

## Chapter 4

## EMISSION SOURCES

Available emission data of Hg, PCBs and  $\gamma$ -HCH for the Northern Hemisphere were collected. Emission sources were divided into several groups according to their geographical location. The key criterion for the selection of this or that region as an aggregate of emission sources is the possible influence of emissions from this region on the Russian North. The number of the selected regions is different for different pollutants. The general division of the Northern Hemisphere into aggregate regions of emission sources is presented in Figure 4.1. For brevity sake we introduce generalized names for some regions, e.g. so-called "Central Asia" actually includes Central, Western, and Southern Asia. Here one should note that composition of some regions varies from pollutant to pollutant. Selected regions of emission sources for all considered pollutants are presented in Table 4.1.



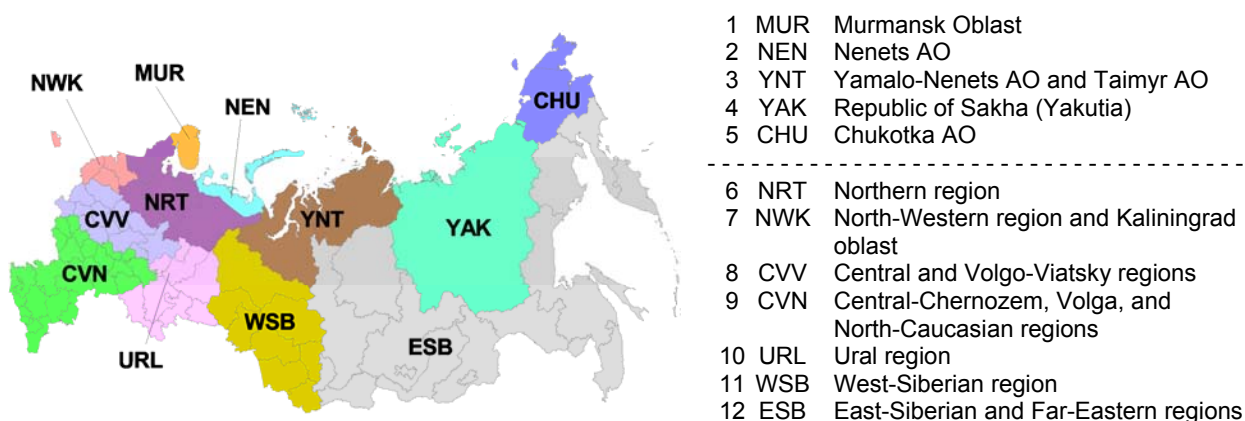
**Figure 4.1.** *Regions of the Northern Hemisphere considered in the source-receptor analysis*

**Table 4.1.** *Selected regions of the Northern Hemisphere*

Hg	PCBs	$\gamma$ -HCH
1. Russia	1. Russia	1. Russia
2. Northern Europe	2. North-western Europe	2. Western Europe
3. Western Europe	3. South-eastern Europe	3. Eastern Europe
4. Eastern Europe	4. Americas	4. Southern Europe
5. Southern Europe	5. South-eastern Asia (including China and Japan)	5. Americas
6. Americas	6. Central Asia (including India and Africa)	6. China
7. Central Asia (including India)		7. India
8. China		8. Asia (Central and South-eastern Asia)
9. Japan		9. Africa
10. South-eastern Asia		
11. Africa		

As one can see from the table among mercury sources China and Japan were isolated as individual emitters. For  $\gamma$ -HCH it seemed important to consider emissions of China and India separately, whereas Northern Europe is not included since  $\gamma$ -HCH emissions in this region are absent in 1996. The Americas (North and South) were considered as one source due to long distances from the Russian North.

Due to close location and significant influence of some regions of the Russian Federation on the Russian North pollution we subdivided the territory of Russia into twelve regions according to the current administrative division and their potential impact on the Arctic ecosystems.



**Figure 4.2.** Location of twelve aggregated regions of Russian Federation chosen for the source-receptor analysis

Location of chosen regions of the Russian Federation is presented in Figure 4.2. The figure contains specification of the regions along with their codes. The first five regions are also considered as receptors. Below the description of emission data for each pollutant of concern, namely, Hg, PCBs, and  $\gamma$ -HCH, is given.

## 4.1. Hg emissions

### *Anthropogenic sources*

Anthropogenic constituent of mercury emission to the atmosphere dominates over industrial and urbanized regions of the world. To evaluate the anthropogenic input of mercury in the Northern Hemisphere we utilize the latest available global emission inventory for 1995 [Pacyna and Pacyna, 2002]. The digital emission data were provided in the framework of the current project by secretariat of AMAP. The original dataset has global coverage with resolution  $1^\circ \times 1^\circ$  and mercury chemical speciation into three forms: elemental  $Hg^0$ , gaseous oxidized  $Hg^{2+}$ , and particulate  $Hg_{part}$ . Besides it distinguishes area and point sources, the latter ones are divided into three categories according to their height (below 50 m, 50-150 m, higher 150 m). To adapt the emission of each species to the model input it has been redistributed to the model grid ( $2.5^\circ \times 2.5^\circ$ ) assuming uniform distribution over a grid cell. It is assumed that sources of the first two height categories emit to the lowest model layer, whereas those of the third one emit to the second layer.

