

## **Chapter 5**

# PTS levels in biota and biomagnification in food chains



#### 5.1. Sampling strategy

Environmental sampling and analysis within the framework of Activity 4 'Biomagnification in Arctic food chains' had two objectives:

- determination of current PTS levels in main biota species, particularly those which are a utilised as part of the traditional diet of the indigenous populations in the pilot areas covered by the project;
- evaluation of the extent to which biomagnification occurs, i.e., the measurement of PTS accumulation in terrestrial, freshwater, and marine food chains, in which humans represent the uppermost trophic level.

These two aims place somewhat different requirements on sampling, sample treatment, and analysis. For the first objective, in order to estimate PTS intake with food, it is necessary to obtain as reliable and representative data as possible on PTS levels in those species and tissues that are widely used as traditional food. For the second objective, it is necessary to determine the average levels of contamination in species representing a range of trophic levels (and in specific tissues of organisms at higher trophic levels), and from this information, evaluate the degree to which PTS are being accumulated and biomagnified in the various food chains that form the basis for food items in the traditional diet.



Figure 5.1. Location of the environmental sampling area on the Kola peninsula.



Figure 5.2. Location of the environmental sampling area in the lower Pechora basin.

To these ends, environmental sampling was carried out in six areas within the four main project regions, these areas being located around settlements with the highest indigenous populations. Bearing in mind that hunting and fishing grounds can be located at some distance from the actual settlements, and that migration of reindeer herds depends upon the season and weather conditions, field sampling was based on prior consultations with local indigenous peoples involved in traditional activities. The environmental sampling areas that were defined following these consultations are shown in Figures 5.1–5.4. It is also important to note that the optimal season for environmental sampling differed between locations. It depends, not only on availability of the specified species, but on the hunting seasons, which may vary between different regions. In addition, sampling of certain species of biota, particularly those species which are obtained by hunting or fishing, had to be arranged in close collaboration with local hunters and fishers. This was important, not only to ensure efficiency in sampling related to these activities, but also from a legal point of view, since licences for the hunting of some species and for marine mammals in particular, can only be obtained by indigenous communities.



Figure 5.3. Location of the environmental sampling areas on the Taymir peninsula.

For these reasons, in addition to the main field sampling expeditions undertaken, additional field work in Chukotka was arranged in order to sample marine species (and particularly marine mammals) over the area shown in Figure 5.5.

The number and type of environmental samples were selected in accordance with the stated objectives of the activity. i.e., to study biomagnification in food chains and to measure PTS levels in traditional food sources of selected indigenous communities. Sampling of environmental media was designed to ensure that reliable data could be obtained for average concentrations of selected contaminants at the sample sites. For example, pooled water samples, which combined a number of replicated samples taken at different depths within the water column (e.g. sub-surface, middle and bottom), were utilized. A similar approach, i.e. using pooled samples, was employed for the lower trophic levels of food chains, and in particular for vegetation such as lichens, mosses, and mushrooms.

For biota species at higher trophic levels, specific organs and tissues known to be important with respect to PTS accumulation, were sampled. Tissue and organ



Figure 5.4. Location of the environmental sampling areas on the Chukotka peninsula.

samples from animals of the same sex and similar age groups were then pooled. An exception to this approach was made in the case of marine mammals, which feed at the top of (in some cases, long) marine food chains and can accumulate particularly high levels of lipophilic contaminants, including organochlorines, due to the high fat content in their bodies, and also high levels of methyl mercury. For these animals, samples were treated and analyzed individually and not pooled. All samples were frozen immediately after delivery to the field camp, and stored frozen until shipped to the laboratory. Samples pooling took place in the laboratory as a part of sample treatment prior to analysis.



Figure 5.5. Location of the area in which marine food chain species were collected around the Chukotka peninsula.

Table 5.1 contains a list of environmental samples collected during field work, and a list of the pooled and individually analyzed samples of environmental media and biota is presented in Table 5.2.

#### 5.2. Analytical methods and quality control

The analytical methods used for PTS determination in individual and pooled environmental and biotic samples were based on internationally recognized methodologies (ISO methods 8288:1986, 6468:1996, 5666:1983, 10382, 11048:1995, 10382, 19258, 14653-2; US EPA methods 200, 245.5, 245.6, 508, 525.1, 550, 608, 680, 8082, 8275a, 8290a, 8310a, PP-006; ASTM methods D 3534-85, D 3557-95, D 3559-96, D 5175-91, D 5412-93, D-5673-96, D5812-96; JAMP, 1999a and 1999b; NOAA, 1998; UNEP, 1993) also taking into account AMAP recommendations. Russian standard methodologies, as certified by the Russian State Standardization Committee (Gosstandart), were also used when appropriate (GOST 17.4.4.02-84, 26929-86, 26927-86, 26932-86, 26933-86, 7636-85, PND F 14.1:2:4.124-97, 14.2:4.74-96, 16.1.7-97, 16.1.4-97 14.2:4.70-96, RD 52.10.556-95, 52.18.180-89, 52.18.578-97, 52.44.590-97, 52.18.191-89, 52.44.592-97).

## 5.2.1. Quantitative determination of chlorinated and brominated organic compounds

Conventional extraction and clean-up procedures were utilised in the analytical treatment of samples. Extraction efficiency was checked by introducing internal standards (PCB-198 and dibromo-octafluorodiphenyl (DBOF)) prior to extraction.

Quantitative analysis of organochlorines (OC) was performed using gas chromatography (GC) with an electron capture detector (ECD). In addition, gas chromatography with mass spectroscopy (GC-MS) was employed for samples with an anomalous composition

	Sample	Туре				Number of s	amples		
Environment	(species)	(organ/ tissue)	Kola	Pechora	Taymir- Dudinka	Taymir- Khatanga	Chukotka- coastal/marine	Chukotka- Kanchalan	Tota
	Soil	Upper layer	30	30	30	30	30	30	180
	3011	Column	10	10	5	5	5	5	40
	Moss		20	20	20	20	20	20	120
	Lichen		20	20	20	20	20	20	120
	Berries	2 types	16 + 4	10 + 10	20 + 0	10 + 8 + 6	12 + 8	10	114
	Mushrooms	2 types	8 + 0	10 + 10	4 + 0	12 + 0	12 + 0	—	56
	Ptarmigan	Muscle	20	20	20	20	20	20	120
		Liver	20	20	20	20	20	20	120
Terrestrial	Water-	Muscle	16	15	20	20	20	12	103
	fowl	Liver	16	15	20	20	20	12	103
	-	Muscle	10	15	15	14	_	15	69
	Hares	Liver	10	15	15	14	_	15	69
		Kidneys	10	15	15	14	_	15	69
		Muscle	10	15	10	10	10	10	65
	Reindeer	Liver	10	15	10	10	10	10	65
		Kidneys	10	15	10	10	10	10	65
	Water		9	8	8	8		8	41
	Sediments		10	10	10	10		10	50
<b>F</b>	Danthaa		10	2	3	3	_		18
Freshwater	Fish (3	Muscle	20 x 3	20 x 3	20 x 3	20 x 3	_	20 x 3	300
	species in each area)	Liver	20 x 3	20 x 3	20 x 3	20 x 3	_	20 x 3	300
Water	/						9		9
	Sediments						10		10
	Seaweed						20		20
	Fish (5	Muscle	_	_		_	151		151
	species)	Liver	_		_		151		151
		Fat					14		14
	Ringed	Muscle	_		_		14	_	14
	seal	Liver					14		14
		Kidneys	_		_		14	_	14
		Fat	_		_		28	_	28
Marine	Other	Muscle	_	_	_	_	28	_	28
	seal .	Liver	_		_		28	_	28
	species	Kidneys	_		_		28	_	28
	-	Fat	_				22		22
		Muscle	_	_		_	22	_	22
	Walrus	Liver					22		22
		Kidneys	_	_	_	_	22	_	22
	-	Fat	_	_			8		8
	Gray	Muscle	_	_		_	8	_	8
	whale	Liver	_	_		_	8	_	8
·····		Kidney	_	_			8		8
Total:			389	420	395	404	846	362	2816

Table 5.1. List of environmental media

and biotic samples obtained in the project study areas.

or high concentrations of pollutants, to confirm the presence of the substances under consideration. Samples in which brominated biphenyls and brominated diphenyl ethers were detected in significant concentrations, were also subjected to additional GS-MS examination.

Quantitative determination was made using an absolute calibration method, using target components and the (DBOF) internal standard that was added to the sample before its analysis.

Routine analyses were performed using a measurement system consisting of a *Fisons Mega-2* chromatograph with *ECD800* detector, and a chromatographic data processing system consisting of a *Multichrome-1.4* and *Kristall-2000M* chromatograph with electron capture detector, an automated sampler, and the chromatographic data processing software, *Chromatec Analytic 1.21*. Analysis of chlorinated compounds by mass-spectrometry was carried out using a *Fisons 8060* gas chromatograph and an *MD800* mass spectrometer operating in the electron shock mode (70 eV). For brominated compounds, the comparable system comprised a *Carlo-Erba 8060* gas chromatograph and *MD800* mass spectrometer as above. Operational control of the above systems, recording of mass-spectra, and their subsequent processing was undertaken using the *MassLab1.3* software package, and the National Institute of Science and Technology (NIST) library of organochlorine compounds.

