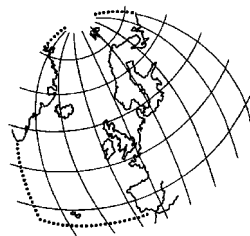


Pilot Study and Intercomparison Exercise on
Atmospheric Inputs of PAHs



OSPAR Commission
2001

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La Convention pour la protection du milieu marin de l'Atlantique du Nord-Est, dite Convention OSPAR, a été ouverte à la signature à la réunion ministérielle des anciennes Commissions d'Oslo et de Paris, à Paris le 22 septembre 1992. La Convention est entrée en vigueur le 25 mars 1998. La Convention a été ratifiée par l'Allemagne, la Belgique, le Danemark, la Finlande, la France, l'Irlande, l'Islande, le Luxembourg, la Norvège, les Pays-Bas, le Portugal, le Royaume-Uni de Grande Bretagne et d'Irlande du Nord, la Suède et la Suisse et approuvée par l'Espagne et la Communauté européenne.

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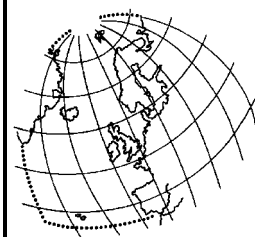
PREFACE

This report provides an overview of the results of the atmospheric part of the PAH Pilot Study - the Intercomparison Exercise. It also includes all detailed information given by the Contracting Parties (CPs) about sampling and analysis methods used in national activities and during the exercise.

The results of the Pilot Study were discussed at the “OSPAR Workshop on the development of guidelines for sampling and analysis of PAH in air and precipitation”, held near Rostock (Germany) in June 1999. After comments had been made by the participating countries to the project organiser, the draft of this report was examined by INPUT 2000 and ASMO 2000. The results of the sampler comparison are presented anonymously.

OSPAR Commission

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1 INTRODUCTION

1.1 Background and aim

Atmospheric transport is a major input pathway of persistent organic pollutants (POPs). Due to their persistence, toxicity and tendency to bioaccumulate in biota, POPs are of great environmental concern. It has been shown that input via the atmosphere accounts for the largest proportion of inputs of PAHs into the open sea [1, 2]. Most PAHs are considered to be semi volatile organic compounds (SOCs) which means that they are transported in the atmosphere in both the gas and particulate phases. The distribution between the phases depends on the PAHs' physical and chemical properties (especially vapour pressure) and concentration, ambient air temperature, humidity and concentration of particles [3, 4]. Wet and dry deposition and chemical transformation remove particle-associated PAHs from the atmosphere. The partitioning between the two phases will affect the removal mechanism. Particle scavenging rather than gas scavenging is the dominant mechanism of removal of PAHs from the atmosphere through precipitation [5]. Generally POPs are mostly inert and chemically stable during transport over long distances, but especially some PAHs participate in atmospheric reactions [6].

The main objective of the CAMP (Comprehensive Atmospheric Monitoring Programme) is to measure the atmospheric input of selected contaminants in precipitation and air. At present PAHs are measured on a voluntary basis and predominantly in precipitation [7]. The situation is that in comparison to the ongoing measurement activities concerning heavy metals only few POPs are measured at a very limited number of stations and not by all countries.

Although analysis of PAHs in air and precipitation has been carried out for many years, there are no harmonised methods. Because of a lack of data comparability an intercomparison exercise was initiated by the OSPAR working group INPUT as part of a PAH Pilot Study. Seven Contracting Parties (CPs) took part (Belgium, Denmark, the Netherlands, Sweden, Norway, Germany, United Kingdom*). The German Federal Environmental Agency (FEA) had organised the intercomparison.

The aim of this Pilot Study was:

- to carry out a field intercomparison of PAH measurements in air and precipitation in order to be able to elaborate recommendations for a harmonised methodology for sampling and analysis and to prepare draft guidelines;
- to check for data comparability using an temporary set of data for CAMP-stations for the same sampling intervals within a period of three months;
- to obtain new information about the distribution of the different share (e. g. wet, gas phase, particulate phase) of deposition and the transboundary transport of PAH in different regions around the North Sea.

The main objective of this experiment was to determine the quality and comparability of PAH measurement data in the CAMP network. At INPUT(2) 1998 [8] it was pointed out that the methodological aspects of the field experiment would take precedence over the explanation of the observations and that the main results of the project would lead to the development of guidelines on PAH monitoring in air and precipitation. More precisely it was to be established whether PAHs in air and precipitation can be determined with different methods with sufficient accuracy.

* separate comparison.

It is not the task of this report to find solutions to all problems concerning PAH measurements in atmospheric samples, but it seems to be clear that a harmonisation of methods and sampling devices and the use of adequate techniques are necessary to increase comparability. The best way would be to have at least a proven and accepted reference method and at least a few acceptable alternatives for use by the CPs.

At present this intercomparison is the first and most comprehensive one with respect to the determination of PAHs in atmospheric samples in the OSPAR region.

1.2 Contracting Parties

After INPUT(1) 1998 [9] the following CPs indicated their willingness to participate in the Intercomparison Exercise:

Belgium

(VMM; Vlaamse Milieumaatschappij)

Denmark

(Denmark's Mijoundersogelser; National Environmental Research Institute)

The Netherlands

(RIVM; National Institute of Public Health and the Environment)*

Norway

(NILU; The Norwegian Institute of Air Research)

Sweden

(IVL, Swedish Environmental Research Institute)

Germany

(NORDUM, Institut für Umwelt und Analytik GmbH & CO. KG,
Project Manager)

*During the Workshop the RIVM informed: The sampler comparison was carried out in cooperation of the RIVM (logistics and intermediary) with Province Noord Holland (owner of PAH-method and samplers), OMEGAM (executor for Province Noord Holland) and Waterworks Noord-Holland (analysis of samples). This set-up implies that the RIVM cannot guarantee the quality of the PAH measurements within CAMP.

After the Workshop on "Guidelines for sampling and analysis of PAHs in air and precipitation" (held near Rostock in June 1999) the United Kingdom (AEA Technology National Environmental Centre) indicated its willingness to participate in a sampler comparison as an additional part of the PAH Pilot Study exercise (see chapter 4.2 Future work).

The German FEA as project leader commissioned the company NORDUM GmbH & CO.KG to manage the Pilot Study and to carry out the exercise within the framework of a research project. The following tasks had to be performed:

- contacting the CPs in order to receive information on current PAH measurements;
- co-ordination of the measuring programme and installation of the samplers in co-operation with the CPs;
- pre-treatment of all parts of the sampler, which may come into contact with the sample;
- analysis of all samples obtained in air and precipitation sampling with the samplers provided;
- collection of all information and data, to compare and evaluate data using statistical methods;
- ensuring data availability through supply of reserve equipment and regular control of field blanks.

1.3 Sampling sites

The following CAMP sites were involved in the field experiment:

- **Ulborg DK1**
Denmark, Westjutland; Location 56°17'N, 8°26'E
- **Knokke B4d**
Belgium; Location 51°21'N, 3°20'E
- **De Zilk NL4**
Netherlands, North Sea coast; Location 52°17'N, 4°30'E
- **Lista N3**
Norway; Location 58°06'N, 6°34'E
- **Rörvik S1**
Sweden, North Sea west-coast; Location 57°25'N, 11°56'E
- **Westerland D1**
Germany, Island of Sylt; Location 54°53'N, 8°19'E

The precipitation measurements in Belgium were not carried out at Knokke, but a test field of the University in Gent.

In view of the common interest of OSPAR and HELCOM as regards PAHs the German HELCOM station Zingst at the Baltic Sea coast was incorporated too.

The CAMP stations are predominantly situated close to the coast. Although the CAMP stations were chosen according to their representativity for concentration levels near the coast, local influences on PAH distribution could not be excluded [8]. Rörvik is a field station situated in a rural area on the Swedish west coast, about 40 km south of Gothenburg. It is also an EMEP monitoring station. De Zilk is located in the dunes of the North Sea coast, 25 km SWW of Amsterdam and 18 km W from Amsterdam Airport. The Danish station Ulborg is located in a forest near the North Sea coast.

1.4 Measuring programme

The measuring concept included a comparison of different air sampler types (high volume and low volume samplers) and precipitation samplers (wet-only and bulk samplers) as well as measurement of PAHs in the gas and particulate phases and in precipitation with methods provided by Germany, which served as "reference methods" for the field experiment.

Table 1. Overview of measuring programme

	CAMP measurements National activities				Pilot Study field experiment (reference method)		
	air		precipitation		air		precipitation
	gas phase	particulate phase	wet-only	bulk	gas phase	particulate phase	wet-only
Belgium	-	+*	+*	-	+	+	+
Denmark	-	+*	-	-	+	+	+
Germany	+*	+*	+	-	+	+	+
The Netherlands	-	+*	-	-	+	+	-
Norway	+	+	-	-	+	+	-
Sweden	+	+	-	+	+	+	+
United Kingdom	+	+	-	-	+	+	-

* experimental phase

sampler comparison

The field experiment was carried out from September to December 1998, a period characterised by increased PAH concentrations in the atmosphere. The annual PAH air concentrations generally show a clear seasonal pattern. Higher levels occur in winter in connection with coal-fired heating and special meteorological conditions. In addition, variations in PAH concentrations are caused by several point and diffuse sources, notably traffic.

The sampler comparison with the United Kingdom was carried out outside the Pilot Study in 1999 (see chapter 4.2: Future work).

Air sampling started on 08/09/1998 at all stations and ended on 17/11/1998. The sampling frequency was weekly. In Norway sampling was done 24 h per week (Wednesday). At each station, a total of 10 samples was collected during the sampling period. The glass cassettes were changed every Tuesday. In agreement with the Swedish monitoring program, the IVL collected one weekly sample at the end of each month. Therefore the sampling period September to December covers only 4 samples.