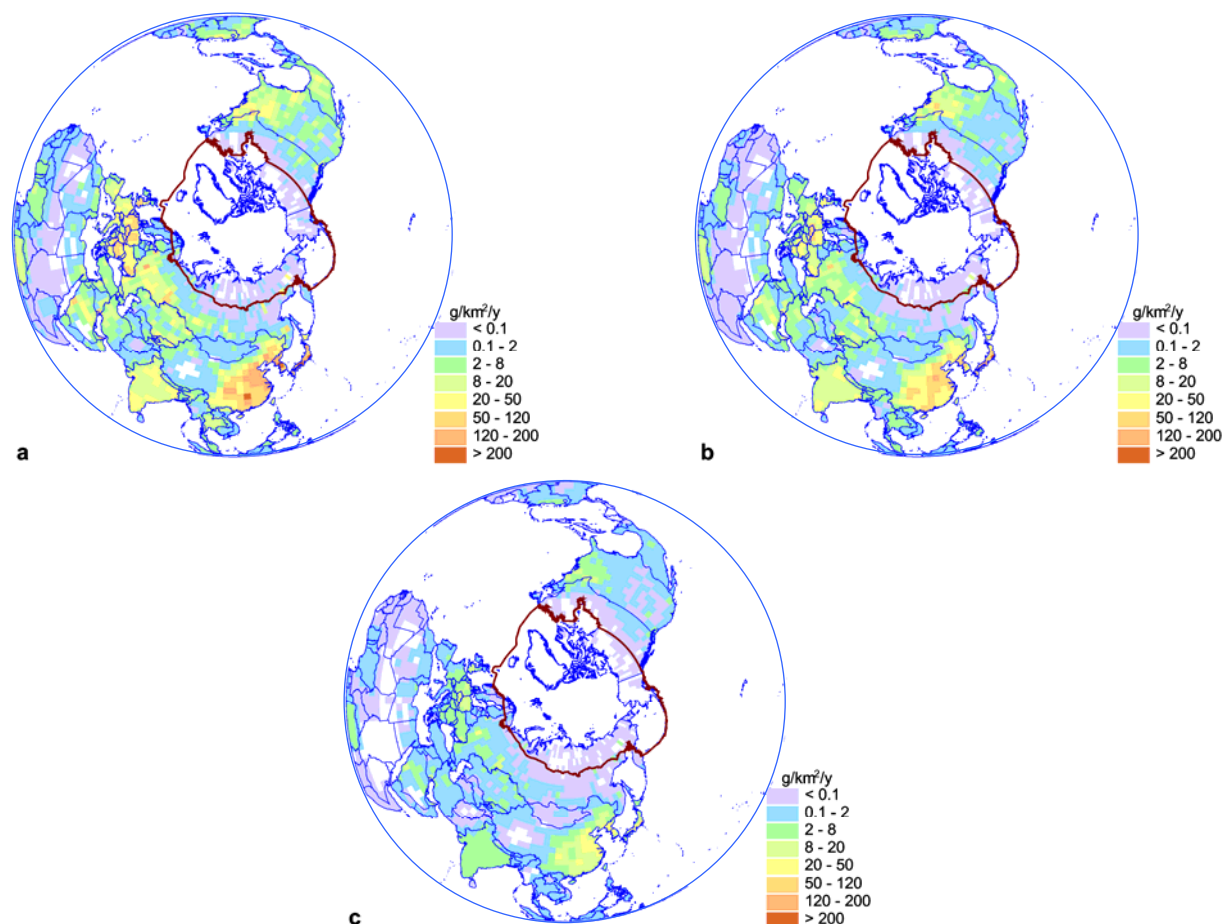
Spatial distribution of anthropogenic mercury emission density in the Northern Hemisphere is presented in Figure 4.3 (for each species individually). As seen from the figures the most significant emission sources are in Eastern Asia, Europe and the Eastern part of North America. Some emissions are also in Hindustan and Arabian Peninsula. The total anthropogenic mercury emission from the Northern Hemisphere is estimated as 1887 tonnes per year.

In order to assess mercury transport to the Russian North the whole hemispheric emission field was divided into several continents and regions (see Table 4.1): Russia, Northern Europe, Western Europe, Eastern Europe, Southern Europe, Africa, Central Asia (including India), South-Eastern Asia (excluding China and Japan), China, Japan, and the Americas.

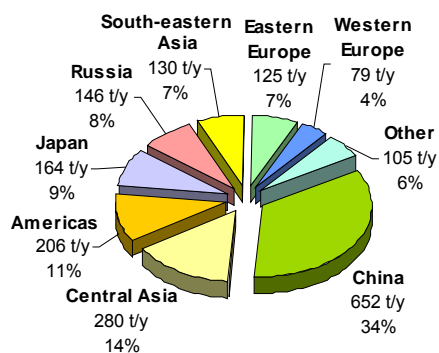
Relative contributions of each continent or region to the total mercury emission in the Northern Hemisphere are presented in Figure 4.4. According to the diagram more than one third (34%) of the

total mercury is emitted from China. Considerable emissions are also in Central Asia (14%), the Americas (11%), Japan (9%), and Russia (8%). The contributions of other regions do not exceed 7%.

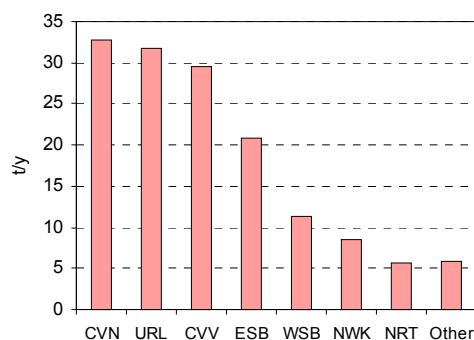
Figure 4.5 shows contributions of different regions of Russian Federation to its total emission. Central-Chernozem, Volga, and North-Caucasian regions (CVN, 22%), Ural region (URL, 22%), and Central and Volgo-Viatsky regions (CVV, 20%) are the sources, which make the main contribution to the total anthropogenic emission of mercury in Russian Federation.



**Figure 4.3.** Spatial distribution of mercury anthropogenic emissions density in the Northern Hemisphere in 1995: (a) –  $Hg^0$ ; (b) –  $Hg^{2+}$ ; (c) –  $Hg_{part}$ ,  $g/km^2/y$



**Figure 4.4.** Relative contribution of different continents and regions to the total anthropogenic emission of mercury in the Northern Hemisphere



**Figure 4.5.** Contribution of different regions to the total anthropogenic emission of mercury in Russian Federation

Annual emissions of each mercury species from different regions in the Northern Hemisphere are summarized in Table 4.2. It should be noted that average speciation (over continents of the Northern Hemisphere) is approximately 58% of  $Hg^0$ , 33% of  $Hg^{2+}$ , and 9% of  $Hg_{part}$ .

**Table 4.2.** Annual anthropogenic emission of mercury species in the Northern Hemisphere, t/y

Region	$Hg^0$	$Hg^{2+}$	$Hg_{part}$
China	372	223	57
Central Asia	151	103	26
Americas	113	72	20
Japan	97	53	15
Russia	94	41	11
South-eastern Asia	80	39	10
Eastern Europe	72	42	11
Western Europe	53	21	6
Africa	33	21	5
Southern Europe	27	10	3
Northern Europe	3	2	1

### Natural sources and re-emission

Estimates of the global natural emission and re-emission of mercury available in the literature are very uncertain (see Table 4.3). The most reasonable of them vary from 700 to 3200 t/y for the continents and from 600 to 2900 t/y for the World Ocean (here we do not consider evidently overestimated values more than  $1 \cdot 10^4$  t/y). Detailed survey of natural emission fluxes was made by the authors in [Travnikov and Ryaboshapko, 2002]. In the current assessment we decided to consider two emission scenarios to evaluate possible uncertainty of natural emission and re-emission. The first one is based on highest emission estimate [Seigneur et al., 2001] – 2000 t/y from land and 2000 t/y from the ocean (Scenario I). The second scenario utilizes the lowest estimate from [Lamborg et al., 2002] – 1460 t/y from land and 800 t/y from the ocean (Scenario II). Here we do not distinguish natural emission and re-emission of mercury.

