)

Table 7.3. Concentrations (geometric mean and range; µg/L plasma) of PTS in maternal and cord blood from various areas of the Taymir AO.
n. d. – not detected

Compound	Kola Peninsula		Nenets AO		Aral (Control area)	
	Lovozero District		Nenetsky District		Urgench , Khozarast	
	maternal, n=7	cord, n=6	maternal, n=21	cord, n=21	maternal, n=12	cord, n=12
HCB	**0.3** (0.2-0.8)	**0.3** (0.1-0.8)	**0.7** (0.2-2.1)	**0.4** (0.2-1.7)	**0.1** (0.05-0.3)	**0.1** (0.03-0.3)
β-HCH	**0.5** (0.1-1.7)	**0.5** (0.1-2.2)	**0.4** (n.d.-1.1)	**0.04** (n.d.-1.9)	**2.9** (0.6-9.5)	**0.7** (n.d.-3.6)
Σ HCH	**0.5** (0.1-1.7)	**0.5** (0.1-2.2)	**0.5** (n.d.-1.2)	**0.04** (n.d.-2.1)	**3.0** (0.6-9.7)	**0.7** (n.d.-3.6)
Oxychlordane	**n.d.**	**0.01** (n.d.-0.05)	**0.02** (n.d.-0.1)	**0.01** (n.d.-0.08)	**0.03** (n.d.-0.6)	**n.d.**
p,p`-DDE	**2.3** (0.8-6.6)	**2.1** (0.6-7.2)	**1.7** (0.1-5.1)	**0.7** (0.1-2.1)	**8.4** (2.5-18)	**2.7** (0.7-5.7)
p,p`-DDT	**0.3** (0.1-0.8)	**0.3** (0.2-0.6)	**0.3** (n.d.-1.9)	**0.1** (n.d.-0.5)	**0.2** (0.1-0.5)	**0.1** (n.d.-0.2)
Σ DDT	**2.7** (1.0-7.5)	**2.4** (0.8-7.7)	**2.0** (0.1-7.4)	**0.7** (0.1-2.7)	**8.7** (2.7-18.2)	**2.8** (0.9-5.8)
Mirex	**0.007** (n.d.-0.01)	**n.d.**	**0.03** (n.d.-0.3)	**0.01** (n.d.-0.02)	**n.d.**	**n.d.**
Σ PCB	**0.7** (n.d.-3.3)	**1.1** (n.d.-5.3)	**1.6** (0.02-6.5)	**0.4** (n.d.-2.4)	**0.1** (n.d.-2.9)	**n.d.**
Σ Toxaphenes	**0.01** (n.d.-0.05)	**0.01** (n.d.-0.03)	**0.01** (n.d.-0.1)	**n.d.**	**0.003** (n.d.-0.01)	**n.d.**
Cd (blood)	**0.3** (n.d.-1.3)	**0.1** (n.d.-0.6)	**0.5** (n.d.-2.8)	**0.2** (n.d.-0.7)	**0.4** (0.2-0.9)	**0.1** (n.d.-0.5)
Pb (blood)	**28** (17-52)	**21** (12-29)	**32** (n.d.-92)	**23** (n.d.-63)	**44** (24-78)	27 (7-54)
Hg (blood)	**0.9** (n.d.-2.4)	**0.9** (n.d.-1.7)	**0.8** (n.d.-5.6)	**0.7** (n.d.-2.7)	**n.d.**	**0.6** (n.d.-1.5)
Se (plasma)	**73** (40-120)	**80** (62-124)	**81** (48-141)	**52** (16-114)	**63** (31-104)	**62** (20-117)
Ferritin (plasma)	**27** (n.d.-135)	**58** (n.d.-230)	**44** (n.d.-146)	**85** (n.d.-293)	**13** (n.d.-172)	**98** (n.d.-529)
Lipid %	**0.3** (0.1-0.7)	**0.3** (0.1-0.7)	**0.5** (0.05-0.8)	**0.1** (0.05-0.3)	**0.5** (0.3-0.7)	**0.4** (0.1-0.8)

Table 7.4. Concentrations (geometric mean and range; µg/L plasma) of PTS in maternal and cord blood from the Kola Peninsula, the Nenets AO, and Aral (control area). n.d. – not detected

Chukchi AO) to 3.3 µg/L (Norilsk) occur in all four regions, with concentrations in maternal blood being 1.5–3 times higher than in cord blood.

Within the Chukchi AO, the highest concentrations of total DDT in cord blood (1.1 µg/L) were found in Chukotsky district, while concentrations in other districts are 2–3 times lower. Levels of DDT in maternal blood from the town of Anadyr, however, are also high (2.7 µg/L). Samples of maternal and cord blood from the Kola Peninsula are similar, as DDT concentrations are high in both, at 2.7 and 2.4 µg/L, respectively.

It should be noted that control blood groups also contain DDT in significant amounts, with mean values varying from 8.7 µg/L in maternal blood to 2.8 µg/L in cord blood. In control blood samples from the Aral area, the concentration of total DDT was as high as 18.2 µg/L in maternal and 5.8 µg/L in cord blood (Table 7.4).