During current CAMP measurements Belgium and the Netherlands measure PAHs in the particulate phase whereas Norway and Sweden measured the PAHs in the combined (particulate and gas) phase. Germany performed measurements of PAHs in the particulate and gas phases separately during the study.

The sampler comparison with UK took place in comparable manner (see chapter 4.2 Future work).

Precipitation sampling was carried out from 01/09/1998 to 30/12/1998. The sampling frequency was monthly. The sampling bottles were changed on Tuesday.

1.5 PAH compounds

PAHs are of a high relevance because of their increasing pollution load in the environment especially in the marine environment. Some PAHs have been classified by the International Agency for Research on Cancer as carcinogenic to animals and probably carcinogenic to humans.

Based on the EPA list published in 1982 (mostly PAHs with carcinogenic effects) the following PAHs (in bold type) were chosen for CAMP [7], adopted by ASMO 1998:

*phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene,
benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene,
benzo(ghi)perylene, indeno(1,2,3-cd)pyrene*

Some of these compounds have been selected within the framework of the UN-ECE Convention on Long Range Transboundary Air Pollution (LRTAP Convention) for inclusion in the list of priority POPs of the Task Force on POPs (underlined compounds). Table A.I (Appendix A) gives an overview of important physical properties of these compounds and of their carcinogenic relevance [10].

2 METHODS

2.1 Air sampling

By pumping an air stream through an air sampler, PAHs adsorbed by particulate matter are usually collected on filters, compounds in the vapour phase are trapped by a back-up solid adsorbent. The use of a filter and a back-up adsorbent is strictly recommended for an assessment of total atmospheric PAH concentrations. Because of discussions about the correct measurement of the gas/particle partitioning, the so-called “particulate phase” was defined as that trapped on a filter, and the “gas phase” defined as that associated with an adsorbent. Not all participants include the gas phase in their current measurement programme. Sampler types, filters and adsorbents used in the field experiment are summarised in Table 2.

Table 2. Types of air samplers used

No. ¹	sampler type	Filter/adsorbent
A.1	low-volume sampler (LVS) MVS 6 (DERENDA) with a sampling head PK 50-PU/G (RIEMER, DIGITEL); adjustable constant flow rate: 2 - 4 m ³ /h = "reference method" (Appendix B)	stainless steel sampling head equipped with a glass cassette containing a glass fibre filter (5 cm d.) and two PUF-plugs (5cm d, 10 cm long); pre-cleaning of filters by heating 10 h to 230°C and of PUF-plugs by soxhlet-extraction with toluene and acetone
A.2a A.2b	home built high volume sampler (HVS) by NILU; the filter holder unit is connected with a high volume vacuum pump using a flow meter; flow rate: 20 - 25 m ³ /h	glass fibre filter (14,2 cm d.) and two PUF-plugs (11 cm d.; 5cm long); pre-cleaning of filters by heating 8 h to 450°C and of PUF-plugs by soxhlet-extraction with acetone and toluene
A.3	PM10 high volume sampler (HVS) (Sierra / Andersen PM10 model 1200 with PM-10 inlet model 321 and volumetric flow, flow rate: 67.7 m ³ /h	Whatman QM-A quartz microfibre filter (20.3 cm x 25.4 cm), no cleaning of filter material
A.4	low volume sampler (LVS); 8 filters in the system consecutively with automatic switching flow rate: 2.4 m ³ /h	glass fibre filters GELMAN type A/C (47 mm d.), no cleaning of filter material
A.5	sampler with a filter holder connected with a vacuum pump, flow rate: 2.4 m ³ /h, regulation of the flow rate by a mass flow controller	filter of a mixed ester of cellulose (Millipore RAWP 1.2 µm, 5 cm d.), no cleaning of filter material
A.6	HVS Andersen GPS-1 fitted with a PM-10 inlet without impactor plates	glass fibre filters and two PUF-plugs, pre-cleaning of PUF-plugs by soxhlet-extraction with toluene and dichloromethane

The sampling procedures belonging to the different sampler types are presented in Table 3.

Table 3. Sampling procedures for air measurements

No.	sampling parameters / procedure
A.1	flow rate: 2 m ³ /h, only for comparison with sampler A.2b: 4 m ³ /h; sampling: weekly on Tuesdays, storage and transport: filters are wrapped in aluminium foil in PE bags, the glass cassettes with PUF plugs are wrapped in aluminium foil and closed in glass transport boxes; standard operation procedures were provided for all participants (see chapter 2.4.1) (Appendix B)
A.2a	flow rate: 25 m ³ /h, sampling: weekly on Tuesdays (last week of the month); working with standard operation procedure
A.2b	flow rate: 25 m ³ /h, sampling 24 h / week (Wednesday); working with standard operation procedure [11]
A.3	two HVS are used, every sampler 3.5 days in a week, flow rate: 67.7 m ³ /h, sampling: weekly on Tuesdays; filters stored and transported in a closed board container
A.4	filters were automatically changed daily, sampling (all filters): weekly on Tuesdays
A.5	sampling weekly on Tuesdays; flow rate: 2.4 m ³ /h

(Method A.6 is included in future work.)

¹ Code numbers for methods used by the participants including sampler type, sampling and analyzing procedure; A = Air

a, b: Participants used the same sampler type, but different sampling and analyzing procedures.

2.2 Precipitation sampling

A distinction should be drawn between two types of precipitation samplers: bulk and wet-only samplers. Bulk samplers are permanently open and collect dry and wet deposition, whereas the wet-only sampler only collects wet deposition from precipitation events. Bulk collectors are more susceptible to contamination. The samplers vary in shape, surface characteristics (size and material of the funnel) and collection mode (adsorbent for in situ compound isolation / non-adsorbent).

Table 4. Types of deposition samplers used

No. ²	sampler type	funnel	sampling
D.1	wet-only sampler (EIGENBRODT), 1.65 m in height; thermostatic system to maintain a constant temperature of 4°C; conductivity sensor fitted with a heating unit, optoelectronic sensor is optional; especially suitable for coastal sites = “reference method” (Appendix B)	glass, cylindrical-conical in shape; collection surface: 0.05 m ²	collecting bottle: 5 l glass bottle
D.2	bulk sampler 1.50 m in height	horizontal Teflon coated surface with 10 cm high edges; collection surface 1 m ² ; bottom declines slightly to a central opening	the PAHs are collected on an adsorbent during sampling, two cylindrical PUF- plugs (5 cm d., 10 cm long)
D.3	wet-only sampler 1.10 m in height; the sampler is equipped with a heating system with a thermostat to avoid freezing of the collected rainwater and to heat the funnel to melt the collected snow; conductivity sensor fitted with a heating unit	plastic funnel has a surface of 0.030 m ² glass funnel has a surface of 0.035 m ²	collecting bottle: 5 l glass bottle

Table 5. Sampling procedures for deposition measurements

No.:	sampling procedure
D.1	<ul style="list-style-type: none"> - monthly changing of the sampling bottles - rinsing the surface of the funnel with methanol in a separate glass bottle - after shaking the precipitation sample subdivision in 1 l transport glass bottles, rinsing of the funnel with hexane in a separate glass bottle (separate analyses of precipitation water, bottle rinse and funnel rinse) - standard operating procedures were provided to all participants (see chapter 2.4) (Appendix B)
D.2	<ul style="list-style-type: none"> - monthly changing of the PUF plugs at the same time; - after the sampling period soot and other particles deposited on the surface were rinsed from the Teflon surface with ethanol, using a Teflon scraper. The ethanol was collected in a separate glass bottle and the surface finally wiped clean with a glass fibre filter. (combined analysis of PUF-plug extract and funnel rinse)
D.3	<ul style="list-style-type: none"> - monthly changing of the sampling bottles, - rinsing the surface of the funnel with methanol in a separate glass bottle - subdivision of precipitation samples, rinsing the sampling bottle with dichloromethane (separate analyses of precipitation water, bottle rinse and funnel rinse)

² Code numbers for methods used by the participants including sampler type, sampling and analyzing procedure, D = Deposition

2.3 Analysis

2.3.1 Sample preparation

FILTER AND PUF PLUGS

The approved methods include soxhlet extraction, extraction under reflux and ultrasonication using a variety of organic solvents like acetone, toluene, cyclohexane and dichloromethane. For the extracts of the PUF plugs a clean-up is necessary before analysis. The filter extracts can be analysed in different ways.

Table 6. Extraction and clean-up methods for air samples

No.	Filters	PUF plugs
A.1	extraction with toluene under reflux for 20 min; no clean-up (Appendix B)	soxhlet extraction with toluene 3 h; clean-up using silica-gel (cyclohexane) (Appendix B)
A.2a	soxhlet extraction with acetone for 24 h; dilution to double volume with water, extraction with pentane / ether 9:1, combined extracts of filter and PUF plugs were fractionated on a silica gel column	
A.2b	soxhlet extraction with cyclohexane; "Grimmer method"; clean-up on HPLC using a silica column	
A.3	1/8 of the loaded filter is soxhlet extracted with dichloromethane for 4.5 h; clean-up over a silica-gel column,	no use of an adsorbent
A.4	two consecutive ultrasonic extractions with dichloromethane for 15 min; no clean-up	no use of an adsorbent
A.5	soxhlet extraction with toluene for 24 h, no clean-up	no use of an adsorbent
A.6	soxhlet extraction with hexane, clean-up on a Florisil column	

DEPOSITION SAMPLES

Table 7. Extraction and clean-up methods for precipitation samples

No.	Precipitation sample / funnel rinse	Adsorbent
D.1	- precipitation: two consecutive liquid-liquid extractions by stirring with hexane for 1 h; no clean-up (in accordance with German standard method DIN 38407-18) [12] funnel rinse: after adding of water to the methanol extraction with hexane (Appendix B)	- no use of an adsorbent
D.2	- funnel rinse: filtration of ethanol with glass fibre filter, soxhlet extraction with acetone 24 h, extraction in pentane / ether 9 : 1, combined extracts with adsorbent fractionation on silica-gel column	- soxhlet extraction with acetone 24 h; extraction in pentane / ether 9:1
D.3	- two consecutive extractions with dichloromethane; no clean-up	- no use of an adsorbent

2.3.2 Equipment for analysis

The analysis of PAH samples is usually carried out by high performance liquid chromatography (HPLC) equipped with a fluorescence detector or gas chromatography mass spectrometry (GC-MS) with electron and negative chemical ionisation methods. Typically HPLC with fluorescence detection requires far less clean up for successful quantification of PAH than GC techniques, but does not allow for use of isotope labelled internal standards.