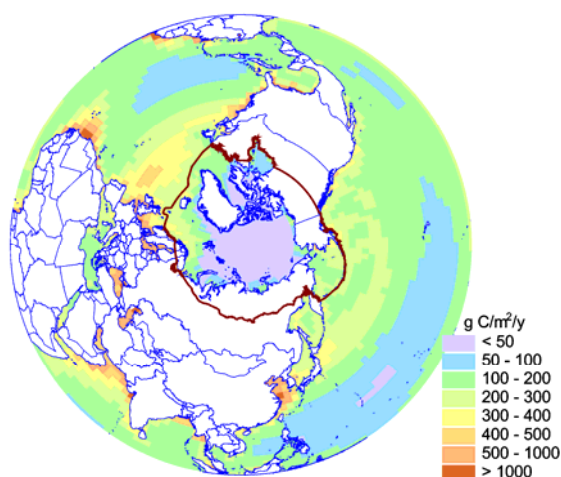
**Table 4.3.** Natural mercury emissions and reemission to the atmosphere

Emission value, t/y			Reference	Note
Land	Ocean	Total		
		$1.9 \cdot 10^5$	Jaworowski et al., 1981 (quoted in Geological Survey of Canada, 1995)	
	2900		Kim and Fitzgerald, 1986	$\pm 1800$ t/y
730	1770	2500	Nriagu, 1989	
		3000	Lindqvist et al., 1991	From 2000 to 9000 t/y
		$2.9 \cdot 10^4$	Geological Survey of Canada, 1995	3500 t/y for Canada only
1000	2000	3000	Fitzgerald and Mason, 1996	1400 t/y of re-emission from the ocean
1400-3200			Lindberg et al., 1998	
1000			Carpi and Lindberg, 1998	
700			Ebinghaus et al., 1999	500 t/y in mercury belts
2000	2000	4000	Seigneur et al., 2001	1500 t/y of re-emission from land
1320	1100	2420	Bergan and Rodhe, 2001	Without re-emission
1460	800	2260	Lamborg et al., 2002	400 t/y of re-emission from the ocean and 460 t/y from land

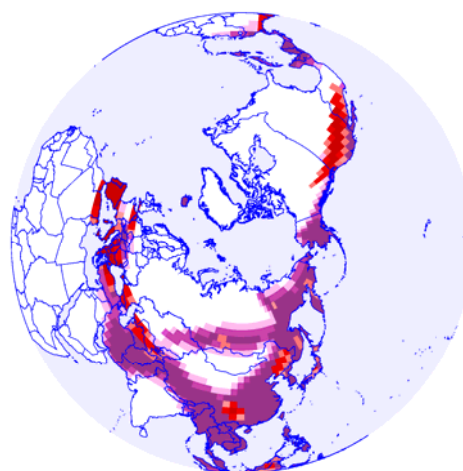
We distinguish five types of the Earth surface: (1) glaciers, (2) seawater, (3) background soils, (4) soil of the geochemical mercury belts, and (5) soil of mercury deposit areas. Mercury emission fluxes differ for different surface types. Glaciers of the Northern Hemisphere include Greenland, permanent ice of the Arctic and high-mountain glaciers. It is presumed that there is no mercury emission from this type of the surface.

To distribute mercury emission over the ocean we accept the idea suggested by *J. Kim and W. Fitzgerald* [1986] that mercury emission intensity is proportional to biological productivity in seawater. For this purpose we utilize monthly mean data on the ocean primary production of carbon (see Fig. 4.6) described in [*Behrenfeld and Falkowski*, 1997] and available through the Internet (<http://marine.rutgers.edu/opp/>). According to the data global primary productivity is equal to  $4.6 \cdot 10^{13}$  kg C/y. Since about 60% of the global ocean primary production falls on the Northern Hemisphere we assess the total ocean mercury emission in the Northern Hemisphere as 1200 t/y for Scenario I and 500 for Scenario II.

The entire continental area in the Northern Hemisphere constitutes approximately 75% of the global land area (excluding Greenland and the Antarctic). Thus, the total natural emission of mercury from land in the Northern Hemisphere can be roughly assessed as 1500 t/y for Scenario I and 1100 for Scenario II. Mercury flux from the land significantly depends on soil mercury content. From this point of view we divide land surface into three categories according to the adopted soil classification: background soils, soils of mercury belts, and soils of mercury deposits. Location of geochemical mercuriferous belts and productive mercury deposits areas are schematically shown in Figure 4.7. These data were generalized from [*Jonasson and Boyle*, 1971; *Gustin et al.*, 1999] and adapted to the model grid. In the current assessment we do not take into account any influence of vegetation on the emission process.



**Figure 4.6.** Spatial distribution of annual primary production of carbon in the ocean of the Northern Hemisphere [*Behrenfeld and Falkowski*, 1997], g C/m<sup>2</sup>/y



**Figure 4.7.** Generalized map of geochemical mercuriferous belts (magenta color) and productive deposit areas (red color) in the Northern Hemisphere [*Jonasson and Boyle*, 1971; *Gustin et al.*, 1999]

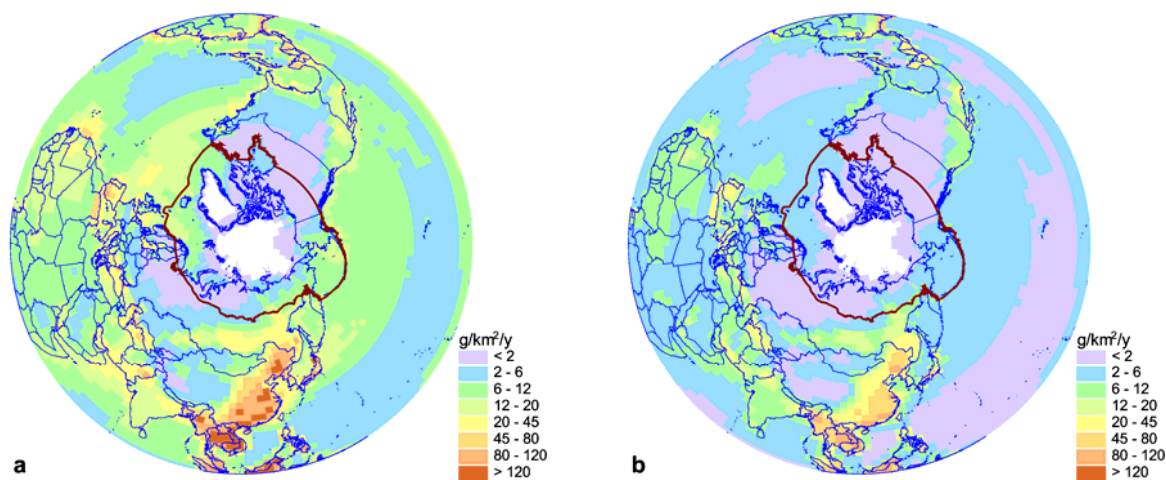
As it was mentioned in Section 2.1 temperature dependence on mercury emission flux can be described by an Arrhenius type equation. Besides, empirically derived activation energies of the process have close values both for background (17.3 - 29.4 kcal/mole) and for enriched soils (25.2 kcal/mole). To parameterize the temperature dependence we choose value 20 kcal/mole for all soil

types. On the contrary, we consider pre-exponential factor depending on the soil type: the factor for background soil is five times lower than for soils of the mercury belts, and ten times lower than for the deposits areas. Besides, the emission flux is assumed to be zero for negative values of the soil temperature in the centigrade scale. Fitting total land emission in the Northern Hemisphere to the adopted value we obtain the following temperature dependence of the mercury flux from soil:

$$F_{Hg} = \begin{cases} A_s \exp(-10^4 / T_s), & T_s > T_0 \\ 0, & T_s \leq T_0 \end{cases}$$

Here mercury flux  $F_{Hg}$  is in  $\text{ng/m}^2/\text{h}$ ;  $A_s$  is equal to  $6.4 \cdot 10^{14}$  for background soils,  $3.2 \cdot 10^{15}$  for the mercury belts, and  $6.4 \cdot 10^{15}$  for deposit areas; surface temperature  $T_s$  is in K and  $T_0 = 273$  K. Currently we do not consider dependence of the mercury emission flux on insolation. It is assumed that mercury is emitted to the atmosphere in the elemental form both from land and from the ocean.