DDE is the most frequently occurring component of total DDT, with the DDE/DDT concentration ratio varying from 3 to 8. Figure 7.3 shows the geographic distribution of geometric mean concentrations of DDE in maternal and cord blood for the regions of Russia involved in the study.

A comparison with the results of the analysis of maternal blood from residents of the Russian North reported by AMAP (AMAP, 2003a), of 1.25–5.0 µg/L of serum, Figure 7.4, indicates that DDT concentrations in maternal blood from three regions of the Russian Arctic, excluding the control region, (1.4–3.3 µg/L of serum) are very similar to previous results. Comparisons of DDT for the Chukchi population are not possible due to the lack of available data prior to the present study.

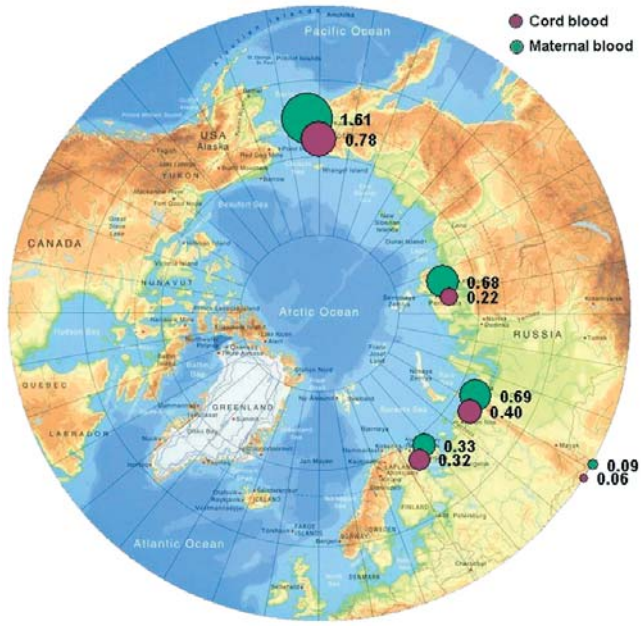

Figure 7.1. Levels of HCB in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

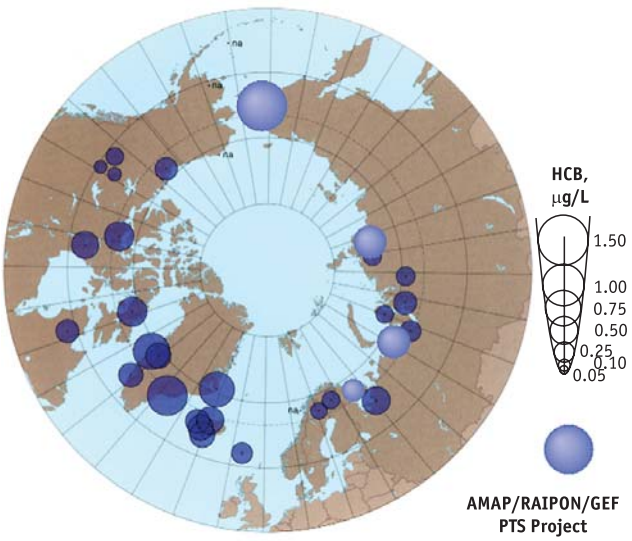

Figure 7.2. Comparison of the results obtained in this project for HCB in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

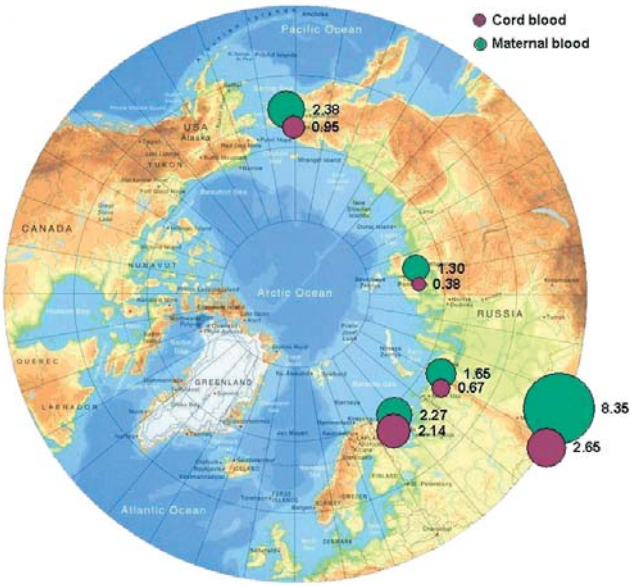

Figure 7.3. Levels of DDE in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