A measurement system consisting of a *Carlo Erba* 8035 chromatograph, and an *Autospec-Ultima (VG)* high resolution mass-spectrometer, operating in electron impact mode (36 eV) and with a resolution of  $\geq 10.000$ , was used for isomer-specific analysis of polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs), brominated compounds and

#### Table 5.2.

List of pooled or individually analyzed samples of environmental media and biota.

		Туре —	Number of samples						
Environmen	Sample (species)	(organ/ tissue)	Kola	Pechora	Taymir- Dudinka	Taymir- Khatanga	Chukotka -coastal/ marine	Chukotka- Kanchala n	Total
	Soil		5	1	1	2	1	1	11
	Moss		3	1	2	2	1	2	11
	Lichen		4	1	2	2	1	2	12
	Berries	2 types	2	2	1	2	2	2	11
	Mushrooms	2 types	1	2	1	1	1	—	6
	Ptarmigan -	Muscle	2	2	2	2	2	2	12
_	rtannigan	Liver	2	2	2	2	2	2	12
Terrestrial	Water-fowl -	Muscle	4	4	5	7	3	8	31
	water-rowt	Liver	4	4	5	7	3	8	31
	_	Muscle	2	2	2	2	—	2	10
	Hares	Liver	2	2	2	2		2	10
		Kidneys	2	2	2	2		2	10
	-	Muscle	6	6	5	4	2	2	25
	Reindeer	Liver	6	б	5	4	2	2	25
		Kidneys	6	6	5	4	2	2	25
Freshwater Sedimen Fish (3 species i	Water		4	3	2	2		1	12
	Sediments		1	1	1	1		1	5
	``_	Muscle	12	13	14	16		10	65
	species in each area)	Liver	12	13	14	16	—	10	65
Water	Water		—		_		3		3
	Sediments		—				1	—	1
	Seaweed		—				2	—	2
	Fish (5	Muscle	_				18	_	18
	species)	Liver	—	—			18	—	18
	_	Fat					14		14
	Ringed seal-	Muscle					14		14
	-	Liver	_				14		14
		Kidneys	_				14		14
	_	Fat	_				28		28
Marine	Other seal	Muscle					28		28
	species _	Liver	_				28		28
		Kidneys	_				28		28
	_	Fat	_				22		22
	Walrus -	Muscle				—	22	_	22
	-	Liver	_				22		22
		Kidneys					22		22
	_	Fat	—		_		8		8
	Gray whale -	Muscle	_		—		8	—	8
		Liver	—		—		8	_	8
		Kidney	_	_	—	_	8	_	8
Total:			80	73	73	80	352	61	719

toxaphenes. Separation of isomers was carried out in a 60 m non-polar *DB-5MS J&W Scientific* column.

All standard solutions of organochlorine pesticides and PCBs used for calibration were produced by Ultra Scientific (USA) and certified by ISO9001. Standards for toxaphenes, brominated diphenyl ethers, and brominated biphenyls were produced by St. Petersburg University.

#### 5.2.2. Quantitative determination of heavy metals

Measurements of mercury were carried out using a (Russian) *Kvant-Z-ETA* atomic absorption spectrophotometer (analogous to the Western *Varian AA-8000* system), operating with a *GRG-106* mercury generator in automatic mode, using Zeeman background correction.

Mercury in samples was reduced to its metal state using tin dichloride, and then transferred in an argon gas flow ('Cold Vapor' method) to a graphite furnace, the internal surface of which was covered with a fine palladium layer to ensure mercury retention in the furnace. The detection limit for mercury in the solutions under consideration was  $0.001 \ \mu g/L$ , with a relative error of 20% at this level of concentration.

Measurements of lead and cadmium were carried out using a *Kvant-Z-ETA* atomic absorption spectrophotometer, with electrochemical atomization of the sample, using Zeeman background correction and a constant aliquot volume of 5  $\mu$ L of sample solution. Prior to any measurements, a palladium modifier (at a concentration of 20  $\mu$ g/L (Pd)) was added to the samples.

### 5.2.3. Quantitative determination

of polyaromatic hydrocarbons (PAHs)

Determination of PAHs in all samples involved liquid extraction, followed by clean-up of extracts to remove substances that could cause interference during analysis. Octafluoronaphthalene (OFN) was introduced as an internal standard to check the extraction efficiency of PAHs. PAH analytical determination was made using High Resolution Liquid Chromatography (HRLC), with target components registered by diode-matrix and fluorescent detectors connected in series. Quantification of PAH levels was made by absolute calibration, using standard solutions of target components and a control based on the internal standard (OFN) solution, which was added to the sample before its analysis. Analysis was performed using a measurement system consisting of an *HP1090M* chromatograph with a standard diodematrix component, a *Spectraphysics* fluorescent detector with programmed excitation wavelength, and Hewlett-Packard hardware/software processing system for chromatographic data.

	Water	Bottom sediments	Soil	Vegetation	Reindeer	Hares	Birds	Fish	Marine mammals	Total
Heavy metals (HM)										
Analysis of blank samples	1	1	1	1	2	1	2	5	4	18
Analysis of replicate samples	1	1	3	1	2	1	2	5	4	19
Analysis of standard solutions	_	1	_	_						1
Analysis of samples with addition of target components					2	1	2	6	4	15
Polycyclic aromatic hydroc	arbons (P/	\Hs)								
Analysis of blank samples	1	1	1	1	2	1	2	5	4	18
Analysis of replicate samples	1	1	3	1	2	1	2	5	4	19
Analysis of standard solutions	_	1	_	_						1
Analysis of samples with addition of target components					2	1	2	6	4	15
Organochlorines: polychlor	rinated bin	henvis (PCBs)								
Analysis of blank samples	1	1	1	1	2	1	2	5	4	18
Analysis of replicate samples	1	1	3	1	2	1	2	5	4	19
Analysis of standard solutions	_	1	_	_						1
Analysis of samples with addition of target					2	1	2	6	4	15
components Chlorobenzenes, polybromi	inated high	and and dinks	nul athar	n nalushlarinat	od comphono					
Analysis of blank samples	1	1	1	1	2	1	2	5	4	18
Analysis of replicate	1	1	3	1	2	1	2	5	4	19
samples Analysis of standard solutions	_	1	_	_						1
Analysis of samples with addition of target components					2	1	2	6	4	15
Organochlorines: HCHs, DD	Ts. cvclodi	enes								
Analysis of blank samples	1	1	1	1	2	1	2	5	4	18
Analysis of replicate samples	1	1	3	1	2	1	2	5	4	19
Analysis of standard solutions	_	1	_	_						1
Analysis of samples with addition of target					2	1	2	6	4	15
components Chlorinated dibenzodioxin	o and dikes	anofiurora								
Analysis of blank	s and didei				1		1		1	
samples Analysis of replicate					0		0		0	
samples Analysis of standard solutions					,		-			
Analysis of samples with addition of target components					1		1		1	

Table 5.3. Quality control analyses performed as part of the analysis of environmental and biotic samples.

5.2. Analytical methods and quality control

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#### Table 5.4.

Comparison of concentrations of brominated compounds in environmental and biotic samples obtained by routine GC, and by high resolution GC-MS methods. TeBD=tetra brominated diphenyl, PeBD=pentabrominated diphenyl, TeBDE=tetrabrominated diphenyl ether, PeBDE=pentabrominated diphenyl ether.

Samples	Routine GC method				High resolution GC-MS method			
Samples	TeBD	PeBD	TeBDE	PeBDE	TeBD	PeBD	TeBDE	PeBDE
Bottom sediments, pg/g dw	< 200	< 200	< 200	< 200	< 2	< 2	3.1 - 24.1	1.0 - 3.0
Soil, pg/g dw	< 200	< 200	< 200	< 200	< 2	< 2	1.5 - 5.4	1.2 - 2.7
Mosses, pg/g dw	< 200	< 200	< 200	< 200	< 2	< 2	7.2 - 11.9	6.2 - 10.9
Lichens, pg/g dw	< 200	< 200	< 200	< 200	< 2	< 2	20.7 - 29.4	5.1 - 10.2
Berries, pg/g ww	< 200	< 200	< 200	< 200	< 2	< 2	3.2 - 21.8	1.0 - 9.5
Reindeer kidney, pg/g ww	< 200	< 200	< 200	< 200	< 2	< 2	136.2 - 233.3	5.1 - 7.1
Hare liver, pg/g ww	< 200	< 200	< 200	< 200	< 2	< 2	123.1 - 258.9	3.1 - 6.5
Fish liver, pg/g ww	< 200	< 200	420	< 200	6.7	< 2	620.2	8.9

All standard solutions for PAHs used for calibration were produced by Ultra Scientific (USA) and certified by ISO9001. The octafluoronaphthalene standard was produced by St. Petersburg University.

