

CO-OPERATIVE PROGRAMME FOR MONITORING AND EVALUATION
OF THE LONG-RANGE TRANSMISSION OF AIR POLLUTANTS
IN EUROPE (EMEP)

**COMPARISON OF EMISSIONS WITH CONCENTRATIONS IN THE AIR
AND PRECIPITATION OF MERCURY, LEAD AND CADMIUM MEASURED
AT SELECTED EMEP STATIONS**

Elisabeth G. Pacyna, Kevin J. Barrett and Jozef M. Pacyna
EMEP Chemical Coordinating Centre, Kjeller, Norway

1 Introduction

Recent estimates indicate a decrease of heavy metal emissions to the atmosphere in Europe and also on a global scale. This decrease applies particularly to lead, cadmium, and mercury emissions. In Europe, the heavy metal emission decrease is estimated by national emission experts in various countries. The results of these estimates are reported to EMEP (EMEP MSC-W, 2002). Independent emission estimates for international programs are in a good agreement with national estimates indicating a decrease of emissions of mercury (Pacyna et al., 2001), lead (Pacyna and Pacyna, 2000) and cadmium (Pacyna and Pacyna, 2001) in Europe and mercury (Pacyna and Pacyna, 2002; Pacyna et al., 2002), lead (Pacyna and Pacyna, 2001), and cadmium (Pacyna and Pacyna, 2001) on a global scale.

The CCC has been collecting the information on concentrations of mercury, lead, and cadmium in air and wet depositions at several EMEP stations for more than a decade. Other programs, such as the OSPAR Commission, HELCOM, and AMAP have also measured these concentrations in Europe (e.g. Barrett, 2001).

An important question in defining policies of protecting the environment is how close the decrease of concentrations of pollutants in various environmental compartments follows the reduction of pollutant emissions. In other words, what is the response of the environment through the change of the state of the environment to the change of environmental pressures caused by various socio-economic and natural drivers. The analysis of these changes, very important from environmental and economic point of view is very difficult to perform.

2 Objective and the Approach

The main objective of this note is to encourage the EMEP Parties to approach the analysis of the relationships between the decrease of their national (and European) emissions of mercury, lead, and cadmium and the decrease of concentrations of concentrations of these pollutants in the air and precipitation, measured at their stations. This analysis is very important for assessing the effects of country's efforts to reduce the flow of heavy metals to the environment.

The above objective is achieved here through a few examples of comparisons between the decreases of emissions and measured concentrations in the air and precipitation for selected countries. However, it is not the intention of this note to present detailed source-receptor relationships for heavy metals in Europe or for specific country. This task requires extensive modelling and is carried out by the EMEP MSC-E (Ilyin et al., 2002) for Europe as a whole.

Data for the Czech Republic (Cd and Pb), Norway (Cd, Pb, Hg), the United Kingdom (Cd and Pb), and the Netherlands (Hg) were selected for the analysis in this work. These countries do have a long time record of Pb, Cd, and Hg measurements at their EMEP stations and report their national emissions for the above mentioned metals for at least a decade. In addition, The United Kingdom would represent the western part of Europe, the Netherlands represents the west/central part, the Czech Republic represents the central/ east part and Norway represents the northern part. Unfortunately, no Southern European country was selected because of short periods of measurements at their stations.

3 Comparison of emission data with measured concentrations

3.1 Lead

The European emission of lead has decreased continuously over the last decade from more than 58 000 tonnes in 1990 to about 23000 tonnes in 2000 (Pacyna and Pacyna, 2000). These emissions have decreased worldwide from more than 330000 tonnes at the beginning of the 1980's to about 120000 tonnes in the mid 1990's (Pacyna and Pacyna, 2001).

The decrease of Pb emissions in the Czech Republic, Norway, and the United Kingdom over the last decade is presented in Figs. 1 through 3, respectively. These data were reported by national agencies to EMEP (EMEP MSC-W, 2002). It can be seen from these estimates that for the Czech Republic the emission decrease was a factor of 2.5, while much larger decrease were estimated for Norway (a factor of 45) and the United Kingdom (a factor of about 7.5). This decrease was mainly due to the decrease of lead additives to gasoline until its final phase-out. The curves in Figs. 1 through 3 indicate clearly the introduction of low-leaded (0.15 g Pb/l gasoline) and unleaded (no lead additives) in these countries. It should be admitted, however, that lead is present in gasoline, also in unleaded gasoline due to its content in crude oil. Unleaded gasoline would contain between 0.010 through 0.013 g Pb/l gasoline). Thus, lead will continue to be emitted from combustion of gasoline, even if this is a combustion of unleaded gasoline.

Concentrations of Pb in the air samples measured at the EMEP stations in the Czech Republic and the United Kingdom are presented in Fig. 4. The two Czech stations CZ01 and CZ03 show very close progressions, with declines 1987 to 2000 of around 75% in concentrations. The period 1995 to 2000 shows the slowest decline. Stations in the UK have reported declines of about 50% between 1989 and 2000, although some stations have not observed for so long. Norwegian results do not indicate a clear time series.

There are few measurements of Pb in precipitation in Europe for the last whole decade. The results for the stations in the United Kingdom and Norway from the late 1980's are presented in Fig. 5. The measurements reported from the UK are discontinuous in the early period, but point towards a possible large fall up to 1992. From then to 1996 there was stability, followed by a decline to 2000. Irish results from the eastern coast (near UK) would agree with a decline post 1996. West coast results have very large interannual variability. Although shifted forward a couple of years, the same pattern is seen in southern Norway at Lista – decline to 1994, stability to 1997/8, then further decline. Those few records that exist from the 1980s in Norway suggest a large decline from then to the present day. Between 1994 and 1998 there was stability across Norway.

In general, the lead decrease of European and individual country emissions discussed in this work is reflected in the decrease of Pb concentrations in the air and precipitation measured at these stations. The answer to the question of to what extent the decrease of Pb measurements is due to the decrease of a given country emissions and to what extent it depends on the reduction of Pb emissions in other European countries is more complicated. This answer would require modelling data. It is the intention of the CCC to perform the second step of the reported work jointly with the MSC-E and include their modelled concentrations into the analysis. At present a study has been made in Germany for the Helmholtz Foundation which indicates that as much as 90 % of the deposition of Pb in the UK is due to the UK emissions (von Storch et al., 2002). This contribution in Norway was calculated to be 76%. No Czech Republic data were estimated, however, in neighbouring Poland this contribution was also 76%. Indeed, the Pb emissions on fine particles from traffic, thus at a release level of up to 1 m can be deposited locally in large amounts.

