CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

EMEP

Cooperative Programme for Monitoring and
Evaluation of the Long-range Transmission
of Air Pollutants in Europe

Lead, Cadmium and Mercury Transboundary Pollution in 2000

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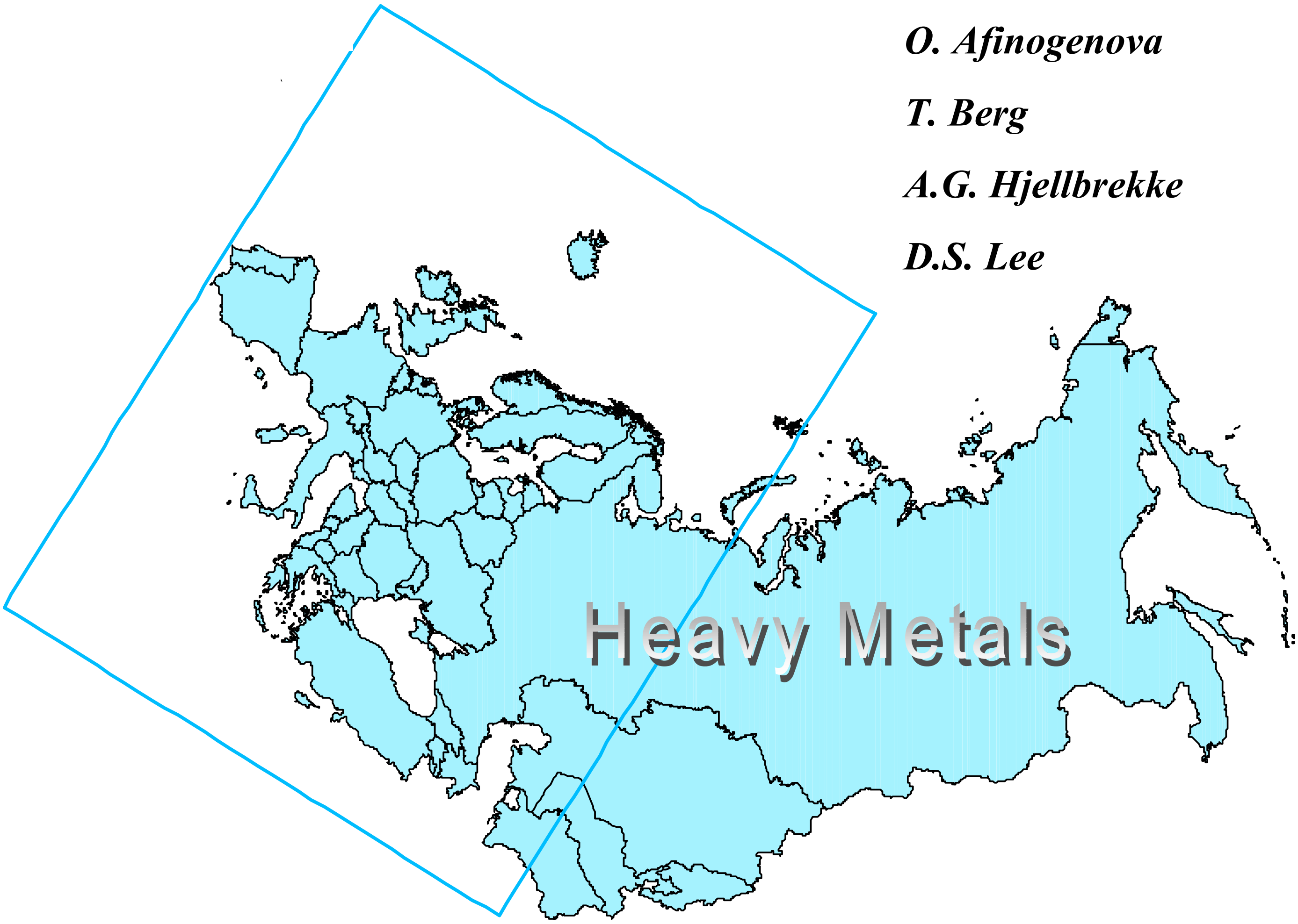

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LEAD, CADMIUM AND MERCURY TRANSBOUNDARY POLLUTION IN 2000

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EXECUTIVE SUMMARY

In accordance with the EMEP work-plan for 2002 approved by the Executive Body for the Convention on Long-Range Transboundary Air Pollution the EMEP Centres provide information about monitoring and model assessment of concentrations, depositions and fluxes of lead, cadmium and mercury for the EMEP domain. Monitoring of heavy metals is supervised by Chemical Coordinating Centre (CCC), the model assessment is the responsibility of Metheorological Synthesizing Centre-East (MSC-E). A brief content of the Report is given below.

The first chapter describes measurement results of lead, cadmium and mercury carried out at the EMEP monitoring network. Some 60 stations have reported data on lead and cadmium concentrations in air and precipitation and around 10 stations have provided similar information about mercury. The concentrations decrease from central to northern Europe. In this chapter the comparison results of analytical methods used for the determination of heavy metal concentrations in precipitation are presented. As noted the quality of measurements improved in comparison with similar study in 1999.

The second chapter presents data on physical-chemical properties of heavy metals and their behaviour in the atmosphere. The description of a number of physical-chemical processes has been modified in comparison with the previous model version. The refined mercury chemical scheme provided more realistic concentrations in precipitation. In parallel boundary concentrations of lead, cadmium and mercury, the parameterization of dry deposition processes have been refined. The current model version computes metal depositions in accordance with land-use type. Such kind of information can be useful for the comparison of atmospheric depositions with critical loads determined for different ecosystems.

The third chapter is dedicated to anthropogenic and natural emissions. At present the EMEP database contains official emission data for 1990 - 2000 submitted to the UN ECE Secretariat. In the absence of official data expert estimates are used. Total anthropogenic emissions of lead, cadmium and mercury for 2000 used in calculations are 11000, 270 and 196 tonnes per year. These values are lower than those used for 1999 by 26%, 18% and 11% respectively. Natural emissions make up an additional source of the metal income to the atmosphere. In the case of mercury natural emissions and re-emissions are considered. For lead and cadmium it is assumed that part of these metals enters the atmosphere with so-called quasi-natural emission, which is the sum of purely natural and secondary supply of previously deposited metals. In the EMEP region mercury natural emission in 2000 was estimated around 208 tonnes, quasi-natural emissions of lead and cadmium - around 7600 and 390 tonnes respectively. These values are 5 – 10% lower than those used for 1999.

The fourth chapter provides computation results for 2000. They involve heavy metal budgets for the EMEP domain as a whole, concentration and deposition fields, estimates of transboundary fluxes between European countries and estimates of loads to seas surrounding Europe. Changes in the obtained results in comparison with 1999 were analysed and the most significant factors influencing these changes have been revealed. First of all among these are changes in emission data. The decline of lead and cadmium emissions as a whole resulted in decreased depositions. The most drastic changes in depositions are noted in countries, in which estimated emissions were substituted by official data. Second, the refinement of meteorological data pre-processing in particular precipitation scheme led to the decrease of precipitation total amount and thereby to reduced lead and cadmium deposition. Mercury depositions also decreased in comparison with 1999 but in this case due to the refined parameterization of dry deposition and emission reduction. For Europe on the whole lead and cadmium depositions cut down around 30% as to mercury the decline is as much as 2 times.

Essential countries-sources of transboundary pollution were identified and the role of indeterminate and national sources was revealed. In Europe as a whole transboundary depositions declined in comparison with 1999.

The comparison of modelling results with available monitoring data showed that in general the model reasonably reproduces European pollution levels. Coefficients of spatial correlation for lead and cadmium are about 0.7 – 0.8. Measured and calculated values are consistent within a factor of 2.

Basic results of this study are summarized in the section “Conclusion”. Annexes provide additional technical information. Detailed information about European pollution levels in individual countries can be found in the Internet (www.emep.int, www.msceast.org).

CONTENTS

INTRODUCTION

This study was accomplished in collaboration with CCC as envisaged by the EMEP work-plan approved by the Executive Body for the Convention on Long-Range Transboundary Air Pollution (CLRTAP) [ECE/EB.AIR/75]. Executive Body for the Convention formulated the following tasks of EMEP in the field of heavy metals for 2002: "Provide monitoring and modelling data on concentrations, depositions and transboundary fluxes of cadmium (Cd), lead (Pb) and mercury (Hg). Develop further the Pb, Cd and Hg transport models in parallel with the development of heavy metal critical limits under the Working Group on Effects (WGE). Analyse trends in Pb and Cd depositions. Further develop emissions data. Support work on review of Protocol on Heavy Metals".

This report provides information on heavy metals monitoring, emissions and modelling activities in the framework of EMEP in year 2000. It is worthwhile to emphasize that countries activities in the field of monitoring have been intensified. The number of stations measuring heavy metal content in the atmosphere increased. Nowadays the database contains information for lead and cadmium concentrations in air and precipitation from about 60 stations and for mercury – from 10 stations. For quality assurance of comparison of analytical methods of heavy metal measurements is curried out. Twenty-nine laboratories took part in the comparison eighteen of them participate in the EMEP programme. This activity of the countries is supervised by Chemical Coordinating Centre (CCC).

Along with monitoring pollution levels are assessed by numerical modeling. This year particular attention was given to improving model parameterization and quality of modelling results. First of all it holds true for processes of dry deposition to various types of the underlying surface. The exchange of scientific ideas with national experts within the framework of the mercury model intercomparison study provides a ground for improvement essentially the scheme of mercury chemical transformations. In particular chemical reaction rates are refined and new reactions are revealed, in which mercury and its compounds participate. The parameterization of mercury input from natural sources is also modified. Alongside with proper understanding of heavy metal behaviour in the atmosphere the reliability and plausibility of model estimates appreciably depend on the quality and completeness of emission data. In recent years the number of countries submitting their emission data to the UN ECE Secretariat is growing. At the same time emissions remain to be the main source of uncertainty of modeling results [*Travnikov*, 2000]. The Workshop on emissions and emission factor estimates held jointly by MSC-E and TFEIP (Moscow, 2001) was dedicated to issues of reliability and uncertainty of emission data.

The MSCE-HM model output provides concentration and deposition fields, transboundary fluxes and pollutant budgets. The budgets include integral indicators – total emission, deposition, advective inflow and outflow in the region etc. The analysis of emissions, concentration, deposition fields and transboundary fluxes give a picture of changes in pollution levels in Europe. Such an analysis was made for each EMEP country. The seas surrounding Europe are considered as regions-receivers, for which inputs from countries to total atmospheric pollution are discussed. The plausibility of modeling results is assessed by their comparison against measurements. Co-operation with national experts contribute significantly to the progress in the investigation of HM long-range transport. In particular investigations in the field of mercury monitoring and airborne transport modelling in the United Kingdom are presented as a separate chapter of the Report. Special Technical Note was prepared jointly by national experts and MSC-E.

Despite the progress made in the field of emission inventories, monitoring and modeling a number of problems still need further research. In particular it refers to mercury atmospheric chemistry and exchange processes between the atmosphere and other environmental compartments. Further refinements are required both for anthropogenic and natural emission. The Report gives the outline of future priorities of investigations in the field of heavy metal airborne transport.

Chapter 1

RESULTS OF HEAVY METALS MONITORING ON Pb, Cd and Hg – 2000

1.1. Introduction

Heavy metals were included in EMEP’s monitoring program in 1999. However, already in 1995, co-operation concerning heavy metals between EMEP and other international programs was extended. This co-operation included the establishment of a database and collection of already available data on heavy metals among the participants. A number of countries have been reporting heavy metals within the EMEP area in connection with different national and international programmes such as HELCOM, AMAP, OSPAR, and MEDPOP. The following heavy metals are included in this report: mercury, cadmium and lead.

1.2. The measurement sites

The location of the measurement sites for which there are data reported for Hg, Pb and Cd for 2000 is given in Table 1.1.

Table 1.1. List of monitoring stations included in the heavy metal data base

Country	Station codes	Station name	Location		Height above sea, m
			Lat.	Long.	
Belgium	BE4	Knokke	51°21'N	3°20'E	0
Czech Republic	CS1	Svratouch	49°44'N	16°02'E	737
	CS3	Kosetice	49°35'N	15°05'E	633
Denmark	DK3	Tange	56°21'N	9°36'E	13
	DK5	Keldsnor	54°44'N	10°44'E	9
	DK8	Anholt	56°43'N	11°31'E	40
	DK10	Nord, Greenland	81°30'N	17°30'W	
	DK15	Faroe Islands	62°18'N	7°04'W	210
	DK20	Bornholm			
	DK31	Ulborg	56°17'N	8°26'E	10
Estonia	EE9	Lahemaa	59°3'N	25°54'E	32
	EE11	Vilsandi	58°23'N	21°49'E	6
Finland	FI9	Utö	59°47’N	21°23’E	7
	FI17	Virolahti II	60°31'N	27°41'E	4
	FI22	Oulanka	66°19'N	29°24'E	310
	FI53	Hailuoto	65°00'N	24°41'E	4
	FI92	Hietajarvi	63°10'N	30°43'E	173
	FI93	Kotinen	61°14'N	25°04'E	158
	FI96	Pallas	67°58'N	24°7'E	566
France	FR90	Porspoder	48°31'N	4°45'W	50

Country	Station	Station name	Location	Height above

	codes		Lat.	Long.	sea, m
Germany	DE1	Westerland	54°55'N	8°18'E	12
	DE3	Schauinsland	47°55'N	7°54'E	1205
	DE4	Deuselbach	49°46'N	7°03'E	480
	DE5	Brotjacklriegel	48°49'N	13°13'E	1016
	DE7	Neuglobsow	53°09'N	13°02'E	62
	DE8	Schmücke	50°39'N	10°46'E	937
	DE9	Zingst	54°26'N	12°44'E	1
Iceland	IS2	Irafoss	64°05'N	21°01'W	61
	IS90	Reykjavik	64°08'N	21°54'W	61
	IS91	Stórhöfdi	63°24'N	20°17'W	118
Ireland	IE1	Valentia Observatory	51°56'N	10°15'W	9
	IE2	Turlough Hill	53°02'N	6°24'W	420
Latvia	LV10	Rucava	56°13'N	21°13'E	18
	LV16	Zoseni	57°08'N	25°55'E	183
Lithuania	LT15	Preila	55°21'N	21°04'E	5
Netherlands	NL9	Kollumerwaard	53°20'N	6°17'E	0
	NL91	De Zilk	52°18'N	4°30'E	4
Norway	NO1	Birkenes	58°23'N	8°15'E	190
	NO39	Kårvatn	62°47'N	8°53'E	210
	NO41	Osen	61°15'N	11°47'E	440
	NO42	Spitsbergen, Zeppelinfjell	78°54'N	11°53'E	474
	NO47	Svanvik	69°27'N	30°02'E	474
	NO55	Karasjok	69°28'N	25°13'E	333
	NO56	Hurdal	60°22'N	11°04'E	300
	NO92	Øverbygd	69°03'N	19°22'E	90
	NO93	Valdalen	62°05'N	12°10'E	800
	NO94	Møsvatn	59°50'N	8°20'E	940
	NO95	Ualand	58°31'N	6°23'E	220
	NO99	Lista	58°06'N	6°34'E	13
Portugal	PT1	Braganca	41°49'N	6°46'W	16
	PT3	V. d. Castelo	40°25'N	7°33'W	16
	PT4	Monte Velho	38°05'N	8°48'W	43
	PT10	Angra do Heroismo	38°74'N	27°13'W	74
Slovak Republic	SK2	Chopok	48°56'N	19°35'E	2008
	SK4	Stará Lesná	49°09'N	20°17'E	808
	SK5	Liesek	49°22'N	19°41'E	892
	SK6	Starina	49°03'N	22°16'E	345
	SK7	Topolniky	47°58'N	17°52'E	113
Sweden	SE2	Rörvik	57°25'N	11°56'E	10
	SE5	Bredkälen	63°51'N	15°20'E	404
	SE11	Vavihill	56°01'N	13°09'E	172
	SE12	Aspvreten	58°48'N	17°23'E	20
	SE51	Arup	55°45'N	13°40'E	157
	SE97	Gårdsjön	58°03'N	12°01'E	113
United Kingdom	GB14	High Muffles	54°20'N	0°48'W	260
	GB90	East Ruston	52°48'N	1°28'E	5
	GB91	Banchory	57°05'N	2°32'E	120

The site codes used are the new EMEP codes introduced during 1992 or codes used in the OSPAR or HELCOM programmes. Stations without these types of codes have been coded with the country ISO code and numbers from 90 and higher.

1.3. Maps of heavy metal concentrations over Europe

Data presentation

Annual averages of Pb, Cd and Hg from the 2000 precipitation and air data are presented in maps (Figs. 1.1 - 1.6). The yearly precipitation mean concentrations have been calculated from daily, weekly or monthly reported values as precipitation-weighted averages. Average air concentrations are arithmetic averages of the reported values.

Lead in precipitation

The stations have been located away from local sources and are as far as possible representative for a larger region. The lowest concentrations of Pb during 2000 are found in northern Scandinavia, Iceland, Ireland and Portugal, where the annual averages are below 1 µg Pb/l (Fig. 1.1). A concentration maximum of about 13 µg Pb/l is seen at the Lithuanian station. It should be noticed that few countries in Southern- and Eastern Europe have reported data for heavy metals in precipitation.

Cadmium in precipitation

In Scandinavia the annual mean values of Cd are below 0.05 µg Cd/l (Fig.1.2). An increasing gradient can be seen south east. The highest concentrations of Cd are reported from the Slovak station SK2 (0.9 µg Cd/l). There are no data reported from Southern Europe (except Portugal with too high detection limit for Cd) and only the Czech Republic, Slovakia and the Baltic States have reported data from Eastern Europe.

Mercury in precipitation

Only a few stations are measuring mercury in precipitation in Europe, and most of them are related to the OSPAR programme. The concentrations are quite similar, and with the exception of the Belgium station, in the range 5 - 20 ng Hg/l for all the stations (Fig. 1.3). The fluxes from Belgium are based on mercury concentrations close to the detection limit of the analysis method used and are therefore uncertain, and the data may only be considered as upper limits.

Lead in aerosols

Figure 1.4 presents the annual averages of Pb in air in 2000. The lowest concentrations (below 1 ng Pb/m^3) can be seen at Svalbard, Iceland and Greenland. Concentration maxima are seen in Latvia and Slovakia. It should be noticed that, with the exception of the Baltic States, Czech Republic and Slovakia, there are no data reported from Southern- and Eastern Europe. Few data are however also reported from Scandinavia and the westernmost part of Europe.

Cadmium in aerosols

Cadmium in aerosols is presented in Figure 1.5. The lowest concentrations (below 0.1 ng Cd/m^3) are reported from the Nordic and the Scottish station. An increasing gradient can be seen southeastward, with the highest concentration maxima at the Slovak and Latvian stations. The lack of data is similarly to Pb in aerosols.

Mercury in air

Concentrations of mercury in air are in the range 1.3 - 1.7 ng/m^3 for all the stations (Fig. 1.6). As for mercury in precipitation, there are only a few stations delivering data on mercury in air, and they are mainly related to the AMAP and the OSPAR programme.

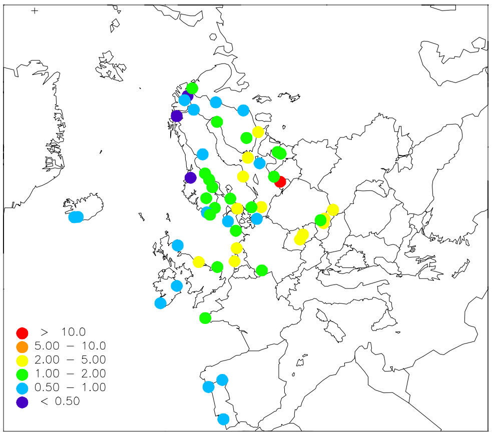

Figure 1.1. *Lead in precipitation in 2000, µg/l*

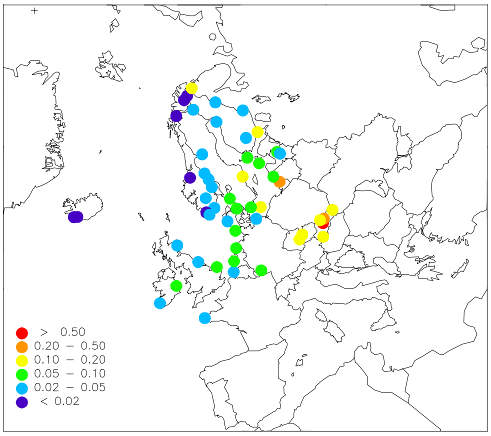

Figure 1.2. *Cadmium in precipitation in 2000, µg/l*

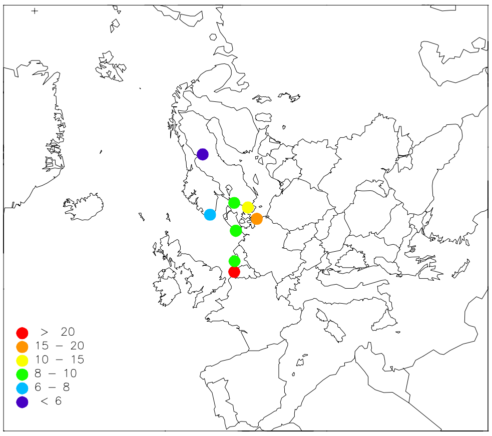

Figure 1.3. *Mercury in precipitation in 2000, ng/l*

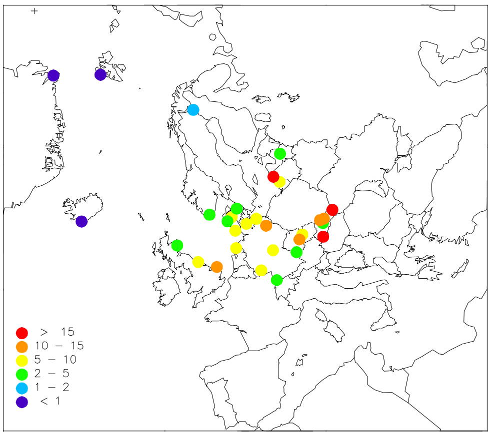

Figure 1.4. *Lead in aerosols in 2000, ng/m^3*

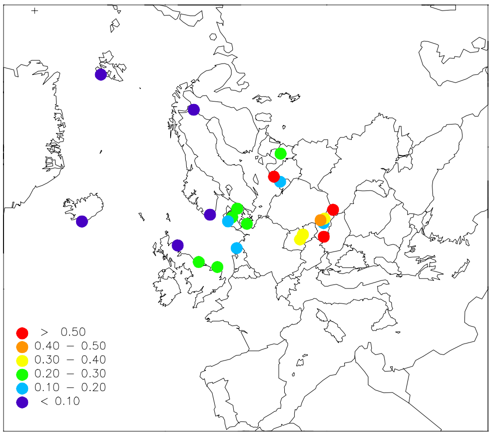

Figure 1.5. *Cadmium in aerosols in 2000, ng/m^3*

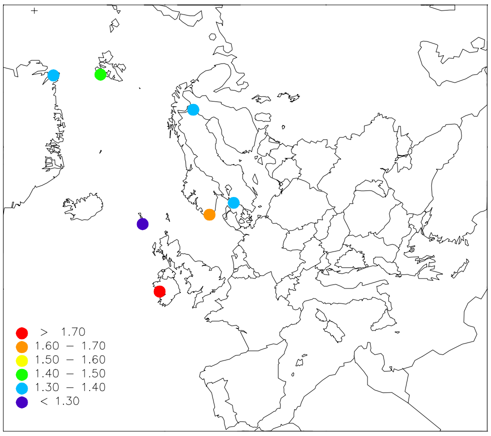

Figure 1.6. *Mercury in air in 2000, ng/m^3*

1.4. Summaries of the data

Annual summaries of heavy metals in precipitation and air are given in Annex A1 and Annex A2, respectively. The definitions are as follows:

W. Mean: the precipitation weighted arithmetic mean value

Min: the minimum value reported for a specific component

Max: the maximum value reported for a specific component

Number: the number of data below the detection limit

Num samples: the number of samples for a specified component

Samp flag: a flag which gives information on the resolution of the reported data. The code used in this report is:

D: daily
D1: one-day each week
D2: two-days each week
W: weekly
WC: weekly with change the first day each month
W1: one week each month
W2: two-weekly
W4: four-weekly
M: monthly
Y: yearly

QA: a flag which gives information on the quality of the data (further details in 2.4)

Arit mean: the arithmetic mean value used for air components only

Arit sd: the arithmetic standard deviation from the arithmetic mean value. It is computed for air components only

Geom mean: the geometric mean value used for air components only

50%: the 50 percentile

A more detailed description of the flags is given in *T. Berg and A.-G. Hjellbrekke* [1998]

Monthly averages of heavy metals are given in Annex A3 and Annex A4. The monthly mean values of precipitation data are precipitation weighted arithmetic averages. Average air concentrations are arithmetic averages of the reported values.

The units used for the results in this report are given in Table 1.2.

Table 1.2. Units used for the measured components

Components	Units for w.mean, min max
Amount precipitation	mm
Heavy metals in precipitation	μg/l
Mercury in precipitation	ng/l
Heavy metals in air	ng/m^3
Mercury in air	ng/m^3

1.5. Quality of the monitoring data

Flagging

In order to provide sufficiently accurate data for EMEP's needs, data of an expected lower accuracy have been flagged (QA) in the tables containing annual summaries and monthly means. The definitions of the quality flags are as follows:

1. High detection limit
2. Site location not regionally representative
3. Sampling problems
4. Analytical problems
5. Sample site located at high altitude
6. Concentration level low when compared to nearby stations
7. Extremely long sampling time
8. Sum of wet deposition + dry deposited particles onto the funnel. Unit: ng/m^2 day
9. Estimated values
10. Extremely high single sample concentrations

11L. More than 25% percentage deviations for both the **low** concentration samples in the 2000 EMEP intercalibration

11H. More than 25% percentage deviations for both the **high** concentration samples in the 2000 EMEP intercalibration

NP. Not participated in the EMEP Intercalibration on heavy metals, 2000.

The data have been checked for outliers. Extremely high values, outside four times standard deviation in a lognormal distribution, have been flagged in the EMEP database and are excluded from this report. A few data with extremely high detection limits are not included in the report (Cd in precipitation from Portugal, Hg in precipitation from Ireland). The Belgium lead data have been excluded from the maps because they are inconsistent. From the same station (BE4) data from both a bulk sampler, a wet-only sampler and an aerosol sampler are delivered. The bulk sampler reports very low concentrations, the wet-only sampler and the aerosol sampler the highest concentrations in Europe. The Belgian laboratory did not participate in the 2000-intercomparison, and the results must be checked in detail before the data are included.

Intercomparisons

Information on the quality of the measurements is also available from the "EMEP Analytical intercomparison of heavy metals in precipitation 2000" [*Uggerud and Skjelmoen*, 2001]. A total of 17 EMEP laboratories participated (Annex A5). Two samples contained trace element concentrations typical of precipitation in Southern Scandinavia, and two samples contained higher concentrations typical of Central Europe. It should be noted that the cadmium concentration given in one of the low concentration samples was extremely low and that 8 of the laboratories delivered results below the detection limit for this sample. It should be emphasised that most laboratories involved measure mainly concentrations similar to the high concentration samples in their monitoring networks, and therefore have less experience than others with low concentration samples. In the discussion below, the cadmium results from the extreme low concentration sample is therefore excluded.

The results (Table A5.3 Annex A5) show that 3 of 19 laboratories reported values below the detection limit for the low concentration sample. Only 2 laboratories were outside 25% from the theoretical value for cadmium in the low concentration sample. For the high concentration samples 1 of 19 laboratories reported values below the detection limit, and 2 laboratories were outside 25% from the theoretical value for cadmium. For lead 2 of 19 laboratories reported values below the detection limit for both the low concentration samples. Three laboratories are outside 25% from the theoretical value for both the low concentration samples, while only 1 of 19 laboratories had high-concentration results outside 25%. For both cadmium and lead, the results were better in 2000 than in the 1999 intercomparison.

The last field intercomparison on heavy metals in precipitation was carried out in the framework of HELCOM-EMEP-OSPAR-AMAP activity during 1996. The exercise was divided in an analytical and a field intercomparison part and included seven heavy metals: Pb, Cd, Cu, Zn, As, Cr, and Ni. The field intercomparison part of the exercise was carried out at the German EMEP station Deuselbach (DE04). The results were extensively discussed at a workshop in Germany, September 1996, and the major conclusion from this meeting was that the agreement between the collectors regarding precipitation amount seems to be satisfactory, and that the outcome of this intercomparison is much more positive than in the case of previous exercises. Furthermore, the results for Pb, Cd and eventually Zn seemed to be acceptable, but problems still remain to be solved for the other heavy metals considered [*WMO*, 1997].

Table 1.3. Percentage deviation from theoretical concentration values [Extract from *Uggerud and Skjelmoen*, 2001]

Element and percent interval	No. of lab.	Lab. Identification *The number in brackets are number of results reported in the particular percent interval by the laboratory*
Cd		
0 - 10%	14	1(2), 3(3), 5(3), 8(2), 14(2), 15(2), 16(1), 19(1), 26(3), 31(3), 33(3), 36(2), 38(1), 39(2)
10 - 25%	11	1(1), 8(2), 14(1), 15(1), 16(2), 19(1), 23(1), 108(1), 32(3), 36(1), 38(2)
> 25%	10	5(1), 7(1), 14(1), 15(1), 16(1), 23(3), 24(4), 31(1), 33(1), 38(1)
Pb		
0 - 10%	15	1(4), 3(3), 5(4), 6(1), 7(2), 8(4), 14(3), 15(4), 16(4), 19(2), 24(2), 26(2), 31(4), 32(4), 33(2), 38(4)
10 - 25%	9	3(1), 6(1), 7(1), 14(1), 24(1), 26(2), 32(1), 36(3), 39(2)
> 25%	6	7(1), 19(2), 23(4), 24(2), 33(2), 39(1)

2000-data

The geographical gradients for Pb, Cd and Hg in precipitation and air seem to be reasonable. Estonian sites have lower concentration values for Pb in precipitation than the adjacent sites in Southern Finland, which seems strange. A similar pattern has also been observed earlier. For Pb, both the Estonian and the Finnish laboratories reported good results in the intercomparison. Portuguese Pb concentrations are low – so they should be. The high concentrations of Pb at the Slovakian sites may be due to industry in the region Ruzomberok – Liptovský Mikauláš [*Rühling et al.*, 1998]. The relatively high concentrations of Cd reported from the Slovakian stations may mainly be due to emissions from cupper smelters in the Legnica - Glogów basin in Southern Poland [*Rühling et al.*, 1998]. High concentrations of Pb are also reported from CZ3 (Kosetice). The main road from Praha to Brno is not far from the station.

Chapter 2

PARAMETERIZATION OF THE HEAVY METAL REGIONAL MODEL

2.1. Behaviour of heavy metals in the atmosphere

Knowledge of properties of modelled substances is important for realistic model parameterization. As to heavy metals of the first priority (Pb, Cd, Hg) physical-chemical properties influencing their behavior in the atmosphere were described in MSC-E previous reports [*Ryaboshapko et al*., 1998; 1999, *Ilyin et al*., 2001]. Our knowledge in this field, however, constantly undergoes replenishment. Each year new data appear in the scientific literature making us correct or even drastically change these or those model parameters.

Pb, Cd, Hg physical-chemical forms in the atmosphere

In the atmosphere heavy metals occur both in the elemental form and as various chemical compounds. By their properties chemical compounds can differ drastically from the metal proper. Thus the first task is to define the list of the most important forms of heavy metal transported in the atmosphere.

Depending on the emission source lead is represented both by the elemental form and by a number of its chemical compounds – $PbSO_4$, Pb_3O_4, $PbO{\cdot}PbSO_4$ etc. [*Finlayson-Pitts and Pitts*, 1986]. Under real atmospheric conditions these compounds are in the solid state in the composition of aerosol particles. Nevertheless the literature provides information that a part of lead can be represented by gaseous compounds of the unknown composition [*Burtseva et al.*, 1986], most likely by methylated forms [*Geological Survey of Canada*, 1995]. Since this information was not widely supported in this work it is considered that lead is present in the atmosphere only in the aerosol form.

Practically nothing is known about chemical forms of cadmium in the atmosphere. There is a good probability that at its emissions by high temperature sources (for example, at coal combustion) such cadmium compounds as oxide, sulphide, sulphate, chloride can be formed [*Yatsenko-Hmelevskaya et al.,* 1994]. These substances are not volatile and have relatively high melting and boiling points. All said above implies that they should occur in the atmosphere in the composition of aerosol particles. As in the case with lead there are indications that gaseous forms of cadmium may exist in the atmosphere [*Burtseva et al*., 1986; *Geological Survey of Canada*, 1995], but in this work cadmium is considered as aerosol matter.

Physical-chemical properties of metallic mercury (temperature dependence of saturated vapor pressure) suggests that under the conditions of the real atmosphere with existing concentrations it can occur only in the gaseous form. Even at the absolute minimum of temperature on the Earth's surface (the Antarctic, Siberia) partial pressure of mercury is several times lower than saturated vapor pressure [*Fursov*, 1983]. Hereinafter gaseous elemental mercury is represented by the symbol Hg^0.

Besides elemental form mercury can be present in the atmosphere as various compounds, part of which possesses noticeable volatility. Of all inorganic compounds first of all mercury chloride ($HgCl_2$)

and mercury hydrate ($Hg(OH)_2$) can be considered as volatile species. The composition of gaseous inorganic mercury in the atmosphere has not been thoroughly investigated up till now [*Ebinghaus et al.*, 1999]. A generalized symbol of the gaseous form of oxidized divalent mercury in this work is HgII.

Organic mercury compounds present a special case. Mainly they can occur in the atmosphere with one or two methyl groups. In the first case a number of compounds is possible – CH_3HgCl, CH_3HgOH etc. A general symbol for this group of compounds is MMM. Twice methylated mercury – $Hg(CH_3)_2$ is denoted by symbol DMM.

While measuring mercury content in the atmosphere methods of total determination both of elemental mercury and all gaseous compounds are often used. This generalized form is usually called "Total Gaseous Mercury" and it is denoted by TGM.

A certain part of mercury is contained within aerosol particles. *W. Schroeder et al*. [1991] surmised that mercury in the solid state can be represented by the following compounds: HgO, HgS, $HgCl_2$, $HgSO_4$, $Hg(NO_3)_2$. Here HgP denotes mercury contained in the composition of aerosol particles.

Properties of aerosol forms of lead, cadmium and mercury in the atmosphere

Availability or lacks of heavy metals in the composition of aerosol particles do not affect behavior of heavy metals except for local conditions near plants of non-ferrous metallurgy. The airborne transport of heavy metals in the solid state first of all is defined by properties of particles-carriers. Above all the distribution with size is referred to such characteristics. In its turn particle sizes define parameters of their scavenging from the atmosphere due to washout (interaction with drops or ice crystals in a cloud and below it) and uptake by the underlying surface. Since in this case properties of the metal itself do not play any role it is reasonable to consider lead, cadmium and aerosol mercury in terms of particles-carriers.

J.Milford and C.Davidson [1985] found that under the conditions of the continental atmosphere mean aerodynamic diameter is 0.55 μm for lead, 0.61 – for mercury and 0.84 for cadmium. Besides they found that in the urban atmosphere the maximum of particle distribution with sizes for lead is shifted to the side of finer particles in comparison with the atmosphere in cleaner regions. Very close values for lead and cadmium were obtained by *M.Kane et al.* [1994] in the marine atmosphere (the North Sea). For lead mean median diameter appeared to be noticeably lower (0.6 μm) than for cadmium (1.0 μm).

J.Injuk et al. [1992] investigated size spectrum of particles carrying lead and cadmium over the North Sea. For lead clear maximum was revealed in submicron range. When air masses were transported from the sea, more than 60% of lead was associated with submicron particles at mean aerodynamic median diameter 0.8 μm. For the European continental atmosphere the authors obtained appreciably lower value – 0.22 μm. For cadmium wide and varying spectrum within the range from 0.09 to 23 μm was identified. Nevertheless about 40% of cadmium is associated with particles less than one micron and 70% - less than 4 microns. In this case an appreciable difference between marine and continental atmosphere was not found – corresponding values of the mean median diameter were 0.72 and 0.75 μm. In the more recent work *J.Injuk et al*. [1998] drew a conclusion that in the region of the North Sea heavy metals have the distribution maximum about 0.5 μm.

Investigations of distribution of aerosol particles carrying heavy metals were carried out in the central part of Europe (Hungary) [*Molnar et al.,* 1995]. For lead one-mode character of distribution with maximum close to 0.5 μm was revealed. For cadmium rather blurred spectrum was obtained. The major portion of cadmium mass is associated with particles of submicron diameter with the implicit maximum within the range of 0.5-1.0 μm.

G.Keeler et al. [1995] studied atmospheric concentrations and distribution with sizes of aerosol mercury in different regions of the USA. It was found that in industrial polluted regions the size spectrum maximum is shifted to the domain of larger particles. In relatively clean regions the distribution maximum is within 0.68 μm.

It is an important fact that distribution with sizes does not significantly change with height. According to data of *A.Kasper et al*. [1998] at height 3000 m the maximum of lead mass distribution with particle sizes (aerodynamic diameter) is accounted for 0.7 μm.

On the base of literature data generalization it is accepted in this work that the characteristic particle size carrying lead is 0.5 μm. For cadmium and mercury relevant values are taken equal to 0.7 μm. It is also admitted that the particle spectrum is invariable with height.

Pb, Cd and Hg background concentrations (boundary concentrations for the regional model)

Transport modelling on the regional scale (within the EMEP domain) presupposes knowledge of metal concentrations at the boundaries of the region. It is necessary for accounting of remote (outside EMEP regio) atmospheric sources of the heavy metals. It is also very important to know concentration vertical profiles at the region boundaries. It should be mentioned that measurements in background regions are scarce and they are not very accurate since concentrations are low and they are often on the level of detection limits of the measurement methods used.

J.Injuk [1992, 1998] carried out extended program of heavy metal measurements in the atmosphere of the North Sea region. In 1988-89 with the use of aircraft it was found that in air masses transported from the north (without any contact with land) lead and cadmium concentrations were 7±2 and 0.4±0.4 ng/m^3 correspondingly [*Injuk et al*. 1998]. The same work contains data of other investigators who found that over the Atlantic far from the shore lead concentrations are on the level of 3 ng/m^3 and those of cadmium within 0.08 - 0.2 ng/m^3. In 1992-94 lead concentration was measured on a sea platform, far from the shore [*Injuk et al*., 1998]. At north-west transport (minimum effect of anthropogenic sources) mean concentration was 10.8 ± 0.8 ng/m^3. Mean concentration of lead measured in summer at a coastal station in Belgium was slightly higher – 14.3 ng/m^3 at minimum value 1.6 ng/m^3.

Later (July – September 1997) *C.Wang et al.* [2000] found that minimum values of lead and cadmium concentrations on the coastal region of North Sea were 3 and 0.05 ng/m^3 respectively. It may be supposed that measured minimum values correspond to background concentrations of these metals.

Lead background concentration in the Atlantic air masses at the western extremity of Europe (Mace Head station) was 2 ng/m^3 in 1990 [*Krasenbrink et al.*, 2000]. Far from the coast the concentration may be considerably lower. For example, *M.Kriews and O.Schrems* [1998] determined median mean concentration of lead over the North Atlantic equal to 0.32 ng/m^3.

M.Ebert et al. [2000] investigated background concentrations of heavy metals in the air transported from the Atlantic and found that in the absence or minimum impact of anthropogenic sources lead concentrations amounted to 3 - 4 ng/m^3. It was estimated that the anthropogenic contribution to lead associated with aerosol did not exceed 25%. Minimum lead concentrations measured in 1993 - 94 in a relatively clean region on the western coast of the Irish Sea [*Chester et al.* 2000b] coincide with these values – 3.6 ng/m^3.

In spring of 1992 *J.Isakson* [1997] took samples for the evaluation of heavy metal background concentrations in Scandinavia. Concentrations in aerosol of air masses transported from the Atlantic and the Arctic were considered as background ones. Measurements were made for two aerosol fractions: fine aerosol (to 2.5 μm) and coarse one (from 2.5 to 10 μm). Minimum lead concentrations were detected in the west of Norway at the Atlantic transport: 0.31 ng/m^3 in the fine fraction and 0.11 ng/m^3 in the coarse one. Higher values were characteristic of southern Norway – 1.0 and 0.25 ng/m^3 respectively. The same values were characteristic of the Arctic air in the north of Finland.

Atmospheric transport from the equatorial Atlantic may define boundary conditions at western and southern boundaries of the EMEP domain. In the tropical Atlantic lead concentrations were 1.01 ± 0.59 ng/m^3 at the same time the major part (0.72 ± 0.46 ng/m^3) was concentrated in the fine fraction (less than 3 μm) [*Johansen et al.*, 2000].

Remote regions of the Pacific Ocean have the lowest concentrations of heavy metals in the atmosphere. According to *D.Cohen* [1999] background lead concentration (particles with diameter less than 2 μm) in the Earth atmosphere are on the level of 1±1 ng/m^3. *S.Santosa et al.* [1997] give higher values for the central and eastern parts of the Pacific. According to their data (1995 - 96) lead concentration was 5 ± 3 ng/m^3.

Investigations demonstrated that aerosol mercury is omnipresent in the atmosphere. *W.Baeyens et al.* [1991] found that over the Atlantic Ocean aerosol mercury concentrations were about 0.07 ng/m^3 (data of 1980). Virtually the same levels were observed in western Sweden (0.05 - 0.06 ng/m^3) and the concentration did not reveal any dependence on the transport direction [*Linqvist et al.*, 1991]. In relatively clean regions of the USA HgP concentrations varied from 0.005 to 0.05 ng/m^3 [*Keeler et al.*, 1995]. In Vermont State maximum concentrations were observed in winter (up to 0.015 ng/m^3) and minimum ones in summer (0.009 ng/m^3). Over the Pacific Ocean HgP concentration varies from 0.0004 to 0.002 ng/m^3 [*Fitzgerald*, 1989].

In September of 1995 at Mace Head station (western extremity of Ireland) an experiment aimed at the determination of concentrations of mercury different forms was carried out [*Ebinhaus et al.*, 1999a]. In this region the impact of European anthropogenic sources is minimum and the atmospheric chemical composition is more likely reflects the situation over the Atlantic. Two methods used for aerosol sampling revealed the difference between each other as much as 5 times. HgP concentrations varied from 0.005 to 0.115 ng/m^3. For oxidized gaseous mercury the difference between various methods used also reached 5 time at the concentration range from 0.013 to 0.094 ng/m^3.

On the US eastern coast in relatively clean regions HgP concentrations in fine particles (size <2.5 μm) is within the range from 0.051 to 0.089 ng/m^3. The contribution of HgP to total mercury concentration is about 1.8% [*EPA USA,* 1997].

T.Berg et al. [1999] estimated that at the EMEP northern boundary TGM concentration is noticeably lower than at the western one. On the average in 1996-97 TGM concentration in the region of Spitsbergen archipelago was 1.4 ng/m^3 and in the north of Finland was even lower – 1.3 ng/m^3.

On the base of summarized measurement data for the USA region *P.Pai et al.* [1997] in their regional model used the following boundary conditions for mercury and its compounds: Hg^0 = 1.6 ng/m^3; HgII = 0.08 ng/m^3 and HgP = 0.01 ng/m^3. In addition it was accepted that within the atmospheric boundary layer HgII and HgP concentrations were invariable with height. On the level of 10^3 Pa the concentrations were assumed to declined to 0.1% of the surface layer value. Hg^0 concentration at this height was accepted as 70% of that in the surface layer.

According to data of *V.Ionov et al*. [1976] metallic mercury concentration decreases exponentially with height. At the height about 1 km the concentration declines **e** times of the surface value. A certain decrease of gaseous mercury concentration with height was observed by *C.Brosset* [1987] when flying over western Sweden. At the height of 2.5-3 km Hg^0 concentration was about 1.5 times lower than the surface one. HgII concentration was more conservative – it was practically independent of height.

According to data of *O.Lindqvist et al.* [1991] elemental mercury concentration in the first 4 km on the US eastern coast declines by 20 - 25%. *K.Kvietkus et al.* [1996] found that TGM concentration decrease with height is considerably less (1.5 times at the height of 8 km) with simultaneous growth of HgP from fractions of ng/m^3 near the ground surface to approximately 1 ng/m^3 at 1.5 km. These data evidence that in the free troposphere aerosol mercury distribution with height is almost uniform (up to 8 km).

There are observational data, which do not confirm TGM concentration variation with height. Flights over Germany showed that TGM concentrations are constant to the height of 3800 m [*Ebinghaus and Slerm*, 2000]. *C.Banic et al.* [1999] believe that mercury concentration (under at standard conditions) does not decline at least at the height of 7 km. *W.Schroeder et al*. [2001] are of the opinion that TGM profile is virtually uniform or slightly declining (10% within the troposphere). Drastic periodic removal of Hg^0 during spring period in the Arctic occurs in the lower 1-km layer. When this event takes place, near the ground surface TGM concentrations can reach zero, then they are restored to the normal values at the height of 1 km.

On the base of the analysis made the following concentrations values are taken at the boundaries of the EMEP domain (Table 2.1).

Table 2.1. Accepted values of near surface (near water) HM concentrations at the EMEP region boundaries, ng/m^3

Boundary	Metal and its form				
	Pb	Cd	Hg^0	HGII, DMM, MMM	HgP
Northern	0.7	0.07	1.6	0	0.02
Eastern	3	0.3	1.7	0	0.03
Southern	2	0.2	1.7	0	0.03
Western	1	0.1	1.7	0	0.02

It is assumed that on the background level mass concentration of lead and cadmium within the height range of the first 1.5 km is kept constant. Then till the level of the tropopause concentrations linearly decline with height to 5% of the surface value. Mass concentration of Hg^0 decreases with height up to 90-% of its surface value on the level of tropopause. HgP mass concentration is constant with height.

Solubility of Pb, Cd and Hg aerosol forms

An important physical-chemical property of the considered heavy metals is their solubility when their particles-carriers enter the water. For all the metals it defines their accessibility for biota (and consequently the extent of a negative impact). For mercury solubility of its compounds is an important characteristic of chemical transformations in the aqueous phase [*Ryaboshapko et al.,* 2001]. Another essential thing is the fact that when measuring concentrations of heavy metals in precipitation, very often only water-soluble fraction is analysed. Hence the intensity of metal scavenging from the atmosphere can be underestimated. In the comparison of model results with measurement data this fact should be taken into account.

Investigations demonstrated that lead solubility in rain water strongly depends on the solution acidity [*Chester et al*., 2000a). In the acid medium (pH=3.5) up to 90% of lead compounds is dissolved, in slightly acid medium (pH=5) – about 50% and in neutral (pH=6) – only 10%. Under the conditions of the North Sea the solubility of aerosol lead in rainwater is 74% on the average [*Chester et al*., 1994]. On the base of monitoring for many years *M.Takeuchi et al.* [2000] concluded that the bulk of lead in rainwater (84%) is in the dissolve form.

R.Ebinghaus et al. [1999] consider that the share of mercury in atmospheric precipitation associated with solid particles varies from 90% in polluted regions to 10% in clean ones. In leaching mercury from aerosol samples by hydrochloric acid solution from 5 to 50% of mercury was transferred to the solution [*Sakata and Marumoto*, 2002]. It is conceivable that in neutral (or slightly acid) water the dissolved fraction may be even less. Among those compounds which could be present in the atmosphere the least soluble are mercury bromide, iodide, sulphide and oxide.

C.Brosset and E.Lord [1991] evidence that 50% of mercury in rainwater is represented by insoluble compounds. *W.Fitzgerald et al*. [1991] and *C.Lamborg et al.* [1995] are of the same opinion. *C.Lamborg et al.* [1995] also indicate that mercury fraction associated with particles is higher in snow than in rain.

On the base of the literature data it is assumed that half of lead, cadmium and mercury in rainwater is contained in the composition of insoluble particles within cloud and rainwater droplets.

Other properties of Pb, Cd and Hg defining their airborne transport

For modelling of mercury transfer from air to the aqueous phase two approaches can be used: the application of Henry's law and the consideration of diffusion process. In this work Henry's law approach is used.

The integral parameter characterizing a possibility of the transport of any substance in the atmosphere is “lifetime”. This parameter is most important for elemental mercury. Knowledge of this parameter allows testing the rationality of model design. *O.Lindqvist and H.Rodhe* [1985] used several ways for the estimation of mercury lifetime in the atmosphere. As a result they obtained values from 1 month to 3 years. The authors believe that most likely this value is 1 year. More recently on the base of model calculations and the comparison with monitoring data *T.Bergan et al.* [1999] came to the conclusion that mercury average lifetime in the atmosphere should be 1.3 years. *C.Lamborg* [2000] with the use of data on radioactive tracers concluded that mercury average lifetime in the atmosphere should be within the range of 0.9 - 2.1 year.

On the base of consideration of mercury atmospheric chemical transformations *C.Seigneur and K.Lohman* [1999] estimated the lifetime of elemental mercury as long as 1.2 years in the absence of clouds, and the availability of clouds increases this value to 1.7 years. They believe that clouds are favorable for the reduction of short-lived oxidized compounds to long-lived elemental form.

The range of estimates of mercury average lifetime in the atmosphere is sufficiently wide. In this work for the hemispherical model it is assumed that the lifetime is within the limits from 1 to 1.5 years.

2.2. Physical-chemical processes in the gas and aqueous phases

Among the metals considered only mercury and its compounds are subject to physical-chemical transformations, which can drastically alter their parameters of scavenging from the atmosphere. To these transformations belong transfers between the gaseous, liquid and solid phases and chemical reactions in the gaseous and aqueous media. It is very important to know temperature dependence of inter-phase equilibrium coefficients and chemical reaction rates since in the troposphere the temperature can vary within 130ºC (from –80 to +50ºC).