#### 5.2.4. Quality control

Analytical quality control and quality assurance involved the execution of a full programme of work including analyses of blank samples, standard solutions, replicate samples, samples spiked with target components, and analysis of samples of different matrix compositions containing known levels of the determined components (Table 5.3). In addition, laboratories involved in the work participated in international intercalibration exercises within the framework of the 'QUASIMEME' Programme, and the AMAP Ring Test on analysis of POPs in human blood samples.

Under an arrangement made through the AMAP Secretariat, the laboratory responsible for analysis of environmental and biotic samples participated in the first stages of Rounds 22, 24 and 25 of the laboratory performance studies organized by 'QUASIMEME'. These concerned the analysis of bottom sediments and biota samples for levels of PAHs, OCs and HMs (Rounds 22 and 24), and the analysis of samples of sea and estuarine waters for OCs, HM and mercury (Round 25).

Calibration standards used were the Russian State Certified Standards and certified standards produced in other countries (by ULTRA Scientific, Wellington Laboratories, etc.). Previously analyzed samples, spiked with specific components at levels approximately 2-4 times greater than those detected during their original analysis, were employed as matrix samples containing known levels of the determined components. In addition, residual material from test samples distributed as part of the 'QUASIMEME' laboratory performance studies, with known composition and published 'assigned' concentration values, were also used as control samples.

As concentrations of toxaphenes, brominated diphenyl ethers and brominated biphenyls in most pooled samples were found to be very low (below the levels of reliable determination for these compounds using routine methods), 40 samples (6 bottom sediment, 6 soil, 6 lichen, 6 berry, 3 reindeer kidney, 4 hare liver, and 3 fish liver samples) were sent for control

analysis using high resolution GC-MS (*Carlo Erba* 8010/Autospec Ultima V6 system, described above) (Table 5.4). The control analyses confirmed the validity of the data obtained using the routine methods.

5.2.5. Processing and presentation of analytical results Results of analyses were grouped according to sampling site and sample types. Concentrations of individual compounds within related groups of substances were summed to provide a total value for the group. For purposes of calculation, where results were below the detection limit, a value of half the detection limit was used if this did not contribute more than 20% of the summed value; otherwise no sum was calculated.

Sums were calculated for the following groups of substances:

ΣHCH: the sum of  $\alpha$ -,  $\beta$ - and  $\gamma$ -isomers of HCH.

ΣDDT: the sum of  $o_i p^2$  and  $p_i p^2$ DDT, -DDE, -DDD.

ΣCHLOR: the sum of *cis*- and *trans*-chlordane and *cis*- and *trans*-nonachlor.

ΣPCB<sub>15</sub>: the sum of 15 PCB congeners (#28, #31, #52, #99, #101, #105, #118, #128, #138, #153, #156, #170, #180, #183, and #187).

 $\Sigma$ PCB<sub>7</sub>: the sum of 7 PCB congeners (#28, #52, #101, #118, #138, #153, and #180); calculated to allow comparison with data obtained in the Russian North in 1994/1995.

Toxaphene: the sum of Parlar-26, Parlar-50, and Parlar-62.

 $\Sigma$ PCDD/F: the sum of all 2,3,7,8-substituted congeners of dibenzo-*p*-dioxin and dibenzofuran.

Environmental contaminants commonly exhibit a log-normal frequency distribution in their concentration values (WHO, 1983). A log-normal distribution was therefore assumed to apply for concentrations of a particular contaminant (and concentration ratios) within any given sample type collected at a particular site. In most cases, therefore, data are reported as the geometric mean concentration (or ratio) and the associated standard deviation. Arithmetic mean concentrations and standard deviations were only calculated when concentration variability was low (i.e. where the standard deviation was less than 30% of the mean for most contaminants). This latter calculation, however, facilitated comparison with results from other studies, where PTS concentrations are commonly reported in terms of mean values and their standard deviations.

Sample type	Area	<b>ΣPCB</b> 15	<b>ΣΡCB</b> 7	ΣΗCB	ΣΗCΗ
	Kola Peninsula, n=4	3.9±0.3	2.8±0.2	0.5 (0.1-0.9) <sup>a</sup>	0.53±0.17
	Pechora basin, n=1	3.2	2.3	1.25	0.74
Lichens	Taymir, west, n=2	3.5±0.3	2.5±0.2	0.5±0.1	$1.4{\pm}0.5$
LICHENS	Taymir, east, n=2	3.5±0.6	2.5±0.4	1.0±0.2	$1.6 \pm 0.4$
	Chukotka, inland, n=2	3.4±0.5	2.2±0.2	0.4±0.1	0.89±0.08
	Chukotka, coast, n=1	3.9	2.5	0.15	0.76
	Kola Peninsula, n=3	12.6±0.1	9.1±0.1	0.2(0.1-0.45) <sup>a</sup>	0.8±0.2
	Pechora basin, n=1	7.7	6.2	0.95	1.4
Mosses	Taymir, west, n=2	11.8±1.8	9.0±1.2	1.0±0.3	2.3±0.5
1103565	Taymir, east, n=2	10.3±0.5	7.7±0.1	0.7±0.1	1.9±0.2
	Chukotka, inland, n=2	13.1±1.0	9.6±0.5	0.5±0.2	0.69±0.04
	Chukotka, coast, n=1	13.1±1.0	10.5	0.24	0.5
	Kola Peninsula, n=2	1.2 – 1.8 <sup>ª</sup>	1.1±0.2	0.18±0.04	0– 0.4 <sup>a</sup>
	Pechora basin, n=2	1.4 – 1.8 <sup>ª</sup>	1.3±0.1	0.25±0.05	0.1 – 0.5 <sup>a</sup>
Berries	Taymir, west, n=1	4.4	3.25	0.21	0– 0.40 <sup>a</sup>
Derries	Taymir, east, n=2	1.5 – 3.0 <sup>ª</sup>	1.2±0.1	0.18±0.01	0– 0.5ª
	Chukotka, inland, n=2	1.1 – 2.1 <sup>a</sup>	$1.1 \pm 0.1$	$0.19{\pm}0.08$	0- 0.6 <sup>a</sup>
	Chukotka, coast, n=2	1.0 – 1.5 <sup>ª</sup>	$1.0 \pm 0.1$	<0.1-0.15 <sup>a</sup>	0- 0.40 <sup>a</sup>
	Kola Peninsula, n=1	0.5 – 1.7 <sup>ª</sup>	$0.4 - 0.9^{a}$	0.11	0- 0.4ª
	Pechora basin, n=2	0.7 – 2.0 <sup>a</sup>	1.0±0.2	0.20±0.05	$0.1 - 0.5^{a}$
Mushrooms	Taymir, west, n=1	1.4 – 2.3 <sup>a</sup>	1.2	0.14	$0.1 - 0.4^{a}$
	Taymir, east, n=1	0.9 – 1.8 <sup>a</sup>	0.88	0.14	0- 0.4 <sup>a</sup>
	Chukotka, coast, n=1	0.5 – 1.7 <sup>a</sup>	$0.2 - 0.7^{a}$	0.05	0-0.4 <sup>a</sup>

Table 5.5a.

Concentrations (mean and standard deviation, or range; ng/g dw) of OCs in vegetation in the Russian Arctic in 2001

<sup>a</sup> A range is given when the standard deviation is greater than 50% of the mean, or the concentration in one of the samples is below the detection limit. When lower and upper limits of the concentration interval were estimated for summed concentrations, any individual values that were below the detection limit were either set to zero or to the detection limit (see Section 5.2.5).

n = number of pooled samples analyzed.

#### 5.3. Results – Terrestrial environment

5.3.1. PTSs in plants and mushrooms

The following species were collected and analysed for PTSs:

Lichens — Cetraria cuculata, Cetraria islandica, Cladina rangiferina, Cladina alpica, Cladina stellaris, Cladina mitis;

Bryophytes – Polytrichum commune, Pleurozium schreberi; Mosses – Dicranum sp., Sphagnum balticum, Hylocomium splendens;

Berries – low-bush cranberry (*Vaccinium vitis-idaea*), cloudberry (*Rubus chamaemorus*), bilberry (*Vaccinium myrtillus*), blueberry (*Vaccinium uliginosum*), crowberry (*Empetrum nigrum*);

Mushrooms – orange-cap boletus (*Leccinum aurantiacum*), brown-cap boletus (*Leccinum scabrum*), mossiness mushroom (*Xerocomus sp.*). The number of individual samples of each vegetation type collected at a given site and used in the preparation of a pooled sample was usually 10, but ranged between 4 and 20 (see Table 5.1). Vegetation was analysed for all PTS listed in Section 1.2.4.