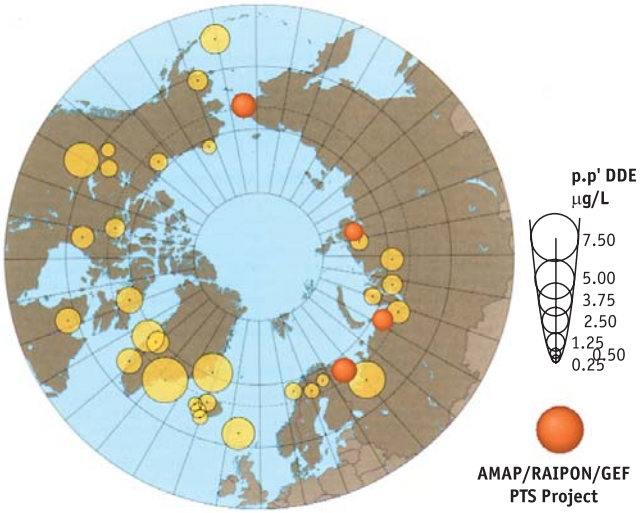

Figure 7.4. Comparison of the results obtained in this project for DDE in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

HCH

Total HCH levels in human blood are mainly determined by β-HCH, this being the most stable compound within the HCH group. Consequently, all subsequent discussions in this chapter concerning HCH levels are based on β-HCH results. The geometric mean values of β-HCH concentrations in maternal and cord blood in the four studied regions of the Russian Arctic are shown in Figure 7.5. The distribution of β-HCH in human blood in the Russian Arctic is similar to that of HCB, with the highest levels (0.8–2.0 µg/L) observed in the blood of residents of Chukotka (Table 7.2). However, one difference is that elevated levels of β-HCH are also found in maternal blood from Norilsk (1.3 µg/L). In all other maternal blood samples (apart from those from the Kola Peninsula) the concentrations of β-HCH are 2–4 times higher than in cord blood.

As for DDT, β-HCH concentrations in control samples from the Aral area are high, with a geometric mean of 2.9 µg/L of plasma. In individual samples, concentrations as high as 9.5 µg/L of plasma were found, which is likely to be the result of the long-term use of pesticides such as HCH, lindane, and DDT in this area.

Concentrations of β-HCH in maternal blood do not exceed values reported in earlier studies by AMAP (AMAP, 2003a) for the Russian North (Figure 7.6).

PCBs

The presence of PCBs in human blood is attributed mainly to the consumption of contaminated foodstuffs. In the diet of people living in coastal areas of the Arctic, sources of PCBs include meat from polar bears, seals, whales, and sea birds and bird eggs, as well as from fish; whilst for those living in continental areas, sources include freshwater fish and other meat and fish products (AMAP, 2002).

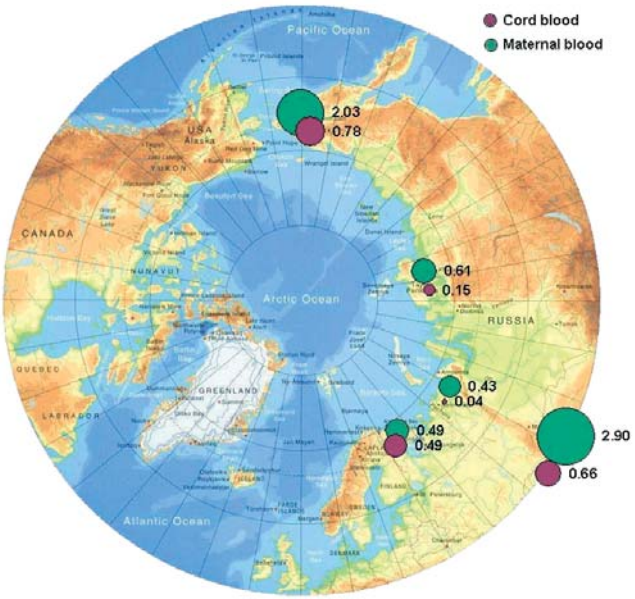

Figure 7.5. Levels of β-HCH in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

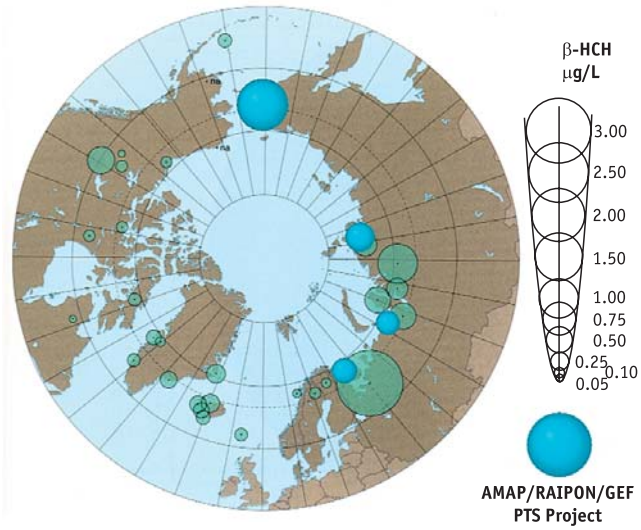

Figure 7.6. Comparison of the results obtained in this project for β-HCH in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

