Final Report WG 14 Part E Field Tests Berlin

Umweltbundesamt
Federal Environmental Agency

CEN / TC 264 / WG 14 :

Reference Method for the Measurement of Pb/Cd/As/Ni in Ambient Air,

Minimum Validation Programme –

Field Test Berlin, 2001

Report for CEN / TC 264 / WG 14,
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1 Introduction

This report is based on the work performed in the framework of CEN/TC264/WG14. Results of the Minimum Validation Programme (field test, Berlin, September – October 2001) are summarized.

The purpose of the field test is to perform the field validation of the proposed draft standard “Reference Method for the Measurement of Pb/Cd/As/Ni in Ambient Air”. The field validation covers all steps including sampling, sample preparation and analysis of samples.

Field validation tests were carried out at four measurement sites (2 industrial sites and 2 urban sites). Field tests in Madrid (urban site) and Avonmouth (industrial site) were performed in spring and summer 2001. After the field test in Berlin (urban site), a field campaign in Hoboken (industrial site) followed in winter 2001.

Four labs participate in the field tests. All sampling is carried out with the same type of samplers : CEN Low Volume PM10 Sampler (Kleinfiltergerät). 10 identical samplers (including 2 reserve instruments) are used in parallel, 20 daily samples are collected at each site. Each lab analyses 2 sets of 20 daily samples from each site. A more detailed description of the field test is provided in the Guidance Document (CEN/TC264/WG14 Document N140Rev5).

The following laboratories participate in the programme:

- Lab A : Centro Nacional de Sanidad Ambiental,
  Instituto de Salud Carlos III (ISCIII), Spain
- Lab B : UK Consortium (Casella Stanger / CRE Group Ltd. /
  Harwell Scientifics Ltd.), UK
- Lab C : Vlaamse Milieumaatschappij (VMM), Belgium
- Lab D : Umweltbundesamt (UBA-DE), Germany /
  Umweltbundesamt (UBA-A), Austria

All four laboratories perform analysis of samples using GF-AAS and two laboratories perform additional voluntary analysis of samples using ICP-MS. As a voluntary contribution, Lab D (UBA-DE) provides additional samplers (3 sequential low volume PM10 samplers and 2 sequential high volume PM10 samplers) for the Berlin campaign. Samples collected with additional samplers are analysed by Lab D (UBA-DE) with ICP/MS only.

The following Table-1 provides a summary of the individual contributions of the participating laboratories (voluntary parts are shaded grey) :

Table-1 : Field test Berlin - Contributions of the participating laboratories

Lab	Filter material	Filter Type	Sampler	Analytical technique
Lab A	quartz	Munktell MK360 (50 mm)	Kleinfiltergerät	GF-AAS
Lab B	membrane	Sartorius Cellulose Acetate 3 µm	Kleinfiltergerät	GF-AAS ICP/MS
Lab C	membrane	Sartorius Cellulose Acetate 3 µm	Kleinfiltergerät	GF-AAS
Lab D	quartz	Munktell MK360 (50 mm)	Kleinfiltergerät	UBA-A : GF-AAS UBA-DE : ICP/MS
Lab D	membrane	Sartorius Cellulose Acetate 3 µm	sequential Low Volume Sampler	ICP/MS
Lab D	quartz	Munktell MK360 (150 mm)	sequential High Volume Sampler	ICP/MS

This report consists of the following parts :

- State and function tests of the CEN samplers in Berlin
- Sampling site characteristics and sampling regime at the site Berlin-Westend
- Technical details of sample preparation and analysis in the participating labs
- Results of the mandatory measurements

Results of the voluntary measurements as well as individual data summaries for the participating labs are included as Annexes 1 – 4.

2 State and Function Tests

The 10 CEN LVS-PM10 samplers arrived in Berlin on 20/08/01. The flow rates of the samplers were checked in the laboratory immediately after delivery. The results are summarized in the following Table-2.

Flow rates given by the sampler readings were checked using different instruments :

- MFM : Mass Flow Meter, provided by Lab A, delivered with the CEN samplers
- Rotameter ERLAP : Rotameter, provided by ERLAP, delivered with CEN samplers
- Rotameter UBA : Rotameter, provided by Lab D (UBA-DE)

Table-2 : Flow rate check after delivery

CEN LVS-PM10 Sampler No.	Date	Amb. Air Temp. °C	Amb. Air Press. mbar	MFM m³/h	Rota ERLAP m³/h	Rota UBA m³/h	Sampler Reading m³/h
				(Ambient Air Conditions)			
1	21/08/01	25	1013	2.24	1.99	2.14	2.29
2	21/08/01	25	1013	2.19	2.01	2.19	2.29
3	21/08/01	25	1013	2.20	1.97	2.12	2.29
4	21/08/01	25	1013	2.21	2.01	2.17	2.29
5	21/08/01	25	1013	2.17	1.97	2.14	2.29
6	21/08/01	25	1013	2.18	1.99	2.17	2.29
7	21/08/01	25	1013	2.32	2.11	2.27	2.29
8	20/08/01	23	1006			1.92	2.30
9	21/08/01	25	1013				1.16
10	21/08/01	25	1013	2.18	2.01	2.19	2.29

Subsequently, all samplers were checked through by the instrument producer, samplers 8 and 9 as well as two other samplers were repaired. After repair flow rates of all samplers were recalibrated by the instrument producer. Since there were

differences in the flow rate readings depending on the instrument used, sampler readings were adjusted to the flow rates given by the instrument provided by ERLAP (Rotameter ERLAP) as originally recommended in the Guidance Document (CEN / TC 264 / WG 14 Document N140). The results of the final flow rate check are summarized in the following Table-3.