#### Levels and trends

#### (a) Organochlorines

Concentrations of organochlorines (OCs) in vegetation that significantly exceeded detection limits are shown in Tables 5.5a and 5.5b. Data for those OCs which occurred at concentrations below the detection limit in most samples are not presented. The level of HCB was above the detection limit in all samples of plants and mushrooms.  $\Sigma PCB_{15}$  and  $\Sigma PCB_7$ ,  $\Sigma DDT$  and  $\Sigma HCH$  were detectable in all samples of lichens and mosses and  $\Sigma PCB_7$  and  $\Sigma DDT$  also in most of the berry

Sample type	Area	<i>p,p</i> '-DDE	<i>p,p</i> '-DDT	ΣDDT	Mirex
	Kola Peninsula, n=4	0.24±0.07	0.4±0.1	1.0±0.3	<0.1
	Pechora basin, n=1	0.75	0.80	2.2	0.52
Lichens	Taymir, west, n=2	1.2±0.6	1.3±0.3	3.1±0.3	0.18±0.03
LICHEIIS	Taymir, east, n=2	0.71±0.13	0.9±0.3	2.9±0.8	<0.1 - 0.3 <sup>a</sup>
_	Chukotka, inland, n=2	0.30±0.03	0.62±0.12	1.39±0.03	<0.1
	Chukotka, coast, n=1	0.24	0.67	1.2	<0.1
	Kola Peninsula, n=3	0.3±0.1	0.4±0.1	1.3±0.1	0.15±0.06
– Mosses –	Pechora basin, n=1	0.72	0.77	2.3	0.44
	Taymir, west, n=2	<0.05 - 1.1 <sup>ª</sup>	1.1±0.3	2.6±0.5	0.5±0.2
	Taymir, east, n=2	0.7±0.1	0.9±0.2	3.0±0.2	0.20±0.02
	Chukotka, inland, n=2	0.3±0.1	0.60±0.03	1.4±0.1	<0.1
	Chukotka, coast, n=1	0.20	0.39	1.0	<0.1
	Kola Peninsula, n=2	<0.1-0.12	1.09±0.04	1.59±0.02	<0.1
	Pechora basin, n=2	<0.1	0.17±0.06	0.1-0.7 <sup>a</sup>	<0.1
Berries	Taymir, west, n=1	0.15	0.28	1.1	<0.1
Derries	Taymir, east, n=2	<0.1-0.13	0.1-0.9 <sup>a</sup>	0.1–1.5 <sup>a</sup>	<0.1
	Chukotka, inland, n=2	0.13±0.03	0.13±0.03	0.1 –0.7 <sup>a</sup>	<0.1
	Chukotka, coast, n=2	<0.1-0.1	<0.1-0.1	0.1 –0.6 <sup>a</sup>	<0.1
	Kola Peninsula, n=1	0 – 0.12 <sup>a</sup>	0.28	0.4 – 0.8 <sup>a</sup>	<0.1
	Pechora basin, n=2	<0.1	<0.1	0-0.6 <sup>a</sup>	<0.1
Mushrooms	Taymir, west, n=1	0.1	0.18	0.5 – 0.8 <sup>a</sup>	<0.1
-	Taymir, east, n=1	<0.1	0.18	0.3 – 0.7 <sup>ª</sup>	<0.1
	Chukotka, coast, n=1	<0.1	<0.1	0-0.6°	<0.1

Table 5.5b. Concentrations (mean and standard deviation, or range; ng/g dw) of OCs in vegetation in the Russian Arctic in 2001 <sup>a</sup> A range is given when the standard deviation is greater than 50% of the mean, or the concentration in one of the samples is below the detection limit. When lower and upper limits of the concentration interval were estimated for summed concentrations, any individual values that were below the detection limit were either set to zero or to the detection limit (see Section 5 2 5)

n = number of pooled samples analyzed. and mushroom samples. The  $\Sigma PCB_7$  value, when multiplied by two, can be used to provide an estimate of the total PCB concentration in mosses and, most likely, also in other plants (AMAP, 1998). Of the DDT group, only  $p,p^2$ DDT occurs in detectable concentration in all berry and most mushroom samples.  $\Sigma DDT$  concentration in berries and mushrooms were therefore estimated using the ratio of  $p,p^2$ DDT/ $\Sigma DDT$  found in lichens and mosses (0.39±0.07). This probably provides a conservative estimate as, at the three sites where  $\Sigma DDT$  in berries could be calculated directly, this ratio was equivalent to 0.5±0.2.

Concentrations of HCB, HCH, and DDT in mosses are comparable to those in lichens, while PCB levels are 2-4 times higher in mosses at all sites. Concentrations of these substances in berries and mushrooms are several times lower than those found in mosses and lichens.

Levels of HCB, HCH, and DDT follow a similar geographical trend, with highest levels found at the two locations on the Taymir Peninsula, and in the lower Pechora basin. In contrast, no geographical trend in PCB levels was observed. With only one exception (berries from Dudinka), all differences in PCB concentrations between the sites could be explained by analytical variability.

PCB levels in the Arctic have been found to be generally decreasing over time. Over the last few years, however, the rate of decrease has been small and levels have remained relatively constant (AMAP, 2002). In accordance with this tendency, mean  $\Sigma PCB_7$  concentrations measured in 2001 in samples of lichens collected near Khatanga, in eastern Taymir (2.5 ng/g) and at Chukotka (2.2 and 2.5 ng/g) were slightly lower than those determined in these areas in 1995 (3.2 and 3.82 ng/g, respectively) (AMAP, 1998). In contrast, the  $\Sigma PCB_7$  concentration for lichens from the Pechora basin in 1995 was below the detection limit, while 2.3 ng/g was found in 2001. An unexpected increase was also observed in the  $\Sigma PCB_7$  concentration in mosses, which in 1994/1995 in the Russian North ranged from 0 to 3.6 ng/g (0-02.4 ng/g on the Taymir



Figure 5.6. PCB congener contributions to  $\Sigma$ PCB<sub>15</sub> levels in lichen in the Russian Arctic in 2001. The congeners shown are the main contributors within each homologue group.

Peninsula; and below the detection limit in the Pechora basin). The  $\Sigma PCB_7$  concentration in mosses in 2001 is significantly higher (10.3–013.9 ng/g).

The PCB congener patterns seen in lichens differ significantly from those occurring in most of the common technical mixtures used in Western countries. In Western products, PCB-138 and 153 dominate, while in the environment of Russian Arctic, PCB-28 makes the greatest contribution to the summed value in samples from all sites. However, relative levels of the congeners PCB-28, 52, 118, 138, 153 and 180 found in remote Arctic areas of North America also differ from those found in American technical mixtures (Wilcke and Amelung, 2000) and are close to those found in the Russian Arctic. Therefore, the PCB composition patterns provided in Figure 5.6 could also be a result of the fractionation of congeners during long-range transport.

Concentrations of **SCBz** (sum of HCB and pentachlorobenzene (PeCBz), not shown in tables) measured in plants in this study, in 2001, are distinctly higher than levels previously reported for the Russian North (see Figure 5.7). In August 1995, on the Taymir Peninsula, concentrations of 0.25 and 0.4 ng/g of  $\Sigma$ CBz were found in lichens and mosses, respectively (AMAP, 1998). Mean concentrations of  $\Sigma$ CBz in lichens and mosses obtained during the current study at two sites on the Taymir Peninsula, were 0.64±0.16 and 1.3±0.3 ng/g, and 0.9±0.1 and 1.4±0.2 ng/g, respectively. Concentration of  $\Sigma$ CBz in 3 samples of lichen collected near Khatanga in 1995 (AMAP, 1998) ranged from 0.16 to 0.66 ng/g, while concentrations of 1.2- $1.5 \text{ ng/g} \Sigma \text{CBz}$  were found at Khatanga in 2001 (see Figure 5.7). In the Pechora basin, mean  $\Sigma$ CBz concentrations in lichens and mosses in 1994/1995 ranged from 0 (i.e., below the detection limit) to 0.08 ng/g(AMAP, 1998), whilst in 2001 values of 0.2-1.0 ng/g were found. Thus, a comparison of the data obtained in 1994/1995 and in 2001, indicates that the concentration of chlorinated benzenes in lichens and mosses (and by inference in air) in the Russian North has shown a tendency to increase during recent years.



Figure 5.7. Mean values and ranges of OC concentrations measured in lichen in Eastern Taymir and the Pechora Basin in 1995 and in 2001. Values for Eastern Taymir were derived from the analysis of three samples in 1995, and two samples in 2001. CBz = sum of HCB and PeCBz, DDT= $\Sigma$ DDT.