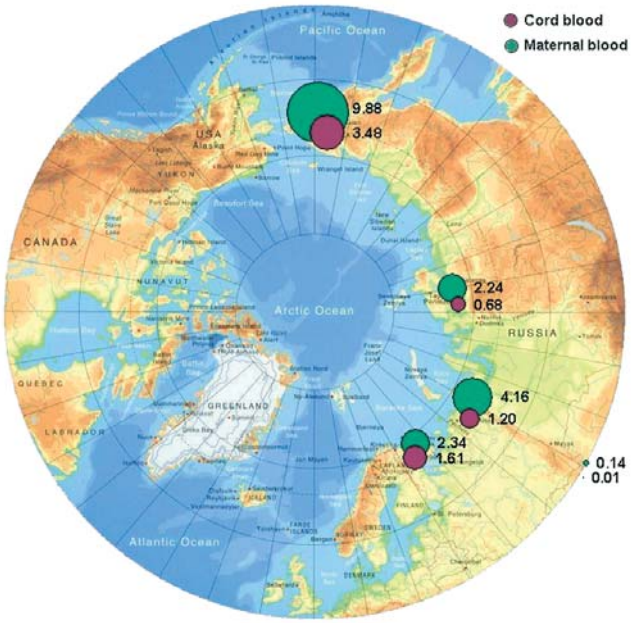

Figure 7.7. Levels of sum of PCBs (shown as Aroclor 1260 equivalents) in maternal and cord blood in Russian Arctic (geometric means, µg/L plasma).

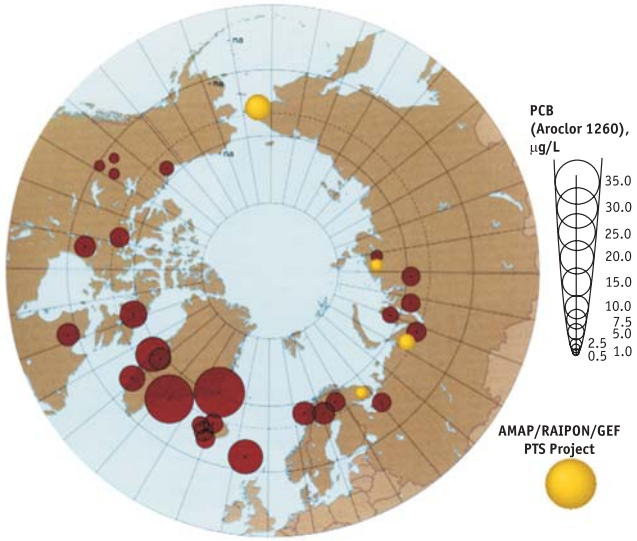

Figure 7.8. Comparison of the results obtained in this project for sum of PCBs (as Aroclor 1260 equivalents) in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

The analysis of maternal and cord blood demonstrates that, as for other toxicants, when examining PCB in humans, the transfer of contaminants from mother to fetus via the blood appears to be impeded by the placental barrier. This is reflected by the ratio of PTS in maternal and cord blood, and differs for residents of different districts (as seen in mean values) and between individuals (as seen in deviations from the mean).

Tables 7.2–7.4 show that the maximum values of total PCBs occur in maternal and cord blood samples of residents of the Chukotsky District of the Chukchi AO (3.9 µg/L and 1.4 µg/L, respectively), with PCB levels as high as 11 µg/L in some individual samples from this area. In the Taymir area, the highest concentrations are found in Dudinka (mean concentration of 2.2 µg/L, with a maximum value of 5.2 µg/L). Figure 7.7 shows the spatial distribution of geometric mean concentrations of total PCBs across the Russian Arctic.

The results were compared with data obtained in earlier studies by AMAP (AMAP, 2003a) on PCB concentrations in maternal blood for various Arctic countries. These included Greenland: 25–35 µg/L of plasma (for indigenous people of coastal areas), Iceland: 20 µg/L, Canada: 2–15 µg/L, and Russia: 2–15 µg/L of plasma. It can be seen from data in Tables 7.2–7.4 and Figure