Inter-phase equilibrium coefficients

All gaseous mercury compounds to this or that extent are soluble in cloud and rain drops. Droplet sizes are small enough therefore the equilibrium between the solution and gas is established rather rapidly. As a rule, equilibrium states are described by Henry's law with allowance made for the temperature effect. The same approach can be used for the description of equilibrium between the atmospheric air and water surface of a sea or lake. In this section for the convenience of comparison the Henry's law coefficients are given in the dimensionless form (being more precise as the ratio of concentration in the liquid to air concentration).

We have not found any publications (for last 5 years) which could change to any extent our ideas about the elemental mercury equilibrium between air and water. In this work we used the temperature dependence obtained in multiple measurements of dimensionless Henry's law constant within the temperature range from 278 to 298ºK represented as a ratio of the concentration in water to the concentration in air [*Ryaboshapko and Korolev*, 1997]:

$$K_{H,fresh} = 0.00984 \cdot T \cdot \exp\left(2800 \cdot \left(\frac{1}{T} - 0.003356\right)\right).$$

It is assumed that the main gaseous mercury compound in the atmosphere is chloride. In the literature most often Henry's law constant values at 298ºK ($3.4 \cdot 10^7$) and at 283ºK ($8.3 \cdot 10^7$) [*Lidqvist et al.*, 1984] are cited. *J.Sommar et al.* [1999b] give higher values of Henry's law constant for $HgCl_2$ – $4.9 \cdot 10^7$ at 298ºK and $3.6 \cdot 10^6$ at 323ºK. *A.Ryaboshapko et al.* [2001] roughly approximated the temperature dependence of Henry' law constant for mercury chloride in the "water-air" system by the expression:

$$K_{H(HgCl2)} = 1.054 \cdot 10^5 \cdot T \cdot \exp\left(5590 \cdot \frac{1}{T} - 0.003356\right).$$

This expression will be used in this report.

For other gaseous mercury compounds and individual reactants Henry's law constant values for different temperatures are given in Table 2.2. As it follows from the Table the major part of DMM in the "air-water" system should be in the gaseous state. The reverse relationship should be for CH_3HgOH, $Hg(OH)_2$ and particularly for HgO.

Table 2.2. Henry's law constants for mercury compounds and different reactants

Compound	K_H	T°K	Reference
$(CH_3)_2Hg$	6.7	273	*Lindqvist and Rodhe*, 1985
	3.2	298	
	3.2	298	*Seigneur et al.*, 1994.
CH_3HgCl	62500	288	*Lindqvist and Rodhe*, 1985
	53000	298	
	53900	298	*Seigneur et al.*, 1994
CH_3HgOH	5900000	288	*Petersen*, 1992
	3700000	293	
$Hg(OH)_2$	625000	283	*Lindqvist and Rodhe*, 1985
	310000	298	
	290000	298	*Seigneur et al.*, 1994
HgO	$3.2 \cdot 10^7$	?	*Petersen et al.*, 1998
Cl_2	270000*	?	*Lin and Pehkonen*, 1998
$^{\bullet}OH$	600	298	In: [*Lin and Pehkonen*, 1998]
$HO2^{\bullet}$	49000	298	In: [*Lin and Pehkonen*, 1998]
SO_2	30	298	In: [*Lin and Pehkonen*, 1998]
H_2O_2	$1.8 \cdot 10^7$	298	In: [*Lin and Pehkonen*, 1998]

The constant for molecular chlorine marked in the table by asterisk was obtained on the following assumptions. Chlorine solubility in cloud drops strongly depends on pH and chloride concentration. *C.-L. Lin and S.Pehkonen* [1998] suggested the formula for calculations of effective Henry's law constant:

$$H_{eff}(M/atm) = 7.61 \cdot 10^{-2} \cdot \left(1 + \frac{1 \cdot 10^{-3.3}}{([CL^-] \cdot [H^+])} + \frac{1 \cdot 10^{-10.8}}{([CL^-] \cdot [H^+]^2)}\right).$$

According to data of *U.Baltensperger et al.* [1998]; *M.Couture et al*. [1998]; *G.Kmiek et al*. [1998]; *R.Vong et al.* [1997] $[H^+]$ and $[Cl^-]$ concentrations in the marine atmosphere can be estimated by an order of magnitude as $3.2 \cdot 10^{-5}$ and $1 \cdot 10^{-4}$ M respectively. Hence it follows that effective Henry's law constant for chlorine will be equal to $1.2 \cdot 10^4$ M/atm or $2.7 \cdot 10^5$ in the dimensionless representation.

Equilibrium conditions for ozone in the "water-air" system were studied by *R.Sander* [1997]. Further we use temperature dependence suggested by him:

$$K_H(O_3) = 0.000951 \cdot T \cdot \exp\left(2325 \cdot \left(\frac{1}{T} - 0.003356\right)\right).$$

Although (as it was demonstrated above) metallic mercury cannot exist in the atmosphere in the liquid or solid states its sorption by aerosol particles is possible. Quantitative characteristics of the process first of all depend on the "gas-solid matter" contact area as well as on the composition of particles.

Lyon et al. [1999] experimentally considered two types of particles – small (diameter 0.3 μm) and coarse (5.7 μm) and accepted that the distribution in the system is proportional to the contact area. The relationship of areas appeared to be equal to 93:7 respectively.

Most likely soot particles posses the highest sorption capability. *C.Seigneur et al*. [1998] analysed literature data published by *S.Krishnan et al*. [1994], *D.Livengood et al*. [1995], Accurex Environmental [995] [cited from *C.Seigneur et al.,* 1998] on Hg^0 and HgII absorption from the gaseous phase by activated charcoal and estimated redistribution coefficients $K_{a/s}$ in the dimension "liter of air to gram of soot". For Hg^0 coefficient $K_{a/s}$ was estimated to be equal to 10 l/g and for HgII –$3 \cdot 10^5$ l/g. *C.Seigneur et al*. [1998] indicate that it is not clear so far whether activated charcoal and atmospheric particles have the same chemical properties. Besides the redistribution value should depend on the temperature but nothing is known about it as yet.

In the comparison of various schemes of mercury liquid-phase chemistry [*Ryaboshapko et al*., 2001] it was demonstrated that mercury partition in the "liquid-solid matter" system considerably affects mercury accumulation in cloud and rain drops. Above all it is influenced by mercury accessibility to chemical transformations in the liquid phase and non-accessibility in the sorbed state. Soot particles contained in drops may serve as the most probable sorbent.

C.Seigneur et al. [1998] analysed data of *L.Thiem et al.* [1976] and *X.Ma et al.* [1996] (cited from *C.Seigneur et al.,* 1998) on the absorption of HgII from water by activated charcoal and estimated the redistribution coefficient $K_{w/s}$ in the dimension "liter of water to gram of soot". For atmospheric conditions in the first approximation the coefficient is equal to 3700 l/g of HgII.

Special experiments with rain water for the determination of partitioning coefficient K_p with shaking of aerosol matter in pure water and for the determination of desorption coefficient K_d showed that these coefficients are of the same order of magnitude [*Seigneur et al*., 1998]. However, K_p varies from 100 to 600 l/g and K_d – from 200 to 1400 l/g. The experiment with adsorption on sampled aerosol matter of dissolved forms made for the determination of the adsorption coefficient K_a revealed that K_a is lower by an order of magnitude than K_d. Most likely it is connected with the occurrence of insoluble mercury forms (oxide and sulphide) in aerosol matter. The nature of aerosol matter can drastically affect coefficient values. Values of pH actually did not influence the investigated coefficients.

Gaseous reactions, their products and oxidant concentrations

In the atmosphere there is a number of chemical substances capable to oxidize elemental mercury and its organic compounds in the gaseous state. Photochemical processes leading to decay of molecules are also possible. The integral indicator of the significance of this or that reaction for mercury atmospheric cycle is mercury lifetime in the atmosphere relative to a given reaction. Based on this indicator it is reasonable to consider only those reactions, which make a tangible contribution to mercury atmospheric cycle. It is also important to know reaction products since their rate of scavenging from the atmosphere essentially depends on their phase state.

It is recognized that ozone is one of most important oxidant in the gas phase. In the majority of modern models describing mercury bahaviour in the atmosphere the second order reaction rate constant of oxidation by ozone suggested by *B.Hall* [1995] and equal to $(3 \pm 2) \cdot 10^{-20}$ cm^3/molec/s at 20ºC is used. First of all it should mention that this estimate has an essential uncertainty. *B.Hall* also investigated the temperature effect of this reaction at 22, 55 and 75ºC. With temperature decrease the reaction rate should decline (activation energy about 10 kJ/mole, pre-exponential multiplier $2.1 \cdot 10^{-18}$ cm^3/molec/s). With the use of these data we obtained the following temperature dependence of this reaction rate:

$$k = 2.1 \cdot 10^{-18} \cdot \exp\left(-\frac{1246}{T}\right) \quad \text{cm}^3/\text{molec/s}.$$

In a rough assessment mean tropospheric temperature is 0ºC, it gives the oxidation reaction rate equal to $2.2 \cdot 10^{-20}$ cm^3/molec/s. At the average concentration of ozone in the troposphere $7.5 \cdot 10^{11}$

molec/m^3 mean lifetime of elemental mercury in the troposphere relative to this reaction is 2 years. Therefore this reaction is one of most important in the atmospheric mercury chemistry.

It is difficult to say what compound may be a product of Hg^0 oxidation by ozone. Most probably the oxide is formed. *G.Petersen et al.* [1998] consider the reaction product to be gaseous. On the contrary experts from *EPA USA* [1997] suppose that the reaction product actually immediately is adsorbed by aerosol particles and then behaves itself in the atmosphere in accordance with properties of particles-carriers. We believe if mercury oxide is the product of oxidation by ozone, it cannot exist in the atmosphere as a gas due to its poor volatility [*Sommar et al.,* 2001; *Schroeder and Munthe,* 1998]. It should be immediately and irreversibly trapped either by particles or by cloud drops.

J.Sommar [1999a, 2001] studied the reaction of elemental mercury oxidation by hydroxyl radical. The reaction can go on in two stages:

$Hg^0 + {}^{\bullet}OH \rightarrow {}^{\bullet}HgOH$

${}^{\bullet}HgOH + O_2 \rightarrow HgO + HO_2^{\bullet}$

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$Hg^0 + {}^{\bullet}OH \rightarrow HgO + HO_2^{\bullet}$ ($k = 8.7 \pm 2.8\ 10^{-14}$ cm^3/molec/s.)

At the mean concentration of atmospheric hydroxyl concentration $1{\cdot}10^6$ molec/cm^3 the Hg^0 lifetime relative to this reaction will be less than a year. Thus this reaction is more important than the reaction of oxidation by ozone. The temperature dependence of the reaction rate is unknown. This high value of the oxidation rate has not been confirmed by any independent laboratory yet, hence one should be careful dealing with this high value.

The reaction of Hg^0 oxidation by chlorine [*Seigneur et al*., 1994; *Tokos et al*., 1998] may be important for the atmosphere over the ocean.

$Hg^0_{gas} + Cl_{2\ gas} \rightarrow HgCl_{2\ gas}$ $K \le 4{\cdot}10^{-16}$ cm^3/molec/s at 25°C.

B.Hall [cited from *Tokos et al.,* 1998] showed that the reaction rate does not depend on temperature in the temperature range considered. In the atmosphere near the oceanic water surface chlorine concentration may be about $3{\cdot}10^9$ molec/cm^3. Under these conditions Hg^0 mean lifetime relative to this reaction will be estimated at days. However, it should be mentioned that in the atmosphere chlorine could exist only at night, only over the ocean and only in the lowest atmospheric layer. This reaction should be considered in the model scheme since the oceanic underlying surface is represented in models both of regional and global scale.

Gaseous hydrogen peroxide may be another oxidant of elemental mercury.

$Hg^0_{gas} + H_2O_{2\ gas} \rightarrow Hg(HO)_{2\ gas.}$

Available in the literature information about this reaction rate is contradictory. For instance, *E.Constanttinou et al*. [1995] use the rate constant equal to $4.1{\cdot}10^{-16}$ cm^3/moles/s at 25ºC. *J.Tokos et al.* [1998] gives a considerably lower value – $6{\cdot}10^{-19}$ cm^3/mole/s. It is essential to note that the reaction rate should strongly depend on temperature. On the base of data on activation energy (-75 kJ/mole) in this work we use the following temperature dependence:

$$k = 8.4 \cdot 10^{-6} \cdot \exp\left(-\frac{9021}{T}\right) \quad \text{cm}^3\text{/molec/s} .$$

If, as before, we assume that mean atmospheric temperature is 0ºC, then the oxidation rate will be $3.7 \cdot 10^{-20}$ cm^3/molec/s. At the mean atmospheric concentration of gaseous H_2O_2 equal to $2.5 \cdot 10^{10}$ molec/cm^3 elemental mercury lifetime in the atmosphere will be about 30 years. Most likely it is the minimum value since hydrogen peroxide is a daytime oxidant [*Lin and Pehkonen*, 1999]. For this reason gas phase oxidation reaction of Hg^0 by hydrogen peroxide may not be considered both in hemispherical and regional simulation.

Mercury organic compounds, for example, DMM are sufficiently rapidly destructed in the atmosphere at the reaction with OH radical [*Niki et al.*, 1983]. The reaction product is either elemental mercury [*Niki et al.*, 1983] or MMM [*Schroeder and Munthe*, 1998]. The reaction rate constant is $2 \cdot 10^{-11}$ cm^3/molec/s. At mean radical concentration $1 \cdot 10^6$ molec/cm^3 atmospheric lifetime of DMM should not exceed several hours [*Lin and Pehkonen*, 1999]. Besides *M.Horvat* [1996] points to a possibility of photochemical destruction of DMM leading to even shorter lifetime.

Theoretically mercury reduction in the gas phase to the elemental state is not excluded. For example, photochemical destruction of molecules containing mercury can lead to formation of Hg^0 but quantitative information on such reactions is not available yet [*Seigneur et al.*, 1994].

Aqueous phase reactions, their products and reactant concentrations

Schemes of liquid phase transformations used in modern models for mercury transport assume a simultaneous action of two mechanisms – oxidation and reduction of elemental mercury. These schemes are described in detail in the work of *A.Ryaboshapko et al.* [2001]. The main oxidants may be dissolved ozone and chlorine as well as hydroxyl radical formed directly in a drop. Sulphite complexes and hydroperoxide radical may be reducing agents. Photoreduction of some compounds is also possible. Modern ideas about liquid phase mercury chemistry are described in detail in the work by *C.-J.Lin and S.Pehkonen* [1999].

Many investigators studied the reaction of Hg^0 oxidation by ozone in the water environment. *C.-J.Lin* and *S.Pehkonen* [1999] take the reaction rate equal to $(4.7 \pm 2.2) \cdot 10^7$ M^{-1} s^{-1}. In order to estimate the uncertainty of this value, Table 2.3 summarizes in the chronological order values used by different modellers. As it follows from the Table the reaction rate published by *J.Munthe* in 1992 is used in models. The dependence of rate on solution temperature and pH may be neglected. It may be supposed that both on regional and global scale the reaction with ozone is the basic one for elemental mercury oxidation.

Hg^0 oxidation by hydroxyl radical takes place only in the daytime since the radical itself is a product of photochemical reactions. *C.-J.Lin and S.Pehkonen* [1997] estimated that the reaction rate equals to $2.0 \cdot 10^9$ $M^{-1}s^{-1}$. *K.Gårdfeldt et al.* [2001a] suggest a very close value – $(2.4 \pm 0.3) \cdot 10^9$ $M^{-1}s^{-1}$.

Table 2.3. Rate constants of Hg^0 oxidation by ozone in the liquid phase, M^{-1} s^{-1}

Rate constant	Dependencies		Reference
	on temperature	on pH	
$(4.7 \pm 2.2) \cdot 10^7$	independent	Independent	*Munthe*, 1992
$4.7 \cdot 10^7$	25C		*Seigneur et al.*, 1994
$4.5 \cdot 10^7$			*Pleijel and Munte*, 1995
$4.7 \cdot 10^7$	25C		*Constantinou et al.*, 1995
$4.5 \cdot 10^7$			*Lin and Pehkonen*, 1997
$4.7 \cdot 10^7$	5C		*Petersen et al.*, 1998
$4.7 \cdot 10^7$		Dependent	*Lin and Pehkonen*, 1998
$(4.7+/-2.2) \cdot 10^7$	no within (5-35°C)	No	*Lin and Pehkonen*, 1999

Herrmann et al. [2000] investigated variations of hydroxyl radical concentrations in cloud water. First of all, the concentration depends on the atmosphere pollution by substances capable either to generate radicals or react with them. Besides there is a strong dependence on a drop size. In the daytime OH concentration variation may be roughly described by a function of square sine.

C-J. Lin and S. Pehkonen [1997] assumed OH concentration in water at noon as $3.7 \cdot 10^{-15}$ M. In this case the constant of reaction of pseudo-first order is $7.4 \cdot 10^{-6}$ s^{-1} [*Lin and Pehkonen*, 1997]. Liquid-phase reactions of oxidation by ozone and OH radical compete: at the ozone air concentration <4 ppb radical oxidation prevails. At concentrations more than 10 ppb the contribution of radical reaction is about 20%, and at 20ppb – only 10%. By recognizing that ozone concentration may decline to low values it is reasonable to consider the reaction of radical oxidation in model scheme of regional and global scale.

Under certain conditions the reaction of Hg^0 oxidation by dissolved chlorine may be important. Being dissolved in the liquid phase chlorine may be in two forms – hypochlorine acid and hypochlorite ion, which relationship depends on solution pH. Oxidation by chlorine can take place mainly in the sea atmosphere and only at night since Cl_2 and HOCl are decomposed at light. Both hypochlorine acids and hypochlorite ion can oxidize mercury [*Lin and Pehkonen*, 1999]:

$$HOCl + Hg^0 \rightarrow Hg^{2+} + Cl^- + OH^- \quad (K = 2.09 +/- 0.06) \cdot 10^6\ M^{-1}\ s^{-1})$$

$$OCl^- + Hg^0 \rightarrow \rightarrow Hg^{2+} + Cl^- + OH^- \quad (K = 1.99 +/- 0.05) \cdot 10^6\ M^{-1}\ s^{-1})$$

Since chlorine content over oceans is sufficiently high, it seems reasonable to include this pathway of oxidation to the calculation scheme of the global level model. In the regional EMEP model the reaction with chlorine in the aqueous phase may be neglected.

It was considered earlier that the main agent responsible for the mercury reduction to the elemental state was sulphite ion forming unstable complexes with mercury ion [*Munthe et al*, 1991]. As a result of complex decays an atom of elemental mercury comes to the liquid phase. Photoreduction of $Hg(OH)_2$ was indicated also as a possible reduction mechanism [*Pleijel and Munthe*, 1995]. During recent years radical mechanism of reduction at the reaction of mercury ion or dissolved compounds with HO_2 radical was investigated [*Lin and Pehkonen*, 1997, 1998].

Chemistry of mercury sulfite complexes is not sufficiently studied up till now. In a general form the scheme of the sulfite mechanism at present is represented in the following way.

At the first step sulfur dioxide is dissolved in a water drop with the formation of three forms of 4-valent sulfur – non-dissociated sulfuric acid, bisulfite-ion and sulfite ion. At real pH values of cloud water within the range of 3.0-5.0 the bulk of S^{IV} is represented by the first two forms, although in any case concentrations of sulfite-ion trace quantities will be higher than concentrations of dissolved mercury.

Sulfite-ion can react with divalent mercury ion forming mercury sulfite. Further it combines another sulfite-ion producing sulfite-mercury complex [*Constantinou et al.*, 1995]:

$$Hg^{2+} + SO_3^{2-} \longleftrightarrow HgSO_3\ (aq);$$

$$HgSO_3\ (aq) + SO_3^{2-} \longleftrightarrow Hg(SO_3)_2^{2-}.$$

Note that *G.Petersenet et al* [1998] consider this pathway to be impossible on the assumption that primary the complex is formed. Then it dissociates with the formation of mercury sulfite. In any case mercury sulfite complex dominates among all other mercury compounds with four-valence sulfur [*Lin and Pehkonen*, 1997].

Mercury sulfite and probably sulfite-mercury complex are decayed and mercury is reduced to the elemental state [*Constantinou et al.*, 1995]:

$Hg(SO_3)_2^{2-}$ --> $Hg^0(aq)$;

$HgSO_3$ (aq) --> $Hg^0(aq) + SO_3^{2-}$.

In a general form the intramolecular redox process may be represented by the following reaction chain [*van Loon et al.,* 2000]:

$$Hg^{2+}_{(aq)} + SO_3^{2-}{}_{(aq)} = Hg^{II}S^{IV}O_3 \rightarrow Hg^0S^{VI}O_3 \rightarrow Hg^0_{(aq)} + S^{(VI)}$$

Thus the availability of S^{IV} in a drop provides the action of negative feedback increasing elemental mercury concentration in a drop and preventing from its additional solution from the ambient air. *G.Petersen et al.* [1998] believe that mercury reduction process is limited by reaction of $Hg(SO_3)_2^{-2}$ dissociation. Data on the rate constants of the indicated reactions are very contradictory. It is demonstrated in Table 2.4.

Table 2.4. Reaction rates of sulphite reduction of mercury in the liquid phase

Reaction	Rate (*k*) / equilibrium (*K*) constant	t°C	Reference
$HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$	$K = 2.5\cdot10^{11}$ M^{-1}	25	*Seigneur et al.*, 1994
$Hg^{2+} + SO_3^{2-} \leftrightarrow HgSO_3(aq)$	$K = 5.0\cdot10^{12}$ M^{-1}	25	*Seigneur et al.*, 1994
$Hg^{2+} + HSO_3^{-} \leftrightarrow Hg(HSO_3)^{-}$			
$Hg^{2+} + SO_3^{2-} \rightarrow HgSO_3$	$k = 5.0\cdot10^{12}$ M^{-1}	25	*Constantinou et al.*, 1995
$Hg^{2+} + 2SO_3^{2-} \rightarrow Hg(SO_3)_2^{2-}$	$k = 1.1\cdot10^{-21} * ([SO_{2\,(g)}] / 10^{-2*pH})^2$ s^{-1}	5	*Petersen et al.,* 1998
$HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$	$K = 2.5\cdot10^{11}$ M^{-1}	25	*Constantinou et al.*, 1995
$Hg(SO_3)_2^{2-} \rightarrow Hg^0$	$k = 1\cdot10^{-4}$ s^{-1}	25	*Constantinou et al.*, 1995
$Hg(SO_3)_2^{2-} \rightarrow Hg^0$	$k = 1.0\cdot10^{-4}$ s^{-1}	25	*Seigneur et al.*, 1994
$Hg(SO_3)_2^{2-} \rightarrow HgSO_3 + SO_3^{2-}$	$k = 4.4\cdot10^{-4}$ s^{-1}	5	*Petersen et al.*, 1998
$HgSO_3 \rightarrow Hg^0 + SO_3^{2-}$	$k = 0.6$ s^{-1}	25	*Constantinou et al.*, 1995
$HgSO_3 \rightarrow Hg^0$	$k = 0.6$ s^{-1}		*Munthe et al.*, 1991
HgSO3 $\rightarrow Hg^0$ + products	$k = 0.6$ s^{-1}		*Lin and Pehkonen,* 1999
$HgSO_3 \rightarrow Hg^0 + SO_4^{2-}$	$k = 0.6$ s^{-1}	25	*Seigneur et al.*, 1994
$Hg(SO_3)_2^{2-} \rightarrow Hg^0$	$k = 0$		*Munthe*, 1994
$Hg(HSO_3)^{-} \rightarrow Hg^0 + S(VI)$	$k = 4\cdot10^{-6}$ s^{-1}		*Munthe et al.*, 1991

While considering the importance sulphite reduction mechanism one should take into account several things. First, if water solution has chloride, mercury ions mainly form mercury chloride [*Prokofiev*, 1981; *Lindqvist et al.*, 1984; *Lin and Pehkonen,* 1998]. At the same time the probability of sulphite compound formations drastically decreases. Under real atmospheric conditions the content of chlorides in cloud water varies from $2\cdot10^{-5}$ to $4\cdot10^{-4}$ M [*Baltensperger et al.*, 1998; *Couture et al.*, 1998; *Kmiec et al.*, 1997]. The content of chlorides is particularly high in the atmosphere over the ocean – up to $4\cdot10^{4}$ M [*Vong et al.*, 1997]. Observations in Europe under EMEP [*Ilyin et al.*, 2001] show that chloride content in precipitation is always higher than $2\cdot10^{-6}$ M used in the work by *G.Petersen et al.* [1998]. The model analysis of chemical scheme sensitivity to chloride content demonstrated that actually sulphite mechanism of reduction starts acting only when chloride concentrations are lower than $5\cdot10^{-6}$ M [*Ryaboshapko et al.*, 2001].

Second, sulfites in cloud water are rapidly oxidized to sulfates. According to data of *C.-J.Lin and S.Pehkonen* [1998] in 5 hours sulphite-ion content becomes negligible and the sulfite reduction mechanism ceases to act (it is assumed that in cloud formation the bulk of sulfur dioxide is dissolved in the liquid phase). It is also important that at high concentrations of sulfite-ion the sufficiently stable complex $Hg(SO_3)_2^{2-}$ is mainly formed [*Lin and Pehkonen*, 1998] (see the Table).

Third, as it was mentioned above the probability of sulfite-ion formation is strongly dependent on solution pH. According to *G.Petersen et al*. [1998] the rate of mercury-sulfite decomposition complex is defined by solution acidity. Model assessments showed [*Ryaboshapko et al.*, 2001] that sulfite reduction mechanism begins to act at pH more than 5.

Finally, fourth, sulfite reduction rate drastically decreases with temperature decrease. According to data of *L.Loon et al*. [2000] at temperature decrease from 25ºC to 0ºC the rate declines more than 20 times.

C.-J.Lin and S.Pehkonen consider that in general SO_2 is not important in mercury reduction since sulfur oxidation to 6-valence state goes on quickly. Ozone is the principal oxidant in the continental atmosphere in the daytime and at night, in the marine atmosphere – in the daytime. At night clorine is the main oxidant in the oceanic atmosphere. Taking into account this opinion and the analysis made above in this work for the EMEP region the sulphite reduction mechanism will be included to the calculation scheme since the levels of pollution by sulfur dioxide in this region are high enough. On the contrary it is not reasonable to consider this mechanism in the global model since over oceans, over remote parts of continents and in the free troposphere SO_2 concentrations account for tenths and even hundredths of fractions of ppb.

Part of oxidized mercury can be represented by hydrate. Under real conditions it can take place only at high pH and when chlorides are practically absent. Under the impact of solar light hydrate can decay forming elemental mercury. *Z.Xiao et al*. [1994] estimated that even at summer noon in the latitude of Stockholm this reaction is very slow ($K = 3 \cdot 10^{-7}$ s^{-1}). In this report in calculations of liquid-phase transformations this reaction is neglected.

C.-J.Lin and S.Pehkonen [1997, 1998] found that hydroperoxide radical can be a very effective reducing agent:

$$HgII + HO_2^{\bullet} \rightarrow Hg0 + prod.$$

According to their data the reaction rate is $1.7 \cdot 10^4$ $M^{-1}s^{-1}$ and typical level of HO_2 radical concentration in the liquid phase is $1 \cdot 10^{-8}$ M. It is particularly important that this radical reacts both with free mercury ions and with molecular compounds of $HgCl_2$ type. At the same time it is assumed that molecules of mercury compounds sorbed by particles are not accessible for this reduction mechanism. The reaction is dependent on pH but the quantitative description of this dependence is not available so far. The diurnal dynamics of the radical concentration was investigated in detail by *H.Herrmann et al*. [2000] under different external conditions. Like in the case with radical OH in the daytime HO_2 concentration variations can be described by a function square sine. On the base of said above it seems important to include this reaction to the model calculation scheme.

It is known that the major part of cloud water does not fall out as precipitation but it is evaporated. For modelling of mercury behaviour in the atmosphere the interpretation of mercury fate after drop evaporation is important. The literature provides very contradictory information on this issue. Earlier it was supposed [*Lindqvist et al.*, 1991] that reactive oxidized mercury after water evaporation is reduced to the elemental form due to photo-dissociation. Only chemically persistent compounds of HgS type are remained in the solid state. *G.Petersen et al.* [1998] in their model assume that at drop evaporation all mercury compounds are transferred to the gaseous phase. Experts of *EPA USA* [1997] consider that after drop evaporation an aerosol particle is formed containing in its composition all earlier dissolved and insoluble mercury compounds. In this report the opinion of *EPA USA* experts [1997] is accepted.

2.3. Scavenging from the atmosphere

Update of dry uptake parameterization of particles in MSCE-HM heavy metal model

This section is intended to describe modification of dry uptake parametrization for MSC-E model of long-range transport of heavy metals. The update refers only to land surfaces, and concern only aerosol compounds - lead, cadmium and particulate mercury. Previous scheme [*Pekar*, 1996] used the following regression formulas to compute dry deposition of lead and cadmium to land surfaces:

$$\left.\begin{aligned} v_d(Pb) &= (0.02 \cdot u_*^2 + 0.01) \cdot (z_0 / 10^{-3})^{0.33} \\ v_d(Cd) &= (0.04 \cdot u_*^2 + 0.02) \cdot (z_0 / 10^{-3})^{0.30} \end{aligned}\right\} \qquad (2.1)$$

where $V_d(Pb)$ and $V_d(Cd)$ are dry deposition velocities for lead and cadmium, cm/s; respectively, u_* is friction velocity, m/s; and z_0 is roughness length, m.

Scheme (2.1) needs modification for two reasons. First, field studies show that dry deposition velocity depends on the stability of the atmospheric surface layer. Parameterization (2.1) provides rather similar deposition velocities at stable and unstable atmospheric stratification. Second, dry uptake scheme should account for different land-use types. The effects community is estimating critical loads and exceedances of heavy metals for different land-use categories. The previous deposition scheme computed deposition velocities for the entire EMEP grid cell disregarding land-use types within a cell with the use of averaged over a cell parameters.

To compute deposition fluxes to different land-use categories database of land-use developed at Coordinating Centre for Effects was used [*Posh et al.,* 1997]. It is represented by eight categories of land-use: (1) deciduous forests, (2) coniferous and mixed forests, (3) arable land, (4) permanent crops, (5) grassland, (6) inland waters, (7) urban area, and (8) other areas (extensive agriculture and natural areas).

When considering dry deposition of a pollutant electric resistance analogy is usually applied. In terms of resistances dry deposition velocity is written as follows:

$$v_d = \frac{1}{r_a + r_b + r_c} \qquad (2.2)$$

In (2.2) r_a is referred to as aerodynamic resistance. A pollutant has to overcome this resistance when transporting within turbulent surface layer. This resistance is a property of the atmosphere and does not depend on a particular type of a pollutant. Term r_b is the resistance of a near-surface laminar layer. Since transport within this layer is controlled mainly by Brownian diffusion, this resistance depends not only external parameters (surface roughness, wind velocity, etc) but also on specific properties of a pollutant. The third resistance - r_c - denotes resistance of surface itself and, in its turn, comprises a number of resistances of surface elements like stomata, cuticle, soil, etc [*Wesely and Hicks*, 2000].

Unlike gaseous compounds, for particles there is one more driving force responsible for their transfer to the underlying surface from the atmosphere - gravitation. Obviously, the greater particle the stronger mechanism of gravitational settling is. In the case of particulate compounds dry deposition velocity is considered as follows [*Wesely and Hicks*, 2000; *Hicks et al.,* 1987; *Ruijgrok*, 1995]:

$$v_d = \frac{1}{r_a + r_{ds} + r_a \cdot r_{ds} \cdot v_g} + v_g \qquad (2.3)$$

In formula (2.3) the sum of laminar resistance and surface resistance is replaced by term r_{ds}, reciprocal of which is called surface deposition velocity: $v_{ds} = 1/r_{ds}$. In (2.3) v_g is velocity caused by gravitational settling.

To parameterize dry deposition velocity to forested areas the model developed by *W. Ruijgrok et al.* [1997] was applied to this work. This work is based on long-term (set of 2-3 days campaigns during about 7 months) measurements carried out in the framework of Dutch Priority Program on Acidification [*Erisman et al.,* 1997; *Wyers and Duyzer*, 1997] in Speulder Forest, the Netherlands. On the basis of the experiments and taking the theoretical model of particle deposition to canopy developed by *W. Slinn* [1982]; *W. Ruijgrok et al*. [1997] developed handy parameterization formulas describing dry deposition velocity of particles depending on friction velocity and relative humidity of air.

In work [*Ruijgrok et al.,* 1997] it was suggested to compute v_{ds} in the following way:

$$v_{ds} = E \cdot \frac{u_*^2}{u_h} \tag{2.4}$$

where u_* - friction velocity, u_h - wind velocity at the canopy top, and E represents total collection efficiency with which vegetation captures particles. E depends on particle size, relative humidity, conditions of the underlying surface and friction velocity. In the paper [*Ruijgrok et al.*, 1997] dependence of E for particles containing SO^{2-}_4, NO^-_3, NH^+_4 and Na^+ on these parameters was presented. Since particles containing Na are characterized by mass median diameter significantly greater than that of priority metals, they are no longer considered in the current work.

Following [*Ruijgrok et al.,* 1997] E is calculated as:

$$E = \alpha \cdot u_*^{\beta} \cdot \left[1 + \gamma \cdot \exp\left(\frac{RH - 80}{20}\right)\right], \qquad \text{if } RH > 80 \tag{2.5}$$

$$E = \alpha \cdot u_*^{\beta}, \qquad \text{if } RH \le 80 \tag{2.6}$$

where RH is the relative humidity in surface layer, %, u_* - friction velocity, m/s; α, β, and γ - empirical coefficients, which are different for dry and wet underlying surface. Coefficients α, β are also dependent on specific pollutant.

It was proposed that if it is raining, the surface is wet, and if there is no rain the surface is dry. Relative humidity was assumed to be 80%. However, in the case of rain event it was assumed that expression in square brackets in formula (2.5) is reduced to $[1 + \gamma]$, thus accounting for some possible increase of the collection efficiency under rainy (and, hence, more humid) conditions. Parameter α was chosen as an average among available values in the work [*Ruijgrok et al.,* 1997], and parameter β was selected as a intermediate value between available ones. The parameters used in MSCE_HM model for computation of dry deposition of Pb, Cd and Hg_{part} are summarized in Table 2.5.

Table 2.5. Parameters used in MSCE_HM model for estimation of dry deposition to forests

Parameter	Wet surface	Dry surface
α	0.082	0.054
β	0.43	0.25
γ	0.37	0.0

Friction velocity u* is computed via parameterization of atmospheric boundary layer [*Pekar*, 1996]. Wind velocity at the canopy top u_h is computed basing on logarithmic wind profile including correction for on the surface layer stability:

$$u_h = u_{ref} \cdot \frac{\left(\ln \frac{FH - DH}{z_{0F}} - \psi_m (FH - DH) \right)}{\left(\ln \frac{z_{ref}}{z_{0F}} - \psi_m (z_{ref}) \right)} \tag{2.7}$$

where u_{ref} - wind velocity at the reference level, z_{ref} - reference height, which is equal to half the lowest model layer, z_{ref} = 50 m, *FH* - height of forest, *DH* - displacement height, z_{0F} - roughness length over forested area, ψ_m - Monin-Obukhov stability correction function for momentum. Similar to the work [*Ruijgrok et al.,* 1997], the following values were accepted in the scheme*:* *FH* = 20 m, *DH* = 15 m and z_{0F} = 2 m. Wind velocity at 50 m height is derived from meteorological data.

Correction function was taken as [*Garrat*, 1999]:

$$\psi_m = 2 \cdot \ln\left(\frac{1 + x}{2} \right) + \ln\left(\frac{1 + x^2}{2} \right) - 2 \cdot arctg(x) + \frac{\pi}{2} \qquad \zeta < 0, \tag{2.8}$$

$$\psi_m = -6 \cdot \zeta\,, \qquad \zeta > 0, \tag{2.9}$$

where $x = (1 - 19 \cdot \zeta)^{1/4}$ and $\zeta = z/L$, *z* is height and *L* is Monin-Obukhov length scale. This approach was applied to deciduous forests and mixed and coniferous forests.

In the case of grass vegetation, an approach developed by *M. Wesley et al. [*1985] for sulfate particles was employed. This approach was also used in other regional-scale models, e.g., [*Brook et al.*, 1999a, *Erisman,* 1993]. According to this approach, deposition velocity v_{ds} (cm/s) is calculated as follows:

$$v_{ds} = 0.002 \cdot u_* \,, \qquad \text{if } L > 0. \tag{2.10}$$

$$v_{ds} = 0.002 \cdot u_* \cdot \left[1 + \left(-\frac{300}{L} \right)^{2/3} \right], \qquad \text{if } L < 0. \tag{2.11}$$

Formula (2.11) can result in extremely high deposition velocity under highly unstable conditions. In MSC-E model it was assumed that L cannot be lower than -10 under convective conditions and if $|L| > 200$ the atmosphere is neutral and formula (2.10) is used. This approach was used to compute deposition to grasslands, arable lands and permanent crops. To compute depositions to land-use categories called "other areas" and to "inland waters", *M. Pekar's* [1996] approach was kept. For urban areas constant deposition velocity of 0.5 cm/s was used.

Different types of land-use are characterized by different roughness lengths z_0, which, in turn, influence dry deposition velocity. Typically, the higher vegetation the greater roughness length. Vegetation cover is characterized by seasonal changes. This, in turn, affects roughness length and dry uptake velocity. For example, in temperate climate deciduous forests shed leaves thereby reducing the area of dry uptake. In northern Europe large areas are covered with snow in winter time, which also both reduces the capacity of dry uptake of particles and makes underlying surface smoother. In this connection consideration of seasonal changes is important matter for parameterization of dry uptake. Three types of seasons are considered in the model: cold, warm and transitional. It was proposed that the transitional season takes place twice a year and its duration is one month each time.

The following scheme for the determination of a season versus the latitude is suggested. Number of transitional month, at which season change takes place, is determined by the following formulas:

$$N_{SW} = 12 - \frac{(\cos\varphi - \cos 40^\circ)\cdot(M_{SW40} - M_{SW75})}{\cos 75^\circ - \cos 40^\circ} \tag{2.12}$$

$$N_{WS} = 3 + \frac{(\cos\varphi - \cos 40^\circ)\cdot(M_{WS75} - M_{WS40})}{\cos 75^\circ - \cos 40^\circ} \tag{2.13}$$

In (2.12) and (2.13) symbols N_{SW} and N_{WS} are integer numbers of months at which warm season changes to cold one and cold to warm, respectively, and φ is the geographical latitude. A number of assumptions were applied to these formulas. It was assumed that north of 75º latitude it is always a cold season, south of 40º - always a warm season. At 40º latitude season change is supposed to occur at 12th month ("fall", December) and at 3rd ("spring", March). At 75º the corresponding season changes are assumed to take place in August and June. The determination of transitional month at other latitudes is made by linear interpolation between cosines of 40º and 75º latitude. Terms M_{SW40} and M_{SW75} mean number of month at which transitional season between warm and cold season is established at 40º and 75º latitude, respectively. Obviously, M_{SW40} = 12 (December), and M_{SW75} = 8 (August). Terms M_{WS75} and M_{WS40} have similar meaning but for the transition from cold to warm season, and M_{WS75} = 6 (June) and M_{WS40} = 3 (March).

For each land-use category and each season type roughness length was determined basing on the literature data [*Brook et al.*, 1999a; *Davidson and Wu*, 1988; *Civerolo et al.*, 2000; *Garrat*, 1999]. The values applied to the model are summarized in Table 2.6. In the Table z_0 for forests is set always 2.0 m for all seasons. However, in order to account for possible reduction of dry uptake in the cold season, dry uptake velocities are multiplied by reduction factors. These factors for different forests are given in Table 2.7. It is important to mention that these factors are arbitrary and they are used because of the lack of data on research of aerosol dry deposition to forests in the cold season.

Table 2.6. Roughness lengths (z_0, m) for different land-use categories and season types used in the model

Land-use class	Season type		
	warm	transitional	cold
Deciduous forests	2.0	2.0	2.0
Coniferous/Mixed forests	2.0	2.0	2.0
Arable lands	0.10	0.05	0.01
Permanent crops	0.10	0.05	0.01
Grassland	0.10	0.05	0.01
Inland waters	0.005	0.005	0.005
Urban area	0.5	0.5	0.5
Other areas	0.05	0.05	0.05

Table 2.7. Reduction factors applied to dry uptake velocities computed for forests

Forest type	Season type		
	warm	transitional	cold
Deciduous forests	1.00	0.75	0.50
Coniferous/Mixed forests	1.00	0.85	0.75

Dry deposition velocities calculated by previously used and current schemes were compared. The comparison of deposition velocities with monthly resolution was performed for gridcells in six regions:

the central part of European Russia, the central part of Germany, the central part of Sweden, the central part of the United Kingdom, the southern part of Spain and the central part of Romania. These regions were selected as they represent different geographical sections of the EMEP domain. In Figure 2.1. a - f deposition velocities for different land-use categories in comparison with that used in previous calculations are shown. These results are based on emission and meteorological data for 1999.

As seen from the Figures, dry deposition velocity over forested areas is an order of magnitude higher than that used in the previous scheme or that over arable lands. It means that elevated dry deposition fluxes are expected in gridcells where forests occupy significant percent of the area. Dry uptake velocities to arable lands are on average somewhat greater than those used in previous scheme, especially in summer season. It can be explained by the fact that current scheme strong increase in dry uptake velocity at unstable conditions. In summertime in Europe convective conditions more probable, so it results in higher average dry uptake velocity. Another reason of explicit seasonal variations of dry uptake velocities for forests and arable lands is their strong dependence on roughness height.

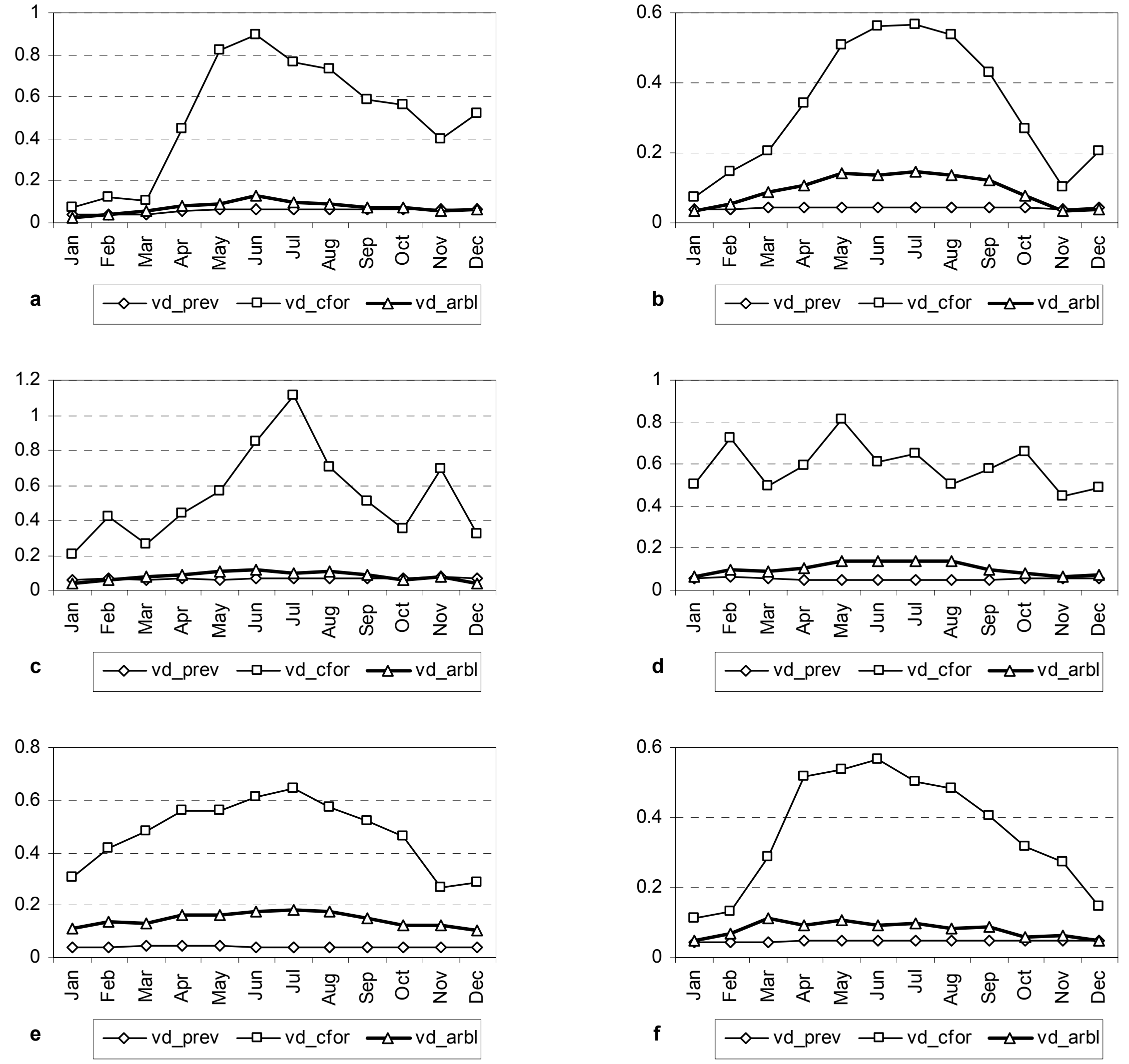


Figure 2.1. *Comparison of deposition velocities (cm/s), used in previous scheme (vd_prev) and in current scheme for coniferous forests (vd_cfor) and for arable lands (vd_arbl).* ***a*** *- Central part of European Russia,* ***b*** *- Central Germany,* ***c*** *- Central Sweden,* ***d*** *- Central United Kingdom,* ***e*** *- southern part of Spain, and* ***f*** *- Central Romania*

It could be interesting to evaluate not only dry uptake velocities, but also dry deposition fluxes based on these velocities. Specific and total annual deposition fluxes computed by two schemes are summarized in the Table 2.8. As seen from the Table, dry uptake velocities obtained by scheme (2.1) are similar to those obtained with the use of approach the of [*Wesley et al*., 1985] applied to arable lands. The computed annual mean velocities of abut 0.1 cm/s for submicron particles seem to be reasonable. Computed mean annual uptake velocities to coniferous/mixed forests are about 0.5 cm/s. *G. P. Wyers* and *A. C. Veltkamp* [1997] reported the mean value of particle dry deposition velocity to a coniferous forest of 0.73 ± 0.1 cm/s. This value is based on measurements carried out in the Dutch forest during a number of months and in different seasons. During the same field studies *G. P. Wyers* and *J. H. Duyzer* [1997] reported measured average dry deposition velocity of sulfate particles as 0.7 ± 0.3 cm/s and for nitrate particles 1.2 ± 0.4 cm/s. The reported ranges were from near zero at the stable atmosphere to 4 cm/s for sulfate and 5 cm/s for nitrate at unstable atmosphere. *L. Horvath et al.* [2001], presented lower limits of dry deposition of ammonium and sulfate particles to spruce forest in May of 0.4 cm/s during daytime and 0.1 cm/s at night. *W. Ruijgrok et al*. [1997] estimated deposition velocity of sulfate particles to fir forest in the Netherlands for nine months to be 1.3 ± 1.2 cm/s during daytime and 1 ± 1.4 cm/s at night. Although these values are 2-3 times greater than those obtained in this work, one should keep in mind that results presented in [*Ruijgrok et al*., 1997] referred to both fine (<2.5 μm) and coarse (> 2.5 μm) fractions, and that the uncertainties of the estimates are high. Therefore, it is possible to conclude that dry uptake velocities applied to MSC-E transport model appear to be reasonable in terms of an order of magnitude.

The computed dry deposition velocities are similar to those derived in contemporary regional-scale models. For example, *J. R. Brook et al*. [1999b] obtained average deposition velocities of sulfates for different forest land-use types ranging from 0.6 to 1.2 cm/s in the warm (July - September) season. Daily averaged velocities to grasslands and agricultural lands for the same period were about 0.35 cm/s (0.1 cm/s at night and 0.7 cm/s in the afternoon), which is approximately 2 - 3 times higher than that in MSC-E model. This difference can probably be attributed to different roughness heights for the warm season applied to this land-use type: z_0 is equal to 10 cm in MSC-E model and 50 cm in work [*Brook et al.,* 1999b]. *Zhang et al*. [2001a] applied process-oriented size-segregated model of dry deposition for Canadian Regional Climate Model and obtained deposition velocity for 0.24 μm sulfate particles of less then 0.35 cm/s for smooth surfaces and between 0.3 - 0.75 cm/s for forest areas.

It is clearly seen from Table 2.8 that modelled dry deposition densities can vary dramatically within a gridcell. For example, deposition density for forest in a Romanian gridcell is four times higher than the density for arable lands. Comparing columns $SD_{\_prev}$, $SD_{\_cfor}$ and $SD_{\_arbl}$ it is obviously seen that previously used deposition scheme could result both in higher and in smaller dry deposition densities to different land-use categories. However, as it comes from the comparison of weight-averaged dry deposition density for these selected gridcells, updated parameterization resulted in higher dry uptake rate.

Analysis of dry uptake velocities in gridcells of different geographical regions exemplifies given how updated scheme operates and what sort of differences with previous scheme it results in. However, this analysis characterizes only several gridcells. In order to demonstrate the effect of introduction of the updated scheme on larger spatial scale, deposition with and without use of the updates mapped.