Table-3 : Final flow rate check before field campaign

CEN LVS-PM10	Date	Amb. Air Temp.	Amb. Air Press.	Rota ERLAP	Rota UBA	Sampler Reading
Sampler		°C	mbar	m³/h	m³/h	m³/h
No.				(Ambient Air Conditions)		
1	30/08/01	24,4	1007	2.30	2,44	2.29
2	30/8	24,3	1007	2,32	2,48	2.29
3	30/8	24,6	1007	2,32	2,46	2.29
4	30/8	24,4	1007	2,33	2.50	2.29
5	30/8	24,5	1006	2,33	2.50	2.29
6	30/8	24,4	1007	2.30	2,46	2.29
7	30/8	24,4	1007	2,32	2,48	2.29
8	03/9	23,8	1005	2,24	2.40	2.29
9	30/8	24,5	1006	2,32	2,46	2.29
10	30/8	24,3	1007	2,29	2,46	2.29

For the calibration of the samplers under ambient air conditions, the MFM could not be used, as this instrument reacts on the slightest air breath. By that, the reading was permanently changing. Therefore, the Rotameter provided by ERLAP was also used for calibrating the samplers in the field. This Rotameter was also delivered together with the samplers to the next measuring site (Hoboken).

3 Sampling site characteristics and sampling regimes

3.1 Site characteristics

The site Berlin-Westend (geographical co-ordinates : 52.5°N, 13.3°E) is an urban background site located in Berlin next to a crowded city highway. The traffic volume at this part of the highway is about 150,000 cars per 24 hours with a proportion of trucks of 10 to 15%. The samplers were installed on a container station. The site is surrounded by the city highway in the east , residential houses in the west and northwest and a cemetery in the south. Besides the traffic emissions, the site is affected by all sorts of emissions from the city such as from house heatings, small trades etc. and resuspended geonic material.

Figure-1 : The Berlin-Westend monitoring site (view towards north-east)

Figure-2a : The Berlin-Westend monitoring site (view towards south)

Figure-2b : The Berlin-Westend monitoring site (view towards north)

3.2 Sampling at the site Berlin-Westend

Sampling at the site Berlin-Westend was carried out using 10 CEN Low Volume PM10 Samplers (Kleinfiltergerät), 3 sequential low volume samplers and 2 sequential high volume samplers during the period of 12/09/01 to 15/10/01. Daily filter exchanges were performed by three technicians from Umweltbundesamt in Berlin : Ms Bettina Süssenbach, Mr Jürgen Kura and Mr Axel Pietsch (referred to as Sues, Ku and Pie in the report forms included in Annex-1).

The samplers were calibrated and cleaned during the field campaign on each Friday. Among the 10 CEN Low Volume PM10 Samplers only one instrument caused problems during the field measurements in Berlin. This instrument was CEN PM10 LVS unit No. 7, which showed a too high flow rate at the first check on 14/09/01. After re-calibrating the sampler no further problems occurred. The flow rates of the 10 LVS units measured by the Rotameter (ERLAP) were in the range of 2.27 and 2.35 m^3/h, though the samplers showed readings of 2.29 or 2.30 m^3/h.

Detailed sampling data is shown in report forms included in Annex-1.

4 Sample Preparation and Analytical Methods

4.1 Sample Preparation

Digestion procedures to be employed for preparation of samples are described in detail in the analytical guidance document (CEN/TC264/WG14 Document N245). However, due to the individual laboratory equipment, changes in the procedures described there may be necessary, but have to be justified and documented. In principle, sample preparation includes microwave digestion in closed vessels using a mixture of nitric acid and hydrogen peroxide at a temperature of 220 °C.

Table-4 : Equipment used by the participating laboratories

- Lab A : Anton Paar / Perkin Elmer Multi-wave system
- Lab B : CEM MARS 5 Microwave system
- Lab C : CEM MARS 5 Microwave system
- Lab D (UBA-A) : Anton Paar / Perkin Elmer Multi-wave system
- Lab D (UBA-DE) : CEM MARS 5 Microwave system (used for the digestion of samples collected with the additional sequential samplers)

Digestion procedures used for sample preparation by the participating laboratories were in accordance with those specified in the analytical guidance document.

4.2 Analysis

Analytical methods to be employed for the analysis of samples are described in detail in CEN/TC264/WG14 Document N245. However, participating laboratories are requested to use the best GF-AAS or ICP/MS method available, although any necessary technical changes to the analytical conditions have to be justified and documented.

All four participating laboratories analysed samples collected with the CEN PM10 samplers (Kleinfiltergerät) using GF-AAS. In addition, two laboratories (Lab B and Lab D) used ICP/MS for voluntary analysis of these samples. Analyses of the samples collected with the sequential samplers were performed by lab D using ICP/MS (voluntary contribution).

For QA/QC purposes, analysis of samples includes field blanks, reagent blanks and laboratory blanks as well as the analysis of certified reference materials (CRMs). CRMs used in the current work are NIST 1648 (Urban Particulate Matter) and NIES No.8 (Vehicle Exhaust Particulate Matter).

4.2.1 GF-AAS

Lab A :

The measurements were carried out using an atomic absorption spectrometer Perkin Elmer model Analyst 100 with deuterium lamp background correction, equipped with graphite furnace Perkin Elmer HGA-800 and autosampler AS-72. The analysis of

Nickel was performed in accordance with Document CEN/TC264/WG14/N245 while the analytical conditions for Pb, Cd and As were identical of those described in document CEN/TC264/WG14/N206.

Lab B :

Measurements were made using atomic absorption spectrometer (Varian Spectra AA-400 Zeeman). The analysis was performed in accordance with Document CEN/TC264/WG14/N245, with the exception that calibration standards deviated (standard addition was used for analysis of CRM NIES No. 8).