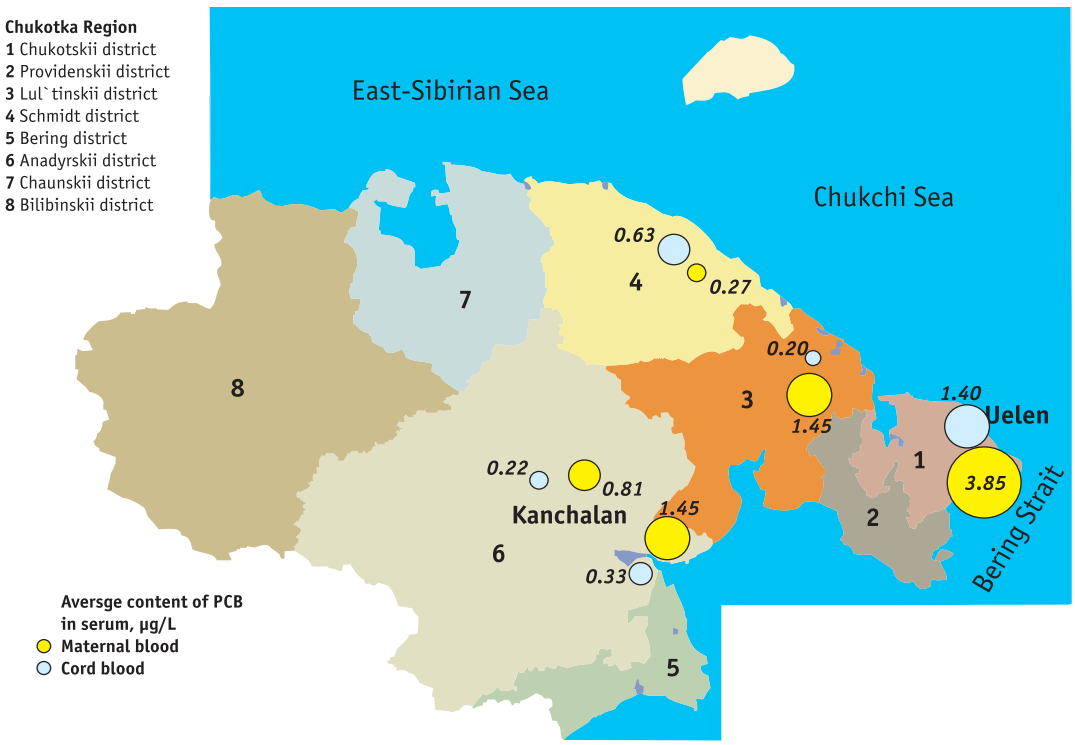

Figure 7.9. PCB levels in various districts of the Chukchi AO.

7.8 that the concentrations of total PCBs in maternal and cord blood sampled in the Russian Arctic during this study, on average, do not exceed the limit value of 5 µg/L of blood, below which toxic effects on humans have not been observed (Klopov, 2000). Figure 7.9 illustrates the distribution of PCBs within different areas of the Chukchi AO.

Of all the PCB congeners, PCB-153 (2,2',4,4',5,5'-hexachlorobiphenyl) occurs in humans most frequently and in the largest amount. Assessment of PCB congeners present in paired maternal and cord blood samples from four regions of the Russian Arctic shows that the distributions of congeners in the paired samples are similar. This means that, when PCBs are transferred to infants via the blood, the PCB congener pattern remains essentially the same. However, the pattern of PCB distribution in the paired blood samples collected on the Kola Peninsula differs from that found in blood of residents of the three other regions. This may be due to peculiarities in the diet of residents in the Kola region. It is worth noting that the distribution patterns found are consistent with data previously obtained from more limited sets of blood samples taken in the same areas (Chashchin *et al.*, 2002).

According to the scientific literature (Chen *et al.*, 1985) the highest recorded levels of total PCBs in blood, were found in those poisoned by PCB-contaminated rice oil in Japan in 1968 (Yusho disease) and in Taiwan in 1979 (Iu-Cheng disease). Blood concentrations of PCBs in the residents of Taiwan who were affected ranged from 10 to 720 µg/L, with the mean value of 38 µg/L. Symptoms of the poisoning showed a close correlation with concentrations of hexachlorobiphenyl (congener PCB-157) in the blood. However, within a year, the maximum concentration in blood had decreased to 99 µg/L (Chen *et al.*, 1985).

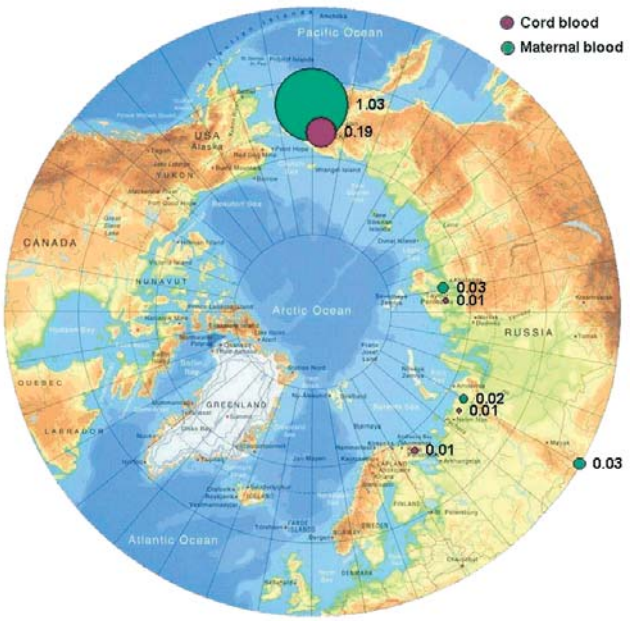

Figure 7.10. Levels of oxychlordane in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

Chlordane and its decomposition products: trans- and cis-chlordanes and oxychlordane

The predominant chlordane component in blood is oxychlordane (often constituting 100% of the sum). It is believed that high concentrations of this compound, found in the blood of indigenous people, are due to the intake of oxychlordane with marine mammal meat. Oxychlordane concentrations in blood from past studies were reported to be 0.25–1.5 µg/L of blood serum for indigenous women in Greenland, and 0.05-0.75 µg/L of blood serum for residents of Canada (AMAP, 2003a). The sum of chlordanes in the blood of women in northwest Greenland, and northern Canada (Quebec) were reported to be 1.4 and 1.6 µg/L of blood serum, whereas for women in the Russian Arctic, levels are found to be 0.1–0.5 µg/L of blood serum (AMAP, 1998).