Table 2.8. Annual mean deposition velocities and annual fluxes of lead to selected gridcells in 1999. Description of symbols in the Table head is given below the table

Region	v_{d_prev}	v_{d_cfor}	v_{d_arbl}	**SD$_{\_prev}$**	**SD$_{\_cfor}$**	**SD$_{\_arbl}$**	DD$_{\_prev}$	DD$_{\_curr}$
Central European Russia	0.06	0.50	0.07	**270**	**940**	**140**	270	290
Central Germany	0.04	0.33	0.09	**150**	**560**	**170**	150	330
Central Sweden	0.07	0.54	0.08	**40**	**260**	**40**	40	180
Central U. K.	0.05	0.59	0.10	**50**	**330**	**70**	50	80
Southern Spain	0.04	0.47	0.14	**150**	**870**	**280**	150	370
Central Romania	0.05	0.36	0.08	**320**	**820**	**200**	320	580

v_{d_prev} - annual mean dry uptake velocity for previous scheme, cm/s
v_{d_cfor} - annual mean dry uptake velocity for coniferous/mixed forests, cm/s
v_{d_arbl} - annual mean dry uptake velocity for arable land, cm/s
SD$_{\_prev}$ - specific dry deposition density of lead obtained by previous scheme, kg/km^2/y
SD$_{\_cfor}$ - specific dry deposition density of lead for coniferous forests, kg/km^2/y
SD$_{\_arbl}$ - specific dry deposition density of lead for arable land, kg/km^2/y
DD$_{\_prev}$ - total dry deposition density in a gridcell obtained by previous scheme, kg/km^2
DD$_{\_curr}$ - total dry deposition density in a gridcell obtained by current scheme, kg/km^2

In Figure 2.2.a and b maps of lead dry deposition without and with use of updated deposition scheme, respectively, are shown. It is clearly seen that the modified scheme results in significantly higher annual dry uptake fluxes over the most part of Europe. As it is expected from the analysis of Figure 2.1 and Table 2.8, the most pronounced changes in dry uptake values were obtained for forested areas. The map of per cent of gridcell area occupied by forests is given in Figure 2.3. It is well seen that in the areas where per cent of forests is relatively high, such as the Scandinavian Peninsula, the north of Russia, the south-west of Germany, the Balkans, the Alps and the north-west of the Iberian Peninsula, the increase of dry deposition is most significant. Some decrease in dry deposition was obtained for Belarus and Turkey. It is connected with lower average roughness lengths used for these regions after introduction of land-use subdivision. On the average for entire land area in EMEP domain, dry deposition increased about 1.5 times.

Dry deposition makes up first tens of percent with regard to total deposition. In Figure 2.4.a demonstrates differences in total deposition resulted from the introduction of the modified scheme. It is clear from the Figure that over land total deposition is mostly increased, especially in forested regions. Over some marginal seas such as the Baltic Sea, the Adriatic Sea, the western part of the Mediterranean, the Barents Sea and Bay of Biscay total deposition is decreased from 5 to 15%. Over other areas the differences lay within ±5%.

The increase of total deposition to areas occupied by specific land-use type can be even greater than that averaged over the entire grid cell. In Figure 2.4.b the increase of total deposition to forested areas is shown. As seen, the highest increase took place in the southern part of the Iberian Peninsula, in Ireland, along southern coast of the North and Baltic Seas as well as in southern part of Italy. Although the most of forest area is located in the Scandinavia Peninsula and in the north of European Russia (see Figure 2.3, the increase of total deposition is moderate. It is explained by the fact that the previous scheme (see formula 2.1) accounted for elevated roughness over forests, also producing relatively high dry deposition velocities. At some gridcells even small decrease took place, but the number of them was few.

For entire EMEP domain the increase in dry deposition on land calculated by new dry uptake scheme made up about 1.5 times. The increase of total deposition to the entire EMEP domain was negligible, whereas the increase only for land area was more than 3%. These Figures indicate that one should not expect significant changes in atmospheric pollutant budget for aerosol compounds because of the introduction of new dry deposition scheme, and essential changes should take place on smaller scales like individual gridcells or groups of gridcells.

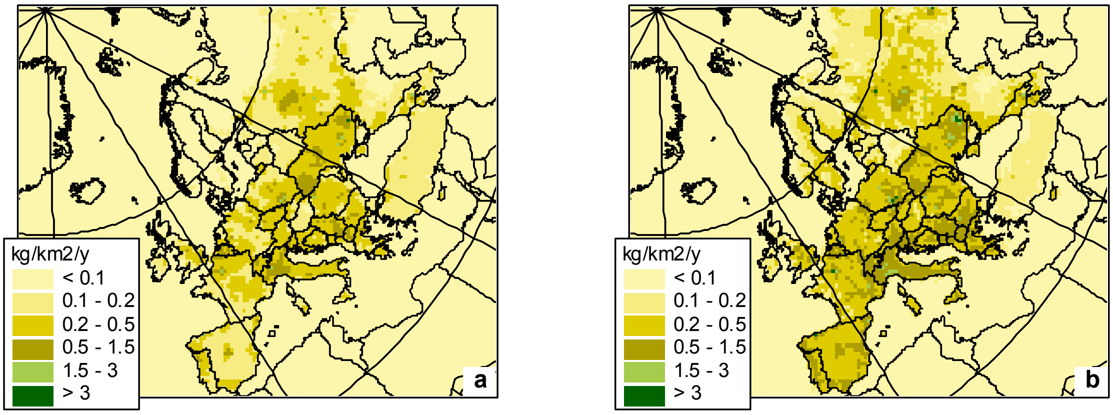


Figure 2.2. *Dry deposition density of lead obtained on the basis of previous deposition scheme -* ***a*** *and updated scheme –* ***b****, kg/km^2/y*

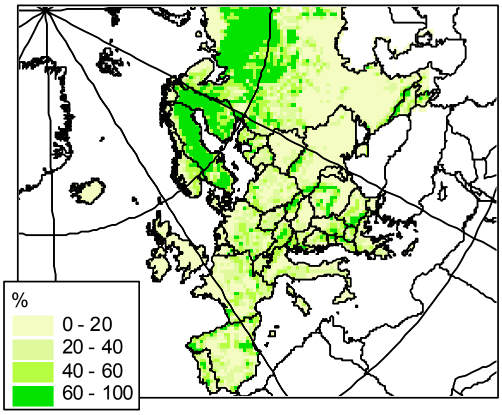


Figure 2.3. *Fraction of gridcell area, covered by forests, %*

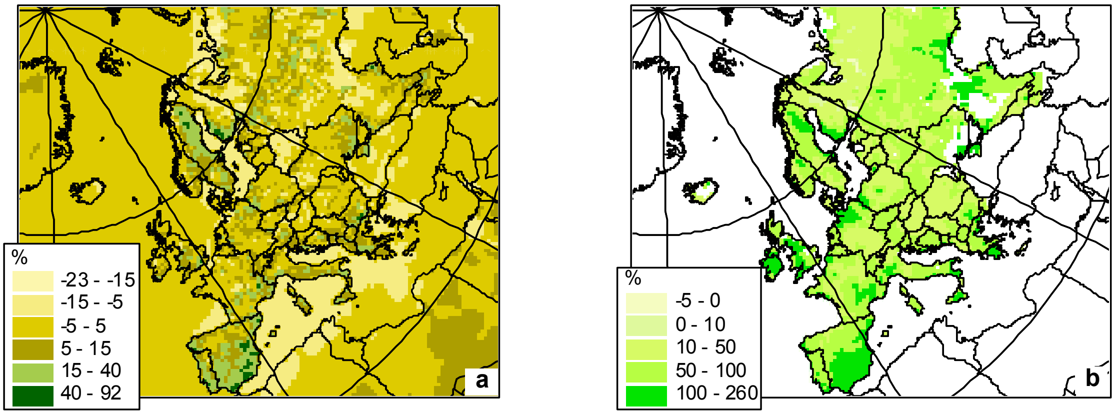


Figure 2.4. *Relative increase, %, in total deposition to Europe as a whole -* ***a*** *and to forested areas -* ***b*** *after modification of dry deposition scheme*

Dry deposition of gaseous mercury compounds

The problem of elemental mercury ability for and the rate of dry uptake by various underlying surface types is very important, and still remains highly uncertain. Some of experts believe that dry uptake of elemental mercury is not a substantial sink on the regional and global scale [*EPA USA*, 1997]. It is usually assumed that the uptake by vegetation is possible if only Hg^0 concentration is above the "compensation point" (about 20 ng/m^3). For the real atmosphere it means that the uptake is realized only at the local scale in the vicinity of the emission source [*Lyon et al.,* 1999]. On the contrary, some experts consider elemental mercury dry uptake as a dominating mechanism of mercury scavenging from the atmosphere [*Lin and Pehkonen*, 1999]. *T. Bergan and H. Rodhe* [2001] noted that although the uptake of Hg^0 is an important mechanism in the global mercury cycle, it is seldom discussed in the literature.

For this reason it is useful to summarize the available information. Measured and accepted in various models dry uptake velocities under various conditions are given in Table 2.9. The information is presented chronologically in order to trace tendencies in understanding of the considered process.

Table 2.9. Elemental mercury measured and estimated velocities of dry uptake by the underlying surface for, cm/s

Type of the underlying surface	Conditions	Velocity	Method	Reference
Deciduous forest	Warm season	<0.01-0.1	Measured	*Lindberg et al.,* 1991
Forest	Winter Summer	0.006 0.12	Model	*Lindberg et al.,* 1992
Land, USA	Always	0	Expert.	*Bullock et al.*, 1994
Continents		0.05-0.1	Expert.	*Bloom et al.,* 1994
Land	Day	0.005	Expert.	*Constantinou et al.*, 1995
Great Lakes	Always	0	Model	*Schroeder*, 1996
Forest	Warm season	>0 (25% of time)	Measured	*Meyers et al.*, 1996
Land, USA	Always	0	Expert.	*Pai et al.*, 1997
Vegetation	C<"CP" Wet foliage	0 >0	Measured	*EPA USA*, 1997
Vegetation	Dry (TGM) Wet (TGM)	1.3 ± 1.8 0.4 ± 0.3	Measured	*Lindberg et al.*, 1998
Land, Europe Water, ice, snow	Warm season Winter, t(C)>0 Winter, t(C)<0 Always	0.03 0.01 0 0	Expert.	*Ryaboshapko et al.,* 1999
Lakes in Sweden	Warm season	0	Measured	*Ebinghaus et al.*, 1999
Vegetation	C>20 ng/m3 C<20 ng/m3	0.06 0	Expert.	*Lyon et al.*, 1999
Soil, USA Forest, USA	Variable water content T<0(C) Night, July Day, July	0.002-0.015 0 0 до 0.15	Measured / Model	*Xu et al.*, 1999
Continents	Always	0.005	Expert.	*Shia et al.*, 1999
Continents Oceans	t(C)>20 0<t(C)<20 t(C)<0 Always	0.03 0-0.03 (linear) 0 0	Expert.	*Bergan and Rodhe,* 2001
Forest Other surface types	 Always	0.001-0.03 0	Expert.	*Petersen et al.*, 2001
All	Always	0	Expert.	*Christensen*, 2001
Soil	Wet, shade	0.005	Measured	*Zhang et al.*, 2001b
Continents	Always	0.01	Expert.	*Seigneur et al.*, 2001

"CP" – Compensation point

The data of Table 2.9 demonstrates that dry uptake velocity of Hg^0 depends on a number of parameters. The underlying surface type and temperature are the most important parameters. On the base of the summarized data the following values can be accepted for the parameterization in numerical models. It is assumed that at negative temperatures the uptake does not exist. The uptake by water and vegetation-free surfaces as well as at nighttime does not take place. For the surface covered with vegetation during daytime the uptake velocity varies with the proportion to the positive part of sinusoid. The sinusoid amplitude in its turn depends on temperature: for forest the maximum is 0.03 cm/s at 20°C and higher, for other types of vegetation is 0.01 cm/s. The uptake velocity decreases linearly to zero with temperature decrease to 0°C.

There are no field measurements of dry uptake of gaseous oxidized mercury, or, at least, it was not easy matter to find them in literature. When describing dry uptake of gaseous oxidized mercury similarity of dry uptake velocity to that of nitric acid is usually assumed. This assumption comes from their similar solubilities in water. Keeping in mind obvious lack of knowledge on this, dry uptake velocity assumed in the model is 0.5 cm/s for all seasons and types of the underlying surfaces. For organic mercury compounds it is accepted that the uptake by the underlying surface is absent.

Wet scavenging

The model description of heavy metal subcloud washout treated as a process of a first order and was described in detail in MSC-E reports for 1998 and 1999 [*Ryaboshapko et al*., 1998; 1999]. Washout ratios for lead and cadmium were calculated on the basis of monitoring of the metal contents simultaneously in precipitation and air [*Berg et al.,* 1996, 1997; *Berg and Hjellbrekke,* 1998] for individual months and the whole year.

It is accepted that particles containing mercury behave like sulfate particles and the equilibrium washout ratio is equal to 7×10^5 [*Petersen et al*., 1995; *Iversen et al*., 1989]. Washout of inorganic gaseous oxidized mercury by the cloud liquid phase is prescribed by the equilibrium washout ratio characteristic of nitric acid: 1.4×10^6 [*Petersen et al*., 1995; *Jonsen and Berge*, 1995].

2.4. Arctic mercury depletion

Rising of Hg content in vulnerable Arctic ecosystems and increase of Hg input to human body in the Arctic is of a particular concern [*AMAP*, 1999]. Only a few years ago it was difficult to find any geophysical explanation of increased Hg content in the Arctic. Mercury behaviours in the atmosphere suggest that elevated Hg depositions in high latitudes are impossible. Indeed, it is commonly accepted that even if Hg^0 was scavenged from the atmosphere due to dry deposition, the process can be realized only in low and middle latitudes through "soil-plant-atmosphere" interaction [*EPA USA,* 1997]. Hg^0 uptake by snow cover is usually disclaimed. Oxidised gaseous and particulate Hg has restricted atmospheric lifetime, and their anthropogenic emissions in middle latitudes cannot account for noticeable contribution to total Hg deposition in the Arctic [*Petersen et al*., 2001; *Ilyin et al*., 2001].

However, recently discovered mercury depletion phenomenon (MDP) during springtime [*Schroeder et al*., 1998] allows hypothesising other ways of high Hg deposition in the Arctic (and Antarctic). Main point of the MDP is an abrupt dropping of TGM concentration in high latitudes during springtime. The drop can be very quick (during few hours) and very deep – practically to total disappearance of elemental mercury. In a short time the TGM concentration can sharply rise to its usual values.

Sometimes the period of super low Hg^0 concentration can lasts several hours and even days [*Lu et al.,* 2002; *Lindberg et al.*, 2002; *Berg et al*., 2001; *Ebinghaus et al*., 2002]. Sharp droppings can repeat several times, and total duration of the phenomenon is about 4-6 weeks. Both in the Northern and Southern Hemisphere the phenomenon can be observed only in springtime [*Lu et al.*, 2002; *Ebinghaus et al*., 2002]. In the Northern Hemisphere it is from mid-March to mid-June.

Elemental mercury has relatively long atmospheric lifetime and theoretically should not have such sharp variations [*Junge*, 1972]. Evidently, elemental mercury must be extremely quickly transformed into any other mercury-containing products. Most likely, they are oxidized mercury compounds presented by either gaseous oxidized forms or particulate oxidized forms. The products were experimentally determined both as RGM and HgP [*Lu et al.*, 2002; *Lindberg et al*., 2002]. The concentration of oxidized mercury can be of the same level as usual TGM concentration (up to 1 ng/m3). Such concentrations are much higher than those ones, which are typically observed in the vicinity of powerful anthropogenic sources.

Very probably that the phenomenon embraces only the first kilometre height of the atmospheric layer [*Ebinghaus et al.,* 2002]. This is supported by aircraft measurements of oxidation products [*Schroeder et al*., 2001; *Lindberg et al*., 2002]. For example, at surface level the RGM concentration was 70 pg/m^3 while at 1 km height – only 2 pg/m^3 [*Lindberg et al*., 2002]. With height the TGM concentration rises and reaches its typical values at 1 km [*Schroeder et al.*, 2001]. This height is practically coincides with the top of the boundary layer. Hence, because the oxidation process is very fast the vertical profile of oxidation products is opposite to the TGM profile.

It is commonly believed that the sunrise in the Arctic provokes quick photochemical (catalytic) oxidation of elemental mercury in reactions with Br-related radicals [*Ebinghaus et al.*, 2002]. Recently *S.Lindberg et al.* [2002] presented a possible mechanism of the Hg depletion. The mechanism suggested can be described by several consecutive steps:

(1) Appearance in the atmosphere of sea-salt aerosol particles in the frozen form (negative air temperature is an obligatory condition).

(2) Influence of UV sun light on concentrated on the particle surface Br/Cl compounds. The compounds can be concentrated on the surface in the process of freezing.

(3) Formation of halogen radicals and halogen oxide radicals as a result of autocatalytical hetherogenic reactions.

(4) Destruction of ozone and oxidation of elemental mercury in the following reactions:

$Br / Cl + O_3 \rightarrow BrO / ClO$

$BrO / ClO + Hg^0 \rightarrow HgO + Br / Cl$

and/or

$Hg^0 + 2\ Br / Cl \rightarrow HgBr_2 / HgCl_2$ (these reactions are preferable).

(5) Abrupt stopping step 2 when air temperature is rising above zero. Creation water drop instead of the frozen particle and dissolution of the salts homogeneously within the drop.

The mechanism seems to be very reasonable. However, it cannot explain an “explosive” character of the beginning of the process. In our opinion such a “trigger” is the formation of areas of open water near seashore or polynyas in ice cover. In springtime ice cover becomes movable due to ice drift provoked by see currents or wind pressure. Such alternations can be very fast – in few hours a wide area of open water can appear even at low air temperature. In this case formation of frozen sea-salt aerosol is quite natural. *S.Lindberg et al.* [2002] showed that elevated levels of RGM are accompanied very often by periods of sea-surface roughness and the formation of marine aerosol.

S.Lindberg et al. [2002] treat the oxidation products primary as RGM, which later can be partly converted into HgP. On the contrary, *Lu et al*. [2002] believe that RGM and HgP are formed simultaneously, at that the formation of HgP is preferable. T.Berg et al. [2002] also observed simultaneous formation both of HgP and RGM. Lifetime of HgP and RGM even in the stable polar atmosphere is much shorter than of Hg^0, and their deposition should lead to additional Hg pollution of the Arctic environment. Measurements of mercury concentration in snow-pack conducted in series with atmospheric observation at Barrow station (Alaska, USA) showed clearly that the depletion phenomenon is accompanied by rise of mercury content in snow [*Lindberg et al.*, 2002]. Canadian experts provided a broad survey of mercury content in snow-pack of northeastern Canada and Greenland. They found that the depletion phenomenon is widespread and lead to considerable rising of mercury content in snow-pack during springtime (Lu et al., 2002). *S.Lindberg et al.* [2002] noted that mercury concentration in snow-pack reaches its maximum leeward from polynyas and open water areas. Besides, the concentrations drops with distance from seashore. These facts confirm that the MDP is closely connected with seashore line.

It was noted in recent works that the depletion is connected with elevated concentrations of BrO. Satellite observations showed that both in Arctic and Antarctic the zones of elevated BrO concentrations have ring structure – they connected with the seashores, and they appear in spring [*Steffen et al*., 2001; *Drummond*, 2001; *Lu et al*., 2002; *Ebinghaus et al*., 2002]. If hypothesis of BrO involvement into Hg depletion is correct, it means that not the whole Arctic is influenced by the phenomenon but only seashore zones. Most likely, that the central parts of the Arctic and Antarctic are not affected by the MDP. Nowadays it is difficult to say how far southward the phenomenon can be extended. It observed at least within the Polar Circle in the Arctic.

Taking into account the said above we can try to find a parameterization of the MDP to include it into the model calculation:

- We assume that MDP can occur only over open seawater areas, which were previously covered with ice during winter period. We exclude a possibility of penetration of BrO precursors through ice cover. Hence, we think that MDP can take place over coastal zones of the Arctic Ocean. Only those grid cells are taken into account, which cover both land and sea.
- We suppose that the water surface was previously covered with ice if air temperature in a given point was permanently lower than -3°C during wintertime (assumed seawater freezing point). Then in springtime the temperature became higher than 0°C, and ice melting started. Besides, during springtime ice-drift becomes stronger and areas of open water appear. Conditionally we "switch on" the MDP module if air temperature during previous 24 hours was higher than 0°C. We understand the conventional character of such a "trigger" because open water can appear at low negative temperatures.
- We assume that total duration of MDP during springtime in any point does not exceed 4 weeks and MDP takes place every day (instantly at noon) during this period. The MDP module can be "switched on" only within the period from April to June.
- We believe that during the MDP concentration of elemental mercury near the surface layer drops down from its usual level to 0.1 ng/m^3. Oxidation of Hg^0 leads to the formation of RGM (50%) and HgP (50%). The oxidized products are partly scavenged from the atmosphere within a given modelling grid cell, partly transported outside it and scavenged later.

- We accept that the MDP covers the lowest 1 kilometre height layer of the atmosphere. Within this layer the intensity of the phenomenon linearly decreases with height to zero at the top of the layer. Hence, during the MDP elemental mercury has rising profile from 0.1 ng/m^3 at the surface to its usual values at 1 km height. Contrary, oxidized forms have dropping profile from their maximum at the surface to their usual values at 1 km height.

2.5. EMEP MSCE-HM model structure

This section is focused on a brief description of transport and deposition model developed to evaluate pollution levels in the EMEP region. Description of the model, recently used for the evaluation of long-range atmospheric transport of lead, cadmium and mercury has been described in work [*Ryaboshapko et al.*, 1999]. This model considers basic processes governing transport and deposition of lead, cadmium and mercury - advection, diffusion, dry and wet removal and mercury chemistry. Current version of regional model underwent significant changes, which are related to modification of dry deposition scheme and parameterization of gas-phase and aqueous-phase chemistry of mercury. Some changes concerned background concentrations of considered compounds, which are described in Section 2.1. In the following sub-sections a brief description of processes, which were not changed, and detailed elucidation of modified parameterizations is given.

Regional EMEP/MSC-E model for calculation of transport, chemical transformations and depositions operates within EMEP region. This region includes Europe, the northern part of Africa, part of Middle East, the North Atlantic and part of the Arctic. EMEP grid consists of 135x111 gridcells with spatial resolution 50 km at 60°N. latitude. A detailed description of the EMEP grid one can find elsewhere [Posh et al., 1997].

Vertical structure of the model is depicted in Figure 2.5. As seen, the model consists of five non-uniform layers along the vertical. Top of the model is at the height of about 4 km. Therefore, the model domain covers the entire atmospheric boundary layer and part of middle troposphere. Thicknesses of the layers are 100, 300, 700, 1000 and 1800 m.

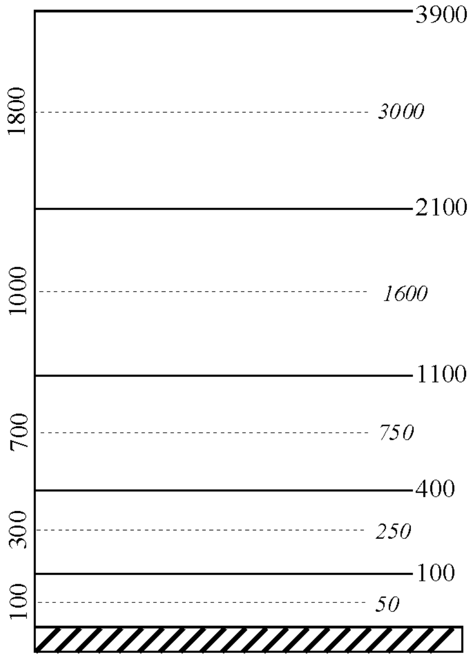


Figure 2.5. *Heights and thiknesses of the model layers, m*

The advection scheme has been developed by *M.Pekar* [1996]. The scheme is conservative, stable and positively defined. The horizontal diffusion is described according to the approach suggested by *Yu.Izrael et al.* [1980]. The model description of vertical turbulent diffusion is based on a classical law: a substance flux is proportional to the concentration gradient. The proportionality factor is the coefficient of turbulent diffusion calculated by the boundary layer parameterisation described in [*Pekar*, 1996]. Vertical diffusion is described by an implicit scheme [*Samarsky*, 1977].

Physical processes used in the model are described in Sections 2.2 - 2.4. They include scavenging, chemical transformations and depletion of mercury in spring. Scavenging of lead, cadmium and mercury encompasses wet removal by precipitation and dry uptake. Wet removal of particulate compounds (Pb, Cd and Hg_{part}) and subcloud scavenging of Hg^{2+} is described using washout ratio approach. Within clouds Hg^{2+} and Hg^0 are rained out via dissolution in a cloud drops. Dry uptake of particulate compounds is differentiated with regard to land-use category of the underlying surface and depends basically on properties of the underlying surface and atmospheric stability. Dry uptake of Hg^0 is calculated depending on the type of vegetation (forests/low vegetation/waters/other lands). Dry deposition velocity of Hg^0 is assumed to exhibits the diurnal cycle. Dry deposition velocity of Hg2+ is prescribed basing on data available in the literature.

Parameterization of chemical processes includes both the aqueous-phase and gaseous-phase reactions and equilibria. In spite of a wide variety of reactions involving mercury species, only several key reactions were introduced into the modelling scheme. They are oxidation of elemental mercury by O_3 and OH-radical, dissolution of Hg^0 and Hg^{2+} in cloud droplets, oxidation of mercury within drops by O_3 with further sorbtion on insoluble particles within drops and partial reduction by dissolved HO_2-radical and because of decomposition of mercury-sulfite complex. Destruction of DMM in air due to reaction with OH-radical is also considered.

Chapter 3

LEAD, CADMIUM AND MERCURY EMISSIONS IN THE EMEP DOMAIN

The accuracy of emission estimates defines the reliability of modelling results. This chapter provides anthropogenic emissions of lead, cadmium and mercury in the EMEP region in 1990-2000 and natural emissions of these metals as well as re-emission of anthropogenic mercury.

3.1. National data on lead, cadmium and mercury anthropogenic emissions

In accordance with agreed procedure Parties to the Convention submit national emission data to UN ECE Secretariat. In 2002 national total emissions for 2000 were submitted by 25 countries for lead and by 22 countries for cadmium and mercury. Official emission data on lead, cadmium and mercury for 1990-2000 are given in Tables 3.1, 3.2, and 3.3. For the considered period 34 countries have provided information on lead at least for one year, 32 countries - on cadmium and on mercury – 33 countries. Only very small number of countries has not provided the information at all. Thus the database of the current state and trends of heavy metal emission variations is available for 11-year period.

It should be mentioned that some countries make a retrospective analysis of emission data. In doing so both emission factors and quantitative characteristics of economic activity are refined. Sometimes when recalculations are performed the difference in emission values may be essential.

Available official emission data for 2000 were used in the calculations. In the case when official data for 2000 were not submitted information for the last reported year was used. For instance, last data of Italy are referred to 1994. These very data were used in the calculations for 2000. If there are no official data at all expert estimates of emissions are used.

It is important to stress that the use of official data for modelling independent of the fact whether a country included all source categories into the official emission data set. For example, Armenia and Turkey estimate emissions from some stationary industrial sources. It results in an appreciable difference between official data and expert estimates. For Turkey expert estimates of mercury emission used in previous calculations [*Ilyin et al.*, 2001] exceed the official data by two orders of magnitude. Sector emission data indicate that in many countries not all possible source categories are considered. As a result emissions in countries and in the region as a whole may be underestimated.

Table 3.1. Official data on lead emissions to the atmosphere in the EMEP region[a], t/y

Country	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	**2000**[b]
Albania											24
Armenia [c]	11	0.82	0.61	0.79	0.34	0.334	0.009	0.009	0.010	0.005	0.0
Austria	***205***	***173***	***118***	***84.1***	***58.9***	***18.5***	***17.3***	***16.4***	***15.1***	***14.1***	13.2
Azerbaijan											145
Belarus	798					148	46.3	42.2	41.2	37.5	46.1
Belgium [d]	601	218	230	230	325	336	302	291	203	212	134
Bosnia&Herzegovina											5
Bulgaria	436					297	279	231	251	224	213
Croatia	466					264	268	190	183	178	178
Cyprus	81	63	66	69	68	67	67	72	69	75	74
Czech Republic	269	240	247	232	202	180	165	180	169	157	108
Denmark	***134***	99.0	87.1	45.0	***31.9***	***28.7***	***15.8***	***8.73***	***7.64***	***7.42***	7.70
Estonia	233	208	121	100	107	87.6	80.2	73.1	54.7	45.0	40.7
Finland	326	247	175	100	60.1	56.6	35	18.5	20.3	14	37.5
France	***4192***	***2795***	***2020***	***1766***	***1570***	***1395***	***1221***	***1073***	***961***	***724***	196
Georgia											112
Germany [e]	2323					632					519
Greece							470				470
Hungary	680	488	208	187	155	127	99.8	89.7	82.2	38.6	36.9
Iceland	12.2	8.9	6.8	5.3	4.6	3.9	1.7	0.4	0.4		0.4
Ireland											83
Italy	4300				2174						2174
Kazakhstan											20
Latvia	20.3	10.1	7.94	6.18	10.3	4.69	***4.57***	***3.4***	***4.64***	***0.2***	0.2
Lithuania						30.2	17.8	19.5	21.8	19.3	19.3
Luxembourg	77.4				52.5	29.8	26.1	17.7	6.8	2.34	1.62
Netherlands	***333***					***159***			***43.9***		43.9
Norway	***186***	***143***	***126***	***86.2***	***22.8***	***21.1***	***9.22***	***8.63***	***8.63***	***7.82***	6.47
Poland	1372	1336	986	997	966	937	960	896	736	***745***	648
Portugal											365
Republic of Moldova	253	220	103	71.2	23.2	33.9	27.9	22.4	7.90	11.2	11.2
Romania											510
Russian Federation	3591	3553	3095	3276	2643	2426	2304	2247	2262	2339	2352
Slovakia	***152***		***149***		***84.0***	***81.1***	***78.4***	***78.7***	***67.2***	***55.4***	75.0
Slovenia	460	386	390	398	406	196	99.0	80.4	60.5	50.2	37.2
Spain	***2834***	***2081***	***1301***	***1194***	***1180***	***974***	***1007***	943	884	826	692
Sweden	540		365		37	37.8		10.8	10.5	10.5	7.59
Switzerland	520	461	401	341	287	226	200	174	149	131	114
The FYR of Macedonia											3.02
Turkey [f]						405	413	336	427		427
Ukraine											420
United Kingdom	***2828***	***2574***	***2356***	***2133***	***1888***	***1577***	***1335***	***1182***	***898***	***548***	496
Yugoslavia											331

a) Recalculated official data are presented in bold.

b) Values obtained by extrapolation of official data and on the base of expert estimates are shaded.

c) Road transport not included.

d) Figure for 1990 refers to Flanders and Wallonia only. Figures for 1991-93 refer to Flanders only.

e) Emission for 2000 is assessed by linear interpolation between 1995 and projected emissions for 2010.

f) The calculation of heavy metal emissions includes emissions from glass production, iron production, primary aluminium production, primary copper production, primary zinc production and blast furnace charging.

Table 3.2. Official data on cadmium emissions to the atmosphere in the EMEP region[a], t/y

Country	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	**2000**[b]
Albania											0.6
Armenia											1
Austria	***2.98***	***2.68***	***2.21***	***2.09***	***1.82***	***1.61***	***1.52***	***1.55***	***1.47***	***1.44***	1.30
Azerbaijan											3
Belarus	7.59					3.48	1.20	1.25	1.45	1.42	1.38
Belgium [c]	9.52	3.00	4.00	1.00	4.40	6.38	4.62	4.60	3.26	3.31	2.75
Bosnia&Herzegovina											0.3
Bulgaria	28.3					12.8	14.3	14.2	14.9	13.6	11.0
Croatia	1.61					0.95	1.04	1.03	1.06	1.05	1.05
Cyprus	0.20										0.20
Czech Republic	4.34	3.92	3.61	3.48	3.52	3.55	2.94	3.00	2.65	2.72	2.85
Denmark	***1.17***	1.23	1.20	1.12	***1.36***	***0.957***	***0.915***	***0.845***	0.775	0.713	0.736
Estonia	1.61	1.49	1.12	0.885	0.937	0.899	0.941	0.978	0.829	0.776	0.681
Finland	6.3	3.4	2.9	2.9	2.4	1.7	1.5	1.1	1.3	0.6	1.4
France	***17***	***17***	***17***	***16***	***15***	***14***	***14***	***13***	***13***	***12***	12
Georgia											2
Germany [d]	31					11					11
Greece							3				3
Hungary	5.52	4.70	4.03	4.14	4.08	3.78	3.41	3.26	3.08	2.99	2.75
Iceland											0.2
Ireland											2
Italy	53.8				29.9						29.9
Kazakhstan											0.4
Latvia	2.46	1.79	1.71	1.68	2.20	1.44	***0.3***	***0.4***	***0.7***		0.7
Lithuania						2.10	2.20	2.20	2.59	2.01	2.01
Luxembourg	0.6				0.5	0.4	0.4	0.3	0.2	0.054	0.051
Netherlands	***1.95***					***1.01***			***1.15***		1.15
Norway	***1.69***	***1.62***	***1.61***	***1.68***	***1.22***	***1.05***	***1.09***	***1.12***	***1.18***	***1.01***	0.746
Poland	91.6	85.0	84.1	91.9	85.8	82.6	91.2	85.8	55.4	***61.7***	50.4
Portugal											3
Republic of Moldova	3.08	3.49	1.69	1.42	0.819	0.594	0.659	0.364	0.328	0.148	0.148
Romania											21
Russian Federation	79.4	68.2	68.8	59.0	56.6	57.4	51.0	50.4	49.0	50.9	50.5
Slovakia	***9.97***		***11.3***		***7.19***	***10.6***	***9.62***	***10.8***	***8.47***	***7.34***	7.90
Slovenia	1.68				1.66	1.71	1.77	1.75	1.67	1.62	1.54
Spain	***14***	***15***	***16***	***15***	***15***	***16***	***15***	15	16	18	19
Sweden	2		1.3		0.7	0.8		0.3	0.26	0.26	0.054
Switzerland	4.2	3.9	3.6	3.1	2.7	2.5	2.3	2.2	2.18	2.18	2.18
The FYR of Macedonia											0.167
Turkey [e]						0.16	0.19	0.21	0.22	0.18	0.18
Ukraine											6.91
United Kingdom	***20.3***	***19.9***	***19.6***	***13.8***	***13.3***	***11.8***	***9.35***	***7.81***	***6.33***	***5.93***	5.22
Yugoslavia											6

a) Recalculated official data are presented in bold.
b) Values obtained by extrapolation of official data and on the base of expert estimates are shaded.
c) Figure for 1990 refers to Flanders and Wallonia only. Figures for 1991-93 refer to Flanders only.
d) Emission for 2000 is assessed by linear interpolation between 1995 and projected emissions for 2010.
e) The calculation of heavy metal emissions includes emissions from glass production, iron production, primary aluminium production, primary copper production, primary zinc production and blast furnace charging.

Table 3.3. Official data on mercury emissions to the atmosphere in the EMEP region[a], t/y

Country	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	**2000**[b]
Albania											0.5
Armenia	0.01	0.01	0.008	0.009	0.001	0.001	0.001				0.001
Austria	***2.59***	***2.51***	***1.98***	***1.75***	***1.54***	***1.50***	***1.41***	***1.44***	***1.25***	***1.23***	1.10
Azerbaijan											0.6
Belarus	0.480					0.265	0.297	0.310	0.392	0.380	0.358
Belgium [c]	8.79	2.00	3.00	1.00	5.82	4.54	5.55	3.52	3.50	3.02	2.25
Bosnia&Herzegovina											0.2
Bulgaria	13.2					6.88	4.70	4.31	4.69	4.06	4.19
Croatia	1.15					0.287	0.297	0.318	0.320	0.307	0.307
Cyprus	0.30										0.30
Czech Republic	7.52	7.42	7.28	7.46	7.17	7.40	5.86	5.54	5.16	3.66	3.84
Denmark	***3.35***	3.23	3.07	3.06	***3.10***	***2.55***	***2.75***	***2.16***	1.95	1.98	2.05
Estonia	1.29	1.18	0.980	0.750	0.798	0.751	0.778	0.773	0.664	0.611	0.553
Finland	1.1	0.9	0.8	0.6	0.7	0.7	0.8	0.6	0.5	0.4	0.6
France	***27***	***28***	***27***	***24***	***24***	***22***	***22***	***17***	***17***	***16***	15
Georgia											0.5
Germany [d]	113					31					29
Greece							13				13
Hungary	6.28	5.83	4.99	5.00	4.72	4.83	4.67	4.47	4.28	4.26	4.20
Iceland											0.05
Ireland											1.95
Italy	20.0				13.2						13.2
Kazakhstan											0.1
Latvia	0.37	0.32	0.27	0.22	0.37	0.17	***0.51***	***0.07***	***0.12***		0.12
Lithuania						0.153	0.159	0.232	0.245	0.253	0.253
Luxembourg	0.3				0.2	0.1	0.1	0.1	0.1	0.286	0.275
Netherlands	***3.03***					***1.07***			0.56		0.56
Norway	***1.67***	***1.56***	***1.41***	***1.10***	***1.17***	***1.08***	***1.10***	***1.12***	***1.09***	***1.14***	0.960
Poland	33.3	32.7	31.9	32.5	32.4	32.3	33.6	33.0	29.5	***27.1***	25.6
Portugal											5
Republic of Moldova	4.25	3.81	3.29	1.85	1.29	0.894	0.954	0.571	0.406	0.180	0.180
Romania											7
Russian Federation	15.6	13.4	11.4	11.8	10.4	10.4	10.1	9.6	9.4	9.9	10
Slovakia	***12.5***		***6.15***		***3.86***	***3.95***	***3.41***	***3.74***	***4.10***	***3.72***	4.45
Slovenia	0.76				0.61	0.65	0.59	0.61	0.63	0.60	0.58
Spain	***21***	***22***	***23***	***21***	***21***	***21***	***19***	20	22	24	23
Sweden	1.5		1.2		0.9	0.9		0.55	0.54	0.54	0.291
Switzerland	6.8	6.1	5.4	4.7	4.0	3.3	3.1	2.9	2.63	2.63	2.63
The FYR of Macedonia											0.048
Turkey [e]						0.043	0.050	0.055	0.058	0.053	0.053
Ukraine											9.03
United Kingdom	***31.7***	***32.4***	***30.4***	***20.0***	***19.5***	***19.0***	***14.4***	***12.2***	***11.1***	***8.83***	8.53
Yugoslavia											3

a) Recalculated official data are presented in bold.
b) Values obtained by extrapolation of official data and on the base of expert estimates are shaded.
c) Figure for 1990 refers to Flanders and Wallonia only. Figures for 1991-93 refer to Flanders only.
d) Emission for 2000 is assessed by linear interpolation between 1995 and projected emissions for 2010.
e) The calculation of heavy metal emissions includes emissions from glass production, iron production, primary aluminium production, primary copper production, primary zinc production and blast furnace charging.

3.2. Uncertainties of emission estimates

Since the emission value is a key factor defining the reliability of modelling results it is necessary to have an idea about the range of possible errors of official data and expert estimates. The Task Force on Monitoring and Modelling requested countries to give possible maximum, minimum and average values of emissions. This approach would provide the quantitative estimate of data uncertainty.

To discuss issues of methodology used for emission evaluation and data accuracy MSC-E and the Task Force on Emission Inventories and Projection held a special workshop (Moscow, Russia, November 21-23, 2001). The workshop stated that for the emission assessment countries use the method of information generalization “bottom - up”, i.e. from emissions of individual sources to national totals. Since absolutely complete account of all sources is a priori impossible, a certain underestimation of emissions can take place.

How much the official data may be in error are demonstrated by the retrospective recalculations of emission values for previous years. It is illustrated by data of Table 3.4, which presents “previous” [*Vestreng*, 2001] and “recalculated” (data reported in early 2002) emission values for some countries. For example, Austria in 2002 recalculated all emissions beginning with 1990. For the interval of 1990-94 the difference between previous and recalculated values for lead is not higher than 3%. For the subsequent years emission values has reduced more than 2 times.

Expert estimates are usually based on available information about the amount of consumed raw material, product output and available emission factors. The quality, completeness and reliability of the emission data define the extent of the obtained data scattering. *J.Berdowski et al*. [1997] believe that the uncertainty of their expert estimates of heavy metal emissions in European countries is within the range of factors 1.5 - 3.5.

As it follows from Table 3.4 national data may also have a considerable uncertainty comparable with the uncertainty of expert estimates. Thus the improvement of inventory quality in countries and the recalculation of emission values, on the one hand, will refine emission trends. On the other hand it will lead to the necessity of repeating model calculations of concentrations and depositions for the previous years.

Table 3.4. Recalculation of national data, t/y

Country	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999
Austria	Lead emissions									
Previous data	201.9	170.3	116.1	81.97	57.06	38.61	35.88	35.35	35.37	33.64
Recalculated data	204.9	172.9	118	84.06	58.91	18.49	17.28	16.39	15.12	14.09
max/min ratio*	1.0	1.0	1.0	1.0	1.0	- 2.1	- 2.1	- 2.2	- 2.3	- 2.4
United Kingdom	Cadmium emissions									
Previous data	21.21	20.82	20.41	19.93	19.15	12.33	10.39	8.75	7.06	6.47
Recalculated data	20.33	19.93	19.58	13.75	13.29	11.82	9.35	7.81	6.33	5.93
max/min ratio*	-1.0	-1.0	-1.0	-1.4	-1.4	-1.0	-1.1	-1.1	-1.1	-1.1
France	Mercury emissions									
Previous data	44	46	47	42	37	31	28	21	19	17
Recalculated data	27	28	27	24	24	22	22	17	17	16
max/min ratio*	-1.6	-1.6	-1.7	-1.7	-1.5	-1.4	-1.3	-1.2	-1.1	-1.1

* - Sign “-“ implies the exceedance of previous data over the recalculated ones

3.3. Spatial and seasonal distribution of anthropogenic emissions

In accordance with the guidelines for reporting emission data countries should report emission spatial distribution with resolution 50x50 km for every fifth year from 1990 (1990, 1995, 2000, etc.). Only Belarus, Finland, Poland, Switzerland and the Ukraine submitted such information for 2000. These data were used in calculations. As to other countries the spatial distribution for the last available year corrected for the new total emission was used. In the absence of official information about spatial distribution expert estimates were used. In this case national total was distributed with resolution 50x50 km in proportion to spatial distribution estimated within the framework of UBA/TNO project [*Berdowski et al.*, 1997] for 1990.

Figures 3.1 - 3.3 show spatial distribution of lead, cadmium and mercury anthropogenic emission in 2000.

Seasonal variations of lead, cadmium and mercury emissions were assumed to be sinusoidal with the amplitude of 10% [*Ryaboshapko et al.*, 1999]. Maximum lead emission occurs in summer, those of cadmium and mercury – in winter.

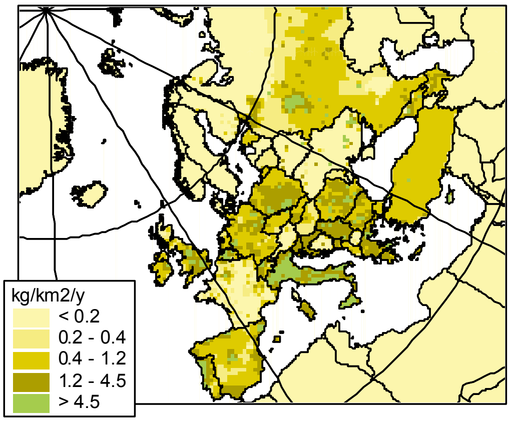


Figure 3.1. *Spatial distribution of lead anthropogenic emission in the EMEP region in 2000 with resolution 50x50 km, kg/km^2/y*

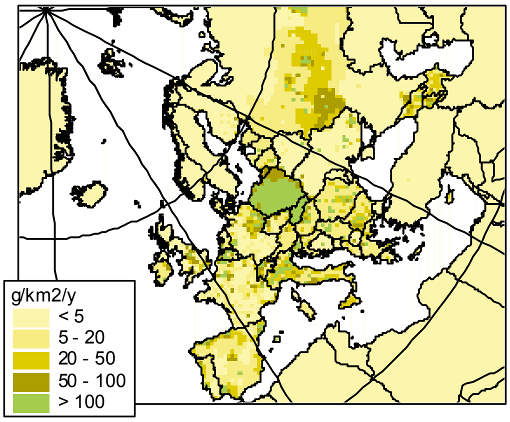


Figure 3.2. *Spatial distribution of cadmium anthropogenic emission in the EMEP region in 2000 with resolution 50x50 km, g/km^2/y*

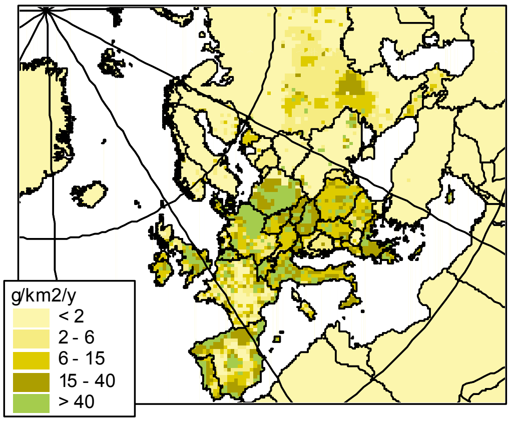
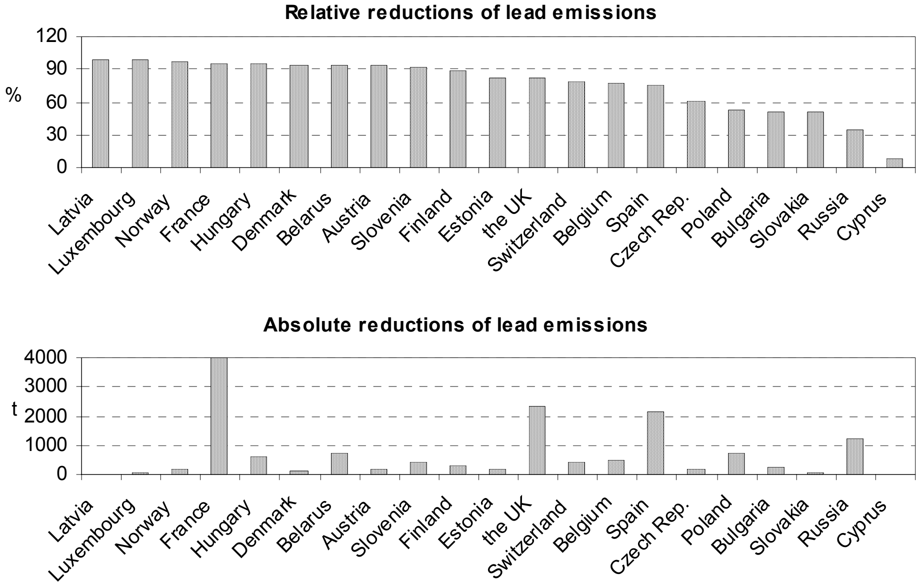


Figure 3.3. *Spatial distribution of mercury anthropogenic emission in the EMEP region in 2000 with resolution 50x50 km, g/km^2/y*

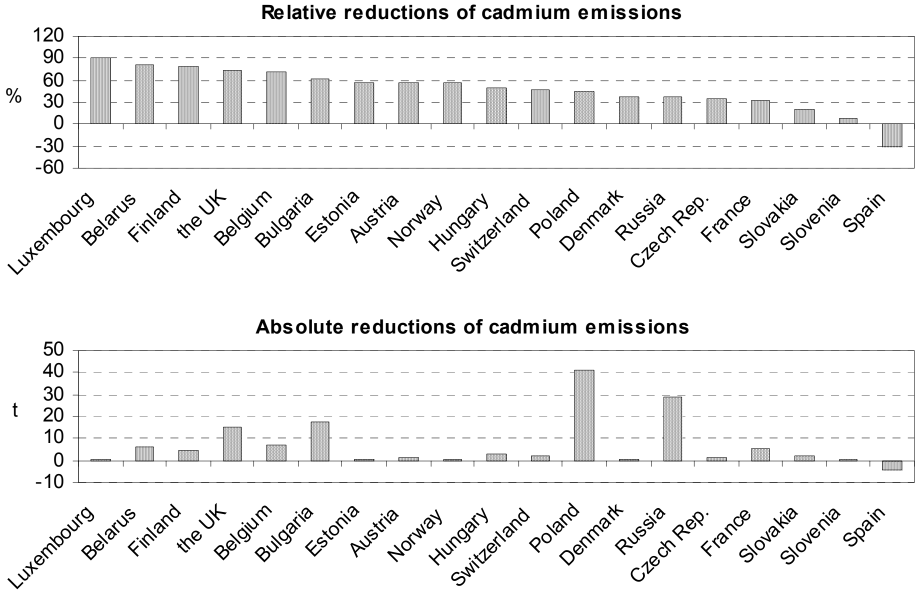
3.4. Trends of lead, cadmium and mercury emissions in individual countries

Information about emission variations in each country and in the entire region is important in view of the implementation of the Protocol on Heavy Metals. As it follows from the Protocol each Party shall reduce its annual atmospheric emissions of each of the metal (lead, cadmium and mercury) due to application of appropriate effective measures. Emission reductions of these metals for 1990-2000 are shown in Figures 3.4, 3.5 and 3.6 for all countries, which reported their national totals for 1990 and 2000. As evident from the figures in the majority of countries the emissions have been reduced. Only in Spain cadmium and mercury emissions have increased.