3.2 Cadmium

European emissions of cadmium to the atmosphere have decreased from about 900 tonnes in 1990 (Pacyna, 1996) to about 360 tonnes/year in the second half of the 1990's (Pacyna and Pacyna 2001). The global emissions have changed from about 7500 tonnes/year in the 1980's to about 3000 tonnes/year in the second half of the 1990's (Pacyna and Pacyna, 2001). An interesting fact is that both, the European and global emissions have decreased from the 1980's to the 1990's by a factor of 2.5. The major sources include non-ferrous metal production, stationary fossil fuel combustion, and waste incineration.

The decrease of Cd emissions in the Czech Republic, Norway, and the United Kingdom over the last decade is presented in Figs. 6 through 8, respectively. These data were reported by national agencies to EMEP (EMEP MSC-W, 2002). It can be seen from these estimates that for the Czech Republic and Norway the emission

decrease was a factor of 1.5, while larger decrease were estimated for the United Kingdom (a factor of about 4.0). This decrease of Cd emissions is mostly related to the employment of highly efficient emission control abatement in Europe to reduce the emissions of particles, mostly electrostatic precipitators (ESPs), multicyclones, and wet scrubbers. Cadmium is emitted to the atmosphere mainly on fine particles. It should be observed that emission reductions in the reported countries are in agreement with the reduction tendency for the whole Europe.

Concentrations of Cd in the air samples measured at the EMEP stations in the Czech Republic, Norway, and the United Kingdom are presented in Fig. 9. The Czech station CZ0001 shows decline, with sharpest drop 1988-93, and flatter decline 1993-2000. This agrees with the Czech station CZ0003, with records from 1988 to only 1996. Reported data from Norway and the UK are variable – potentially thus influenced by its variable weather. Clear decline of Cd concentrations at the UK stations is measured from the first half of the decade towards the second half.

Similarly to the Pb measurements, there are only a few measurements of Cd in precipitation in Europe for the period of one decade. The results for the stations in the United Kingdom and Norway from the late 1980's are presented in Fig. 10. The British results are too discontinuous to provide either supporting or contradictory advice obtained from the Irish east coast (not discussed in this work, however) that there is a clear decline of Cd concentrations in precipitation since 1994 until present. It is even though that the British stations have spanned from 1987 to 2000. Records from the Atlantic coastline - north with an apparent message are from Norway. Records from Birkenes (NO01) and from Lista (NO99) made at different times but set together in a sequence suggest a steady and strong decline in concentrations 1987-2000. There is no obvious change in the rate of change, but then the degree of interannual variability is seen to be very high on occasions. Indeed, whilst there is some support from other sites for the Lista-Birkenes change, the discontinuities added to very great variability makes this somewhat tentative.

The cadmium decrease of European and individual country emissions discussed in this work is reflected in the decrease of Cd concentrations in the air and precipitation measured at these stations. These decreases vary from a factor of 1.5 to about 4.0. This range is closer than the similar range for Pb due to the fact that the implementation of emission control equipment for cadmium was quite broad in the European countries and has happened gradually. The implementation of Pb emission reduction policies, basically the introduction on the market low-leaded and unleaded gasoline was more restricted to certain deadlines widely variable between the European countries. Further cooperation with the EMEP MSC-E and national experts is needed to explain to what extent the decline in the measured Cd concentrations in the air and precipitation is a result of the decrease of the metal emissions in the country of measurements or rather due to the decrease of the total European emissions.

3.3 Mercury

European emissions of mercury from anthropogenic sources to the atmosphere have decreased from about 630 tonnes in 1990 (Pacyna, 1996) through 340 tonnes in 1995 (Pacyna et al., 2001) and to about 200 tonnes in 2000 (EMEP MSC-W, 2002). The

global anthropogenic emissions have changed from about 3600 tonnes/ year in the 1980's to about 2000 tonnes/ year in the second half of the 1990's (Pacyna and Pacyna, 2002; Pacyna et al., 2002). Thus, the European emissions have decreased by a factor of 3, while the global emissions by a factor of less than 2. The main anthropogenic source of Hg is combustion of coal. Introduction of flue gas desulfurization (FGD) in the European power plants to remove sulfur dioxide, but also gaseous Hg has contributed the most to the European emission decline of this element. This introduction of FGD equipment was less pronounced in other parts of the globe, particularly in Asia. This is the main explanation for the difference between the degree of the Hg emission decline in Europe and worldwide.

The decrease of Hg emissions from anthropogenic sources in the Netherlands and Norway over the last decade is presented in Figs. 11 and 12, respectively. These data were reported by national agencies to EMEP (EMEP MSC-W, 2002). It can be seen from these estimates that in the Netherlands the Hg emissions have been reduced by a factor of 6, while in Norway by a factor of 1.7. Both countries belong to the group of countries contributing the least to the total anthropogenic emissions of Hg in Europe. Coal combustion, the main emission source of Hg in Europe is not the primary source of these emissions in these countries, rather incineration of wastes (Norway) and some industrial processes (the Netherlands).

There are very few stations having a long record for Hg concentrations in the air and precipitation. Concentrations of Hg in the air samples measured at the EMEP station in Norway (and Sweden not discussed in this work) is presented in Fig. 13. These concentrations vary between 1 and 2 ng/m³ not showing any specific trend.

The Hg concentrations in precipitation at the Dutch station are shown in Fig. 14. A clear decrease of these concentrations from 1996 to 2000 is observed, resembling nicely the decrease of Dutch anthropogenic emissions of the element in the period (see Fig. 11).

It is rather difficult to compare directly the changes in Hg emissions with the measured concentrations of the element in Europe. The first reason for this difficulty is the fact that only a few stations within the EMEP network measure Hg concentrations, and even fewer have a record of these concentrations from the past. The other reason is the fact that there are also natural emissions of Hg in Europe, such as evasion of Hg from land with high content of Hg either through the geological composition of rocks (around the past and present Hg mines) or past deposition of Hg from the atmosphere. The other natural source is volcano eruptions and venting. It is estimated that between 200 and 250 tonnes of Hg is emitted annually from these natural emission sources in Europe (Pacyna et al., 2001). They are quite unevenly distributed over Europe with more natural emissions in the South.

Mercury, emitted primarily in a gaseous form can be transported with air masses on very long distances (a few thousand kilometres) are considered as a global contaminant. Therefore, concentrations measured at the EMEP stations can be affected by the emissions in a given country, other countries and Europe, and possibly by emissions originating outside Europe. This greatly adds to the complicated explanation of relationships between emissions and measured concentrations.