Lab C :

The analysis was done with GF-AAS with Zeemann correction – Perkin Elmer SIMAA apparatus. Cd and Pb were analysed together. As and Ni were analysed mono-elementally. The detailed analytical conditions are described in document CEN/TC264/WG14/N262.

Lab D :

All measurements according to the requirements of MVP WG 14 were performed using a simultaneous graphite furnace atomic absorption spectrometer SIMAA 6000, Perkin Elmer, with transverse heated graphite atomizer (THGA). The analysis was performed in accordance with Document CEN/TC264/WG14 N245.

4.2.2 ICP-MS

Lab B :

The analysis was performed on a TJA Solutions PQ-ExCell ICP/MS instrument. Calibration standards were prepared from a single-element 1000µg/ml certified standard solution at 0.1, 0.5, 1.0, 10, 25, 100 and 250 µg/l (in the case of Pb only). A 10 µg/ml multi-element stock solution was prepared by dilution of appropriate aliquots of single-element certified standard solutions. A secondary multi-element stock solution was prepared at 100 µg/l by dilution of 1 ml of the 1000 µg/ml standard to 100 ml using 16% nitric acid. An internal standard stock solution was used prepared at 10 µg/ml by dilution of appropriate aliquots of the single element certified standard solutions using 16% nitric acid. This solution contained germanium, yttrium, indium and bismuth. The calibration standards were prepared by diluting appropriate

volumes of the secondary multi-element stock solution and 400 µl of the internal standard stock solution to 100 ml using 16% nitric acid.

Lab D :

Measurements were made using a Varian Ultramass ICP/MS instrument. The samples collected with the CEN samplers (Kleinfiltergerät), digested and previously analysed with GF-AAS by Lab D (UBA-A), were reanalysed using the following analytical conditions :

Before analysis of samples using ICP-MS, samples were diluted with deionised water and internal standards were added. Blank values presented in the report forms as **[µg/L]** are related to diluted solutions. Thus only values calculated as **[ng/m3]** are directly comparable to the results of the other laboratories. The following dilution factors were applied prior to analysis:

- Samples and blanks: dilution factor 2
- NIST 1648: dilution factors 2 (for Cd, As, Ni) and 20 (for Pb)
- NIES No.8: dilution factors 2 (for Cd, As, Ni) and 4 (for Pb)

The same calibration procedure was used for samples, blanks and CRM solutions. The following calibration standards were employed:

- Standard blank solution
- Operating standard – 1 solution (element conc.: 20 µg/l As, Pb, Cd, Ni)
- Operating standard – 2 solution (element conc.: 100 µg/ As, Pb, Cd, Ni)
- Internal Standards : Sc, In

Comparable analytical conditions were applied for the analysis of the samples collected with additional samplers.

5 Results (mandatory measurements)

5.1 Blank Values and CRM Recovery Rates

Tables 4 - 6 below show concentrations of Pb, Cd, As and Ni in blanks as determined by the participating laboratories, whereas Tables 7 – 8 show recovery rates for certified reference materials (CRMs). Results of voluntary measurements are included in the tables, but are shaded grey. Lab A did not provide data on filter blanks. The complete data set is included in Annexes 1 and 4.

The following abbreviations for identification of individual data sets are used :

KFG : CEN Low Volume PM10 Sampler (Kleinfiltergerät)

sLVS : sequential Low Volume Sampler

sHVS : sequential High Volume Sampler

Table-4 : Reagent blank concentrations [ng/m3] (standard deviation in brackets)

Laboratory - Sampler	Filter material	Analytical technique	Determinant							
			Pb		Cd		As		Ni	
			mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)
Lab A - KFG	quartz	GF-AAS	0,490	0,054	0,023	0,010	0,003	0,120	0,763	0,198
Lab B - KFG	membrane	GF-AAS	-0,004	0,004	-0,003	0,000	-0,002	0,002	0,007	0,004
Lab C - KFG	membrane	GF-AAS	0,202	0,071	0,027	0,010	-0,239	0,120	1,540	0,437
Lab D - KFG	quartz	GF-AAS	0,586	0,227	0,019	0,012	-0,205	0,073	0,346	0,161
Lab B - KFG	membrane	ICP/MS	0,002	0,001	0,001	0,000	0,000	0,000	0,007	0,004
Lab D - KFG	quartz	ICP/MS	0,641	0,200	0,035	0,014	0,084	0,080	0,068	0,134
Lab D - sLVS	membrane	ICP/MS	0,051	0,040	0,013	0,004	-0,007	0,075	0,051	0,040
Lab D - sHVS	quartz	ICP/MS	0,054	0,038	0,013	0,005	0,018	0,057	0,071	0,040

Table-5 : Filter blank concentrations [ng/m3] (standard deviation in brackets)

Laboratory - Sampler	Filter material	Analytical technique	Determinant							
			Pb		Cd		As		Ni	
			mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)
Lab A - KFG	quartz	GF-AAS								
Lab B - KFG	membrane	GF-AAS	-0,008	0,001	-0,002	0,001	-0,003	0,002	0,003	0,001
Lab C - KFG	membrane	GF-AAS	0,364	0,075	0,014	0,006	-0,134	0,121	1,159	0,405
Lab D - KFG	quartz	GF-AAS	0,783	0,337	0,003	0,003	-0,068	0,046	0,852	0,326
Lab B - KFG	membrane	ICP/MS	0,003	0,000	0,001	0,000	0,003	0,000	0,007	0,001
Lab D - KFG	quartz	ICP/MS	0,948	0,340	0,025	0,002	0,080	0,112	0,729	0,357
Lab D - sLVS	membrane	ICP/MS	0,082	0,047	0,007	0,002	0,096	0,062	-0,073	0,064
Lab D - sHVS	quartz	ICP/MS	0,141	0,039	0,011	0,003	0,051	0,055	0,344	0,076