Relative reductions of lead emissions

Absolute reductions of lead emissions

Figure 3.4. *Relative (%) and absolute (t) reductions of lead emissions in individual countries during 1990-2000*


Relative reductions of cadmium emissions

Absolute reductions of cadmium emissions

Figure 3.5. *Relative (%) and absolute (t) reductions of cadmium emissions in individual countries during 1990-2000*

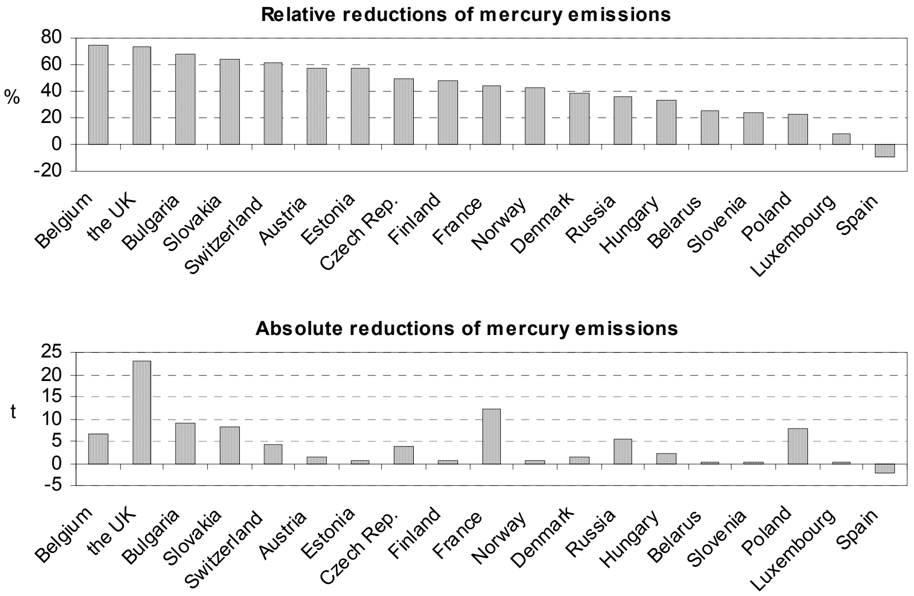


Figure 3.6. *Relative (%) and absolute (t) reductions of mercury emissions in individual countries during 1990-2000*

During last decade lead emissions were most essentially reduced. First of all it is conditioned by the fact that the majority of countries rejected the consumption of leaded gasoline. Cadmium and mercury emission reductions are slower. The highest contribution to lead emission reduction in the EMEP region was made by France, the emission decline amounts to 4000 tonnes. The greatest contribution of cadmium emission decline in the EMEP region was made by Poland and of mercury – by the United Kingdom.

3.5 Natural emission of lead and cadmium in the EMEP domain

J.Nriagu [1989] estimated different natural pathways of lead and cadmium to the atmosphere on the global scale. In accordance with his data the main natural sources of these metals to the atmosphere are soil wind-borne particles, volcanoes, sea-salt spray, forest fires and biogenic particles. For Europe volcanic sources are not so important. The other sources can give a noticeable contribution to the atmospheric balances of these metals over Europe.

It is possible to assume that in Europe the intensity of wind-borne soil particles, the intensity of wild forest fires and the intensity of biogenic particulate input correspond to mean global values [*Nriagy,* 1989]. In this case these sources can motivate the rate of the inflow to the European atmosphere of lead as aerosol particles equal to 54 g/km^2/y and of cadmium - 3.7 g/km^2/y.

Clearly heavy metals can enter the European atmosphere as a constituent of sea-salt particles. However, one should bear in mind that sea-salt particles can be essentially enriched in heavy metals relative to macro-components (sodium, chlorine) because they are accumulated in the surface microlayer at the "ocean-atmosphere" interface [*Brimblecombe*, 1986; *Dick,* 1991]. It was evaluated [*Ryaboshapko et al*., 1999] that the mean rates of lead and cadmium inputs from the World Ocean are 4 and 0.2 g/km^2/y, respectively. For the conditions of the seas adjacent to Europe most likely these values can be considered as the lower limit in view of higher content of these metals in shelf waters.

The intensity of natural emissions of lead and cadmium depends on many environmental factors variable in time: temperature, presence of snow cover, soil moisture, wind speed. Hence it is logical to suppose that there is a seasonal cycle of natural emission intensity. We assume here that the sea surface emits the metals evenly in time and space. As for the other sources, they can be dependent mainly on existence of snow cover. At present it assumed that the emissions from these sources are equal zero when air temperature drops to zero and lower. Otherwise, the emissions are evenly distributed over land in time and space.

Natural mercury emissions on the global scale

It is certain that the atmosphere is an intermediate link in the global mercury cycle. According to various estimates [*Lindvist and Rodhe*, 1985; *Lamborg et al*., 2002] the lifetime of elemental mercury, the most long-lived form of mercury in the atmosphere, is about a year. The main mechanism of metallic mercury removal from the atmosphere is its oxidation. The oxidized forms are scavenged faster on the underlying surface – for the periods of days. Aerosol mercury in the lower stratosphere is a special case [*Murphy et al.*, 1998]. Its lifetime can be long and it is defined by the stratospheric-tropospheric exchange.

Mercury in these or those quantities can be found virtually in all the surface media. Elemental and some forms of oxidized mercury due to their volatility are permanently coming to the atmosphere. The Earth surface covered by ice may be considered the only exclusion. Low mercury content in glacier materials and attendant low temperature make glaciers free from mercury emissions to the atmosphere.

High temperature of the Earth mantle zone contributes to high mercury mobility. It continuously diffuses to the lithosphere surface. In the zones of deep geological fractures these processes go on more intensively. Here are located so-called mercury geochemical belts where mercury concentrations in the upper layer appreciably exceed their average values. In some regions of mercury belts the intensive accumulation of mercury resulted in the formation of deposits and areas of dispersion [*Bailey et al*., 1973; *Jonasson and Boyle*, 1971]. It is clear that regions with high concentrations in surface rock are characterized by high mercury emissions to the atmosphere.

Metallic mercury is poorly dissolvable in water, however, in the form of different compounds it is found everywhere both in fresh and seawater. Concentrations in seawater vary from region to region within an order of magnitude [*Bayenes et al*., 1991]. Physical-chemical processes in surface layers of water lead to the formation of volatile forms – elemental and methylated mercury. In its turn it causes supersaturating of surface water layers relative to air concentrations. Supersaturating levels can reach 4 orders of magnitude [*Baeyens et al.*, 1991]. When the equilibrium is disturbed mercury flux to the atmosphere from the ocean should take place.

On the base of said above according to the character of natural mercury emissions to the atmosphere the Earth surface may be divided into five main types: glaciers (zero emission), sea water, usual soils, soils of the mercury belts and soil (or rocks) of areas of mercury deposits. Within the scales of oceans and continents the fresh water reservoirs due to their insignificant sizes should be referred to appropriate types of land.

Emissions of background and natural enriched soils

Mercury content in soils of the World outside the geochemical mercury belts varies several times. For cultivated soils of the World *A.Vinogradov* [1957] gives the range from 0.03 to 0.07 ppm. *V.Fursov* [1983] investigated Euroasian soils in detail and found a wider range (0.03 - 0.09 ppm). Mercury content in the US soils is even more variable – from 0.008 to 0.4 ppm [*EPA USA*, 1997]. Most likely the upper limit belong to soils of a geochemical mercury belt. For the US clean soils *S. Williston* [1968] estimates the variation range from 0.02 to 0.04 ppm.

The capacity of the soil reservoir relative to mercury is at least by three orders of magnitude higher than that of the atmosphere. In soil mercury is chemically toughly bound [*Biester and Nehrke*, 1997]. For the most part it is in the oxidized form, often as humic complexes. To destruct these complexes and to remove mercury it is necessary to heat them to 220 - 320ºC. Mercury lifetime in soil relative to its volatilization is from hundreds to thousands years [*Trakhtenberg and Korshun, 1990; Ebinghaus et al*., 1999] therefore in comparison with the reservoir capacity the emission intensity is very low.

The interpretation of data on mercury emission from soil is impeded by the fact that for the most part of a year soils are covered by vegetation. It is supposed that soils emit mercury and vegetation above soil uptakes it via the gas exchange process [*Lindberg et al*., 1992]. To assess the global natural emissions to air the net flux from a given vegetation ecosystem is important. Unfortunately these data are very scares in the literature because it is difficult technically to make an experiment above the canopy of a forest with height 20-30 m.

At present two main methods of soil emission assessment are in use: the chamber method on the soil surface and method of measurement of the vertical concentration gradient in the atmosphere. Both methods are rough. The comparison of the methods [*Poissant et al*., 1999] demonstrated that the correlation is comparatively low. That is way it is impossible to obtain sufficiently accurate estimates of mercury fluxes from soil to air. The situation is aggravated by the fact that depending on external conditions the flux direction can alternate.

Table 3.5 gives emission intensity values measured by different methods. As it follows from the Table the emission fluxes from soils vary within a wide range – up to two orders of magnitude. It is important that all the measurements were carried out in middle latitudes. There are no data on tropical forests, savannas and deserts. In addition the Table shows that the emission intensity has clear diurnal and seasonal variations, i.e. depends on external conditions. The authors of the works presented in the Table point out that as the external condition changes the flux not only can drop to zero but also changes its direction.

Investigations carried out round the clock and over a year show that soil temperature and insolation intensity are the most important external factors. Only a minor fraction of mercury is represented by the elemental form, the bulk – by the oxidized form. It means that while emitting oxidized mercury should be reduced. This process can go on with energy consumption. Reduction mechanisms can be both biotic and abiotic. In the first case the intensity of biotic reduction should depend on temperature and it should drop to zero at soil freezing. In the second case the reduction process can take place on the surface as result of photolysis of mercury-containing complexes. Most likely both mechanisms are in operation simultaneously.

A number of works confirm obvious dependence of the emission intensity on soil temperature [*Bouldala et al*., 2000; *Carpi and Lindberg*, 1998; *Zhang et al.*, 2001b; *Engle et al.*, 2001]. Thus, on evidence of *F.Bouldala et al*. [2000] soil temperature is the most important parameter defining the intensity of its emission. The flux from soil may be parameterized by an equation of Arrhenius type:

$$\ln(F) = -\frac{E_a}{R \cdot T} + C\,,$$

here: F is the flux; E_a is the activation energy; R is the universal gas constant (1.9872 kcal/mol/T(K°)); T is the soil temperature, K°; C is the constant.

For Canadian forest soils it is obtained that E_a = 14.6 kcal/mol, a C = 25.7 (when soil temperature was measured at 0.5 cm depth).

Table 3.5. Intensity of mercury emissions to the atmosphere from unenriched soils, ng/m^2/h

Region	Measurement conditions	Flux	Reference
USSR Republics of Central Asia	(B)*	5.9	*Fursov*, 1983
USSR Republics of Central Asia	(G)*	2.6	*Fursov*, 1983
Canada Ontario	Average for the Province for a year	0.18	*Innanen*, 1998
Canada, Nova Scotia	(B)	0.3-2.3	*Boudala et al.*, 2000
Canada, South Quebec	Grass, vegetation, noon	8.3	*Poissant and Casimir*, 1998
USA, Tennessee	Mean value	5	*Kim et al.*, 1995
USA, Tennessee	(B), shadowed soil under the forest canopy, daytime, summer	2-7	*Carpi and Lindberg*, 1998
USA, Tennessee	(B), open field, daytime, summer	12-45	*Carpi and Lindberg*, 1998
USA, forests of middle latitudes. Similar forests make up 25% of all the forests on the Earth	(G) grown up deciduous forest, mean value	37	*Lindberg et al.,* 1998
USA, forests of middle latitudes	(G) planting of spruce	7.8	*Lindberg et al.,* 1998
USA forest soils	Mean value	<0.2	*Munthe*, 1993
USA, Tennessee	Summer-autumn	7.5±7	*Schroeder and Munthe*, 1998
USA deciduous forests	Mean value	100±80	In: [*Schroeder and Munthe,* 1998]
USA deciduous forests	(G) mean annual value	10-50	In: [*Schroeder*, 1995]
USA deciduous forests	(G) mean for warm season	- 2.2 - + 7.5	In: [*Schroeder*, 1995]
The south part of UK	Mean value	7	*Lee et al.*, 1998
Sweden, boreal forests	Mean annual value	0.11	*Lindqvist et al.*, 1991
Sweden, deciduous forests	(B), summer, daytime	1.4	In: [*Schroeder*, 1995]
Sweden, coniferous forests	(B), summer, daytime	0.3-0.6	In: [*Schroeder*, 1995]
Sweden, coniferous forests	(B), mean annual value	-1.1 - + 1.0	In: [*Schroeder*, 1995]
Sweden, field	(B), summer, daytime	0.1-0.9	In: [*Schroeder*, 1995]
Sweden, soils	Mean flux, summer	1.1±0.4	*Schroeder et al.*, 1989
South-western Sweden	Soil, t>1°C	0.3	*Xiao et al.*, 1991
USA. Agricultural field	July, mean value	37	*Xu et al.,* 1999
USA, deciduous forests	July, mean value	24	*Xu et al.,* 1999
USA, mixed forests	July, mean value	18	*Xu et al.,* 1999
Boreal forests	Mean value	1-10	*Schroeder and Munthe,* 1998
Natural land	Global value	2-7	*Bergan and Rodhe,* 2001

(B)* - chamber method; (G) –gradient method.

In the same geographical region *A.Carpi and S.Lindberg* [1998] studied the dependence of intensity of mercury emissions to air from natural soils on external factors. Soil temperature and insolation were taken as the main factors. Like previous authors they found that the dependence of the flux on temperature might be described by Arrhenius type equation. In measurements the activation energy varied from place to place from 18 to 24.9 kcal/mol. For practical use the authors expressed temperature dependence as simple regression equations for two forest sites and two cites in an open field (temperature in ˚C):

Undisturbed forest soil (under canopies): $\log F\ (\mathrm{ng/m^2/h}) = 0.059 \cdot T_s - 0.6$

$\log F\ (\mathrm{ng/m^2/h}) = 0.028 \cdot T_s + 0.2$

Open field, cultivated soil: $\log F\ (\mathrm{ng/m^2/h}) = 0.043 \cdot T_s + 0.2$

$\log F\ (\mathrm{ng/m^2/h}) = 0.057 \cdot T_s - 1.7$

Coefficients of these equations point to a high space variability of the emission, which depends not only on temperature. It should be noted that measurement sites were located at rather small distance from each other.

L.Poissant and A.Casimir [1998] also found that dependence of the emission on temperature obviously follows Arrenius type equation. When temperature was measured at 5 cm depth the activation energy value was found as 20.5 kcal/mol. The flux can be estimated using the equation:

$$F_{Hg}(ng/m^2/h) = -10.548 \cdot \frac{1000}{T} + 36.161$$ where T - temperature, K.

For background soils of Michigan State of the USA the emission intensity is on the level of 2 ng/m^2/h at variations from 1.4 to 2.4 ng/m^2/h [*Zhang et al.*, 2001b]. Only in one very shadowed place at high moisture content it was found that the intensity of mercury absorption by soil is -0.3 ng/m^2/h corresponding to dry uptake rate about 0.005 cm/s. On the open field the flux was appreciably higher – 7.6 ± 1.7 ng/m^2/h. According to these authors the emission intensity first of all depends on insolation and to less extent on temperature, although the correlation with temperature is high and clear linear dependence is observed:

$$F(ng/m^2/h) = 0.6382 \cdot (T - 273) - 9.3892 \ .$$ where T - temperature, K.

This regression equation was derived for the totality of forest and open-field sites.

The authors consider mercury exchange in the system “air-soil” as the surface physical-chemical process based on adsorption. The linear relationship between ln(F) and 1/T is interpreted as an evidence that the exchange process is a process of zero order. For background soils of Michigan the calculated activation energy value is 29.4 kcal/mol. It is noticeably higher than for other background soils:

Tennessee, the USA – (17.3 - 25.8) [*Kim et al.*, 1995];

Tennessee, the USA – (18.0 - 24.9) [*Carpi and Linberg*, 1998];

Quebec, Canada – 20.5 [*Poissant and Casimit*, 1998].

H.Zhang et al. [2001b] found that soil temperature is directly connected with insolation. The regression equation for the totality of all forest and open sites looks as follows:

$$(T - 273)_{mean} = 0.022 \cdot SR + 14.9 \, ,$$

where SR – is solar radiation, W/m^2

Summer measurements of emissions from soils covered by grass in Canadian Province South Quebec made by *L.Poissant and A.Casimir* [1998] showed that diurnal variations of soil emissions coincide with variations of insolation. At night the flux was observed on the level of 1 ng/m^2/h. In the daytime the flux value lagged behind of solar radiation peak.

From data of *A.Carpi and S.Lindberg* [1998] the sunlight makes greater impact than temperature. On exposure to soil the sunlight reduces oxidized mercury to elemental one. In one of experiments a liniar dependence of logarithm of mercury flux (in dimension ng/m^2/h) upon solar radiation flux SR (W/m^2) is obtained:

$$\log\,(Hg\ flux) = 0.0013 \cdot SR + 0.3 \ .$$

S.Lindgerg et al. [1998] found that the intensity of mercury emissions by mature forests of middle latitudes is about 70000, by young planting – 30000 and by forest soils – 2000 ng/m^2/y. Hence they have made the global summarization presented in Table 3.6.

Table 3.6. Global natural emissions of mercury on land [*Lindberg et al.*, 1998], t/y

Surface type	Area, km^2	Range of emission values
Taiga forests in high latitudes	$1.37{\cdot}10^7$	10 - 100
Forests of temperate zone of middle latitudes	$1.04{\cdot}10^7$	300 - 700
Tropical forests of low latitudes	$1.76{\cdot}10^7$	540 - 1200
Woodless soils		500 - 1000
Forest soils in winter		80 - 160
Total		1400 - 3200

S.Lindberg et al. [1995] investigated the emission (being more precise re-emission) from earlier polluted soils. They showed that variations are temperature dependent and within the range +7ºC - +29ºC the flux intensity (*F*) can be described by the following empirical dependence:

$$\log F\ \ (ng/m^2/h) = 0.065 \cdot T_S - 17.1,\quad \text{where T - temperature, K.}$$

Soil mercury flux highly correlated with water vapor flux [*Poissant and Casimir*, 1998]:

$$F_{Hg}(ng/m^2/h) = 42.64 \cdot F_{H_2O}(ng/m^2/h) + 1.4965\ .$$

In its turn it means that the higher is air humidity the lower is emission:

$$F_{Hg}(ng/m^2/h) = -0.0633 \cdot RH(\%) + 7.4026\ .$$

Wetting of soil by rain is another factor affecting the soil emission intensity [*Lindberg et al.*, 1999; *Benesch et al.*, 2001; *Carpi and Lindberg*, 1998; *Engle et al.*, 2001]. The mechanism of the phenomenon is not clear so far. *S.Lindberg et al.* [1999] believe that three reasons are possible: (1) the substitution of elemental mercury atom by water molecule on the sorption surface; (2) rapid reduction of oxidized mercury in the liquid phase; (3) displacement of soil air by water. Most likely the wetting effect is of a short-time character and it cannot affect long-term values of the emissions. For instance, in experiments of *H.Zhang et al.* [2001b] watering of soil by water amount 11 mm caused a rapid growth of the flux from 3.0 to 5.6 ng/m^2/h (the increase by 87% during 15 minutes). Water molecules possess higher capability to absorption by the surface of soil particles than elemental mercury atoms.

Soils of the mercury belts contain essentially more mercury than background soils. Besides in these cases the variability of values is also considerably higher. For mercury anomaly in the zone of a mercury belt *I.Trakhtenberg and M.Korshun* [1990] give the range of Hg content in soils from 0.3 to 12 ppm. Mercury content is even higher in desert soils of Nevada – up to 25 ppm [*Engle et al.*, 2001]. *O.Lindqvist et al.* [1991] believe that mean annual emission value within the mercury geochemical belts is 10000 ng/m^2/y.

It is natural that the mercury flux to air should be higher the higher is its content in soil. *M.Gustin et al.* [1999b] investigated this dependence both in laboratory and under field conditions. The experiment results can be approximated by the linear regression equation:

$$\log F\ \ (ng/m^2/h) = 1.10 \cdot \log C\ \ (ppm) + 0.52 \qquad \text{(measured in laboratory)}$$

$$\log F\ \ (ng/m^2/h) = 1.26 \cdot \log C\ \ (ppm) + 0.25 \qquad \text{(measured in field)}$$

Both equations give close results (within the range of 1-1000 ppm) at least by the order of magnitude).

American and European specialists carried out a series of investigations of soil mercury emissions within the geochemical mercury belt in Nevada, the USA [*Gustin et al.*, 1999a]. The maximum mercury flux reached 600 ng/m^2/h. *M.Engle et al.*. [2001] found that mean diurnal emission is about 17 ng/m^2/h. At night when temperature dropped down to –4ºC the emission actually ceased and it reached its maximum at noon (temperature +20ºC). The authors approximated the diurnal emission variation by Gauss curve with maximum at noon. Under laboratory conditions it was also observed that at constant temperature the enhancement of illumination leads to the sharp increase of mercury release.

Emissions from other lithospheric sources

Appreciable mercury emissions on relatively local scales result from volcanic activity. On fumarole fields of Kilauea volcano *F.Davies and G.Notcutt* [1996] found extremely high concentrations of TGM – from 2700 to 40600 ng/m^3. According to the estimate of *S.Siegel and B.Siegel* [1984] mercury flux only from this volcano is 260 t/y. From the evidence of *J.Nriagu and C.Decker* [2001] during 1980 – 2000 European volcanoes released 40 tonnes of mercury, volcanoes of both Americas – 2160 tonnes and in the whole World – 7182 tonnes. Thus mean annual value for all the volcanoes is 360 t/y though it is clear that this flux is highly sporadic. *W.Fitzerald* [1996] obtained appreciably lower values (from 20 to 90 t/y). He believes that the volcanic contribution to the global mercury cycle does not exceed 3%.

A certain contribution to natural emissions can be made by forest fires and biomass burning. In reality these sources can hardly be purely natural sources. *J.Nriagu* [1989] estimated the flux only from wild forest fires as 20 t/y. *P.Artaxo et al.* [2000] found very high mercury concentrations in air during the season of biomass burning in Brazil (up to 1000 ng/m^3). From their viewpoint mercury can enter the atmosphere both from the burning biomass itself and from soil being heated.

Sea surface emissions

Numerous measurements of mercury concentrations simultaneously in air and water (both in fresh water and seawater) showed that everywhere water is supersaturated by elemental mercury and by DMM. The extent of supersaturation reaches several orders of magnitude [*Baeyens et al*., 1991]. According to Henry's law "excessive mercury" enters the atmosphere. Both fresh and marine waters are supersaturated by the volatile mercury forms, and at present it is difficult to say whether mechanisms of mercury excess formation in sea and fresh water differ. According to measurements of *K.Gårdfeld et al*. [2001b] the emission from fresh water is by an order of magnitude higher than from seawater. Below literature data will be summarized separately for fresh water and marine ecosystems.

There are two hypotheses relative to the role of biota in mercury emissions from the water surface. For example, *J.Kim and W.Fitzgerald* [1986] indicate a direct connection between mercury emission intensity and biological productivity in water. On the other hand, *A.Amiot* [1995] found that the removal of particles, bacteria and colloids from lake water samples does not influence the concentration of dissolved elemental mercury. The more so, sample sterilization slightly increases the concentration of dissolved Hg0.

One of the first measurements of mercury emissions from seawater was made by *V.Fursov* [1983]. His data evidence that the mean flux to air from the surface of the Aral Sea is 1.6 ± 0.3 ng/m^2/h.

Unfortunately this paper does not answer the question whether observations were made round the clock and what was the season. For the first time *J.Kim and W.Fitzgerald* [1986] assessed the role of the ocean on the global scale. They measured mercury flux to the atmosphere in the east of the equatorial Pacific in the zone of elevated biological productivity. It was found that the highest mercury concentrations in water are characteristic of cold, enriched by nutrients zones in equatorial upwelling. In the North Atlantic *R.Mason et al.* [1998] estimated mean emission value equal to 11000 ng/m^2/y. On the average over the World Ocean the emission intensity is 6500 ng/m^2/y [*Lindqvist et al*., 1991]. *T.Bergen and H.Rodhe* [2001] accept in their model that emissions from the sea surface smoothly change from the equator to the poles from about 9000 to 0 ng/m^2/y.

If the emission intensity of the sea surface is proportional to area of "water-air" contact then the availability of dependence on wind speed (on sea roughness) becomes natural. W.Bayens et al. [1991] found that the emission intensity varies from 0.05 to 0.74 ng/m^2/h depending on the wind speed. When on wave crests appear "white horses" the intensity can increase up to 20 ng/m^2/h. The authors suggest an empirical formula for the dependence of mercury intensity flux from the ocean on the wind speed (V) within the range from 0 to 30 m/s:

$$F\,(ng\ Hg\,/\,m^2\,/\,y) = 1000 \cdot \left(0.43 + V^{1.13} + \left(\frac{V}{10} \right)^{4.25} \right).$$

K.Gårdleld et al. [2001b] found that seawater emission in the region of the western coast of Sweden is on the average 0.61 ng/m^2/h at the range from –2.72 to +8.84 ng/m^2/h. Thus in their experiments the water surface was mercury sink time to time though on the whole the flux was directed from water to air. The flux increased with temperature increase. It was explained by solubility decline with temperature growth and correspondingly the supersaturating increase.

For the central part of the Baltic Sea mean diurnal flux in summer (average temperature 17.3ºC) was about 1 ng/m^2/h and in winter (average temperature 3.3ºC) decreases as much as 2 times [*Wängberg et al*., 1999]. The authors did not find a pronounced diurnal cycle and came to the conclusion that the flux was a function of water temperature and wind speed. Mean annual emission intensity for the Baltic Sea as a whole was estimated equal to 7000 ng/m^2/y.

In addition to elemental mercury seawater is obviously supersaturated by dimethylated mercury. There is small number of DMM flux measurements. This complicates the determination of integral values. *R.Pongratz and K.G.Heumann* [1999] measured DMM in different regions of the World Ocean at different depths. They found that the depth profile of DMM concentrations actually coincides with the profile of chlorophyll-a. According to their assessment DMM flux to the atmosphere from the basin of the Antarctic Ocean (between 51 and 71 latitudes) amounts to 210 t/y and from the Arctic Ocean – 240 t/y. Even neglecting the contribution of the other oceans this value indicates the significance of DMM emission input to the global atmospheric mercury cycle.

Emissions from fresh water bodies

The range of mercury fluxes from fresh water reservoirs as a rule is between 2000 and 20000 ng/m^2/y [*Libndqvist et al.,* 1991]. The intensity depends on a number of factors among which the most important are: mercury content in water, the amount of dissolved organic compounds, temperature and wind speed.

W.Schroeder [1996] obtained mean annual value of the flux intensity for Ontario Lake equal to 5600 ng/m^2/y. *F.Bouldala* [2000] in August 1997 carried out round the clock comprehensive investigations on two Canadian lakes. Mercury concentration in the lakes differed about 2 times. First, it was demonstrated that the emission intensity depends on mercury concentration in the lake water. Second, for both lakes a pronounced diurnal variation was observed – the flux in the daytime was higher than at night by an order of magnitude. The authors concluded that the most important factors defining the flux value are wind speed and solar radiation. The effect of wind has double explanation: (1) vertical mixing speeds up the inflow of dissolved elemental mercury to the upper water layer; (2) mixing accelerates the inflow to the surface of oxidized mercury where it photochemically is reduced to elemental mercury and removed to the atmosphere. *F.Boudala* [2000] derived an empirical dependence of the emission intensity on at once two factors – wind speed and insolation intensity:

$$F = B \cdot V^{i} + C\,,$$

where F – flux, ng/m^2/h; R – solar radiation, kW/m^2; V – wind speed, m/s.

For a lake with higher content of mercury: B = 2.454; i = 1.5; C = 1.1.

W.Fitzgerald et al. [1991] evaluated mercury budget for Little Rock Lake, the USA. Emission to the atmosphere is an important component of mercury budget in the lake. Mean annual emission was estimated equal to 700 ng/m^2/y, but during a year the intensity varies essentially from 2.5 ± 0.3 ng/m^2/day in October to 5.0 ± 2.5 ng/m^2/day in August.

L.Poissant and A.Casimir [1998] measured mercury fluxes from the surface of the St. Lawrence River and compared them with fluxes from soils of this region. They concluded that on the whole the exchange intensity in the system “soil-air” is 6.8 times higher that in the system “water-air”. In the daytime emissions from the water surface are weak (maximum 1 ng/m^2/h) and at night water surface absorbs mercury from the atmosphere (maximum 0.5 ng/m^2/h). Besides they suggested an empirical equation of emission dependence on wind speed over the water surface:

$$F\,(ng\,/\,m^2\,/\,h) = -1.3244 \cdot V(m\,/\,s) + 1.4167\,.$$

A considerable number of measurements of mercury fluxes for the water underlying surface were made in Sweden in the end of the 80-s [*Schroeder et al*., 1989; *Xiao et al*., 1991]. In the daytime during warm season the mean flux from the lake water was 7.9 ng/m^2/h (at water temperature within the range of 13 – 23ºC). At night the emission was 2-3 times lower. In September at water temperature 12-17ºC the flux varied from 3.2 to 20 ng/m^2/h [*Schroeder et al.*, 1989]. When temperature lowered down to 2ºC the flux was negligible.

Later measurements of fluxes from the river water gave mean value 11 ng/m^2/h with the variation range from –2.5 to +88.9 ng/m^2/h [*Gårdfeldt et al.,* 2001b]. Like in the case of seawater sometimes the authors pointed to a realized possibility of mercury absorption by the surface. The flux to the atmosphere is well correlated with the solar radiation flux. It is possible that under the impact of light organic complexes in water are reduced due to the formation of radicals. The concentration of mercury dissolved in water grows linearly with insolation and it can be described by the equation:

$$C\,(water) = 0.0206 \cdot SR - 0.8628\,,$$

where $C(water)$ – concentration, ng/l; SR – solar radiation flux, W/m^2.

The concentration of mercury dissolved in water (then the supersaturating extent) depends on temperature both of water and air. *K.Gårdfeldt et al.* [2001b] suggest the following empirical relationships:

$$C\,(water) = -28.326 \cdot \frac{1000}{T_W} + 98.458\,;$$

$$C(water) = -14.517 \cdot \frac{1000}{T_A} + 52.081,$$

where T_W and T_A – temperature of water and air in Kelvin degrees, respectively.

Integral values of global natural emissions

It is interesting to compare estimates of global natural emission intensities obtained by different authors and used in global models. For the convenience the data are collected in Table 3.7 separately for land and sea surface.

Table 3.7. Natural mercury emissions to the atmosphere

Emission value, t/y			Reference	Note
Land	Ocean	Total		
		190000	*Jaworowski et al.*, 1981 (quoted in Geological Survey of Canada, 1995)	
	2900		*Kim and Fitzgerald,* 1986	+/-1800
730	1770	2500	*Nriagu*, 1989	
		3000	*Lindqvist et al.*, 1991	From 2000 to 9000
		29000	*Geological Survey of Canada*, 1995	3500 t/y for Canada only
1000	2000	3000	*Fitzgerald and Mason,* 1994	1400 t/y of re-emission from land
1400-3200			*Lindberg et al.*, 1998	
700			*Ebinghaus et al.*, 1999	500 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
1000	800	1800	*Lamborg et al.*, 2002	400 t/y of re-emission from the ocean

Sufficiently simple estimates evidence that very high values of emissions contradict measurement data. For instance, the upper limit of mercury atmospheric content is a reliable value – about 6000 tonnes. If the flux is equal, for example, to 190000 t/y, then mercury lifetime in the atmosphere should be about 10 days. In its turn it means that an essential vertical gradient of concentration should be observed. Since in reality any pronounced gradient is not detected, natural emission of about 10000 t/y and higher seems unreasonably high.

Diurnal and seasonal cycles of natural emissions

The literature data discussed above suggest that the main parameters defining the intensity of natural emissions both from soils and water objects are the temperatures of the underlying surface and insolation. The soil temperature can be measured at different depths. In any case, however, round the clock it is a poorly varying parameter. At the diurnal variation of air temperature by 20ºC the soil temperature variation even at the minimum depth is much lower. For this reason in the diurnal cycle natural emission intensity may be considered independent of temperature.

The insolation depends upon the point position on the Earth surface, season and cloud availability. Diurnal variations of the illumination intensity may be approximated by a function of sinus with allowance made for the latitude of a given place and season. The influence of cloudiness has not been studied so far therefore this factor is forcedly excluded from the consideration.

It is clear that the underlying surface temperature and insolation in middle and high latitudes have a pronounced seasonal cycles. The surface temperature can vary from negative values to more than +40ºC. On the base of literature data it is accepted that natural emissions ceased when the temperature drops to 0ºC and lower. The insolation in diurnal and seasonal cycles can be calculated at each model step as a function of latitude of a given place and the day of a year. Naturally, there is no sense to take into account diurnal variations of insolation if temporal resolution of calculations is of order of months and longer.

Undoubtedly mercury release by volcanoes is extremely variable in time. However, in deficiency of operational information the flux of volcanic mercury is taken constant in time.

Natural mercury emission in the EMEP region

To give a pattern of spatial distribution of natural mercury emissions the globe surface may be divided into 5 categories. Glacier surfaces, from which there are no emissions, may be referred to the first category. Thus the first category will involve the Antarctic, Greenland, permanent ice of the Arctic and high-mountain glaciers. The World Ocean should be referred to the second category. The surface of the continents may be divided depending on mercury content in soils. The main part of the continental surface (the third category) is characterized by soil mercury content within the range of 0.01-0.1 ppm. The fourth category includes those zones of the geochemical mercury belts where concentrations in rocks do not reach the levels characteristic of mercury deposits. Finally regions with the main mercury deposits represent the fifth category. The last two categories can be distributed in accordance with the map of mercuriferous suggested by *I.Jonasson and R.Boyle* [1971] or *M.Gustin et al.* [1999a].

In Europe there are some geochemical mercury belts, which should cause drastic non- uniformity of the natural emission field [*Bailey et al.*, 1973]. Firstly, almost entire southern Europe is in the mercury belt zone. Suffice it to say that 50% of mercury mining in the World falls at the region of the Mediterranean Sea [*Trakhtenberg and Korshun,* 1990]. It is important that the belt encompasses both the south of Europe and the north of Africa where emissions were not assessed earlier. At the same time such countries as Algeria are the main producers of mercury in the World [*Hylander*, 2001]. Secondly, the manifestation of the mercury belt is characteristic of Belgium, the Netherlands, Luxemburg and the United Kingdom. Finally thirdly, the whole territory of Iceland is in the zone of the mercury belt.

A certain contribution to natural emissions is made by volcanoes. According to data of Italian specialists during quiet periods the volcanoes of Italy emit about 55 tonnes of mercury per year [*Ferrara et al.*, 1999]. *R.Ebinghaus et al.* [1999] mentioned that geysers of Iceland are a noticeable source of mercury. For modelling purposes the information about the height of mercury input to the atmosphere is important. The values of volcanic emissions, their location and height are given in Table 3.8.

Table 3.8. Characteristics of some volcanic sources of mercury

Source	Co-ordinates		Characteristic emission height (above sea level), m	Mean annual mercury emission, t/y
	Latitude	Longitude		
Etna Volcano	37045’ N	14059’ E	3240	47
Stromboli Volcano	38048’ N	15013’ E	920	8.8
Volcano Volcano	38023’ N	14059’ E	500	0.9
Geothermal provinces of Iceland	650 N	180 W	300	0.08*

* on the basis of [*Edner et al.*, 1991] and on the assumption that at least 10 geysers are active

O.Travnikov and A.Ryaboshapko [2002] estimated natural emission flux of mercury in the Northern Hemisphere. In was assumed that the emission from land depends on temperature and it is higher in the zones of mercuriferous belts than in other land areas. The emission from sea surfaces is assumed to be in proportion to organic carbon primary production [*Kim and Fitzgerald,* 1986]. The same principles were applied when estimating spatial and temporal distribution of natural mercury emissions within the EMEP domain. The map of mean annual spatial distribution of natural mercury emission intensities over the EMEP domain with spatial resolution 50x50 km is presented in Figure 3.7. Maximum values are characteristic of the southern Europe where the geochemical mercury belt is extended and the surface temperature as a rule is above 0°C. For the region as a whole natural emission is 208 t/y. The land emits 193 t/y and the sea surface - 15 t/y.

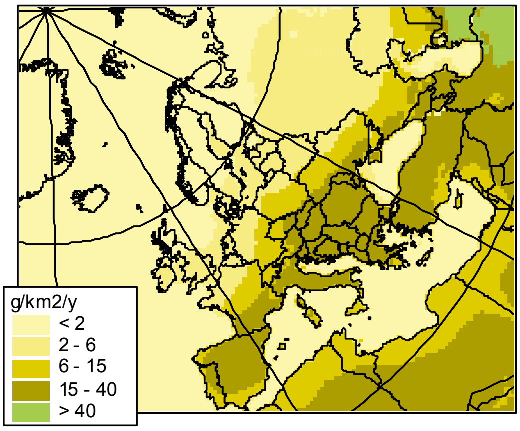


Figure 3.7. *Spatial distribution of mercury natural emissions in EMEP region, g/km^2/y*

Anthropogenic mercury re-emission to the atmosphere in the EMEP region

Significance of re-emission of previously accumulated anthropogenic mercury in soils is determined first of all by the capacity of soils to retain mercury and by mercury lifetime in soils relative to different removal mechanisms. One can consider three such mechanisms: (1) hydrological run-off into water bodies; (2) washout from upper soil layers to deep ones; (3) evasion to the atmosphere or re-emission.

Earlier we estimated that the low limit of estimate of mercury lifetime in soils (relative to evasion to the atmosphere) could be about 100 years [*Ryaboshapko et al.*, 1998]. In literature it is possible to find estimates from 150 to 10000 years [*Wallschläger et al.*, 2000; *Lee et al.*, 1998]. For the following calculations the value of mercury life-time in soils relative to the flux into the atmosphere (400 y) published by *I.Trakhtenberg and M.Korshun* [1990] is used.

W.Fitzgerald and R.Mason [1996] estimated that the bulk (190000 t or 95%) of anthropogenic mercury emitted to the atmosphere during recent 100 years, at present is being accumulated by soils. According to estimates of *I.Trakhtenberg and M.Korshun* [1990] process rate constant relative to volatilization is 0.0025 y^{-1} and relative to the runoff to water basins - 0.0011 y^{-1}. Based on these values it is possible to evaluate the range of conceivable values of re-emission to the atmosphere of Europe.

On the assumption that all earlier emitted anthropogenic mercury is uniformly distributed with soils of all continents, then for Europe re-emission value could be only 32 t/y. This is minimum estimate, since the bulk of emissions during recent 100 years took place in Europe and European soils accumulated much more mercury per unit soil mass than soils of other continents. In addition, a part of anthropogenic mercury entered soils (or in-land water bodies) directly from industrial plants. This share of mercury (practically equal to the atmospheric load) can also volatile to the atmosphere as re-emission.

Mercury lifetime in soils exceeds considerably the period of really noticeable anthropogenic impact (the last 100 years). It means that there was no significant redistribution of previously deposited mercury. Hence the re-emission field should be similar to the field of total deposition for the last 100 years. About 75% of deposited mercury during the last 100 years on a given region is still remained in the soils of this region.

The total re-emission in Europe was estimated on the basis of a number of assumptions [*Ryaboshapko et al*., 1998]. The total direct anthropogenic emission in Europe for the end of the 80-s was assessed as 726 t/y [*Petersen et al*., 1995]. According to *A.Ryaboshapko and V.Korolev* [1997] about half of this amount (let it be 350 t/y) deposited on the territory of Europe. Let us admit like *W.Fitzgerald and R.Mason* [1996] that during recent hundred years a linear growth of emissions is observed (and deposition respectively) and one hundred years ago the deposition from direct anthropogenic sources was negligible. Reasoning from these assumptions and rates of mercury removal from the soil [*Trakhtenberg and Korshun*, 1990] we find that in Europe nowadays anthropogenic mercury re-emission in the EMEP region caused by direct anthropogenic emissions in Europe makes up 36 t/y. Besides, a part of mercury deposition in the EMEP region was resulted from globally distributed sources outside Europe. If we assume that the total emission in Europe during XIX and XX centuries amounted to 1/3 of the global one and that mercury of non-European origin was evenly distributed in soils of all continents the value of re-emission in Europe from these sources should be about 11 t/y. Thus the total re-emission from soils of the EMEP region at the beginning of the 90-s should not exceed 47 t/y or 10% of the modern value of direct anthropogenic emission.

It was mentioned above that mercury is firmly fixed with soil and the bulk of mercury deposited in previous years is still contained in soil. Then it is possible to assume that during last 50-100 years the configuration of direct anthropogenic emission field did not undergo considerable changes. The resulting re-emission field should comply with mean climatic deposition field. Two factors, however, can distort the re-emission field configuration: on the one hand, the temperature decrease is accompanied by re-emission intensity reduction, on the other, the same is happened at the increase of organic carbon content in soil. Under European conditions to a certain extent these effects compensate each other - from the north to the south both mean temperature and organic carbon content are increased. Here we presume in the first approximation that the re-emission field configuration complies with the deposition field produced by direct anthropogenic emissions for 1995.

The violation of global atmospheric mercury cycle by human activity inevitably should lead to the increase of mercury content in the oceanic surface layer and consequently to the growth of emission intensity from the sea surface. In work [*Ryaboshapko et al*, 1998] it was assumed that re-emission from sea surfaces is evenly distributed in the EMEP domain, and its flux is 0.7 g/km^2/y. A combined re-emission field over both land and ocean used further in calculations is shown in Figure 3.8.

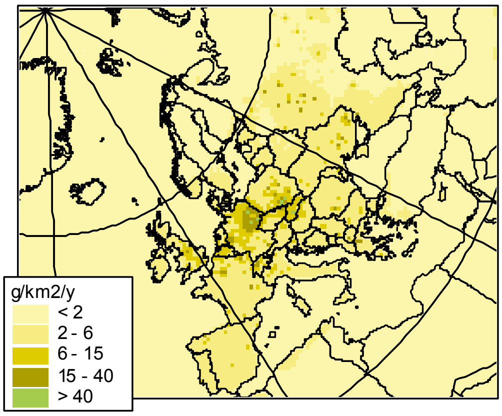


Figure 3.8. *Field of mercury re-emission in the EMEP region, g/km^2/y*

When considering re-emission one should bear in mind an important thing that irrespective of chemical mercury form in deposition, re-emission is mainly represented by the elemental and maybe methylated forms. Re-emission in aerosol form caused by aeolian soil weathering can give but a small contribution (to 2%) on the local scale and in the course of short periods. Like natural emission re-emission depends on temperature and on sun insolation.

Chapter 4

RESULTS OF THE CALCULATIONS FOR 2000

The updated version of the regional model, described in Chapter 2, was used to evaluate concentration and deposition fields in the EMEP area. The results were obtained on the base of the emission data (Chapter 3) and the meteorological data for 2000. This Chapter is devoted to description and analysis of results obtained by the MSCE-HM model. These results are mass budgets for the EMEP region as whole, fields of air concentrations and depositions, deposition budgets for individual countries and for regional seas surrounding Europe. In addition to this, effects of Arctic mercury springtime depletion phenomenon on depositions in the Arctic are considered. Current version of MSCE_HM model underwent some modifications, which, in turn, led to differences between the results for 1999 and for 2000. These differences were analyzed. Comparison of measured and calculated values demonstrated that the model results reasonably agree with monitoring data.

4.1. Atmospheric budgets for the EMEP area

Lead and cadmium

Before analysing the modelling results for 2000 and their comparison with the results for 1999 brief overview of changes concerning input data and the model is given. Changes of the emissions in 2000 led to decrease of pollution levels in Europe. Lead and cadmium anthropogenic emission data decreased 26% and 18%, respectively. Approach to estimates of quasi-natural emissions of these metals was also modified. This resulted in about 11% decrease of this emission in EMEP region (see Chapter 2). The decrease of the emissions should lead to decrease of the depositions to EMEP region as a whole.

In the calculations for 2000 the precipitation amounts used were lower over most of EMEP region, than those used for 1999. This difference in precipitation caused by improvements of meteorological pre-processing procedure. Annual precipitation amounts in 1999 and in 2000 are demonstrated in Figure 4.1.a and b. As seen from the map, nearly over entire EMEP region annual precipitation in 2000 are lower than those in 1999. On average, precipitation amounts over entire EMEP changed from 620 to 440 mm/y. Lower annual precipitation results in lower wet deposition fluxes. The changes of precipitation affects cadmium wet scavenging to greater extent than wet scavenging of lead, because mean annual washout coefficient for cadmium is assumed to be more than twice higher (see Chapter 2).

Other changes have less effect on depositions and concentrations in Europe. Modification of dry deposition scheme slightly changed budget for EMEP as whole (see Chapter 2). Revision of boundary concentrations can have some effect on pollution level in the vicinity of the boundaries of the modelling domain, but does not significantly influence central parts of the EMEP region.

Before doing analysis of spatial pattern of the concentrations and depositions it makes sense to examine integral budget articles characterizing atmospheric pollution of the EMEP region as a whole. These articles are calculated in operational regime. They are total or quasi-natural emission, wet and dry depositions, inflow to the region and outflow out of the region due to advective wind flows.

Analysis of these integral budget articles can help to identify the most important budget components for the region as a whole, to assure that model conserves mass of the pollutant and to determine if the region is a net "receptor" of "emitter" with regard to the atmosphere of the globe.

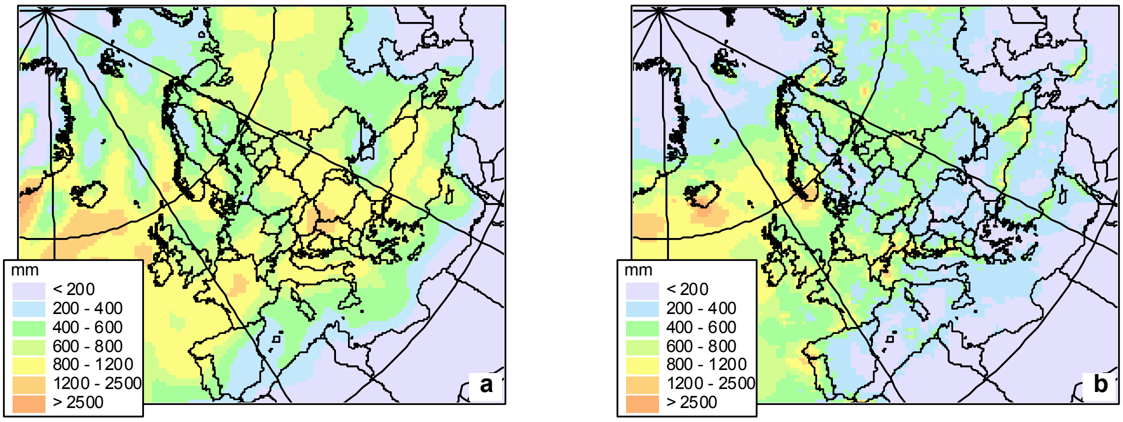


Figure 4.1. *Annual precipitation amounts, mm, used in calculations for 1999 - **a** and in 2000 - **b***

In Table 4.1. the most important budget components for lead and cadmium in 2000 and 1999 are summarized. As seen from the budget articles for 2000, total amounts entering EMEP domain through lateral and top boundaries are lower than those leaving the domain. Therefore, the EMEP region is the net "emitter" of these metals to the global atmosphere according to model assumptions used. Wet deposition is dominant for region as a whole both over land areas and over marine surfaces in comparison with dry deposition. On the average, the contribution of dry deposition to the total deposition makes up 23 % for lead and 17 % for cadmium.

Table 4.1. Atmospheric budgets of lead and cadmium for EMEP domain in 2000, t/y

Budget item	Pb-2000	Pb-1999	Cd-2000	Cd-1999
Total emission	18843	23699	664	783
Quasi-natural emission	*7641*	*8565*	*394*	*425*
Direst anthropogenic emission	*11201*	*15134*	*270*	*331*
Inflow through lateral boundaries	5176	7000	134	144
Inflow from the free troposphere	5339	5060	134	124
Total depositions	16703	22565	588	767
Dry deposition to land	*3538*	*2457*	*84*	*110*
Dry deposition to sea surfaces	*348*	*312*	*18*	*15*
Wet deposition to land	*7510*	*12360*	*271*	*398*
Wet deposition to sea surface	*5307*	*7434*	*215*	*345*
Outflow through lateral boundaries	7149	7682	203	174
Outflow trough the model top	5541	5361	141	110

In comparison with the budget for 1999 [*Ilyin et al.*, 2001], budget components and their ratios are different. Wet deposition of lead and cadmium decreased mainly due to emission changes and also because of changes in precipitation amounts. Dry deposition increased about 40 % for lead mostly because of introduction of new parameterization, which takes into account a significant increase of dry uptake velocity over forested areas. For cadmium the role of dry deposition (ratio of dry to total deposition) to EMEP only slightly increased. This is connected with the fact that previously used deposition scheme for cadmium caused high enough deposition velocities. It is shown in Chapter 2 that boundary concentrations of lead in the current model version are lower than those in the previous version. This fact resulted in some decrease of lead transport into the region due to advection. Advective inflow of cadmium into the region remained approximately the same.

Mercury

Atmospheric mercury budget articles for 2000 are presented in Table 4.2, and for 1999 - in Table 4.3. As seen from the Table 4.2., a huge mass of atmospheric mercury enters and leaves EMEP reservoir via lateral boundaries. This is conditioned mostly by elemental form of mercury, which is a long-living atmospheric species (atmospheric lifetime is about one year). Thus, it is capable of transporting over the global scale. Since other mercury forms - Hg_{part}, Hg^{2+}_{gas} and DMM have lifetimes from hours to days, most of these species deposited within the region, and do not move far from their emission sources. Hg_{part}, however, can also be generated in the atmosphere due to gaseous and aqueous chemical transformations (Chapter 2). This can explain the fact that depositions of Hg_{part} are about twice larger than its emissions.