Finally, complicated and variable scheme of chemical reactions of Hg in the atmosphere after emissions adds to the complexity of factors that need examination when the source receptor analysis of Hg behaviour in the atmosphere is undertaken.

Taking into account all complexity factors mentioned above it can be roughly and preliminarily suggested that the fairly well documented decrease of anthropogenic emissions of Hg in Europe and its individual countries is reflected by the decrease of Hg concentrations measured at least in the precipitation samples. This statement should be taken with caution and further analyzed within the EMEP.

4 Final remarks

Decrease of Pb, Cd, and Hg anthropogenic emissions and decrease of Pb, Cd, and Hg concentrations measured in air and precipitation samples at the EMEP stations over the last decade are documented in the EMEP. These decreases in emissions and concentrations can be related to each other as illustrated in this work. The discussion of this relationship is easier for Pb and Cd than for Hg due to the fact that the two former elements are emitted, transported, and deposited on particles, while Hg appears mostly in a gaseous form. Atmospheric chemistry of Pb and Cd is also less complex than the Hg chemistry.

The approach presented here is based on rather limited body of measured data, particularly for Hg. Therefore, the suggestions defined here should be considered with caution. It was not the intention to present and assess the European trends in emissions and concentrations of heavy metals in Europe.

There is, however, no doubt that the comparison undertaken in this work should be continued at a total EMEP and individual country levels. Concerning the total EMEP level, the next step of the work would involve the joint study with modellers from the EMEP MSC-E. The contribution from modellers would add to the explanation on to what extent emissions reductions at sources within a given country contribute to the concentrations measured at a given station in this country and what is the amount of the "foreign source" contribution.

An example from Germany (von Storch et al., 2002) proves that the individual EMEP Parties themselves may undertake the assessment of the relationships between emissions and measured concentrations. This activity may greatly add to the conclusions from source-receptor studies within EMEP. It was the intention of this work to provide some examples that will encourage the Parties to approach such assessment.

References

Barrett, K. (2001) Observations from coastal stations in 1999. Comprehensive Atmospheric Monitoring Programme. Kjeller, Norwegian Institute for Air Research (NILU OR 2/2001).

- EMEP MSC-W (2002) Preliminary status on emission reporting to the Convention on Long range Transboundary Air Pollution (Note to the TFEIP in Cordoba, 6-8 May, 2002). Oslo, Norwegian Meteorological Institute.
- Ilyin, I., Ryaboshapko, A. and Travnikov, O. (2002) Heavy metal contamination on european and hemispherical scale. Moscow, The EMEP Meteorological Synthesizing Centre-East (EMEP Status Report 3/2002).
- Pacyna, E.G. and Pacyna, J.M. (2002) Global emission of mercury from anthropogenic sources in 1995. *Water Air Soil Poll.*, 137, 149-165.
- Pacyna, E.G., Pacyna, J.M. and Pirrone, N. (2001) European emissions of atmospheric mercury from anthropogenic sources in 1995. *Atmos. Environ.*, 35, 2987-2996.
- Pacyna, J.M. (1996) Emission inventories for heavy metals and persistent organic pollutants in Europe. In: *Report and proceedings of the workshop on the assessment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development, Moscow, 24-26 September*. Geneva, World Meteorological Organization (WMO/GAW no. 117).
- Pacyna, J.M. and Pacyna, E.G. (2000) Atmospheric emissions of anthropogenic lead in Europe: improvements, updates, historical data and projections. Geesthacht, GKSS Forschungszentrum (GKSS Report 2000/31).
- Pacyna, J.M. and Pacyna, E.G. (2001) An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.*, 9, 269-298.
- Pacyna, J.M., Pacyna, E.G., Steenhuisen F., and Wilson, S. (2002) Mapping 1995 global anthropogenic emissions of mercury. *Atmos. Environ.*, accepted for publication.
- von Storch, H., Costa-Cabral, M., Hagner, C., Feser, F., Pacyna, J.M. and Pacyna, E.G. (2002) Four decades of gasoline lead emissions and control policies in Europe: a retrospective assessment. *Sci Total Environ.*, submitted.

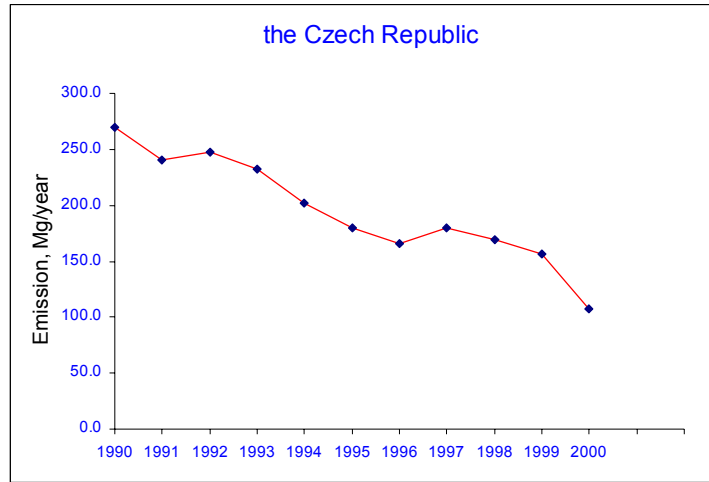


Figure 1: *Pb emissions from anthropogenic sources in the Czech Republic (in Mg/year).*

