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"Reference method for the determination of Hg deposition"

Minimum Validation Programme CEN/TC 264/WG 25
Field test at Central European industrial site, Šoštanj, Slovenia

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INTRODUCTION

There are currently only the European standard method for the determination of the mercury concentration in water samples (EN 13506), but no standard method exist for the determination of mercury in precipitation. The purpose of described field test was to develop a draft standard for mercury deposition, as defined in the Directive. The field validation included all steps of the draft standard including sample preparation, sampling and analysis of the samples. The field validation enables to demonstrate that the drafted reference method is fit for purpose.

Methods for different types of deposition samplers (bulk, Bergerhoff and wet only) were tested and the experiments for their evaluation were defined and optimized. Sampling and analytical methods were tested over a 6 months period at local/industrial (Šoštanj, Slovenia) and background (Sweden) (coastal/rural) sites.

Bulk, Bergerhoff and wet-only samplers were used to obtain parallel precipitation samples for mercury analysis. It was proposed that equipment currently used in Europe should be tested over a 6 month period at both sites. Duplicate deposition samplers were used to collect for a six months sapling period enough precipitation volumes for analysis by two laboratories to perform an extensive inter-comparison analysis exercise.

The equipment in Slovenia was installed at industrial site in Šoštanj, where coal fired power plant (ŠTPP) and coal mine are located. The aim of intercomparison was to evaluate the reproducibility of bulk, Bergerhoff and wet-only samplers as well as compare the sampling methods.

Sampling site description (Industrial, Šoštanj, Slovenia)

The Šalek Valley is one of the most polluted regions in Slovenia. It is located in the northern part of Slovenia, between the Kamniško - Savinjske Alps and the Karavanke range. The valley is very densely populated. In the centre of the valley is the town Velenje, where Slovenia's biggest coal (lignite) mine is located. Underground reserves of coal are estimated to be about 600 million tons. The second biggest town in the valley is Šoštanj, where over 30% of Slovenian electrical power is produced. Surrounding the valley, small industry and farming are present. The valley lies about 300 m above sea level.
Because of underground coal exploitation, the ground is gradually subsiding and forms hollow depressions that are filled with water. These processes caused the formation of Lake Škale, Lake Velenje, and Lake Šoštanj.

Figure 1. Map of Slovenia with Šalek Valley.

The valley is approximately 10 km long, 5 km wide and extends in the W - E direction. The colder area is along the northern margin of the valley, where the highest peak, Smrekovec (1577 m above the sea level), is also located. The highest air temperatures are usually in July (with an average of 18.8 °C for the period 1961-1990), and the lowest in February (with an average of -1.0 °C for the period 1961-1990) (Mekinda - Majaron, 1995). The difference between the annual absolute highest and absolute lowest air temperature is more than 60 °C. Air humidity is highest in October and November and lowest in April and May. The annual amount of precipitation in the northern part of valley is about 1300 mm, and in the eastern part is about 1100 mm. June and July are the wettest months (average 145-149 mm per month) while January and February are the driest (average 60-62 mm per month).

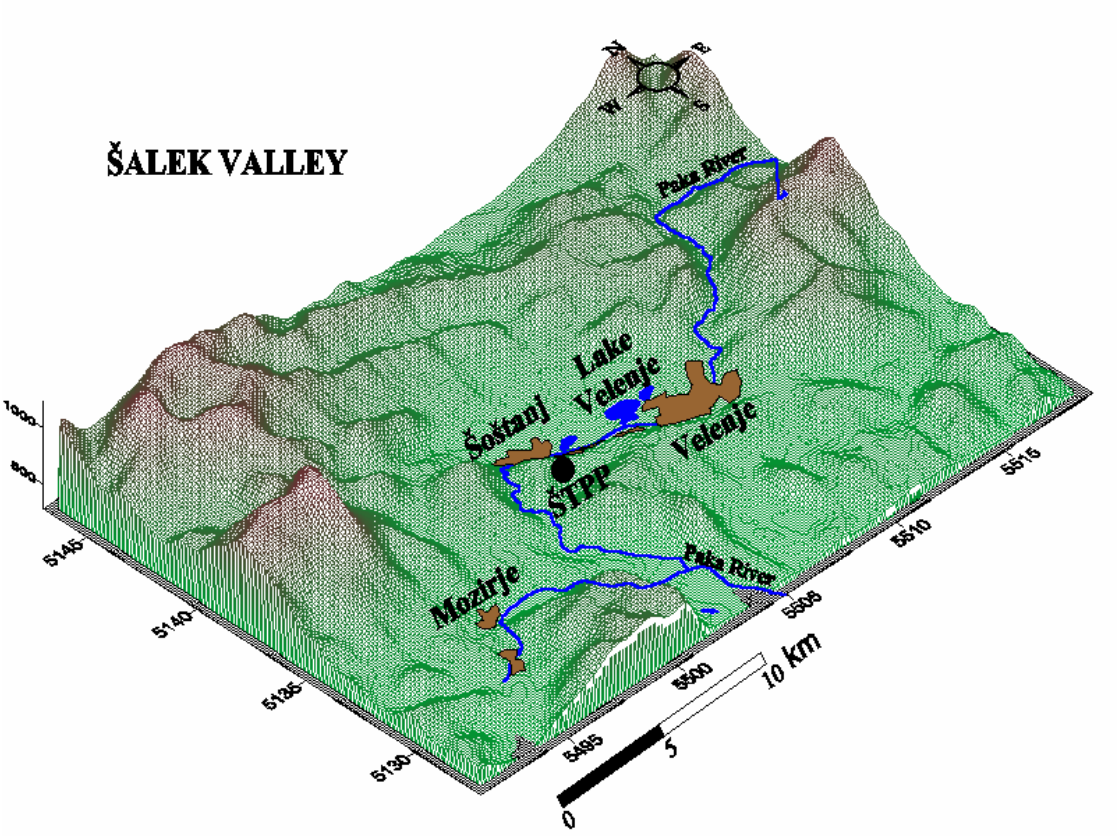

Figure 2. Topography of Šalek Valley.

In autumn and winter there is a very frequent temperature inversion that usually does not exceed a height of 1000 m above sea level. Because of the longer nights and lower height of the sun, the duration of the periods of temperature inversion is longest at the end of autumn and at the beginning of winter. There are two regions of temperature inversions: the lowest, basement inversion is usually between 360 m and 460 m above sea level and the highest, subsidence inversion, is between 750 and 1000 m above sea level.

Wind direction and velocity are locally the most changeable factors and are highly dependent upon the configuration of the terrain. Wind is an important factor for the dispersion of pollutants from the ŠTPP. Generally the prevailing wind directions in the Šalek Valley are east (23.3 %), west (15.7 %) and northeast (11.8 %), that coincide with the direction of the valley axis. Data for Velenje and Šoštanj show that more than 50 % of winds are calm, about 40 % of winds have speeds between 0.5 to 1.5 m/s, and only 5 % of winds have speeds between 1.5 and 3 m/s. Winds in Velenje almost never exceed a speed of 3 m/s. In Šoštanj only 1 to 3 % of winds with speeds between 3 to 5 m/s were observed. Winds are weakest at the bottom of the valley and strengthen with height.

The Šoštanj coal-fired thermal power plant (Fig 3) was built after the Second World War. The combined power of all five units is 775 MW, and represents the biggest electro-energetic system in Slovenia. Yearly, the ŠTPP produces about 3.5M MWh of electrical power and 450000 MWh of heat, and for this 4M tons of coal (lignite) is burned with a heat value of 9.5 MJ kg^{-1}.

Figure 3. Šoštanj thermal power plant - view from north (source: http://www.te-sostanj.si/predstavitev/elektr-01.htm).

The ŠTPP's stacks are 100, 150 and 230 m high. Basement temperature inversion protects the bottom of the valley against pollution. At the greatest heights, subsidence inversion trapping stack gases that then accumulate under the air layer with the temperature inversion. Thus, gases sink above the valley slopes, but do not reach the bottom of the valley.

Emissions from individual heating systems, industrial boilers and traffic are less than one percent of the total emissions from the ŠTPP.

Sampling site

The sampling site was located approximately 2 km NE-E from the power plant, between coal ash landfill expanding towards NW , coal mine on S and E and freshwater Lake Velenje (Fig 4 and 5). The sampling site was located 46.36937°N, 15.08332°E and 370 m above the sea level.

Figure 4. Sampling location (46.36937°N, 15.08332°E, 370 m a.s.l.).

The samplers were located to not interfere with each other. However they were co-located at a distance less than 3m. The collectors were not been exposed to strong winds, and were not been sheltered by tall trees or buildings. There were no obstacles such are trees, buildings or topographical features above 30 m from the rim of the collectors. Supply of the electricity was necessary for wet-only and bulk samplers.

The site was operated by the Department of Environmental Sciences, ‘’Jožef Stefan’’ Institute.

The sampling site is called ‘’At Kinološko društvo’’ and is a part of regular air and deposition pollution monitoring network operated by ŠTPP.

In nearby vicinity of sampling site is a weather observation site operated by Slovenian Environmental Agency.

The field tests started in January 2007 and last until beginning of September 2007.

Figure 5. Sampling location.

MATERIALS AND EQUIPEMENT

Sampling equipment

Mercury was collected in special precipitation samplers. Funnels and collecting bottles were made from Teflon or borosilicate glass. The sampling vessels were bulk samplers which are open at all times, wet-only samplers which are open only during precipitation event and wide mouthed jars (i.e. Bergerhoff samplers).

Bulk samplers

Two bulk samplers were used to collect precipitation samples at the industrial site. Bulk samplers were produced by IVL (Sweden). Funnel and capillary was made of borosilicate glass with collecting vessel made of Teflon. The horizontal opening of the funnel was 82 mm (collecting area was 52.8 cm^2). Bulk samplers are shown on following figures.

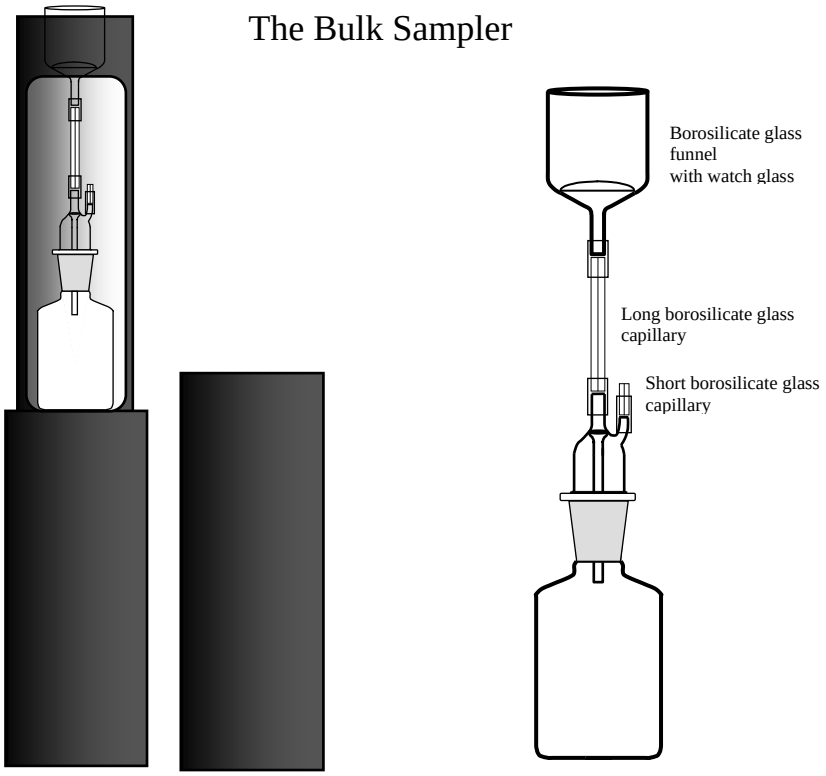

Figure 6. The bulk sampler.