Resulting spatial distribution of mean annual mercury emission from natural sources is shown in Figure 4.8 for both scenarios. As one can see from the figure the highest mercury emissions from land correspond to mercuriferous belts and deposit areas (compare with Fig. 4.7). Mercury fluxes at the high latitudes are considerably lower even for the mercury belts due to low soil temperature. Emission flux from seawater is lowest in the Middle Pacific and the highest in internal seas and coastal waters at low latitudes. There is no mercury emission from Greenland and from seawater near the pole because of permanent glaciers.

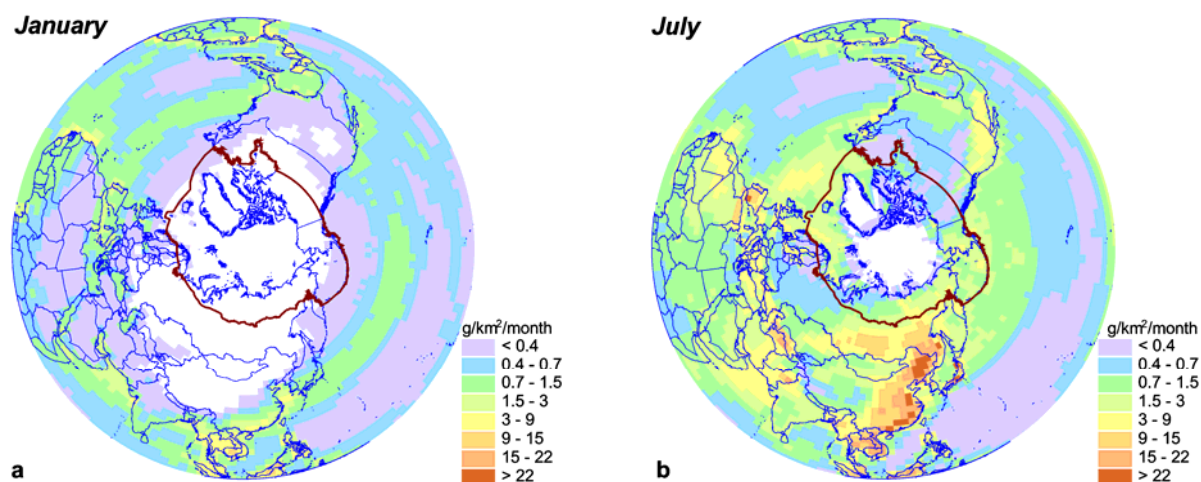


**Figure 4.8.** Spatial distribution of mean annual natural emission density of mercury in the Northern Hemisphere: (a) – Scenario I, (b) – Scenario II

Figures 4.9.a and 4.9.b illustrate seasonal variation of natural mercury emission basing on Scenario I. As one can see variation of land emission flux is considerably higher (up to an order of magnitude) than that of seawater due to greater amplitude of land surface temperature alteration. Moreover, a significant part of the surface has no mercury emission in wintertime due to negative surface temperatures.

To assess influence of natural sources from different parts of the Northern Hemisphere the emission field was divided into 8 general parts: Europe, Asia, the Americas, Africa, the Atlantic Ocean, the Pacific Ocean, the Indian Ocean, and the Arctic Ocean.





**Figure 4.9.** Spatial distribution of monthly mean natural emission density of mercury in the Northern Hemisphere (Scenario I), g/km<sup>2</sup>/month

## 4.2. PCB emissions

This section outlines the data on PCB emissions which were used in the AMAP project for the assessment of the impact of the different regions of the Northern Hemisphere on the contamination of the Russian North. The global emission inventory of 22 PCB congeners for 1930-2000 was prepared by *K.Breivik et al.* [2002b]. The inventory was based on historical data on global production and consumption of these PCBs [Breivik et al., 2002a]. A concise review of the data presented in papers [Breivik et al., 2002a,b] and of the Northern Hemisphere PCB emission sources selected for modeling purposes is given below.

### 4.2.1. PCB emission estimates according to [Breivik et al., 2002a,b]

Mixtures of chlorinated biphenyls with varying numbers of chlorine atoms and with different sets of individual homologues and congeners have been produced in many countries under various trade names: Aroclor (USA), Clophen (West Germany), Kanechlor (Japan), Delor (Czechoslovakia), Pyroclor (United Kingdom), Sovol, Sovtol (Russia) and others. The total global production of PCBs from 1930 to 1993 amounted to approximately 1.3 million t. More than 70% was accounted for by tri-, tetra and penta-chlorinated biphenyls. To quantify the production of the 22 selected congeners for the period under consideration, data on the production and chemical composition of the individual technical mixtures (for example, Aroclor 1242) were used. In the absence of required data from some producers, the annual production of individual congeners and homologues were estimated by a set of annual production-weighted default compositions.

The authors assessed the global consumption pattern by compiling information on import, export and national consumption of PCBs by country and year, including restrictions on PCB imports in various countries and regions. The inventory of PCB global consumption involves estimates for 114 countries. The results suggest that almost 97% of the intentionally produced PCBs have been used in the Northern Hemisphere.

To go from data on the prolonged historical production of PCBs to calculations of historical global emissions (from 1930 to 2000), a dynamic mass balance model was developed, parameterized and

applied. With the use of a 1-year time step, four usage sub-categories (open usage, small capacitor usage, nominally closed usage and closed usage), four disposal source categories (landfills, open burning, waste incineration and destruction) and two accidental release pathways (spillage to soil and fires) were considered. The contribution of an individual congener to the total emission for a specific year and country was determined from information on annual national consumption and by means of a number of model parameters: usage factors, product lifetimes, disposal factors, accidental release factors, degradation factors and emission factors.

Taking into account the uncertainties of model parameters in the default emission estimate (i.e. Mid estimate) two additional scenarios were considered – High and Low emissions. Some of the most relevant model parameters were adjusted within reported or anticipated ranges. The emissions of 22 individual PCB congeners were evaluated for 114 countries for the period of 1930 to 2000, with allowance made for High, Middle and Low emission scenarios. The total historical global emissions of the 22 PCB congeners for the Low and High scenarios were 440 and 91722 t. The default (Mid) emission value was estimated at 7709 t. The relative importance of historical emissions from three major source categories (usage, waste disposal and accidental release) and total historical emissions by congener were estimated in this paper for the three emission scenarios. Table 4.4 shows some estimates obtained with the use of the High emission scenario for four selected PCB congeners.