Table 8. Equipment and calibration procedures

No.	Method	calibration
A.1 / D.1	HPLC (SHIMADZU) with wavelength-programmable fluorescence detector ; SUPERCOSIL LC-PAH 250 mm column with 4.6 ID; gradient elution acetonitrile / water (Appendix B)	external calibration with SRM 1647
A.2a / D.2	GC-MS (Varian Saturn 2000 with ion trap) operating in electron impact mode using full scan 45 - 350 a.m.u.; capillary column (CP-Sil-8 CB, Chrompack, Holland)	internal standards b,b'binaphtyl and bromonaphtalene
A.2b	GC/MS (HP-5973) in selected ion mode with electron impact ionisation	one-point calibration using 37 PAHs with 7 deuterated internal standards
A.3	HPLC with programmed fluorescence detection	external calibration with certified standard SRM 1647, some supplementary certified components
A.4/ D.3	HPLC analysis with programmed fluorescence detection; elution with acetonitrile/water 50/50 for 5 min, to 100 % acetonitrile in 20 min ; column Vydac 201 TP54, 5 µm, 4.6 mm i.d., 250 mm	external calibration with certified standard SRM 1647

2.4 Quality assurance and quality control (QA / QC)

The CAMP Principles [7] recommend a minimum programme to ensure that comparable quality data is established. The “method performance criteria and quality control measures for the determination of POPs in ambient air and precipitation” in accordance with AMAP (1994) [13] and EMEP (Guidelines recommended in Lillehammer 1997) can serve as a basis for such a programme [11].

2.4.1 Field operation

SAMPLING EQUIPMENT

All LVS provided by Germany were calibrated for correct volume reading before use. The measurement electronics show the volume of sampled air with 0.01 m³ accuracy. The deviation of the controller is < 1 %. To ensure extensive data completeness a reserve device was provided by Germany.

The HVS of Netherlands is working with a volumetric flow control accuracy with a deviation < 1 % over a 24-hour sampling period. In the case of the NILU home built HVS the flow is measured using rotameter reading at the start and at the end of sampling, assuming a linear flow decrease during the sampling period (standard operation procedure [11]).

For wet-only-sampling the conductivity and optoelectronic sensors installed on the EIGENBRODT sampler are regularly checked by staff in accordance with working instructions.

SAMPLE HANDLING, STORAGE AND TRANSPORT

At all sites the staff worked with operation procedures containing detailed instructions concerning changing of samples and storage and transport of the samples during the field experiment. Standard operation procedures for the LVS “reference sampler” and wet-only “reference sampler” were provided by Germany.

METHOD PERFORMANCE CRITERIA FOR SAMPLE COLLECTION

The use of a solid adsorbent for sampling of volatile compounds requires a back-up adsorbent for break-through control. Break-through rates have to be determined during method development. Because the breakthrough of volatile PAH depends on temperature and concentration level, differences between summer and winter have to be taken into account. If the sampling method is changed, especially the flow rate, the break-through has to be controlled as well. The back-up PUF plug should contain less than 5 % of the sample [11].

The three sampling methods A.1, A.2.a and A.2.b, which include the measurement of PAHs in the gas phase, were tested for breakthrough. To avoid breakthrough at least two PUF plugs were used. Their size depends on the type of sampler and the used flow rate.

FIELD BLANKS

A field blank was prepared, stored, transported and analysed in the same way as an exposed sample in order to check for possible sample contamination during field and other operations. In the case of the volatile PAHs, the back-up adsorbent used to control breakthrough can also be used as field blank as long as break-through rates are low.

For the sampling period of 10 weeks one field blank of filter and PUF plugs was taken at each station and was included in the “reference method”. Only the volatile PAHs phenanthrene, anthracene and fluoranthene could be detected. The lowest measured values were ten times higher than those of the blanks, that is the reason why they can be ignored.

The field blanks for deposition sampling using the “reference method” included the following samples: high purity water with adding of 10 ml hexane in one litre glass bottle for transport, 200 ml methanol, used for funnel rinsing in 500 ml transport glass bottle, 60 ml hexane, used for rinsing of the sampling bottle. In parallel to each sampling period a high purity water blank was included. Blank checks of hexane and methanol were carried out once during the field experiment. Blanks were only obtained for the volatile PAH.

PRECISION OF FIELD INSTRUMENTS AND MEASUREMENT SYSTEMS

To assess the precision of the data two identical samplers should be run in parallel.

The HVS A.2b and the LVS “reference method” A.1 were tested for their precision in the measurement of PAHs. Including both the gas and the particulate phases the precision is below 20 % for all PAHs and below 10 % for most compounds (see Table D.II Appendix D).

The wet-only sampling “reference method” (D.1) was also checked for precision. The precision is below 14% for all PAHs (see Table E.II Appendix E).

2.4.2 Laboratory operations

Aspects of method validation including compound identification and quantification criteria should be investigated before the analysis of real samples. They are summarised in the “Method performance criteria and quality control measures for the determination of POPs in ambient air and precipitation” according to AMAP (1994) [13] and EMEP (Guidelines, Lillehammer 1997) [11].

QUALITY CONTROL MEASURES

Reference material:

A standard reference material was analysed by the participants (SRM 1649 Urban Dust). The reference material is certified for all PAHs of the measuring programme. The results are presented in Tables C.I - C.III in Appendix C. Including the different analysis methods the scatters (relative standard deviations) of the individual PAHs between the labs are below 25 % (see Table C.II) and the deviations of the measured mean values of all labs from the certified values are +/- 15 % (see Table C.III).

Blank values:

Analytical blanks were considered by all participants.

3 RESULTS

3.1 Sampler comparison

As the sampling method provided by Germany for both air and precipitation was used at all stations, the methods CPs used in parallel are evaluated in comparison to the German method. It must be pointed out that the method provided by Germany was used as “reference method” during the Pilot Study. The method was checked for important quality parameters (reproducibility of parallel samplers, recovery and breakthrough, storage and transport of samples, field blanks) (see Appendix B).

Data availability for air measurements is shown in Table D.I in Appendix D and for precipitation measurements, in Table E.I in Appendix E. Data from the sampler comparisons LVS A.4 / A.1 “reference method” and LVS A.5 / A.1 could not be included, since problems with the LVS A.4 occurred and the data from the LVS A.5 were not available at the time the samplers were evaluated (see chapter 4.2 Future work).

During the experiment few technical problems were observed. Only three samples of the LVS A.1 are missing due to sampler failure. Special problems were observed in Lista, where the sampler was installed on a pallet on the lawn at the station approximately 50 m from the beach. Since samples were changed outdoor, sometimes during strong rain events, wet samples and/or interrupted sampling occurred. Three samples were excluded from the sampler comparison.

3.1.1 Air measurements

REMARK:

For the air measurements the following definitions served as the basis. The “particulate phase” covers that part of the sample which is collected on the filter. The “gas phase” is that part which is captured by the two PUF plugs fitted in line.

Substantial issues were included in the sampler comparison, which are important for the discussion of the comparability of methods:

- the flow rate required for different sampler types (high-volume sampler / HVS, low-volume sampler / LVS);
- sampling time and sampling intervals;
- sampling system (particulate phase (fraction TSP = total suspended particulates, PM10 = fraction $\leq 10 \mu\text{m}$)); gas phase).

Weekly sampling with the “reference method” (A.1) is compared with two types of HVS:

- HVS (home built) in weekly sampling (A.2a) and 24 h sampling (A.2.b); and
- the PM10 HVS (Sierra / Andersen) (A.3).

The following results were obtained with respect to concentrations of individual PAH compounds in air (particulate phase; particulate and gas phase).

In Tables D.II and D.III (Appendix D) the results of the sampler comparison are summarised (mean of relative standard deviations of the paired air samples; deviation of the mean values of PAH concentrations during the sampling period (methods of the participants in comparison to “reference method”). Not all PAH compounds selected for the sampler comparison were analysed by all participants.

The sampler comparison including sample handling and analysis allows the following conclusions to be drawn:

- the analysis of a reference material SRM 1649 “urban dust” has shown that the analytical agreement between the participants is acceptable and is not a main source of the variations found in the sampler comparison;
- field blanks did not occur, so that contamination problems during sample handling should be excluded as an error. PUF-plugs have to be cleaned before use;
- the variations between the LVS reference method (A.1) and the three HVS methods (A.2a, A.2b, A.3) are mainly due to the sampling devices, the sampling frequency and sample handling.