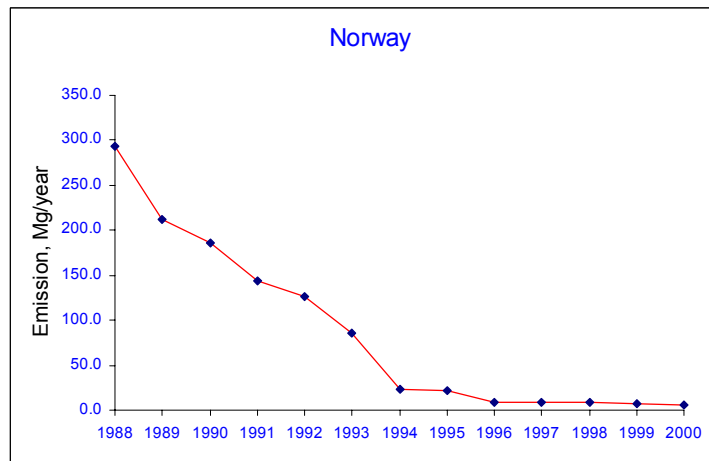


Figure 2: *Pb emissions from anthropogenic sources in Norway (in Mg/year).*

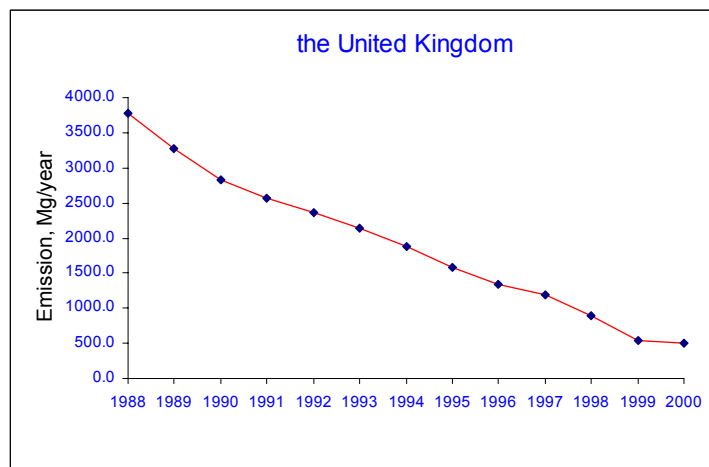


Figure 3: *Pb emissions from anthropogenic sources in the United Kingdom (in Mg/year).*

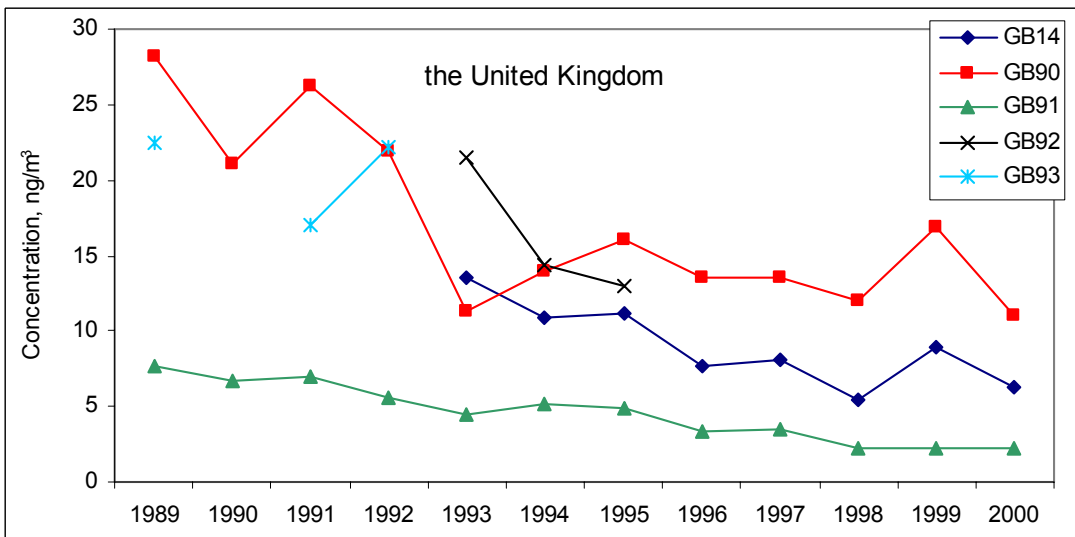
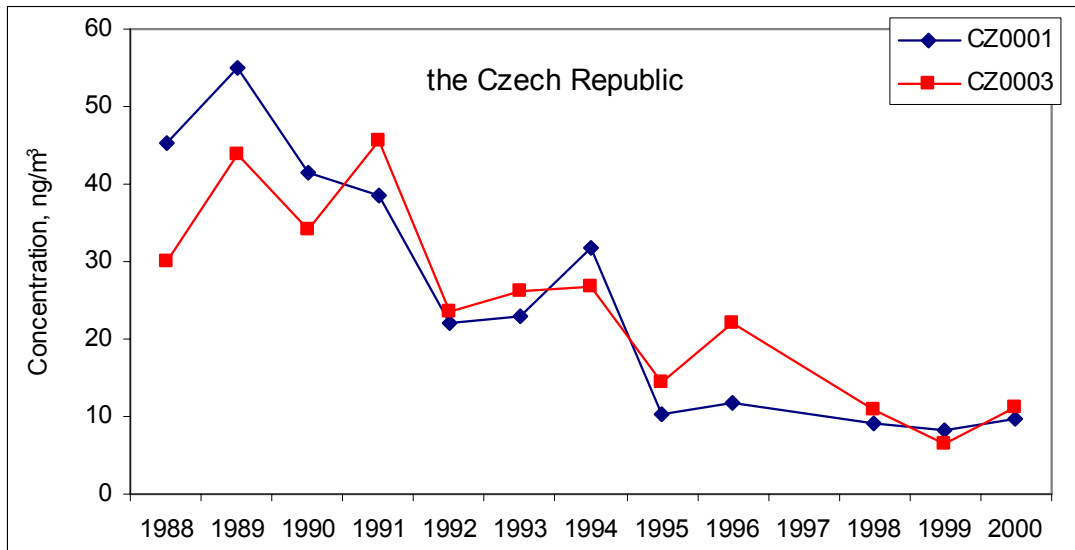


Figure 4: *Pb* concentration in aerosols measured at the EMEP station in the Czech Republic and the United Kingdom (in ng/m^3).