Table 4.2. Atmospheric budgets of mercury for EMEP domain for 2000, t/y

Budget item	Mercury forms				
	Hg^0	Hg^{+2}_{gas}	Hg^{+2}_{part}	DMM	ΣHg
Total emission	343	57	30	26	456
Natural emission	*187*	*0*	*0.1*	*21*	*208*
Direct anthropogenic emission	*109*	*57*	*30*	*0*	*196*
Re-emission	*47*	*0*	*0*	*5*	*52*
Inflow through lateral boundaries	8560	0	60	0	8620
Inflow from the free troposphere	18250	0	130	0	18380
Total depositions	38	55	123	0	216
Dry depositions	*17*	*23*	*17*	*0*	*57*
Wet depositions	*21*	*32*	*106*	*0*	*159*
Outflow through lateral boundaries	10850	1.4	1.4	110	10960
Outflow trough the model top	16150	120	1	0.1	16270

Table 4.3. Atmospheric budgets of mercury for EMEP domain for 1999, t/y

Budget item	Mercury forms				
	Hg^0	Hg^{+2}_{gas}	Hg^{+2}_{part}	DMM	ΣHg
Total emission	365	64	35	27	491
Natural emission	*198*	*0*	*0.1*	*22*	*220*
Direct anthropogenic emission	*120*	*64*	*35*	*0*	*219*
Re-emission	*47*	*0*	*0*	*5*	*52*
Inflow through lateral boundaries	9230	0	63	0	9293
Inflow from the free troposphere	16980	0	160	0	17140
Total depositions	183	59	248	0	490
Dry depositions	*154*	*15*	*40*	*0*	*209*
Wet depositions	*29*	*44*	*208*	*0*	*281*
Outflow through lateral boundaries	11129	2	172	1	11304
Outflow trough the model top	14974	2	154	0.1	15130

In comparison with the results for 1999 [*Ilyin et al.*, 2001] integral values of the anthropogenic and natural emissions did not changed significantly. Anthropogenic emissions in 2000 were about 11% and natural emissions - about 5% lower than the corresponding values for 1999. Total re-emission value remained the same. However, other budget components changed significantly. First of all, dry uptake of elemental mercury went down from approximately 180 t/y to 17 t/y. This is connected with the modification of dry uptake scheme for elemental mercury (see Chapter 2). Wet depositions of Hg^0, Hg_{part} and $Hg^{2+}{}_{gas}$ also decreased. The main reason for this is lower amounts of precipitation in 2000 used in the calculations in comparison with those in 1999. Another reason is the introduction of the radical reactions in the aqueous-phase mercury chemical scheme, which led to more probable reduction of mercury in the liquid phase and weaker dissolution in the cloud droplets. In addition to this, temperature dependence of Hg^0 oxidation rate by ozone was introduced, which led to slower oxidation in upper (colder) atmospheric layers of the model. Slower oxidation of Hg^0 finally led to lower atmospheric content of Hg_{part}. That is why, despite potential increase of dry deposition capacity due to introduction of new scheme for dry uptake of particles, overall dry uptake of Hg_{part} decreased in comparison with the results for 1999. Total depositions to the EMEP region decreased from 490 t/y to about 216 t/y. In these estimates the effect caused by mercury spring-time depletion was not considered. As discussed in section 4.5., current parameterization of this phenomenon could add up about 17 t of depositions on annual level in the northern parts of EMEP.

4.2. Concentration and deposition fields over the EMEP region

Lead

Mean annual calculated concentrations of lead in air are demonstrated in Figure 4.2. As seen, over most part of Europe the concentrations do not exceed 15 ng/m^3. In some areas, associated with significant emissions the concentrations can exceed 30 ng/m^3. These areas are Italy, the eastern Ukraine, the south of Poland, central Russia and Romania.

Especially large areas with elevated air concentrations are located in Italy, where they extend over more than a half of its territory. This can be explained by very high emission density in this country (see Chapter 3). However, it is worth mentioning that official emission data from Italy refer to 1994, and could be higher than that in 2000. Maximum computed concentrations are in northern Italy (210 ng/m^3), in Romania (170 ng/m^3) and in the Ukraine (130 ng/m^3). Relatively low air concentrations are observed in the north of Scandinavia, Spitzbergen (Norway), Iceland and in Komi Republic of Russia, where lead concentrations in air are lower than 2 ng/m^3.

In comparison with the calculation results obtained for 1999, modelled concentration values for Europe as whole did not change significantly. On one hand, decrease of the emissions should lead to decrease of the concentrations. On the other hand, lower precipitation amounts results in weaker wet removal, and, consequently, to rise of concentrations. In some areas decrease of the concentrations was obtained. For example, on Scandinavian Peninsula air concentrations become lower because of modification of quasi-natural emission parameterization (see Chapter 3). In France or in the Ukraine the decrease is associated with changes concerning the emission data. For some parts in Europe some increase of the concentration caused mainly by changes associated with precipitation differences.

A map of total (wet and dry) depositions of lead is shown in Figure 4.3. Similar to the map of air concentrations, zones of elevated depositions are seen in Poland, Italy, Central Russia, the east of the Ukraine, the United Kingdom, Balkan Countries. In these countries the depositions of lead often exceed 1.2 kg/km^2/y, and in some gridcells are even greater than 4.5 kg/km^2/y. Relatively low computed depositions are obtained for the north of Scandinavia, where they are below 0.2 kg/km^2/y in some areas. Low depositions are indicated in the northern part of Africa. This can be explained by lack of the data on emissions from anthropogenic sources in this area and by low precipitation in arid climate.

Calculated total depositions values of lead decreased in comparison with the results for 1999. The decrease is associated with the decrease of the emission estimates and with lower model precipitation amounts in 2000 comparing to those in 1999.

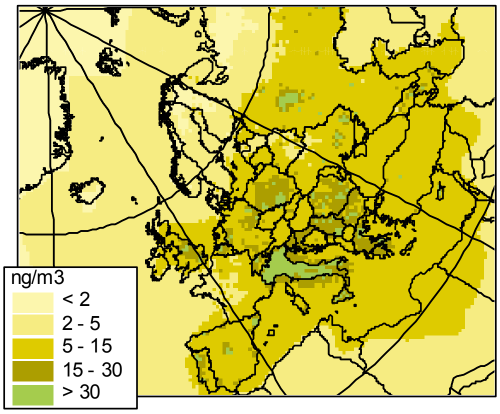


Figure 4.2. *Annual mean air concentrations of lead in 2000, ng/m^3*

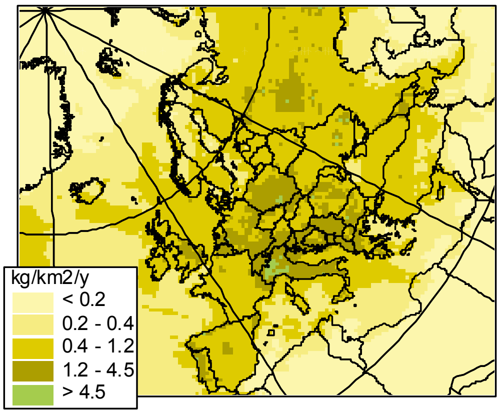


Figure 4.3. *Total (wet and dry) depositions of lead in 2000, kg/km^2/y*

Cadmium

A map of calculated air concentrations of cadmium is demonstrated in Figure 4.4. As seen, air concentrations in Europe mainly range from 0.1 to 1 ng/m^3. Especially high pollution levels were computed for Poland, which is characterized by large areas of elevated cadmium concentrations. In some gridcells these concentrations exceed 3 ng/m^3. Relatively high concentrations of cadmium are also obtained for Belgium, Italy, the United Kingdom, Russia, the Ukraine and Balkan countries. In these countries air concentrations often exceed 0.3 ng/m^3. Highest computed air concentrations are located in Romania (18.7 ng/m^3), Bulgaria (7.4 ng/m^3) and in Italy (Sicily, 5.7 ng/m^3). Relatively low concentration values were produced for the Arctic and the northern part of Africa. In the north of Scandinavia the concentrations typically lay below 0.1 ng/m^3.

In comparison with the results obtained in calculations for 1999 [*Ilyin et al.*, 2001] it is possible to say that for Europe as a whole modeled concentration values rose. Some decrease of the emission values causes the decrease of concentration, but lower precipitation leads to higher content in air. Integral effect of these two factors leads to the increase of air concentrations of cadmium. In the Ukraine the emission estimates went down much greater (more than 6 times) than those for Europe as a whole (18%). Due to this huge decrease in the emission estimates concentrations in the Ukraine also dropped.

The map of total cadmium depositions is shown in Figure 4.5. As seen from the Figure, zones of high depositions conform to zones of high concentrations. The highest depositions are computed for Romania (750 g/km^2/y), Poland (370 g/km^2/y), Bulgaria (260 g/km^2/y). Relatively clean areas are the north of Sweden and Finland, Spitzbergen (Norway), Iceland and the north of Russia. In these areas depositions are below 20 g/km^2/y.

In comparison with the results for 1999 it becomes clear that on the average for Europe the modeled depositions decreased. First, some decrease of anthropogenic emission and estimates of quasi-natural emissions can be noted. In addition to this, in 2000 precipitation amounts were lower, than those used in simulations for 1999. This resulted in weaker removal, and, consequently, in the rise of air concentrations and decrease of total deposition.

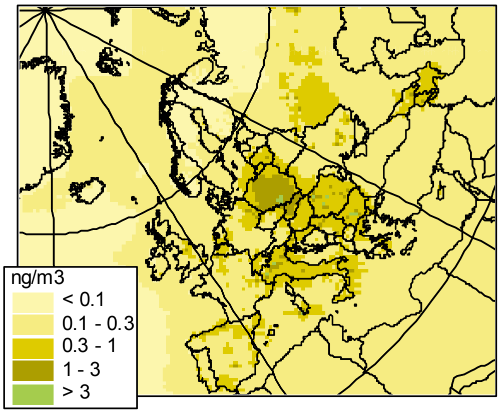


Figure 4.4. *Annual mean concentrations of cadmium in 2000, ng/m^3*

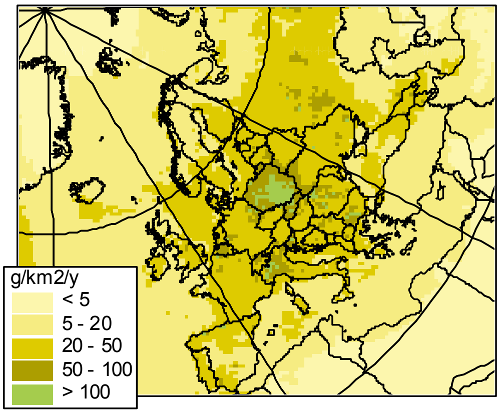


Figure 4.5. *Total (wet and dry) depositions of cadmium in 2000, g/km^2/y*

Mercury

In Figure 4.6 a map of mercury air concentration is presented. At monitoring stations so-called total gaseous mercury (TGM) is usually measured. That is why it makes sense to demonstrate maps of this species. TGM includes gaseous mercury species in the atmosphere. In the model TGM is a sum of Hg^0, Hg^{2+}_{gas} and DMM. As seen, the field of TGM concentrations is smoother than that of lead and cadmium concentrations in air. It is explained by the fact that most of TGM is composed of elemental mercury, which lifetime is rather long (about one year) and it causes significant transport and mixing in horizontal and vertical direction. Maximum concentrations of TGM in 2000 are obtained in the central part of Greece and reach 6.3 ng/m^3. Another maxima are located in Slovakia (4.2 ng/m^3), Poland (4.1 ng/m^3) and the eastern part of Germany (4.0 ng/m^3). Regions with relatively low air concentrations are in the north of Scandinavia, where computed concentrations lay within 1.7 - 1.9 ng/m^3.

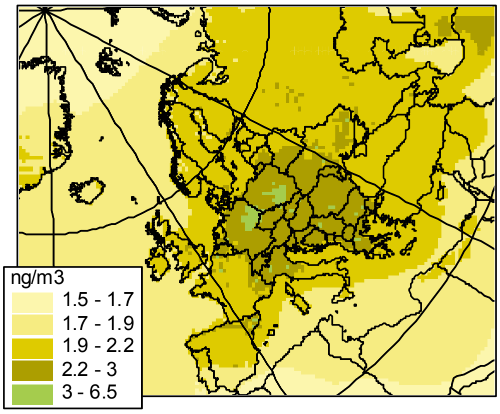


Figure 4.6. *Annual mean concentrations of TGM in 2000, ng/m^3*

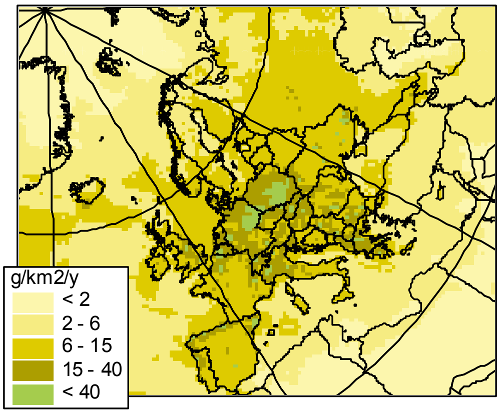


Figure 4.7. *Total (wet and dry) depositions of mercury in 2000, g/km^2/y*

According to the modelling scheme, three forms of mercury are scavenged from the atmosphere - Hg^0, Hg_{part} and $Hg^{2+}{}_{gas}$. It is assumed that DMM is not removed from the atmosphere. The map of total mercury depositions is demonstrated in Figure 4.7. Unlike field of TGM concentrations, deposition fields are not so smooth. The main reason for this is different removal rates of different mercury forms. Total depositions of mercury are mostly formed by depositions of oxidized mercury forms - Hg_{part} and Hg^{2+}. Since a considerable fraction of these forms has basically anthropogenic origin, the deposition maxima are usually strongly associated with the anthropogenic sources. Areas of elevated depositions are located in Poland, the east Germany, the north-east of Spain, in Greece and the north of France. Maxima are 250 g/km^2/y (Greece), 155 g/km^2/y (Poland) and 130 g/km^2/y (France). Relatively low depositions are distinguished in the central part of Scandinavian Peninsula. Typically computed depositions there do not exceed 8 g/km^2/y.

In calculations for 1999 the anthropogenic emission used was nearly the same, and natural emission was 5% lower. However, in comparison with depositions for 1999 [*Ilyin et al.*, 2001] it is clear that the computed depositions of mercury in 2000 are considerably lower than those in 1999. The reasons are associated with modifications of parameterizations, emission changes and precipitation amounts. The effects of these changes are discussed above (section 4.1).

4.3. Transboundary transport estimates

Contributions to depositions for each EMEP country due to the transboundary transport were estimated. Detailed matrices for lead, cadmium and mercury are given in Annex C. In these matrices countries - emitters are lined along the horizontal, and regions-receptors along vertical. Abbreviations of the names of the regions are given in Annex B. In addition to region names, identification of contribution from indeterminate sources, which includes natural, secondary anthropogenic and remote anthropogenic sources is given by code "IND".

In this section more simplified version of the matrices is present. In Tables 4.4 – 4.6 for each EMEP country three major countries-sources of transboundary pollution for each metal are shown. In addition to this, contributions from indeterminate sources are given.

The analysis of these tables obviously demonstrates that the most important anthropogenic polluters for each country are the country's neighbours. For example, main contributors of lead to Hungary are Italy (16%), Yugoslavia (10%) and Romania (10%). Depositions from transboundary anthropogenic sources are ranges from 10 to 70%. A significant contribution is conditioned by quasi-natural sources and input from outside of the EMEP region (IND). It is important to stress that this fraction does not indicate pure natural contribution to depositions, but in fact is a combination of natural inputs, inputs from remote anthropogenic sources and inputs due to previous anthropogenic pollution.

In the case of cadmium the contribution of the anthropogenic transboundary sources mainly ranges from 10 to 50%, and in some countries, which are located close to main sources, the contribution exceeds 30%. However, even if contribution of transboundary anthropogenic depositions is not very high for a country as a whole, it causes notable fraction in the vicinity of the state borderlines.

In comparison with the results for 1999, it is possible to say that absolute values of lead deposition to countries in 2000 generally decreased. An overall tendency of the increase of contribution from indeterminate sources can be indicated. It is connected with the decreasing of anthropogenic emission estimates. In some countries, however, absolute input of transboundary deposition increased. For example, for the Ukraine in previous calculations [*Ilyin et al.*, 2001] expert lead emission estimates were used. This year the Ukrainian official data for 2000 were used, which are about 6 times lower than the expert estimates. This resulted in higher contribution of transboundary depositions.

Table 4.4. Main countries - sources of transboundary pollution and their contributions to depositions of **lead** on countries - receptors

Country - receiver	Major countries - sources (input in %)						Contribution of own sources, %	IND*
Albania	Italy	23	Greece	13	Yugoslavia	12	11	31
Armenia	Azerbaijan	23	Georgia	10	Turkey	10	0.0	50
Austria	Italy	45	Germany	5	Switzerland	3	3	27
Azerbaijan	Russia	6	Georgia	5	Turkey	2	44	40
Belarus	Poland	17	Russia	6	Italy	5	9	39
Belgium	France	9	the UK	7	Germany	6	47	24
Bosnia & Herzegovina	Italy	31	Croatia	14	Yugoslavia	12	2	29
Bulgaria	Romania	12	Yugoslavia	10	Greece	7	36	21
Croatia	Italy	29	Yugoslavia	4	Slovakia	3	35	21
Cyprus	Turkey	6	Italy	4	Greece	3	57	26
Czech Rep.	Germany	14	Poland	11	Italy	11	24	25
Denmark	Germany	16	the UK	10	Poland	5	3	47
Estonia	Poland	7	Russia	7	Germany	4	21	43
Finland	Russia	9	Poland	4	Germany	3	8	61
France	Italy	14	Spain	12	the UK	3	16	46
Georgia	Russia	11	Azerbaijan	5	Turkey	4	42	31
Germany	Italy	9	Switzerland	5	Belgium	4	42	26
Greece	Italy	9	Bulgaria	6	Yugoslavia	4	48	24
Hungary	Italy	16	Yugoslavia	10	Romania	10	9	26
Iceland	the UK	1.3	Germany	0.6	Poland	0.4	0.3	95
Ireland	the UK	8	Spain	0.9	Portugal	0.7	34	55
Italy	Spain	1.3	Croatia	0.8	Switzerland	0.7	81	14
Kazakhstan	Russia	21	Ukraine	4	Romania	2	2	63
Latvia	Poland	13	Russia	6	Germany	6	0.1	49
Lithuania	Poland	20	Russia	8	Germany	5	9	38
Luxembourg	Germany	16	France	13	Belgium	11	4	37
Malta	Italy	31	Spain	4	Greece	3	0	58
Macedonia	Yugoslavia	19	Greece	16	Italy	13	2	28
Italy	Spain	4	Greece	3	Croatia	1	31	58
Netherlands	Belgium	23	the UK	11	Germany	11	15	28
Norway	the UK	5	Germany	4	Poland	4	1.5	75
Poland	Germany	8	Czech Rep.	5	Italy	4	52	20
Portugal	Spain	6	the UK	0.3	France	0.1	66	27
Rep. Moldova	Romania	29	Italy	7	Yugoslavia	4	5	32
Romania	Yugoslavia	7	Italy	6	Bulgaria	3	51	20
Russia	Ukraine	3	Poland	2	Italy	1.4	46	40
Slovakia	Poland	11	Italy	10	Czech Rep.	6	24	24
Slovakia	Italy	40	Croatia	11	Yugoslavia	2	18	21
Spain	Portugal	10	Italy	2	France	0.5	51	36
Sweden	Poland	7	Germany	6	the UK	3	1.4	65
Switzerland	Italy	38	France	3	Spain	2	34	19
Turkey	Greece	5	Italy	4	Romania	2	31	45
Ukraine	Romania	9	Poland	6	Russia	6	29	32
the UK	Ireland	3	France	1.1	Spain	1.0	59	32
Yugoslavia	Italy	12	Romania	4	Croatia	3	50	19

*IND. – Indeterminate sources: input from natural, and previous and remote anthropogenic sources

Table 4.5. Main countries - sources of transboundary pollution and their contributions to depositions of **cadmium** on countries - receptors

Country - receiver	Major countries - sources (input in %)						Contribution of own sources, %	IND*
Albania	Italy	15	Yugoslavia	6	Bulgaria	4	12	55
Armenia	Azerbaijan	10	Georgia	5	Russia	0.6	35	48
Austria	Italy	19	Slovenia	5	Poland	3	13	43
Azerbaijan	Armenia	4	Georgia	4	Russia	1.4	31	58
Belarus	Poland	33	Romania	4	Russia	4	6	37
Belgium	France	27	Germany	3	the UK	2	31	31
Bosnia & Herzegovina	Italy	15	Yugoslavia	8	Croatia	3	5	54
Bulgaria	Romania	9	Yugoslavia	6	Italy	2	53	23
Croatia	Italy	18	Yugoslavia	5	Slovenia	4	13	48
Cyprus	Italy	4	Bulgaria	1.8	Greece	1.4	10	78
Czech Rep.	Poland	21	Germany	8	Slovakia	7	19	31
Denmark	Poland	10	Germany	9	France	5	9	54
Estonia	Poland	17	Russia	4	Germany	3	9	49
Finland	Poland	9	Russia	4	Germany	1.9	8	68
France	Spain	9	Italy	5	Switzerland	1.4	26	55
Georgia	Russia	8	Azerbaijan	4	Armenia	4	34	48
Germany	France	7	Poland	6	Italy	4	29	40
Greece	Bulgaria	16	Italy	7	Romania	3	15	49
Hungary	Romania	15	Slovakia	13	Yugoslavia	5	18	30
Iceland	Poland	0.6	the UK	0.2	Germany	0.2	3	95
Ireland	the UK	2.0	Spain	0.8	France	0.8	25	70
Italy	Spain	1.6	France	1.3	Switzerland	0.6	59	35
Kazakhstan	Russia	11	Poland	2.2	Romania	2.1	1.2	77
Latvia	Poland	23	Lithuania	9	Russia	4	9	42
Lithuania	Poland	35	Russia	5	Germany	3	17	29
Luxembourg	France	23	Germany	9	Belgium	5	4	48
Macedonia	Bulgaria	20	Yugoslavia	8	Italy	6	5	46
Malta	Spain	2	France	1.0	Bulgaria	0.5	15	78
Netherlands	Belgium	17	France	15	Germany	6	15	39
Norway	Poland	7	Germany	2	France	1.3	5	78
Poland	Germany	4	Slovakia	4	Czech Rep.	2	69	14
Portugal	Spain	11	France	0.3	the UK	0.1	33	56
Rep. Moldova	Romania	26	Poland	8	Bulgaria	6	2	44
Romania	Poland	4	Bulgaria	4	Yugoslavia	4	59	21
Russia	Poland	5	Romania	1.7	Ukraine	1.5	34	52
Slovakia	Poland	13	Romania	6	Hungary	6	48	17
Slovenia	Italy	19	Croatia	4	Austria	1.6	35	32
Spain	Portugal	3	Italy	1.1	France	0.7	45	50
Sweden	Poland	15	Germany	3	Romania	2	0.2	66
Switzerland	Italy	19	France	8	Spain	2	33	36
Turkey	Bulgaria	4	Italy	2	Romania	2	0.5	81
Ukraine	Poland	15	Romania	12	Russia	4	14	41
the UK	France	3	Ireland	3	Spain	1.3	29	60
Yugoslavia	Italy	6	Bulgaria	6	Romania	4	40	34

*IND. – Indeterminate sources: input from natural, and previous and remote anthropogenic sources

Table 4.6. Main countries - sources of transboundary pollution and their contributions to depositions of **mercury** on countries - receptors

Country - receiver	Major countries - sources (input in %)						Contribution of own sources, %	IND*
Albania	Greece	17	Yugoslavia	4	Italy	3	16	54
Armenia	Azerbaijan	5	Georgia	2	Greece	0.3	0.1	92
Austria	Italy	8	Germany	4	Switzerland	3	15	56
Azerbaijan	Georgia	1.3	Russia	0.6	Ukraine	0.3	19	78
Belarus	Poland	19	Germany	5	Ukraine	3	4	57
Belgium	France	38	Germany	4	the UK	3	30	20
Bosnia & Herzegovina	Yugoslavia	7	Italy	5	Hungary	2	6	68
Bulgaria	Romania	9	Greece	7	Yugoslavia	3	36	40
Croatia	Italy	11	Hungary	4	Yugoslavia	4	6	61
Cyprus	Greece	4	Bulgaria	0.5	Italy	0.5	42	52
Czech Rep.	Germany	18	Poland	14	Slovakia	2	31	26
Denmark	Germany	16	Poland	3	France	3	40	31
Estonia	Poland	8	Germany	5	France	1.1	19	57
Finland	Poland	4	Germany	3	France	0.9	3	82
France	Spain	7	Switzerland	2	Italy	1.4	43	43
Georgia	Azerbaijan	1.3	Russia	0.9	Ukraine	0.8	15	79
Germany	France	4	Switzerland	2	Poland	2	61	23
Greece	Bulgaria	3	Romania	0.7	Italy	1	69	24
Hungary	Slovakia	14	Romania	3	Yugoslavia	3	42	29
Iceland	the UK	0.3	France	0.2	Germany	0.2	0.0	99
Ireland	the UK	3	France	0.7	Spain	0.4	44	51
Italy	France	3	Spain	2	Switzerland	1.0	52	41
Kazakhstan	Russia	6	Ukraine	3	Poland	1.2	0.7	85
Latvia	Poland	13	Germany	7	Lithuania	2	4	61
Lithuania	Poland	21	Germany	7	Czech Rep.	1.3	7	53
Luxembourg	France	16	Germany	6	Belgium	4	35	34
Macedonia	Greece	33	Yugoslavia	5	Bulgaria	5	2	48
Malta	Spain	4	France	3	Greece	2	0	76
Netherlands	France	20	Belgium	13	Germany	12	16	30
Norway	Germany	3	Poland	3	Denmark	1.2	6	83
Poland	Germany	10	Czech Rep.	4	Slovakia	2	61	18
Portugal	Spain	6	France	0.2	the UK	0.1	51	43
Rep. Moldova	Romania	18	Poland	4	Ukraine	4	7	55
Romania	Hungary	4	Poland	3	Yugoslavia	3	41	39
Russia	Ukraine	3	Poland	3	Germany	1.2	13	76
Slovakia	Hungary	11	Poland	6	Czech Rep.	3	49	24
Slovenia	Italy	12	Austria	2	Hungary	2	24	52
Spain	Portugal	3	France	0.8	the UK	0.1	55	41
Sweden	Germany	7	Poland	7	Denmark	4	1	73
Switzerland	France	10	Italy	7	Spain	1.4	47	33
Turkey	Greece	5	Bulgaria	2	Romania	1.2	0.3	86
Ukraine	Poland	7	Romania	3	Slovakia	2	32	46
the UK	France	2	Ireland	2	Germany	0.7	56	37
Yugoslavia	Romania	3	Greece	3	Hungary	3	37	44

*IND. – Indeterminate sources: input from natural, and previous and remote anthropogenic sources

Changes in relative contributions of total lead anthropogenic transboundary depositions were not significant. The largest decrease of the contribution can be mentioned for the Netherlands (from 68 to 57%) and Republic of Moldova (from 68 to 57%). Significant change (from 48% to 12%) was obtained for Malta. This can be explained by relatively remote location of the country from anthropogenic sources.

The increase of contribution of transboundary lead deposition can be mentioned for Macedonia (from 34 to 70%), Armenia (from 23 to 50%), the Ukraine (from 14 to 40%) and France (from 26 to 38%). This increase is connected with changes concerning the emission data. For example, in France the emission reduced more than 4 times. For the Ukraine expert estimates were replaced by its official data that resulted in 6 times decrease. Therefore, the role of depositions from domestic sources went down, and the role of depositions from transboundary sources rose.

Absolute values of cadmium transboundary depositions for 2000 decreased in most of countries in comparison with those for 1999. Relative contributions of cadmium transboundary depositions in comparison with results for 1990 also decreased. In 1999 one of the main countries-sources of cadmium transboundary contribution were the Ukraine and Macedonia. For 2000 emission lead and cadmium estimates for these countries were much lower than those for 1999. Therefore, their places of major contributors were replaced by other countries.

Similar to lead and cadmium, absolute values of the transboundary depositions of mercury in 2000 decreased in comparison with those for 1999 in most countries. For some countries, some rise of these depositions can be mentioned. The rise is connected with variability of meteorological conditions. Relative contribution of transboundary transport to depositions for 2000 increased for the majority of countries. The increase is connected with the diminished role of indeterminate sources followed modifications of the model, first of all, updated parameterizations of natural emissions, of dry deposition of Hg^0 and of the atmospheric chemistry.

In Table 4.6 contributions to mercury depositions of main countries - sources, relative importance of indeterminate sources as well as contribution of domestic sources are shown. It could be useful to remind that mercury springtime depletion phenomenon was not considered in the country-to-country calculations.

Substantial changes in the model parameterizations and in evaluation of natural mercury emissions caused differences in regional transboundary budgets in comparison with results for 1999. Absolute values of the anthropogenic transboundary depositions in 2000 diminished in comparison with those for 1999 in most of countries. In some countries some rise of these depositions can be indicated, which is connected with variability of meteorological conditions.

Relative contribution of transboundary transport to depositions for 2000 increased for the majority of countries. The increase is connected with the diminished role of indeterminate sources followed modifications of the mercury model.

4.4. Atmospheric input of heavy metals to marginal seas

When calculating country-to-country matrix European marginal seas are treated as individual receptors. Therefore, country-to-country approach could be applied to distinguish the most important countries - sources of atmospheric pollution to seas. For example, calculations of depositions to selected sub-basins of the Baltic Sea are carried out every year in the framework of HELCOM. Example of analysis of lead depositions is given for the North Sea. In Figure 4.8 inputs of main contributors of deposition to the sea are demonstrated. Obviously, major anthropogenic contributors are situated along the North Sea coast. They are the United Kingdom (23%), Germany (6%), Belgium (4%) and France (3%). Other European countries contribute 12% of lead depositions. The rest is originated from the indeterminate sources.

Contribution of depositions from the anthropogenic sources varies over the sea area. Figure 4.9 shows spatial distribution of the anthropogenic input to depositions over the sea. As seen from the Figure, zone of the highest contribution of the anthropogenic sources is located in the southern part of the sea, near coasts of Belgium, the southern part of the United Kingdom and the Netherlands. In these areas the contribution is 60 - 85%. Further to the north the input of anthropogenic sources decreases, and near coasts of Norway, northern part of the United Kingdom and Faroe Islands does not exceed 25%. However, the role of quasi-natural emissions in remote parts of the seas could be overestimated. Quasi-natural emissions need to be studied in more detail.

Total depositions and deposition densities of lead, cadmium and mercury to the Baltic, the North, the Mediterranean, the Black and the Barents Seas are given in Table 4.7.

It is seen from the table that maximum densities of these metals are found for the North Sea. The lowest deposition densities were obtained for the Mediterranean Sea. However, the density is underestimated because no data on anthropogenic sources from Northern Africa or Middle East were available. In comparison with results for 1999 [*Ilyin et al.*, 2001] the most significant changes in modelled depositions of the three metals took place in the Black Sea. The main reason for this is a significant reduction of emission values from major contributors - the Ukraine and Turkey. Another reason is the decrease of precipitation amount used in calculations for 2000 in comparison with the amount for 1999. In case of mercury modifications in the model parameterisations also resulted to overall reduction of depositions. The lowest deposition density both of lead and cadmium and mercury is obtained for the Mediterranean Sea. However, depositions to the Mediterranean Sea are likely to be underestimated because anthropogenic sources in Middle East and Northern Africa were not taken into account.

Table 4.7. Total depositions (ΣD, t/y) and mean deposition densities (DD g/km^2/y) of lead, cadmium and mercury to basins of regional seas in 2000.

Sea	Parameter	Pb	Cd	Hg
North	*ΣD*	*491*	*18*	*7*
	DD	**661**	**24**	**9**
Baltic	*ΣD*	*190*	*10*	*3*
	DD	**452**	**23**	**8**
Mediterranean	*ΣD*	*1065*	*37*	*11*
	DD	**422**	**15**	**4**
Black	*ΣD*	*277*	*10*	*3*
	DD	**598**	**21**	**6**
Barents	*ΣD*	*249*	*11*	*2.5*
	DD	**179**	**8**	**1.8**

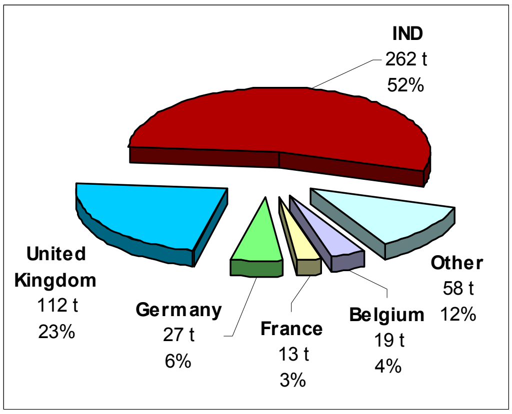


Figure 4.8. *Contributions (%) and absolute inputs (t/y) of various sources to lead deposition on the North Sea. IND means indeterminate sources: input from natural, secondary anthropogenic and remote anthropogenic sources*

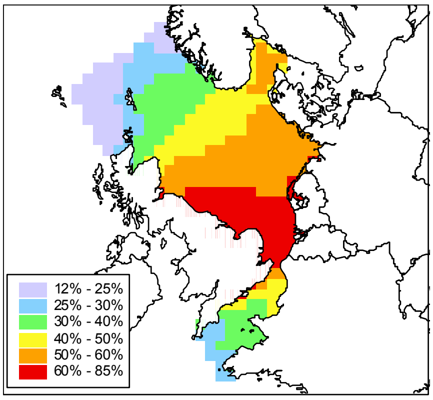


Figure 4.9. *Contribution of anthropogenic sources to lead deposition over the North Sea, %*

4.5. The role of the Arctic mercury depletion

In Section 2.4 a Mercury Depletion Phenomenon (MDP) module was formulated and parameterised. Then it was incorporated into the transport/scavenging model to calculate concentration and deposition of different mercury forms. The MDP module gives its additional effect in the Arctic in certain time. It means that mercury species connected with the Arctic depletion are added to those transported to the Arctic from remote anthropogenic and natural sources.

To reveal the effect of the MDP the model was run twice – without and with the MDP module. Since the products of elemental mercury oxidation in the course of the MDP have relatively short lifetimes they should be removed from the atmosphere not far from the place of their formation. Hence, the effect should be most evidently displayed along the Arctic Ocean seashore. It is proved by Figures 4.10.a and b. In the first case mercury deposition in the Arctic is relatively low. The highest value within the Polar Circle is 12 g /km^2/y during 2000. Usually it does not exceed 8 g/km^2/y. The pattern is sharply changed when the MDP module is used. Along the seashore one can find a pronounced zone of elevated mercury deposition. The highest deposition value in this case is 45 g /km^2/y of mercury. This level of mercury load on ecosystems is comparable with those in Central Europe or in the North-eastern USA.

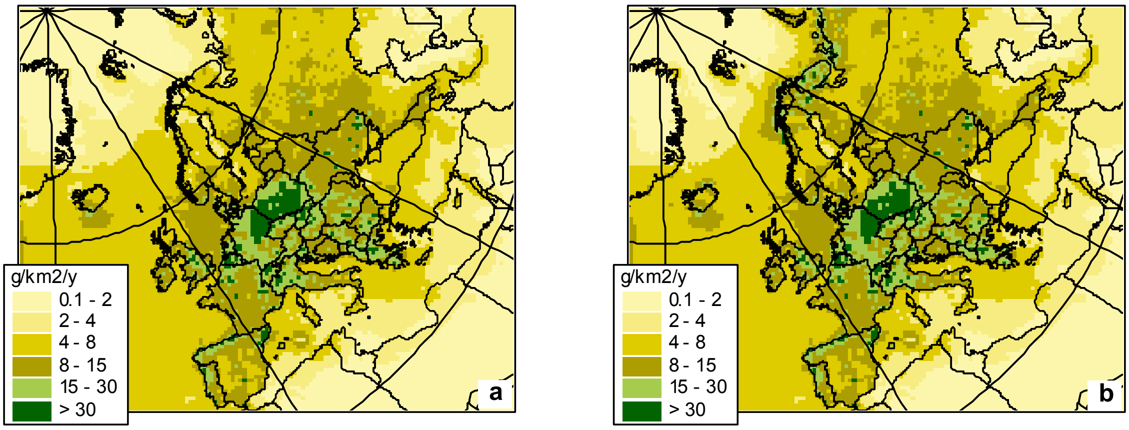


Figure 4.10. *Total mercury deposition fields in the Arctic in 2000, g/km^2/y:* ***a*** *– without Hg depletion;* ***b*** *– with Hg depletion*

Without consideration of the MDP total deposition value within the Arctic Circle over the EMEP grid is 16 tonnes in 2000. When the MDP module is „switched on“ the total annual deposition over the same area reaches 33 tonnes. It means that the Hg load on European part of the Arctic caused only by MDP is about 17 tonnes. The value means that at least 50% of mercury total deposition in the European Arctic is caused by the Hg depletion phenomenon. It should be noted that this deposition falls on springtime when Arctic ecosystems are especially vulnerable to any toxic influence. During this period mercury can actively enter metabolic processes of the Arctic life.

The MSCE-HM model does not give a possibility to assess Hg deposition over the whole Arctic because the domain covers only about a quarter of the Arctic. Nevertheless, we believe that the intensity of the phenomenon is the same over the Siberian Arctic and American Arctic. Hence, in the first approximation we can say that MDP is responsible for additional deposition of about 70 tonnes of mercury over the Arctic annually.

Before the discovery of the MDP there were several experimental evidences showing elevated depositions of mercury in the Arctic, which were difficult to explain in the framework of traditional conceptions about mercury fate in the atmosphere. Abnormally high concentrations of Hg were found in moss material along the Arctic shore of Scandinavia [*Steinnes and Andersson*, 1991; *Reimann et al.*, 1997]. The concentrations there were of the same level as in the southernmost parts of Norway.

Measurements in fresh snow during and just after MDP demonstrated that during springtime the Hg concentrations permanently increase and reach their maximum by the beginning of snow melting [*Lu et al.*, 2002; *Lindberg et al.*, 2002]. In comparison with the winter period (January) Hg concentration in spring snow can be 10-100 times higher [*Lindberg et al.*, 2001; *Scott et al.*, 2001; *Berg et al.*, 2002]. *J.Lu et al.* [2002] carried out a detail survey of mercury content in snow-pack in the Canadian Arctic and in Greenland and found that the concentration could be as high as 160 ng/L. They estimated that total deposition over the Arctic seas and Hudson Bay could be 50 t of mercury a year. *S.Lindberg et al.* [2002] gives their rough estimate for the whole Arctic in the range of 150-300 t/yr. They also note that about 10-20% of this amount can re-emit to the atmosphere during snow melting period.

The first attempt to assess the role of the MDP in Arctic contamination with the use of a global transport model was made by *J.Christensen* [2001]. He showed that more than 100 t of mercury a year could be additionally deposited over the Arctic due to the MDP. Let us note, however, that in accordance with *J.Christensen's* calculations effects of the MDP become apparent mainly in the European Arctic. In calculations performed by *O.Travnikov and A.Ryaboshapko* [2002], additional 40 tonnes is deposited to the Arctic due to MDP.

The comparison of our estimate of Hg deposition over the Arctic with the other experimental and modelling values shows a good agreement. Of course, the phenomenon is recently discovered and many of its features are not well known yet. Hence, any estimates of the MDP consequences are of a preliminary character. However, it is clear that the phenomenon should be taken into account when any assessment of the Arctic pollution is given.

An interesting and extremely important problem was risen by *S.Lindberg et al.* [2002] – is this phenomenon new or is it essential natural characteristic of the Arctic? The authors came to the conclusion that intensity of the MDP increased sharply during last 30-50 year. The reason to this is in recent climatic changes in the Arctic resulting in enlargement of open water and polynya areas as well as in decreasing of ice thickness. If so, the importance of the MDP from ecological viewpoint will rise in the future.

4.6. Comparison of models with observations and requirements to monitoring data

In order to confirm quality and reliability of the modelling results, the modelled data were compared with monitoring data. Since no data for 2000 were available at the moment of calculations, verification was carried out on the basis of 1999. For this purpose supplementary run was performed with the use of emission and meteorological data for 1999. Measurement data were provided by Chemical Co-ordinating Centre (CCC) [*Berg et al.*, 2001]. Comparison was carried out for annual mean concentrations in air and in precipitation of lead, cadmium and mercury. Uncertainties of the measured data were evaluated on the basis of the results of analytical methods intercomparison. Uncertainty of the modelling results, as was estimated by *O. Travnikov* [2000], is about 25%, If the uncertainty associated with the emission data is neglected. However, due to large uncertainty of the emission data (e.g., see Chapter 3) overall uncertainty of the modelling results is much higher.

Lead

The criteria of selection of measurement data for the comparison have already been discussed and formulated in work [*Ilyin et al.*, 2001]. Briefly, they are the following. If monthly mean data for three or more months were missed the annual mean value did not take part in the comparison. If annual precipitation amounts, collected at measurement site and those used in the model differed more than 1.5 times, the measurement data were also excluded from the comparison. Selected data on measured concentrations in air and precipitation on lead and corresponding modelled values are given in Table 4.8.

Comparison of modelled and measured concentrations of lead in air is demonstrated in Figure 4.11. In this Figure error whiskers at measurement values indicate errors of analytical method. Analytical error was estimated on the basis of results of intercomparison of analytical methods [*Berg and Aas,* 2000; *Uggerud and Skjelmoen*, 2001]. For each country these errors are different, and they are summarised in Table 4.9. It is important to mention that this error is actually only a part of overall measurement error, because it does not include, e.g., sampling errors.

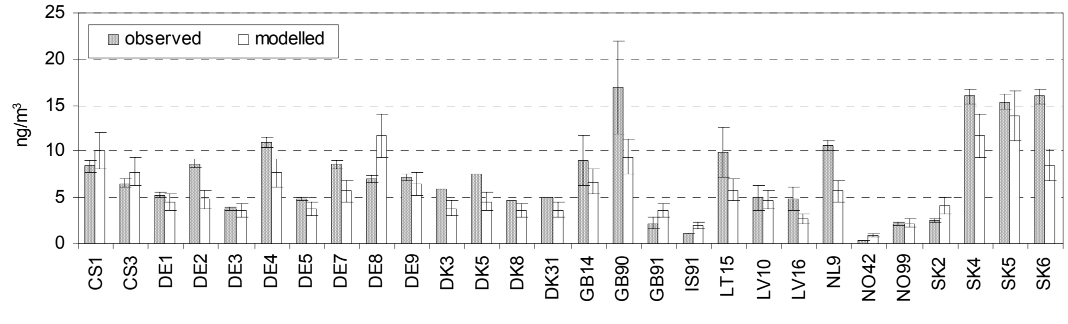


Figure 4.11. *Comparison of modelled and measured concentrations of lead in air in 1999, ng/m^3*

As seen, for most of sites modelled values are in reasonable agreement with measured ones. For most of the sites the model slightly underestimates concentrations in air. However, at the same time for some sites the model overestimates measurements. The most significant overestimation could be indicated for background sites NO42 (2.3 times) and IS91 (2.0 times). This could be connected with either overestimated natural emissions in the areas of the location of these sites or due to high model concentration in air at lateral boundaries of the modelling domain. Evident overestimation is also indicated for site DE8. This site is located in the eastern part of Germany, where emission density was relatively high. Since we used spatial distribution of German emissions for 1990 [*Berdowski et al.,* 1997], emission levels in this part of Germany are probably too high, and this can result in too high modelling values.

Table 4.8. Measurement data on lead in air and precipitation used in the comparison

Country	Site code	Concentrations in air, ng/m^3		Concentration in precipitation, µg/l	
		Observed	Modelled	Observed	Modelled
Czech Rep.	CZ1	8.4	10.03	4.66	1.60
	CZ3	6.6	7.82		
Germany	DE1	5.3	4.45	1.22	0.82
	DE2	8.7	4.82		
	DE3	3.8	3.56		
	DE4	11.0	7.67	2.47	1.32
	DE5	4.8	3.81		
	DE7	8.6	5.67		
	DE8	7.0	11.74		
	DE9	7.2	6.51	1.21	1.00
Denmark	DK3	5.9	3.84		
	DK5	7.6	4.58		
	DK8	4.7	3.54	1.80	0.68
	DK31	5.1	3.69	0.9	0.67
Finland	FI9			2.99	0.59
	FI36			0.73	0.42
	FI92			1.14	0.54
	FI93			1.31	0.66
	FI95			0.50	0.46
United Kingdom	GB14	9.0	6.72		
	GB90	16.8	9.40	1.89	1.71
	GB91	2.2	3.53	0.91	0.71
Iceland	IS91	1.0	2.00		
Lithuania	LT15	9.9	5.83	3.31	0.99
Latvia	LV10	5.0	4.76		
	LV16	4.9	2.75		
The Netherlands	NL9	10.6	5.67	1.65	1.16
Norway	NO41			1.01	0.46
	NO42	0.4	0.97		
	NO47			0.95	0.47
	NO55			0.45	0.46
	NO56			1.17	0.52
	NO93			0.69	0.43
	NO94			1.02	0.56
	NO99	2.2	2.21	1.60	0.64
Sweden	SE5			0.71	0.38
	SE12			2.22	0.6
	SE51			2.38	0.72
	SE97			1.65	0.54
Slovakia	SK2	2.5	4.13		
	SK4	15.9	11.68		
	SK5	15.4	13.83		
	SK6	15.9	8.54		

In Table 4.10 statistical parameters of model validation are summaraized. As seen, the model reasonably reproduces spatial pattern of pollution levels (correlation coefficient is 0.80). On average, model underestimates measurements by about 30 %. In comparison with calculations for 1999 given in [*Ilyin et al.*, 2001], average model results now are about 10% lower. It is connected with lower emission data used in these calculations.

Comparison of concentrations in precipitation is demonstrated in Figure 4.12. As seen, model results are lower than measurement values. For some sites this underestimation is significant - up to 5 times. These differences can be connected with a number of reasons. Uncertainty of the analytical methods of lead measurements is not higher than 30% (Table 4.9). Inherent uncertainty of the model (without uncertainty of the emission data) is about 25% [*Travnikov*, 2000]. Therefore, one can hardly expect that uncertainties of the model or measurements can explain such a difference. Uncertainty of the emission data, in its turn, is the main source of the uncertainty of the modelling results [*Travnikov,* 2000]. As was shown in Chapter 3, revision of the emission data can lead to large (up to 2.4 times) differences in the total emission for a country. Therefore, most probable reason is uncertainties of the emission data.

Table 4.9. Average error of analytical method for national laboratory (lead). Based on [*Berg and Aas,* 2000, *Uggerud and Skjelmoen*, 2001]

Country	Error, %
Czech Republic	8
Germany	5
Finland	4
the UK	30
Lithuania	27
Latvia	26
the Netherlands	5
Norway	7
Slovakia	5

Table 4.10. Statistical parameters of model validation for lead for 1999. C_{obs} – measurement results averaged over all sites, C_{mod} – model results averaged over all sites, R – correlation coefficient

Parameter	Concentration in air, ng/m^3	Concentration in precipitation, µg/l
C_{obs}	7.38	1.64
C_{mod}	5.85	0.74
C_{obs}/C_{mod}	1.26	2.18
R_{air}	0.80	0.67

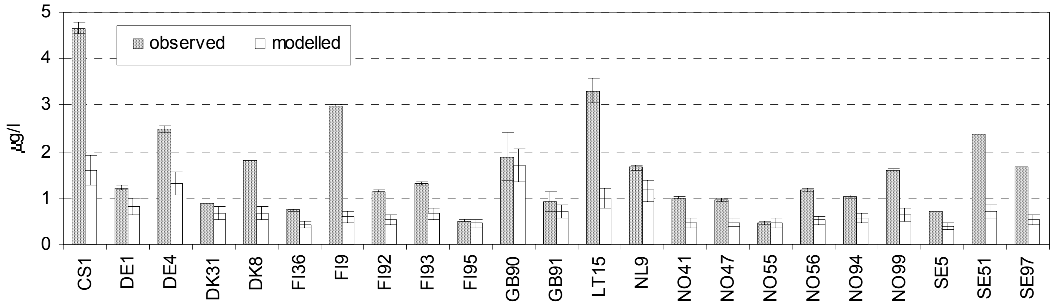


Figure 4.12. *Comparison of modelled and measured concentrations of lead in precipitation in 1999, µg/l*

Cadmium

Similar to lead, in Table 4.11 measurement and modelled data of cadmium used in the verification are summarized.

In Figure 4.13 a diagram showing modelled and measured values and their uncertainties is demonstrated. As seen from the Figure, the model satisfactorily reproduced concentrations of cadmium in air. Differences between modelled and observed air concentrations for Czech, German, Danish, British, and Lithuanian sites do not exceed 50 %. Some differences are indicated for Slovak stations SK4 and SK5 for which model overestimates measured data. Most probably this is connected with the fact that these sites are located in mountainous areas and their altitudes are about 800 - 900 m a. s. l. The highest discrepancy is indicated for Norwegian site NO42, where model value is about twice as high as measured one. Possible reason for this could be overestimation of background concentrations of cadmium or its emission due to natural mechanisms.