SAMPLER COMPARISON HVS (A.2A, A.2B) / LVS (A.1) - COMBINED GAS AND PARTICULATE PHASE

Weekly sampling (A.2a / A.1)

For most PAH compounds there is a good agreement between the weekly PAH concentrations in the gas and the particulate phase measured with HVS and LVS. It can be concluded that the LVS reference method (A.1) and the HVS (A.2a) correlate very well for all PAH compounds determined in the complete sample ($R^2 > 0.95$, with the exception of benzo(ghi)perylene ($R^2 = 0.73$) and indeno(1,2,3-cd)pyrene ($R^2 = 0.84$)). With the exception of benzo(a)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene the mean values of the relative standard deviations are between 9% and 50% (see Table D.II in Appendix D). The comparison of the mean weekly concentrations of the HVS and LVS methods shows that for some volatile compounds (anthracene, fluoranthene, pyrene, benzo(a)anthracene) the values measured with HVS are 30% to 59% lower (Table D.III in Appendix D). The deviations in order of +/- 20 % found for the other compounds (exception: benzo(ghi)perylene) were considered negligible and need not be discussed.

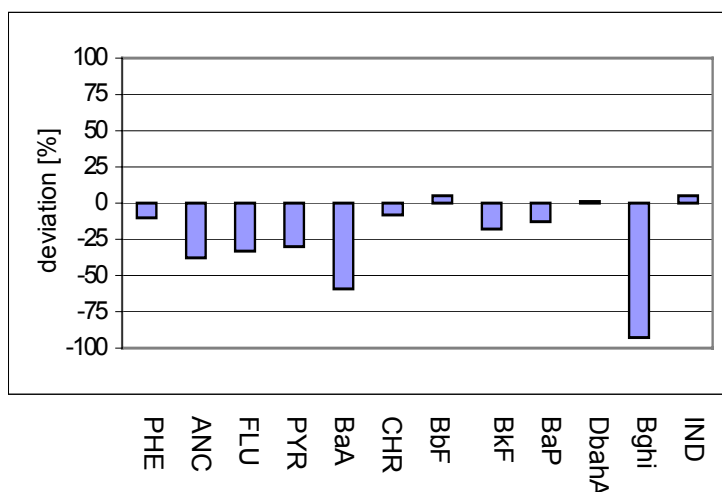


Figure 1. Deviation of the mean weekly values of concentrations of individual PAHs in the gas and particulate phase measured with HVS (A.2a) in comparison to the values measured with LVS (A.1a) “reference method” (September - December 1998, one week a month)

24 h-HVS (A.2b) - Weekly sampling (A.1)

The same HVS used in method A.2a for weekly sampling were run 24 h a week in comparison to the weekly sampling with the LVS “reference method”. The mean concentrations of both methods in this sampling period show good agreement for the volatile compounds anthracene, fluoranthene, pyrene and benzo(a)anthracene (deviations of A.2.a in comparison to A.1 between +/- 6 % and 22 % (see Table D.III in Appendix D).

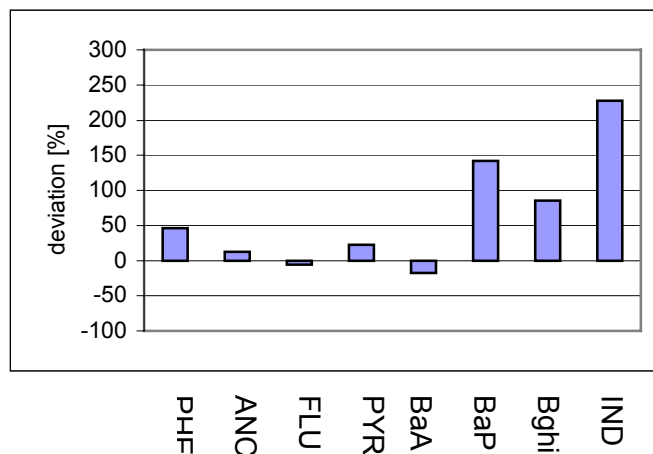


Figure 2. Deviation of the mean values of concentrations of individual PAHs in the gas and particulate phase measured with HVS (A.2b) (24h sampling a week) in comparison to the values measured with LVS (A.1a) “reference method” (weekly sampling) (September - November 1998)

The large deviations for the particle bound PAHs benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(ghi)perylene and indeno(1,2,3-cd)pyrene have to be considered in connection with some interference in the GC-MS analysis used for method A.2b. Nevertheless this differences can be caused by large temporal variations of PAH concentrations in ambient air. Individual situations with high or low concentrations may occur, and if they happen during a 24 h sampling the influence on the mean of the whole sampling period may be large.

SAMPLER COMPARISON PM10 HVS (A.3) / LVS (A.1) (WEEKLY SAMPLING) - PARTICULATE PHASE

In general it can be concluded that the LVS reference method A.1 and the PM10 HVS A.3 correlate very well for all measured particle bound PAH components (individual PAHs $R^2 > 0.75$; sum of 10 PAHs $R^2 = 0.98$; ($n=6$)). A loss was observed for the more volatile compounds fluoranthene, pyrene, benzo(a)anthracene and chrysene in the PM10 HVS (loss of fluoranthene and pyrene 69% and 65% (see Table D.III in Appendix D) in comparison to values measured with A.1). The main reasons for the loss are probably the adsorption of PAH gas-phase substances on the impactor plate and the untreated filter storage over many weeks. For the more volatile PAHs the scatter is between 38% and 68%, for the other compounds between 19% and 29% (see Table D.II in Appendix D).

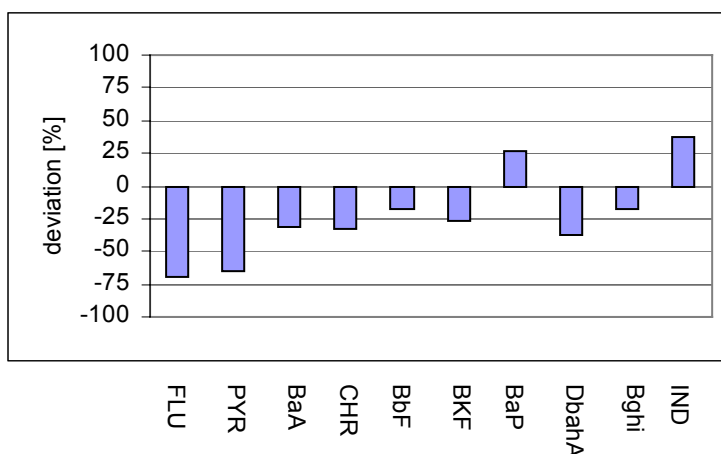


Figure 3. Deviation of the mean weekly values of concentrations of individual particle bound PAHs measured with HVS (A.3) in comparison to the values measured with LVS (A.1a) “reference method” (September - November 1998)

The HVS with the PM10 inlet can be considered as a one-stage impactor, which is based on selection of the PM10 particles by internal separation, followed by collection of the PM10 mass on a glass fibre filter. The particulate phase includes mainly those particles with an aerodynamic diameter less than or equal to 10 micrometers. This sampling system seems to have a greater influence on the collection of the more volatile compounds. Size fractionating air samplers, such as cascade impactors, have been used to study the distribution of PAHs with particle size. Sampling artefacts are known to occur in the use of cascade impactors [14, 15]. The volatilisation artefact was found to be important for PAH compounds with intermediate vapour pressures (from phenanthrene / anthracene to benzo(a)anthracene / chrysene [15]).

There is general agreement that most PAHs are associated with fine particles (i.e. 2.5 μm [16]). Allen [17] claimed that PAHs are associated predominantly with aerosols $< 2 \mu\text{m}$. Especially benzo(a)pyrene is associated with atmospheric particles with diameters in the respiratory range $< 0.26 \mu\text{m}$ [18]. For small particles ($< 10 \mu\text{m}$) the sampler construction in connection with the wind direction and speed can influence only slightly the collection efficiency [16]. However, the sampling of large particles is much more complicated, but they are not so important for PAHs, as was found in sampler tests (AEAT, UK) [19] for particles $< 5 \mu\text{m}$.

3.1.2 Precipitation measurements

Main parameters, which are important for the comparability of methods were included in the sampler comparison:

- the sampler type: wet-only and bulk;
- the sampling mode: adsorbent, non-adsorbent (collection of precipitation in a glass bottle);
- funnel size, shape and material.

Because it is well documented that an adsorption of PAHs on the funnel surface occurs, a funnel rinse was carried out and the rinse added to the deposition sample [20 - 22]. The cleaning of the collection surface and the addition of the rinse to the deposition sample must be carried out in accordance with quality requirements [11].

In Tables E.II and E.III (Appendix E) the results of the sampler comparison are summarised (mean of relative standard deviations of the paired deposition samples; deviation of the mean values of PAH deposition in the sampling period of the methods (method of the participants in comparison to the “reference method”).

For the sampler comparison including sample handling and analysis the following conclusions are drawn:

SAMPLER COMPARISON BULK-SAMPLER (D.2) / WET-ONLY-SAMPLER (D.1) “REFERENCE METHOD”

The mean values of monthly PAH deposition show considerable differences between the methods, which vary among the individual compounds. Larger amounts of PAH deposition were obtained with bulk-sampling in comparison to the wet-only-sampling (see Table E.III in Appendix E).

Several reasons can be responsible for the differences, because the design of the samplers as well as sample handling and analysis differ considerably. The bulk-sampling method D.2 used an adsorbent for an in situ accumulation of PAHs during the sampling period. The precipitation from wet-only sampling was collected in bottles, which were cooled during sampling, so that losses of PAH during the monthly sampling can be excluded. Field blanks of the wet-only-sampling method were checked.

Further measurements have to be carried out to clarify the differences between the two methods (see chapter 4.2 Future work).