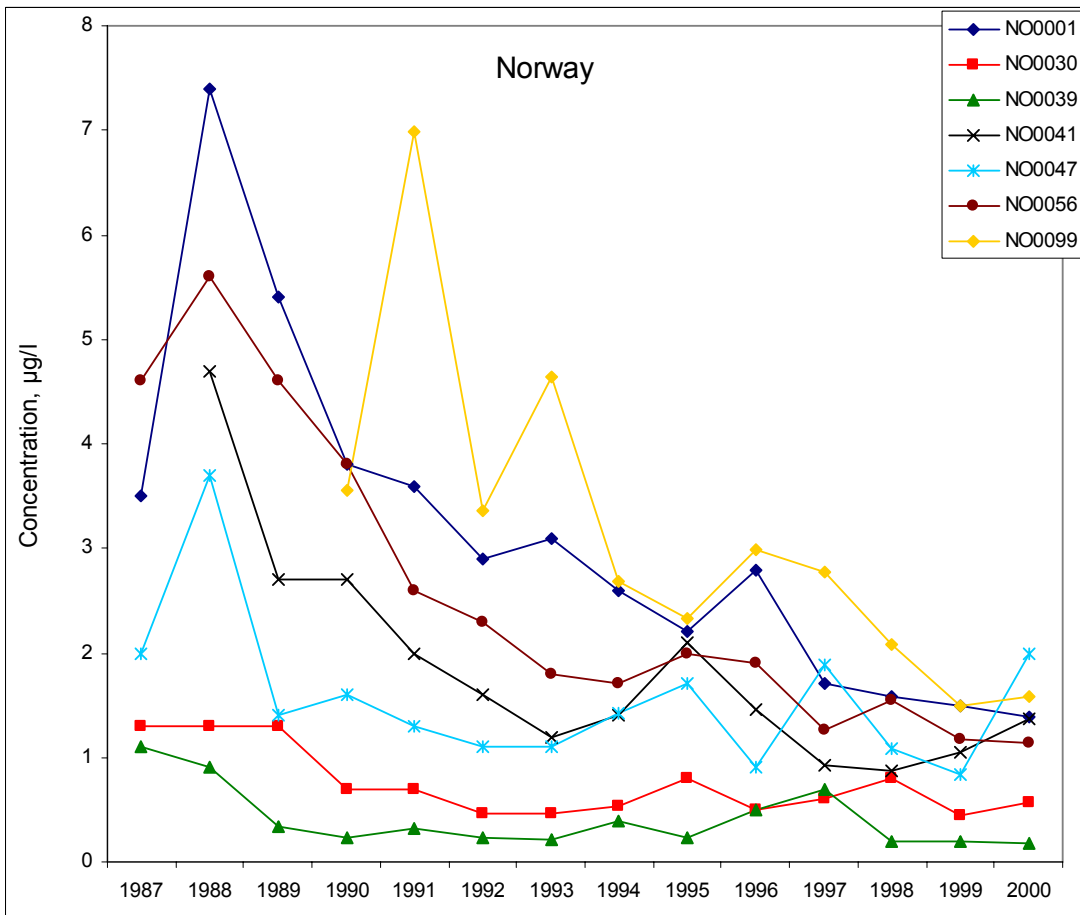
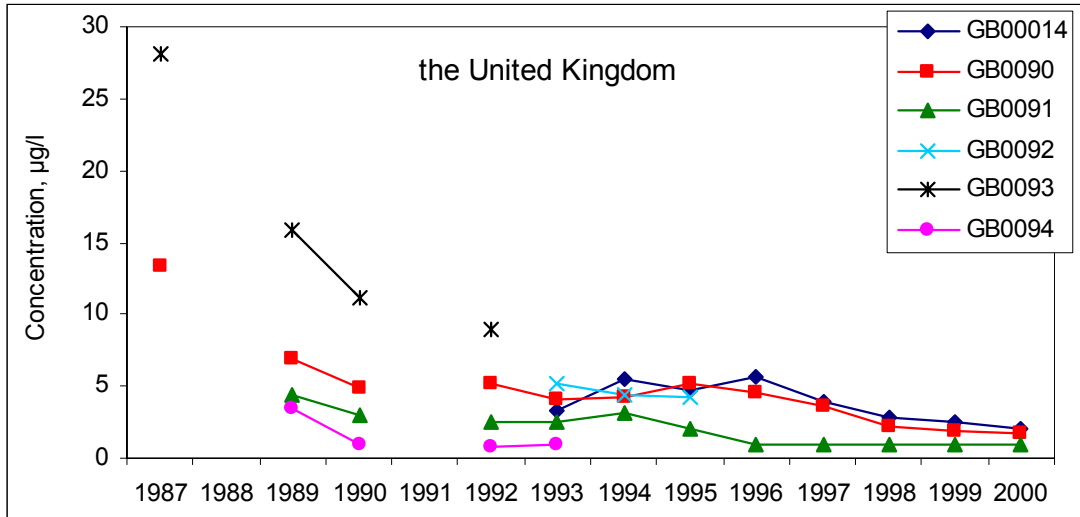


Figure 5: Pb concentration in precipitation, measured at the EMEP stations in the United Kingdom and Norway (in µg/l).

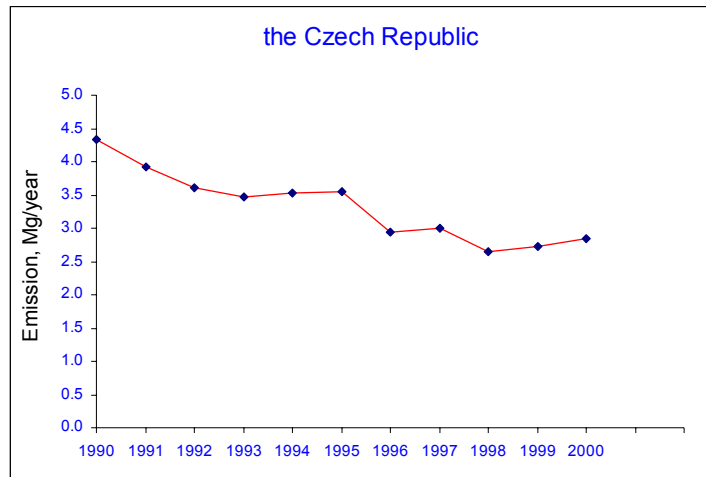


Figure 6: Cd emissions from anthropogenic sources in the Czech Republic (in Mg/year).

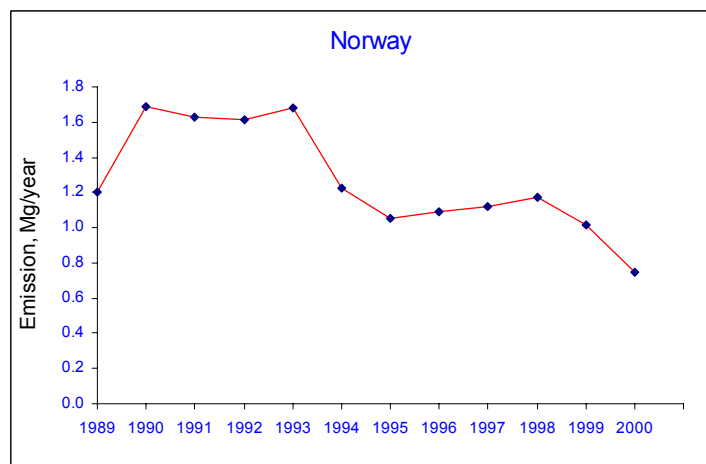


Figure 7: Cd emissions from anthropogenic sources in Norway (in Mg/year).