Table 4.11. Measurement data on cadmium in air and precipitation used in the comparison

Country	Site code	Concentration in air, ng/m^3		Concentration in precipitation, µg/l	
		Observed	Modelled	Observed	Modelled
Czech Republic	CZ1	0.30	0.30	0.27	0.07
	CZ3	0.40	0.21		
Germany	DE1	0.18	0.13	0.06	0.03
	DE2	0.21	0.11		
	DE3	0.09	0.06		
	DE4	0.20	0.10	0.11	0.04
	DE5	0.12	0.10		
	DE7	0.30	0.19		
	DE8	0.26	0.28		
	DE9	0.18	0.22	0.05	0.04
Denmark	DK3	0.22	0.16		
	DK5	0.18	0.14		
	DK8	0.21	0.12	0.05	0.03
	DK31	0.15	0.14	0.03	0.03
Finland	FI9			0.08	0.03
	FI36			0.02	0.03
	FI92			0.04	0.03
	FI93			0.04	0.04
	FI95			0.01	0.03
United Kingdom	GB14	0.13	0.15		
	GB90	0.25	0.15	0.04	0.04
	GB91	0.08	0.10	0.06	0.03
Iceland	IS91	0.19	0.08		
Lithuania	LT15	0.29	0.30	0.10	0.06
Latvia	LV10	0.13	0.21		
	LV16	0.16	0.15		
The Netherlands	NL9	0.21	0.16	0.13	0.04
Norway	NO41			0.04	0.03
	NO42	0.02	0.04		
	NO47			0.09	0.03
	NO55			0.02	0.03
	NO56			0.03	
	NO94			0.04	0.03
	NO99	0.06	0.08	0.03	0.03
Poland	PL4			0.08	0.06
Sweden	SE5			0.05	0.02
	SE12			0.08	
	SE51			0.10	0.03
	SE97			0.05	0.03
Slovakia	SK2	0.27	0.21		
	SK4	0.46	0.89		
	SK5	0.64	1.07		
	SK6	0.65	0.61		

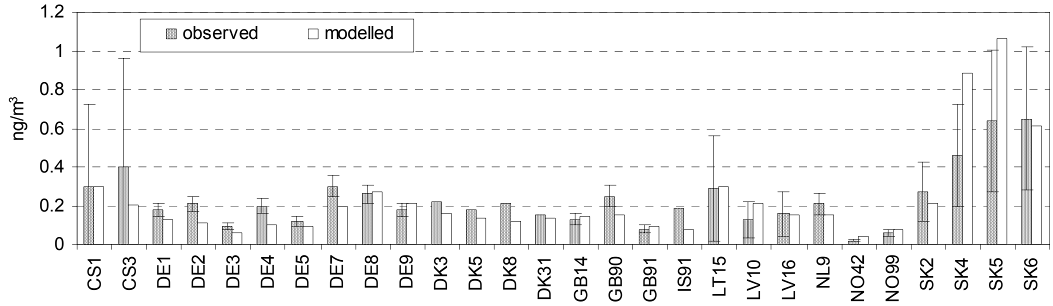


Figure 4.13. *Comparison of modelled and measured concentrations of cadmium in air in 1999, ng/m³*

When comparing this Figure with similar Figure for lead, it becomes evident that measurements of cadmium are more uncertain than those of lead. This is basically due to the fact that cadmium concentrations in the atmosphere are about 1 - 2 orders of magnitude lower than those of lead, and that is why it is more complicated task to measure cadmium concentrations in the atmosphere. Relative errors of analytical methods used in the comparison are given in the Table 4.12.

Table 4.12. Average error of analytical method for national laboratories (cadmium). Based on [*Berg and Aas,* 2000; *Uggerud and Skjelmoen*, 2001]

Country	Error, %
Czech Republic	141
Germany	19
Finland	12
the UK	23
Lithuania	95
Latvia	72
the Netherlands	27
Norway	28
Poland	43
Slovakia	57

In Figure 4.14 comparison of calculated and measured cadmium concentrations in precipitation is given. For most of measurement stations underestimation of observed concentrations is seen.

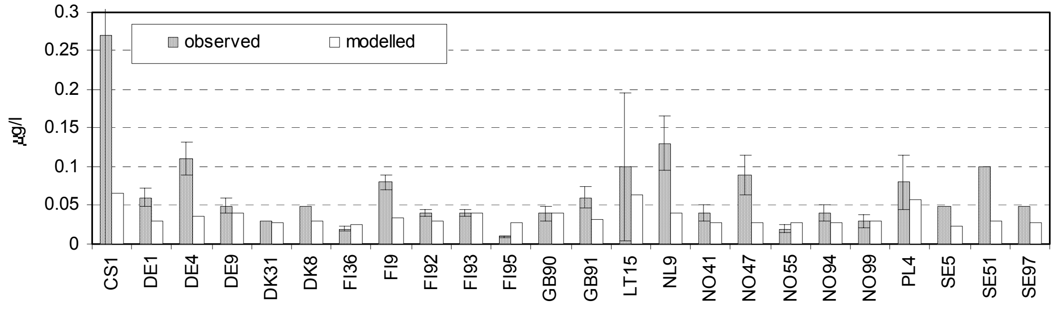


Figure 4.14. *Comparison of modelled and measured concentrations of cadmium in precipitation in 1999, µg/l*

Especially high discrepancy between modelled and measured values can be indicated for Czech site CZ1 and Dutch site NL9. In former case it is possible to note that analytical error is even greater than 100% (Table 4.12), but in later case the difference can not be simply attributed to complexity of the measurements. High underestimation is also mentioned for Scandinavian sites: NO47 (Norway) and SE51 (Sweden). In case of Norway it is possible to suggest that the underestimation is conditioned by missing emission sources, possibly local sources, either in Norway or in neighbouring countries, because for other Norwegian sites the differences are not so significant. As for Swedish sites, the underestimation is inherent to all sites used in the comparison, so it is possible to suggest either underestimation of emissions or imperfection of measurement methods used at Swedish measurement network. Obviously, uncertainties of model parameterizations can also contribute to discrepancies between modelled and measured values both in air and in precipitation.

In Table 4.13 statistical parameters characterizing the situation for Europe as a whole are given. Relatively high correlation coefficients confirm that the model captured spatial pattern of concentrations in air and in precipitation. It is also clear that on average concentrations in air are reproduced rather well. However, modelled concentrations in precipitation are about twice lower than measured ones for Europe as a whole. Partly this disagreement is conditioned by too high measured concentrations, e. g. at Czech or Dutch sites This fact reveals the need of further improvements of wet removal schemes. To solve this task co-operation with national experts, working both in the field of measurements and modelling, could be highly fruitful.

Table 4.13. Statistical parameters of model validation for cadmium for 1999. C_{obs} – measurement results averaged over all sites, C_{mod} – model results averaged over all sites, R – correlation coefficient

Parameter	Concentration in air, ng/m^3	Concentration in precipitation, µg/l
C_{obs}	0.23	0.07
C_{mod}	0.23	0.04
C_{obs}/C_{mod}	1.02	1.88
R_{air}	0.86	0.67

Mercury

Modification of aerosol dry deposition scheme did actually not affect final results for lead and cadmium. In case of mercury, however, the model was subjected by more substantial changes. These are new way of setting of natural emission, modifications of atmospheric chemistry scheme, new scheme of dry uptake for elemental mercury. All these changes affected on final modelling results, such as concentrations in air in concentrations in precipitation.

In Table 4.14 measured and modelled values of TGM concentrations in air and total mercury concentrations in precipitation in 1999 are summarized. These data were used in the model validation. Similar to lead and cadmium, averaged modelled and measured values are given in Table 4.15. Unfortunately, there are only five monitoring sites measuring concentration in air, and nine measuring concentration in precipitation, from which the data are available, and they all are situated in the northern part of Europe. Because of so few numbers of sites there is no sense to compute correlation coefficient, and it was omitted in Table 4.15.

In Figure 4.15 comparison of mean annual modelled and measured TGM concentrations is demonstrated. As seen, for most of the sites the model reasonably reproduced measured values. The difference between modelled and measured concentrations does not exceed 40%.

In Figure 4.16 modelled concentrations in precipitation are compared against measurements. For Finnish site FI96 and German site DE9 the model produced too high concentrations in precipitation. On one hand, these large differences could be explained by the complexity of mercury behaviour in the atmosphere, and, hence, complexity of modelling of this behaviour. On the other hand, measurements of mercury concentrations in the atmosphere is also very complicated task, and the measurement results could contain considerable uncertainty. For the rest seven sites the agreement between modelled and measured values is reasonable. For these sites modelled and measured values agree better than factor of 2, which mean that the model complies to contemporary requirements of long-range heavy metal transport models [*Ilyin et al.*, 2000].

In comparison with the results for 1999, presented in the previous report [*Ilyin et al.*, 2001], current results are in better agreement with measured values. For example, ratio of observed- to-modelled concentration of mercury in precipitation averaged for all available monitoring sites of sites in calculations for 1999 [*Ilyin et al.*, 2001] was 0.5, while now it is 0.6. Excluding site DE9 from the comparison leads to even better agreement with measurements comparing to previous results. This means that modifications of the MSCE_HM model described in Chapter 2, resulted in better agreement with the data obtained by long-term monitoring.

Table 4.14. Measurement data and model results on mercury in air and precipitation used in the comparison

Country	Site code	Concentration in air, ng/m^3	Modelled	Concentration in precipitation, ng/l	Modelled
Germany	DE1			10.0	10.9
	DE9			11.7	43.3
Finland	FI96	1.4	2.0	5.0	14.1
Ireland	IE31	1.8	2.0		
The Netherlands	NL91			11.1	19.1
Norway	NO42	2.0	1.6		
	NO99	1.9	2.1	8.6	9.5
Sweden	SE2	1.4	2.0	9.4	10.2
	SE5			4.2	6.8
	SE11			10.4	11.8
	SE12			8.2	9.0

Table 4.15. Statistical parameters of model validation for mercury for 1999. C_{obs} – measurement results averaged over all sites, C_{mod} – model results averaged over all sites, R – correlation coefficient

Parameter	TGM concentration, ng/m^3	Concentration in precipitation, ng/l
C_{obs}	1.9	8.7
C_{mod}	2.0	15.0
C_{obs}/C_{mod}	0.9	0.6

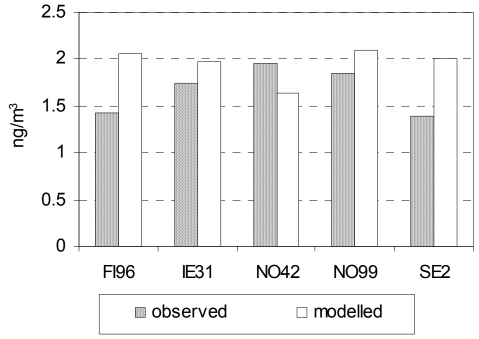


Figure 4.15. *Comparison of modelled and measured concentrations of TGM in air in 1999, ng/m^3*

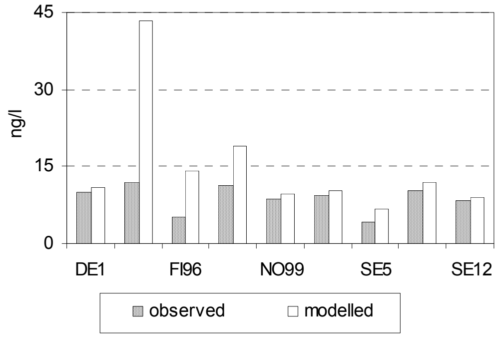


Figure 4.16. *Comparison of modelled and measured concentrations of mercury in precipitation in 1999, ng/l*

Chapter 5

MEASUREMENTS AND MODELLING OF ATMOSPHERIC MERCURY IN THE UK: A UK CONTRIBUTION TO THE EMEP METEOROLOGICAL SYNTHESIZING CENTRE EAST ANNUAL REPORT

Abstract. This Chapter to the annual report of the EMEP Meteorological Synthesizing Centre-East is a contribution in-kind from the United Kingdom to the overall activities of the Centre. Here, some of the measurements that have been made in the UK are described and summarized. A simple European-scale model has been constructed and used to characterize the UK atmospheric Hg budget. The data and model results reported here represent a country-case study and may be used for comparison to other model studies and measurement programmes.

5.1. Introduction

Heavy metal contamination of ecosystems and air quality has been of concern for some time. Although ambient levels of trace metals in the atmosphere have, in general, fallen since the 1970s, some metals remain a problem. Mercury (Hg) in the atmosphere is unique amongst metals, as it is found predominantly in the gas phase as elemental gaseous Hg (Hg^0). Mercury is primarily emitted in this form, along with particulate phase Hg (Hg-p) and reactive gaseous Hg (RGM) [*Sloss*, 1995].

The characteristics of these different forms of Hg greatly affect their residence time in the atmosphere: Hg^0 has a lifetime of approximately 1 year [*Bergan et al.*, 1999]; Hg-p is present as a sub-micron sized particle and typically has a lifetime of the order 10 days; RGM is assumed to behave similarly to nitric acid (HNO_3), being readily removed by dry and wet deposition, thus having a lifetime (in the boundary layer) of hours to a few days. The long lifetime of Hg^0 is a consequence of its lack of chemical reactivity and its slow removal by dry deposition. The dominant oxidation pathway to divalent Hg (HgII), predominantly Hg-p, is thought to be via ozone (O_3), proceeding at average rates of 0.01% h^{-1} [*Pai et al.*, 1997] Other atmospheric chemistry has been identified [*Lin and Pehkonen,* 1999], along with some rather unusual chemistry in the Polar regions [*Schroeder et al.*, 1998], but other than this particular process, the atmospheric chemistry is characterized by rather slow oxidation pathways with some even slower reduction pathways. Thus, Hg^0 is well mixed across the Northern Hemisphere and latitudinal transects indicate somewhat lower concentrations in the Southern Hemisphere [*Slemr et al.*, 1981].

The speciation of the different forms of Hg in terms of emissions is not well known; nor is it for ambient concentrations. This is because of a paucity of measurements both from sources and in the ambient atmosphere. The lack of measurements is partially a result of the difficulty of making speciated measurements. Reliable automatic instruments for the routine measurement of total gaseous mercury (TGM, where TGM=Hg^0 + RGM) have been available for ~10 years. From the few measurements of RGM and the more easily made measurements of Hg-p, it appears that in most circumstances, Hg^0 dominates TGM by approximately one order of magnitude. Closer to sources, however, it is apparent that RGM may be present as a larger fraction of TGM, depending upon proximity and the industrial process.

At present, it is thought that man-made sources of Hg dominate the total emission and inventory estimates in Europe indicate that this emission is declining. Natural sources are rather difficult to define as it has been found that many terrestrial and aquatic ecosystems emit Hg^0, possibly as a consequence of processing (by unknown mechanisms) of previously deposited Hg-p.

The particular problem associated with Hg emissions into the atmosphere is not air quality *per se*, but rather the deposition of Hg onto ecosystems and its subsequent terrestrial/biological processing into the toxic form, methyl Hg. Methyl Hg accumulates in biota, particularly fish, and ingestion of fish products contaminated by methyl Hg represents the primary threat to human health. However, it should be pointed out that other health hazards in particular regions of the world exist. For example, open-air roasting of gold with cinnabar in South America, and contamination of watercourses from gold mining activities represents a serious localized problem [*Akagi et al*., 1995].

Since the human health hazard is primarily from ingestion of biota, and given that there is significant atmospheric, terrestrial and biological processing between emission source and human receptor, the source-receptor relationship is particularly intractable. Because of this, it is important to quantify the atmospheric inputs to ecosystems via measurements and modelling.

In this paper, some of the efforts made towards this in the UK are reviewed. In Section 5.2, some of the available measurements are presented; in Section 5.3, some of the atmospheric modelling efforts are described. Finally, the emergent issues are discussed in Section 5.4, making recommendations for future scientific efforts with regard to measurements and modelling, setting this in the perspective of UK activities contributing to the wider EMEP requirements.

5.2. Measurements of total gaseous and particulate phase mercury

There are very few measurements of Hg in the atmosphere of the UK; these have been reviewed in detail by *D. Lee et al*. [2000]. Long-term measurements of Hg-p in various urban and rural locations were analysed by *D.Lee et al*. [1994]; measurements of total gaseous mercury (TGM) were made at a site in central southern England for a period of approximately 1 year by *D. Lee et al*. [1998]; more recently, TGM measurements have been made by the Centre for Ecology and Hydrology in Southern Scotland [*E. Nemitz*, personal communication] but these have not, as yet, been reported but early results indicate mean concentrations similar to those found in southern England.

Gas-phase measurements of Hg have been made at a rural site in central southern England using a Tekran vapour phase instrument [*Lee et al*. 1998]. This instrument measures TGM and as such, is an operationally defined measurement of Hg^0 + RGM.

The measurements were made over a period of approximately 1 year. The average concentration was 1.68 ng/m^3, the overall distribution being shown in Figure 5.1. A time-series of daily average concentrations is shown in Figure 5.2. It is difficult to discern much structure from this figure, with no clear indication of any seasonality.

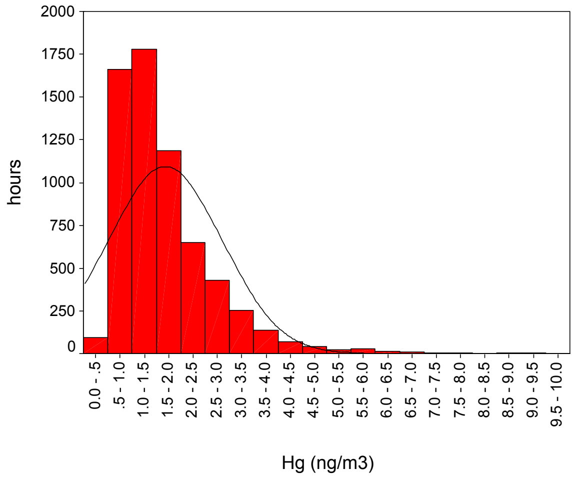


Figure 5.1. *Frequency distribution of hourly measurements of TGM [(data source: Lee et al., 1998]*

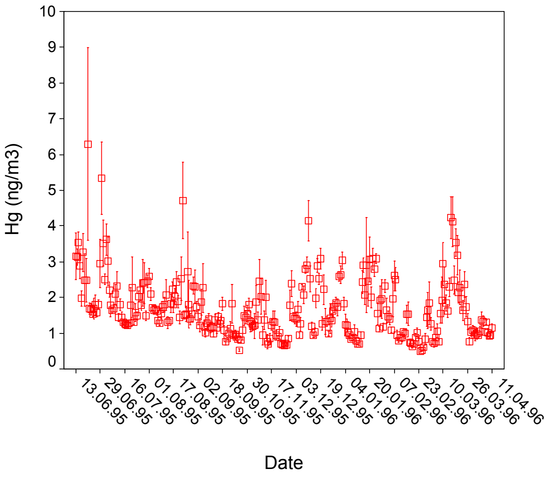


Figure 5.2. *Average daily concentrations (with 95% confidence limits shown) of TGM [data source: Lee et al., 1998]*

An analysis of the TGM data by wind sector (Fig. 5.3) showed almost uniform concentrations with a background of approximately 1.5 ng/m^3. Enhancements were shown in easterly and westerly winds. The explanation offered for these enhancements was the location of an industrial smelting plant to the west and larger concentrations originating from central and eastern Europe possibly explaining the enhancement to the east [*Lee et al.*, 1998]. The TGM concentrations do, however, exhibit some structure on shorter time-scales: there is a clear diurnal variation in the data (Fig. 5.4), indicative of a surface source. Radon typically shows a similar diurnal pattern of concentrations building up below nocturnal boundary layers. The typically lower average wind speeds at night at this site also illustrate this phenomenon (Fig. 5.5).

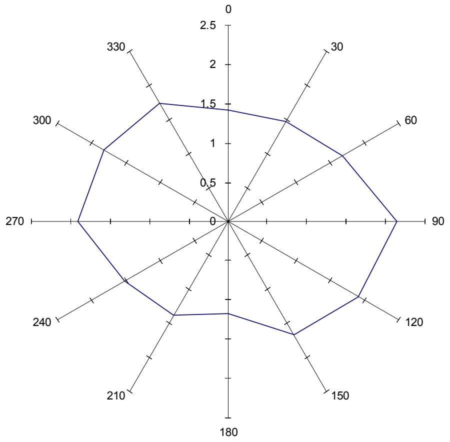


Figure 5.3. *Sector plot of TGM concentrations, ng/m^3 [data source: Lee et al., 1998]*

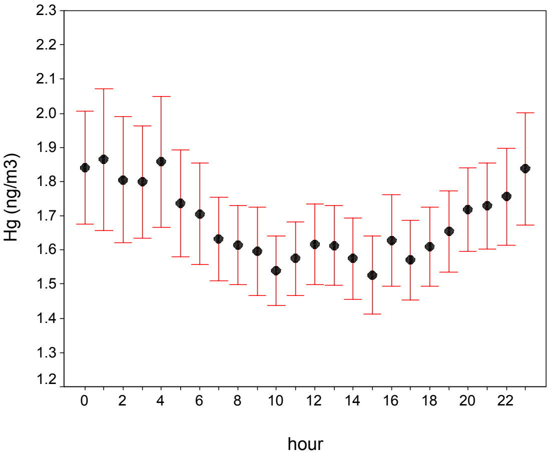


Figure 5.4. *Average concentrations of TGM (all data) sorted by hour of day (with 95% confidence limits shown) [(data source: Lee et al., 1998]*

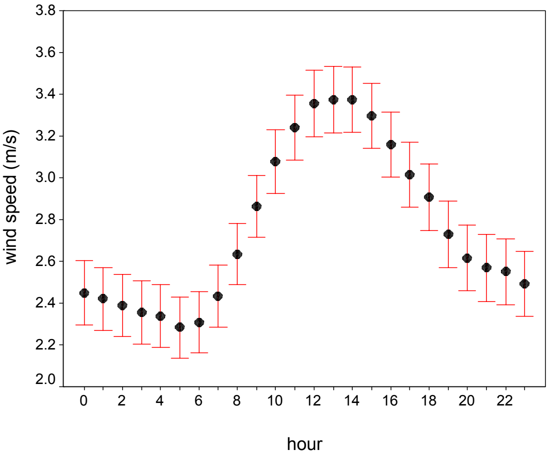


Figure 5.5. *Average wind speeds sorted by hour of day (with 95% confidence limits shown) [data source: Lee et al., 1998]*

Particle phase Hg has been measured over some years at a number of rural and urban sites in the UK. Since the particles are sampled by drawing ambient air through a filter paper, the technique is prone to unquantified sampling artifacts, with a potential interference from RGM, which is believed to be of the same order concentration. There should be no interference from Hg^0. Figure 5.6 shows concentrations of Hg-p at an urban and rural site. Two features are immediately apparent: over the period of data collected, the urban Hg-p concentrations are of the order 5 to 10 time greater than the rural ones; further, there is a clear trend in the urban data but not the rural data. Unfortunately, no more recent data are available.

There are no reliable measurements of wet deposition for the UK.

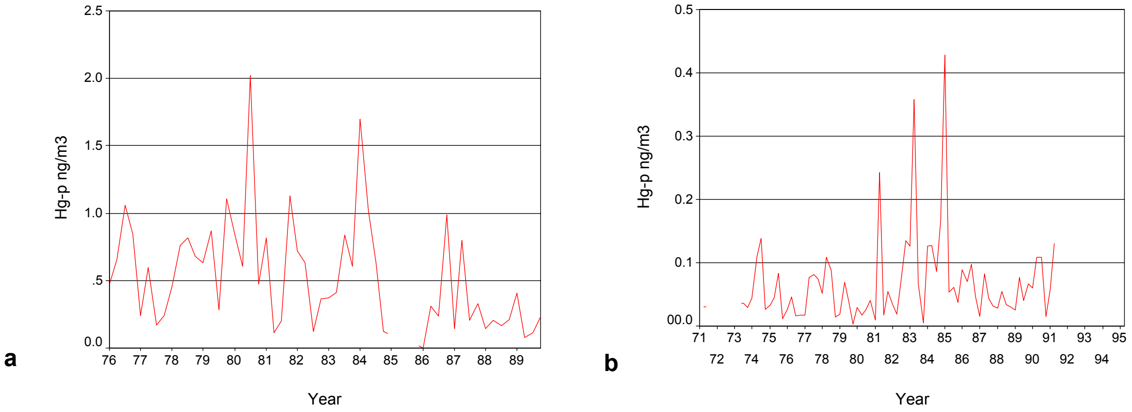


Figure 5.6. *Long-term concentrations of Hg-p at an urban site -* ***a*** *and at a rural site -* ***b*** *in the UK, ng/m^3 [data source: Lee et al., 1994]*

5.3. Modelling

Background

A number of modelling activities are underway in Europe but these are relatively few, compared to e.g., efforts to model acid deposition or photochemical oxidants. Currently, long-range transport modelling efforts are confined to Germany (GKSS), Russia (EMEP MSC-East) and the UK (QinetiQ). Other regional-scale models are currently under development in Greece, Bulgaria and Denmark. The status of long-range transport modelling of Hg has been reviewed by *G.Petersen* [1996] and *D.Lee et al.* [2000].

Modelling of the UK budget with RCTM-Q—model approach

The QinetiQ RCTM-Q (Regional Chemistry Transport Model-Quicksilver) model is a statistical long-term straight-line Lagrangian 1D trajectory model [*Lee et al.*, 1998]. It follows the evolution of the composition of an air parcel in the boundary layer, incorporating emissions (in three forms: Hg^0, Hg-p and RGM), vertical diffusion (between 10 layers), chemistry and deposition.

Modelled surface concentrations of Hg^0 at a resolution of 50 × 50 km across Europe are shown in Figure 5.7 and at 20 × 20 km across the UK (Fig. 5.8). The model has been shown to perform adequately against the fairly sparse measurement database of Hg^0 concentrations.

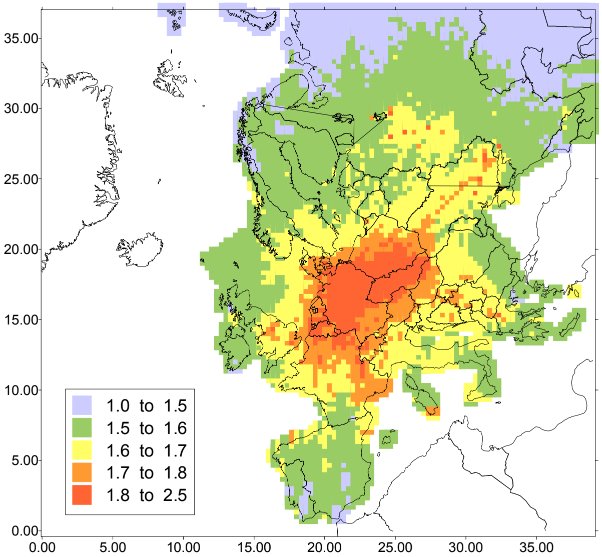


Figure 5.7. *Modelled Hg^0 concentrations over Europe, ng/m^3*

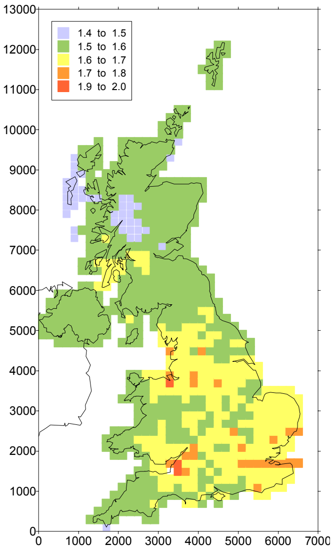


Figure 5.8. *Modelled Hg^0 concentrations over the UK, ng/m^3*

Using the UK as an example, deposition budgets have been calculated to illustrate the sensitivity of the model to some of the parameters used. Firstly, a base case is calculated in which best estimates of emissions and parameterizations of deposition and chemistry are used. Then, the sensitivities to the speciation of emissions, the impact of hemispheric background concentrations, and dry deposition rates were investigated.

Sensitivity of the UK deposition budget to emissions speciation

Emissions for the UK of 12.7 tonnes were estimated to comprise 65% Hg^0, 23% RGM and 12% Hg-p for low-level sources (3.4 t/y), and 67% Hg^0, 25% RGM and 8% Hg-p for high-level sources (9.3 t/y) [*Lee et al.*, 2000]. Using the same overall UK emission term, simulations were then run for 'low' and 'high' scenarios of Hg^0 of 30%, 50%, 20% (Hg^0, RGM, Hg-p) and 80%, 15%, 5% (Hg^0, RGM, Hg-p). The results are given in Table 5.1.

Table 5.1. UK deposition terms in t/y, emissions speciation sensitivity study

Deposited form of Hg	Base case	Low Hg^0 scenario	High Hg^0 scenario
dry Hg^0	1.98	1.95	1.99
wet Hg^0	0.00	0.00	0.00
dry RGM	5.49	8.89	4.24
wet RGM	0.88	1.37	0.70
dry Hg-p	0.14	0.20	0.11
wet Hg-p	1.39	1.73	1.26
Total	9.88	14.1	8.30

The base case scenario resulted in a total deposition term of approximately 10 t/y, which is dominated by dry deposition of RGM (56%). Depending upon the assumption of the emissions speciation, total deposition was modelled to be 42% higher, or 16% lower than the base case for the same emissions. This demonstrates the sensitivity of the model to the emissions speciation assumptions.

The differences from the base case arose principally from the fraction of Hg emitted in the form of RGM. Elemental gaseous Hg dry deposits at a rather low rate (1.55×10^{-4} m/s); RGM and Hg-p are assumed to behave like HNO_3 and sub-micron aerosol, respectively (Petersen *et al.*, 1995), with dry deposition velocities of 4×10^{-2} m/s and 1.5×10^{-3} m/s and washout coefficients of 9×10^{-6} s^{-1} and 1.3×10^{-5} s^{-1}, for RGM and Hg-p, respectively, assumed. Thus, if RGM behaves like HNO_3, then any change in this emitted form will result in a large change in total UK Hg deposition.

Contribution of background sources

In a further experiment, trajectories were initialized to zero concentrations of Hg^0 and Hg-p rather than the 1.5 ng/m^3 and 0.01 ng/m^3 assumed as the Northern Hemispherical background. The implied contribution of background concentrations was 25% of the UK total deposition (Table 5.2). In order to determine the deposition arising from Hg^0 oxidation and dry deposition, a further simulation excluded all emissions across the model domain and only Hg^0 concentrations were initialized. This resulted in a deposition of 2.47 t/y to the UK: of this, 73% was from dry deposited Hg^0 and 27% from Hg-p (from oxidized Hg^0). This emphasizes the importance and sensitivity of the model to the dry deposition rate for Hg^0, a very poorly understood and quantified parameter.

Table 5.2. UK deposition terms in t/y, trajectory initialization sensitivity study

Deposited form of Hg	Base case	Zero initialization	Hg^0 initialization only
dry Hg^0	1.98	0.18	1.79
wet Hg^0	0.00	0.00	0.00
dry RGM	5.49	5.49	0.00
wet RGM	0.88	0.88	0.00
dry Hg-p	0.14	0.11	0.08
wet Hg-p	1.39	0.71	0.60
Total	9.88	7.37	2.47

Attribution studies

One of the advantages of the simplicity of the RCTM-Q model is that it allows many simulations to be run in a short time, so that attribution of deposition to emissions can be easily explored. As an illustration of this, the contribution of non-UK European sources to UK deposition was calculated by excluding UK emissions and subtracting the contribution from a simulation in which only initializations of trajectories were included. The results are given in Table 5.3.

Table 5.3. Modelled deposition budgets of speciated Hg, t/y

Deposited form of Hg	Base case	Non-UK European sources only
dry Hg^0	1.98	0.13
wet Hg^0	0.00	0.00
dry RGM	5.49	2.30
wet RGM	0.88	0.42
dry Hg-p	0.14	0.05
wet Hg-p	1.39	0.42
Total	9.88	3.32

The UK contribution to itself was calculated to be 4.1 t/y. From the results, it was calculated that 25% of the deposition arose from the Northern Hemispherical background concentrations; 41% came from UK sources; 34% from other European countries. Given the dominance of the impacts of RGM on the UK budget and that much of it is from UK sources, it is unsurprising that the largest fraction of deposition comes from domestic sources. However, as has been demonstrated, the sensitivity studies on emissions speciation show that the budget is rather sensitive to this. The modelled UK Hg budget is summarized in Figure 5.9.

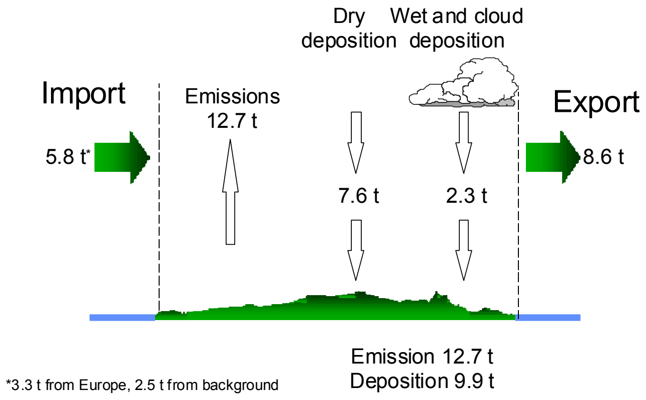


Figure 5.9. *Summary of modelled UK Hg budget, t/y*

5.4. Discussion

The measurements of TGM are, in general, in good agreement with other measurements of TGM in Europe, scant those these are. Presently, there is no routine monitoring network across Europe, let alone the UK, for TGM. This is obviously a major handicap in any monitoring and assessment work. There are moves under the auspices of the European Framework Directive that will require Member States to monitor Hg, although the details are not yet finalized. Because Hg^0, the principal constituent of TGM, has a long atmospheric lifetime, it is no surprise that concentrations are not so variable and that annual average concentrations are not so very different to those found at other sites.

Various measurements of TGM have been made, reviewed and summarized elsewhere [*Lee et al.,* 2000]. Concentrations closer to the principal source areas in central Europe tend to be of the order 2 ng/m^3, whilst a transect of sites from central to northern Europe showed a clear gradient down to approximately 1.5 ng/m^3 at the northernmost site [*Schmolke et al*., 1999].

There are only limited measurements of other atmospheric Hg species: in the UK, some measurements are still being made of Hg-p, continuing the long record of measurements made at sites such as Chilton and Windermere. Unfortunately, the measurements after 1990 are of limited use; an analysis of the data by *D. Lee et al*. [2000] demonstrated that there was a step change in concentrations, which was directly attributable to a change in analytical methodology. No measurements of RGM have been made in the UK and no reliable measurements of wet deposited Hg-p exist, despite some attempts [e.g. *Playford et al*., 1995].

In terms of the modelling, the long-term straight-line trajectory model approach is rather simplistic and a better model is required for the UK. However, despite its simplicity, it has been useful in providing an initial estimate of the UK budget and identifying important differences in attribution between this and other models. Moreover, the model's sensitivity to various parameters, especially the speciation of emissions and the dry removal rates has helped to point the way to prioritizing measurement and process studies. Possibly most important of all are measurements of speciated emissions and dry deposition rates of Hg^0. There is substantial evidence emerging that Hg^0 exchange is bi-directional [*Xu et al*., 1999], rather than being a simple deposition process. It is critical for the modelling that careful process studies are initiated.

As has been shown, Hg is a global pollutant and concentrated in the Northern Hemisphere: thus, so-called 'background' concentrations of $Hg^0$are a substantial fraction (of the order 60 to 83%) of concentrations over Europe. Because of this, any model will be sensitive to the background concentrations, however they are treated. Because of this, it is important to initiate global-scale modelling studies. Some global models exist but this aspect remains underdeveloped. It is recommended that global and regional approaches are developed in tandem. An illustration of the importance of this is the apparently increasing background concentrations of TGM measured at the Wank Mountain after 1996 [*Slemr*, 2000], prior to which, concentrations had been steadily declining [*Slemr and Scheel*, 1998]. The tentative explanation to this phenomenon, which cannot be explained with current knowledge of European emissions, is that increasing coal burning in the Far East is releasing Hg, which is causing hemispherical background levels to increase. Such issues could be explored with global models.

5.5. Conclusions

Measurements of TGM in central southern England showed a mean annual concentration of the order 1.7 ng/m^3 (in 1996), which is in agreement with the spatial gradient implied from other measurements across Europe of this long-lived species. These measurements implied a surface source of Hg, which is currently not accounted for in the emissions inventory. Process studies of TGM exchange would assist in confirming, or otherwise, the importance of this. It is important to initiate more measurements in the UK and establish some long-term measurements.

Only one UK-specific modelling study of Hg has been undertaken. It was found that the model was rather sensitive to the emissions speciation because of the greatly different lifetimes of the species involved. Other sensitivities were explored and it was found that the contribution of hemispheric background concentrations was greater than 60%, which results in rather large uncertainties in the modelling in the absence measurements at more remote locations and global model studies.

In terms of the UK budget for Hg, in addition to emissions speciation, the model was found to be sensitive to the assumed dry deposition rate of Hg^0. This urgently requires more studies of Hg^0 dry deposition over various surfaces, including seawater, and a characterization of bi-directional exchange.

It is recommended that the UK stay active in this atmospheric research arena and contribute actively towards the EMEP programmes in terms of both measurements and modelling.

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CONCLUSIONS

- Atmospheric budgets of lead, cadmium and mercury in 2000 were evaluated for each EMEP country. Areas with elevated concentrations and depositions were identified. Total calculated lead, cadmium and mercury depositions to EMEP region in 2000 amounted to about 16700, 600 and 220 t, respectively. Calculated depositions of lead and cadmium to Europe as whole in 2000 became about 30% lower, and of mercury - about twice lower in comparison with 1999. Transboundary depositions were computed as country-to-country matrices and the most important countries - sources were identified. In addition to this, a role of domestic sources and indeterminate sources was indicated. Atmospheric depositions and deposition densities to European marginal seas were calculated.

- On the base of monitoring data European pollution levels were mapped. Lead concentrations in precipitation range from less than 1 to 13 μg/l, cadmium – from less than 0.05 to 0.9 μg/l and mercury – from 5 to 20 ng/l. Gradient of the pollution levels from central Europe to the north is indicated.

- Advances have been made in the area of heavy metal monitoring in the atmosphere. Twenty-nine laboratories participated in the last intercomparison of analytical methods used for the determination of heavy metal concentrations. The quality of chemical analysis of samples improved in comparison with similar intercomparison of 1999. Measurements of aerosol and gaseous forms of oxidized mercury responsible for the bulk of depositions are still few in number and they are characterized by a considerable uncertainty.

- Official emission data for 2000 have been submitted on lead by 25 countries, on cadmium and mercury by 22 countries. Estimated total anthropogenic emissions of lead, cadmium and mercury for 2000 are lower by 30, 18 and 11% than corresponding values for 1999.

- Uncertainty of heavy metal anthropogenic emission remains one of main sources of the uncertainty of modeling results. The estimate of annual emission for a country can vary up to two times as a result of retrospective refinement of emission data.

- Natural emission values have been also refined. Estimated total natural emission in the EMEP domain in 2000 was 208 tonnes of mercury, quasi-natural emissions of lead and cadmium – 7600 and 390 tonnes respectively. It might be well to point out that these estimates are highly uncertain.

- The calculation scheme of mercury atmospheric transformations was complemented by new reactions as a consequence calculated concentrations of mercury in precipitation became more realistic. Boundary concentrations of heavy metals were made more precise. The calculation scheme of dry deposition was also improved by the account of underlying surface type. According to the refined scheme specific depositions to areas covered by forests are noticeably higher than those to the surface with shortish vegetation – grasslands, arable lands etc.

- Recently discovered phenomenon of spring mercury concentration depletion in the Arctic can result to an appreciable increase of depositions to vulnerable northern ecosystems. Further experimental and theoretical research is needed for the improvement of the process parameterization.

- Comparison of modelled and measured data for 1999 indicated that the modified model reasonably reproduces observed values of concentrations in air and in precipitation. Computed concentrations in air agree with measured values within 30% for most of monitoring sites. As for concentrations in precipitation, modelled heavy metal concentrations on average are within a factor of 2.

- In the future with the use of refined emissions it is planned to proceed with the assessment of concentrations, depositions and transboundary fluxes in the EMEP countries as well as with the analysis of trends. The improvement of transport and deposition models will go on in parallel with better understanding of metals' behaviour in the atmosphere. It is also planned to start collecting information about properties and atmospheric cycling of metals of the second priority (As, Cu, Ni, Cr, Zn). The co-operation with the Task Force on Effects in respect of the comparison of deposition levels with critical loads will continue. The collaboration with national experts engaged in transport and deposition model intercomarison study is in progress.
- More detailed information about EMEP Centres' activity in the field of heavy metals can be found in the Internet site www.emep.int.

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Ireland	Environmental Protection Agency (EPA)
Latvia	Latvian Hydrometeorological Agency
Lithuania	Institute of Physics
Netherlands	National Institute for Public Health and Environmental Protection (RIVM)
Norway	Norwegian Institute for Air Research (NILU)
Poland	Institute of Environmental Protection
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Annex A1

Annual statistics for heavy metals in precipitation

BE0004R **Knokke** **Belgium**
Wet-only

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.76	0.70	1.40	13	14		M
Hg	30.00	10.00	50.00	3	14	1	M
Pb	28.15	6.00	93.00	0	9	2,3,4	M
Precip	-	28.60	98.10	0	14		M

BE0004R **Knokke** **Belgium**
Bulk

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.26	0.05	1.13	3	11		
Pb	5.96	0.69	32.41	1	12		
Precip	-	55.7	177.8	0	12		

CZ0001R **Svratouch** **Czech Republic**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.17	0.05	0.68	0	44		W
Pb	3.59	0.40	9.00	0	45		W
Precip	-	0.0	58.6	3	52		W

CZ0003R **Kosetice** **Czech Republic**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.18	0.06	1.01	0	45		W
Pb	3.46	0.40	18.50	0	46		W
Precip	-	0.0	39.8	3	51		W

DE0001R **Westerland** **Germany**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.07	0.02	0.21	0	45		W
Hg	9.59	0.80	51.70	0	47		W
Pb	1.09	0.19	3.67	0	45		W
Precip	-	0.0	58.1	8	53		W
Precip (Hg)	-	0.0	58.1	8	53		W

DE0004R **Deuselbach** **Germany**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.06	0.01	0.29	0	50		W
Pb	1.78	0.48	9.11	0	50		W
Precip	-	0.0	61.8	1	53		W

DE0009R **Zingst** **Germany**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.00	0.25	0	47		W
Hg	15.22	4.40	64.80	0	47		W
Pb	0.95	0.04	5.96	0	47		W
Precip	-	0.0	65.4	5	53		W

DK0008R **Anholt** **Denmark**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.06	0.03	0.11	0	12		M
Pb	2.33	0.95	8.37	0	12		M
Precip	-	22.7	87.4	0	12		M

DK0020R

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.11	0.04	0.32	0	11		M
Pb	2.53	1.27	6.11	0	11		M
Precip	-	26.4	78.5	0	11		M

DK0031R **Ulborg** **Denmark**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.03	0.09	0	10		M
Pb	0.86	0.57	1.93	0	10		M
Precip	-	45.2	142.2	0	10		M

EE0009R **Lahemaa** **Estonia**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.07	0.03	0.20	0	12		M
Pb	1.28	0.50	7.20	8	12		M
Precip	-	13.7	106.3	0	12		M

EE0011R **Vilsandi** **Estonia**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.06	0.03	0.14	0	9		M
Pb	0.83	0.50	1.70	4	9		M
Precip	-	8.4	96.0	0	12		M

FI0008R

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.01	0.11	0	12		M
Pb	0.46	0.15	3.60	0	12		M
Precip	-	5.4	51.5	0	12		M

FI0009R **Uto** **Finland**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.10	0.03	0.53	0	11		M
Pb	3.01	0.64	10.17	0	11		M
Precip	-	0.6	88.2	0	12		M

FI0017R Virolahti II Finland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.10	0.03	0.21	0	12		M
Pb	2.87	0.42	5.35	0	12		M
Precip	-	9.0	82.3	0	12		M

FI0022R Oulanka Finland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.03	0.00	0.09	0	12		M
Pb	0.64	0.10	2.75	0	12		M
Precip	-	18.5	62.2	0	12		M

FI0053R Hailuoto Finland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.01	0.14	0	12		M
Pb	1.50	0.33	4.69	0	12		M
Precip	-	12.4	89.3	0	12		M

FI0092R Hietajarvi Finland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.01	0.26	0	12		M
Pb	0.96	0.19	8.98	0	12		M
Precip	-	15.3	86.0	0	12		M

FI0093R Kotinen Finland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.01	0.23	0	12		M
Pb	1.15	0.33	7.82	0	12		M
Precip	-	8.6	143.8	0	12		M

FI0096R Pallas Finland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.00	0.11	0	12		M
Pb	0.65	0.14	2.72	0	12		M
Precip	-	10.4	92.1	0	12		M

FR0090R Porspoder France

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.01	0.05	0	12		M
Pb	1.81	1.06	4.85	0	12		M
Precip	-	24.2	227.7	0	12		M

GB0014R High Muffles United Kingdom

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.03	0.17	0	12	11LH	M
Pb	2.11	1.12	6.60	0	11	11LH	M
Precip	-	18.7	200.5	0	12		M

GB0090R East Ruston United Kingdom

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.09	0.02	0.41	0	12	11LH	M
Pb	1.66	0.60	4.00	0	13	11LH	M
Precip	-	23.5	96.8	0	13		M

GB0091R Banchory United Kingdom

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.02	0.19	0	12	11LH	M
Pb	0.90	0.40	1.69	0	12	11LH	M
Precip	-	23.0	185.2	0	12		M

IE0001R Valentia Obs. Ireland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.03	0.07	11	12	NP	M
Pb	0.50	0.25	1.00	10	12	NP	M
Precip	-	42.5	308.9	0	12		M

IE0002R Turlough Hill Ireland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.08	0.03	0.11	5	11	NP	M
Pb	0.63	0.25	2.80	7	11	NP	M
Precip	-	42.3	390.0	0	12		M

IS0002R Irafoss Iceland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.01	0.72	16	47		W
Pb	0.56	0.10	4.67	0	47		W
Precip	-	0.0	93.3	2	59		W

IS0090R Reykjavik Iceland

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.01	0.01	0.08	31	51		W
Pb	0.61	0.20	3.06	0	51		W
Precip	-	0.0	58.6	3	58		W

LT0015R Preila Lithuania

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.25	0.03	4.88	0	48		WC
Pb	13.24	0.90	327.00	0	48		WC
Precip	-	0.0	31.6	4	52		WC

LV0010R Rucava Latvia

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.10	0.01	0.32	0	10		M
Pb	1.56	0.20	5.30	0	10		M
Precip	-	9.2	94.1	0	10		M

LV0016R Zoseni Latvia

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.01	0.17	0	10		M
Cu	1.37	0.20	5.80	0	10		M
Pb	1.05	0.10	3.10	1	10		M
Precip	-	16.3	90.3	0	10		M
Zn	14.12	3.60	36.70	0	10		M

NL0009R Kollumerwaard Netherlands

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.09	0.06	0.15	0	11		W4
Pb	2.19	1.07	4.79	0	11		W4
Precip	-	23.9	95.2	0	11		W4

NL0091R

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.06	0.02	0.24	1	12		W4
Hg	9.87	4.00	49.00	0	46		W4
Pb	3.11	2.05	7.82	0	12		W4
Precip	-	18.4	211.4	1	52		W4
Precip (Hg)	-	0.0	43.2	1	52		W4

NO0001R Birkenes Norway

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.03	0.01	0.18	10	56		WC
Pb	1.39	0.15	6.66	0	56		WC
Precip	-	0.1	191.7	0	63		WC

NO0039R Kaarvatn Norway

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.01	0.00	0.17	16	51		WC
Pb	0.18	0.03	1.20	0	51		WC
Precip	-	0.0	88.5	3	63		WC

NO0041R Osen Norway

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.00	0.35	8	54		WC
Pb	1.37	0.14	12.43	0	54		WC
Precip	-	0.0	89.7	2	62		WC

NO0047R Svanvik Norway

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.12	0.02	1.92	0	55		WC
Pb	1.99	0.19	38.02	0	55		WC
Precip	-	0.0	33.2	2	62		WC

NO0055R **Karasjok** **Norway**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.00	0.13	11	48		WC
Pb	0.56	0.09	6.20	0	48		WC
Precip	-	0.0	32.4	2	63		WC

NO0056R **Hurdal**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.00	0.20	4	58		WC
Pb	1.13	0.18	10.15	0	58		WC
Precip	-	0.0	93.1	2	63		WC

NO0092R **Øverbygd** **Norway**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.00	0.12	5	47		WC
Pb	0.37	0.09	4.50	0	46		WC
Precip	-	0.0	67.8	15	62		WC

NO0093R **Valdalen** **Norway**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.03	0.00	0.15	19	54		WC
Pb	1.01	0.06	5.64	0	54		WC
Precip	-	0.0	64.9	2	63		WC

NO0094R **Moesvatn** **Norway**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.00	0.19	10	48		WC
Pb	1.02	0.05	5.78	0	48		WC
Precip	-	0.0	92.1	1	52		WC

NO0095R **Ualand** **Norway**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.00	0.11	12	56		WC
Pb	0.71	0.13	5.86	0	57		WC
Precip	-	0.0	167.5	4	63		WC

NO0099R **Lista** **Norway**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.01	0.24	4	55		WC
Hg	7.32	3.20	20.20	0	11		M
Pb	1.57	0.25	6.27	0	55		WC
Precip	-	27.4	402.4	2	62		WC

PT0001R **Braganca** **Portugal**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.42	0.42	0.42	53	53	NP	D
Pb	0.99	0.65	10.39	48	53	NP	D
Precip off	-	0.00	77.90	228	366		D

PT0003R **V. Do Castelo** **Portugal**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.43	0.42	1.28	98	99	NP	D
Pb	0.82	0.65	5.83	92	99	NP	D
Precip off	-	0.00	63.30	184	366		D

PT0004R **Monte Velho** **Portugal**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.42	0.42	0.42	31	31	NP	D
Pb	0.67	0.65	1.68	29	31	NP	D
Precip off	-	0.00	57.80	311	366		D