Figure 7. Bulk samplers used at industrial site (Šoštanj, Slovenia).

Wet – only samplers

Two wet-only samplers were used. Samplers were produced by N-CON Systems, USA. The sampler was designed for collection of wet only mercury deposition samples for routine collection of wet fall to provide reliable samples for precipitation chemistry. It provides prompt opening and closing of the sample container and is sensitive to light snow, drizzle or heavy fog. Collected sample was heated or cooled to 5°C, depending on ambient temperature. The horizontal opening of the funnel was 115 mm (collecting area was 103.9 cm^2) Samplers used are shown on following pictures.

Figure 8. Wet - only samplers.

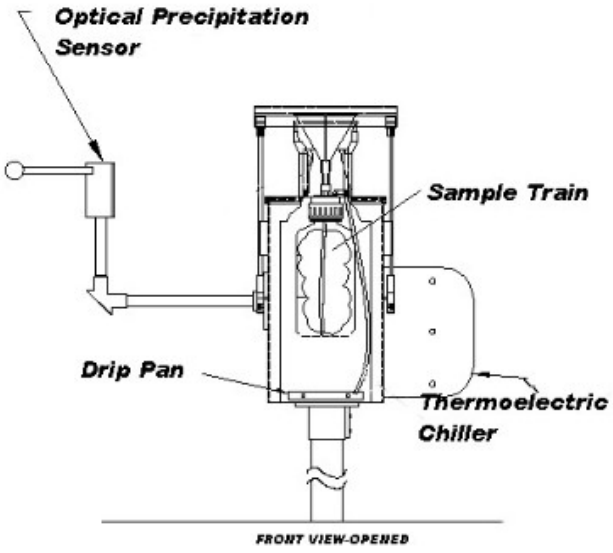

Figure 9. Schematic presentation of wet – only sampler.

Bergerhoff samplers

Four Bergerhoff samplers were used to collect deposition. Two samples were collected on weekly basis and two on monthly basis. The horizontal opening of the sampling vessel was 90 mm (collecting area was 63.6 cm^2).

Figure 10. The Bergerhoff samplers.

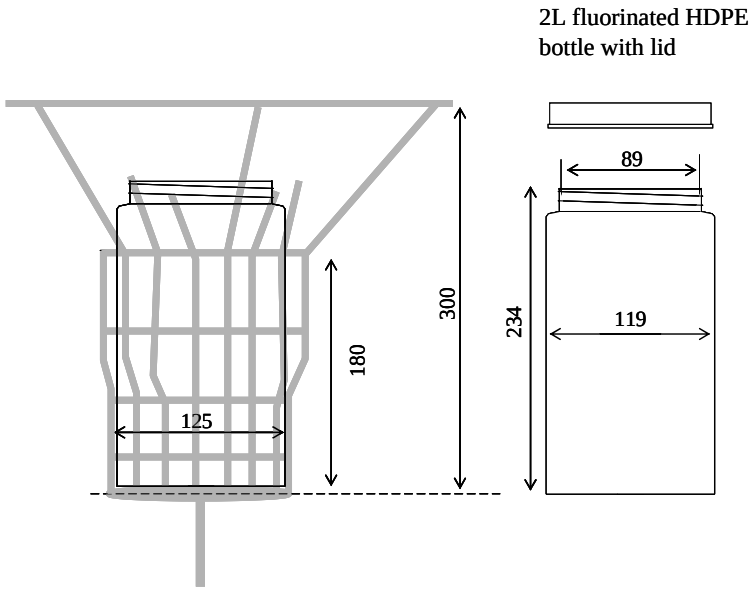

Figure 11. Bergerhoff collector. The sampler consists of a fluorinated HDPE (of 2 l volume and 89 mm diameter opening) collector bottle supported by a steel basket with a "bird ring".

Cleaning of precipitation collectors, sample vessels, sample containers and labware

All parts of precipitation collectors that were in contact with the sample, sample vessels, sample containers and labware were cleaned extensively before use. Cleaning steps were as follows:

1. Wash with alkaline laboratory detergent. Rinse thoroughly with de-ionised Milli-q water.
2. Lench in a solution of 2 % HCl overnight. Rinse thoroughly with de-ionised Milli-q water.
3. If a wet-only or bulk sampler was used 100 ml of 2 % HCl (suprapur) was added to the sampling bottle prior to exposure.
4. Glass funnels, capillaries or bottles that were believe to be contaminated were leached with BrCl solution for at least 24 hand than cleaned followed the upper procedure.

Powder free latex gloves were used during all steps of the cleaning procedure. All cleaned equipment was double bagged during storage and transport to the sampling site.

SAMPLING PROCEDURE

All samples, replacement sample bottles and other labware were handled with care in order to avoid contamination during sample bottle replacement, transport and storage. During all steps of sample bottle replacement powder free latex gloves were used. All bottles were kept in double plastic bags during transport and storage. All equipment needed for the sample bottle exchange were transported in plastic box and placed on clean plastic surface during the procedure.
Funnel and capillary in bulk and wet-only sampler were rinsed with deionised Milli-q water before installing new bottle. If visible materials were present funnel and capillary were disconnected and rinsed separately. If funnel and capillary were visibly dirty even after rinsing, they were replaced with new newly washed pieces.
The complete sample was send to the laboratory in the sampling vessel. The sample amount was measured by weight in the laboratory. The empty sampling bottles were weighted before use and than weighted after sampling period.
Samples for storage were refrigerated (5°C) and kept in dark. Samples will be stored for 6 months provided that the long term stability will be checked.
Before storage, the samples collected by Bergerhoff samplers were preserved by addition of 5 ml hydrochloric acid (30%, suprapur) per litre of sample. 100 ml of 2% HCl (suprapur) was added to wet-only and bulk sampling vessel prior to exposure.

Field blanks

The funnel in bulk and wet only samplers were rinsed with a known volume (500 ml) of 5 % (v/v) HCl (suprapur). The rinsing solution was collected in empty and clean sampling bottle. The rinsing solution was treated like normal precipitation sample. Field blanks were taken twice in the period of 6 months.

Analytical procedure

Analysis of samples was performed following the analytical methods described in EMEP reference method, using atomic absorption spectrometry (AAS). Mercury in precipitation samples were oxidized with BrCl, followed by UV irradiation, $SnCl_2$ reduction, gold amalgamation and AAS detection.

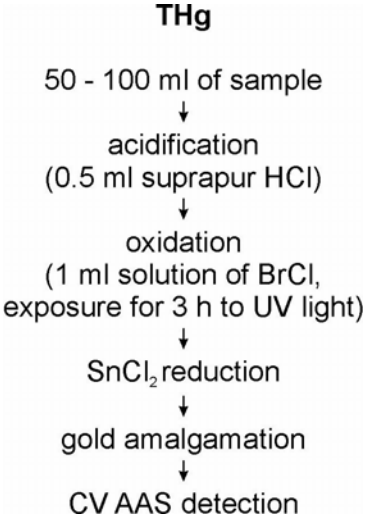

Figure 12. Schematic presentation of analytical method used.

Instrumentation

Following equipment was used:

- Naglene Teflon vessels, 125 or 250 mL
- Three-way Teflon valve, Cole Parmer
- Two-way Teflon valve, Cole Parmer
- Borosilicate glass reduction vessel
- Borosilicate neutralization cell
- Gold trap quartz tubes
- Quartz sand coated with gold, Brooks Rand
- GPC 145 multifunction controller
- Flow meters, Cole Parmer
- Teflon tubes, Cole Parmer
- Teflon fittings, Cole Parmer
- LCD AAS detector, Milton Roy
- Recorder, 1mV to 5 V, Cole Parmer
- UV lamps, 2×30W, 254 nm, Cole Parmer

Sample storage and handling

Precipitation samples were handled with care, to prevent Hg contamination. Samples were stored in the collection bottles, double bagged, in the dark refrigerator at 5°C.

Storage time prior to analysis was 1 to maximum 5 days. Powder free latex gloves were used at all times of analytical steps.

Reagents and material

Following reagents and material were used for cleaning and analysis:

- deionised Milli-Q water, Millipore
- Laboratory detergent Micro 90
- HNO_3 for cleaning (65%, pro analysi, Merck)
- HCl for cleaning (30%, pro analysi, Merck)
- HNO_3 (65%, suprapur, Merck)
- HCl (30%, suprapur, Merck)
- $SnCl_2$ (pro analysi, Merck)
- H_2SO_4, 96%, suprapur, Merck
- $HgCl_2$, pro analysi, Merck
- $KBrO_3$, pro analysi, Merck
- KBr, pro analysi, Merck
- $NH_2OH.HCl$, pro analysi, Merck
- Silicagel, Kemika
- NaOH, pro analysi, Merck
- $KMnO_4$, pro analysi, max. 0.000005% Hg, Merck
- Nitrogen, 4.6, Messer

Pre-treatment

The collected samples were preserved with HCl prior to storage. Before analysis chemical oxidation step was performed using BrCl and UV irradiation. Excess BrCl was removed using $NH_2OH.HCl$.

Reduction step

Bubbler blank values were checked regularly prior and after analysis of sample by addition of 1.0 ± 0.5 mL $SnCl_2$ into reduction vessel. After bubbler blank, CRM and calibration standard (1.0 ng Hg) has been measured an aliquot of the pre-treated precipitation sample was added to the reduction vessel. The reduction and purging lasted for 2 min.

Detection

The mercury was thermally desorbed (500 °C) from gold trap directly into the AAS detector using mercury-free N_2 as a carrier gas.

Calculation of the results

Hg concentration in analyzed samples was calculated by following equation:

$$c_{vz} = \left(\frac{h_{vz} - h_{bb}}{h_{st} - h_{bb}} \cdot \frac{1}{V_{vz}} \cdot c_2 \cdot V_2 \cdot 1000 \right) - \left(\frac{h_{sl} - h_{bb}}{h_{st} - h_{bb}} \cdot \frac{1}{V_{sl}} \cdot c_2 \cdot V_2 \cdot 1000 \right)$$

Where:
c_{vz} = concentration of Hg in sample
h_{vz} = sample peak height
h_{bb} = bubbler blank peak height
h_{st} = standard peak height
h_{sl} = blank sample peak height

c_2 = concentration of Hg in standard solution
V_{vz} = sample volume
V_2 = standard solution volume
V_{sl} = blank sample volume

Quality control – Quality assurance

Certified reference material ORMS-3 was checked prior each set of analysis. Obtained values are reported within the section “Results”

RESULTS

Meteorological parameters

Meteorological parameters were measured by Agency for the Environment of the Republic of Slovenia by standard meteorological observation methods. Results in tabular form are presented in Appendix 1. Basic meteorological parameters are presented on Figures 12 – 15.