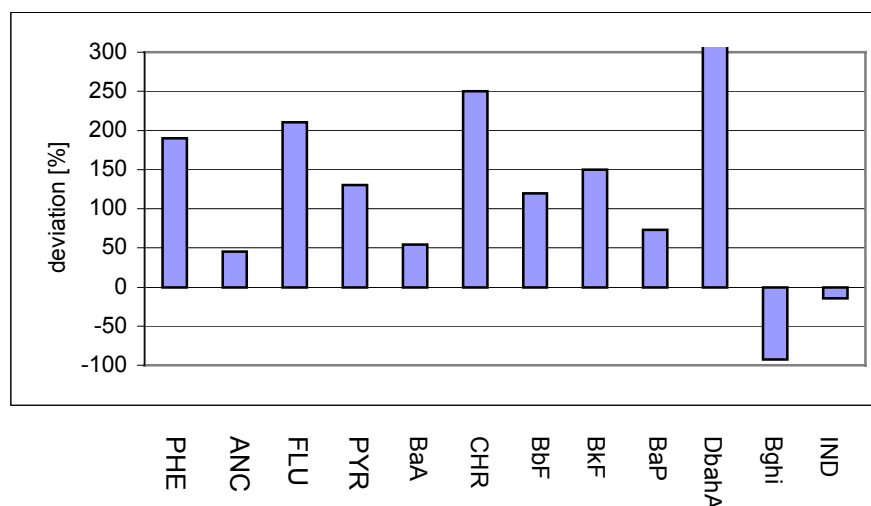


Figure 4. Deviation of the mean monthly values of depositions of individual PAHs measured with bulk-sampling (D.2) in comparison to the values measured with wet-only-sampling (D.1) “reference method” (October - December 1998)

SAMPLER COMPARISON WET-ONLY-SAMPLER (D.3) / WET-ONLY-SAMPLER (D.1) (“REFERENCE SAMPLER”)

For a comparison of analysis methods subdivided precipitation samples of the “reference sampler” were analysed both by D.1 and by D.3. While the analysis of PAH concentrations in sub samples by D.1 (for 5 sampling periods two separate transport bottles with the sub samples were sent to the project manager) indicates a good reproducibility (< 10% for most compounds), the analysis results differ considerably between the two labs (relative standard deviations of three paired samples over 90% for individual PAH compounds).

There are considerable differences between the PAH deposition measured with both methods (see Tables E.II and E.III in Appendix E). These differences are caused by the type of sampler especially the funnel shape as well as by problems in analysis. The method of the VMM was tested during the sampler comparison for the first time. The proportions of PAHs in rinses of the plastic funnel and the glass funnel (D.3, a sampler with a glass funnel was used additionally in the last month) differ considerably. Especially for the plastic funnel they vary considerably among the three sampling periods, so that it seems that the plastic funnel can cause problems when the funnel rinse is added to the deposition sample. Field blanks were checked in every sampling period, so that contamination should not be the problem. Further measurements have to be carried out to clarify the differences of both methods (see chapter 4.2 Future work).

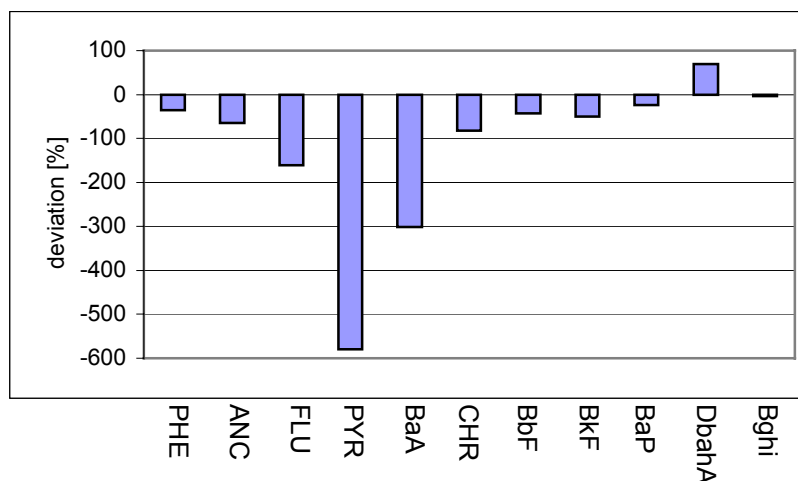


Figure 5. Deviation of the mean monthly values of depositions of individual PAHs measured with wet-only-sampling (D.3) in comparison to the values measured with wet-only-sampling (D.1) “reference method” (October – December 1998)

3.2 Spatial and temporal variations of PAH concentrations and depositions

3.2.1 PAH concentrations in the gas and particulate phases

The concentration of PAHs in ambient air was to be determined using the “reference method” separately for the gas and particulate phases at 7 stations (see Appendix F).

Given the importance of the vapour phase burden for volatile PAH compounds, the phases trapped on the filter and adsorbed by an adsorbent were analysed separately. With the use of filters alone only the particle bound PAHs can be measured, but there are sampling artefacts, discussed in the literature [14 - 16]. The particle fraction can be either underestimated as a result of “blow-off”, or overestimated if vapour phase PAHs have adsorbed onto the trapped particles. The use of a sampling system as combination of a filter and a back-up adsorbent can address these problems for measuring the total PAH concentration in air. The determination of partitioning of PAHs between the vapour and particulate phases is important for gaining an understanding of atmospheric processes, but several factors including possible error sources may affect the distribution of POP during sampling.

The following results were obtained for the 10-week sampling period from 08/09/1998 to 17/11/1998 (six weeks were included (week 1-4 and 9-10), because only for these sampling intervals complete data sets were available from all stations):

- A spatial variation of PAH concentrations in air is observable. The weekly PAH concentrations follow the order of

- De Zilk > Knokke > Zingst > Westerland ~ Ulborg ~ Lista ~ Rörvik for the sum of both phases
- De Zilk > Knokke > Zingst > Westerland ~ Lista ~ Rörvik ~ Ulborg for the gas phase
- Zingst > De Zilk ~ Knokke > Westerland ~ Ulborg = Rörvik > Lista for the particulate phase

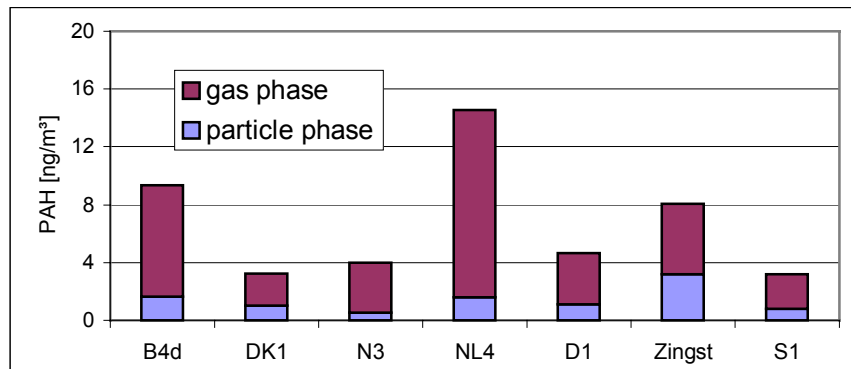


Figure 6. Mean values of weekly concentrations of the sum of PAH concentrations in the gas and particulate phases at the different sampling sites from 08/09/1998 to 17/11/1998

- A clear temporal variation is evident for all stations and for gas-particle partitioning. Measurements show a sudden simultaneous increase in PAH concentrations especially in the particulate phase at the stations De Zilk, Knokke, Zingst, Ulborg and Westerland.
- At all sites the lighter three- and four-ring compounds were the most abundant in air, notably phenanthrene, fluoranthene and pyrene. Phenanthrene consistently accounts for about 40 -50% of the total PAH concentration in air at each site. The higher molecular compounds are less abundant. Similar PAH profiles were reported by other authors [21, 23]. These volatile compounds are mainly in the gas phase (phenanthrene over 90 %). Conversely, beginning with benzo(a)pyrene up to indeno(1,2,3-cd)pyrene these PAHs were primarily associated with the particulate fraction on the filter. The four-ring PAHs pyrene, benzo(a)anthracene and chrysene were distributed more or less equally between the two phases [3].

3.2.2 PAH depositions

The “reference method” was used to measure PAH depositions during the period of the sampler comparison at 5 stations (3 CAMP stations, Zingst, which is included in HELCOM and Gent (measuring field) (see Appendix G).

The following results were obtained with respect to monthly PAH deposition from October till December 1998:

- The mean values of monthly PAH deposition from October to December 1998 show the following order: Gent > Zingst > Rörvik ~ Ulborg ~ Westerland.
- A temporal variation is evident for Zingst and Rörvik with a sudden increase from October to November. This is in agreement with the air measurements.
- At all sites the more volatile compounds phenanthrene, fluoranthene and pyrene have the highest depositions. Deposition samples dominated by less volatile PAH which exist to a great extent to particles.
- The proportion of PAH adsorbed on the funnel surface is between 4 % and 38 % during this study period. Similar results were obtained in earlier investigations with wet-only-sampling [20, 22].