PT0010R

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.42	0.42	0.42	38	38	NP	D
Pb	1.67	0.65	16.50	17	38	NP	D
Precip off	-	0.00	139.90	4	52		D

SE0002R **Rorvik** **Sweden**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Hg	8.76	5.80	12.60	0	12		M
Precip	-	26.9	106.0	0	12		M

SE0005R **Bredkalen** **Sweden**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.01	0.11	3	12		M
Hg	5.52	3.10	15.30	0	12		M
Pb	0.71	0.23	2.32	0	13		M
Precip	-	12.0	123.0	0	13		M

SE0011R **Vavihill** **Sweden**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Hg	12.52	8.70	28.80	0	12		M
Precip	-	36.1	139.5	0	12		M

SE0012R **Aspvreten** **Sweden**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.11	0.06	0.17	0	4		M
Pb	3.52	2.05	6.16	0	4		M
Precip	-	15.0	23.0	0	4		M

SE0051R **Arup** **Sweden**

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.02	0.12	0	12		M
Pb	2.00	0.79	3.61	0	12		M
Precip	-	24.0	111.0	0	12		M

SE0097R Gårdsjon Sweden

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.05	0.01	0.10	0	13		M
Pb	1.58	0.76	3.11	0	13		M
Precip	-	25.0	193.0	0	13		M

SK0002R Chopok Slovakia

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.94	0.20	3.00	0	12		M
Pb	4.43	2.00	7.00	0	12		M
Precip	-	37.5	189.3	0	12		M

SK0004R Stara Lesna Slovakia

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.32	0.10	2.60	0	12		M
Pb	2.24	1.00	10.00	0	12		M
Precip	-	8.5	136.0	0	12		M

SK0005R Liesek Slovakia

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.13	0.10	0.40	0	12		M
Pb	1.96	1.00	5.00	0	12		M
Precip	-	27.3	207.2	0	12		M

SK0006R Starina Slovakia

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.17	0.10	0.30	1	11		M
Pb	3.00	1.00	5.00	0	12		M
Precip	-	5.3	220.9	0	12		M

SK0007R Kode SK0007R ikke funnet

January 2000 - December 2000

Component	W. mean	Min	Max	Num bel	Num sampl	QA flag	Samp flag
Cd	0.19	0.10	0.30	0	11		M
Pb	3.11	1.00	5.00	0	12		M
Precip	-	7.7	71.5	0	12		M

Annex A2

Annual heavy metal concentrations in air

BE0004R Knokke Belgium

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb          42.00   8.06  41.28   1.22  30.00  40.00   54.00 100.0    0    12
```

CZ0001R Svratouch Czech Republic

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.32   0.30   0.22   2.45   0.04   0.21    1.61  15.8    0    58        D1
Pb           9.80   8.80   7.44   2.14   0.50   7.91   58.87  15.8    0    58        D1
```

CZ0003R Kosetice Czech Republic

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.33   0.26   0.24   2.20   0.03   0.23    1.21  15.6    0    57        D1
Pb          11.13  16.49   6.52   2.64   0.51   5.73  108.59  15.6    0    57        D1
```

DE0001R Westerland Germany

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb           6.46   2.67   5.85   1.65   2.20   6.60   10.70 100.0    0    12         M
```

DE0003R Schauinsland Germany

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb           2.86   1.06   2.67   1.50   1.30   3.00    4.80 100.0    0    12         M
```

DE0004R Deuselbach Germany

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb           9.22   1.95   9.03   1.24   5.70   8.70   13.20 100.0    0    12         M
```

DE0005R Brotjacklriegel Germany

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb           4.55   1.49   4.31   1.44   2.10   4.70    7.30 100.0    0    12         M
```

DE0007R Neuglobsow Germany

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb          11.51   4.81  10.19   1.77   3.00  12.00   17.90 100.0    0    12         M
```

DE0008R Schmucke Germany

```
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min     50%    Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb           6.50   2.49   6.07   1.47   2.70   5.30   11.90 100.0    0    12         M
```

```
DE0009R       Zingst                 Germany
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Pb           7.19   5.44   5.55   2.12   2.10   4.50   17.00 100.0    0    12        M

DK0003R       Tange                  Denmark
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.27   0.52   0.15   3.48   0.00   0.18    8.92  95.1  302   348        D
Pb           5.88   8.35   3.18   3.22   0.08   3.43   77.24  95.1    2   348        D

DK0005R       Keldsnor               Denmark
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.30   0.29   0.17   3.31   0.00   0.22    2.04  97.8  279   358        D
Pb           7.56   9.18   4.19   3.29   0.09   5.05   85.72  98.1    3   359        D

DK0008R       Anholt                 Denmark
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.13   0.26   0.17   2.97  -0.85   0.10    1.02  99.7  316   365  NP    D
Pb           4.93   6.83   2.28   4.14  -0.18   2.49   50.50 100.0   11   366  NP  D

DK0010G       Greenland              Denmark
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Hg           1.39   0.47   1.24   1.82   0.03   1.52    2.91  62.7  188  5511        H
Pb           0.59   0.93   0.20   6.34   0.00   0.22    4.46  86.6   15    51  NP    W
Zn           0.83   1.09   0.41   3.75   0.02   0.41    4.67  86.6   26    51  NP     W

DK0015G       Faroe Islands
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Hg           1.28   0.46   1.20   1.44   0.09   1.20    3.40  59.3    5  5207        H

DK0031R       Ulborg                 Denmark
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.14   0.27   0.17   2.99  -0.52   0.11    1.16  99.5  318   364  NP    D
Pb           4.26   5.61   2.02   4.21  -0.61   2.44   48.36  99.7   35   365  NP

FI0096R       Pallas                 Finland
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.04   0.04   0.03   2.58   0.00   0.02    0.20  99.3    0    56        W
Hg           1.34   0.14   1.35   1.11   1.10   1.40    1.60  13.1    0    43        W
Pb           1.07   1.04   0.71   2.47   0.06   0.65    5.17  99.3    0    56        W

GB0014R       High Muffles           United Kingdom
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.23   0.18   0.18   1.86   0.09   0.14    0.70  99.9    0    12        M
Pb           6.34   2.10   6.02   1.38   4.00   5.05    9.70  92.2    0    11        M

GB0090R       East Ruston            United Kingdom
January 2000 - December 2000
             Arit   Arit   Geom   Geom    Min    50%     Max     %  Num   Num   QA Samp
Component    mean     sd   mean     sd                        anal  bel sampl flag flag
Cd           0.23   0.19   0.22   1.83   0.08   0.19    0.80 100.0    0    13        M
Pb          11.02   8.77  10.05   1.85   3.20   8.80   34.70 100.0    0    13        M
```

GB0091R **Banchory** **United Kingdom**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.04	0.02	0.04	1.68	0.01	0.04	0.09	92.3	2	12		M
Pb	2.16	0.86	2.10	1.49	1.15	2.08	3.60	92.3	0	12		M

IE0031R **Mace Head** **Ireland**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Hg	1.78	0.19	1.77	1.11	1.17	1.77	3.04	86.1	0	7567		H

IS0091R **Storhofdi** **Iceland**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.09	0.10	0.05	2.76	0.01	0.04	0.32	95.9	0	24		W2
Hg(aerosols)	1.73	0.71	1.46	1.84	0.27	1.84	2.89	95.9	0	24		W2
Pb	0.53	0.24	0.47	1.68	0.17	0.54	1.10	95.9	0	24		W2

LT0015R **Preila** **Lithuania**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.17	0.13	0.12	2.53	0.01	0.12	0.54	99.7	0	52		W
Pb	5.77	4.65	4.17	2.29	0.80	3.20	19.90	99.7	0	52		W

LV0010R **Rucava** **Latvia**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.51	0.45	0.33	2.72	0.05	0.42	1.82	98.2	0	52		W
Pb	15.44	15.51	9.69	2.78	1.20	9.99	70.80	98.2	0	52		W

LV0016R **Zoseni** **Latvia**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.22	0.19	0.15	2.68	0.01	0.17	0.86	94.0	0	49		W
Pb	4.86	4.22	3.31	2.57	0.31	3.35	20.70	94.0	1	49		W

NL0009R **Kollumerwaard** **Netherlands**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.17	0.15	0.11	2.73	0.02	0.13	0.67	24.9	13	91		D
Pb	8.82	11.13	5.62	2.72	0.30	5.91	96.66	24.9	0	91		D

NO0042G **Zeppelin, Spitsbergen** **Norway**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.02	0.03	0.02	2.32	0.00	0.01	0.14	28.1	13	53		D2
Hg	1.62	0.08	1.62	1.05	0.53	1.61	1.88	31.1	0	2728		H
Pb	0.62	0.97	0.21	5.72	0.01	0.23	3.97	28.1	4	53		D2

NO0099R **Lista** **Norway**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.07	0.05	0.05	2.19	0.01	0.05	0.28	93.7	0	49		W
Hg	1.63	0.53	1.53	1.45	0.56	1.54	2.60	5.2	0	19		D1
Pb	2.44	2.17	1.78	2.22	0.36	1.73	10.37	93.7	0	49		W

SE0002R **Rorvik** **Sweden**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Hg	1.36	0.24	1.34	1.18	1.00	1.30	2.60	25.7	0	94		D2

SK0002R **Chopok** **Slovakia**

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.15	0.17	0.10	2.38	0.04	0.11	0.97	73.8	0	46		W
Pb	3.67	3.31	2.02	3.55	0.15	2.85	13.34	72.2	1	45		W

SK0004R Stara Lesna Slovakia

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.33	0.19	0.29	1.71	0.09	0.27	0.95	85.2	0	52		W
Pb	10.29	7.29	8.55	1.80	2.87	7.83	34.54	85.2	0	52		W

SK0005R Liesek Slovakia

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.41	0.21	0.37	1.68	0.10	0.38	1.10	85.5	0	51		W
Pb	11.70	4.48	10.88	1.53	3.89	11.72	21.35	85.5	0	51		W

SK0006R Starina Slovakia

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.57	0.49	0.42	2.20	0.05	0.38	2.31	62.6	0	104		D
Pb	17.94	17.38	12.55	2.45	1.54	11.27	80.03	62.6	0	104		D

SK0007R

January 2000 - December 2000

Component	Arit mean	Arit sd	Geom mean	Geom sd	Min	50%	Max	% anal	Num bel	Num sampl	QA flag	Samp flag
Cd	0.51	0.34	0.41	1.94	0.09	0.44	1.67	65.1	0	120		D
Pb	17.79	11.15	14.86	1.84	4.65	13.97	49.80	65.1	0	120		D

Annex A3

Monthly mean values on data for heavy metals in precipitation

BE0004R cadmium (Wet-only)	**0.700**	**0.700**	**1.090**	**0.765**	**0.700**	**0.700**	**0.700**	**0.873**	**0.989**	**0.700**	**0.700**	**0.700**
BE0004R lead (Wet-only)	22.062	10.044	38.655	42.217	19.367	27.812	35.666	74.015	37.578	30.303	15.036	9.150
BE0004R lead (Bulk)	2.570	2.860	5.300	27.814	17.774	10.620	7.995	2.780	2.654	1.139	1.693	3.386
BE0004R mercury (Wet-only)	0.010	0.025	0.030	0.030	0.030	0.034	0.013	0.030	0.030	0.030	0.040	0.045
BE0004R cadmium (Bulk)	0.068	0.083	0.277	0.477	0.346	0.691	0.944	0.110	0.063	0.050	0.050	0.735
CZ0001R cadmium	0.115	0.100	0.116	0.112	0.106	0.134	0.159	0.445	0.211	0.231	0.267	0.457
CZ0001R lead	2.941	2.939	3.030	2.732	4.415	4.295	2.267	6.690	4.445	5.963	4.113	4.516
DE0001R lead	1.626	1.910	0.810	0.720	1.110	0.740	0.700	1.600	1.000	0.730	1.560	0.890
DE0001R cadmium	0.078	0.057	0.070	0.081	0.057	0.069	0.036	0.106	0.055	0.059	0.079	0.059
DE0001R mercury	6.985	8.900	4.300	11.600	8.300	9.600	5.800	20.400	8.100	4.700	9.800	18.900
DE0001R cadmium	0.081	0.057	0.072	0.080	0.057	0.067	0.040	0.105	0.052	0.063	0.077	0.056
DE0001R lead	1.694	1.817	0.787	0.735	1.023	0.811	0.687	1.481	1.026	0.786	1.523	0.889
DE0001R mercury	7.634	8.190	4.618	11.660	8.820	9.661	5.444	17.439	8.615	4.939	12.015	16.020
DE0004R cadmium	0.078	0.055	0.064	0.065	0.085	0.078	0.029	0.077	0.049	0.045	0.047	0.060
DE0004R lead	2.275	1.431	2.136	2.788	2.559	2.211	0.988	2.646	1.228	1.421	1.856	1.848
DE0009R mercury	13.970	6.588	5.662	10.078	19.739	19.649	20.319	19.587	13.269	15.444	7.285	24.498
DE0009R lead	1.247	1.132	0.818	0.928	1.078	0.395	0.434	0.558	1.318	2.552	0.902	1.084
DE0009R cadmium	0.189	0.028	0.031	0.030	0.052	0.025	0.017	0.025	0.037	0.089	0.033	0.037
DK0008R cadmium	0.097	0.080	0.028	0.043	0.047	0.039	0.050	0.108	0.047	0.069	0.055	0.062
DK0008R lead	2.286	1.569	1.035	2.972	2.667	1.075	2.485	7.821	1.626	2.482	2.033	1.984
DK0020R lead	1.666	2.479	2.291	5.887	2.474	1.277	1.524	5.773	1.448	2.635	3.037	3.037
DK0020R cadmium	0.079	0.037	0.043	0.090	0.125	0.047	0.076	0.171	0.320	0.155	0.103	0.103
DK0031R cadmium	0.032	0.037	0.034	0.030	0.031	0.080	0.083	0.043	0.041	0.030	0.046	0.046
DK0031R lead	0.682	0.578	0.848	1.476	1.485	1.887	0.866	0.787	0.906	0.659	0.585	0.585
EE0009R cadmium	0.090	0.080	0.060	0.070	0.030	0.060	0.050	0.070	0.050	0.070	0.080	0.200
EE0009R lead	0.500	0.500	2.100	2.100	0.500	0.500	0.500	0.500	0.500	1.300	0.500	7.200
EE0011R lead	1.700	1.200	1.400	1.500	0.500	0.500	0.500	-	-	0.500	1.200	-
EE0011R cadmium	0.140	0.080	0.090	0.060	0.040	0.040	0.050	-	-	0.030	0.080	-
FI0008R cadmium	0.005	0.006	0.024	0.045	0.017	0.017	0.019	0.012	0.007	0.112	0.021	0.011
FI0008R lead	0.150	0.230	1.100	0.770	0.480	0.410	0.510	0.340	0.190	3.600	0.660	0.290
FI0009R cadmium	0.528	0.108	-	0.131	0.091	0.052	0.028	0.029	0.025	0.232	0.182	0.112
FI0009R lead	10.170	3.870	-	4.840	4.430	1.360	0.710	0.870	0.640	8.790	5.350	3.680
FI0017R cadmium	0.046	0.074	0.138	0.141	0.090	0.037	0.035	0.030	0.035	0.214	0.134	0.156
FI0017R lead	2.270	2.840	4.740	4.520	3.400	1.030	1.130	0.420	1.070	5.350	4.620	2.100
FI0022R cadmium	0.017	0.015	0.022	0.094	0.035	0.031	0.019	0.003	0.030	0.039	0.031	0.008
FI0022R lead	0.400	0.290	0.640	2.750	0.850	0.560	0.460	0.100	0.520	1.220	0.840	0.220
FI0053R cadmium	0.046	0.030	0.055	0.102	0.041	0.031	0.026	0.014	0.042	0.141	0.045	0.020
FI0053R lead	1.640	0.960	1.820	3.320	1.400	1.280	0.730	0.330	0.890	4.690	1.250	0.690
FI0092R lead	0.830	0.440	0.800	8.980	1.640	0.580	0.490	0.190	0.520	2.160	1.140	0.650
FI0092R cadmium	0.037	0.011	0.039	0.256	0.058	0.021	0.017	0.012	0.026	0.080	0.067	0.032
FI0093R cadmium	0.019	0.027	0.022	0.226	0.033	0.060	0.034	0.009	0.026	0.076	0.077	0.045
FI0093R lead	0.770	1.080	0.830	7.820	0.870	0.750	0.760	0.330	0.370	2.240	1.460	1.020
FI0096R cadmium	0.012	0.016	0.022	0.013	0.021	0.020	0.040	0.014	0.016	0.112	0.013	0.003
FI0096R lead	0.380	0.380	0.650	0.500	0.680	0.510	1.170	0.360	0.410	2.720	0.410	0.140
FR0090R cadmium	0.020	0.010	0.040	0.040	0.020	0.040	0.050	0.050	0.010	0.010	0.020	0.020
FR0090R lead	3.020	2.160	1.200	1.440	1.370	1.790	4.850	2.350	1.060	1.260	2.200	1.610
GB0014R cadmium	0.040	0.164	0.086	0.070	0.053	0.030	0.030	0.030	0.030	0.030	0.041	0.060
GB0014R lead	1.560	1.560	4.933	3.120	2.894	1.800	1.125	1.550	1.463	1.353	2.148	2.363

GB0090R cadmium	0.191	0.211	0.140	0.410	0.105	0.050	0.040	0.031	0.040	0.021	0.030	0.040
GB0090R lead	2.193	2.660	3.595	3.434	2.476	0.600	1.362	1.405	1.500	0.651	0.800	1.100
GB0091R cadmium	0.079	0.183	0.062	0.028	0.017	0.076	0.049	0.076	0.056	0.025	0.037	0.025
GB0091R lead	0.675	0.746	1.197	1.320	1.032	1.412	0.982	1.688	0.871	0.586	0.624	0.466
IE0001R cadmium	0.025	0.025	0.070	0.025	0.025	0.025	0.050	0.050	0.050	0.050	0.050	0.050
IE0001R lead	0.250	0.250	1.000	0.250	0.250	0.250	0.500	0.500	0.500	0.500	1.000	0.500
IE0001R mercury	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000
IE0002R lead	0.700	1.000	2.800	0.250	1.200	0.250	0.500	0.500	0.500	0.500	0.500	-
IE0002R cadmium	0.025	0.070	0.110	0.100	0.070	0.025	0.050	0.050	0.050	0.100	0.110	-
IE0002R mercury	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	50.000	-
IS0002R cadmium	0.081	0.021	0.012	0.009	0.011	0.010	0.011	0.010	0.006	0.010	0.016	0.042
IS0002R lead	0.809	0.804	0.617	0.834	0.399	0.562	0.282	0.328	0.324	0.295	0.635	2.436
IS0090R cadmium	0.028	0.008	0.008	0.016	0.021	0.009	0.012	0.005	0.007	0.006	0.005	0.005
IS0090R lead	0.441	0.349	0.430	1.633	0.909	0.895	0.673	0.388	0.386	1.192	0.922	0.453
LT0015R cadmium	0.519	0.241	0.180	0.124	0.134	0.103	0.333	0.235	0.122	0.086	0.555	0.202
LT0015R lead	48.122	24.738	10.762	8.211	7.591	10.175	7.994	7.334	2.623	2.322	7.845	4.289
LV0010F cadmium	-	0.090	0.140	0.310	0.010	0.010	-	0.320	0.230	0.110	0.030	0.030
LV0010F lead	-	5.300	2.500	4.300	0.200	0.300	-	0.500	3.000	0.600	0.400	1.700
LV0010F precipitation_amount	-	53.500	51.700	16.100	28.700	48.800	-	58.200	9.200	44.900	94.100	50.900
LV0016F cadmium	-	0.030	0.100	0.060	0.010	0.010	-	0.010	0.060	0.080	0.010	0.170
LV0016F lead	-	2.700	2.100	0.400	0.100	0.100	-	0.100	1.800	0.900	0.400	3.100
LV0016F precipitation_amount	-	37.600	75.400	30.400	25.700	64.100	-	90.300	16.300	45.900	47.300	36.600
NL0009R cadmium	0.067	0.067	0.075	0.145	0.104	0.083	0.057	0.069	0.097	0.107	-	-
NL0009R lead	1.308	1.766	2.516	4.634	2.585	2.177	1.524	1.685	2.474	2.390	-	-
NL0091R cadmium	0.052	0.046	0.080	0.153	0.063	0.089	0.026	0.065	0.043	0.042	0.049	0.054
NL0091R lead	2.830	2.541	2.782	6.708	3.213	4.485	3.012	3.674	2.093	2.657	3.183	3.650
NL0091R mercury	8.966	8.541	11.814	19.836	9.820	19.538	8.790	31.416	13.418	5.780	5.823	5.683
NO0001R cadmium	0.017	0.031	0.014	0.065	0.044	0.030	0.019	0.013	0.027	0.045	0.026	0.025
NO0001R lead	0.661	0.937	0.730	2.383	1.224	1.068	0.618	1.029	1.549	2.096	1.423	1.261
NO0039R cadmium	0.005	0.004	0.003	0.013	0.015	0.010	0.004	0.022	0.021	0.034	0.048	0.025
NO0039R lead	0.151	0.120	0.150	0.245	0.460	0.160	0.222	0.102	0.142	0.502	1.043	0.286
NO0039R precipitation_amount	202.356	138.025	210.509	41.082	60.287	177.962	66.785	148.440	35.605	25.541	1.242	75.288
NO0041R cadmium	0.030	0.021	0.027	0.054	0.077	0.032	0.022	0.047	0.040	0.099	0.022	0.013
NO0041R lead	0.510	0.609	3.120	1.592	1.137	0.855	1.310	2.204	1.920	2.096	0.632	0.428
NO0041R precipitation_amount	25.287	37.580	11.911	94.203	68.248	109.268	101.498	125.287	60.477	213.981	187.325	71.433
NO0047R cadmium	0.058	0.099	0.124	0.140	0.093	0.079	0.147	0.061	0.124	0.057	0.383	0.215
NO0047R lead	0.497	0.969	1.556	2.077	1.492	2.155	2.435	1.346	2.144	1.330	8.732	2.353
NO0047R precipitation_amount	24.841	19.521	31.019	45.095	28.153	25.987	63.357	65.147	35.446	27.261	14.681	15.160
NO0055R cadmium	0.020	0.014	0.038	0.029	0.014	0.032	0.017	0.008	0.009	0.021	0.014	0.008
NO0055R lead	0.197	0.343	0.212	1.113	0.435	0.903	0.581	0.385	0.249	1.123	0.796	0.358
NO0055R precipitation_amount	24.044	7.994	7.580	16.624	34.618	63.185	28.148	26.147	49.395	12.390	16.846	17.802
NO0056R cadmium	0.021	0.043	0.017	0.067	0.020	0.026	0.029	0.022	0.054	0.071	0.036	0.030
NO0056R lead	0.755	0.867	0.260	2.190	0.791	0.828	0.551	0.585	2.029	1.800	0.923	0.724
NO0056R precipitation_amount	38.154	36.400	16.784	117.197	90.160	103.821	130.860	76.624	52.835	257.707	326.146	82.867
NO0092R cadmium	0.016	0.021	0.012	0.017	0.029	0.024	0.019	0.022	0.007	0.019	0.015	0.020
NO0092R lead	0.301	0.206	0.241	0.418	0.342	0.303	0.445	0.592	0.332	1.178	1.514	0.198
NO0092R precipitation_amount	107.070	50.796	120.955	35.637	62.325	59.141	51.944	80.255	75.254	30.732	3.121	55.191
NO0093R cadmium	0.025	0.036	0.040	0.029	0.023	0.046	0.005	0.002	0.011	0.041	0.033	0.007
NO0093R lead	0.497	0.272	0.339	0.869	0.512	0.687	0.336	0.192	0.716	2.295	1.713	0.872
NO0093R precipitation_amount	36.752	32.740	21.020	60.064	79.237	66.305	101.751	82.229	24.459	130.828	146.020	39.969
NO0094R cadmium	0.008	0.015	0.043	0.035	0.042	0.039	0.016	0.027	0.048	0.041	0.095	0.038
NO0094R lead	0.987	0.566	0.348	1.273	1.014	0.669	0.277	0.371	0.469	1.273	2.310	0.644
NO0094R precipitation_amount	59.201	56.876	46.338	57.514	81.212	121.846	69.770	59.872	66.303	233.757	135.700	59.459
NO0094R vanadium	0.135	0.083	0.064	0.232	0.199	0.145	0.065	0.070	0.190	0.138	0.168	0.104
NO0095R cadmium	0.010	0.011	0.006	0.038	0.022	0.022	0.006	0.052	0.040	0.020	0.022	0.018
NO0095R lead	0.617	0.493	0.286	1.072	0.703	0.807	0.356	0.813	0.803	0.729	0.768	0.867
NO0095R precipitation_amount	256.242	292.261	145.859	118.694	172.834	152.166	49.173	148.058	147.230	477.070	385.797	249.332
NO0099R cadmium	0.021	0.014	0.015	0.050	0.050	0.030	0.025	0.029	0.059	0.048	0.036	0.038

NO0099R lead	1.416	0.895	0.589	2.291	1.764	1.566	0.799	1.727	1.810	1.856	1.736	1.385
NO0099R mercury	6.200	3.300	9.100	12.600	12.400	15.966	7.200	-	3.200	6.800	3.900	11.700
PT0001R cadmium	0.425	0.425	0.425	0.425	0.425	-	0.425	-	0.425	0.425	0.425	0.425
PT0001R lead	0.645	0.645	0.645	0.645	0.645	-	0.645	-	0.645	0.745	0.645	1.448
PT0003R lead	0.645	0.645	1.357	1.126	0.645	0.645	0.645	0.645	0.645	0.645	0.984	0.645
PT0003R cadmium	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.434	0.425
PT0004R cadmium	0.425	0.425	0.425	0.425	0.425	-	-	-	0.425	0.425	0.425	0.425
PT0004R lead	0.645	0.645	1.680	0.712	0.645	-	-	-	0.645	0.645	0.645	0.645
PT0010R lead	1.464	3.713	0.903	1.093	2.114	1.835	1.432	1.051	1.313	4.163	4.516	1.327
PT0010R cadmium	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425	0.425
SE0002R mercury	8.300	10.600	6.600	10.400	10.800	6.900	5.800	12.600	10.700	6.500	9.500	8.000
SE0005R cadmium	0.010	0.030	0.040	0.030	0.082	0.110	0.018	0.011	0.070	0.040	0.020	0.058
SE0005R lead	0.468	0.905	0.700	0.790	0.525	0.430	0.448	0.252	2.320	0.995	0.720	0.804
SE0005R mercury	4.000	4.900	15.300	6.900	11.900	6.000	5.000	5.100	6.600	3.100	3.700	3.600
SE0011R mercury	17.600	19.100	11.000	12.200	28.800	11.200	9.100	10.800	9.200	8.700	10.100	12.200
SE0012R cadmium	0.060	0.060	0.060	0.170	-	0.120	-	-	-	-	-	-
SE0012R lead	2.540	2.515	2.050	6.160	-	2.730	-	-	-	-	-	-
SE0051R cadmium	0.120	0.080	0.080	0.080	0.050	0.020	0.020	0.040	0.040	0.070	0.050	0.040
SE0051R lead	2.680	2.540	1.930	3.140	2.480	0.790	1.120	1.780	1.820	3.610	2.820	1.810
SE0097R cadmium	0.026	0.033	0.100	0.083	0.024	0.025	0.080	0.053	0.047	0.070	0.050	0.050
SE0097R lead	1.421	1.324	1.810	2.921	1.329	1.126	0.760	1.418	1.967	2.450	1.610	1.090
SK0002R cadmium	0.900	0.200	0.300	0.300	1.500	1.900	1.900	3.000	0.900	0.500	0.300	0.400
SK0002R lead	7.000	5.000	6.000	4.000	6.000	4.000	3.000	5.000	2.000	6.000	5.000	2.000
SK0004R cadmium	2.600	1.000	0.200	0.300	0.100	0.200	0.400	0.100	0.100	0.400	0.200	0.100
SK0004R lead	5.000	3.000	2.000	1.000	2.000	2.000	1.000	2.000	3.000	10.000	2.000	4.000
SK0005R cadmium	0.100	0.100	0.100	0.400	0.200	0.100	0.100	0.100	0.100	0.200	0.100	0.100
SK0005R lead	4.000	5.000	2.000	2.000	2.000	2.000	1.000	2.000	1.000	3.000	1.000	2.000
SK0006R cadmium	0.100	0.200	0.200	0.100	0.200	0.100	-	0.100	0.100	0.200	0.300	0.300
SK0006R lead	4.000	5.000	4.000	1.000	1.000	3.000	2.000	2.000	2.000	3.000	4.000	5.000
SK0007R cadmium	0.100	0.200	0.100	0.200	0.100	-	0.100	0.100	0.200	0.300	0.300	-
SK0007R lead	4.000	4.141	1.000	1.000	3.000	2.000	2.000	2.000	3.000	4.000	5.000	-
SK0007R precipitation_amount	40.100	83.200	28.300	24.900	7.700	62.600	18.500	41.500	26.400	56.000	41.700	-

Annex A4

Monthly mean values on data for heavy metals in air

BE0004R lead	54.000	45.000	39.000	33.000	40.000	35.000	30.000	34.000	44.000	47.000	51.000	52.000
CZ0001R cadmium	0.365	0.298	0.340	0.434	0.434	0.244	0.117	0.120	0.292	0.504	0.346	0.310
CZ0001R lead	7.625	9.430	10.330	8.282	8.282	5.670	3.730	6.188	10.658	21.556	10.978	11.625
CZ0003R cadmium	0.356	0.284	0.260	0.262	0.275	0.225	0.327	0.154	0.412	0.560	0.310	0.410
CZ0003R lead	6.794	5.168	8.446	6.830	8.725	4.442	6.205	4.842	12.546	20.794	11.930	29.547
DE0001R lead	7.300	6.600	3.000	7.900	6.600	4.200	2.200	3.500	8.300	10.700	8.000	9.300
DE0003R lead	1.300	1.500	3.500	3.200	3.000	4.800	3.100	3.800	3.800	2.400	2.000	1.900
DE0004R lead	13.200	10.800	8.000	7.300	8.100	8.500	5.700	10.500	9.900	9.400	10.600	8.700
DE0005R lead	5.400	4.100	3.700	7.300	5.500	4.700	3.300	5.500	5.700	4.900	2.500	2.100
DE0007R lead	12.000	6.200	3.000	10.400	17.900	14.000	15.600	4.200	10.700	15.400	12.700	15.700
DE0008R lead	6.900	5.100	5.500	8.400	11.900	4.700	5.300	5.300	9.400	7.600	2.700	5.100
DE0009R lead	5.800	4.500	2.100	7.600	3.000	3.300	3.000	2.300	8.100	17.000	16.100	13.500
DK0003R lead	6.084	5.248	3.555	7.834	4.931	1.642	1.396	2.277	6.234	10.480	8.288	10.655
DK0003R cadmium	0.295	0.233	0.168	0.242	0.490	0.122	0.140	0.183	0.281	0.420	0.265	0.306
DK0005R lead	7.055	6.449	4.008	10.183	5.310	4.527	2.717	3.320	9.440	15.457	11.816	10.342
DK0005R cadmium	0.333	0.344	0.177	0.357	0.205	0.221	0.163	0.174	0.297	0.519	0.444	0.326
DK0008R cadmium	0.266	0.221	0.164	0.217	0.163	0.197	0.150	0.194	0.221	0.292	0.277	0.240
DK0008R lead	4.388	3.745	1.866	6.987	3.122	3.277	1.309	2.183	6.210	10.843	9.268	6.071
DK0010G lead	1.162	2.427	1.638	0.702	0.324	0.065	0.019	0.015	0.029	0.061	0.240	0.547
DK0010G mercury	1.767	1.702	1.456	1.044	0.839	1.426	1.521	1.383	-	-	-	-
DK0015G mercury	-	-	-	-	1.924	1.961	1.338	0.880	1.180	1.109	1.116	1.186
DK0031R cadmium	0.117	0.170	0.116	0.193	0.057	0.136	0.049	0.020	0.159	0.176	0.212	0.300
DK0031R lead	3.446	4.055	1.933	6.815	3.669	3.477	1.619	1.524	5.173	7.832	6.137	5.695
FI0096R cadmium	0.032	0.059	0.040	0.035	0.024	0.027	0.047	0.023	0.024	0.096	0.039	0.025
FI0096R lead	0.825	0.902	1.069	0.846	0.859	0.659	1.386	0.454	0.867	2.749	1.439	0.745
FI0096R mercury	1.475	1.533	1.450	1.400	1.320	1.425	1.320	1.267	1.233	1.220	-	1.238
GB0014R cadmium	0.700	0.266	0.149	0.230	0.145	0.120	0.110	0.101	0.420	0.130	0.260	0.120
GB0014R lead	6.600	5.055	4.106	5.100	4.990	4.500	4.600	6.694	8.600	9.665	9.600	9.600
GB0090R cadmium	0.427	0.211	0.380	0.216	0.094	0.180	0.110	0.189	0.160	0.188	0.360	0.270
GB0090R lead	20.068	10.617	8.823	6.470	3.587	6.200	8.290	9.087	8.700	9.168	25.100	15.900
GB0091R cadmium	0.067	0.033	0.025	0.015	0.090	0.051	0.024	0.030	0.056	0.053	0.042	0.040
GB0091R lead	1.673	1.154	1.337	1.710	2.080	1.307	2.017	2.020	3.381	2.982	2.945	2.561
IE0031R mercury	1.855	1.875	1.934	2.025	1.995	1.801	1.788	1.663	1.531	1.686	1.677	1.681
IS0091R cadmium	0.077	0.166	0.181	0.071	0.151	0.022	0.076	0.048	0.023	0.027	0.032	0.141
IS0091R lead	0.711	0.814	0.625	0.776	0.526	0.382	0.640	0.243	0.491	0.220	0.502	0.562
IS0091R mercury	0.643	1.467	1.106	2.029	1.426	1.379	2.368	1.336	1.900	2.343	2.400	1.998
LT0015R cadmium	0.164	0.118	0.102	0.267	0.132	0.125	0.080	0.028	0.149	0.230	0.395	0.306
LT0015R lead	8.097	4.469	2.910	8.820	3.065	2.627	2.452	1.590	2.940	9.700	12.960	9.807
LV0010R lead	5.603	3.438	3.296	27.307	45.722	15.550	25.164	9.017	5.993	10.991	17.123	17.147
LV0010R cadmium	0.158	0.088	0.107	1.016	1.236	0.763	0.470	0.211	0.243	0.520	0.577	0.691
LV0016R lead	4.275	1.272	2.624	8.763	3.061	3.020	11.601	2.523	2.354	7.401	7.449	4.654
LV0016R cadmium	0.090	0.048	0.160	0.560	0.190	0.165	0.180	0.113	0.156	0.377	0.261	0.227
NL0009R cadmium	0.293	0.150	0.149	0.293	0.122	0.125	0.052	0.080	0.210	0.243	0.164	0.220
NL0009R lead	22.126	6.375	6.530	12.319	6.428	5.083	2.446	4.847	10.752	11.247	7.858	9.754
NO0042G cadmium	0.039	0.053	0.047	0.022	0.010	0.002	0.000	0.006	0.000	0.007	0.005	0.017
NO0042G lead	1.278	1.733	1.646	0.815	0.391	0.071	0.062	0.050	0.027	0.260	0.303	0.553
NO0042G mercury	-	1.952	1.895	1.155	0.885	1.407	1.467	1.353	1.623	1.551	1.621	1.674
NO0099R cadmium	0.047	0.041	0.071	0.107	0.080	0.052	0.028	0.044	0.110	0.083	0.055	0.078
NO0099R lead	0.923	1.251	2.733	3.677	2.580	2.368	1.154	1.230	3.823	3.719	2.897	2.959

NO0099R mercury	2.000	1.700	1.250	-	1.775	1.880	1.470	-	1.640	2.190	0.560	1.518
SE0002R mercury	1.386	1.350	1.389	1.300	1.386	1.338	1.233	1.125	1.178	1.617	1.562	1.571
SK0002R cadmium	0.054	0.075	0.242	0.355	0.221	0.110	0.258	0.175	0.136	0.076	0.143	0.064
SK0002R lead	0.748	1.561	2.487	9.843	7.091	4.168	2.260	4.628	5.642	2.925	2.567	0.413
SK0004R cadmium	0.387	0.261	0.322	0.356	0.402	0.309	0.125	0.249	0.319	0.512	0.382	0.370
SK0004R lead	9.468	6.278	6.304	8.334	10.935	9.284	4.369	7.483	11.604	21.358	15.768	12.302
SK0005R cadmium	0.388	0.543	0.478	0.403	0.438	0.425	0.165	0.444	0.453	0.628	0.233	0.316
SK0005R lead	12.165	11.058	11.173	12.232	13.975	13.512	4.952	9.632	13.436	14.390	10.142	13.857
SK0006R cadmium	0.646	0.482	0.384	0.579	0.360	0.245	0.254	0.586	0.324	1.154	1.063	0.684
SK0006R lead	17.548	13.299	11.746	12.794	10.652	9.004	8.485	18.812	9.336	42.568	36.696	24.760
SK0007R cadmium	0.705	0.575	0.420	0.617	0.345	0.280	0.177	0.322	0.596	0.646	0.849	0.649
SK0007R lead	21.758	13.077	11.853	17.367	12.777	12.038	7.206	11.787	23.913	26.600	30.555	26.281

Annex A5

Results from the 2000 intercomparison

Table A5.1. Participating laboratories in the EMEP intercompaarison of heavy metals in precipitation 2000. The numbers in front are used in tables

No	Laboratory identification
1	Federal Environmental Agency, Austria
3	Czech Hydrometeorological Institute, Czech Republic
5	Finnish Meteorological Institute, Finland
6	Laboratories Wollf, France
7	IfE Leipzig GmbH, Umweltlaborator., Germany
8	Umweltbundesamt, Germany
14	RIVM Laboratory of Inorganic Analytical Chemistry, The Netherlands
15	The Norwegian Institute for Air Research, Norway
16	Inst. Of Meteorology and Water Management, Poland
19	Instituto de Salud Carlos III, Centro Nacional de Sanidad Ambiental Area de Contaminacion Atmosferica, Spain
23	AEA Technology, National Environmental Techn. Centre, United Kingdom
24	Federal Hydrometeorological Institute, Yugoslavia
26	Ontario Ministry of Environment, Canada
31	Slovak Hydrometeorological Institute, Slovakia
32	Institute of physics, Aerosol research laboratory, Lithuania
33	Latvian Hydrometeorological Agency, Latvia
36	Hydrometeorological Institute of Slovenia, Slovenia
38	Estonian Environmental Research Centre, Estonia
39	Institute of Environmental Protection, Poland

Table A5.2. Analytical results for Cd in synthetic precipitation samples

Cd
SAMPLE NO.: H1
THEORETICAL VALUE: 0.090
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 0.127
MEDIAN: 0.100
STANDARD DEVIATON: 0.140
REL. ST. DEVIATION (%): 110.001

RUN 2:
NUMBER OF LABORATORIES: 23
ARITHMETIC MEAN VALUE: 0.099
MEDIAN: 0.100
STANDARD DEVIATON: 0.018
REL. ST. DEVIATION (%): 18.581

RESULTS IN DECREASING ORDER:
6 < 2
24 0.780 *
39 < 0.3
19 < 0.2
115 0.140
118 0.140
119 0.117
14 0.110
112 0.110
117 0.110
7 0.105
8 0.104
110 < 0.1
1 0.100
38 0.100
120 0.100
121 0.100
15 0.099
31 0.098
3 0.097
5 0.090
26 0.090
36 0.090
123 0.086
33 0.081
23 0.075
32 0.075
16 0.061

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: H2
THEORETICAL VALUE: 0.007
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 0.035
MEDIAN: 0.014
STANDARD DEVIATON: 0.068
REL. ST. DEVIATION (%): 193.915

RUN 2:
NUMBER OF LABORATORIES: 11
ARITHMETIC MEAN VALUE: 0.016
MEDIAN: 0.011
STANDARD DEVIATON: 0.010
REL. ST. DEVIATION (%): 66.267

RESULTS IN DECREASING ORDER:
6 < 2
39 < 0.3
24 0.250 *
19 < 0.2
110 < 0.1
112 < 0.1
118 < 0.1
120 < 0.1
115 < 0.06
117 < 0.05
26 < 0.05
3 < 0.04
1 < 0.04
73 0.038
119 < 0.03
32 < 0.03
38 0.03
36 < 0.02
121 < 0.02
8 0.006
33 0.020
31 0.019
7 0.016
15 0.011
5 0.010
14 0.010
16 0.008
23 0.005

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: H3
THEORETICAL VALUE 1.000
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 1.207
MEDIAN: 1.000
STANDARD DEVIATON: 1.441
REL. ST. DEVIATION (%): 119.418

RUN 2:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 0.937
MEDIAN: 1.000
STANDARD DEVIATON: 0.186
REL. ST. DEVIATION (%): 19.847

RESULTS IN DECREASING ORDER:
24 8.500 *
6 < 2
19 1.150
112 1.090
31 1.062
115 1.060
16 1.030
118 1.020
119 1.020
7 1.017
8 1.010
3 1.000
5 1.000
14 1.000
15 1.000
39 1.000
108 1.000
70 1.000
26 0.980
1 0.970
33 0.957
38 0.920
36 0.900
110 0.900
121 0.900
32 0.850
23 0.620
123 0.610
117 0.220

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Cd
SAMPLE NO.: H4
THEORETICAL VALUE 1.400
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 1.478
MEDIAN: 1.407
STANDARD DEVIATON: 0.852
REL. ST. DEVIATION (%): 57.669

RUN 2:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 1.325
MEDIAN: 1.403
STANDARD DEVIATON: 0.277
REL. ST. DEVIATION (%): 20.873

RESULTS IN DECREASING ORDER:
24 5.600 *
6 < 2
108 1.600
16 1.540
19 1.500
39 1.500
31 1.486
118 1.470
3 1.450
14 1.450
115 1.450
7 1.440
112 1.440
119 1.420
8 1.410
33 1.403
15 1.400
120 1.400
1 1.360
26 1.350
5 1.300
36 1.300
110 1.300
121 1.300
32 1.260
38 1.240
23 1.000
123 0.810
117 0.200

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Table A5.3. Analytical results for Pb in synthetic precipitation samples

Pb

SAMPLE NO.: H1
THEORETICAL VALUE 2.000
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 2.397
MEDIAN: 2.000
STANDARD DEVIATON: 2.746
REL. ST. DEVIATION (%): 114.579

RUN 2:
NUMBER OF LABORATORIES: 25
ARITHMETIC MEAN VALUE: 1.865
MEDIAN: 2.000
STANDARD DEVIATON: 0.434
REL. ST. DEVIATION (%): 23.251

RESULTS IN DECREASING ORDER:
24 15.700 *
6 < 10
39 < 3
118 2.400
119 2.320
3 2.200
8 2.170
31 2.110
5 2.100
14 2.100
112 2.100
117 2.100
1 2.050
16 2.000
110 2.000
33 0.480
120 2.000
121 2.000
38 1.980
115 1.940
15 1.900
123 1.900
26 1.700
36 1.700
32 1.600
23 1.500
7 1.420
108 < 1.4
19 0.850

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Pb

SAMPLE NO.: H2
THEORETICAL VALUE 4.500
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 4.857
MEDIAN: 4.500
STANDARD DEVIATON: 2.494
REL. ST. DEVIATION (%): 51.346

RUN 2:
NUMBER OF LABORATORIES: 26
ARITHMETIC MEAN VALUE: 4.398
MEDIAN: 4.470
STANDARD DEVIATON: 0.756
REL. ST. DEVIATION (%): 17.193

RESULTS IN DECREASING ORDER:
24 16.770 *
6 < 10
39 7.000
120 5.000
23 4.930
119 4.890
5 4.800
8 4.750
122 4.740
14 4.700
110 4.600
117 4.600
115 4.550
1 4.500
121 4.500
108 < 1.4
38 4.440
31 4.420
3 4.400
15 4.300
118 4.200
16 4.100
32 4.100
26 3.850
7 3.740
36 3.600
33 3.580
19 3.170
23 2.900

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Pb

SAMPLE NO.: H3
THEORETICAL VALUE 58.000
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 57.013
MEDIAN: 57.600
STANDARD DEVIATON: 6.292
REL. ST. DEVIATION (%): 11.036

RUN 2:
NUMBER OF LABORATORIES: 27
ARITHMETIC MEAN VALUE: 57.274
MEDIAN: 57.600
STANDARD DEVIATON: 3.910
REL. ST. DEVIATION (%): 6.826

RESULTS IN DECREASING ORDER:
117 72.000 *
123 68.000
14 64.000
5 61.000
8 60.800
3 59.900
118 59.800
119 59.300
112 58.670
110 58.500
16 58.000
121 58.000
115 57.810
31 57.770
6 57.600
33 57.560
1 57.000
120 57.000
7 56.600
19 56.150
32 55.000
26 54.700
15 54.000
108 53.900
38 53.700
24 51.630
39 51.000
36 49.000
23 35.000 *

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Pb

SAMPLE NO.: H4
THEORETICAL VALUE 45.000
UNIT: ng/ml

RUN 1:
NUMBER OF LABORATORIES: 29
ARITHMETIC MEAN VALUE: 43.794
MEDIAN: 45.000
STANDARD DEVIATON: 3.782
REL. ST. DEVIATION (%): 8.635

RUN 2:
NUMBER OF LABORATORIES: 28
ARITHMETIC MEAN VALUE: 44.251
MEDIAN: 45.000
STANDARD DEVIATON: 2.924
REL. ST. DEVIATION (%): 6.608

RESULTS IN DECREASING ORDER:
123 50.500
117 48.600
8 47.800
14 47.200
5 47.000
31 46.540
3 45.800
112 45.800
115 45.620
110 45.600
119 45.500
38 45.200
118 45.100
16 45.000
23 31.000 *
121 45.000
1 44.400
120 44.000
33 43.410
15 43.000
32 42.600
7 42.500
26 42.300
19 42.100
24 41.750
108 39.400
6 39.300
36 39.000
39 39.000

< : DATA UNUSED IN RUN 1 AND 2
* : DATA UNUSED IN RUN 2

Annex B

Codes of countries, regions and seas

Country/Region/Sea	Code	Country/Region/Sea	Code
Albania	AL	Norway	NO
Armenia	AM	Poland	PL
Austria	AT	Portugal	PT
Azerbaijan	AZ	Republic of Moldova	MD
Belarus	BY	Romania	RO
Belgium	BE	Russian Federation (European part)	RU
Bosnia and Herzegovina	BA	Slovakia	SK
Bulgaria	BG	Slovenia	SI
Croatia	HR	Spain	ES
Cyprus	CY	Sweden	SE
Czech Republic	CZ	Switzerland	CH
Denmark	DK	The Former Yugoslav Republic of Macedonia	MK
Estonia	EE	Turkey	TR
Finland	FI	Ukraine	UA
France	FR	United Kingdom	GB
Georgia	GE	Yugoslavia	YU
Germany	DE		
Greece	GR		
Hungary	HU	Africa	AF
Iceland	IS	Asia	AS
Ireland	IE	Atlantic	ATL
Italy	IT	Baltic Sea	BAS
Kazakhstan	KZ	Black Sea	BLS
Latvia	LV	Caspian Sea	CAS
Lithuania	LT	English Channel	ECH
Luxembourg	LU	North Sea	NOS
Malta	MT	Mediterranean Sea	MED
Netherlands	NL	Arctic	ARC