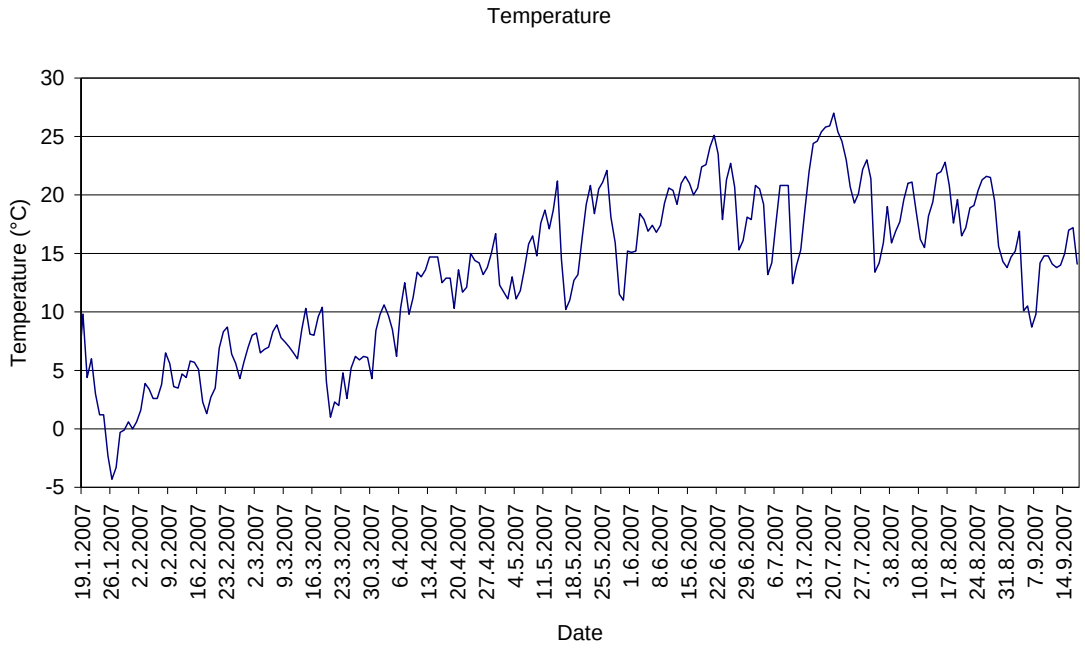

Figure 13. Average air temperature at sampling site in Šoštanj (in°C).

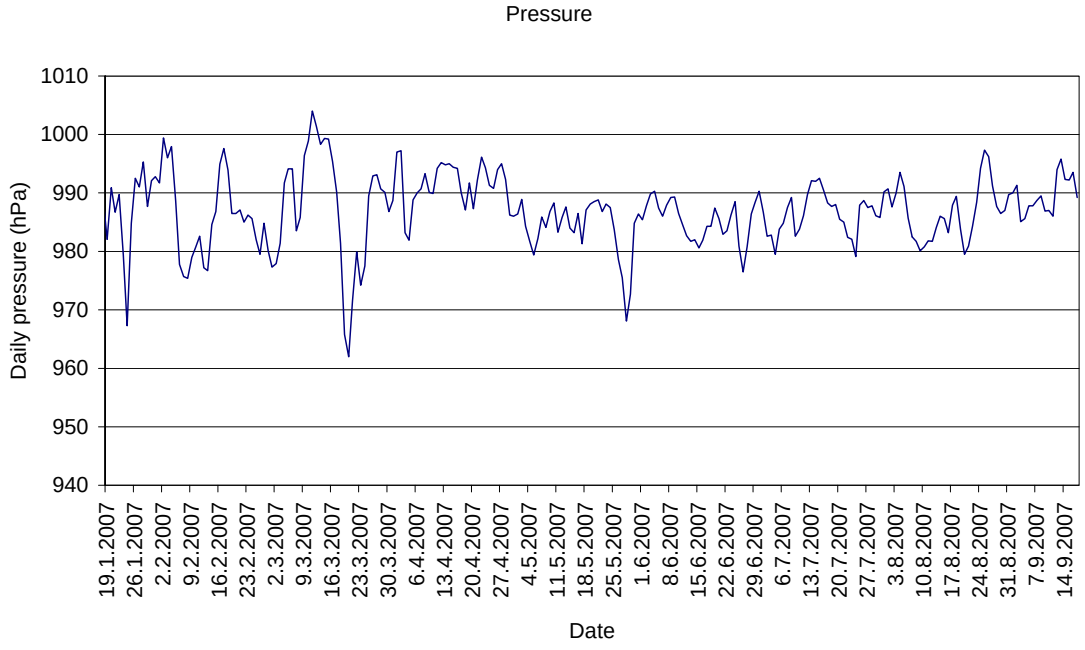

Figure 14. Average air pressure at sampling site in Šoštanj (in hPa).

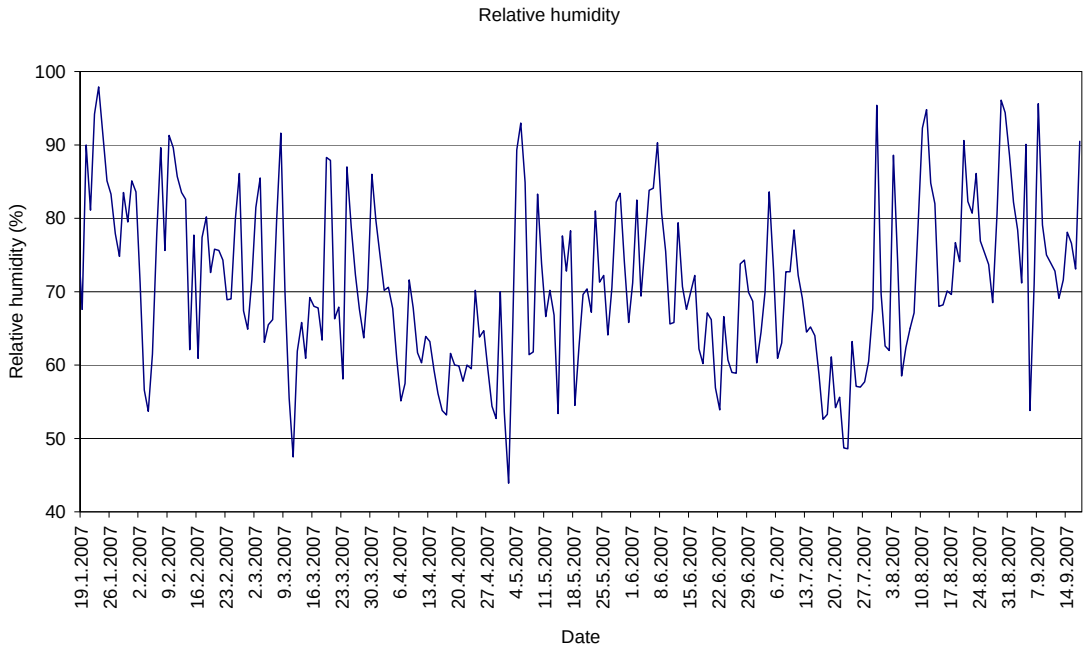

Figure 15. Average air humidity at sampling site in Šoštanj (in %).

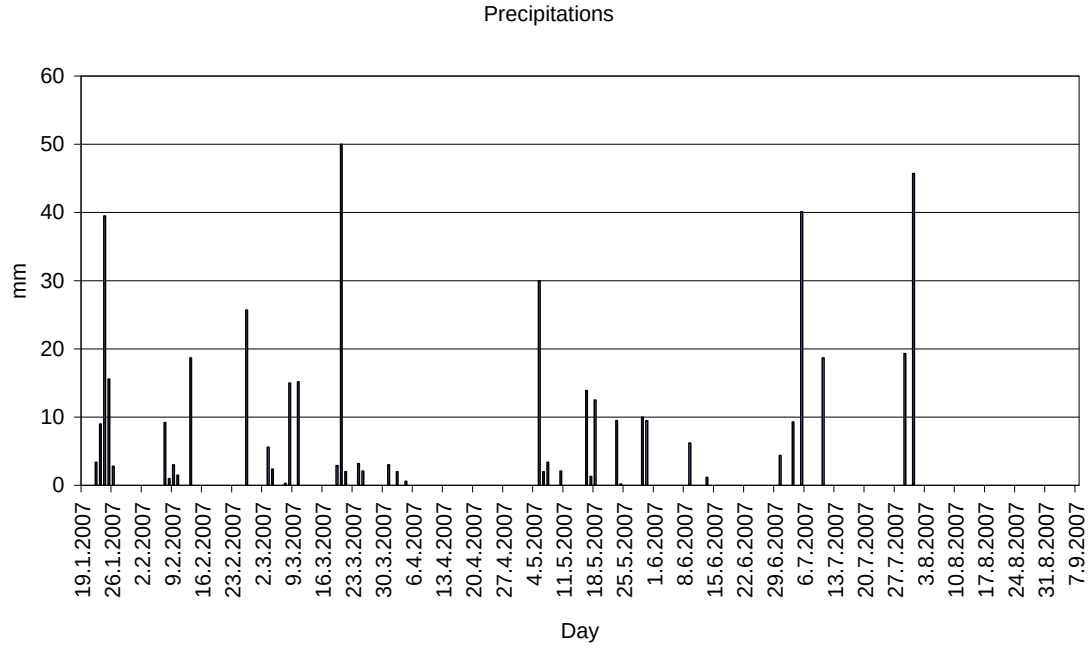

Figure 16. Average amount of precipitations at sampling site in Šoštanj (in mm).

Hg deposition

Hg deposition was calculated using following equation:

$$Dep_{THg} = \frac{M_{THg}}{A_{Samp}} \cdot \frac{1}{7}$$

Where:
Dep_{THg} = total Hg deposition (ng/m^2/day)
M_{THg} = mass of THg per sample (sampler blanks were substracted)(ng/sample)
A_{Samp} = sampler collecting area (m^2)

Graphical presentation of results is shown on following figures (Fig. 23 - 27). Results in numeric form are given in Appendix 2.

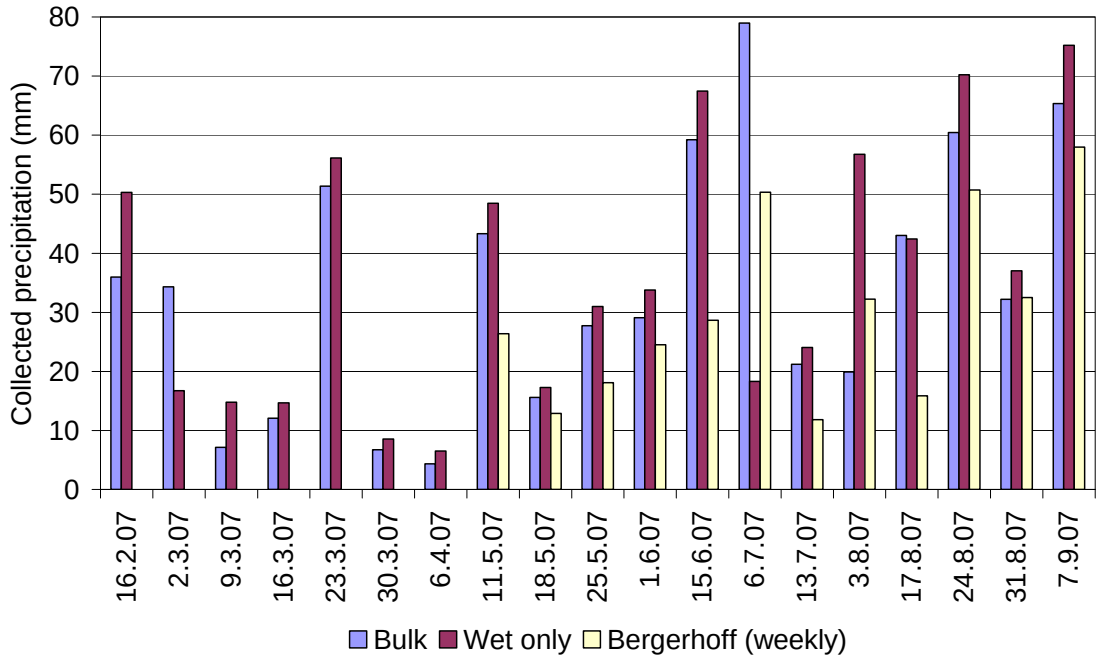

Figure 17. Collected amount of precipitations by different sampler type (in mm).