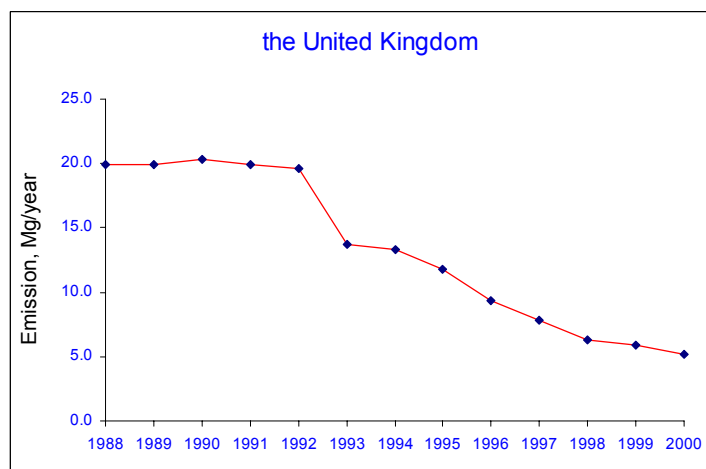


Figure 8: Cd emissions from anthropogenic sources in the United Kingdom (in Mg/year).

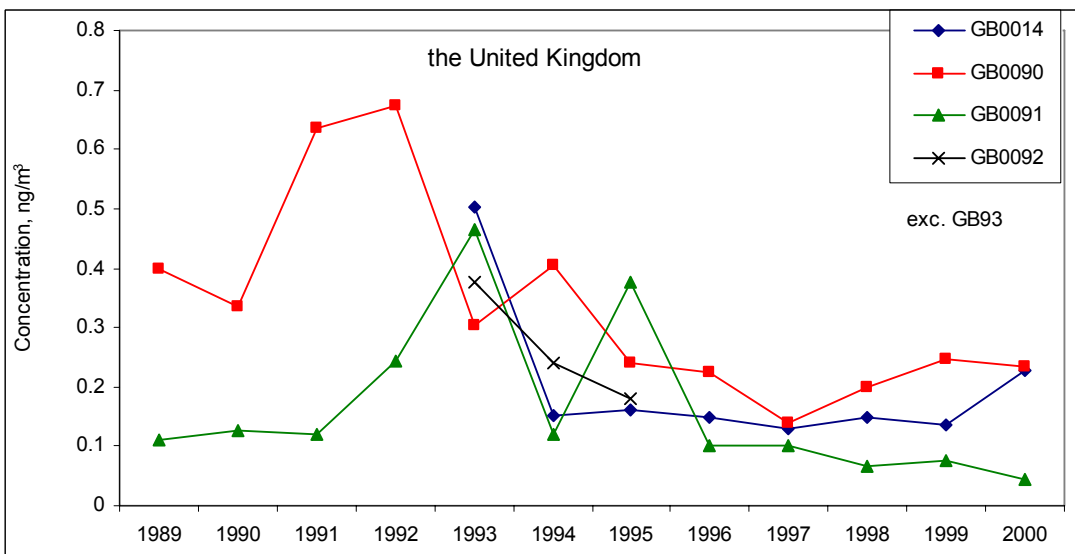
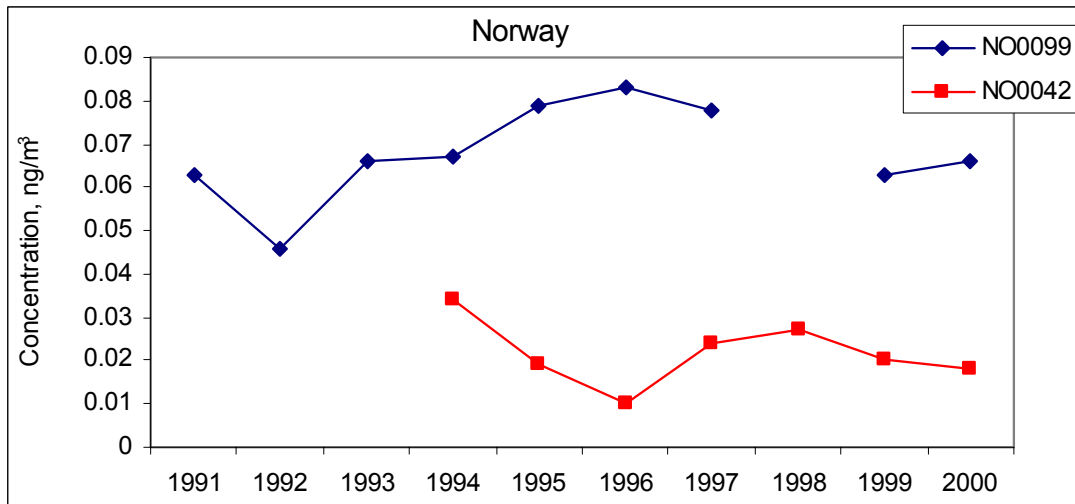
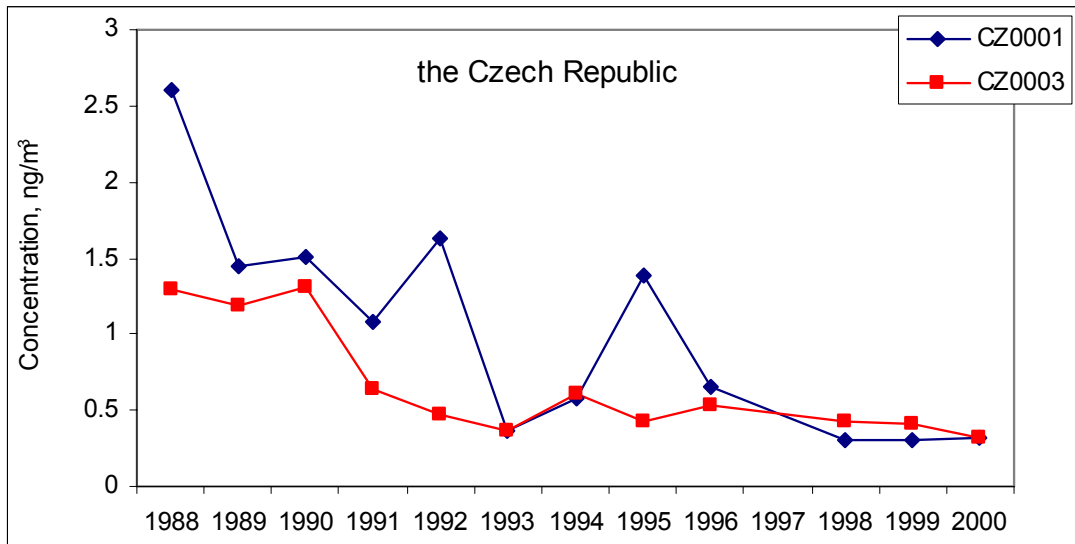


Figure 9: Cd concentration in aerosols measured at the EMEP stations in the Czech Republic, Norway, and the United Kingdom (in ng/m³).

