CONCENTRATIONS OF GASEOUS TRACE ELEMENTS SUCH AS MERCURY IN THE AMBIENT AIR OF THE NETHERLANDS

Ruud Meij

KEMA, RO, Box 310
NL 6800 ET ARNHEM
The Netherlands

Tel.: +31-26-3562225 fax: +31-26-4454659
E-mail: r.meij@kema.nl

ABSTRACT

Around the world, there is increasing concern about mercury in the environment. Sources of mercury emissions to the air include municipal waste incineration plants, coal-fired power plants and municipal sewage sludge disposal. The emission of mercury from coal-fired power plants in the Netherlands is well documented. However, to assess the environmental consequences of the emissions of mercury and other trace elements, it is necessary to know the background concentrations in the ambient air.

Over a period of a year, a measuring station was in operation at Arnhem (the Netherlands) to sample the ambient air. Active carbon was used as an adsorption medium: a method developed by KEMA. The sampling periods were one to two months, so that a total of nine duplicated measurements were made.

The ambient concentrations of the gaseous trace elements arsenic, boron, bromine, antimony, selenium, mercury and iodine in the air were determined. The averaged concentrations were as follows: arsenic 1.2 ± 0.15, boron 60 ± 2, bromine 50 ± 0.7, antimony 0.4 ± 0.06, selenium 0.8 ± 0.6, mercury 1.4 ± 0.15 and iodine 6 ± 1.7 ng•m^{-3}

On the basis of these results, it does not appear that the ambient mercury concentrations in this area are problematic.

1 INTRODUCTION

In order to study the environmental impact of coal-fired units in the Netherlands, it is necessary not only to quantify emissions and calculate immissions, but also to know the background ambient atmospheric concentrations. Only once these concentrations are known is it possible to determine the extent to which the situation is affected by the use of coal for power generation. The Dutch background concentrations of many elements and compounds were determined in 1982 and 1983 as part of the NOK-LUK programme (a national research programme concerned with coal-fired plant and the associated pollution; PEO, 1985). However, the data on the environmentally significant element gaseous mercury was based upon measurements carried out over a mere two-month period at four locations. The average concentration

suggested by the NOK-LUK research was 0.3 ng•m^{-3}, while data published elsewhere indicated that 4 ng•m^{-3} was more realistic.

Meanwhile, concern about the presence of mercury in the environment has grown. Mercury has been recognised as an environmental hazard since the fifties, when many people in Japan died and still more contracted serious conditions of the central nervous system as a result of eating fish contaminated with mercury. Since 1984, a national research programme has been running in Sweden, looking at the impact of mercury on the environment. Like Canada and northern parts of the US, Sweden has a problem with mercury, because the granite bedrock reduces the soil's buffer capacity. As a result, acidification easily occurs in lakes affected by acidic deposition. A side-effect of this process is that the mercury present in the humus layer is released by the acidic rainwater. The mercury in the humus layer is of anthropogenic origin, having accumulated as a result of deposition from the air over many years. The mercury concentrations in the water are not a direct threat to plants, animals or people. However, it appears that inorganic mercury is converted into methyl mercury, which can find its way into fish. Human consumption of fish affected in this way could cause poisoning similar to that which occurred in Japan. The Swedish authorities have accordingly set a limit on the mercury concentration in fish, namely 1 milligram per kilo, dry weight. In 10 300 of Sweden's 83 000 lakes, this level is exceeded, making the fish unsuitable for human consumption. With a view to preventing the situation getting worse, the Swedes are seeking to cut mercury deposition by 80 per cent. Unfortunately, most of the mercury deposited in Sweden comes from other countries, so the Swedes are pressing for a pan-European strategy to reduce mercury emissions, comparable with that previously implemented for sulphur dioxide (Lindqvist, 1991a; Lindqvist, 1991b). In the *Fifth Environmental Action Programme: Towards Sustainability*, a European Community programme of policy and action in relation to the environment and sustainable development, several objectives are set. For mercury, the objective is a reduction in emissions of at least 70 per cent by 1995 (EC, 1993).

Sources of mercury emissions to the air include municipal waste incineration plants, coal-fired plants (Sloss, 1995) and municipal sewage sludge disposal plants (Carpi and Lindberg, 1997).