The results of analysis of maternal and umbilical cord blood in the present study (Figure 7.10) show that the highest concentrations of oxychlordane occur in the blood of women and children living in Chukotsky District of the Chukchi AO (with geometric mean levels of 1.0 and 0.2 µg/L, respectively). This is an order of magnitude higher than in the other regions where samples were taken. However, the elevated levels of oxychlordanes in maternal blood in Chukotsky district are close to levels found in women living in Greenland and consuming the meat of marine mammals. A comparison of levels of oxychlordane found in maternal blood in this study and during previous studies is shown in Figure 7.11.

Toxaphene and mirex

Blood samples were analyzed for three enantiomers of toxaphene, Parlar-26, -50, and -62 (based on the Parlar standards). Of these, Parlar-26 (octachlorocamphene) and Parlar-50 (nonachlorocamphene) were the enantiomers that were primarily detected. Tables 7.2–7.4 provide total concentrations for the toxaphenes studied, as determined in blood samples.

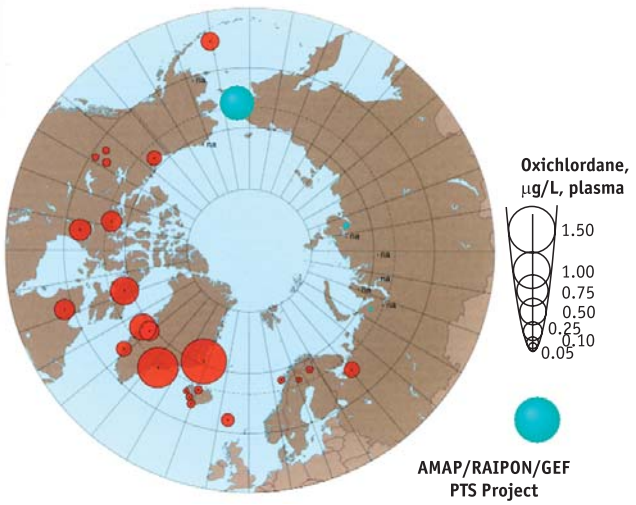

Figure 7.11. Comparison of the results obtained in this project for oxychlordane in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

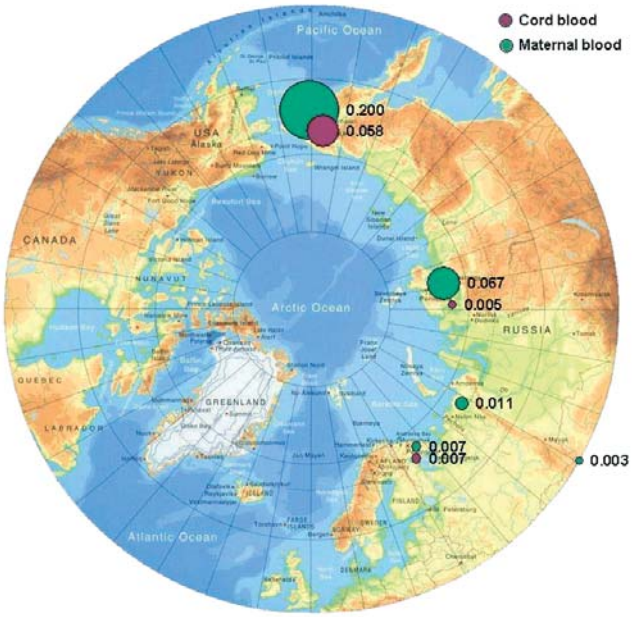

Figure 7.12. Levels of total toxaphenes in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

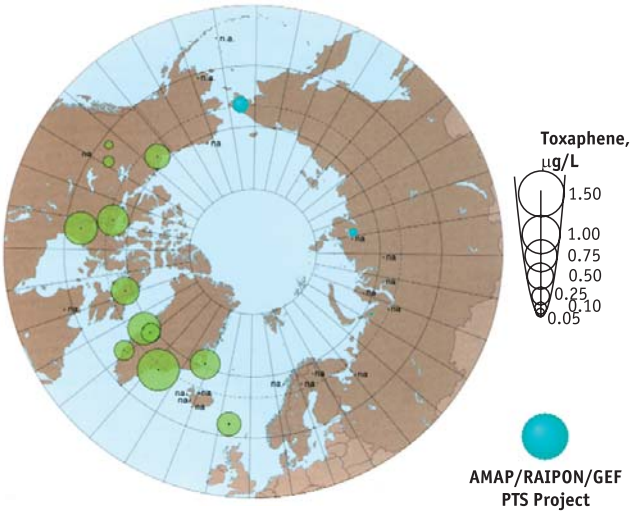

Figure 7.13. Comparison of the results obtained in this project for toxaphene in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

The concentration of toxaphenes in human blood, like that of mirex, is known to be higher among indigenous people whose traditional diet includes marine mammals and fish (AMAP, 2003a), with the highest levels of toxaphenes observed in inhabitants of Greenland and northern Canada (up to 1.5 µg/L of blood).