Table-6 : Field filter blank concentrations [ng/m3] (standard deviation in brackets)

Laboratory - Sampler	Filter material	Analytical technique	Determinant							
			Pb		Cd		As		Ni	
			mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)	mean value (ng/m3)	standard deviation (ng/m3)
Lab A - KFG	quartz	GF-AAS	1,443	0,185	0,034	0,018	-0,152	0,107	1,313	0,260
Lab B - KFG	membrane	GF-AAS	0,015	0,022	-0,003	0,000	0,000	0,005	0,007	0,002
Lab C - KFG	membrane	GF-AAS	0,540	0,093	0,017	0,008	-0,191	0,089	1,483	1,511
Lab D - KFG	quartz	GF-AAS	1,230	0,967	-0,001	0,009	-0,168	0,118	2,792	1,744
Lab B - KFG	membrane	ICP/MS	0,003	0,001	0,001	0,000	0,002	0,001	0,008	0,001
Lab D - KFG	quartz	ICP/MS	1,577	0,917	0,023	0,010	0,045	0,106	2,369	1,812
Lab D - sLVS	membrane	ICP/MS	0,109	0,104	0,051	0,067	0,048	0,032	0,425	0,163
Lab D - sHVS	quartz	ICP/MS	0,149	0,083	0,028	0,008	0,084	0,074	0,918	0,194

Table-7 : CRM recovery rates (%) for NIST 1648

Laboratory - Sampler	Analytical technique	Determinant							
		Pb 6550 ± 80 mg/kg		Cd 75 ± 7 mg/kg		As 115 ± 10 mg/kg		Ni 82 ± 3 mg/kg	
		%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
Lab A - KFG	GF-AAS	98,2	6430	95,9	72	102,2	118	95,7	79
Lab B - KFG	GF-AAS	98,7	6463	93,6	70	107,6	124	92,5	76
Lab C - KFG	GF-AAS	98,6	6461	95,6	72	104,3	120	97,8	80
Lab D - KFG	GF-AAS	96,8	6339	93,6	70	109,6	126	96,3	79
Lab B - KFG	ICP/MS	97,9	6411	106,2	80	110,7	127	94,1	77
Lab D - KFG	ICP/MS	95,1	6230	96,0	72	104,4	120	96,9	79
Lab D - sLVS	ICP/MS	99,0	6483	100,4	75	111,2	128	90,4	74
Lab D - sHVS	ICP/MS	95,4	6248	96,1	72	108,0	124	88,9	73

Table-8 : CRM recovery rates (%) for NIST No. 8

Laboratory - Sampler	Analytical technique	Determinant							
		Pb 219 ± 9 mg/kg		Cd 1.1 ± 0.1 mg/kg		As 2.6 ± 0.2 mg/kg		Ni 18.5 ± 1.5 mg/kg	
		%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg
Lab A - KFG	GF-AAS	101,6	223	94,1	1,0	107,3	2,8	93,6	17,3
Lab B - KFG	GF-AAS	101,3	222	87,7	1,0	83,1	2,2	93,6	17,3
Lab C - KFG	GF-AAS	104,1	228	91,7	1,0	101,0	2,6	100,1	18,5
Lab D - KFG	GF-AAS	100,4	220	85,5	0,9	129,6	3,4	96,4	17,8
Lab B - KFG	ICP/MS	96,0	210	96,1	1,1	112,6	2,9	90,3	16,7
Lab D - KFG	ICP/MS	103,1	226	97,7	1,1	128,8	3,3	100,3	18,6
Lab D - sLVS	ICP/MS	99,7	218	99,1	1,1	140,9	3,7	89,6	16,6
Lab D - sHVS	ICP/MS	97,0	212	93,0	1,0	133,1	3,5	88,4	16,4

Recovery rates for Pb, Cd, As and Ni in the certified reference material NIST 1648 were generally within the ranges set by CEN / TC 264 / WG 14, i.e. within 90 – 110 % for Pb and Cd and within 85 – 115 % for As and Ni. These targets would be met also for the elements Pb and Ni in CRM NIES No. 8.

5.2 Field samples

Figures 3 - 6 below show daily mean concentrations of Pb, Cd, As and Ni in air as determined by the participating labs in the samples collected during the field test in Berlin. Since concentrations of Pb and As were rather high on 30/09/01 and 15/10/01 (compared to the other days) two different scales were chosen for presentation of these data. The complete data set is included in Annex-1.

The following abbreviations are used :

Table-9 : Abbreviations

Code	Lab	Sampler	Analytical Technique	Code	Lab	Sampler	Analytical Technique
A 1	A	KFG-1	GF-AAS	A 2	A	KFG-2	GF-AAS
B 3	B	KFG-3	GF-AAS	B 4	B	KFG-4	GF-AAS
B 3, ms	B	KFG-3	ICP/MS	B 4, ms	B	KFG-4	ICP/MS
C 5	C	KFG-5	GF-AAS	C 6	C	KFG-5	GF-AAS
D 7	D	KFG-7	GF-AAS	D 8	D	KFG-8	GF-AAS
D 7, ms	D	KFG-7	ICP/MS	D 8, ms	D	KFG-8	ICP/MS

Figure 3a : Field Test Berlin - Daily Mean Lead Concentrations (CEN PM10 LVS)