In 1992, an article by Slemr & Langer appeared in *Nature*, indicating that mercury concentrations in the atmosphere had increased as a result of anthropogenic emissions. The reported increase was greater in the Northern Hemisphere than in the Southern Hemisphere. The authors' conclusions were based upon measurements carried out above the Atlantic Ocean in 1977, 1978, 1979, 1980 and 1990, from the southern tip of South America to Bremerhaven. There was apparently 6 000 tons of mercury, 92 per cent of it metallic, in the atmosphere. The average residence time of this atmospheric mercury was about one year, and three quarters of it had been released by human activity, in particular the combustion of coal (Slemr & Langer, 1992).

Mercury pollution is also causing considerable concern in the US.

Against this background, KEMA was asked by the Netherlands' electricity generating companies to monitor the ambient atmospheric concentrations of various substances, including mercury, in Arnhem. The measurement technique used, which was based on active carbon, had previously been developed by KEMA itself. Monthly or bimonthly average values were obtained.

As well as measuring mercury levels, the concentrations of gaseous elemental arsenic, boron, bromine, antimony and selenium were also determined. During one of the measurement periods, iodine, fluorine and chlorine were also measured.

2   EXPERIMENTAL

The samples were collected on KEMA's site in Arnhem. Ambient air was drawn in through the underside of the sampler, one metre above ground level, at a rate of $2\,l\bullet min^{-1}$. The air was then led over so-called small carbon cartridges. Sampling lasted for between 800 and 1 500 hours (a period of one to two months). The carbon cartridges were made of quartz and had two compartments, each about 0.05 metres long, with a diameter of 0.01 metres. Approximately two grams of active carbon was placed in each compartment, held in place by wads of quartz wool, which also served to exclude particulate material. The active carbon, which was shaped into rounded forms, was supplied by the Japanese company KUREHA (BAC lot. no. MP 62176, diameter between 0.1 and 1 millimetre). The carbon cartridges were placed in a holder heated to about 20°C to exclude moisture condensation. Each measurement was duplicated. Prior to use, the carbon cartridges were loaded on a clean bench; after sampling, they were then emptied in a similar environment, so as to avoid all forms of contamination. Two additional carbon cartridges completed an identical journey during each measurement period, acting as exterior control samples.

The active carbon sampling technique had previously been developed by KEMA to measure gaseous trace elements in flue gases. A metallic mercury calibration gas was prepared in the laboratory, then the efficiency under various conditions was established (Meij *et al*., 1989; Meij, 1991a).

After sampling, the active carbon was analysed at ECN by means of INAA to determine the concentrations of arsenic, bromine, antimony, selenium and mercury (Sloot and Das, 1974). In one case, chlorine, fluorine and iodine concentrations were also determined. Boron was released using nitrous acid as a digection procedure and the amount released measured by ICP. The carbon from both compartments of each cartridge was analysed to provide information on the degree of penetration.

The prevailing meteorological parameters were recorded at a KEMA weather station in the nearby town of Wageningen. The parameters measured at this station were the hourly average temperature one metre above ground level and the wind direction and speed ten metres above ground level. The data collected was grouped in bands for the same periods that the ambient atmospheric measurements were in progress. De results are presented in tables 2, 3 and 5.

3   RESULTS AND DISCUSSION

The annual average concentrations determined are presented in table 1, which also shows the corresponding figures from the NOK-LUK programme (PEO, 1985). The boron and bromine concentrations measured in the KEMA experiments proved close to the NOK-LUK data. Although higher than the NOK-LUK figures, the mercury concentrations measured were lower than those recorded by Slemr & Langer in October and November of 1990 in the air above the North Atlantic (range: 1.41 – 3.41; average 2.247 ng•m⁻³) (Langer & Slemr, 1992).

Table 1 Average ambient atmospheric concentrations (in ng•m^{-3}) of the gaseous elements arsenic, boron, bromine, antimony, selenium and mercury, measured over a period of a year at Arnhem, the Netherlands.

| ng•m^{-3} | KEMA-results | | | | | NOK-LUK |
	low	high	mean	±	std.	1983
As, arsenic	0.5	3.3	1.2	±	0.15	
B, boron	0.3	254	60	±	2	50
Br, bromine	27.5	77.6	50.1	±	0.70	50
Hg, mercury	0.5	4.3	1.4	±	0.15	0.3
I, iodine[1]	2.9	9.1	6			
Sb, antimony	0.1	0.8	0.4	±	0.06	
Se, selenium	0.3	1.3	0.8	±	0.58	

[1] only one measurement (February)

The KEMA data also indicated that the concentrations were subject to seasonal variation. The data on arsenic, boron, bromine, antimony, selenium and mercury from each measurement period are presented in graphical form in figure 1. The duplicate measurements are placed next to each other per measuring period. No duplicate measurement was made in December because one of the pumps failed in that month.