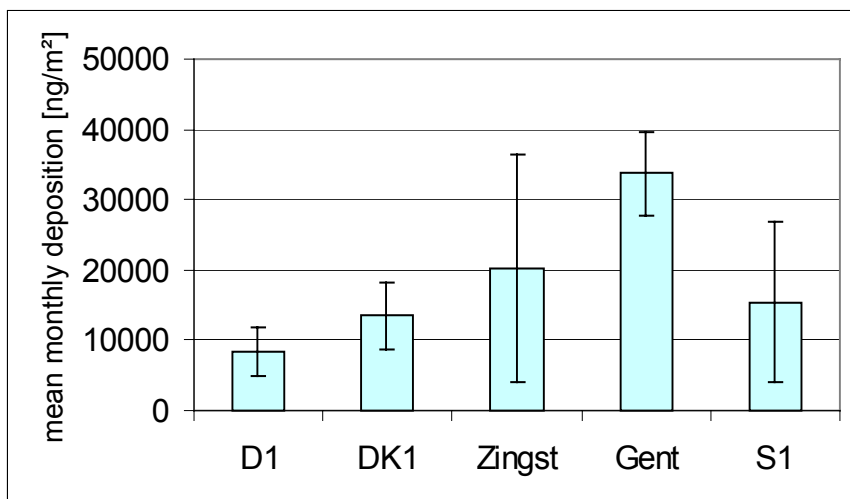


Figure 7. Mean values of monthly depositions from October till December 1998 at the different sampling sites

4 CONCLUSIONS

The results confirm that different chemical and physical properties of the individual PAH compounds reflect different air sampling characteristics. They correspond with comparable results from other sources of literature. Once present in the atmosphere, the PAHs further partition between the particulate and gas phases depending on the prevailing physical conditions within the atmosphere and the particular physical characteristics of the compounds themselves. Recent investigations including the field experiment show that gaseous PAHs account for a considerable proportion of the PAH concentration in air. If PAHs are adopted as a mandatory CAMP parameter to the CAMP, the determination of the PAH concentration in the gas phase may not be neglected.

In general it can be concluded that there is good agreement between the methods for the measurement of PAH concentrations in ambient air, although there are some problems with individual PAH compounds, such as loss of volatile PAHs in the use of a PM 10 sampling head or differences especially for particle bound PAH using weekly LVS and 24 h HVS.

During and after the Pilot Study additional methodological investigations supporting this study were carried out. The results of these extra activities will not change the outcome and the results of the final report of the Pilot Study on Atmospheric Inputs of PAHs; this is the reason why the current report was published in this form. Later on, there will be an extension to this report including the missing data.

Precipitation measurements were found to involve the largest problems. Sampling methods for POPs in precipitation have been and will continue to be the subject of in-depth discussion within the framework of monitoring programmes [7, 11], whereas for air measurements the situation seems less complicated. The Intercomparison Exercise also confirms that QA/QC is an important element of the measuring programme.

4.1 Recommendations

The results including sampling and analytical problems were discussed among the participants at the "OSPAR Workshop on guidelines for sampling and analysis of PAH in air and precipitation" and some main recommendations were established.

The use of a LVS is recommended, since it represents an economic device for achieving the objectives of the measurements conducted under CAMP. Air measurements should include both the particulate and gas

phases, since considerable proportions of volatile PAH compounds are present in the gas phase (use of a filter-adsorber system). Weekly sampling is recommended for the initial phase to quantify the atmospheric input. Analyses should be carried out preferably weekly, biweekly if there are problems with the detection limit. Monthly data reflect mainly seasonal variations.

In the CAMP principles the use of a wet-only sampler is recommended for precipitation measurements. After each sampling period the surface of the funnel should be rinsed with a water mixable polar solvent (methanol, ethanol). The rinse should be added to the sample. A sampling period from one week to one month is possible.

For analysis of PAHs the following methods were used: HPLC with programmable fluorescence detection and GC-MS.

Generally it is recommended to follow the “Method performance criteria and quality control measures for the determination of persistent organic pollutants (POP) in ambient air and precipitation” according to AMAP (1994) [13] and EMEP (Guidelines recommended in Lillehammer 1997) [11]. Standard operation procedures must be defined separately for sampling and analysis. Field blanks should be checked 2 to 3 times per year. The SRM 1649a “Urban dust” is used as a quality standard. It should be used once per year.

4.2 Future work

Beyond the results of the Pilot Study investigation, it is necessary on the one hand to confirm the results and on the other hand to clarify questions that are still open.

Air measurements

- Additional parallel measurements with LVS (“reference method” A.1) and HVS (A.2a) will be performed, using the same procedure as during the field experiment (one weekly sample in a month from July till October 1999)
responsible: Germany / Sweden (IVL)
- Inclusion of the UK in the comparison of air volume sampler (parallel sampling HVS A.6 / LVS (“reference method” A.1) (August till October 1999).
responsible: Germany / UK (AEAT)
- The current validation of the Belgian LVS (A.4) method is ongoing (comparison with a HVS).
responsible: Belgium
- The data of Denmark were not available yet. They will be reported later.
responsible: Denmark

Precipitation measurements

- In the context of a research project planned by Sweden a long-term comparison of bulk (D.2) and wet only (EIGENBRODT (D.1)) sampling is to be conducted over a one-year period. Germany / NORDUM had supplied the sampler.
responsible: Germany / Sweden
- The analysis of precipitation sub samples collected as part of the field experiment has not yet been carried out.
responsible: Denmark
- Examination showed differences in the application of the extraction methods for precipitation samples (comparison of D.1 and D.3). Germany / NORDUM had supplied the sampler.
responsible: Belgium / Germany

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Appendix A

Table A.I. Properties and structure of selected PAHs [10]

Compound (IUPAC name)	abbrev.	Mol. wt.	Vapour pressure at 25°C [kPa]	boiling point [°C]	Carcinogenic	structure
Phenanthrene	PHE	178	$2.3 \cdot 10^{-5}$	339 - 340		
Anthracene	ANC	178	$36 \cdot 10^{-6}$	340	(+)	
Fluoranthene	FLU	202	$6.5 \cdot 10^{-7}$	375 - 393		
Pyrene	PYR	202	$3.1 \cdot 10^{-6}$	360 - 404		
Benzo(a)-Anthracene	BaA	228	$1.5 \cdot 10^{-8}$	435	+	
Chrysene	CHR	228	$5.7 \cdot 10^{-10}$	441 - 448	+	
Benzo(b)-fluoranthene	BbF	252	$6,7 \cdot 10^{-8}$	481	+	
Benzo(k)-fluoranthene	BkF	252	$2.1 \cdot 10^{-8}$	480 - 481	+	
Benzo(a)-pyrene	BaP	252	$7.3 \cdot 10^{-10}$	493 - 496	+	
Benzo(ghi)-perylene	BghiP	278	$1.3 \cdot 10^{-11}$	525	+	
Dibenzo(a,h)-anthracene	DBaA	278	$1.3 \cdot 10^{-11}$	524	+	
Indeno(1,2,3-cd)pyrene	IND	276	$\sim 1.0 \cdot 10^{-11}$	-	+	

**Determination of PAHs in ambient air (particle and gas phase) -
“reference method” provided by Germany for the field experiment**

	sampling weekly	<ul style="list-style-type: none">- low volume sampling device (DERENDA) (flow rate: 2 - 4 m³/h)- sampling head PK 50-PU/G (RIEMER) glass fibre filters (d. 5 cm) and glass cassette with 2 PUF plugs (d.5cm, 5cm long)- pre-cleaning of filters (heating 10 h, 230°C) and PUF plugs (soxhlet extraction with toluene and acetone, drying under vacuum and storage in glass cassettes)
	storage and transport	<ul style="list-style-type: none">- filters are folded and wrapped in aluminium foil and put into plastic bags- PUF plugs stored in the glass cassettes wrapped in aluminium foil and put into closed glass vessels;- storage at room temperature
toluene	extraction	<ul style="list-style-type: none">- separate extraction of filter and PUF-plugs- PUF plugs 3 h in a soxhlet-apparatus- filters 20 min boiling with reflux condenser
cyclohexane	clean-up	<ul style="list-style-type: none">- no clean-up of filter extracts- clean-up of PUF-plug extracts with silica gel
acetonitrile	HPLC analysis programmable fluorescence detector	<ul style="list-style-type: none">- SUPELCOSIL LC-PAH 250 mm column- water / acetonitrile gradient- calibration with SRM 1647d
	detection limits:	<p>- PHE, BaA, CHR, BbF, BkF, BaP, DbahA, BghiP 0.003 ng/m³ (for 2 m³/h) - A 0.001 ng/m³; FLUOR, PYR 0.006 ng/m³; IND 0.015 ng/m³</p>
	QA / QC	<ul style="list-style-type: none">- working with operation procedures- regular control of field blanks- analysis of SRM 1649 urban dust
	- reproducibility (parallel samplers (n=5)) :	<ul style="list-style-type: none">- particle phase: 3.9 % - 21 %- gas phase: 7.3 % - 27 %- sum of both phases: 4.8 % - 21 %
	- recovery:	<ul style="list-style-type: none">- breakthrough of back-up plug < 5 % of the first plug- Deviation of parallel sampling 1*6 days and 3*2 days lies in the reproducibility of the method.- no losses of volatile PAH from loaded PUF plugs during 6-week storage at room temperature

Determination of PAHs in precipitation - "reference method" of the field experiment provided by Germany

funnel rinse with methanol	sampling monthly <i>precipitation sample</i>	<ul style="list-style-type: none">- wet-only sampler (EIGENBRODT) with a conductivity sensor (or optoelectronic sensor)- collection of precipitation via a glass funnel (0.05 m²) in a glass bottle- heating of the sampler interior and funnel in winter, cooling with a refrigerator in summer
	storage and transport	<ul style="list-style-type: none">- monitoring¹⁾: after sampling hexane is added to the precipitation sample in the sampling bottle, storage in a refrigerator, transport in cooling box- field experiment²⁾: sub-samples were taken after shaking the sampling bottle, rinsing of the sampling bottle with hexane, hexane was added to the sub-sample, transport in parcels
hexane DIN 38 407 F18	extraction	<ul style="list-style-type: none">- stirring with hexane directly in the sampling bottle or in the transport bottle (sub-samples) (two separate extractions for 1 h are combined)- no clean-up of the extracts
acetonitrile	HPLC analysis programmable fluorescence detector	<ul style="list-style-type: none">- SUPELCOSIL LC-PAH 250 mm column- water / acetonitrile gradient- calibration with SRM 1647d
detection limits: - PHE, BaA, CHR, BbF, BkF, BaP, DbahA, BghiP 1 ng/l (for 1 l sample) - A 0.5 ng/l ; FLUOR, PYR 2 ng/l ; IND 5 ng/l		
<i>deposition sample</i> (sum of PAH amount on the funnel and in precipitation)		
	QA / QC	<ul style="list-style-type: none">- working with operation procedures- regular control of field blanks- analysis of SRM 1649 urban dust
		<ul style="list-style-type: none">- reproducibility (parallel samplers (n=4)): - sum of PAH 4.3 % - individual PAH 5.6 % - 14 %
		<ul style="list-style-type: none">- recovery: - re-extraction of precipitation samples- no losses of PAH during 1-week storage of samples at room temperature and in a refrigerator with and without adding of hexane