Chapter 5

Area	NAP	ACNLE	BIPN	NAP2M	FLE	ACNE	PA
Kola Peninsula, n=4	179 (124-258)	1.3 (<0.5-7.9)	1.5 (<0.5–10)	45 (33-65)	12 (5.8-22)	1.2 (<0.5-5.7)	75 (33-142)
Pechora basin, n=1	188	10.0	13.1	30	5.3	<0.5	237
Taymir, west, n=2	177 (164-192)	8.5 (7.1-10.2)	7.4 (5.3-10.3)	29 (21-40)	9.8 (8.2-11.6)	<0.5	31 (26-38)
Taymir, east, n=2	315 (262-378)	9.2 (6.8-12.5)	39 (33-45)	73 (59-91)	18 (15-21)	4.7 (3.5-6.3)	123 (105-144)
Chukotka, inland, n=2	79 (63-100)	<0.5	<0.5	13 (11–14)	8.7 (6.8-11)	<0.5	65 (61-70)
Chukotka, coast, n=1	505	7.9	<0.5	71	21	8.7	129
Kola Peninsula, n=3	174 (86-432)	17 (13-21)	37 (28-50)	60 (48-78)	26 (20-35)	6 (4.2-9.8)	141 (110–166)
Pechora basin, n=1	335	16	<0.5	91	13	<0.5	131
Taymir, west, n=2	626 (512-765)	23 (16-35)	116 (102-132)	64 (54-75)	19 (19 –20)	6.5 (5.8-7.4)	66
Taymir, east, n=2	275 (261-290)	11 (8.8-15)	35 (30-40)	208 (177-245)	13 (8.9-18)	<0.5	64
Chukotka, inland, n=2	123 (112-134)	26 (24-28)	15 (13-17)	20 (19-21)	8.5 (7.8-9.2)	<0.5	61
Chukotka, coast, n=1	144	<0.5	<0.5	28	27	5.0	136
	Kola Peninsula, n=4 Pechora basin, n=1 Taymir, west, n=2 Taymir, east, n=2 Chukotka, inland, n=2 Chukotka, coast, n=1 Kola Peninsula, n=3 Pechora basin, n=1 Taymir, west, n=2 Taymir, east, n=2 Chukotka, inland, n=2	Kola Peninsula, n=4   179 (124-258)     Pechora basin, n=1   188     Taymir, west, n=2   177 (164-192)     Taymir, east, n=2   315 (262-378)     Chukotka, inland, n=2   79 (63-100)     Chukotka, coast, n=1   505     Kola Peninsula, n=3   174 (86-432)     Pechora basin, n=1   335     Taymir, west, n=2   626 (512-765)     Taymir, east, n=2   275 (261-290)     Chukotka, inland, n=2   123 (112-134)	Kola Peninsula, n=4   179 (124-258)   1.3 (<0.5-7.9)	Kola Peninsula, n=4   179 (124-258)   1.3 (<0.5-7.9)	Kola Peninsula, n=4179 (124-258)1.3 (<0.5-7.9)	Kola Peninsula, n=4 179 (124-258) 1.3 (<0.5-7.9) 1.5 (<0.5-10) 45 (33-65) 12 (5.8-22)   Pechora basin, n=1 188 10.0 13.1 30 5.3   Taymir, west, n=2 177 (164-192) 8.5 (7.1-10.2) 7.4 (5.3-10.3) 29 (21-40) 9.8 (8.2-11.6)   Taymir, east, n=2 315 (262-378) 9.2 (6.8-12.5) 39 (33-45) 73 (59-91) 18 (15-21)   Chukotka, inland, n=2 79 (63-100) <0.5 <0.5 13 (11-14) 8.7 (6.8-11)   Chukotka, coast, n=1 505 7.9 <0.5 71 21   Kola Peninsula, n=3 174 (86-432) 17 (13-21) 37 (28-50) 60 (48-78) 26 (20-35)   Pechora basin, n=1 335 16 <0.5 91 13   Taymir, west, n=2 626 (512-765) 23 (16-35) 116 (102-132) 64 (54-75) 19 (19-20)   Taymir, east, n=2 275 (261-290) 11 (8.8-15) 35 (30-40) 208 (177-245) 13 (8.9-18)   Chukotka, inland, n=2 123 (112-134) 26 (24-28) 15 (13-17) 20 (19-21) 8.5 (7.8-9.2)	Kola Peninsula, n=4 179 (124-258) 1.3 (<0.5-7.9) 1.5 (<0.5-10) 45 (33-65) 12 (5.8-22) 1.2 (<0.5-5.7)   Pechora basin, n=1 188 10.0 13.1 30 5.3 <0.5   Taymir, west, n=2 177 (164-192) 8.5 (7.1-10.2) 7.4 (5.3-10.3) 29 (21-40) 9.8 (8.2-11.6) <0.5   Taymir, east, n=2 315 (262-378) 9.2 (6.8-12.5) 39 (33-45) 73 (59-91) 18 (15-21) 4.7 (3.5-6.3)   Chukotka, inland, n=2 79 (63-100) <0.5 <0.5 13 (11-14) 8.7 (6.8-11) <0.5   Chukotka, coast, n=1 505 7.9 <0.5 71 21 8.7   Kola Peninsula, n=3 174 (86-432) 17 (13-21) 37 (28-50) 60 (48-78) 26 (20-35) 6 (4.2-9.8)   Pechora basin, n=1 335 16 <0.5 91 13 <0.5   Taymir, west, n=2 626 (512-765) 23 (16-35) 116 (102-132) 64 (54-75) 19 (19 -20) 6.5 (5.8-7.4)   Taymir, east, n=2 275 (261-290) 11 (8.8-15) 35 (30-40) 208 (177-245) 13 (8.9-18) <0.5   Chukotka, inla

Table 5.6a. Concentrations (geometric means and ranges; ng/g dw) of PAHs<sup>a</sup> in vegetation in the Russian Arctic in 2001.

<sup>a</sup> NAP = Naphthalene, ACNLE = Acenaphthylene, BIPN = Biphenyl, NAP2M = 2-Methylnaphthalene, FLE = Fluorene, ACNE = Acenaphthene, PA= Phenanthrene.

The mean  $\Sigma$ HCH concentration in 3 samples of lichens collected near Khatanga in 1995 (AMAP, 1998) was twice as high as those measured in the current study in the same area (3.42 and 1.6 ng/g, respectively). In contrast,  $\Sigma$ HCH concentrations in lichens and mosses in the Pechora basin in 1995 ranged from 0.17 to 0.38 ng/g, whilst concentrations of 0.74–1.4 ng/g were found in this area in 2001. Despite the difference in values, these results are unlikely to be indicative of a trend, as there is known to be a high degree of spatial variability in levels of contamination from HCH across the Russian North. In 1994/1995, the concentration of  $\Sigma$ HCH, as a function of sampling site, varied within two orders of magnitude, even for samples taken in the same area (AMAP, 1998).

No temporal trend in  $\Sigma$ DDT concentrations in lichens and mosses was evident in the Russian North. The mean concentration of  $\Sigma$ DDT in 3 samples of lichens collected near Khatanga in 1995 (AMAP, 1998) was almost the same as that found in 2001 (2.96 and 2.9 ng/g, respectively). The range of  $\Sigma$ DDT concentrations (0.7–3 ng/g) determined in lichens and mosses in five other areas in the Russian North in 1994/1995 (AMAP, 1998) is consistent with data obtained from the current study (1.0–3.1 ng/g). Concentrations of  $\Sigma$ DDT,  $\Sigma$ HCH, and  $\Sigma$ CBz found in lichens in the Russian Arctic in 2001 are all comparable with those found in the Canadian Arctic in 1993/4. PCB concentrations in Canada in 1993/4 were several times lower, while toxaphene levels were significantly higher, than those measured in Russia in 2001 (AMAP, 1998).

Mirex has not been used in the fSU/Russia. However, it does occur at detectable concentrations in some samples of lichens and mosses, presumably as a result of long-range atmospheric transport from remote sources. The geographical distribution pattern of Mirex is similar to that of  $\Sigma$ DDT,  $\Sigma$ HCH and HCB. In the most highly contaminated areas (the Pechora basin and the Taymir peninsula), Mirex concentration in lichens and mosses ranged from 0.2 to 0.5 ng/g. However, in the majority of samples collected in less contaminated areas (on the Kola peninsula, and Chukotka), Mirex concentrations were below the detection limit of 0.1 ng/g. The similarity between the spatial distribution observed for  $\Sigma$ DDT,  $\Sigma$ HCH, and HCB, and that of Mirex indicates that trans-boundary transport is at least an important source, and most likely the main source of contamination in the Russian Arctic for these compounds.

Samples of plants and mushrooms were also analyzed for other OCs listed in Section 1.2.4, with the exception of PCDD/Fs. Of these substances, only heptachlor was detected in some samples of lichen and mosses, in concentrations ranging from 0.1 to 0.3 ng/g. As all of these samples were collected in the Pechora basin and the Taymir peninsula, the spatial pattern of heptachlor distribution appears, at least qualitatively, similar to that of Mirex,  $\Sigma$ DDT,  $\Sigma$ HCH, and HCB.