Annex C

Country-to-country deposition matrices for 2000

Table C1. Matrix of **lead** country-to-country depositions in 2000, t/y

	al	**am**	**at**	**az**	**by**	**be**	**ba**	**bg**	**hr**	**cy**	**cz**	**dk**	**ee**	**fi**	**fr**	**ge**	**de**	**gr**	**hu**	**is**	**ie**	**it**	**kz**	
al	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.6	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1	5.5	0.1	0.0	0.0	9.9	0.0	**al**
am	0.0	0.0	0.0	3.8	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	1.7	0.0	0.1	0.0	0.0	0.0	0.1	0.0	**am**
at	0.0	0.0	4.3	0.0	0.0	0.8	0.0	0.4	4.0	0.0	1.6	0.0	0.0	0.0	1.4	0.0	6.1	0.4	0.6	0.0	0.1	58.6	0.0	**at**
az	0.0	0.0	0.0	26.2	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.2	0.0	0.0	0.0	0.3	0.1	**az**
by	0.1	0.0	0.1	0.0	15.8	0.7	0.0	1.6	1.4	0.0	2.6	0.1	0.4	0.2	0.7	0.1	6.0	1.7	0.6	0.0	0.2	7.7	0.0	**by**
be	0.0	0.0	0.0	0.0	0.0	26.8	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	4.9	0.0	3.3	0.0	0.0	0.0	0.2	0.8	0.0	**be**
ba	0.3	0.0	0.1	0.0	0.0	0.1	1.5	0.8	10.1	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.4	1.2	0.3	0.0	0.0	22.2	0.0	**ba**
bg	0.5	0.0	0.1	0.1	0.1	0.1	0.0	54.1	1.5	0.1	0.3	0.0	0.0	0.0	0.1	0.1	0.6	10.4	0.4	0.0	0.0	9.3	0.0	**bg**
hr	0.1	0.0	0.2	0.0	0.0	0.1	0.2	0.7	40.2	0.0	0.2	0.0	0.0	0.0	0.4	0.0	0.6	0.9	0.6	0.0	0.0	33.0	0.0	**hr**
cy	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.9	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.0	0.0	0.3	0.0	**cy**
cz	0.0	0.0	0.8	0.0	0.0	0.7	0.0	0.2	1.6	0.0	22.6	0.0	0.0	0.0	1.0	0.0	13.2	0.2	0.5	0.0	0.1	10.3	0.0	**cz**
dk	0.0	0.0	0.0	0.0	0.0	1.2	0.0	0.0	0.1	0.0	0.2	0.9	0.0	0.0	0.7	0.0	4.1	0.0	0.0	0.0	0.2	0.7	0.0	**dk**
ee	0.0	0.0	0.0	0.0	0.2	0.3	0.0	0.1	0.2	0.0	0.3	0.0	7.4	0.3	0.2	0.0	1.6	0.1	0.1	0.0	0.1	1.3	0.0	**ee**
fi	0.0	0.0	0.1	0.0	0.6	1.2	0.0	0.5	0.6	0.0	1.0	0.2	3.6	14.8	1.1	0.1	6.0	0.4	0.2	0.0	0.3	4.6	0.0	**fi**
fr	0.0	0.0	0.0	0.0	0.0	7.7	0.0	0.1	0.8	0.0	0.1	0.0	0.0	0.0	72.0	0.0	8.3	0.3	0.0	0.0	1.6	63.3	0.0	**fr**
ge	0.0	0.0	0.0	4.8	0.0	0.0	0.0	0.3	0.1	0.2	0.0	0.0	0.0	0.0	0.0	37.9	0.1	0.4	0.0	0.0	0.0	0.7	0.0	**ge**
de	0.0	0.0	1.0	0.0	0.1	18.3	0.0	0.2	1.9	0.0	5.7	0.2	0.0	0.0	14.7	0.0	211.7	0.3	0.3	0.0	1.4	45.7	0.0	**de**
gr	1.1	0.0	0.0	0.0	0.0	0.1	0.0	7.5	1.0	0.1	0.1	0.0	0.0	0.0	0.2	0.1	0.3	65.4	0.2	0.0	0.0	12.6	0.0	**gr**
hu	0.1	0.0	0.5	0.0	0.0	0.2	0.1	0.9	9.9	0.0	1.3	0.0	0.0	0.0	0.3	0.0	1.5	0.8	9.4	0.0	0.0	15.8	0.0	**hu**
is	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.3	0.0	0.0	0.1	0.2	0.1	0.0	**is**
ie	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.2	0.0	0.0	0.0	16.2	0.2	0.0	**ie**
it	0.3	0.0	0.3	0.0	0.0	0.3	0.1	0.8	7.1	0.1	0.2	0.0	0.0	0.0	4.4	0.0	1.2	2.8	0.2	0.0	0.1	718.8	0.0	**it**
kz	0.0	0.0	0.0	2.6	0.3	0.1	0.0	0.7	0.5	0.1	0.3	0.0	0.1	0.1	0.2	1.0	0.8	0.5	0.1	0.0	0.0	2.3	3.6	**kz**
lv	0.0	0.0	0.0	0.0	0.5	0.3	0.0	0.2	0.3	0.0	0.4	0.1	1.1	0.1	0.3	0.0	2.4	0.1	0.1	0.0	0.1	1.7	0.0	**lv**
lt	0.0	0.0	0.0	0.0	1.0	0.3	0.0	0.2	0.4	0.0	0.7	0.1	0.2	0.1	0.3	0.0	2.9	0.2	0.1	0.0	0.1	2.1	0.0	**lt**
lu	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.5	0.0	0.0	0.0	0.0	0.2	0.0	**lu**
mt	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**mt**
nl	0.0	0.0	0.0	0.0	0.0	11.5	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	2.5	0.0	5.4	0.0	0.0	0.0	0.4	0.6	0.0	**nl**
no	0.0	0.0	0.0	0.0	0.2	2.1	0.0	0.2	0.3	0.0	0.8	0.4	0.2	0.3	1.6	0.0	7.3	0.3	0.2	0.0	0.8	2.0	0.0	**no**
pl	0.1	0.0	0.7	0.0	1.1	2.4	0.1	1.2	4.4	0.0	27.3	0.3	0.1	0.1	2.6	0.0	40.6	1.1	2.1	0.0	0.5	20.9	0.0	**pl**
pt	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	**pt**
md	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.1	0.5	0.0	0.2	0.0	0.0	0.0	0.1	0.0	0.3	0.7	0.1	0.0	0.0	2.2	0.0	**md**
ro	0.4	0.0	0.2	0.1	0.2	0.3	0.1	10.3	4.7	0.0	1.5	0.0	0.0	0.0	0.4	0.1	2.7	4.6	2.7	0.0	0.1	18.0	0.0	**ro**
ru	0.6	0.0	0.6	12.2	12.5	4.3	0.2	11.7	7.5	0.8	7.3	0.6	13.4	7.3	4.4	14.4	26.4	11.9	2.5	0.0	1.1	46.2	5.0	**ru**
sk	0.1	0.0	0.3	0.0	0.0	0.2	0.0	0.4	2.4	0.0	4.2	0.0	0.0	0.0	0.3	0.0	1.8	0.4	2.4	0.0	0.0	6.9	0.0	**sk**
si	0.0	0.0	0.2	0.0	0.0	0.1	0.0	0.3	6.2	0.0	0.1	0.0	0.0	0.0	0.2	0.0	0.4	0.2	0.2	0.0	0.0	22.1	0.0	**si**
es	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	2.1	0.0	0.3	0.2	0.0	0.0	0.3	6.7	0.0	**es**
se	0.1	0.0	0.1	0.0	0.5	2.5	0.0	0.7	0.7	0.0	1.6	0.9	0.8	2.1	1.8	0.0	11.1	0.8	0.3	0.0	0.5	4.4	0.0	**se**
ch	0.0	0.0	0.1	0.0	0.0	0.3	0.0	0.0	0.3	0.0	0.0	0.0	0.0	0.0	2.6	0.0	1.8	0.0	0.0	0.0	0.1	38.5	0.0	**ch**
mk	1.0	0.0	0.0	0.0	0.0	0.0	0.0	3.3	0.4	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.1	5.6	0.1	0.0	0.0	4.3	0.0	**mk**
tr	0.4	0.0	0.1	3.4	0.1	0.1	0.0	8.0	1.3	7.7	0.3	0.0	0.0	0.0	0.4	5.6	0.8	19.6	0.3	0.0	0.0	15.9	0.0	**tr**
ua	0.4	0.0	0.3	0.8	2.8	1.1	0.1	10.0	5.5	0.2	4.3	0.1	0.4	0.2	1.2	0.9	9.4	8.2	2.7	0.0	0.2	27.3	0.1	**ua**
gb	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0	2.8	0.0	2.1	0.0	0.0	0.0	8.5	1.3	0.0	**gb**
yu	1.5	0.0	0.1	0.0	0.0	0.1	0.2	5.4	6.2	0.0	0.5	0.0	0.0	0.0	0.3	0.0	1.0	4.1	1.0	0.0	0.0	22.5	0.0	**yu**
af	0.4	0.0	0.0	0.0	0.0	0.2	0.1	2.3	1.3	0.7	0.1	0.0	0.0	0.0	1.0	0.1	0.5	11.3	0.1	0.0	0.1	32.0	0.0	**af**
as	0.1	0.0	0.0	10.1	0.0	0.0	0.0	1.0	0.3	3.5	0.1	0.0	0.0	0.0	0.1	1.1	0.2	4.5	0.0	0.0	0.0	4.5	0.2	**as**
atl	0.1	0.0	0.1	0.1	0.7	7.1	0.0	0.7	1.2	0.0	1.9	0.5	1.0	1.6	11.2	0.1	16.1	0.7	0.4	0.2	27.2	13.2	0.1	**atl**
grl	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.1	0.1	0.0	**grl**
bas	0.1	0.0	0.2	0.0	0.6	2.9	0.0	0.7	1.3	0.0	2.3	0.9	3.9	3.6	2.3	0.0	19.3	0.8	0.4	0.0	0.5	7.8	0.0	**bas**
red	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**red**
bls	0.3	0.0	0.1	1.3	0.5	0.2	0.1	11.0	1.9	0.8	0.7	0.0	0.1	0.1	0.4	9.6	1.7	9.2	0.5	0.0	0.1	12.5	0.1	**bls**
cas	0.0	0.0	0.0	13.3	0.1	0.0	0.0	0.2	0.1	0.2	0.1	0.0	0.0	0.0	0.0	1.5	0.2	0.3	0.0	0.0	0.0	0.8	0.5	**cas**
nos	0.0	0.0	0.1	0.0	0.1	18.6	0.0	0.1	0.7	0.0	1.6	1.1	0.1	0.1	12.7	0.0	27.2	0.1	0.2	0.0	9.0	7.1	0.0	**nos**
mdt	3.0	0.0	0.2	0.1	0.1	0.7	0.3	11.5	14.6	12.2	0.6	0.0	0.0	0.0	8.2	0.3	2.1	79.5	0.6	0.0	0.3	323.7	0.0	**mdt**
SUM	**16**	**0**	**11**	**79**	**38**	**117**	**4**	**151**	**144**	**32**	**94**	**7**	**33**	**31**	**163**	**78**	**451**	**256**	**31**	**0**	**71**	**1664**	**10**	**SUM**
	al	**am**	**at**	**az**	**by**	**be**	**ba**	**bg**	**hr**	**cy**	**cz**	**dk**	**ee**	**fi**	**fr**	**ge**	**de**	**gr**	**hu**	**is**	**ie**	**it**	**kz**	

continued

	lv	lt	lu	nl	no	pl	pt	md	ro	ru	sk	si	es	se	ch	mk	tr	ua	gb	yu	ind	SUM	
al	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.6	0.2	0.1	0.0	0.5	0.0	0.0	0.1	0.2	0.2	0.1	5.0	13.3	**43**	**al**
am	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	1.7	0.1	0.0	0.0	8.3	**17**	**am**
at	0.0	0.0	0.0	0.2	0.0	1.6	0.5	0.0	1.2	0.5	0.7	3.8	2.0	0.0	4.5	0.0	0.2	0.2	1.1	1.6	34.8	**131**	**at**
az	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.1	3.6	0.0	0.0	0.0	0.0	0.0	0.0	1.4	0.3	0.0	0.1	24.0	**60**	**az**
by	0.0	1.5	0.0	0.3	0.0	28.5	0.3	0.2	7.4	9.8	1.8	0.3	1.1	0.1	0.5	0.0	0.6	5.4	1.7	2.7	65.8	**168**	**by**
be	0.0	0.0	0.1	1.0	0.0	0.3	0.4	0.0	0.0	0.0	0.0	0.0	1.4	0.0	0.2	0.0	0.0	0.0	3.9	0.0	13.4	**57**	**be**
ba	0.0	0.0	0.0	0.0	0.0	0.4	0.2	0.0	1.1	0.4	0.2	0.4	0.9	0.0	0.1	0.0	0.3	0.2	0.1	8.4	20.9	**71**	**ba**
bg	0.0	0.0	0.0	0.0	0.0	1.2	0.1	0.1	18.1	1.8	0.5	0.2	0.5	0.0	0.1	0.2	1.4	1.9	0.2	14.5	31.7	**150**	**bg**
hr	0.0	0.0	0.0	0.0	0.0	0.4	0.2	0.0	1.2	0.4	0.2	3.0	1.3	0.0	0.2	0.0	0.3	0.2	0.2	5.1	24.6	**115**	**hr**
cy	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	2.3	**9**	**cy**
cz	0.0	0.0	0.0	0.3	0.0	10.7	0.2	0.0	0.8	0.4	1.8	0.5	0.9	0.0	1.8	0.0	0.0	0.1	1.2	1.2	24.3	**96**	**cz**
dk	0.0	0.0	0.0	0.6	0.0	1.2	0.2	0.0	0.1	0.1	0.1	0.0	0.4	0.1	0.1	0.0	0.0	0.0	2.7	0.1	12.4	**26**	**dk**
ee	0.0	0.3	0.0	0.1	0.0	2.6	0.1	0.0	0.7	2.4	0.2	0.0	0.3	0.1	0.1	0.0	0.0	0.3	0.6	0.4	15.4	**36**	**ee**
fi	0.0	0.5	0.0	0.5	0.1	8.0	0.4	0.1	2.2	17.0	0.5	0.1	1.3	0.5	0.5	0.0	0.2	1.4	2.6	1.0	113.1	**185**	**fi**
fr	0.0	0.0	0.2	1.1	0.0	0.5	10.2	0.0	0.2	0.1	0.1	0.2	52.5	0.0	10.6	0.0	0.0	0.1	11.8	0.3	206.4	**449**	**fr**
ge	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.6	10.2	0.0	0.0	0.1	0.0	0.0	0.0	4.0	1.1	0.0	0.3	28.1	**89**	**ge**
de	0.0	0.1	0.5	6.0	0.0	12.5	2.5	0.0	0.9	0.8	0.6	0.8	8.9	0.0	25.4	0.0	0.1	0.2	15.6	1.2	132.1	**510**	**de**
gr	0.0	0.0	0.0	0.0	0.0	0.5	0.1	0.0	3.1	0.9	0.2	0.1	1.0	0.0	0.1	0.2	1.7	0.9	0.1	4.9	32.9	**136**	**gr**
hu	0.0	0.0	0.0	0.1	0.0	2.4	0.2	0.0	10.3	0.6	6.4	1.4	0.7	0.0	0.3	0.0	0.1	0.3	0.3	10.3	25.6	**100**	**hu**
is	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.0	0.2	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.6	0.0	41.3	**43**	**is**
ie	0.0	0.0	0.0	0.0	0.0	0.1	0.3	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	3.7	0.0	26.0	**48**	**ie**
it	0.0	0.0	0.0	0.1	0.0	0.5	2.0	0.0	1.1	0.4	0.2	2.3	11.8	0.0	5.8	0.0	0.3	0.3	0.9	2.5	124.4	**889**	**it**
kz	0.0	0.1	0.0	0.1	0.0	1.8	0.1	0.1	3.1	36.4	0.3	0.1	0.3	0.0	0.1	0.0	1.3	6.6	0.3	1.1	112.2	**177**	**kz**
lv	0.0	1.7	0.0	0.1	0.0	5.3	0.1	0.0	0.9	2.4	0.2	0.1	0.3	0.1	0.1	0.0	0.0	0.4	0.8	0.5	19.8	**41**	**lv**
lt	0.0	4.6	0.0	0.1	0.0	10.8	0.1	0.0	1.1	4.1	0.4	0.1	0.4	0.1	0.2	0.0	0.0	0.6	0.9	0.6	20.3	**53**	**lt**
lu	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.1	0.0	0.0	0.0	0.1	0.0	1.2	**3**	**lu**
mt	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	**0**	**mt**
nl	0.0	0.0	0.0	7.3	0.0	0.3	0.3	0.0	0.0	0.0	0.0	0.0	0.8	0.0	0.2	0.0	0.0	0.0	5.6	0.0	13.7	**49**	**nl**
no	0.0	0.1	0.0	1.0	2.5	6.1	0.5	0.0	1.5	2.2	0.4	0.1	1.6	0.3	0.3	0.0	0.1	0.5	7.8	0.8	125.6	**168**	**no**
pl	0.0	0.4	0.0	0.9	0.1	275.4	0.8	0.1	9.0	4.0	9.5	1.0	2.8	0.1	2.3	0.0	0.1	2.7	5.0	5.2	104.2	**529**	**pl**
pt	0.0	0.0	0.0	0.0	0.0	0.0	87.4	0.0	0.0	0.0	0.0	0.0	8.3	0.0	0.0	0.0	0.0	0.0	0.4	0.0	36.0	**132**	**pt**
md	0.0	0.0	0.0	0.0	0.0	1.1	0.1	1.7	8.9	0.7	0.2	0.1	0.2	0.0	0.1	0.0	0.3	1.1	0.1	1.2	9.9	**31**	**md**
ro	0.0	0.1	0.0	0.1	0.0	7.1	0.2	0.8	160.7	3.5	3.2	0.6	1.0	0.0	0.4	0.1	0.9	3.2	0.6	21.2	62.4	**313**	**ro**
ru	0.1	3.8	0.1	1.7	0.3	61.5	2.0	1.3	43.0	1464.6	6.0	1.4	6.6	0.8	2.8	0.1	16.7	89.8	10.1	16.1	1275.9	**3195**	**ru**
sk	0.0	0.0	0.0	0.1	0.0	7.6	0.1	0.0	3.7	0.5	16.8	0.5	0.4	0.0	0.3	0.0	0.0	0.2	0.4	2.9	16.4	**69**	**sk**
si	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.6	0.2	0.1	9.8	0.8	0.0	0.2	0.0	0.1	0.1	0.1	1.1	11.4	**55**	**si**
es	0.0	0.0	0.0	0.1	0.0	0.0	43.8	0.0	0.0	0.0	0.0	0.0	217.1	0.0	0.2	0.0	0.0	0.0	1.9	0.1	156.0	**429**	**es**
se	0.0	0.5	0.0	1.1	0.5	14.3	0.5	0.1	3.6	4.7	0.9	0.1	1.6	2.7	0.6	0.0	0.2	1.6	5.1	1.6	126.3	**195**	**se**
ch	0.0	0.0	0.0	0.1	0.0	0.1	0.5	0.0	0.0	0.0	0.0	0.1	2.1	0.0	34.5	0.0	0.0	0.0	0.6	0.1	18.6	**100**	**ch**
mk	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	1.0	0.3	0.1	0.0	0.2	0.0	0.0	0.6	0.2	0.3	0.0	6.6	9.6	**34**	**mk**
tr	0.0	0.0	0.0	0.0	0.0	1.7	0.2	0.2	8.4	7.5	0.4	0.2	1.6	0.0	0.2	0.1	126.5	5.1	0.3	4.5	183.5	**404**	**tr**
ua	0.0	0.5	0.0	0.5	0.0	37.4	0.7	2.5	54.7	36.6	6.8	0.9	2.5	0.1	1.0	0.1	5.0	174.2	2.6	12.2	191.5	**606**	**ua**
gb	0.0	0.0	0.0	0.7	0.0	0.7	1.2	0.0	0.1	0.1	0.0	0.0	2.6	0.0	0.2	0.0	0.0	0.0	151.9	0.0	81.2	**256**	**gb**
yu	0.0	0.0	0.0	0.1	0.0	1.0	0.2	0.0	6.9	0.9	0.6	0.4	1.0	0.0	0.2	0.2	0.3	0.7	0.3	90.8	35.1	**182**	**yu**
af	0.0	0.0	0.0	0.0	0.0	0.5	2.1	0.0	2.0	0.7	0.1	0.2	10.6	0.0	0.3	0.0	2.9	0.7	0.5	2.5	245.3	**319**	**af**
as	0.0	0.0	0.0	0.0	0.0	0.4	0.1	0.0	1.1	4.5	0.1	0.0	0.5	0.0	0.1	0.0	10.7	1.1	0.1	0.8	231.1	**276**	**as**
atl	0.0	0.4	0.1	2.5	1.0	14.0	44.4	0.1	3.8	26.3	1.0	0.3	52.9	0.4	1.3	0.0	0.3	2.4	71.1	1.9	3138.2	**3446**	**atl**
grl	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	84.4	**86**	**grl**
bas	0.0	1.0	0.0	1.1	0.1	24.5	0.6	0.1	3.4	7.4	1.1	0.3	2.0	0.8	0.9	0.0	0.2	1.2	5.4	2.0	90.0	**190**	**bas**
red	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	**0**	**red**
bls	0.0	0.1	0.0	0.1	0.0	4.7	0.2	0.8	22.1	25.7	0.9	0.3	0.9	0.0	0.3	0.1	21.3	21.1	0.5	6.7	120.0	**277**	**bls**
cas	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.9	11.1	0.1	0.0	0.1	0.0	0.0	0.0	1.5	1.8	0.1	0.3	66.9	**101**	**cas**
nos	0.0	0.1	0.1	10.0	0.6	8.7	3.8	0.0	0.8	1.0	0.5	0.2	9.3	0.2	1.3	0.0	0.0	0.2	112.2	0.8	262.2	**491**	**nos**
mdt	0.0	0.0	0.0	0.2	0.0	2.1	6.6	0.2	9.6	3.4	0.6	1.7	66.3	0.0	1.6	0.2	20.5	3.2	2.2	13.0	475.8	**1065**	**mdt**
SUM	**0**	**16**	**1**	**38**	**5**	**560**	**215**	**9**	**401**	**1700**	**64**	**32**	**481**	**6**	**100**	**2**	**222**	**332**	**435**	**254**	**8346**	**16702**	**SUM**
	lv	**lt**	**lu**	**nl**	**no**	**pl**	**pt**	**md**	**ro**	**ru**	**sk**	**si**	**es**	**se**	**ch**	**mk**	**tr**	**ua**	**gb**	**yu**	**ind**	**SUM**	

Table C2. Matrix of **cadmium** country-to-country depositions in 2000, kg/y

	al	**am**	**at**	**az**	**by**	**be**	**ba**	**bg**	**hr**	**cy**	**cz**	**dk**	**ee**	**fi**	**fr**	**ge**	**de**	**gr**	**hu**	**is**	**ie**	**it**	**kz**	
al	128	0	1	0	0	0	2	42	3	0	1	0	0	0	5	0	2	31	4	0	0	164	0	**al**
am	0	299	0	87	0	0	0	1	0	0	0	0	0	0	0	39	0	0	0	0	0	1	0	**am**
at	1	0	437	0	1	14	2	21	27	0	31	1	0	0	70	0	55	2	37	0	2	638	0	**at**
az	0	71	0	577	0	0	0	3	0	0	0	0	0	0	0	70	1	1	0	0	0	3	1	**az**
by	2	0	13	0	459	14	2	74	8	0	64	11	8	6	42	1	155	8	49	0	3	81	0	**by**
be	0	0	1	0	0	586	0	0	0	0	2	1	0	0	505	0	54	0	0	0	5	10	0	**be**
ba	8	0	8	0	0	1	92	43	58	0	4	0	0	0	11	0	8	6	19	0	0	278	0	**ba**
bg	12	1	6	1	2	1	3	3113	8	0	7	0	0	0	6	3	11	62	31	0	0	118	0	**bg**
hr	4	0	16	0	0	1	11	35	284	0	4	0	0	0	18	0	9	4	32	0	0	399	0	**hr**
cy	0	0	0	0	0	0	0	2	0	11	0	0	0	0	0	0	0	2	0	0	0	4	0	**cy**
cz	1	0	90	0	1	14	1	8	10	0	665	2	0	0	56	0	291	1	35	0	2	118	0	**cz**
dk	0	0	2	0	0	27	0	1	1	0	8	93	0	0	55	0	100	0	2	0	4	9	0	**dk**
ee	0	0	2	0	6	5	0	7	1	0	8	5	133	10	14	0	44	0	6	0	1	15	0	**ee**
fi	1	0	7	1	15	22	1	21	3	0	26	17	67	559	60	1	133	2	14	0	3	45	0	**fi**
fr	1	0	4	0	0	171	0	3	4	0	4	3	0	0	4258	0	121	1	2	0	31	897	0	**fr**
ge	0	91	0	103	1	0	0	10	0	0	0	0	0	0	1	851	1	2	1	0	0	7	0	**ge**
de	1	0	104	0	3	387	1	10	11	0	257	19	1	1	942	0	4091	2	20	0	24	539	0	**de**
gr	26	0	3	0	1	1	2	441	5	0	3	0	0	0	9	1	6	433	10	0	0	197	0	**gr**
hu	3	0	52	0	1	3	7	45	57	0	27	1	0	0	14	0	28	5	718	0	0	181	0	**hu**
is	0	0	0	0	0	1	0	0	0	0	0	0	0	1	3	0	3	0	0	52	2	0	0	**is**
ie	0	0	0	0	0	3	0	0	0	0	0	0	0	0	12	0	3	0	0	0	386	2	0	**ie**
it	8	0	23	0	0	5	4	32	40	0	4	0	0	0	191	0	14	14	12	0	2	8475	0	**it**
kz	1	17	2	71	8	2	1	36	3	0	5	1	2	2	8	24	16	3	10	0	0	28	68	**kz**
lv	0	0	3	0	12	7	0	8	2	0	13	7	20	5	18	0	66	1	8	0	1	20	0	**lv**
lt	0	0	4	0	24	7	0	9	2	0	21	7	3	3	20	0	82	1	12	0	1	24	0	**lt**
lu	0	0	0	0	0	5	0	0	0	0	0	0	0	0	25	0	10	0	0	0	0	2	0	**lu**
mt	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	**mt**
nl	0	0	1	0	0	259	0	0	0	0	3	2	0	0	229	0	97	0	1	0	7	9	0	**nl**
no	1	0	4	0	4	35	0	9	1	0	21	36	3	8	82	0	154	1	10	1	9	19	0	**no**
pl	3	0	78	0	34	50	5	61	29	0	704	32	2	3	160	0	1413	6	198	0	8	240	0	**pl**
pt	0	0	0	0	0	1	0	0	0	0	0	0	0	0	6	0	1	0	0	0	1	1	0	**pt**
md	1	0	2	0	1	1	1	62	2	0	4	0	0	0	3	0	7	5	10	0	0	26	0	**md**
ro	11	1	22	1	6	4	8	490	27	0	34	2	1	1	19	2	58	30	191	0	1	217	0	**ro**
ru	12	81	49	279	436	69	10	522	39	2	169	46	219	249	217	317	557	67	186	0	13	476	123	**ru**
sk	1	0	41	0	1	3	2	21	16	0	88	1	0	0	14	0	38	2	230	0	1	81	0	**sk**
si	1	0	23	0	0	1	1	15	51	0	2	0	0	0	9	0	4	1	11	0	0	272	0	**si**
es	0	0	0	0	0	8	0	1	1	0	0	0	0	0	86	0	4	1	0	0	4	143	0	**es**
se	2	0	10	0	14	49	1	36	3	0	48	87	13	76	116	1	287	4	29	0	6	48	0	**se**
ch	0	0	9	0	0	6	0	1	1	0	1	0	0	0	162	0	10	0	0	0	1	404	0	**ch**
mk	26	0	1	0	0	0	1	198	2	0	1	0	0	0	2	0	2	41	5	0	0	59	0	**mk**
tr	9	172	4	70	3	1	2	381	6	21	5	1	0	0	13	117	11	123	14	0	0	204	0	**tr**
ua	10	6	34	14	94	21	8	539	31	0	104	11	7	8	67	18	231	55	219	0	4	309	3	**ua**
gb	0	0	1	0	0	52	0	0	0	0	3	3	0	0	170	0	32	0	1	0	168	16	0	**gb**
yu	39	0	15	0	1	2	15	256	29	0	11	1	0	0	13	1	19	24	67	0	0	285	0	**yu**
af	6	1	2	0	0	2	2	64	5	2	1	0	0	0	37	1	4	39	4	0	1	385	0	**af**
as	2	52	1	210	1	0	0	42	1	7	1	0	0	0	3	21	3	22	2	0	0	48	2	**as**
atl	1	0	11	1	18	128	1	23	5	0	44	35	15	54	581	1	289	3	28	92	582	151	1	**atl**
grl	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	0	2	0	0	0	0	0	0	**grl**
bas	2	0	21	0	20	65	2	45	9	0	81	108	82	178	159	0	592	5	42	0	8	95	0	**bas**
red	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**red**
bls	8	34	9	28	14	3	3	636	11	2	16	2	2	2	18	250	36	68	41	0	1	165	1	**bls**
cas	0	34	1	373	2	0	0	11	1	0	1	0	0	0	2	40	4	2	3	0	0	9	11	**cas**
nos	0	0	16	0	3	433	1	3	4	0	58	117	2	3	983	0	637	1	18	2	175	98	0	**nos**
mdt	106	3	23	2	2	14	20	763	96	43	16	2	0	1	476	6	42	661	48	0	6	6940	0	**mdt**
SUM	**437**	**864**	**1157**	**1822**	**1191**	**2487**	**213**	**8144**	**898**	**92**	**2571**	**655**	**583**	**1174**	**9972**	**1769**	**9836**	**1742**	**2381**	**149**	**1463**	**22958**	**213**	**SUM**
	al	**am**	**at**	**az**	**by**	**be**	**ba**	**bg**	**hr**	**cy**	**cz**	**dk**	**ee**	**fi**	**fr**	**ge**	**de**	**gr**	**hu**	**is**	**ie**	**it**	**kz**	

continued

	lv	**lt**	**lu**	**nl**	**no**	**pl**	**pt**	**md**	**ro**	**ru**	**sk**	**si**	**es**	**se**	**ch**	**mk**	**tr**	**ua**	**gb**	**yu**	**ind**	**SUM**	
al	0	0	0	0	0	8	1	0	16	3	6	2	11	0	0	5	0	2	1	61	601	1102	**al**
am	0	0	0	0	0	1	0	0	1	5	0	0	0	0	0	0	0	1	0	0	408	846	**am**
at	0	1	0	5	0	104	3	0	53	9	89	158	37	0	76	0	0	3	10	31	1473	3391	**at**
az	0	0	0	0	0	4	0	0	4	25	1	0	1	0	0	0	0	4	0	1	1065	1834	**az**
by	23	170	0	7	3	2484	2	3	324	266	202	11	20	0	9	1	0	140	16	54	2831	7570	**by**
be	0	0	3	27	0	18	3	0	1	0	1	0	37	0	4	0	0	0	46	0	582	1886	**be**
ba	0	0	0	0	0	27	1	0	35	6	21	20	21	0	2	1	0	3	1	148	982	1807	**ba**
bg	0	2	0	1	0	80	1	1	512	32	48	7	9	0	2	7	1	29	1	372	1352	5840	**bg**
hr	0	0	0	1	0	23	2	0	37	7	23	90	26	0	3	1	0	3	1	107	1072	2215	**hr**
cy	0	0	0	0	0	0	0	0	1	0	0	0	1	0	0	0	0	0	0	1	88	112	**cy**
cz	0	1	0	6	1	727	2	0	37	7	235	25	18	0	34	0	0	3	11	23	1090	3513	**cz**
dk	0	1	0	17	2	105	1	0	5	3	8	1	12	0	3	0	0	0	26	2	563	1052	**dk**
ee	41	38	0	2	2	245	0	0	33	57	20	2	6	0	2	0	0	7	5	8	690	1418	**ee**
fi	29	53	0	10	14	634	2	1	89	300	50	4	22	7	8	0	0	26	19	16	4846	7125	**fi**
fr	0	1	9	30	1	25	77	0	4	2	4	7	1451	0	231	0	0	1	133	3	9133	16613	**fr**
ge	0	1	0	0	0	12	0	0	15	205	2	0	1	0	0	0	1	14	0	4	1212	2541	**ge**
de	1	5	15	138	4	908	17	0	30	17	69	30	200	0	509	0	0	4	157	21	5725	14261	**de**
gr	0	1	0	0	0	33	1	1	94	13	16	4	20	0	1	11	1	13	1	77	1378	2804	**gr**
hu	0	1	0	2	0	156	1	0	598	13	521	65	12	0	5	1	0	19	3	208	1153	3902	**hu**
is	0	0	0	0	1	10	0	0	0	2	0	0	2	0	0	0	0	0	3	0	1678	1760	**is**
ie	0	0	0	1	0	6	2	0	0	0	1	0	12	0	0	0	0	0	30	0	1091	1553	**ie**
it	0	0	0	2	0	25	15	0	27	5	18	56	238	0	92	1	0	3	7	34	5112	14461	**it**
kz	2	7	0	1	0	128	1	1	117	601	25	4	6	0	2	0	1	108	2	23	4372	5712	**kz**
lv	201	200	0	3	2	513	1	0	45	80	29	3	6	0	3	0	0	10	7	10	930	2233	**lv**
lt	24	532	0	3	2	1059	1	0	54	158	43	4	7	0	4	0	0	14	8	11	893	3039	**lt**
lu	0	0	5	0	0	1	0	0	0	0	0	0	4	0	1	0	0	0	2	0	53	110	**lu**
mt	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	4	**mt**
nl	0	0	1	224	1	24	2	0	1	1	2	0	21	0	3	0	0	0	62	0	596	1547	**nl**
no	3	11	0	20	298	452	2	0	64	40	37	2	29	1	5	0	0	10	56	14	5055	6500	**no**
pl	5	41	1	23	6	22203	5	1	527	148	1233	50	57	0	46	1	0	109	49	110	4599	32242	**pl**
pt	0	0	0	0	0	0	777	0	0	0	0	0	260	0	0	0	0	0	3	0	1325	2376	**pt**
md	0	1	0	0	0	80	1	25	275	15	23	2	4	0	1	0	0	15	1	26	467	1064	**md**
ro	1	6	0	2	1	516	2	9	7631	75	306	25	20	0	6	4	1	66	5	459	2770	13033	**ro**
ru	156	370	1	33	26	4685	11	18	1655	34080	579	51	124	6	44	4	8	1525	73	298	51216	99100	**ru**
sk	0	1	0	1	0	551	1	0	240	10	1999	24	8	0	6	0	0	18	3	59	719	4180	**sk**
si	0	0	0	0	0	10	1	0	20	4	14	501	14	0	3	0	0	1	1	20	470	1450	**si**
es	0	0	0	2	0	1	354	0	0	0	0	1	5691	0	3	0	0	0	16	1	6241	12559	**es**
se	17	56	1	26	57	1332	2	1	197	114	105	6	31	16	11	1	0	37	40	33	5689	8604	**se**
ch	0	0	0	1	0	3	3	0	1	0	1	2	44	0	695	0	0	0	5	1	753	2107	**ch**
mk	0	0	0	0	0	11	0	0	30	5	8	2	4	0	0	51	0	5	0	80	452	988	**mk**
tr	1	3	0	1	0	85	1	2	202	71	26	6	28	0	2	3	48	59	2	72	7598	9368	**tr**
ua	12	54	0	11	4	3104	6	36	2580	831	692	38	52	0	18	4	4	2944	23	245	8765	21217	**ua**
gb	0	1	0	20	2	39	8	0	2	1	4	0	73	0	4	0	0	0	1659	1	3431	5692	**gb**
yu	0	1	0	1	0	70	2	0	187	16	69	20	22	0	3	9	0	11	2	1777	1505	4474	**yu**
af	0	0	0	1	0	15	16	0	29	9	6	5	194	0	4	1	1	4	3	21	7179	8044	**af**
as	0	1	0	0	0	18	0	0	21	44	4	1	6	0	1	1	2	12	0	9	8503	9042	**as**
atl	13	39	2	54	127	941	486	1	138	521	94	9	2249	3	22	0	0	43	667	28	146248	153750	**atl**
grl	0	0	0	0	0	7	0	0	1	3	0	0	0	0	0	0	0	0	1	0	3218	3239	**grl**
bas	70	134	1	31	15	2650	4	1	198	229	153	16	45	10	19	1	0	35	53	45	4528	9752	**bas**
red	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8	9	**red**
bls	4	12	0	2	1	347	2	13	771	295	88	13	19	0	5	3	14	351	4	160	6078	9534	**bls**
cas	0	2	0	0	0	35	0	0	32	155	7	1	2	0	0	0	1	31	0	6	3578	4347	**cas**
nos	3	12	3	325	83	752	28	0	37	25	62	9	261	1	26	0	0	5	1477	16	12244	17923	**nos**
mdt	1	2	0	5	1	152	66	3	325	62	73	71	1823	0	38	13	15	46	22	245	25188	37418	**mdt**
SUM	**613**	**1762**	**46**	**1042**	**657**	**45415**	**1915**	**121**	**17298**	**38571**	**7019**	**1351**	**13261**	**47**	**1955**	**126**	**100**	**5734**	**4719**	**4940**	**368800**	**588264**	**SUM**
	lv	**lt**	**lu**	**nl**	**no**	**pl**	**pt**	**md**	**ro**	**ru**	**sk**	**si**	**es**	**se**	**ch**	**mk**	**tr**	**ua**	**gb**	**yu**	**ind**	**SUM**	

Table C3. Matrix of **mercury** country-to-country depositions in 2000, t/y

	al	**am**	**at**	**az**	**by**	**be**	**ba**	**bg**	**hr**	**cy**	**cz**	**dk**	**ee**	**fi**	**fr**	**ge**	**de**	**gr**	**hu**	**is**	**ie**	**it**	**kz**	
al	78	0	0	0	0	0	1	5	0	0	1	0	0	0	2	0	2	85	2	0	0	16	0	**al**
am	0	0	0	8	0	0	0	0	0	0	0	0	0	0	0	3	0	1	0	0	0	0	0	**am**
at	0	0	205	0	0	3	0	2	3	0	23	1	0	0	33	0	59	3	30	0	1	104	0	**at**
az	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	7	0	1	0	0	0	0	0	**az**
by	0	0	3	0	76	3	0	9	1	0	27	10	3	1	17	0	94	11	26	0	1	9	0	**by**
be	0	0	0	0	0	317	0	0	0	0	1	1	0	0	404	0	40	0	0	0	2	1	0	**be**
ba	2	0	3	0	0	0	39	4	10	0	2	0	0	0	6	0	8	11	14	0	0	35	0	**ba**
bg	4	0	2	0	0	0	1	683	1	0	3	0	0	0	3	0	8	129	17	0	0	13	0	**bg**
hr	1	0	5	0	0	0	6	4	45	0	2	0	0	0	11	0	8	7	29	0	0	83	0	**hr**
cy	0	0	0	0	0	0	0	0	0	27	0	0	0	0	0	0	0	2	0	0	0	0	0	**cy**
cz	0	0	34	0	0	3	0	1	1	0	621	3	0	0	25	0	359	2	25	0	1	16	0	**cz**
dk	0	0	1	0	0	6	0	0	0	0	4	259	0	0	22	0	104	0	1	0	1	1	0	**dk**
ee	0	0	1	0	1	1	0	1	0	0	3	4	86	1	5	0	25	1	3	0	0	1	0	**ee**
fi	0	0	2	0	2	4	0	2	0	0	10	14	21	80	23	0	74	4	6	0	1	4	0	**fi**
fr	0	0	1	0	0	76	0	0	0	0	2	3	0	0	3656	0	83	2	1	0	10	115	0	**fr**
ge	0	0	0	10	0	0	0	2	0	0	0	0	0	0	1	112	1	3	1	0	0	1	0	**ge**
de	0	0	34	0	0	97	0	1	1	0	178	35	0	0	432	0	6400	2	13	0	8	78	0	**de**
gr	14	0	1	0	0	0	1	93	1	0	2	0	0	0	4	0	5	2106	6	0	0	20	0	**gr**
hu	1	0	20	0	0	1	2	6	9	0	15	1	0	0	8	0	23	8	777	0	0	26	0	**hu**
is	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	2	0	0	0	1	0	0	**is**
ie	0	0	0	0	0	1	0	0	0	0	0	0	0	0	6	0	3	0	0	0	398	0	0	**ie**
it	2	0	7	0	0	1	1	4	4	0	2	0	0	0	125	0	12	19	7	0	1	2486	0	**it**
kz	0	0	1	6	1	1	0	5	0	0	3	1	1	0	4	2	12	5	5	0	0	3	12	**kz**
lv	0	0	1	0	1	1	0	1	0	0	6	7	9	1	6	0	39	2	5	0	0	2	0	**lv**
lt	0	0	1	0	4	1	0	1	0	0	9	8	1	0	8	0	46	1	6	0	0	3	0	**lt**
lu	0	0	0	0	0	3	0	0	0	0	0	0	0	0	10	0	4	0	0	0	0	0	0	**lu**
mk	11	0	0	0	0	0	0	22	0	0	1	0	0	0	1	0	2	158	3	0	0	6	0	**mk**
mt	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**mt**
nl	0	0	0	0	0	88	0	0	0	0	2	2	0	0	140	0	85	0	0	0	2	1	0	**nl**
no	0	0	1	0	0	6	0	1	0	0	9	31	1	1	26	0	85	2	5	0	4	2	0	**no**
pl	1	0	24	0	7	12	1	8	3	0	485	42	1	0	73	0	1224	12	122	0	3	32	0	**pl**
pt	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	0	0	**pt**
md	0	0	0	0	0	0	0	9	0	0	1	0	0	0	1	0	4	8	6	0	0	3	0	**md**
ro	3	0	6	0	1	1	3	83	3	0	16	2	0	0	11	0	41	52	140	0	0	30	0	**ro**
ru	3	0	12	20	50	15	2	69	4	1	68	41	69	23	95	24	322	92	90	0	6	52	13	**ru**
sk	0	0	13	0	0	1	1	3	2	0	51	1	0	0	7	0	27	4	173	0	0	11	0	**sk**
si	0	0	8	0	0	0	0	1	6	0	1	0	0	0	6	0	4	1	7	0	0	52	0	**si**
es	0	0	0	0	0	2	0	0	0	0	0	0	0	0	51	0	3	1	0	0	2	8	0	**es**
se	0	0	2	0	1	9	0	3	0	0	20	113	3	5	43	0	207	6	12	0	2	5	0	**se**
ch	0	0	3	0	0	1	0	0	0	0	0	0	0	0	107	0	11	0	0	0	0	72	0	**ch**
tr	3	0	1	6	0	1	1	90	1	12	3	1	0	0	8	11	10	199	9	0	0	20	0	**tr**
ua	2	0	9	1	8	4	2	69	3	0	44	10	2	1	30	1	141	69	126	0	1	36	0	**ua**
gb	0	0	0	0	0	14	0	0	0	0	2	4	0	0	80	0	25	0	1	0	72	2	0	**gb**
yu	14	0	5	0	0	0	7	32	5	0	5	1	0	0	7	0	14	52	50	0	0	33	0	**yu**
af	5	0	1	0	0	1	1	30	1	2	2	0	0	0	31	0	7	204	6	0	1	73	0	**af**
as	1	0	0	20	0	0	0	6	0	9	1	0	0	0	2	2	3	38	2	0	0	6	0	**as**
atl	0	0	3	0	1	31	0	3	0	0	18	28	4	4	297	0	166	6	13	0	309	16	0	**atl**
grl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	2	0	0	0	0	0	0	**grl**
bas	1	0	5	0	3	13	0	5	1	0	39	274	38	22	63	0	603	9	21	0	3	9	0	**bas**
red	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**red**
bls	2	0	2	2	1	1	1	133	1	1	6	2	1	0	10	26	21	111	20	0	0	20	0	**bls**
cas	0	0	0	47	0	0	0	2	0	0	1	0	0	0	1	3	3	3	1	0	0	1	1	**cas**
nos	0	0	4	0	0	119	0	0	0	0	28	160	1	0	463	0	498	1	11	0	54	11	0	**nos**
mdt	38	0	7	0	0	4	7	154	14	42	8	2	0	0	379	0	32	1418	30	0	2	1094	0	**mdt**
SUM	**189**	**0.29**	**431**	**222**	**159**	**845**	**80**	**1549**	**122**	**96**	**1726**	**1065**	**240**	**140**	**6749**	**192**	**10951**	**4850**	**1827**	**0**	**890**	**4617**	**27**	**SUM**
	al	**am**	**at**	**az**	**by**	**be**	**ba**	**bg**	**hr**	**cy**	**cz**	**dk**	**ee**	**fi**	**fr**	**ge**	**de**	**gr**	**hu**	**is**	**ie**	**it**	**kz**	

continued

	lv	lt	lu	nl	no	pl	pt	md	ro	ru	sk	si	es	se	ch	mk	tr	ua	gb	yu	ind	SUM	
al	0	0	0	0	0	2	0	0	3	0	1	0	4	0	0	1	0	1	0	20	265	490	**al**
am	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	168	183	**am**
at	0	0	1	1	0	23	1	0	7	1	15	25	12	0	35	0	0	1	4	6	755	1354	**at**
az	0	0	0	0	0	1	0	0	1	3	0	0	0	0	0	0	0	2	0	0	422	539	**az**
by	2	10	0	1	1	397	1	2	37	23	38	1	6	1	3	0	0	70	6	9	1176	2076	**by**
be	0	0	11	14	0	3	1	0	0	0	0	0	9	0	2	0	0	0	31	0	213	1051	**be**
ba	0	0	0	0	0	5	0	0	8	0	5	3	7	0	1	0	0	1	1	43	438	648	**ba**
bg	0	0	0	0	0	15	0	1	166	3	10	1	4	0	1	1	0	15	1	53	744	1880	**bg**
hr	0	0	0	0	0	5	1	0	7	0	6	20	10	0	1	0	0	1	1	27	446	726	**hr**
cy	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	34	65	**cy**
cz	0	0	1	1	0	283	1	0	5	0	46	4	6	0	14	0	0	1	5	5	508	1972	**cz**
dk	0	0	0	4	1	22	0	0	0	0	1	0	3	1	1	0	0	0	11	0	202	648	**dk**
ee	4	2	0	0	1	35	0	0	3	4	4	0	1	1	1	0	0	3	2	1	260	456	**ee**
fi	2	3	1	2	4	97	1	0	9	20	8	0	6	4	3	0	0	14	8	3	1976	2408	**fi**
fr	0	0	27	8	0	7	29	0	1	0	1	1	560	0	127	0	0	1	93	1	3622	8428	**fr**
ge	0	0	0	0	0	3	0	0	2	7	1	0	1	0	0	0	0	6	0	1	586	737	**ge**
de	0	0	38	55	1	252	5	0	4	1	14	4	57	0	254	0	0	2	76	4	2429	10478	**de**
gr	0	0	0	0	0	6	0	0	21	1	4	1	7	0	1	3	0	7	1	19	721	3044	**gr**
hu	0	0	0	0	0	34	0	0	63	1	260	11	5	0	2	0	0	2	1	47	546	1871	**hu**
is	0	0	0	0	0	1	0	0	0	0	0	0	1	0	0	0	0	0	2	0	805	816	**is**
ie	0	0	0	0	0	1	1	0	0	0	0	0	3	0	0	0	0	0	23	0	455	894	**ie**
it	0	0	0	0	0	6	5	0	4	0	4	12	82	0	50	0	0	1	4	7	1975	4824	**it**
kz	0	0	0	0	0	23	0	1	13	117	5	0	2	0	1	0	0	52	1	3	1583	1863	**kz**
lv	23	13	0	0	1	72	0	0	5	4	6	0	2	1	1	0	0	5	2	2	345	565	**lv**
lt	2	47	0	1	1	138	0	0	6	7	8	0	2	0	1	0	0	6	3	2	353	668	**lt**
lu	0	0	22	0	0	0	0	0	0	0	0	0	1	0	1	0	0	0	1	0	21	63	**lu**
mk	0	0	0	0	0	2	0	0	6	0	1	0	2	0	0	8	0	2	0	25	230	481	**mk**
mt	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1	1	**mt**
nl	0	0	2	112	0	6	1	0	0	0	0	0	6	0	1	0	0	0	36	0	208	694	**nl**
no	0	0	1	2	148	73	1	0	5	2	7	0	7	2	1	0	0	3	19	2	2147	2596	**no**
pl	0	2	2	5	2	7371	2	1	49	9	252	7	17	1	18	0	0	55	22	22	2099	11986	**pl**
pt	0	0	0	0	0	0	678	0	0	0	0	0	75	0	0	0	0	0	2	0	567	1326	**pt**
md	0	0	0	0	0	13	0	25	64	1	5	0	1	0	0	0	0	13	0	5	198	361	**md**
ro	0	0	0	0	0	97	1	6	1519	6	81	4	8	0	3	0	0	30	3	96	1443	3691	**ro**
ru	10	17	2	6	7	680	4	8	179	3626	102	6	38	5	17	0	1	730	35	46	20331	26922	**ru**
sk	0	0	0	0	0	93	0	0	23	1	789	4	3	0	3	0	0	2	2	12	386	1613	**sk**
si	0	0	0	0	0	2	0	0	2	0	3	103	5	0	1	0	0	0	0	3	221	427	**si**
es	0	0	0	0	0	0	191	0	0	0	0	0	3648	0	1	0	0	0	9	0	2729	6646	**es**
se	1	2	1	4	20	197	1	0	13	6	17	1	10	37	4	0	0	14	16	4	2096	2876	**se**
ch	0	0	1	0	0	1	1	0	0	0	0	0	15	0	510	0	0	0	3	0	361	1089	**ch**
tr	0	0	0	0	0	19	1	1	43	9	7	1	12	0	1	0	11	28	1	12	3215	3738	**tr**
ua	1	3	1	2	1	556	2	21	258	92	157	5	15	1	7	0	0	2560	10	41	3624	7918	**ua**
gb	0	0	1	4	0	9	3	0	0	0	1	0	19	0	1	0	0	0	1918	0	1268	3425	**gb**
yu	0	0	0	0	0	14	0	0	57	1	15	3	7	0	1	1	0	4	1	644	778	1753	**yu**
af	0	0	0	0	0	8	11	0	16	2	3	1	139	0	2	0	0	8	3	12	4777	5348	**af**
as	0	0	0	0	0	6	0	0	5	7	2	0	3	0	0	0	0	7	1	2	3933	4057	**as**
atl	1	2	3	10	38	139	346	0	11	32	16	1	974	2	9	0	0	16	442	5	50120	53067	**atl**
grl	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	1	0	2403	2412	**grl**
bas	6	8	2	6	7	472	1	0	20	15	28	2	13	14	7	0	0	18	22	7	1400	3155	**bas**
red	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5	6	**red**
bls	0	1	0	0	0	51	0	7	156	51	17	2	7	0	2	0	2	184	2	24	1920	2787	**bls**
cas	0	0	0	0	0	6	0	0	4	24	1	0	1	0	0	0	0	15	0	1	858	974	**cas**
nos	0	1	6	93	45	141	8	0	3	1	12	1	67	2	9	0	0	2	1027	3	3945	6717	**nos**
mdt	0	0	1	1	0	30	29	1	70	6	16	11	1364	0	15	2	3	25	13	57	6384	11258	**mdt**
SUM	**53**	**112**	**126**	**338**	**282**	**11416**	**1328**	**77**	**2870**	**4085**	**1970**	**236**	**7244**	**72**	**1115**	**18**	**19**	**3909**	**3867**	**1275**	**138695**	**216070**	**SUM**
	lv	**lt**	**lu**	**nl**	**no**	**pl**	**pt**	**md**	**ro**	**ru**	**sk**	**si**	**es**	**se**	**ch**	**mk**	**tr**	**ua**	**gb**	**yu**	**ind**	**SUM**	