1) method is used at the German monitoring stations Zingst and Westerland

2) method was tested and used for the field experiment (reproducibility in analysis of sub samples < 10 % for individual PAH)

Results of the analysis of the standard reference material SRM 1649 Urban Dust

Table C.I. Number of analyses and relative standard deviations of the methods of the participants [in brackets %]

No.	method	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
A.1	HPLC	5 (11)	5 (5.9)	5 (8.1)	5 (8.4)	5 (3.4)	5 (8.9)	5 (7.4)	5 (7.6)	5 (9.2)	5** (20)	5 (14)	5 (4.2)
A.2a	GC-MS	1	1	1	1	1	-*	-*	-*	1	1*	1	1
A.3	HPLC	-	-	1	1	1	1	1	1	1	1	1	1
A.4	HPLC	4 (11)	4 (9)	4 (5)	4 (5)	4 (5)	4 (4)	4 (2)	4 (1)	4 (6)	4** (9)	4 (3)	4 (3)

* co elution of compounds; ** outliers

Table C.II. Values of the measured PAH concentrations in comparison to the certified values [mg/kg]

		PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
certified values		4.14	0.432	6.45	5.29	2.21	3.05	6.45	1.91	2.51	0.29	4.01	3.18
		+/- 0.37	+/- 0.082	+/- 0.18	+/- 0.25	+/- 0.073	+/- 0.06	+/- 0.45	+/- 0.03	+/- 0.03	+/- 0.023	+/- 0.91	+/- 0.72
measured values	mean	4.41	0.400	6.47	5.41	2.52	3.48	5.75	1.87	2.23	0.30	4.17	3.43
	sd	0.22	0.092	0.41	0.76	0.48	0.04	0.38	0.04	0.47	-	0.72	0.79
	sd (%)	4.9	23.2	6.3	14.0	19.1	1.1	6.6	1.9	21.1	-	17.3	22.9
	d (%)	+6.5	-8.3	+0.3	+2.3	+14.0	+14	-11	-2.1	-11.2	+3.4	+4.0	+7.8

sd = standard deviation; sd (%) = relative standard deviation; d = deviation of measured mean values from certified mean value

Table C.III. Deviation of measured PAH concentrations of the participants in comparison to certified values (mean values); [%]

	method	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
A.1	HPLC	+8.5	-5.5	+8.1	+22	+26	+15	-10	-1.6	+3.8	-	+8.1	-14
A.2a	GC-MS	+0.48	+16	-2.8	-12	+1.8	-	-	-	+5.6	-	-19	+5.3
A.3	HPLC	-	-	2.3	-3.6	-9.5	+15	-5.4	-0.5	-4.4	+3.4	+17	-2.5
A.4	HPLC	+10	-35	-6.5	+3.0	+38	+13	-17	-4	-38	-	13	43

Appendix D

Results of the sampler comparison - PAH measurements in air

Table D.I. Number of paired weekly samples of the sampler comparison HVS (A.2a, A.2b, A.3) and LVS “reference method” (A.1) (planned samples: 10, except for 2.a: 4)

	phase	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
A.2a	particulate	4	4	4	4	4	4	4	4	3	4	4	4
A.2.b	and gas	7	7	7	7	7	0	0	0	7 (4)*	0	7	7 (1)*
A.3	particulate	0	0	6	6	6	6	6	6	6	6	6	6

Table D.II. Means of relative standard deviations of PAH concentrations of the sampler comparison HVS (A.2a, A.2b, A.3) and LVS “reference method” (A.1) and precision of the “reference method” (A.1) and HVS (A.2.a); [%]

	Phase	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
Sampler comparison HVS (A.2a, A.2b, A.3) and LVS “reference method” (A.1)													
A.2a	Particulate	9	34	31	11	60	30	29	18	21	50	96	66
A.2b	and gas	25	60	23	23	61	-	-	-	65 (77*)	-	42	62 (13*)
A.3	Particulate	-	-	54	68	51	38	20	20	19	29	27	26
Precision of one method (parallel sampling)													
A.1 (n=5)	Particulate	7.0	21	9.4	13	6.7	4.5	3.9	5.4	9.0	**	6.0	19
	Particulate and gas	7.0	15	7.8	10	13	21	4.8	5.4	9.0	**	6.0	19
A.2a (n=6)	Particulate and gas	5.4	19	6.7	6.8	18	-	-	-	12	-	12	7.4

* without interference; ** values near and below detection limit

Table D.III. Deviation of the mean values of PAH concentrations of HVS methods (A.2a, A.2b, A.3) in comparison to the LVS reference method (A.1) (September to December 1998 (A.2a); September to November 1998 (A.2b, A.3)); [%]

	Phase	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
A.2a	Particulate and gas	-10	-38	-33	-30	-59	-8	+5	-18	-13	+1	-93	+5
A.2b		+46	+12	-6	+22	-18	-	-	-	+142	-	+85	+228
A.3	Particulate	-	-	-69	-65	-32	-33	-17	-27	+27	-38	-18	+37

< 25 %	25 % - 50 %	> 50 %
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Appendix E

Results of the sampler comparison - PAH measurements in precipitation

Table E.I. Number of paired monthly samples of the sampler comparison (D.2, D3) and “reference method” (D1) (planned samples: 3)

	deposition	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
D.2	bulk	3	3	3	3	3	3	1*	3	2*	2**	2**	2**
D.3	wet-only	3	3	3	3	3	3	3	3	3	3	3	3

* two values of BbF and one value of BaP with interference of GC-MS-analysis; ** one value below detection limit

Table E.II. Means of relative standard deviations of PAH depositions of parallel sampling with bulk and wet-only-sampler (D.2; D3, plastic funnel) and wet-only reference method (D.1) and precision of the reference method (D.1);[%]

	deposition	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
Sampler comparison (D2, D.3) and “reference method” (D.1)													
D.2	bulk	68	41	69	69	49	73	52	37	53	84	120	11
D.3	wet-only	38	99	55	107	102	30	37	28	27	130	22	42
Precision of one method (parallel sampling)													
D.1 (n=4)	wet-only	6.4	5.6	6.4	12	8.4	9.4	14	14	13	12	5.9	7.0

Table E.III. Deviation of the mean values of PAH depositions of bulk- and wet-only sampling (D.2, D.3) in comparison to the wet-only “reference method” (D1), [%]

	deposition	PHE	ANC	FLU	PYR	BaA	CHR	BbF	BkF	BaP	DbahA	Bghi	IND
D.2	bulk	+190	+45	+210	+130	+54	+250	+120	+150	+73	+1050	-93	-14
D.3	wet-only	-35	-64	-161	-580	-302	-82	-43	-50	-23	+69	-3.7	+23

< 25 %	25 % - 50 %	> 50 %
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Appendix F

Weekly PAH concentrations in ambient air (gas and particulate phase) at different sites from September - November 1998, weeks 1-10 from 08/09/1998 - 17/11/1998
("reference method")