Sample type	Area	ANT	FLU	PYR	BAA	CHR	BBF	BKF
	Kola Peninsula, n=4	2.0 (1.3-3.3)	41 (21-70)	18 (12-28)	1.2 (0.7-2.4)	16 (11-21)	14 (9.7-19)	3.7 (2.4-6.1)
	Pechora basin, n=1	2.3	14	2.7	1.0	18.2	4.0	1.6
Lichens	Taymir, west, n=2	1.6 (1.1-2.3)	7.6 (5.7-10.1)	6.2 (5.4-7.1)	0.7 (0.5-1.0)	12 (9.2-16)	2.5 (2.1-3.1)	1.0 (0.8 –1.2)
Lichens	Taymir, east, n=2	11 (9.0-12)	115 (85-152)	69 (54-88)	5.2 (3.6-7.3)	16 (12-20)	31 (27-35)	9.0 (6.6-12)
	Chukotka, inland, n=2	1.1 (0.8-1.4)	10 (8.8–11)	7.4 (7.0-7.7)	0.6 (0.5-0.8)	3.8 (3.3-4.5)	2.6 (2.2-3.0)	1.1 (1.0-1.1)
	Chukotka, coast, n=1	2.8	27	13	1.5	9.6	2.3	2.2
	Kola Peninsula, n=3	1.3 (1.0-2.1)	18 (14-22)	15 (14-17)	2.8 (2.2-3.2)	12 (8.6-16)	6.8 (4.3-5.8)	4.8 (1.7-9.4)
	Pechora basin, n=1	1.7	13	10.4	1.3	17	6.1	3.1
Mosses	Taymir, west, n=2	3.9 (3.8-4.0)	12 (11-13)	18 (15-22)	1.0 (0.8-1.2)	6.2 (5.7-6.8)	2.3 (2.0-2.7)	1.2 (1.0-1.3)
103363	Taymir, east, n=2	9.3	45	47	6.5	21	20	11
	Chukotka, inland, n=2	0.7 (0.6-0.8)	9.2 (8.6-9.9)	5.6 (4.1-1.7)	0.5 (0.4-0.7)	12 (12-13)	3.0 (2.9-3.1)	1.0 (0.8-1.2)
	Chukotka, coast, n=1	2.4	12	16	1.1	17	10.4	4.3

Table 5.6b. Concentrations (geometric means and ranges; ng/g dw) of PAHs<sup>a</sup> in vegetation in the Russian Arctic in 2001.

<sup>a</sup> ANT= Anthracene, FLU = Fluoranthene, PYR = Pyrene, BAA = Benz[a]anthracene, CHR = Chrysene, BBF = Benzo[b]fluoranthene, BKF = Benzo[k]fluoranthene.

#### (b) PAHs

Geometric means and ranges of concentrations of PAHs in lichen and mosses are provided in Tables 5.6a and 5.6b. PAH composition is similar at all sites, naphthalene, 2-methylnaphthalene with and phenanthrene contributing 70-90% of the value of  $\Sigma$ PAH in both lichen and mosses. The highest concentrations, and especially those of heavier PAHs, are normally found near Khatanga. Lichens and mosses were also analyzed for benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, dibenz[*ah*]anthracene, indeno[1,2,3-cd] pyrene and benzo[ghi] perylene. In the most cases, concentrations of these compounds were below the detection limit of 0.5 ng/g. Perylene, indeno[1,2,3-*cd*] pyrene and benzo[*ghi*] perylene were, however, found in concentrations which ranged from 1 to 10 ng/g in several samples, primarily from the Kola and Taymir peninsulas. A notable exception was the concentration of benzo[*ghi*]pervlene found in mosses from Eastern Taymir, which was as high as 30 ng/g.

Naphthalene levels determined in berries and mushrooms are normally several times lower than those found in lichen and mosses. The difference in concentrations occurring between the two groups of plants increases with the molecular weight of the substance in question, and for the heaviest PAHs can be as much as two orders of magnitude. This may indicate that the greater efficiency of lichens and mosses for interception of gaseous and particulate PAHs from the air is partially offset by the ability of plants and mushrooms to take up PAHs with logK<sub>ow</sub> < 4 from the soil and translocate them to the aboveground parts of the plant (McLachlan, 1996).

#### (c) Brominated flame-retardants

Vegetation samples were analyzed for 2,2',4,4'-tetrabromodiphenyl; 2,2',4,4',5-pentabromodiphenyl; 2,2', 4,4'-tetrabromodiphenyl ether; and 2,2',4,4',5-penta-

0.4 8 Kola, Peninsula Pechora Basin Taimvr, Dudinka Taimyr, Khatanga Chukotka, Kanchalan Chukotka, Lavrentiva 6 0.3 Hg and Cd, mg/kg dw Pb, m g/kg dw 4 0.2 2 0.1 0 Cd(L) Hg (L) Pb(M) Cd(M) Hq(M) Pb(L)

Figure 5.8. Concentrations of HMs in lichen (L) and mosses (M) in the Russian Arctic in 2001.

bromodiphenyl ether. In all samples these substances were below the detection limit of 0.2 ng/g dw.

#### (d) Heavy metals

The heavy metals, mercury (Hg), lead (Pb) and cadmium (Cd) were detected in all samples of lichens, mosses and mushrooms (see Figure 5.8 and Table 5.7). In the majority of berry samples, Hg and Cd were below the detection limits (0.001 and 0.005  $\mu$ g/g, respectively), while the Pb level was detectable in all samples. Pb concentrations ranged from 2.6 to  $4.5 \,\mu g/g$  in mosses, from 0.9 to 4.1  $\mu$ g/g in lichens, from 0.04 to 0.1  $\mu$ g/g in mushrooms and from 0.01 to 0.05  $\mu$ g/g in berries. Concentrations of Hg and Cd in samples of lichens and mosses ranged from 0.01 to 0.2  $\mu$ g/g. No pronounced spatial trend was observed in HM contamination of lichens and mosses (see Figure 5.8). The relatively high Hg concentration in mosses collected at Chukotka is, very likely, due to a single anomalous sample, and was not confirmed by data for lichen from the same location. The only notable spatial tendency was a slight decreasing gradient in Cd concentrations from the Kola Peninsula towards Chukotka.

Table 5.7. Concentrations (mean and standard deviations;  $\mu g/g$  dw) of HMs in vegetation in the Russian Arctic in 2001. <sup>a</sup> Range is given when the standard deviation is greater than 50% of the mean, or the concentration in one of samples is below the detection limit. <sup>b</sup> Concentration detected in both samples.

Sample type	Area	Hg	Pb	Cd
	Kola Peninsula, n=4	0.04±0.01	2.80±0.25	0.12±0.02
	Pechora basin, n=1	0.039	1.78	0.051
Lichens	Taymir, west, n=2	0.021±0.003	1.7±0.2	0.096±0.014
LICHEIIS	Taymir, east, n=2	0.061±0.002	4.1±0.2	$0.080 \pm 0.008$
	Chukotka, inland, n=2	0.03±0.01	0.9±0.5	0.043±0.006
	Chukotka, coast, n=1	0.062	2.4	0.056
	Kola Peninsula, n=3	0.04±0.02	3.9±0.1	0.23±0.02
	Pechora basin, n=1	0.053	4.5	0.10
Mosses	Taymir, west, n=2	$0.089 \pm 0.008$	2.62±0.05	0.11±0.02
Mosses	Taymir, east, n=2	$0.089 \pm 0.008$	4.1±0.2	0.14±0.01
	Chukotka, inland, n=2	0.071±0.003	3.70±0.06	0.092±0.006
	Chukotka, coast, n=1	0.23	2.8	0.069
	Kola Peninsula, n=2	<0.001	0.018±0.001	<0.005
	Pechora basin, n=2	<0.001	0.016±0.003	<0.005
Berries	Taymir, west, n=1	<0.001	0.012	<0.005
Derries	Taymir, east, n=2	<0.001	0.025±0.005	<0.005
	Chukotka, inland, n=2	<0.001	0.029±0.011	<0.005
	Chukotka, coast, n=2	<0.001	0.008 - 0.050 <sup>a</sup>	0.008 <sup>b</sup>
	Kola Peninsula, n=1	0.018	0.041	0.082
	Pechora basin, n=2	$0.010 \pm 0.001$	0.022 - 0.058 <sup>a</sup>	$0.086 \pm 0.026$
Mushrooms	Taymir, west, n=1	0.041	0.072	0.072
	Taymir, east, n=1	0.023	0.097	0.060
-	Chukotka, coast, n=1	0.007	0.072	0.032

Comparison between data obtained in 1995 (AMAP, 1998) and 2001, indicates that an increase in the Hg deposition rate in Chukotka may have taken place during this period. Hg levels in lichens and mosses in 1995 (0.02 and 0.03  $\mu$ g/g, respectively) were several times lower than those found in 2001 (0.06 and 0.15  $\mu$ g/g, respectively). A similar temporal trend in Hg concentration in lichen is observed on the Taymir Peninsula (0.01  $\mu$ g/g in 1995, and 0.06  $\mu$ g/g in 2001).

For the other HMs and sample sites, changes over time are less significant, with the exception of a decrease by an order of magnitude (from 0.9 to 0.06  $\mu$ g/g) in Cd concentration in lichen from Chukotka. However, over the same period, an increase in Cd levels in mosses was also observed in this area. Given the similar pathways for Cd uptake in mosses and lichen, these results suggest that the above-mentioned differences in HM concentrations occurring between 1995 and 2001 are most likely a reflection of normal intersample variability. Similar to the majority of OCs, HM concentrations measured in lichen and mosses in Russia in 2001 are consistent with concentration ranges obtained in the Canadian Arctic in 1993/4.

#### 5.3.2. PTS in reindeer

Samples of reindeer (Rangifer tarandus) tissues were collected at all 6 sites in the four regions. The number of individual tissue/organ samples collected at a given site and combined in the preparation of pooled samples was 2-3 in most cases, but ranged from 1 to 6 (see Table 5.2). Pooled samples were prepared from tissue samples of animals of the same sex and with an age difference of less than 2 years. The ages of animals ranged from 1 to 8 years, and equal numbers of animals of each sex were sampled at all sites, except for Western Taymir, where tissue samples from 3 male and 2 female reindeer were collected. Samples were grouped according to sex, (female and male), age group (1-3 years and 4-8 years), and tissue type (liver, kidney, or muscle). Reindeer muscle, liver and kidney were analysed for all PTS listed in Section 1.2.4.