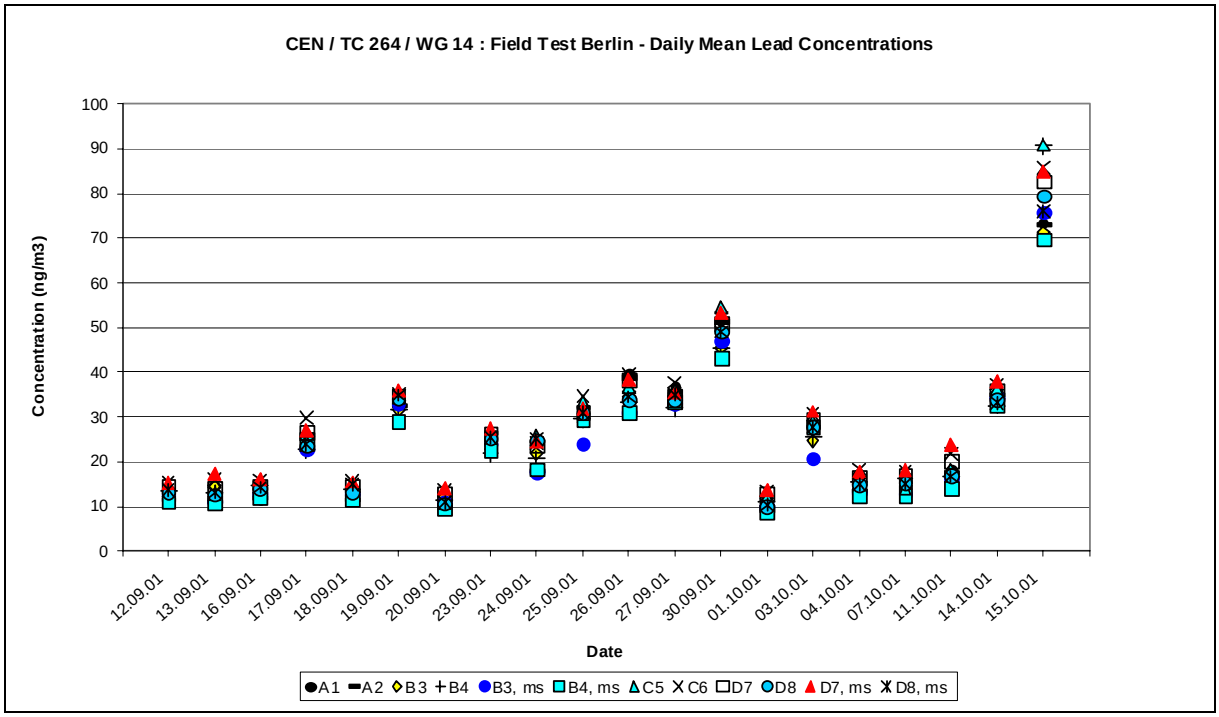


Figure 3a : Field Test Berlin - Daily Mean Lead Concentrations (CEN PM10 LVS)

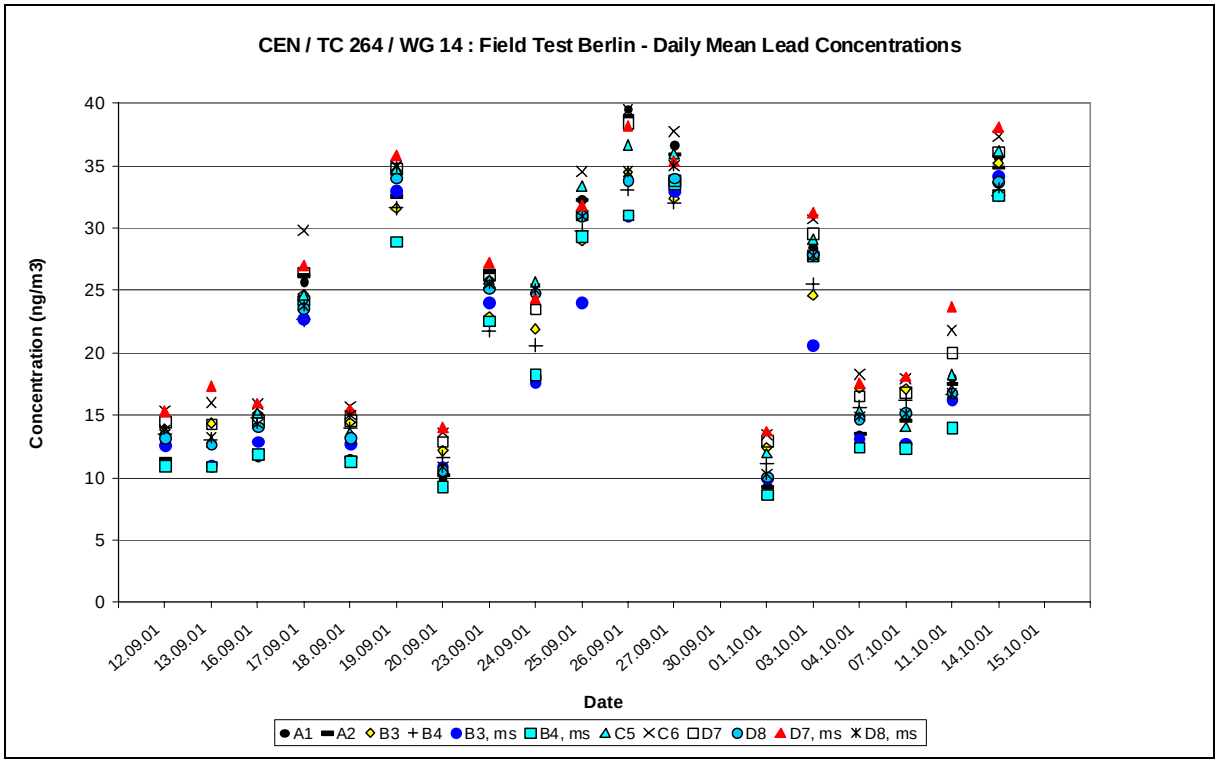


Figure 4 : Field Test Berlin - Daily Mean Cadmium Concentrations (CEN PM10 LVS)