Toxaphene levels occurring in the blood of women in the Russian Arctic are much lower (0.007–0.2 µg/L), and the concentrations in cord blood are found to be lower still, at 0.003–0.06 µg/L. The concentrations of toxaphenes in cord blood areless than 30% of those found in maternal blood, and the placenta barrier, therefore, appears to prevent a major part of the toxaphene transfer to the fetus via blood. An exception to this is the ratio of toxaphene concentrations in maternal and umbilical cord blood for women from the Kola Peninsula.

Figure 7.12 shows the geographic distribution of toxaphenes in the regions of the Russian Arctic studied, and Figure 7.13 compares the results obtained with the earlier AMAP results (AMAP, 2003a). The highest concentrations of toxaphenes were detected in the blood of women from Chukotsky District of the Chukchi AO (geometric mean of 0.20 µg/L), with toxaphene concentrations as high as 0.8 µg/L occurring in individual samples.

The pattern observed for toxaphenes can also be seen in the distribution of mirex in maternal and cord blood in the Arctic regions of Russia. Concentrations of mirex range from 0.007–0.12 µg/L in maternal blood, and from less than the detection limit to 0.03 µg/L in cord blood. The highest geometric mean concentrations of mirex were found for maternal and cord blood from Chukotsky District, up to 0.5 µg/L in individual samples. By comparison, the mirex concentration in umbilical cord blood reported for a group of women in Arctic Canada was determined to be 0.01–0.65 µg/L (CACAR, 1997).

Mercury

Mercury concentrations in human blood are primarily governed by diet. For example, blood mercury concentrations measured in women in the Russian Arctic were 1.6–1.9 times higher for women whose diet included a higher level of intake of traditional foods (fish and reindeer meat), compared to those who consumed these foods rarely, with geometric mean values for blood mercury equal to 2.5 and 1.3 µg/L of blood, respectively (Klopov, 2000). Mercury levels in blood below 20 µg/L are regarded as acceptable according to WHO guidelines (Klopov, 2000).

The results of the analysis of blood taken from women giving birth and from cord blood (Tables 7.2–7.4) show mercury levels within the ranges reported previously for areas of the Russian Arctic (Klopov, 2000). Slightly higher values were found in the blood of women giving birth in Anadyrsky District of the Chukchi AO (2.0 µg/L), and the Dudinka area of the Taymir AO (2.3 µg/L) (see Tables 7.2 and 7.3). In individual blood samples from Dudinka, mercury concentrations were as high as 18–20 µg/L.

For women from the control areas, mercury concentrations were below the detection limit (<1.0 µg/L). In the mother-infant pair samples, mercury concentration in umbilical cord blood did not show a significant decrease in levels when compared to maternal blood samples, suggesting that the placenta is not an effective barrier in protecting the fetus from mercury transfer. The geographic distribution of mercury concentrations in blood in the regions of the Russian Arctic under study are shown in Figure 7.14, whilst Figure 7.15 compares the results obtained with data from AMAP (AMAP, 2003a).

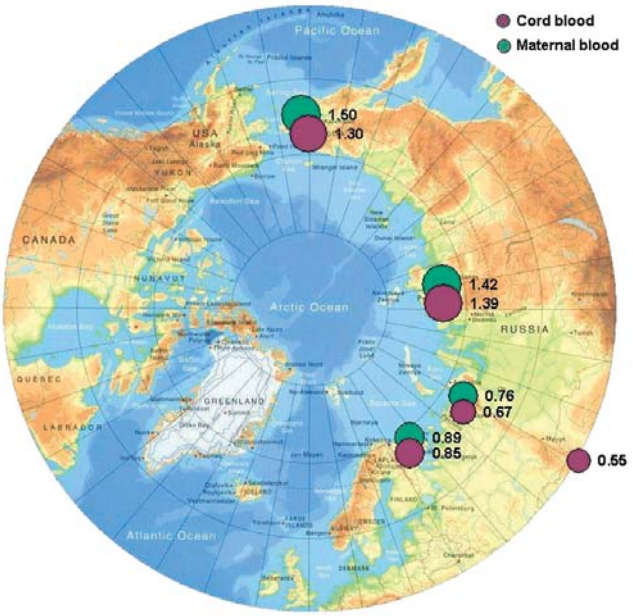

Figure 7.14. Levels of mercury in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).