### PTS concentration relationships with reindeer sex, age, and tissue type

#### (a) Organochlorines

Concentration dependence on animal sex, age, and tissue type was investigated for OCs that exhibited concentrations above detection limits in most cases (p,p<sup>2</sup> DDT, p,p<sup>2</sup>DDE, PCB-118, PCB-153 and HCB).

Ratios of (geometric mean) concentrations of various OCs between male and female reindeer were in the range 1.1 to 1.3, and were found to be independent of site, age group, and tissue type. The difference between these values and unity had very low statistical significance and therefore mean concentrations were calculated using data for both sexes.

Similarly, differences in OC concentrations between the two age groups, and between different tissue types were not statistically significant, the ratios for 'old/young' reindeer groups ranging from 0.8 to 1.3 (1.1–1.3 for p,p<sup>2</sup>DDT, p,p<sup>2</sup>DDE, PCB-118 and PCB-153 and 0.8 for HCB).

The geometric mean of the liver/muscle lipid concentration ratios, from the data collected in this study, was 1.5. Based on this value, somewhat higher concentrations of OCs might be expected in liver tissue when compared with muscle. However, the geometric means of both the liver/muscle and kidney/muscle concentration ratios for all of the OCs investigated were close to unity and independent of site.

From these results, it was decided to calculate mean concentrations based on data from both age groups; values for OCs in muscle tissue only are presented in Tables 5.8a and 5.8b.

Area	$\Sigma PCB_{15}$	HCB	ΣHCH
Kola Peninsula, n=6	1.7 (1.2-2.47)	0.27 (0.13-0.45)	0.47 (0.2-0.9)
Pechora basin, n=6	2.2 (1.7-2.7)	0.18 (0.14-0.35)	0.54 (0.28-2.49)
Taymir, west, n=5	1.4 (1.1-2.0)	0.09 (<0.05-0.30)	0.42 (0.24-0.91)
Taymir, east, n=4	1.3 (0.59-4.3)	0.12 (<0.05-0.29)	0.55 (0.31-0.91)
Chukotka, inland, n=2	2.8 (1.9-4.0)	0.24 (0.21-0.28)	0.47 (0.42-0.53)
Chukotka, coast, n=2	1.3 (1.2-1.3)	0.06 (0.06-0.06)	1.18 (1.16-1.20)

Table 5.8a. Concentrations (geometric mean and range; ng/g ww) of OCs in muscle of reindeer in the Russian Arctic in 2001.

Area	<i>p,p</i> '-DDE	<i>p,p</i> '-DDT	ΣDDT
Kola Peninsula, n=6	0.11(<0.05-0.24)	0.17(0.10-0.28)	0.49(0.25-0.63)
Pechora basin, n=6	0.11(<0.05-0.22)	0.28(0.13-1.1)	0.59(0.37-1.3)
Taymir, west, n=5	0.10(<0.05-0.17)	0.24(0.18-0.46)	0.51(0.28-0.69)
Taymir, east, n=4	0.10(<0.05-0.17)	0.21(0.12-0.33)	0.56(0.50-0.64)
Chukotka, inland, n=2	1.2(0.96-1.4)	0.88(0.51-1.5)	2.65(2.07-3.4)
Chukotka, coast, n=2	0.19(0.19-0.20)	0.13(0.13-0.13)	0.44(0.43-0.45)

Table 5.8b. Concentrations (geometric mean and range; ng/g ww) of OCs in muscle of reindeer in the Russian Arctic in 2001.

#### (b) Heavy metals

As for OCs, the concentrations of HMs in reindeer tissues do not show any significant sex dependence. However, a slight, but consistent increase in concentrations does occur with increasing age of the animals sampled. Concentration ratios between the two age groups (3 years and under, and over 3 years) are similar for all HMs, sites, and tissue types; the geometric means of the age ratios, calculated for almost 30 samples, equal to 1.8, 1.7 and 1.9 for Hg, Pb, and Cd, respectively. Figure 5.9 shows examples of age depend-

ency of HM concentrations in reindeer tissues for the two locations where samples included the greatest range of age groups. Similar relationships between concentrations and age are observed in samples from other sites. In all reindeer tissues, HM concentrations increase in direct proportion to the age of the animal sampled. This implies that the effective rate of HM accumulation in various tissues, expressed in  $\mu g/g$  per year, is independent of age, at least in the sampled mean age interval of 1.5–7.5 years. The only reasonably clear deviation from direct proportionality is the relatively low level of muscle contamination, primarily for Hg, seen in the youngest animals of 1.5-2.5 years of age. This possibly indicates that a steady state liver/kidney concentration ratio is established quite rapidly, whilst a steady state distribution of HM between the liver and muscle may require several years to develop.

The HM distribution between reindeer tissues, appears similar for both age groups and sexes. Only for Hg are liver/muscle and kidney/muscle ratios about

Figure 5.9. Relationships between HM concentration in reindeer tissues and age, for the Kola peninsula (1) and the Pechora basin (2).









3 times higher for younger animals. Relative concentrations of HMs in the muscle, liver and kidney appear, respectively, in the ratios of 1:5:5 for Pb, 1:11:33 for Cd and 1:11:42 for Hg in reindeer over 3 years of age, and 1:31:136 for Hg in younger reindeer (figures are based on the geometric means of the ratios for pooled samples). The degree of variability between liver/muscle and liver/kidney concentration ratios for HMs within a herd is greatest for Hg. The level of variability between reindeer herds is similar. The liver/muscle concentration ratios are slightly lower than those calculated for Swedish herds, but the difference was not statistically significant (see Figure 5.10). As the distribution of HMs between tissues is herd specific, the age concentration ratios for HMs are relatively constant, and concentration variability within a herd is quite low, mean concentrations of Hg, Pb and Cd were calculated separately for all three tissue types and are shown only for the oldest age group. The calculation of separate mean concentrations for each age group does not significantly improve the representativeness of the results, because the variability found in concentrations of HMs within a herd is low.

#### Levels and trends

#### (a) Organochlorines

Concentrations of OCs reliably detected in reindeer muscle are given in Tables 5.8a and 5.8b. Levels of PCB, HCB, HCH and DDT vary within fairly narrow ranges and do not follow any pronounced spatial trend, although somewhat higher levels of PCB, HCB, and DDT are found in inland Chukotka (see Figure 5.11).



Figure 5.10. Geometric means and ranges of HM liver/muscle concentration ratios in Swedish and Russian reindeers. The Swedish data were for 10 herds (AMAP, 1998) and the Russian data for 6 herds.



Figure 5.11. Geometric means and ranges of OC concentrations in reindeer muscle in the Russian Arctic in 2001. PCB=  $\Sigma$ PCB<sub>15</sub>, HCH= $\Sigma$ HCH, DDT= $\Sigma$ DDT.

OCs in reindeer show no correlation with the spatial trends found for OC contamination in lichen. All concentrations are far below the maximum permissible concentrations (MPC) for OCs in meat, established by the Russian Ministry of Health; the MPC of 0.1 mg/kgfor  $\Sigma$ HCH and  $\Sigma$ DDT, given in Chapter 3, is equivalent to 100 ng/g. Concentrations for all OCs measured in reindeer liver in 2001 coincide with the lower end of corresponding ranges obtained for the Russian North in 1994/1995 (AMAP, 1998) Values are also in reasonably good agreement with data on reindeer muscle OC contamination reported from Canada and Norway (AMAP, 1998). For example, the following concentrations of OCs were found in muscle samples from two Canadian reindeer herds: 1 ng/g for  $\Sigma$ HCH, 1-2 ng/gfor  $\Sigma$ DDT and 2-10 ng/g for  $\Sigma$ PCB. The ranges of the geometric means for OC concentrations determined in Russia in 2001 were 0.4-1.2 ng/g for  $\Sigma$ HCH; 0.4 -2.6 ng/g for  $\Sigma$ DDT; and 1.3-2.8 ng/g for  $\Sigma$ PCB. The Canadian data for summed PCB concentrations included more PCB congeners than did the Russian 2001 data. The agreement between the Canadian and Russian reindeer data is similar to that seen in the data concerning OCs measured in lichen and mosses in Russia in 2001, and in Canada in 1994.

Area	pg WHO- TEQ/g ww	pg WHO- TEQ/g lipids	pg WHO- TEQ/pg*
	Mu	iscle	
Kola Peninsula	0.98	20	0.20
Pechora basin	0.10	2.2	0.13
Taymir, west	0.031	1.3	0.11
Taymir, east	0.083	0.75	0.17
Chukotka, inland	0.066	4.3	0.10
Chukotka, coast	0.053	2.6	0.059
	Ŀi	ver	
Kola Peninsula	6.5	105	0.22
Pechora basin	2.4	38	0.20
Taymir, west	0.71	18.2	0.24
Taymir, east	0.49	8.0	0.23
Chukotka, inland	0.22	5.1	0.12
Chukotka, coast	0.24	4.2	0.21

Table 5.9. Concentrations (expressed as TEQ) of PCDD/Fs in reindeer tissues the Russian Arctic in 2001.