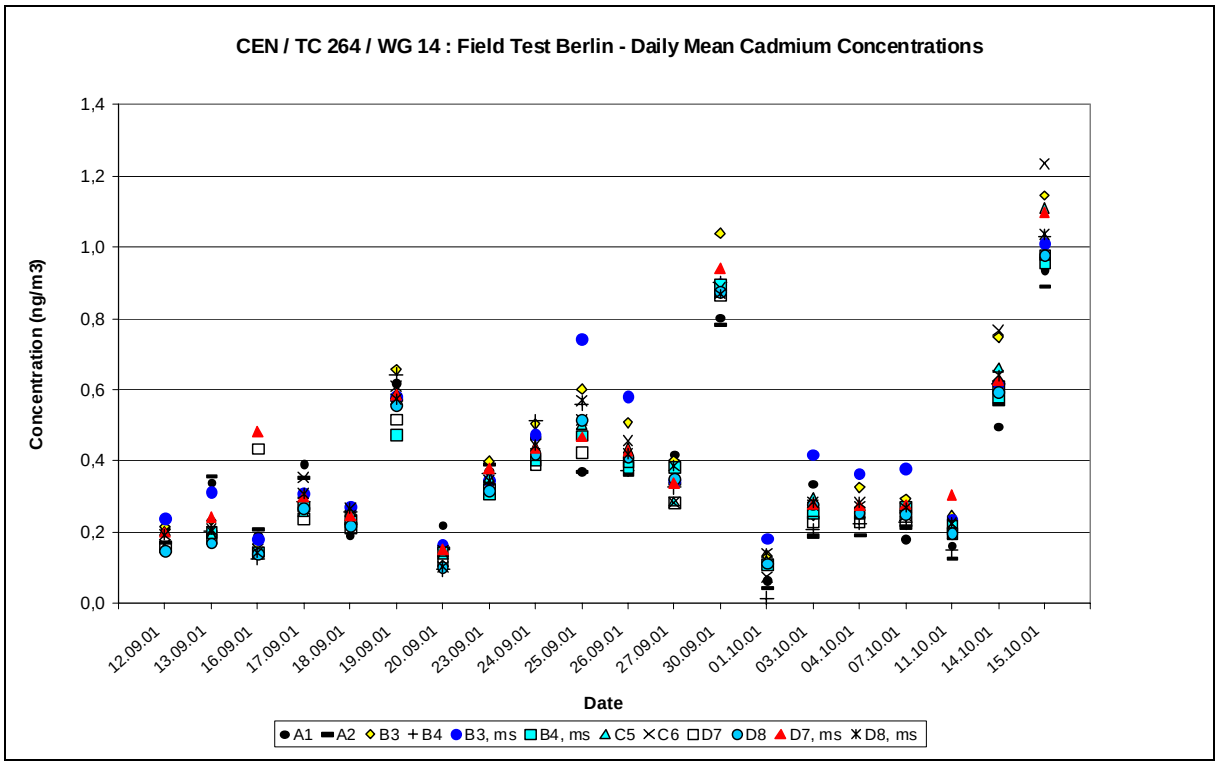


Figure 5a : Field Test Berlin - Daily Mean Arsenic Concentrations (CEN PM10 LVS)