Measurements were continued for more than a year, which included the summer of 1990. High temperatures (between 25 and 30°C) were recorded during spells in the May/June and July/August measurements periods. In the winter of 1990/1991, cold spells (with hourly average temperatures falling to minus 12°C) were recorded in the January and February/March measurement periods (see table 2). During these cold spells, there were also heavy snow falls. Wind speeds were fairly consistent throughout the experimental period, and there were no very strong winds (see table 3). Generally speaking, the prevailing wind was from the south-west. In the summer, however, north-westerlies prevailed, while the cold spell was characterised by north-easterlies (see table 4).

The bromine, antimony and mercury concentration data displays a clear seasonal correlation. The highest concentrations were recorded in the winter and the lowest in the summer. There are three possible explanations for this phenomenon. First, emissions may rise in the winter, particularly in Eastern Europe, where coal is an important fuel, both for spatial heating and for electricity generation. Second, the variations may reflect seasonal changes in the prevailing wind direction. Third, winter conditions are liable to hamper dispersal, because the inversion layer is lower. A similar pattern of mercury concentrations has been observed in Sweden, albeit at a higher overall level. Another feature of the Swedish situation was that concentrations were higher in the south than in the north: 1.5 to 2 ng•m^{-3} in the summer and 3 to 4 ng•m^{-3} in the winter (Lindqvist, 1991a).

Mercury emissions from Dutch power stations are low, partly because the coals fired contain relatively little mercury and partly because the plants have flue gas desulphurisation systems, which remove at least 50 per cent of the mercury. The total mercury removal in the installation is an average 72%. The emission factor is about 1 mg*GJ^{-1} or 9 µg•kWh^{-1}.
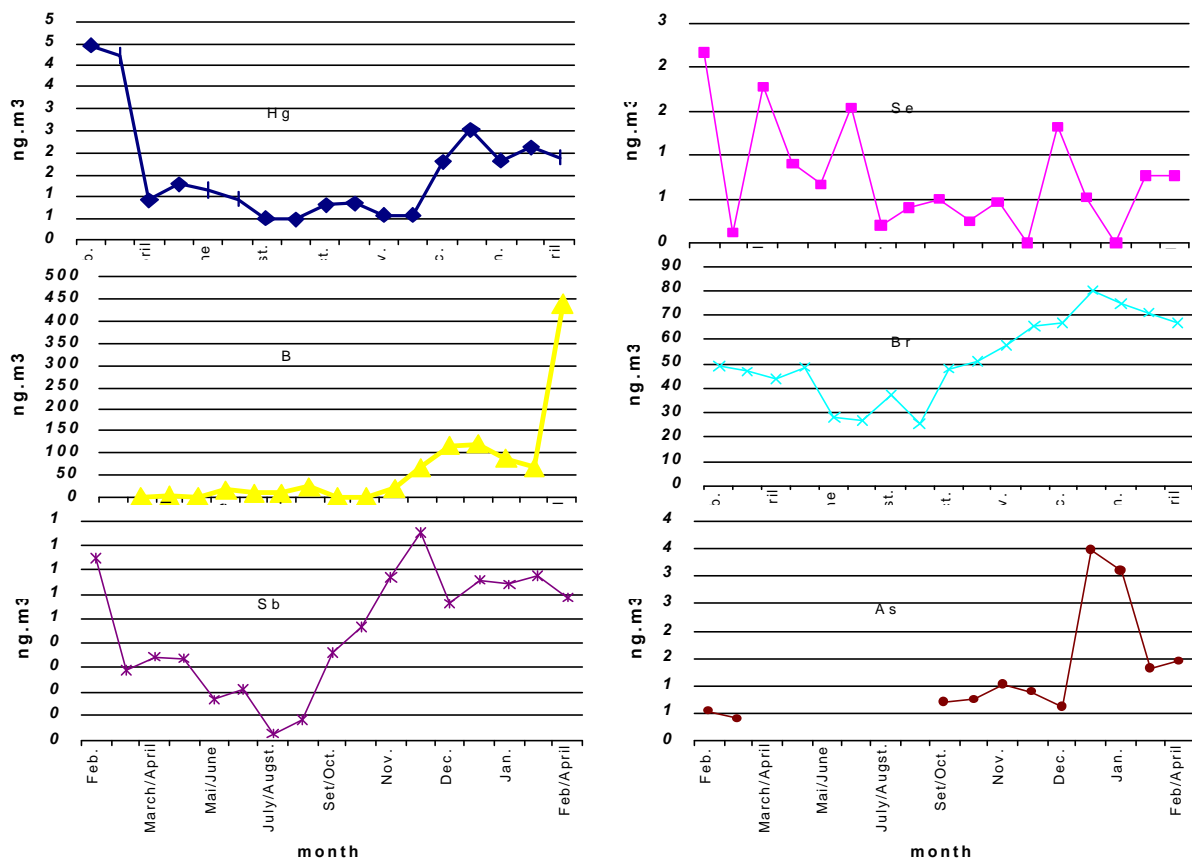
Figure 1   The monthly or bimonthly average ambient atmospheric concentrations of gaseous arsenic, boron, bromine, antimony, selenium and mercury at Arnhem, the Netherlands; for each period the duplicate figures are give.