**Table 4.4.** *Total historical emissions (t) and relative importance of historical emissions from the major source categories (%) for four individual congeners (High scenario)*

Emission, t	PCB-28	PCB-118	PCB-153	PCB-180
	11658	3047	2596	1037
Contributions:				
Use, %	83	13	16	5
Waste disposal, %	6	54	49	58
Accidental release, %	11	33	35	37

According to the data presented, usage is the predominant emission pathway for less chlorinated PCB congeners; for more chlorinated PCBs it is waste disposal (especially open burning). One of the most substantial results of this work is the assessment of the temperature impact on both the absolute value of PCB emissions as well as on the PCB emission patterns.

Thus in the work [Breivik *et al.*, 2002b] temporal and spatial distribution of the global emissions of individual PCB congeners, which is a reflection of the global consumption pattern, were determined for the first time. The diversity of historical usage, waste disposal and accidental release pathways made the problem of filling the gaps between the consumption and emissions difficult and led to an equally complex and diverse true emission pattern. Due to the tremendous uncertainties at the temporal and spatial scales involved in this emission inventory, the actual emission values should be considered as order-of-magnitude estimates.

#### 4.2.2. *PCB emission sources in the Northern Hemisphere*

Spatial distribution of PCB emissions in the Northern Hemisphere obtained on the basis of the High emission scenario available in [Breivik *et al.*, 2002b] and used for modeling within the framework of this project is shown in Figure 4.10 with the example from 1996. The total emissions of 22 PCB congeners from the Northern Hemisphere in 1996 are equal to 662 t. The four considered congeners made a combined contribution of about 20% to this value. At the same time, total emissions of PCB-28 from the Northern Hemisphere in 1996 was about 80 t, that of PCB-118 – about 23 t, that of PCB-153 – about 16 t and that of PCB-180 – about 4.5 t. For emission distribution over the grid with spatial

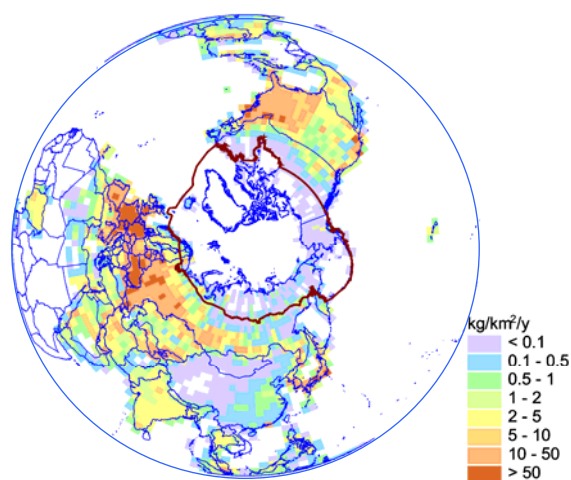


resolution  $2.5^{\circ} \times 2.5^{\circ}$ , a 1990 population distribution data set available from the CGEIC website (<http://www.ortech.ca/cgeic>) was used. Population density is considered a suitable surrogate parameter, as the PCB consumption is generally linked to the use of electrical equipment [Breivik *et al.*, 2002a].

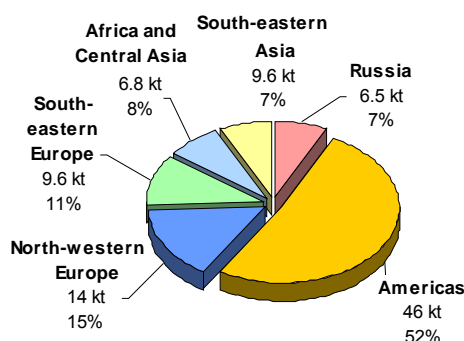
To investigate the impact of different PCB sources on the contamination of the considered regions-receptors within the Russian North six main groups were set apart:

1. Americas
2. North-western Europe
3. South-Eastern Europe
4. Central Asia and Africa
5. South-eastern Asia
6. Russia.

According to K.Breivik *et al.* [2001b] contributions of these groups to PCB total emissions during the period from 1930 to 2000 are presented in Figure 4.11. The chief contribution of Americas to PCB emissions in the Northern Hemisphere is accounted for by the USA. From the perspective of total production, the USA produced PCBs from 1930 to 1977 amounting to about 642 kt making up more than half of the historically produced PCBs. At the same time, the USA was responsible for as much as 46% of the total historical global PCB consumption. A sizable contribution of North-western Europe (15%) to historical total emissions in the Northern Hemisphere was made mostly by inputs from West Germany (total production approximately 159 kt), France (total production approximately 135 kt) and the United Kingdom (total production approximately 67 kt), the region being at the same time a major consumer of PCBs (7.1%, 4.1% and 2% of total historical global consumption, respectively). During the considered period Russia was responsible for 7% of the total emission within the Northern Hemisphere. Russian production of PCBs amounted to 173.8 kt, 60% of which utilized in the national consumption, which was 7.9% of total global consumption. Southern and Eastern Europe contributions to historical total emissions in the Northern Hemisphere total 11%. Czechoslovakia, Spain and Italy produced PCBs in substantial quantities in this region. The contribution of South-eastern Asia to historical emissions of the Northern Hemisphere was 7%. In this region, Japan played a dominant role (total production approximately 59 kt; contribution to global consumption - about 4%).

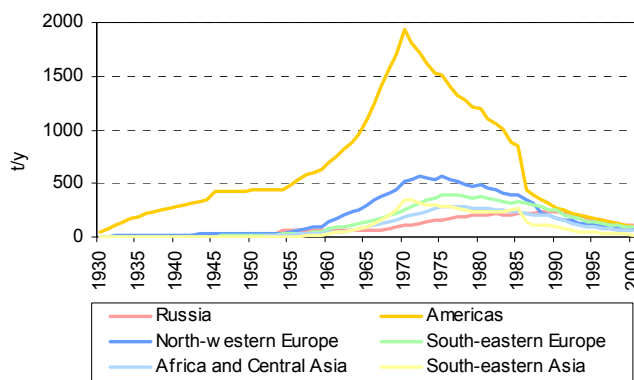


**Figure 4.10.** Spatial distribution of the total emissions of 22 PCB congeners in the Northern Hemisphere in 1996, kg/km<sup>2</sup>/y



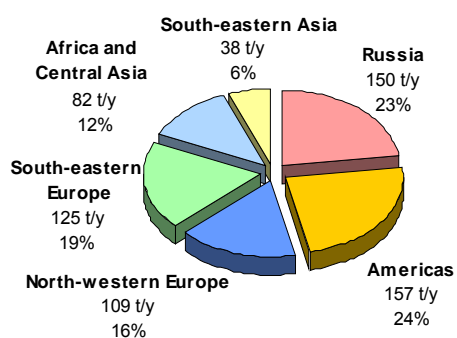
**Figure 4.11.** Distribution of PCB historical emissions in the Northern Hemisphere (1930-2000)

PCB emission dynamics in the major source groups of the Northern Hemisphere in 1930-2000 estimated on the basis of data available in [Breivik *et al.*, 2002a] is plotted in Figure 4.12. In the majority of countries, PCB emissions have reached their maximum by the 70s, i.e. during a period of widespread intensive consumption of products containing these chemicals. PCB peak production in 1970 amounted to 75.5 kt. At that time, the USA made the largest contribution to emissions. Western Europe (namely West Germany) and Japan also contributed significantly. In these countries and in a number of others, PCB emissions had drastically decreased by the 1980s due to limitation or complete prohibition of use of these species. In Russia emissions were at a maximum in the 1990s. The temporal variation in emissions in Russia shown in Figure 4.12 reflects the prolonged period of PCB production and consumption there. In fact PCB production ceased in Russia only in 1993 and the consumption of PCB-containing products still persists [AMAP, 2000].