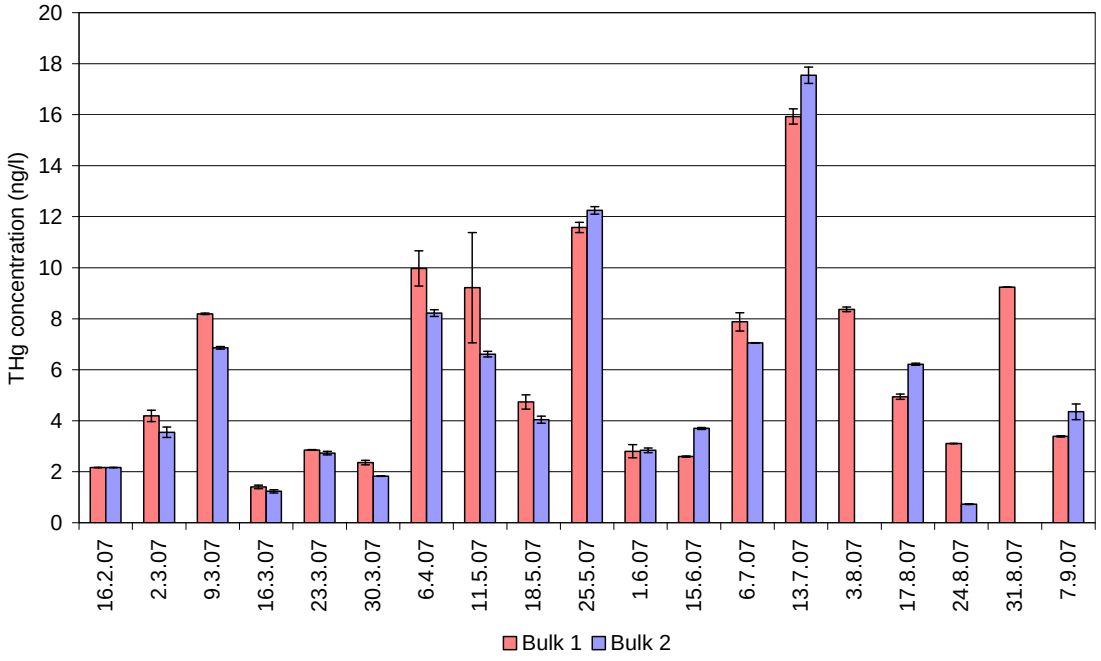

Figure 18. Total Hg concentration in deposition samples collected by “Bulk” samplers (in ng/l).

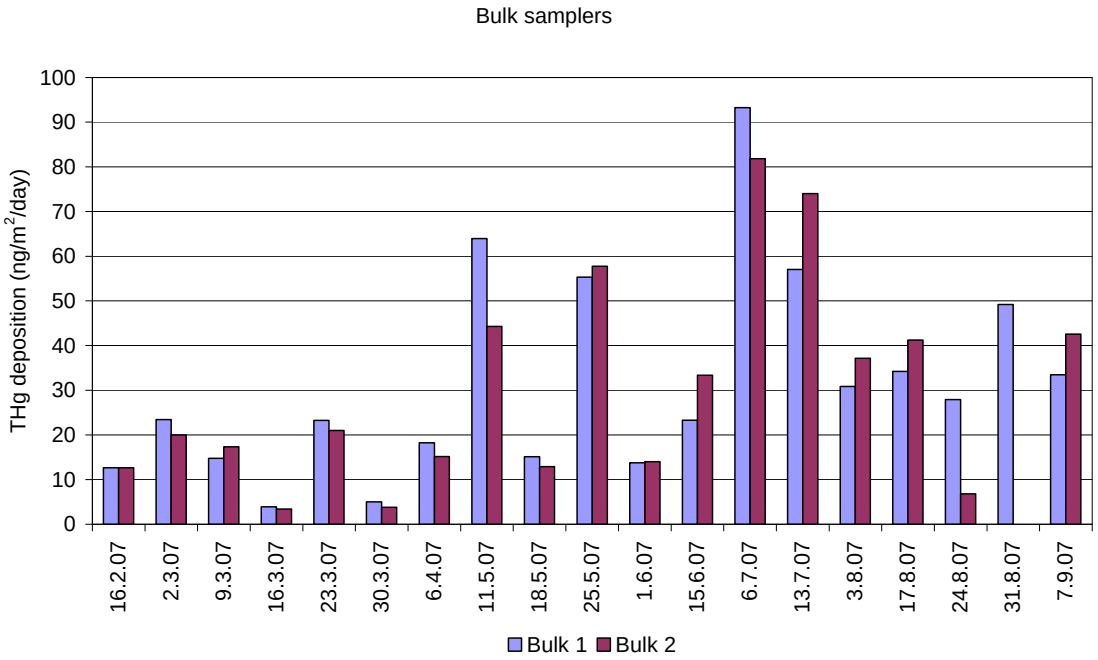

Figure 19. Total mercury deposition rate calculated for "Bulk samplers" (in ng/m^2/day).

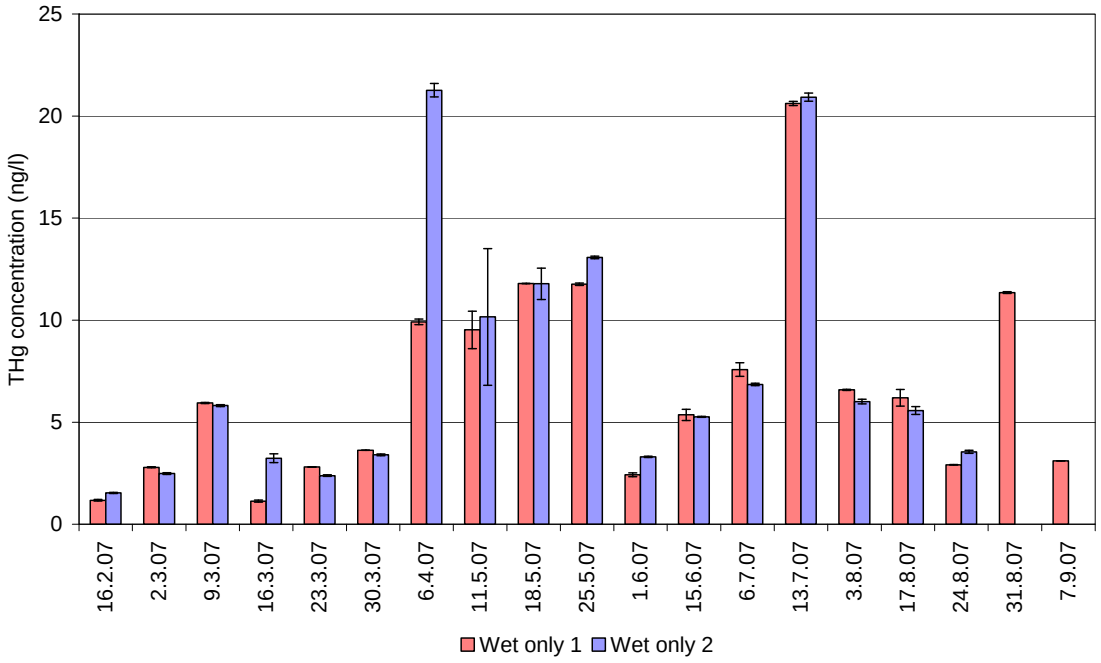

Figure 20. Total Hg concentration in deposition samples collected by "Wet-only" samplers (in ng/l).

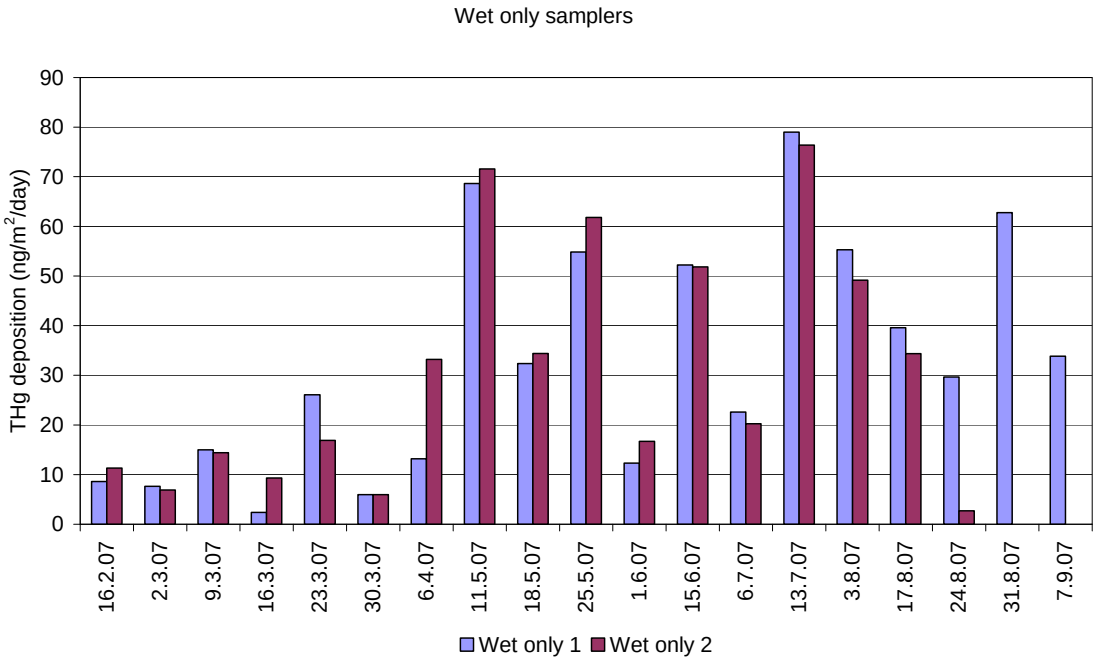

Figure 21. Total mercury deposition rate calculated for “Wet-only” samplers (in ng/m^2/day).

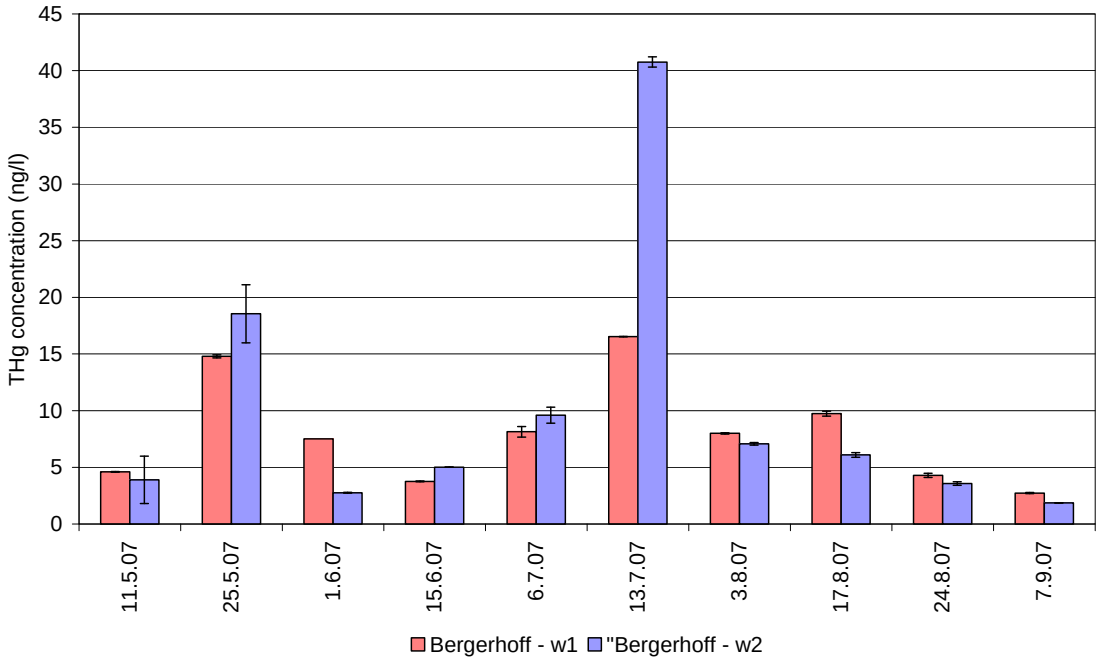

Figure 22. Total Hg concentration in deposition samples collected by “Bergerhoff” samplers on weekly basis (in ng/l).