The NOK-LUK programme data indicated that the background concentration of aerosol-bonded antimony was 2.4 ng•m^{-3}. Taking gaseous antimony into account, the overall background concentration was calculated to be 2.8 μg•m^{-3}.

Arsenic concentrations were not measured in the chemical analysis of the samples from the second, third or forth measurement periods (March 1990 to August 1990). An acceptable level of accuracy could not be achieved because the concentrations in the period up to and including December were only 20 to 60 per cent above the control levels. In the last two measurement periods, the concentrations were 100 to 200 per cent higher than the control levels. No clear seasonal pattern was discerned in the arsenic concentrations, which generally hovered around 1 ng•m^{-3}, except in January 1991, when a level of 3.3 ng•m^{-3} was recorded. The coldest daily temperatures were recorded in this month, and the wind was from the east or the north-east 23 per cent of the time. The NOK-LUK figure for the concentration of aerosol-bonded arsenic was 3.2 ng•m^{-3}. Thus, taking gaseous arsenic into account, the background concentration was more than 30 per cent higher.

Table 2 The relative distribution of ambient air temperatures, divided into bands of 3°C, as a function of the measurement period.

		class	1	2	3	4	5	6	7	8	9	10	11	12	15
		°C	-15/-12	-12/-9	-9/-6	-6/-3	-3/0	0/3	3/6	6/9	9/12	12/15	15/18	18/21	27/30
1	90-02-02	90-03-06	0%	0%	0%	0%	3%	12%	30%	35%	12%	7%	1%	0%	0%
2	90-03-06	90-05-02	0%	0%	0%	1%	3%	9%	17%	30%	26%	8%	4%	2%	0%
3	90-05-02	90-07-03	0%	0%	0%	0%	0%	4%	2%	9%	27%	24%	16%	10%	1%
4	90-07-03	90-09-03	0%	0%	0%	0%	0%	5%	0%	1%	11%	27%	24%	11%	4%
5	90-09-04	90-11-05	0%	0%	0%	0%	1%	5%	7%	18%	27%	23%	14%	5%	0%
6	90-11-05	90-12-05	0%	0%	0%	3%	8%	18%	32%	21%	16%	4%	0%	0%	0%
7	90-12-06	91-01-07	0%	0%	0%	0%	9%	26%	34%	29%	1%	0%	0%	0%	0%
8	91-01-09	91-02-11	0%	5%	9%	13%	27%	24%	13%	6%	2%	0%	0%	0%	0%
9	91-02-11	91-03-29	0%	1%	3%	3%	9%	16%	15%	20%	22%	10%	2%	0%	0%

Table 3 The relative distribution of wind speeds, divided into bands of 3 m•s^{-1}, as a function of the measurement period.

	class	1	2	3	4	5	6	7
	m/s	0-3	3-6	6-9	9-12	12-15	15-18	18-21
90-02-02	90-03-06	13%	40%	24%	16%	6%	1%	0%
90-03-06	90-05-02	37%	42%	17%	4%	0%	0%	0%
90-05-02	90-07-03	72%	24%	4%	0%	0%	0%	0%
90-07-03	90-09-03	72%	23%	5%	0%	0%	0%	0%
90-09-04	90-11-05	57%	31%	10%	2%	0%	0%	0%
90-11-05	90-12-05	58%	33%	6%	4%	0%	0%	0%
90-12-06	91-01-07	21%	49%	21%	5%	4%	0%	0%
91-01-09	91-02-11	50%	34%	13%	3%	0%	0%	0%
91-02-11	91-03-29	53%	33%	12%	2%	0%	0%	0%

Table 4   The relative distribution of wind directions, divided into bands of 30°, as a function of the measurement period.