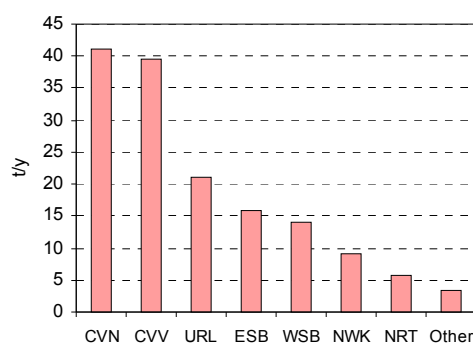


**Figure 4.12.** PCB emission dynamics in countries and regions in 1930-2000, t/y

In comparison with the distribution of contributions of the major source groups to the total historical emissions in the Northern Hemisphere (Fig. 4.11), a similar distribution for 1996 (selected for model computations) differs appreciably. Figure 4.13 demonstrates the relative contribution of the major source groups to the total PCB emissions of the Northern Hemisphere in 1996, estimated on the basis of data from [Breivik *et al.*, 2002a]. Thus the USA's contribution to emissions within the Northern Hemisphere had decreased almost in half by 1996. In contrast, the combined contribution of East and South Europe reached 19% and the contribution of Russia increased up to 23% and actually became equal to that of the USA. A detailed division of Russian sources into 12 groups was made in accordance with the following criteria - location (in the Arctic zone or nearby), PCB quantities in functioning equipment, in wastes and the amounts of PCBs released into the environment. According to the inventory of PCBs in the Russian Federation [AMAP, 2000], the highest amount of PCBs in PCB-containing equipment was detected in the Central-Chernozem, Volga and North Caucasus regions (34% in whole). The highest PCB amount in wastes was detected in the Urals region (46%) [AMAP, 2000]. These regions are also distinguished by the maximum total amount of PCBs released from functioning and phased out equipment [AMAP, 2000].



**Figure 4.13.** Contribution of the major source groups of the Northern Hemisphere to the total PCB emissions in 1996



**Figure 4.14.** Contributions of different Russian regions to PCB emissions in 1996

Contributions to PCB emissions of region-sources within the Russian Federation (Fig.4.2) [Breivik *et al.*, 2002b] are illustrated in Figure 4.14. The diagram demonstrates that the main contribution to PCB total emissions in the Russian Federation originate in the central and southern regions of the European part of Russia. This is in agreement with the estimates presented in the *AMAP Report* [2000].

#### **4.2.3. Seasonal variations of PCB emissions**

Model calculations of individual PCB congeners were carried out on the basis of the global emission inventory of PCBs given in the work [Breivik *et al.*, 2002b]. This expert estimate does not include an evaluation of the seasonal variation of PCB emissions. The climatic (temperature) dependence of emissions was determined only for such source categories as soils and landfills. The emission factors (for temperatures of 5, 10 and 20°C) developed for these sources were allocated to the considered countries, based on global temperature maps. However, according to [Breivik *et al.*, 2002b] these source categories presumably contribute less to the total emissions. Nevertheless K.Breivik *et al.* [2002b] mentioned that temperature is expected to affect the emission pattern of PCBs that are capable of volatilization at ambient temperatures (the continuous sources).

It can be supposed that in actuality PCB emissions vary seasonally having higher values in summer (warmer months) due to more active volatilization in accordance with individual PCB congener volatility. At present, however, quantifying seasonal variations is difficult because of uncertainties in emission factors, the absence of necessary data and peculiarities of contributions made by various source categories to PCB emissions in specific countries. Furthermore, in a number of other expert estimates of PCB emissions, for instance, for the European region [Baart *et al.*, 1995] the characteristics of total emission variability over the year are also not available. Therefore in model calculations seasonal variations of PCB emissions were not taken into account.

#### **4.2.4. Uncertainties of PCB emission estimates**

Basic uncertainties involved in estimates of the global consumption and emissions of PCB individual congeners according to K. Breivik *et al.* [2002 a,b] are:

##### ***Uncertainties in estimates of global production and consumption***

1. Due to deficient information, the inventory of PCB global production did not include the amount of these substances produced in factories of Poland, East Germany and Austria.
2. Data on production reported for a period in excess of one year (e.g. a 5-year period) were uniformly distributed over the indicated period.
3. The highest uncertainty in the global production estimate lies in default homologue and congener composition (e.g. for France, Spain and Italy) and variability between characteristic technical mixture compositions.
4. For individual congeners the uncertainty in the global production estimate increased for the period after the 70s due to the increased number of PCB producers. Nevertheless, recent data are more accurate than the data from the past.
5. In realization of the method of global consumption estimation, a number of assumptions were made. Reliable information was available only for countries with traditionally high consumption of PCBs. For other countries, assumptions based on trade between different countries and regions were made using Gross Domestic Product as a surrogate parameter.

6. Approximately 70 non-OECD countries are not involved in the estimate; otherwise, the probable consumption in them would be about 6% of the total export in countries of this category. It is presumed that it introduced minor uncertainties into the general inventory.

### ***Uncertainty in the emission estimate***

1. The representativeness and accuracy of emission factors are the major source of uncertainties in a given estimate of emissions.
2. The global movement of PCB-containing products and wastes between countries was not considered in detail.
3. In view of the deficiency of reasonable estimates of the detailed spatial patterns, potential “point sources” of PCB atmospheric emissions were not considered separately. For the same reason incidental or unwanted formation of PCBs and emissions from the combustion process (de novo synthesis) were also not considered.

Uncertainties of estimates in global consumption and emissions will grow with the increase of the specification level (e.g. more detailed usage and waste disposal categories). Clearly the supposed uncertainties in emission estimates appear higher than the uncertainty in production estimates.