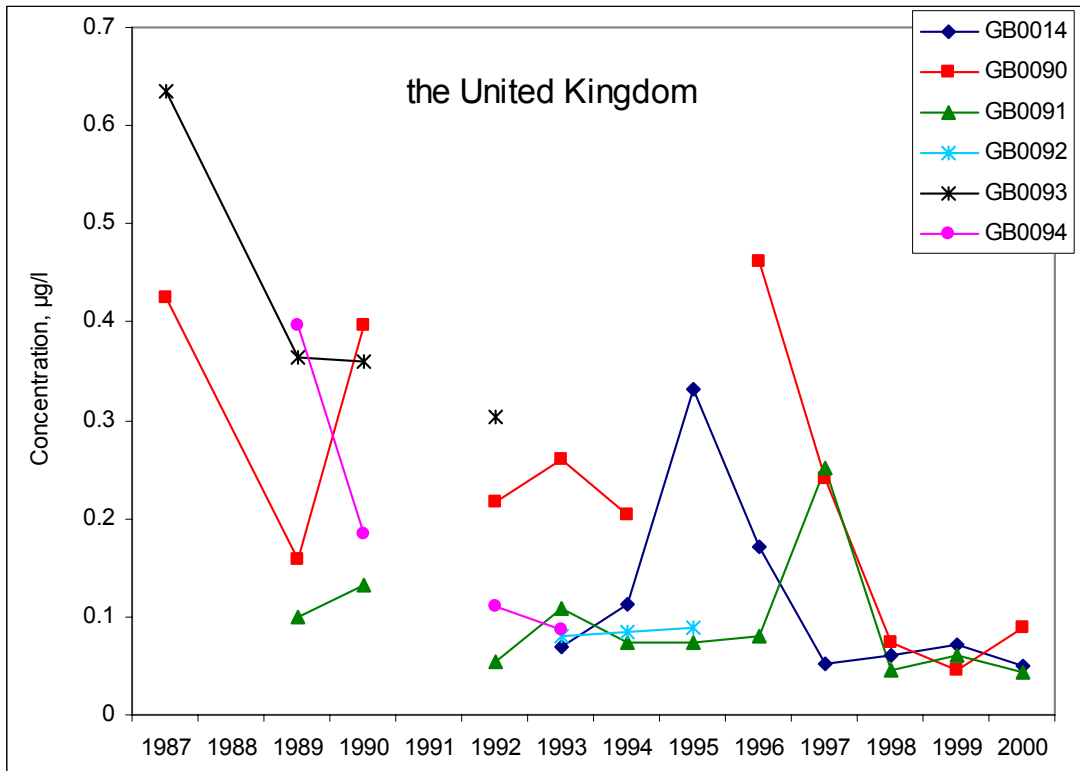
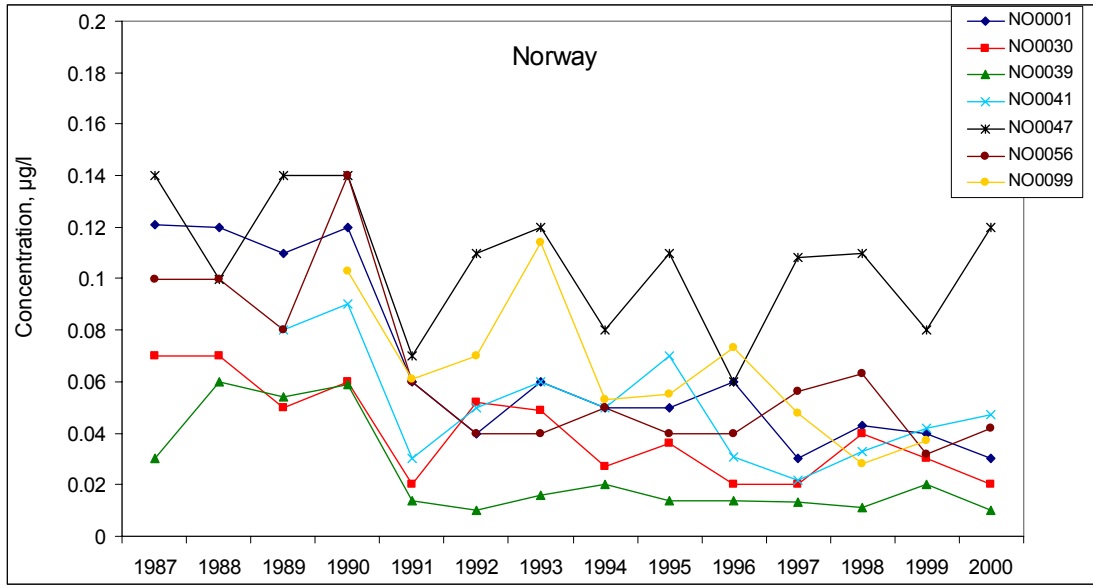


Figure 10: Cd concentration in precipitation measured at the EMEP stations in Norway and the United Kingdom (in µg/l).

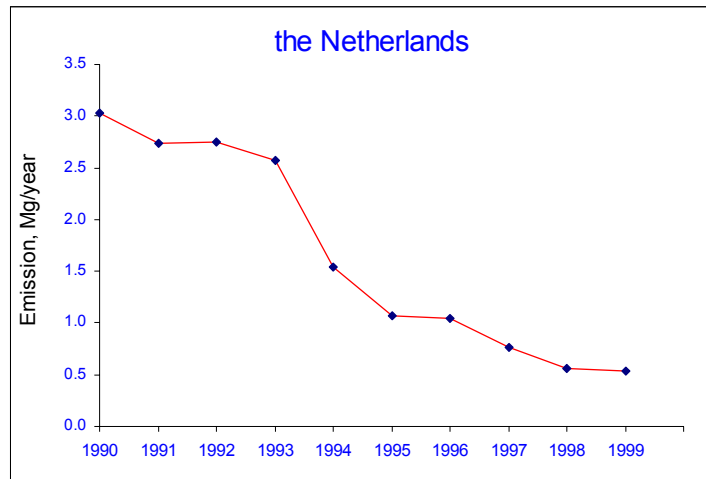


Figure 11: Hg emissions from anthropogenic sources in the Netherlands (in Mg/year).