		sector	1	2	3	4	5	6
		degrees	15-45	45-75	75-105	105-135	135-165	165-195
1	90-02-02	90-03-06	0%	0%	0%	2%	10%	14%
2	90-03-06	90-05-02	9%	10%	3%	3%	8%	12%
3	90-05-02	90-07-03	7%	3%	3%	6%	4%	10%
4	90-07-03	90-09-03	9%	8%	7%	5%	4%	4%
5	90-09-04	90-11-05	2%	3%	5%	10%	7%	7%
6	90-11-05	90-12-05	6%	6%	5%	11%	11%	8%
7	90-12-06	91-01-07	5%	6%	1%	1%	13%	20%
8	91-01-09	91-02-11	10%	23%	13%	11%	6%	7%
9	91-02-11	91-03-29	5%	10%	9%	15%	10%	13%
		sector	7	8	9	10	11	12
		degrees	195-225	225-255	255-285	285-315	315-345	345-15
1	90-02-02	90-03-06	24%	23%	20%	5%	1%	0%
2	90-03-06	90-05-02	8%	21%	15%	6%	3%	3%
3	90-05-02	90-07-03	11%	10%	12%	10%	11%	13%
4	90-07-03	90-09-03	7%	10%	9%	7%	15%	14%
5	90-09-04	90-11-05	16%	16%	10%	8%	9%	5%
6	90-11-05	90-12-05	9%	10%	11%	7%	7%	11%
7	90-12-06	91-01-07	26%	15%	8%	1%	1%	2%
8	91-01-09	91-02-11	7%	5%	2%	1%	5%	9%
9	91-02-11	91-03-29	13%	9%	5%	3%	6%	4%

The selenium concentrations recorded were 100 to 200 per cent higher than the control levels and no clear seasonal pattern was discerned. The NOK-LUK figure for the concentration of aerosol-bonded selenium was 1.8 ng•m^{-3}. Thus, taking gaseous selenium into account, the background concentration was about 50 per cent higher.

No seasonal pattern was detected in boron concentrations either, although consecutive figures did rise sharply, from 1 to 254 ng•m^{-3}. The average concentration of 60 ng•m^{-3} is surprisingly close to the NOK-LUK figure of 50 ng•m^{-3}. The duplicate measurements were good for all measurement periods except the last one. Other authors have reported ambient atmospheric concentrations of gaseous boron of between 1.8 and 460 ng•m^{-3} (FOGG et al., 1984). The data reported here is consistent with such earlier findings. The highest concentrations recorded elsewhere were in Japan. The main sources of boron are sea water and volcanoes. Gaseous boron has a residence time in the troposphere of 19 to 36 days.

The active carbon from the first measurement period was additionally analysed for the presence of chlorine, fluorine and iodine. De ambient atmospheric concentrations of gaseous chlorine calculated from the analytical data were 3.75 and 3.95 µg•m^{-3}, which is about a hundred times lower than one would expect (the NOK-LUK figure was 30 µg•m^{-3}). The sampling technique used was evidently not suitable for the measurement of chlorine concentrations. Fluorine concentrations could not be measured, since the highest

concentrations recorded were below the detection limit (<100 ng•m^{-3}; NOK-LUK 50 ng•m^{-3}). In this context, it is worth noting that KEMA's active carbon sampling technique has been extensively used for the analysis of flue gases at coal-fired power stations, but that the technique has proved to be ineffective for extracting chlorine or fluorine. The iodine concentration was found to be 6 ng•m^{-3} (the average of two measurements of 3 and 9 ng•m^{-3}, respectively).

4   CONCLUSIONS

- The average background concentrations of the gaseous trace elements arsenic, antimony, selenium and mercury, measured at Arnhem in the period 1990 to 1991, were approximately 1 ng•m^{-3}. The concentrations of boron and bromine were approximately 50 ng•m^{-3}. Iodine was measured in one measurement period only, when the concentration was found to be 6 ng•m^{-3}.

- The ambient atmospheric concentration of gaseous mercury measured in the Netherlands in 1983 (0.3 ng•m^{-3}) was probably lower than the true level. The higher concentrations measured by KEMA in 1990-1991 are themselves fairly low compared with the figures reported by other authors.

- Concentrations of the gaseous trace elements bromine, antimony and mercury are subject to seasonal variation. The highest ambient atmospheric concentrations occur in the winter and the lowest in the summer.

- The boron concentrations measured varied considerably over time.

ACKNOWLEDGEMENTS

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