## **4.3. $\gamma$ -HCH emissions**

This section discusses data on emissions of  $\gamma$ -HCH, an isomer of hexachlorocyclohexane (HCH), used in modeling in the AMAP project. HCH is an organochlorine insecticide of a complex action widely used all over the world since the 1940s [Li *et al.*, 1996]. This insecticide has two main compositions - technical HCH (with a range of  $\gamma$ -HCH content from 8 to 15%) and lindane (containing not less than 99% of  $\gamma$ -isomer). By the end of the 1970s the application of technical HCH was the basic source of  $\gamma$ -HCH. Its maximum usage in 1981 was approximately 334 kt [Li *et al.*, 1998]. The majority of the developed countries prohibited the application of HCH in the 1970s. At that time the usage of technical HCH in North America was prohibited in Canada and the USA, but it was still used in Mexico until 1983 [Walker *et al.*, 1999]. At a later time lindane becomes the basic source of  $\gamma$ -HCH. For instance, in China the production and application of technical HCH was prohibited in 1983 and in 1991 lindane was coming into use [Li *et al.*, 1998, Macdonald *et al.*, 2000]. In Europe 81 kt of lindane [Breivik *et al.*, 1999] was applied from 1970 to 1996. Due to the prohibition of lindane in a number of countries, according to [Breivik *et al.*, 1999]  $\gamma$ -HCH use in Europe in 1996 was about one third of its level observed in the 1970s. Nevertheless in some countries of the Northern Hemisphere it was still in use until the late 1990s [AMAP, 1998; Walker *et al.*, 1999].

### **4.3.1. Data on $\gamma$ -HCH use and emissions in the Northern Hemisphere**

The official data on  $\gamma$ -HCH emissions submitted by countries to the UN ECE Secretariat are used for the assessment of gridded emissions in the Northern Hemisphere. Only 13 countries have submitted their totals for at least one year for the period of 1990-2000 [Vestreng and Klein, 2002]. In the 1990s a number of expert estimates of  $\gamma$ -HCH application and emissions both on the regional and global scale

were made. In particular *Y.-F. Li et al.* [1996] have collected data on global use of technical HCH and  $\gamma$ -HCH for 1980 and 1990 and distributed over the grid with spatial resolution  $1^\circ \times 1^\circ$  in accordance with the distribution of cultivated land areas. In further works [*Li et al.*, 1998; *Li*, 1999a,b] the global inventory of HCH use and its spatial distribution have been refined. Within the framework of the POPCYCLING-Baltic project an inventory of  $\gamma$ -HCH use and emissions and their spatial distribution in Europe from 1970 to 1996 was made [*Breivik et al.*, 1999; *Pacyna et al.*, 1999]. As there is no integral pattern of  $\gamma$ -HCH emissions in the Northern Hemisphere at the moment, some emission scenarios based on official and expert estimates had to be worked out. A brief description of  $\gamma$ -HCH emission data for 1990-96 used in modeling is given below.

### 4.3.2. Official data on HCH use and emissions

Table 4.5 demonstrates the official data for Europe and the USA used in modeling [*Vestreng and Klein*, 2002].

It should be mentioned that application of these data to model calculations was complicated by the absence of comments on HCH isomer composition. For this reason, it was accepted that the available data refer to  $\gamma$ -HCH emissions.

**Table 4.5.** Official HCH emission data used in modeling, t/y

Country	Official emission data						
	1990	1991	1992	1993	1994	1995	1996
Austria					12.000	8.056	8.640
Croatia	9.400						12.800
Denmark					0.061		
Germany					15.000		
Hungary	9.281	0.060	0.012	0.462	0.798	1.650	2.400
Netherlands	0		0		0	0	0
Norway			0	0	0	0	0
Spain	9.204	9.204	6.705	5.917	10.650	9.598	9.730
United Kingdom	100.013	86.189	74.756	65.250	57.301	50.616	44.963
USA							0.235

In the former USSR  $\gamma$ -HCH was used extensively as a pesticide during the years 1987-91. In spite of its prohibition in 1990, the use of remaining quantities in agriculture, forest and municipal economy continued until 1996 [*Fedorov and Yablokov*, 1999, *List of chemical and biological ...*, 1994]. Thus  $\gamma$ -HCH use in Russia in 1997 was assumed to be zero. The use of  $\gamma$ -HCH in the European part of Russia in 1990, equal to 923 tonnes was estimated on the basis of the data on pesticide application in this region [*Revich et al.*, 1999]. To get from  $\gamma$ -HCH use to its emissions, an emission factor for lindane agricultural use equal to 0.5 was employed [*Atmospheric Emission Inventory Guidebook*, 1999]. For the Asian part of the Russian Federation,  $\gamma$ -HCH emissions in 1990-96 were evaluated on the basis of information about the application of this insecticide in agriculture in different regions of the Russian Federation available in reports by Roshydromet [*Year-books*, 1992, 1993, 1999]. Aside from that, the amount of  $\gamma$ -HCH used in the Irkutsk region were estimated on the basis of data from *L.P. Ignatieva and M.F. Savchenko* [1994]. According to the obtained data,  $\gamma$ -HCH application tended to decrease from 1987 to 1997. Table 4.6 shows the dynamics of  $\gamma$ -HCH emissions over European and Asian Russia estimated by interpolation of published national data on the use of this pesticide.

Information about lindane use in Uzbekistan was found in [*Ananieva et al.*, 1990].

**Table 4.6.** Dynamics of  $\gamma$ -HCH emissions over European and Asian Russia, t/y

Russia	1990	1991	1992	1993	1994	1995	1996
European part	461.5	395.6	329.6	263.7	197.8	131.9	65.9
Asian part	47.8	29.0	12.3	5.1	2.3	1.1	0.5

### 4.3.3. Expert estimates of $\gamma$ -HCH use and emissions in a number of countries and regions in the Northern Hemisphere

Because official data are inadequate for the compilation of  $\gamma$ -HCH emission scenario for the Northern Hemisphere, they were complemented by expert estimates. In particular data on  $\gamma$ -HCH emissions in Europe from 1970 to 1996 [Pacyna *et al.*, 1999] was used, determined under the POPCYCLING-Baltic project from the inventory of the application of this insecticide in European counties [Breivik *et al.*, 1999]. In this expert estimate, the spatial distribution of  $\gamma$ -HCH emissions and use in Europe were determined on the basis of crop area as a surrogate parameter.

**Table 4.7.**  $\gamma$ -HCH application in a number of countries of the Northern Hemisphere in 1990, t/y

Country	Use in 1990
Algeria	14
Canada	284
China	100
Honduras	137
India	7650
Mexico	261
Niger	397
Pakistan	3
USA	114
Total	8960

To assess emission totals, in some countries within the Northern Hemisphere we employed expert estimates of  $\gamma$ -HCH application on the global scale from [Li *et al.*, 1996; Li *et al.*, 1998 and Li *et al.*, 1999a]. Table 4.7 presents data on the use of this insecticide in 1990 [Li *et al.*, 1996 and Macdonald *et al.*, 2000].

According to [Macdonald *et al.*, 2000], since 1995 usage of  $\gamma$ -HCH in China has been approximately 500 t/y and since 1991  $\gamma$ -HCH use in India has remained at approximately 3600 t/y.

### 4.3.4. $\gamma$ -HCH emission sources in the Northern Hemisphere

The scenario of  $\gamma$ -HCH emissions in the Northern Hemisphere for 1990-96 based on official data and expert estimates is shown in Table 4.8. According to these data the total  $\gamma$ -HCH emissions from the Northern Hemisphere in 1996 amounted to 3445 t.