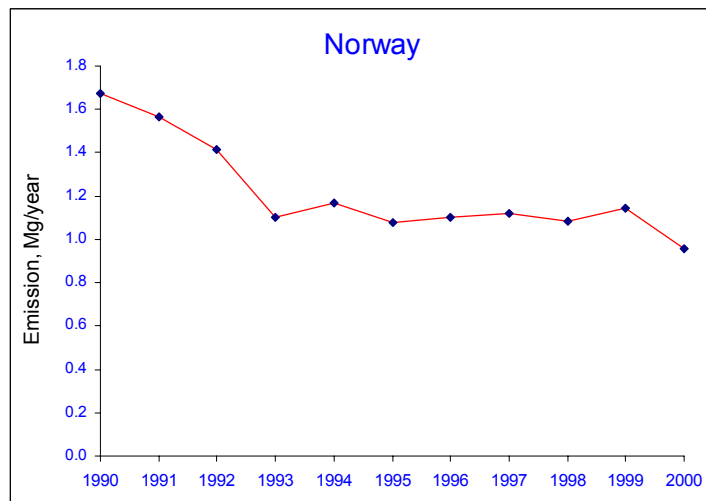


Figure 12: Hg emissions from anthropogenic sources in Norway (in Mg/year).

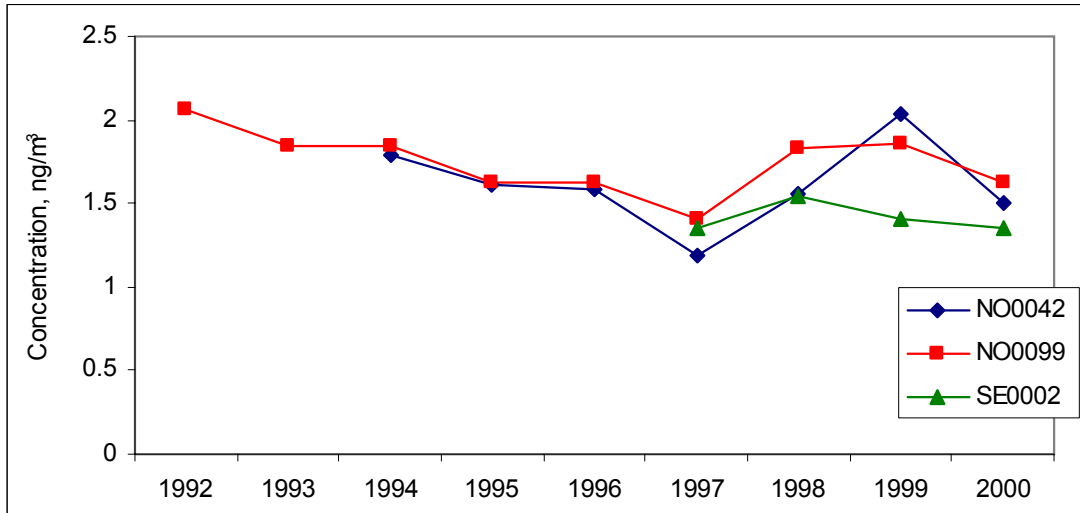


Figure 13: Hg concentration in samples in air and aerosol measured at the EMEP stations in Norway and Sweden (in ng/m^3).

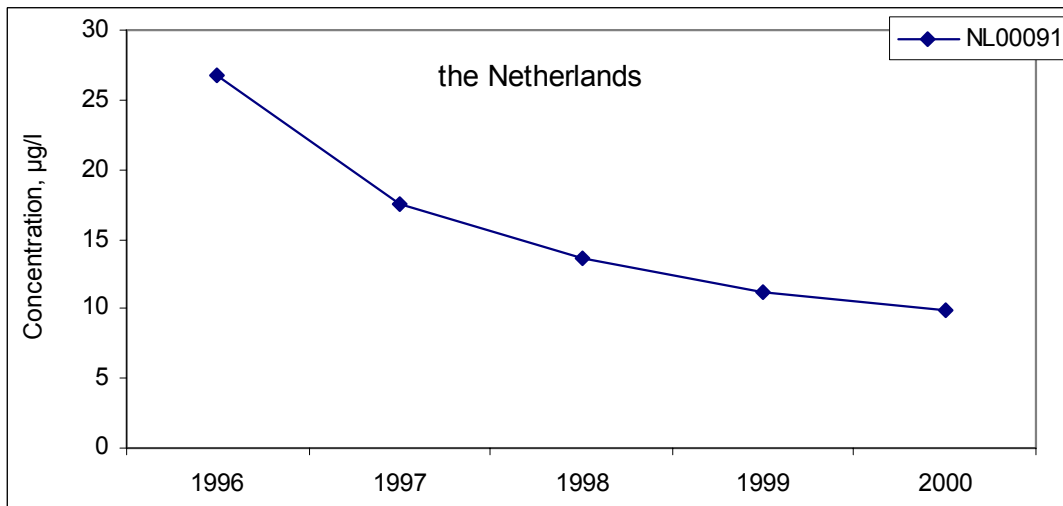


Figure 14: Hg concentration in precipitation measured at the EMEP station in the Netherlands (in $\mu\text{g}/\text{l}$).

A list of EMEP stations discussed in this note:

Station code	Station name	Country	Location		Height above the sea, m
			Lat.	Long.	
CZ0001	Svratouch	the Czech Republic	49°44'N	16°02'E	737
CZ0003	Košetice	"	49°35'N	15°05'E	534
NL0091	De Zilk	the Netherlands	52°18'N	4°30'E	4
NO0001	Birkenes	Norway	58°23'N	8°15'E	190
NO0030	Jergul	"	69°24'N	24°36'E	255
NO0039	Kårvatn	"	62°47'N	8°53'E	210
NO0041	Osen	"	61°15'N	11°47'E	440
NO0042	Spitsbergen, Zeppelinfjell	"	78°54'N	11°53'E	474
NO0047	Svanvik	"	69°27'N	30°02'E	474
NO0056	Hurdal	"	60°22'N	11°04'E	300
NO0099	Lista	"	58°06'N	6°34'E	13
SE0002	Rörvik	Sweden	57°25'N	11°56'E	10
GB0013	Yarner Wood	the United Kingdom	50°36'N	3°43'W	119
GB0014	High Muffles	"	54°20'N	0°48'W	260
GB0090	East Ruston	"	52°48'N	1°28'E	5
GB0091	Banchory	"	57°05'N	2°32'E	120
GB0092	Isle of Wight	"	50°42'N	1°18'W	35
GB0093	Staxton Wold	"	54°11'N	0°26'W	35
GB0094	Lough Erne	"	54°24'N	8°03'W	35