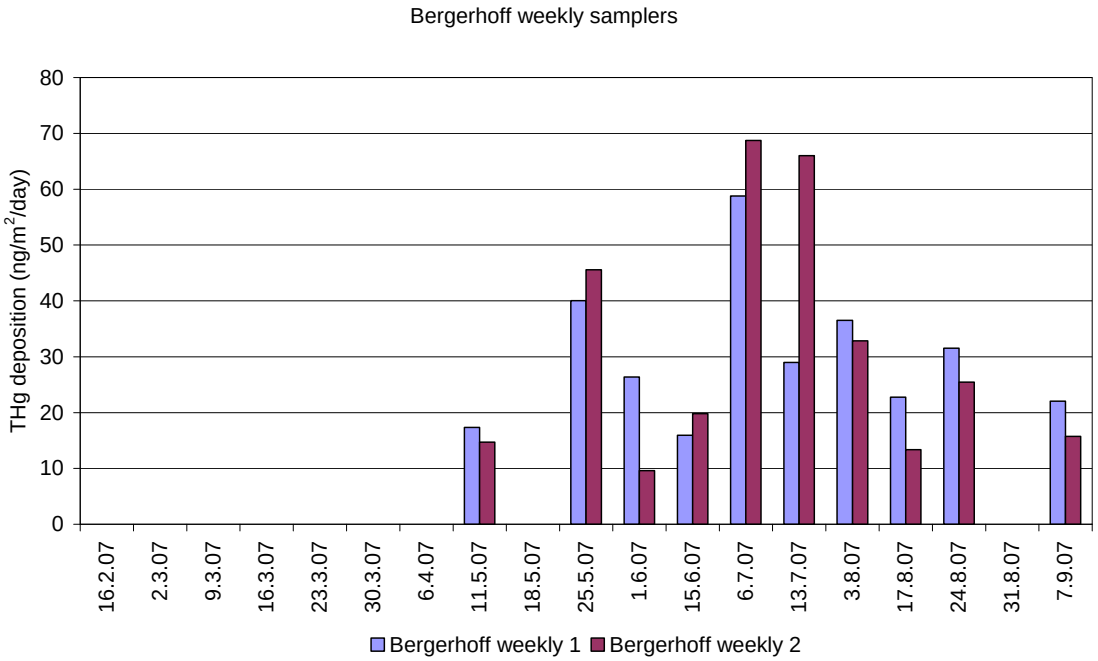

Figure 23. Total mercury deposition rate calculated for “Bergerhoff” samplers collected on weekly basis(in ng/m^2/day).

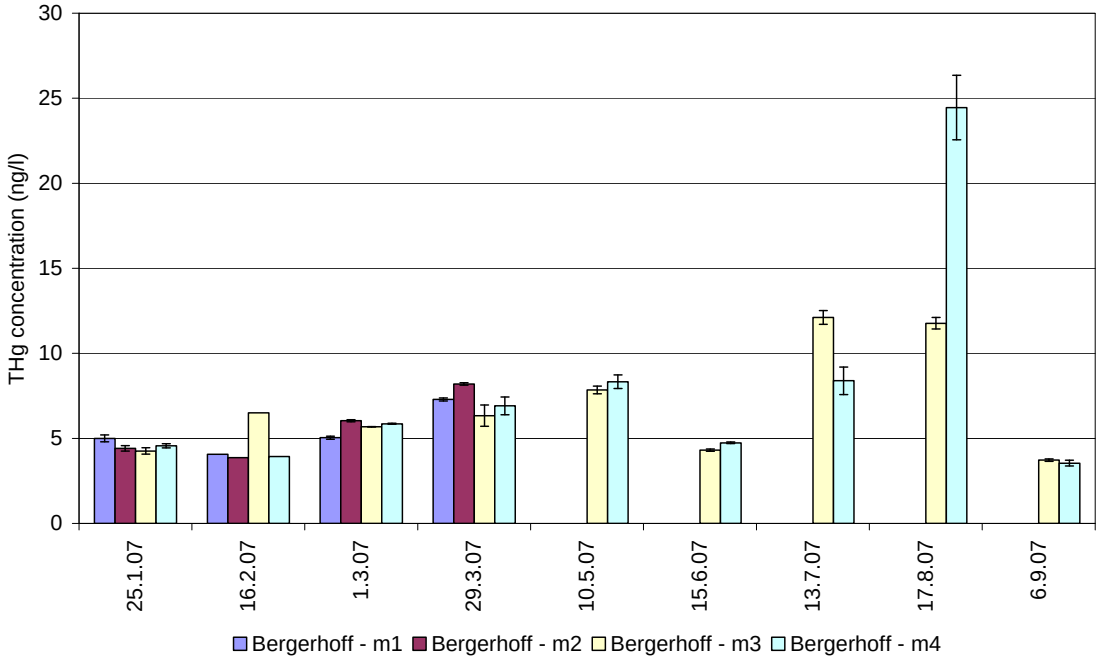

Figure 24. Total Hg concentration in deposition samples collected by “Bergerhoff” samplers on monthly basis (in ng/l).

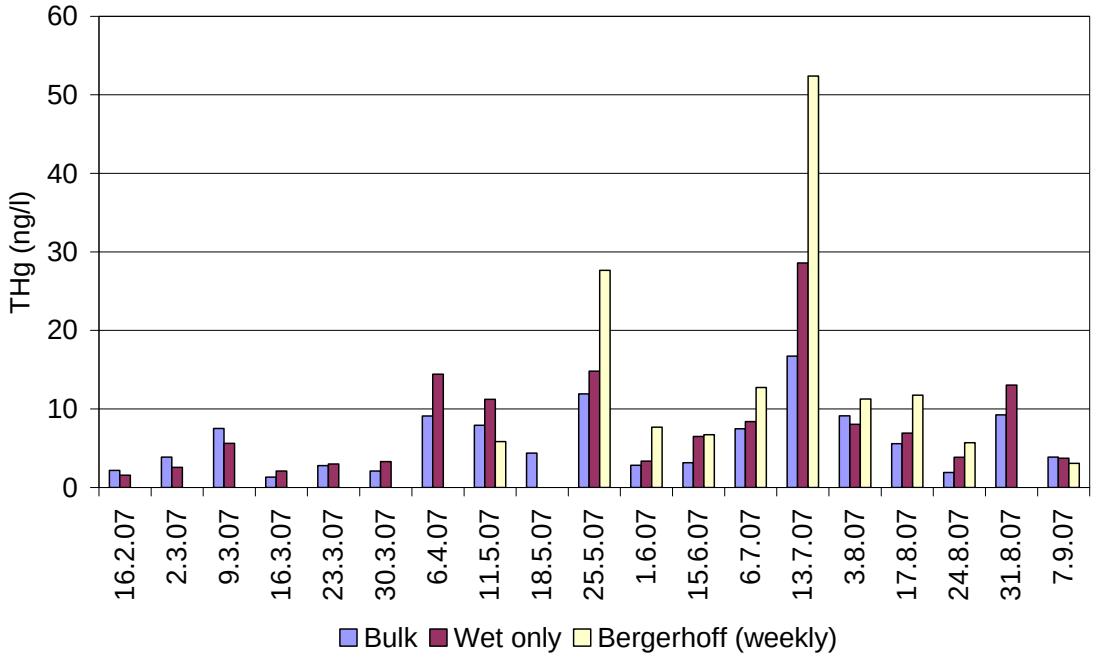

Figure 25. Comparison of THg concentrations in different deposition samples (in ng/l).

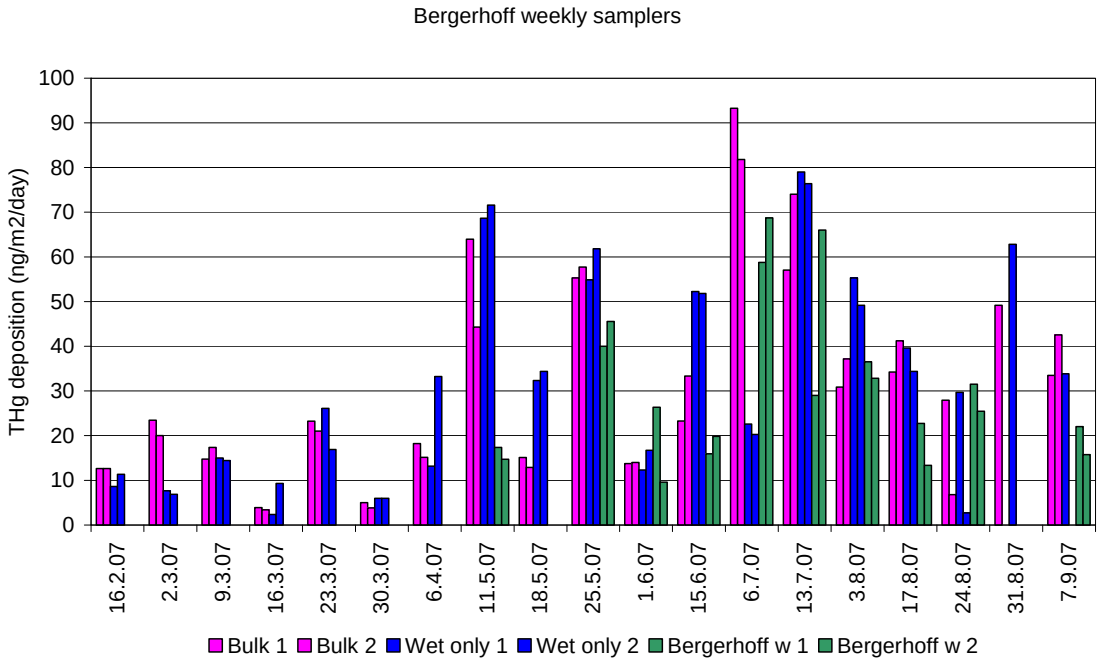

Figure 26. Comparison of THg deposition rates for different samplers (in ng/m^2/day).