**Table 4.8.**  $\gamma$ -HCH emissions in the Northern Hemisphere based on official data and expert estimates, t/y

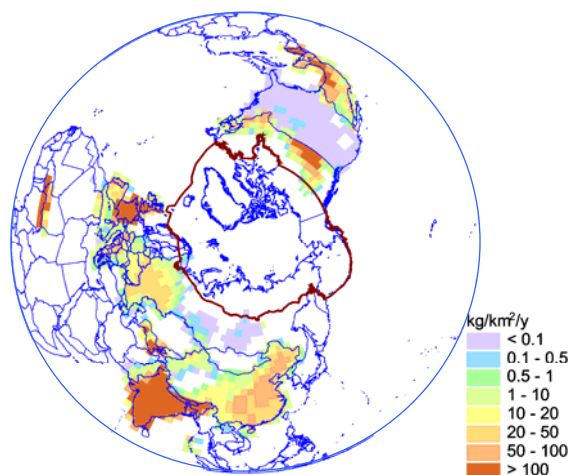
Sources	1990	1991	1992	1993	1994	1995	1996
Americas	398	389	379	370	360	351	341
Asia	84	84	83	83	83	83	83
Eastern Europe	37	22	17	19	18	20	20
Western Europe	419	362	642	643	658	633	632
Southern Europe	337	295	277	21	25	33	47
Northern Europe	3	5	4	3	0	0	0
Africa	206	206	206	206	206	206	206
Russia	509	425	342	269	200	133	66
China	50	50	50	50	50	250	250
India	3825	1800	1800	1800	1800	1800	1800



The approach of *J.Pacyna et al.* [1999b] was used to obtain  $\gamma$ -HCH emission distribution. We used crop area distribution for the evaluation of emission distribution in the Northern Hemisphere over the grid with spatial resolution  $2.5^\circ \times 2.5^\circ$ .  $\gamma$ -HCH emission distribution for 1996 selected for calculations is demonstrated in Figure 4.15.

For the model calculations, nine groups of sources in the Northern Hemisphere were formed:

1. Americas
2. Eastern Europe
3. Western Europe
4. Southern Europe
5. Russia
6. Asia
7. Africa
8. China
9. India

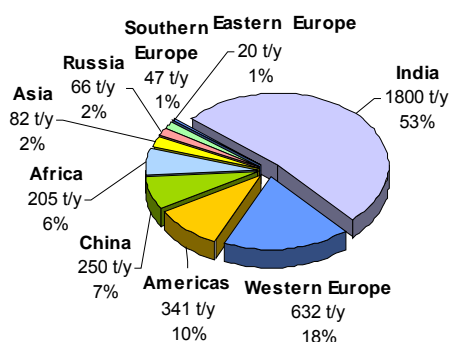


**Figure 4.15.**  $\gamma$ -HCH emission spatial distribution in the Northern Hemisphere in 1996, kg/km<sup>2</sup>/y

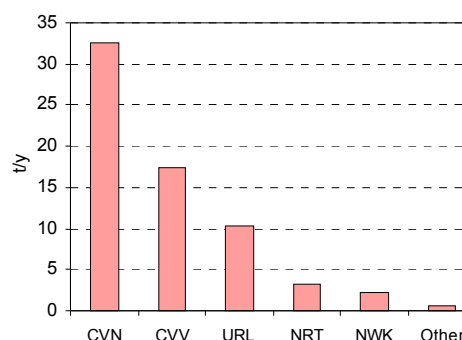
China and India were isolated as separate sources as historically they were significant producers and consumers of this insecticide over a long period of time. For instance, in connection with extensive application of technical HCH in the 60s and 70s China's consumption of  $\gamma$ -HCH was highest in the world [Macdonald et al., 2000]. Beginning from 1994 Northern European emissions are assumed to be zero and for this reason this region was not included as a group of sources in model calculations for 1996. Russian sources are presented in Figure 4.2.

Figure 4.16 demonstrates contributions of source groups identified in our scenario to  $\gamma$ -HCH overall emissions within the Northern Hemisphere in 1996.

As seen from the diagram the highest contribution made the following sources – India, since it was the most significant consumer of this insecticide in agriculture in this time period and Western Europe. Russia's contribution in the indicated year totalled 2%.



**Figure 4.16.** Contribution of different sources to  $\gamma$ -HCH emission in the Northern Hemisphere for 1996



**Figure 4.17.** Contributions of different regions of the Russian Federation to  $\gamma$ -HCH emissions for 1996

As mentioned above, the territorial proximity of a number of regions of the Russian Federation to the Arctic set the stage for finer specification of Russian  $\gamma$ -HCH sources. Figure 4.17 illustrates contributions of Russian region-sources to  $\gamma$ -HCH total emission as it follows from the scenario used.

Figure 4.17 shows that the largest emission value (33 t) from Russia was released from sources located in Central-Chernozem, Volga and North-Caucasus regions.

### 4.3.5. Seasonal variations of $\gamma$ -HCH emissions

According to [Strand and Hov, 1996] the use of pesticides varies over the year and is concentrated in the growing season. The seasonal trend is most characteristic in mid-latitudes where the growing season is short. In connection to this, the application in the 30°N - 60°N latitude zone is therefore assumed to follow the function:

$$2F_{appl} = \frac{F_{totappl}}{365} \left[ \sin \left( 2\pi \frac{\text{day}}{365} - \frac{\pi}{2} \right) + 1 \right] \quad (4.1)$$

where  $F_{appl}$  is the daily emission to the atmosphere and soil;

$F_{totappl}$  is the annual emission;

day is the Julian day.

In the tropics the application of pesticides is assumed to be constant over the year [Strand and Hov, 1996].

### Uncertainties in $\gamma$ -HCH emission estimates

The main uncertainty is connected with the country-based usage of  $\gamma$ -HCH which may be uncertain in itself. K.Breivik *et al.* [2001] believe that uncertainties of  $\gamma$ -HCH consumption in Europe [Breivik *et al.*, 1999] are the consequences of the following peculiarities of the original data:

- Uncertainties regarding whether usage in a given region reported for active ingredient or plus diluting agents;
- The distinction between technical HCH and lindane usage when no information on the subject is given;
- The use of ratios describing HCH to total insecticide usage in estimating HCH consumption (in countries where only information on insecticide usage was available).

As it was mentioned in [Pacyna *et al.*, 1999], the accuracy of data increases from the 1970s to the 1990s reflecting the availability of more reliable information. According to [Li, 1999b] in some regions of the Northern Hemisphere data on the consumption of this insecticide were not kept while in other regions this information was confidential.

Another source of uncertainties arises from distribution of estimated emission over cropland areas as HCH consumption for other purposes unconnected with agriculture was not considered. On the other hand the distribution of emissions over cropland areas results in the appearance of an artificial value of  $\gamma$ -HCH emissions even in the Murmansk Oblast where some agricultural land is available. In the assessment of emissions on the basis of consumption values we used averaged emission factor for lindane applied in agriculture thereby introducing an additional uncertainty. This approach does not

take into account that the share of  $\gamma$ -HCH emitting directly to the air to a great extent depends on the method of the pesticide application.

Substantial source of uncertainties in this emission scenario originates from the rather rough description of seasonal variations of  $\gamma$ -HCH emissions used in the model.

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