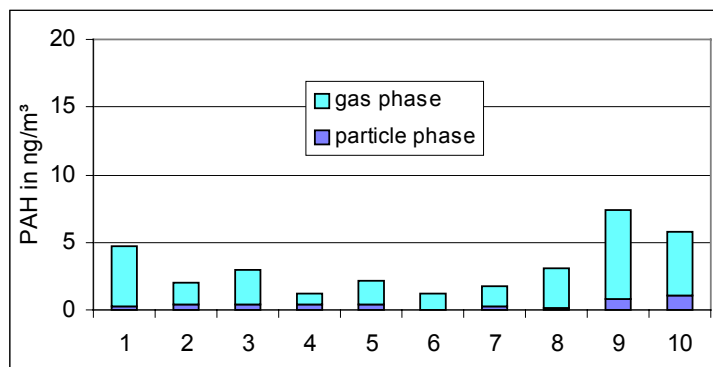


Figure F1. N3 Lista

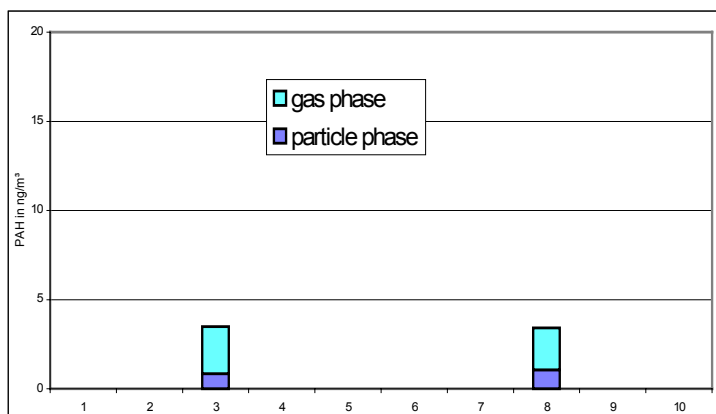


Figure F2. S1 Rörvik

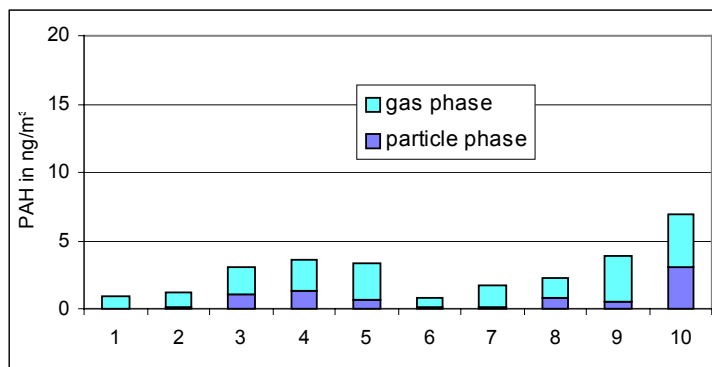


Figure F3. DK1 Ulborg

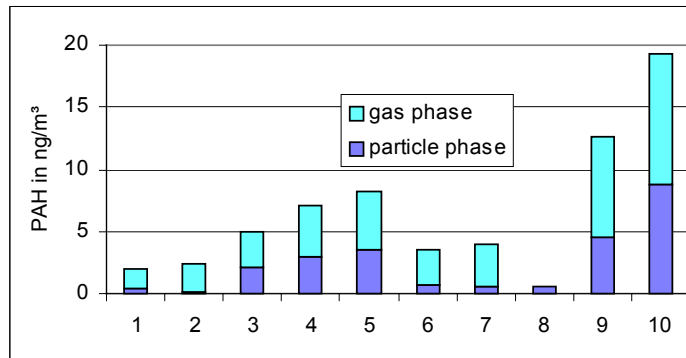


Figure F4. Zingst

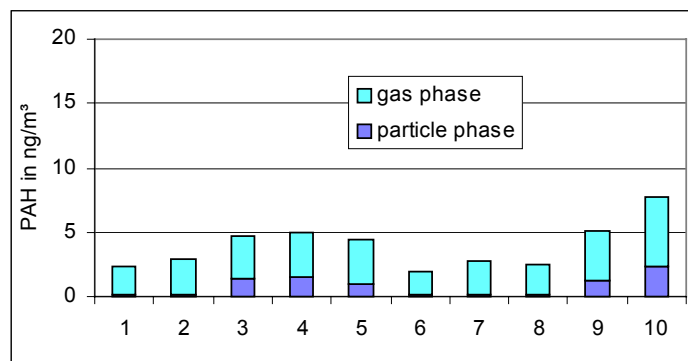


Figure F5. D1 Westerland

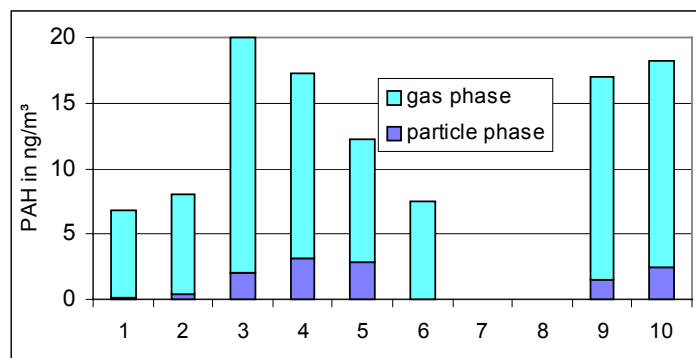


Figure F6. NL4 De Zilk

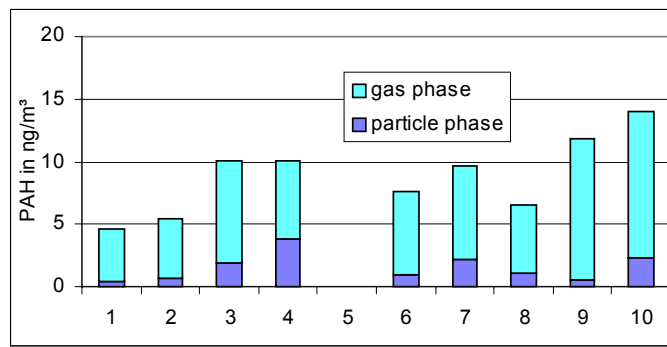


Figure F7. B4d Knokke

Appendix G

Monthly PAH depositions at different sites from October - December 1998
“reference method”

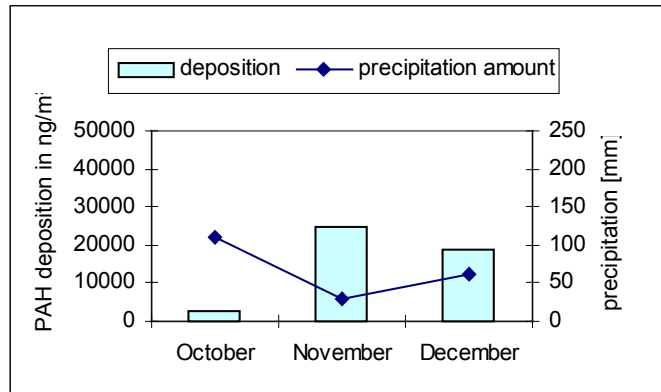


Figure G1 S1 Rörvik

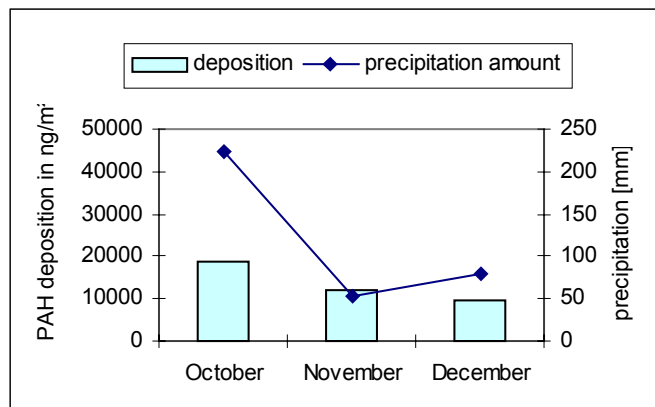


Figure G2. DK1 Ulborg

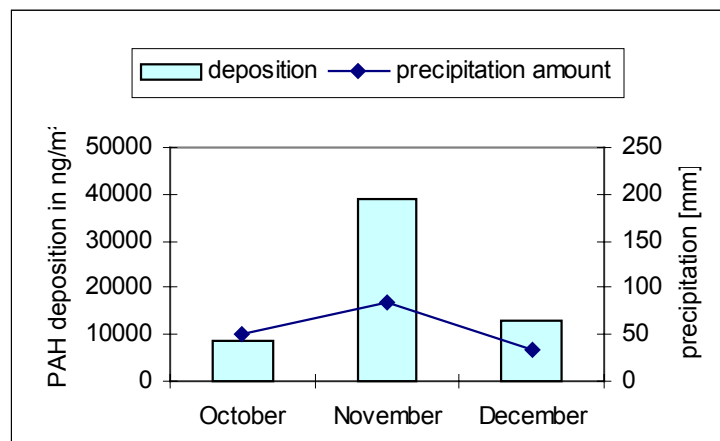


Figure G3. Zingst

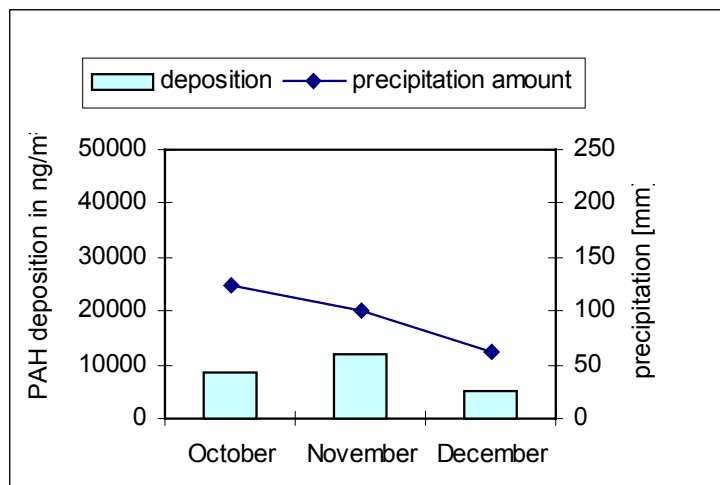


Figure G4. D1 Westerland

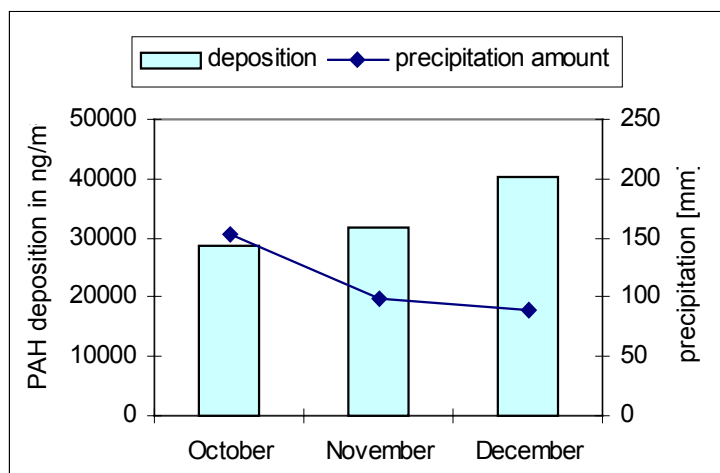


Figure G5. Gent (test field of the University)

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