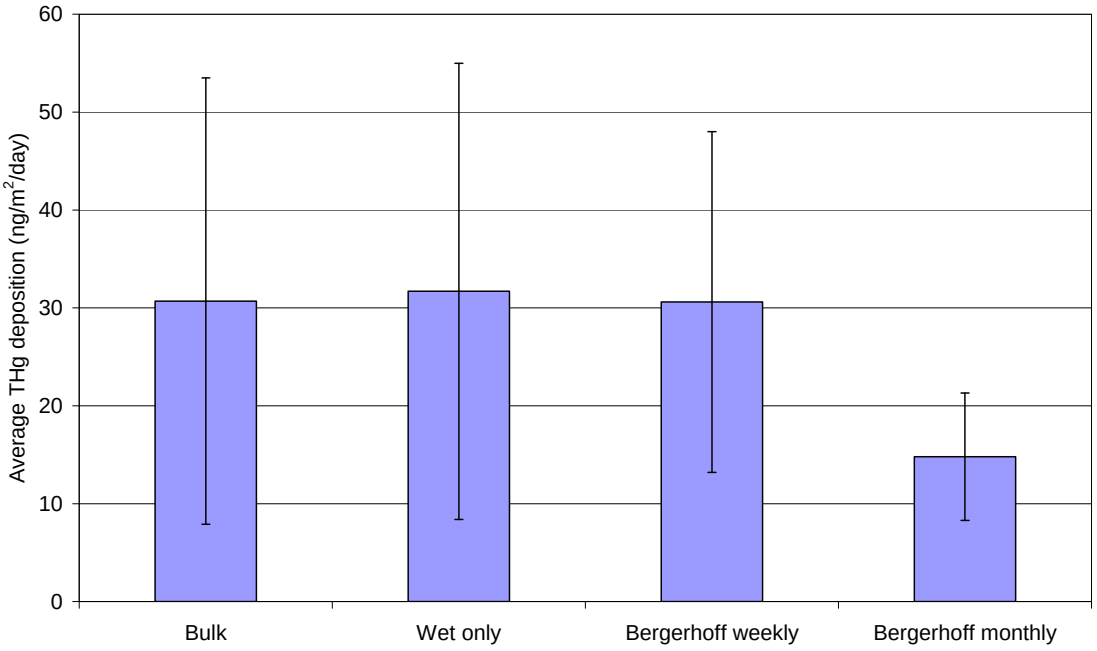

Figure 27. Comparison of average yearly THg deposition rate for different deposition sampler types (ng/m^2/day).

Table 1. THg concentration measured in certified reference material ORMS-3.

Date	THg concentration (ng/l) Certified value: 12.6 ± 1.1	Std. deviation
22.2.2007	13.4	
23.3.2007	9.10	
2.3.2007	12.9	1.5
14.3.2007	13.9	0.3
26.3.2007	12.0	0.2
2.4.2007	10.9	0.7
2.4.2007	11.5	0.2
24.5.2007	13.8	0.8
28.5.2007	12.4	0.2
1.6.2007	12.2	0.8
22.8.2007	13.3	0.4

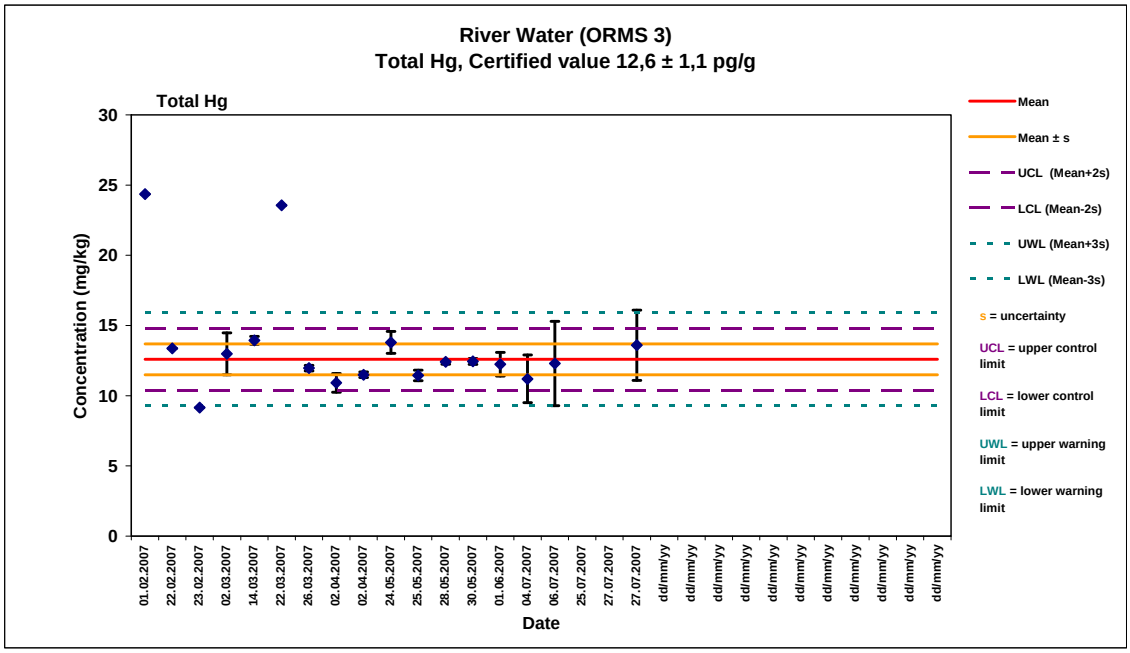

Figure 28. QA/QC chart for certified reference material ORMS-3.

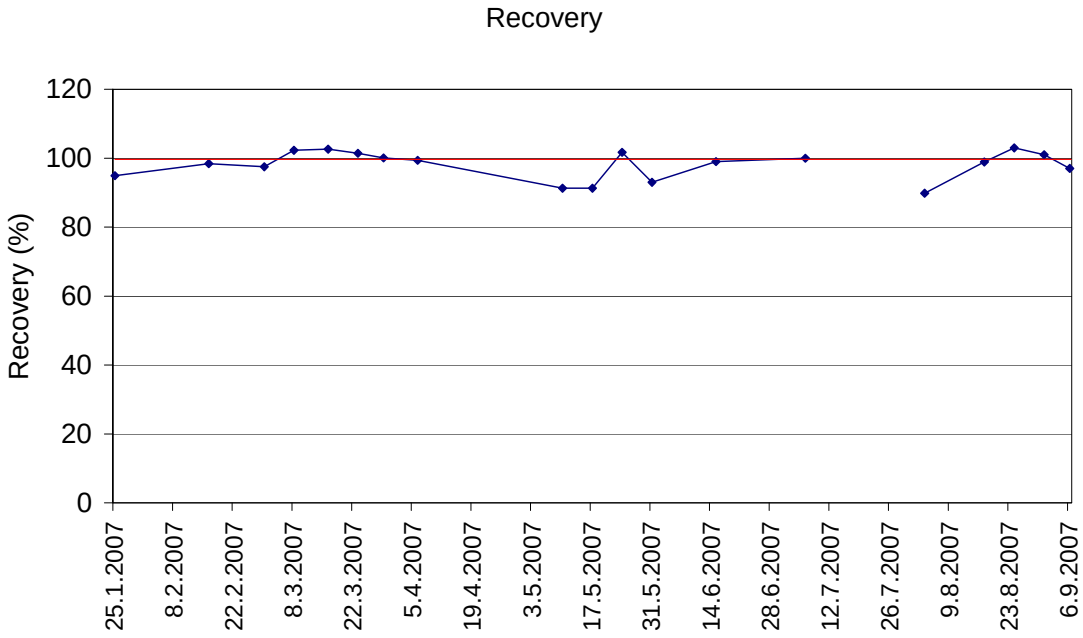

Figure 29. Recovery during analysis of THg deposition samples.

APPENDIX 1

Meteorological data

Table 2. Average meteorological parameters for the day with precipitation event.

Date	Precipitations (mm)	Air Pressure [hPa]	Air temperature [°C]	Air relative humidity [%]	Average wind direction [°]	Average wind speed [m/s]
22.1.2007	3.4	989.7	3	94.2	167.4	0.6
23.1.2007	9	979.4	1.2	97.9	210.4	0.5
24.1.2007	39.5	967.3	1.2	91.5	197.1	0.8
25.1.2007	15.6	984.8	-2.3	85.1	143.3	0.5
26.1.2007	2.8	992.5	-4.3	83.3	135.6	0.5
7.2.2007	9.2	975.7	3.8	89.6	148.9	0.7
8.2.2007	1	975.4	6.5	75.6	155.9	1.4
9.2.2007	3	979	5.6	91.3	185.6	0.6
10.2.2007	1.5	980.7	3.6	89.6	247	0.8
13.2.2007	18.7	976.7	4.4	82.6	216.1	1
26.2.2007	25.7	979.5	4.3	86.1	219.3	1.1
3.3.2007	5.6	981.4	6.5	85.5	180.5	0.9
4.3.2007	2.4	991.7	6.8	63.1	189.8	1.2
7.3.2007	0.3	983.5	8.9	79.8	127.1	0.9
8.3.2007	15	985.8	7.8	91.6	296.5	1.3
10.3.2007	15.2	998.9	7	55.5	161.6	2.1
19.3.2007	2.9	965.8	4	88.3	201.4	0.9
20.3.2007	50	962	1	87.9	241.5	1
21.3.2007	2	971.6	2.3	66.3	160.6	1.4
24.3.2007	3.2	977.5	2.6	87	146.8	1.4
25.3.2007	2.1	989.5	5.2	78.8	252.6	1.2
31.3.2007	3	988.7	8.4	79.7	265.1	0.7
2.4.2007	2	997.2	10.6	70.2	192.5	0.9
4.4.2007	0.6	981.9	8.5	67.7	179.6	1.2
5.5.2007	30	979.4	11.8	93	170	0.7
6.5.2007	2	982.2	13.6	84.9	186.5	1
7.5.2007	3.4	985.9	15.8	61.4	202.4	1.2
10.5.2007	2.1	988.3	17.6	73.8	167.3	1.2
16.5.2007	13.9	986.5	10.2	72.8	199.4	1.3
17.5.2007	1.3	981.3	11	78.3	256.6	1.4
18.5.2007	12.5	987.1	12.7	54.5	204.9	1.8
23.5.2007	9.5	988.1	18.4	81	190.4	1
24.5.2007	0.2	987.5	20.5	71.3	152.8	1.1
29.5.2007	10	972.7	11.5	83.4	150.4	1.2
30.5.2007	9.5	984.8	11	74.1	224.3	1.4
9.6.2007	6.2	989.3	19.3	75.5	212.3	1.2
13.6.2007	1.2	981.7	21	70.7	193	1.1
30.6.2007	4.4	990.3	17.9	68.7	182.5	1.5
3.7.2007	9.3	982.8	19.2	70	164.6	1.4
5.7.2007	40.1	983.8	14.2	73	221.3	1
10.7.2007	18.7	983.8	12.4	78.4	164.9	1.4
29.7.2007	19.3	986.1	21.4	67.7	179.5	1.2
31.7.2007	45.7	990.2	14.2	69.7	188	1.1

Table 3. Wind speed and direction measured at the sampling location.

Date	Max. wind speed (m/s)	Average wind direction [°]	Average wind speed (m/s)	Precipitation (mm)	Wind
2.1.2007	10.3	253.1	1.7	12	
3.1.2007	8.1	211.3	1.1	0.5	
9.1.2007	3.3	259	0.6	0.4	
22.1.2007	5	167.4	0.6	3.4	
23.1.2007	3.3	210.4	0.5	9	
24.1.2007	6.9	197.1	0.8	39.5	
25.1.2007	4.5	143.3	0.5	15.6	
26.1.2007	3.3	135.6	0.5	2.8	
7.2.2007	4	148.9	0.7	9.2	
8.2.2007	11.9	155.9	1.4	1	
9.2.2007	5.2	185.6	0.6	3	
10.2.2007	3.9	247	0.8	1.5	
13.2.2007	7.3	216.1	1	18.7	
26.2.2007	7.5	219.3	1.1	25.7	
3.3.2007	8	180.5	0.9	5.6	
4.3.2007	9.3	189.8	1.2	2.4	
7.3.2007	4.7	127.1	0.9	0.3	
8.3.2007	12.5	296.5	1.3	15	
10.3.2007	13.2	161.6	2.1	15.2	
19.3.2007	11.8	201.4	0.9	2.9	
20.3.2007	7.9	241.5	1	50	
21.3.2007	8.7	160.6	1.4	2	
24.3.2007	7.1	146.8	1.4	3.2	
25.3.2007	6	252.6	1.2	2.1	
31.3.2007	4.6	265.1	0.7	3	
2.4.2007	5	192.5	0.9	2	
4.4.2007	8.7	179.6	1.2	0.6	
5.5.2007	5.3	170	0.7	30	
6.5.2007	7.6	186.5	1	2	
7.5.2007	6.9	202.4	1.2	3.4	
10.5.2007	7.6	167.3	1.2	2.1	
16.5.2007	7.5	199.4	1.3	13.9	
17.5.2007	7.8	256.6	1.4	1.3	
18.5.2007	9.7	204.9	1.8	12.5	
23.5.2007	10.6	190.4	1	9.5	
24.5.2007	5.9	152.8	1.1	0.2	
29.5.2007	6.9	150.4	1.2	10	
30.5.2007	9.2	224.3	1.4	9.5	
9.6.2007	7.4	212.3	1.2	6.2	
13.6.2007	5.1	193	1.1	1.2	
30.6.2007	7.8	182.5	1.5	4.4	
3.7.2007	6.5	164.6	1.4	9.3	
5.7.2007	6.7	221.3	1	40.1	
10.7.2007	10.3	164.9	1.4	18.7	
29.7.2007	6	179.5	1.2	19.3	
31.7.2007	5.7	188	1.1	45.7	

APPENDIX 2

THg results

Table 4. Results for “Bulk” samplers.