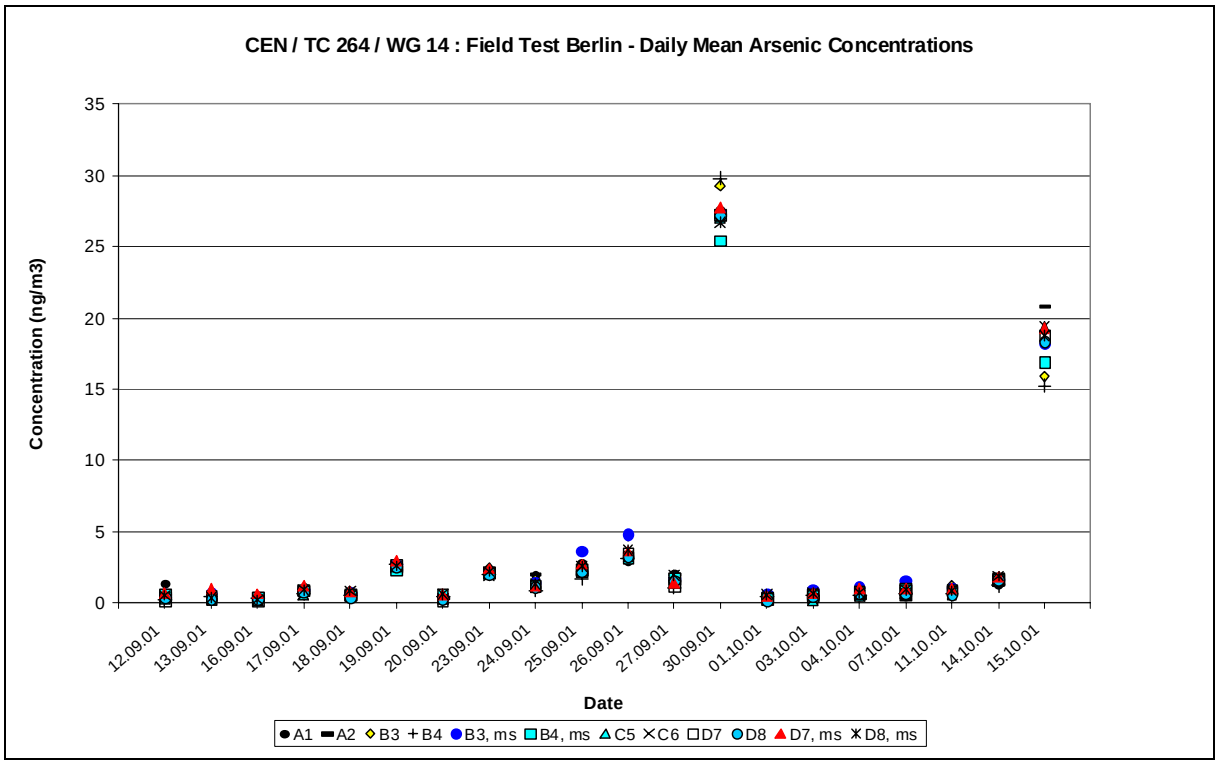


Figure 5b : Field Test Berlin - Daily Mean Arsenic Concentrations (CEN PM10 LVS)

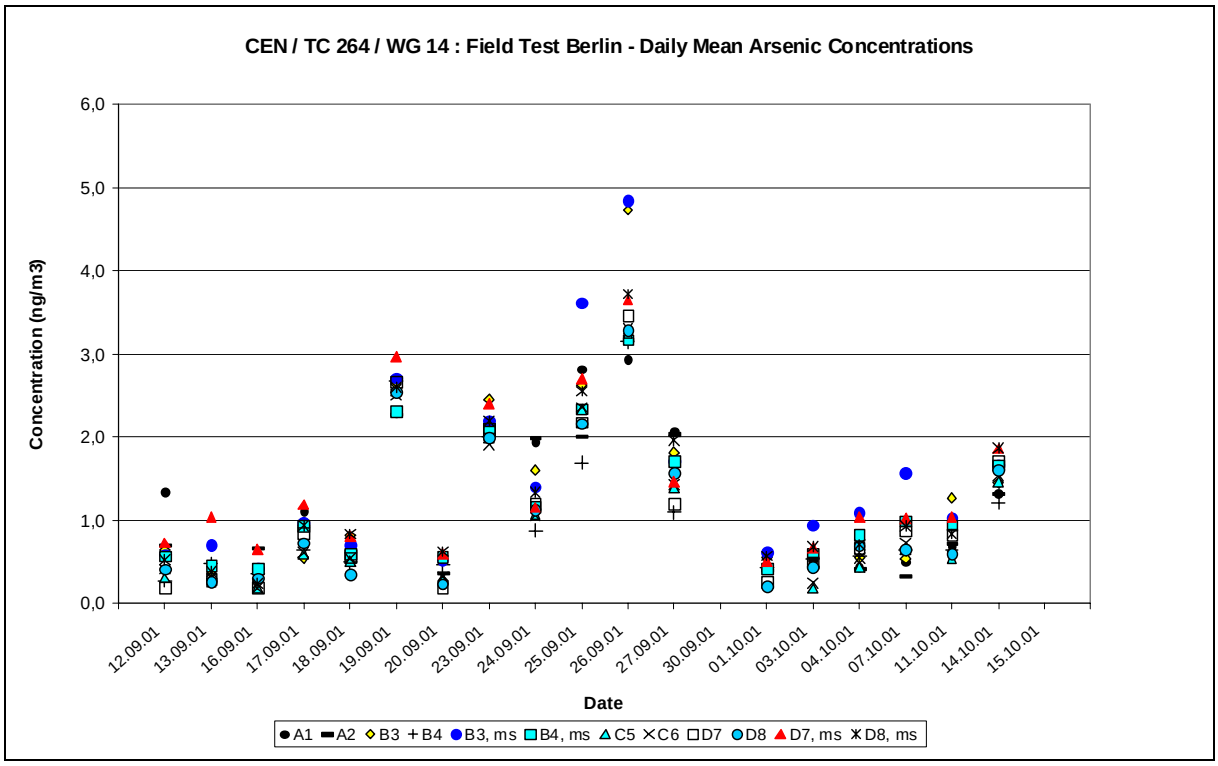
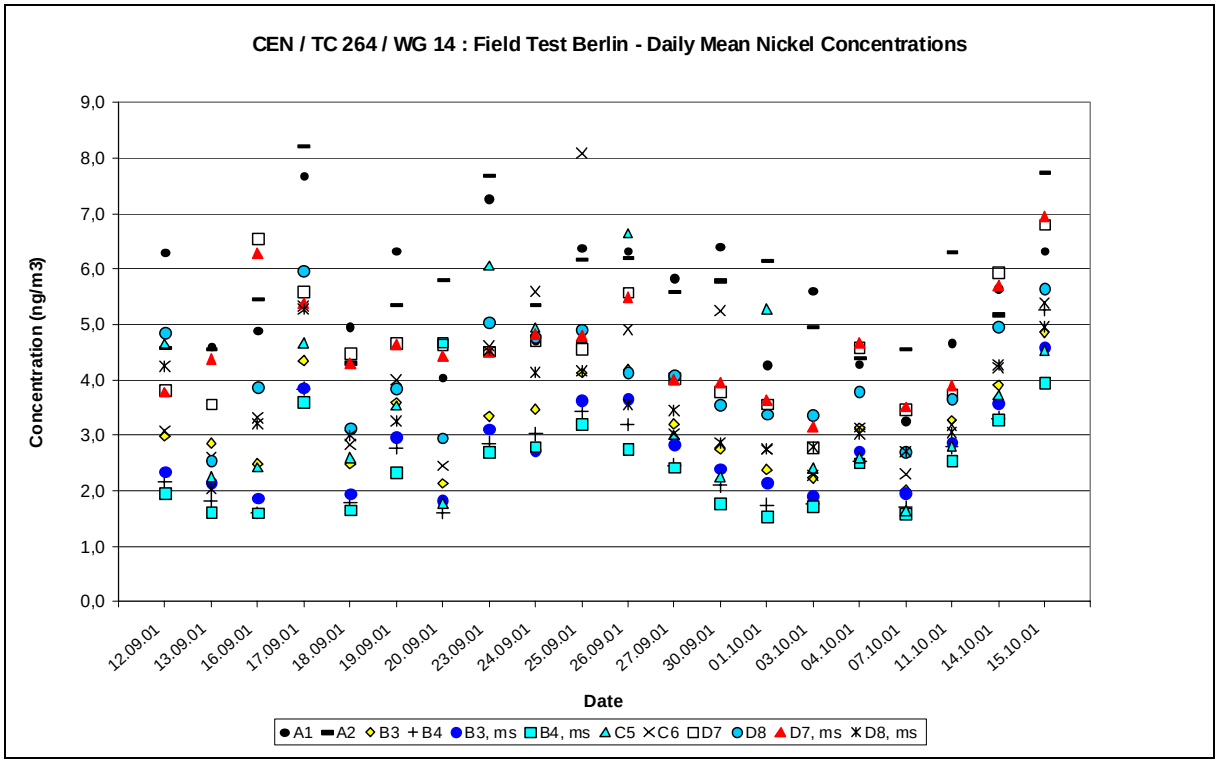