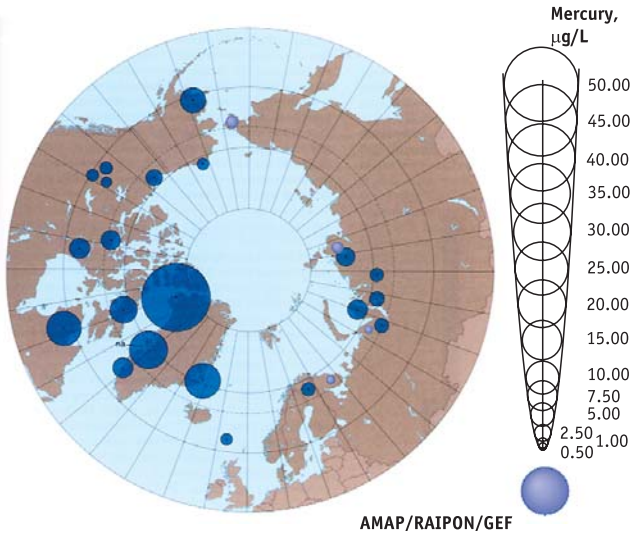

Figure 7.15. Comparison of the results obtained in this project for mercury in maternal blood with results from the AMAP circumpolar blood monitoring study (AMAP, 2003a).

Lead

The distribution of lead concentrations in maternal and umbilical cord blood in the Russian Arctic regions is similar to that of mercury. As for mercury, the placental barrier does not appear to prevent the transfer of lead to the fetus via blood, the lead concentration in umbilical cord blood ranging from 75–93% of the concentration in maternal blood. Lead concentrations are found to range from 13.3 µg/L (Norilsk) to 43 µg/L (Chukotsky District of the Chukchi AO) in cord blood, and 20 µg/L (Norilsk) to 52 µg/L (Iul'tinsky District of the Chukchi AO) in maternal blood (Tables 7.2–7.4).

Figure 7.16 shows the spatial distribution of blood concentrations of lead in the regions of the Russian Arctic under study. As can be seen from the figure, the highest concentrations of lead are found in indigenous women of the Chukchi AO. These levels are somewhat higher than those reported for women living in other regions (which vary from 21.3–32.2 µg/L of blood), but these results may be explained by specific characteristics of selected donor groups (Klopov, 2000).

Cadmium

The results of blood analysis for the four regions of the Russian Arctic indicate that cadmium concentrations in maternal and cord blood range from 0.3–1.1 µg/L, and 0.1–0.3 µg/L, respectively (Tables 7.2–7.4). These concentrations are lower than the WHO guideline value of 2.0 µg/L, for a concentration posing no risk of harmful effects of cadmium exposure (Klopov, 2000). However, there are individual blood samples from both the Chukotsky and Anadyrsky Districts of the Chukchi AO, which exceed this limit by a factor of two.

Figure 7.17 shows the spatial distribution of blood cadmium concentrations in the regions of the Russian Arctic studied. It is worth noting that concentrations of cadmium found in women giving birth were higher for residents of Chukotka and Taymir, than for women living on the Kola peninsula, or in Aral (control area). Concentrations of cadmium in women from the Kola Peninsula were found to be lower than concentrations in the control area samples.

7.4. PTS levels in blood of the general adult indigenous population

7.4.1. Characteristics of PTS levels in blood of the general adult indigenous population

With some exceptions, PTS concentrations in the blood of the general adult population are around 3–5 times, and for mercury, 9 times higher than those in maternal blood in the various areas (Table 7.5). These facts can be explained, at least partially, by the

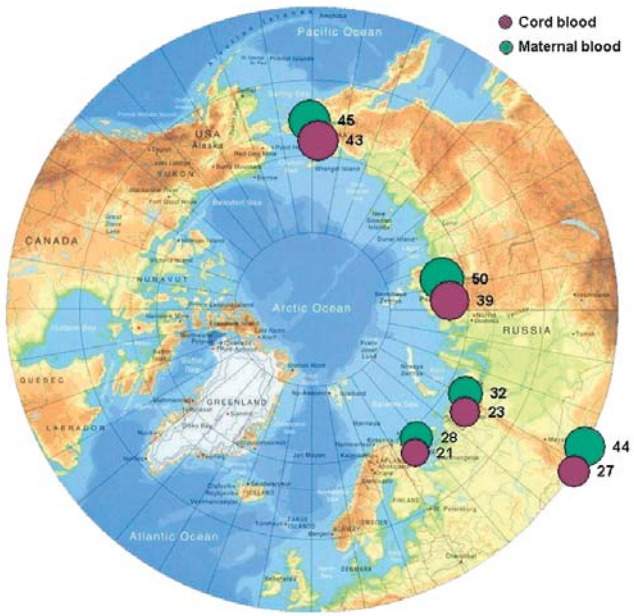

Figure 7.16. Levels of lead in maternal and cord blood in the Russian Arctic (geometric means, µg/L plasma).