Exposure date	Collecting date	Sample code		Amount of precipitation (mm)	Amount of collected sample (Acid+sample) (ml)	Amount of collected precipitations (ml)	THg concentration (ng/l)	Std. dev.	THg in sample (ng/sample)	THg in sample-FBLK (ng/sample)	THg deposition (ng/m2/day)	THg deposition - FBLK (ng/m2/day)	% FBLK
19.1.2007	26.1.2007	BL1/	26.1.2007	70.3			3.77	0.27					
19.1.2007	26.1.2007	BL2/	26.1.2007				3.76	0.16					
26.1.2007	2.2.2007	BL1/	2.2.2007	0	no sample	no sample							
26.1.2007	2.2.2007	BL2/	2.2.2007		no sample	no sample							
2.2.2007	9.2.2007	BL1/	9.2.2007	13.2	no sample	no sample							
2.2.2007	9.2.2007	BL2/	9.2.2007		no sample	no sample							
9.2.2007	16.2.2007	BL1/	16.2.2007	20.2	290.0	190.0	1.61	0.00	0.47	0.39	12.6	10.5	17.1
9.2.2007	16.2.2007	BL2/	16.2.2007		290.0	190.0	1.61	0.00	0.47	0.39	12.6	10.5	17.1
16.2.2007	23.2.2007	BL1/	23.2.2007	0	no sample	no sample							
16.2.2007	23.2.2007	BL2/	23.2.2007		no sample	no sample							
23.2.2007	2.3.2007	BL1/	2.3.2007	25.7	280.4	180.4	3.09	0.22	0.87	0.79	23.4	21.3	9.2
23.2.2007	2.3.2007	BL2/	2.3.2007		282.1	182.1	2.62	0.20	0.74	0.66	20.0	17.8	10.8
2.3.2007	9.3.2007	BL1/	9.3.2007	23.3	121.3	21.3	4.49	0.03	0.54	0.46	14.7	12.6	14.7
2.3.2007	9.3.2007	BL2/	9.3.2007		154.2	54.2	4.16	0.05	0.64	0.56	17.4	15.2	12.5
9.3.2007	16.3.2007	BL1/	16.3.2007	15.2	164.0	64.0	0.87	0.07	0.14	0.06	3.9	1.7	55.9
9.3.2007	16.3.2007	BL2/	16.3.2007		163.4	63.4	0.77	0.06	0.13	0.05	3.4	1.2	64.0
16.3.2007	23.3.2007	BL1/	23.3.2007	54.9	380.1	280.1	2.26	0.01	0.86	0.78	23.2	21.1	9.3
16.3.2007	23.3.2007	BL2/	23.3.2007		362.4	262.4	2.14	0.07	0.78	0.70	21.0	18.8	10.3
23.3.2007	30.3.2007	BL1/	30.3.2007	5.3	136.3	36.3	1.36	0.09	0.19	0.11	6.0	2.9	43.2
23.3.2007	30.3.2007	BL2/	30.3.2007		134.8	34.8	1.05	0.01	0.14	0.06	3.8	1.7	56.5
30.3.2007	6.4.2007	BL1/	6.4.2007	5.6	122.6	22.6	5.49	0.69	0.67	0.59	18.2	16.0	11.9
30.3.2007	6.4.2007	BL2/	6.4.2007		123.4	23.4	4.54	0.13	0.56	0.48	15.2	13.0	14.3
6.4.2007	13.4.2007	BL1/	13.4.2007	0	no sample	no sample							
6.4.2007	13.4.2007	BL2/	13.4.2007		no sample	no sample							
13.4.2007	20.4.2007	BL1/	20.4.2007	0	no sample	no sample							
13.4.2007	20.4.2007	BL2/	20.4.2007		no sample	no sample							
20.4.2007	27.4.2007	BL1/	27.4.2007	0	no sample	no sample							
20.4.2007	27.4.2007	BL2/	27.4.2007		no sample	no sample							
27.4.2007	4.5.2007	BL1/	4.5.2007	0	no sample	no sample							
27.4.2007	4.5.2007	BL2/	4.5.2007		no sample	no sample							
4.5.2007	11.5.2007	BL1/	11.5.2007	37.5	333.4	233.4	7.09	2.16	2.36	2.28	64.0	61.8	3.4
4.5.2007	11.5.2007	BL2/	11.5.2007		324.0	224.0	5.05	0.11	1.64	1.56	44.3	42.1	4.9
11.5.2007	18.5.2007	BL1/	18.5.2007	27.7	182.5	82.5	3.06	0.28	0.56	0.48	15.1	12.9	14.3
11.5.2007	18.5.2007	BL2/	18.5.2007		182.4	82.4	2.61	0.14	0.48	0.40	12.9	10.7	16.8
18.5.2007	25.5.2007	BL1/	25.5.2007	9.7	247.7	147.7	8.25	0.20	2.04	1.96	55.3	53.1	3.9
18.5.2007	25.5.2007	BL2/	25.5.2007		245.3	145.3	8.70	0.15	2.13	2.05	57.7	55.6	3.7
25.5.2007	1.6.2007	BL1/	1.6.2007	19.5	253.1	153.1	2.01	0.26	0.51	0.43	13.8	11.6	15.7
25.5.2007	1.6.2007	BL2/	1.6.2007		254.0	154.0	2.04	0.09	0.52	0.44	14.0	11.9	15.4
1.6.2007	8.6.2007	BL1/	8.6.2007	0	no sample	no sample							
1.6.2007	8.6.2007	BL2/	8.6.2007		no sample	no sample							
8.6.2007	15.6.2007	BL1/	15.6.2007	7.4	411.6	311.6	2.09	0.02	0.86	0.78	23.3	21.1	9.3
8.6.2007	15.6.2007	BL2/	15.6.2007		413.7	313.7	2.98	0.04	1.23	1.15	33.4	31.2	6.5
15.6.2007	22.6.2007	BL1/	22.6.2007	0	no sample	no sample							
15.6.2007	22.6.2007	BL2/	22.6.2007		no sample	no sample							
22.6.2007	29.6.2007	BL1/	29.6.2007	0	no sample	no sample							
22.6.2007	29.6.2007	BL2/	29.6.2007		no sample	no sample							
29.6.2007	6.7.2007	BL1/	6.7.2007	53.8	521.5	421.5	6.61	0.36	3.45	3.37	93.3	91.1	2.3
29.6.2007	6.7.2007	BL2/	6.7.2007		512.4	412.4	5.90	0.01	3.02	2.94	81.8	79.6	2.6
6.7.2007	13.7.2007	BL1/	13.7.2007	18.7	198.9	98.9	10.6	0.30	2.11	2.03	57.0	54.9	3.8
6.7.2007	13.7.2007	BL2/	13.7.2007		225.2	125.2	12.2	0.32	2.74	2.66	74.0	71.9	2.9
13.7.2007	20.7.2007	BL1/	20.7.2007	0	no sample	no sample							
13.7.2007	20.7.2007	BL2/	20.7.2007		no sample	no sample							
20.7.2007	27.7.2007	BL1/	27.7.2007	0	no sample	no sample							
20.7.2007	27.7.2007	BL2/	27.7.2007		no sample	no sample							
27.7.2007	3.8.2007	BL1/	3.8.2007	56	203.4	103.4	5.61	0.09	1.14	1.06	30.9	28.7	7.0
27.7.2007	3.8.2007	BL2/	3.8.2007		206.6	106.6	6.65	0.12	1.37	1.29	37.2	35.0	5.8
3.8.2007	10.8.2007	BL1/	10.8.2007	Not evaluated yet	no sample	no sample							
3.8.2007	10.8.2007	BL2/	10.8.2007		no sample	no sample							
10.8.2007	17.8.2007	BL1/	17.8.2007		333.0	233.0	3.80	0.10	1.27	1.19	34.2	32.1	6.3
10.8.2007	17.8.2007	BL2/	17.8.2007		321.4	221.4	4.74	0.04	1.52	1.44	41.2	39.1	5.3
17.8.2007	24.8.2007	BL1/	24.8.2007		412.6	312.6	2.50	0.01	1.03	0.95	27.9	25.7	7.8
17.8.2007	24.8.2007	BL2/	24.8.2007		425.6	325.6	0.59	0.01	0.25	0.17	6.8	4.6	31.9
24.8.2007	31.8.2007	BL1/	31.8.2007		269.6	169.6	6.74	0.00	1.82	1.74	49.2	47.0	4.4
24.8.2007	31.8.2007	BL2/	31.8.2007		270.6	170.6							
31.8.2007	7.9.2007	BL1/	7.9.2007		446.8	346.8	2.77	0.02	1.24	1.16	33.5	31.3	6.5
31.8.2007	7.9.2007	BL2/	7.9.2007		443.0	343.0	3.55	0.21	1.57	1.49	42.6	40.4	5.1
Average				16.6	280.1	180.1	4.1	0.18	1.14	1.06	30.7	28.6	14.4
St. Dev				20.6	112.7	112.7	2.7	0.35	0.84	0.84	22.8	22.8	15.7

Table 5. Results for “Wet - only” samplers.