\* – ratio of PCDD/F concentration in pg WHO-TEQ/g to that in pg/g



Figure 5.12. Levels of PCDD/Fs in muscle of reindeer, hare,

waterfowl (molluscivores), fish (whitefish species), and terrestrial birds (browsers) in the Russian Arctic in 2001.

Samples of reindeer tissue were also analyzed for the other OCs listed in Section 1.2.4. In the majority of samples, all of these additional OCs exhibited levels below the detection limit. Only Mirex and some of the cyclodienes were found in concentrations close to the detection limit (about 0.1 ng/g), and then only in a few samples. This is again consistent with results of previous studies carried out in Canada and in the Russian North in 1995 (AMAP, 1998).

#### (b) PCDD/Fs

Concentrations of 2,3,7,8-substituted PCDD/Fs were analyzed using pooled samples of reindeer tissue. The results are presented in Table 5.9.

PCDD/F levels in reindeer in the Russian Arctic follow a distinct spatial distribution, that is reflected in other terrestrial mammals, birds, and fish (see Figure 5.12). The highest PCDD/F levels are found at the Kola Peninsula, where they are an order of magnitude greater than those found at other sites. After correction for tissue lipid content, residual differences still remain in PCDD/F concentrations between the various tissues types. In contrast to other OCs, PCDD/F levels occurring in the liver of reindeer are, on average, 7 times higher than those in the muscle. Maximum contamination levels were found in liver tissue from the Kola Peninsula (6.5 pg WHO-TEQ/g) and from the Pechora basin (2.4 pg WHO-TEQ/g). The liver concentrations associated with these TEQ values, and also those in muscle of reindeer from the Kola Peninsula, exceed the maximum permissible level for meat, established by the Russian Ministry of Health, which is 0.9 ng/g. All other concentrations measured were below this level.

Three congeners (2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, and 2,3,4,7,8-PeCDF) contribute more than half (and up to 85%) of the total WHO-TEQ in the majority of samples. The average contribution of 2,3,4,7,8-PeCDF, and the most toxic of the dioxins to the total TEQs are similar in waterfowl, terrestrial birds, fish and marine mammals (4.4% and 4.7%, respectively). In terrestrial animals, the average contribution of 2,3,4,7,8-PeCDF is significantly higher, whilst the contribution from the most toxic dioxins is almost the same (13% and 4.2%, respectively). For this reason, the ratio of concentration in pg WHO-TEQ to weight concentration for terrestrial animals is also higher.

#### (c) PAH

Reindeer tissue was analyzed for the same PAH set as vegetation. The geometric means and ranges of PAH concentrations determined in reindeer muscle in the Russian Arctic in 2001 are shown in Tables 5.10a and 5.10b. Results obtained from two sites in Chukotka were treated as one data set, due to the similarity of contamination levels and the small number of samples analyzed. PAH concentrations in liver were, on average, 3-5 times higher than those in muscle, while concentrations found in kidney and muscle are comparable.

Area	NAP	NAP2M	FLE	PA
Kola Peninsula, n=6	21(12-32)	3.5(<2-11)	<0.5-5.1	16(3.6-83)
Pechora basin, n=6	14(2.1-29)	3.2(<2-6.7)	2.1(<0.5-8.5)	13(1.6-36)
Taymir, west, n=5	19(12-28)	5.5(3.1-13)	<0.5-9.8	19(8.7-77)
Taymir, east, n=5	8.1(<2-30)	5.5(2.1-14)	<0.5-6.6	12(2.9-49)
Chukotka, n=4	21(6.8-40)	18(11-23)	6.8(4.5-13)	11(8.6-13)

Table 5.10a. Concentrations (geometric mean and range; ng/g ww) of PAHs<sup>a</sup> in reindeer muscle in the Russian Arctic in 2001.

a NAP = Naphthalene, NAP2M = 2-Methylnaphthalene, FLE = Fluorene,

PA = Phenanthrene

Area	ANT	NT FLU PYR		BAA	
Kola Peninsula, n=6	<0.5-1.4	<0.5-1.1	2.2(<0.5-8.8)	0.6(<0.5-2.6)	
Pechora basin, n=6	<0.5-2.3	<0.5-1.6	2.5(<0.5-14)	1.0(<0.3-4.2)	
Taymir, west, n=5	<0.5-2.2	1.0(<0.5-5.7)	2.8(<0.5-15)	<0.5-2.1	
Taymir, east, n=5	<0.5-2.8	<0.5-1.3	<0.5-8.6	<0.3-1.7	
Chukotka, n=4	0.8(0.6-1.3)	2.9(1.7-4.0)	0.7(<0.5-1)	<0.3	

Table 5.10b. Concentrations (geometric mean and range; ng/g ww) of PAHs<sup>a</sup> in reindeer muscle in the Russian Arctic in 2001. <sup>a</sup> ANT = Anthracene, FLU = Fluoranthene, PYR = Pyrene, CHR = Chrysene

As for OCs, no trend in spatial distribution was found. The PAH composition pattern in reindeer tissues reflects that found in lichen. Naphthalene, 2-methylnaphthalene and phenanthrene contribute well over half of the  $\Sigma$ PAH value. Reindeer tissues were also analyzed for the other PAH listed in Section 5.3.1.(b). In the majority of samples these PAHs were below the corresponding detection limits (0.5-2 ng/g) or, in a few samples of liver tissue, were only slightly above detection limits.

#### (d) Brominated flame-retardants

Samples of reindeer tissues were analyzed for 2,2', 4,4'-tetrabromodiphenyl, 2,2', 4,4',5-pentabromodiphenyl, 2,2', 4,4'-tetrabromodiphenyl ether, and 2,2',



Figure 5.13. Means and ranges of HM concentrations in reindeer liver (wet weight) in the Russian Arctic in 2001. Red lines indicate the maximum permissible concentrations allowed by food safety standards.

4,4',5-pentabromodiphenyl ether. In all samples these occurred at levels below the detection limit of 0.2 ng/g ww.

#### (e) Heavy metals

Concentrations of HMs in reindeer tissues are shown in Table 5.11 and Figure 5.13. Levels of Pb are below the corresponding MPCs in all tissues, although the difference in the case of liver is guite small. Cadmium and Hg levels in all tissues, and at all sites, except for Hg in tissues from Chukotka, are either close to or exceed corresponding MPCs. The greatest disparity between observed levels of the metals under the scope and MPCs occurred in kidney tissue from the Pechora basin, which exceeded the MPC by two and a half times.

The spatial distribution of HM concentrations in reindeer liver tissue is shown in Figure. 5.13. HM levels in other tissues follow a similar pattern. As for OCs, there is no pronounced correlation with the spatial distribution of HMs in lichen. For all HMs, however, the least contaminated areas are inland Chukotka and the east Taymir (Khatanga) regions. As mentioned above, the HM concentration relationship with reindeer age is almost directly proportional, at least for the first few years of the animals' life. The coefficients for this rela-

Table 5.11. Concentrations (mean and	Tissue	Area	Hg	Pb	Cd
standard deviation; g/g ww) of HMs in tissues of reindeer (>3 years of age) in the Russian Arctic in 2001. <sup>a</sup> Hg level in one sample was close to the detection limit (0.001 ng/g ww), and below the detection limit in another. <sup>b</sup> Hg level in both samples was close to the detection limit. <sup>c</sup> Concentration range.	Muscle	Kola Peninsula, n=3	0.010±0.002	0.05±0.02	0.043±0.014
		Pechora basin, n=3	$0.015 \pm 0.005$	0.09±0.02	0.074±0.009
		Taymir, west, n=2	0.014±0.002	0.09±0.01	0.061±0.01
		Taymir, east, n=2	0.0005-0.001 <sup>a, c</sup>	0.012-0.035 <sup>c</sup>	0.016±0.002
		Chukotka, inland, n=2	0.001 <sup>b</sup>	0.013±0.002	0.026±0.005
	Liver	Kola Peninsula, n=3	0.062±0.009	0.27±0.04	0.51±0.14
		Pechora basin, n=3	0.11±0.05	0.37±0.18	0.63±0.13
		Taymir, west, n=2	0.07±0.02	0.33±0.10	0.50±0.20
		Taymir, east, n=2	0.039±0.017	0.14±0.02	0.31±0.07
		Chukotka, inland, n=2	0.030±0.004	0.16±0.02	0.34±0.06
	- Kidney -	Kola Peninsula, n=3	0.24±0.02	0.21±0.05	2.0±0.9
		Pechora basin, n=3	0.36±0.08	0.34±0.16	2.5±0.9
		Taymir, west, n=2	0.33±0.06	0.31±0.15	2.1±1.3
		Taymir, east, n=2	0.12±0.01	0.12±0.02	2.1±1.3
		Chukotka, inland, n=2	0.15±0.03	0.12±0.02	0.78±0.07