Exposure date	Collecting date	Sample code	Amount of precipitation (mm)	Amount of collected sample (Acid+sample) (ml)	Amount of collected precipitation (ml)	THg concentration (ng/l)	Std. dev.	THg deposition (ng/m2/day)	THg in sample (ng/sample)	THg in sample-FBLK (ng/sample)	THg deposition - FBLK (ng/m2/day)	% FBLK
19.1.2007	26.1.2007	W1/26.1.2007	70.3			4.44	0.12					
		W2/26.1.2007				4.30	0.05					
26.1.2007	2.2.2007	W1/2.2.2007	0		no sample							
		W2/2.2.2007			no sample							
2.2.2007	9.2.2007	W1/9.2.2007	13.2		no sample							
		W2/9.2.2007			no sample							
9.2.2007	16.2.2007	W1/16.2.2007	20.2	620.8	520.8	1.01	0.04	8.6	0.63	0.55	7.5	12.8
		W2/16.2.2007		624.5	524.5	1.32	0.03	11.3	0.82	0.74	10.2	9.8
16.2.2007	23.2.2007	W1/23.2.2007	0		no sample							
		W2/23.2.2007			no sample							
23.2.2007	2.3.2007	W1/2.3.2007	25.7	272.8	172.8	2.04	0.02	7.7	0.56	0.48	6.6	14.5
		W2/2.3.2007		274.8	174.8	1.82	0.04	6.9	0.50	0.42	5.8	16.1
2.3.2007	9.3.2007	W1/9.3.2007	23.3	255.3	155.3	4.27	0.03	15.0	1.09	1.01	13.9	7.4
		W2/9.3.2007		252.1	152.1	4.16	0.05	14.4	1.05	0.97	13.3	7.7
9.3.2007	16.3.2007	W1/16.3.2007	15.2	221.4	121.4	0.78	0.05	2.4	0.17	0.09	1.3	46.6
		W2/16.3.2007		283.6	183.6	2.39	0.21	9.3	0.68	0.60	8.2	11.9
16.3.2007	23.3.2007	W1/23.3.2007	54.9	764.8	664.8	2.48	0.01	26.1	1.90	1.82	25.0	4.3
		W2/23.3.2007		601.3	501.3	2.04	0.04	16.9	1.23	1.15	15.8	6.6
23.3.2007	30.3.2007	W1/30.3.2007	5.3	185.0	85.0	2.35	0.00	6.0	0.43	0.35	4.9	18.5
		W2/30.3.2007		193.0	93.0	2.24	0.04	5.9	0.43	0.35	4.8	18.6
30.3.2007	6.4.2007	W1/6.4.2007	5.6	157.9	57.9	6.07	0.14	13.2	0.96	0.88	12.1	8.4
		W2/6.4.2007		177.4	77.4	13.6	0.33	33.2	2.41	2.33	32.1	3.4
6.4.2007	13.4.2007	W1/13.4.2007	0		no sample							
		W2/13.4.2007			no sample							
13.4.2007	20.4.2007	W1/20.4.2007	0		no sample							
		W2/20.4.2007			no sample							
20.4.2007	27.4.2007	W1/27.4.2007	0		no sample							
		W2/27.4.2007			no sample							
27.4.2007	4.5.2007	W1/4.5.2007	0		no sample							
		W2/4.5.2007			no sample							
4.5.2007	11.5.2007	W1/11.5.2007	37.5	609.8	509.8	8.18	0.92	68.7	4.99	4.91	67.5	1.7
		W2/11.5.2007		597.8	497.8	8.70	3.35	71.6	5.20	5.12	70.4	1.6
11.5.2007	18.5.2007	W1/18.5.2007	27.7	272.5	172.5	8.63	0.00	32.4	2.35	2.27	31.2	3.5
		W2/18.5.2007		286.3	186.3	8.73	0.77	34.4	2.50	2.42	33.3	3.3
18.5.2007	25.5.2007	W1/25.5.2007	9.7	419.6	319.6	9.50	0.06	54.9	3.99	3.91	53.7	2.1
		W2/25.5.2007		424.6	324.6	10.6	0.06	61.8	4.49	4.41	60.7	1.9
25.5.2007	1.6.2007	W1/1.6.2007	19.5	451.8	351.8	1.98	0.09	12.3	0.89	0.81	11.2	9.0
		W2/1.6.2007		449.9	349.9	2.70	0.03	16.7	1.21	1.13	15.6	6.7
1.6.2007	8.6.2007	W1/8.6.2007	0		no sample							
		W2/8.6.2007			no sample							
8.6.2007	15.6.2007	W1/15.6.2007	7.4	797.2	697.2	4.76	0.28	52.2	3.79	3.71	51.1	2.2
		W2/15.6.2007		804.9	704.9	4.68	0.03	51.8	3.77	3.69	50.7	2.2
15.6.2007	22.6.2007	W1/22.6.2007	0		no sample							
		W2/22.6.2007			no sample							
22.6.2007	29.6.2007	W1/29.6.2007	0		no sample							
		W2/29.6.2007			no sample							
29.6.2007	6.7.2007	W1/6.7.2007	53.8	290.9	190.9	5.64	0.33	22.6	1.64	1.56	21.5	5.0
		W2/6.7.2007		289.1	189.1	5.09	0.06	20.3	1.47	1.39	19.1	5.5
6.7.2007	13.7.2007	W1/13.7.2007	18.7	356.6	256.6	16.10	0.10	79.0	5.74	5.66	77.8	1.5
		W2/13.7.2007		342.6	242.6	16.20	0.20	76.4	5.55	5.47	75.2	1.5
13.7.2007	20.7.2007	W1/20.7.2007	0		no sample							
		W2/20.7.2007			no sample							
20.7.2007	27.7.2007	W1/27.7.2007	0		no sample							
		W2/27.7.2007			no sample							
27.7.2007	3.8.2007	W1/3.8.2007	66	697.5	597.5	5.76	0.03	55.3	4.02	3.94	54.1	2.1
		W2/3.8.2007		681.9	581.9	5.24	0.11	49.2	3.57	3.49	48.0	2.3
3.8.2007	10.8.2007	W1/10.8.2007	Not evaluated yet		no sample							
		W2/10.8.2007			no sample							
10.8.2007	17.8.2007	W1/17.8.2007		549.0	449.0	5.24	0.41	39.6	2.88	2.80	38.5	2.9
		W2/17.8.2007		532.8	432.8	4.69	0.19	34.4	2.50	2.42	33.3	3.3
17.8.2007	24.8.2007	W1/24.8.2007		829.5	729.5	2.80	0.01	29.7	2.16	2.08	28.6	3.8
		W2/24.8.2007		107.9	7.9	1.84	0.07	2.7	0.20	0.12	1.6	40.4
24.8.2007	31.8.2007	W1/31.8.2007		484.8	384.8	9.41	0.04	62.8	4.56	4.48	61.6	1.8
		W2/31.8.2007		105.7	5.7							
31.8.2007	7.9.2007	W1/7.9.2007		881.5	781.5	2.79	0.00	33.8	2.46	2.38	32.7	3.3
		W2/7.9.2007			no sample							
Average				436.5	336.5	5.4	0.22	31.7	2.3	2.2	30.5	8.2
St. Dev				224.5	224.5	4.0	0.56	23.3	1.7	1.7	23.3	10.0

Table 6. Results for “Bergerhoff” samplers. Samples were collected on weekly basis

Exposure date	Collecting date	Sample code		Amount of precipitation (mm)	Amount of collected sample (ml)	THg concentration (ng/l)	Std. dev.	THg deposition (ng/m2/day)
4.5.2007	11.5.2007	B1/	11.5.2007	37.5	167.8	4.6	0.03	17.3
		B2/	11.5.2007		167.9	3.9	2.09	14.7
18.5.2007	25.5.2007	B1/	25.5.2007	9.7	120.4	14.8	0.13	40.0
		B2/	25.5.2007		109.4	18.6	2.56	45.6
25.5.2007	1.6.2007	B1/	1.6.2007	19.5	156.3	7.51		26.4
		B2/	1.6.2007		155.2	2.76	0.04	9.6
1.6.2007	8.6.2007	B1/	8.6.2007	0	no sample			
		B2/	8.6.2007		no sample			
8.6.2007	15.6.2007	B1/	15.6.2007	7.4	188.7	3.76	0.04	15.9
		B2/	15.6.2007		175.8	5.02	0.00	19.8
15.6.2007	22.6.2007	B1/	22.6.2007	0	no sample			
		B2/	22.6.2007		no sample			
22.6.2007	29.6.2007	B1/	29.6.2007	0	no sample			
		B2/	29.6.2007		no sample			
29.6.2007	6.7.2007	B1/	6.7.2007	53.8	321.6	8.14	0.46	58.8
		B2/	6.7.2007		318.7	9.60	0.70	68.7
6.7.2007	13.7.2007	B1/	13.7.2007	18.7	78.0	16.5	0.02	29.0
		B2/	13.7.2007		72.1	40.8	0.45	66.0
13.7.2007	20.7.2007	B1/	20.7.2007	0	no sample			
		B2/	20.7.2007		no sample			
20.7.2007	27.7.2007	B1/	27.7.2007	0	no sample			
		B2/	27.7.2007		no sample			
27.7.2007	3.8.2007	B1/	3.8.2007	56	203.4	7.99	0.06	36.5
		B2/	3.8.2007		206.6	7.08	0.11	32.8
3.8.2007	10.8.2007	B1/	10.8.2007	0	no sample			
		B2/	10.8.2007		no sample			
10.8.2007	17.8.2007	B1/	17.8.2007	Not evaluated yet	104.0	9.74	0.21	22.8
		B2/	17.8.2007		97.5	6.10	0.20	13.4
17.8.2007	24.8.2007	B1/	24.8.2007		327.2	4.29	0.18	31.5
		B2/	24.8.2007		317.6	3.57	0.15	25.5
24.8.2007	31.8.2007	B1/	31.8.2007		206.6			
		B2/	31.8.2007		206.9			
31.8.2007	7.9.2007	B3/	7.9.2007		360.7	2.72	0.05	22.0
		B4/	7.9.2007		376.7	1.86	0.02	15.7
Average				15.6	201.8	9.0	0.39	30.6
St. Dev				20.7	94.7	8.8	0.71	17.4

Table 7. Results for “Bergerhoff” samplers. Samples were collected on monthly basis.

Exposure date	Collecting date	Days exposed	Sample code		Amount of precipitation (mm)	Amount of collected sample (ml)	THg concentration (ng/l)	Std. dev.	THg deposition (ng/m2/day)
18.1.2007	25.1.2007	8	B1/	25.1.2007	45.8	213.6	5.00	0.20	21.0
		8	B2/	25.1.2007		213.6	4.41	0.16	18.5
		8	B3/	25.1.2007		213.6	4.26	0.19	17.9
		8	B4/	25.1.2007		213.6	4.56	0.12	19.1
25.1.2007	16.2.2007	21	B1/	16.2.2007	37.8	219.0	4.06	0.00	6.7
		21	B2/	16.2.2007		230.2	3.86	0.00	6.7
		21	B3/	16.2.2007		215.2	6.50	0.00	10.5
		21	B4/	16.2.2007		216.5	3.93	0.00	6.4
16.2.2007	1.3.2007	12	B1/	1.3.2007	22.9	303.4	5.04	0.09	20.0
		12	B2/	1.3.2007		305.3	6.04	0.06	24.2
		12	B3/	1.3.2007		303.5	5.68	0.01	22.6
		12	B4/	1.3.2007		305.5	5.86	0.03	23.5
1.3.2007	29.3.2007	28	B1/	29.3.2007	98.9	419.1	7.29	0.09	17.2
		28	B2/	29.3.2007		370.9	8.20	0.07	17.1
		28	B3/	29.3.2007		444.5	6.34	0.63	15.8
		28	B4/	29.3.2007		370.0	6.91	0.52	14.4
29.3.2007	10.5.2007	42	B3/	10.5.2007	43.1	166.0	7.85	0.23	4.9
		42	B4/	10.5.2007		138.6	8.33	0.4	4.3
10.5.2007	15.6.2007	36	B3/	15.6.2007	64.3	297.0	4.31	0.07	5.6
		36	B4/	15.6.2007		264.6	4.74	0.05	5.5
15.6.2007	13.7.2007	28	B3/	13.7.2007	72.5	284.9	12.11	0.41	19.4
		28	B4/	13.7.2007		260.3	8.39	0.81	12.3
13.7.2007	17.8.2007	35	B3/	17.8.2007	56	216.0	11.77	0.34	11.4
		35	B4/	17.8.2007		175.1	24.45	1.90	19.2
17.8.2007	6.9.2007	21	B3/	6.9.2007	Not evaluated	754.7	3.72	0.07	21.0
		21	B4/	6.9.2007		755.8	3.54	0.17	20.0
Average					55.16	302.71	6.81	0.25	14.81
St. dev.					23.52	152.91	4.26	0.40	6.54