Figure 6 : Field Test Berlin - Daily Mean Nickel Concentrations (CEN PM10 LVS)



All data reported for lead were used for the generation of Figure-3 and Figure-7. However some data were excluded for the generation of Figures 4 – 6 and 8 –10 :

Cd : Lab B, Sampler 4 : 1 value excluded (assumed outlier)
Lab D, Sampler 7 : 1 value excluded (assumed outlier)
As : Lab C, Sampler 5 : 1 value excluded (negative concentration value)
Lab C, Sampler 6 : 1 value excluded (negative concentration value)
Ni : Lab D, Sampler 8 : 1 value excluded (ICP/MS only; contamination).

Besides these exceptions, daily mean concentrations for Pb, Cd and As show good agreement between all CEN PM10 Samplers. However for Ni, daily mean concentrations show much more variability between the samplers.

Figures 7 - 10 below show period mean concentrations of Pb, Cd, As and Ni in air as determined by the participating labs in the samples collected during the field test in Berlin. The abbreviations explained in Table-9 are used.

Figure 7 : Field Test Berlin - Period Mean Lead Concentrations (CEN PM10 LVS)

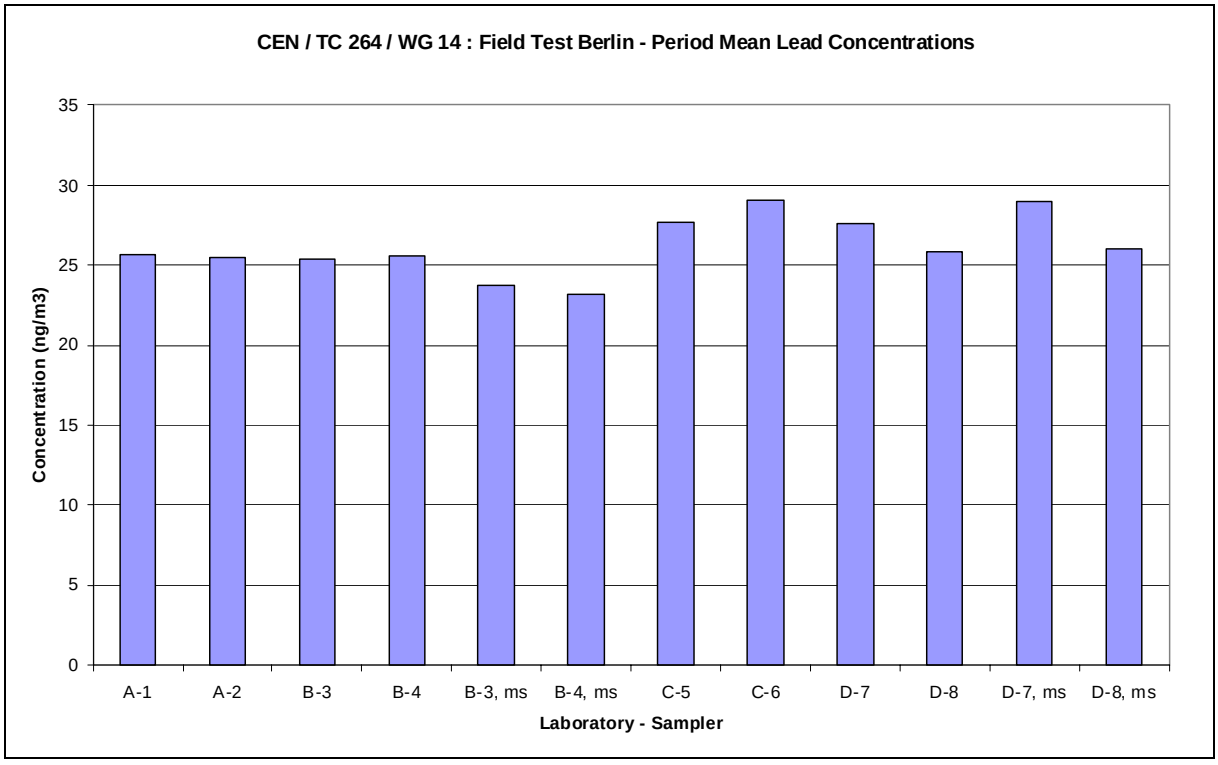


Figure 8 : Field Test Berlin - Period Mean Cadmium Concentrations (CEN PM10 LVS)

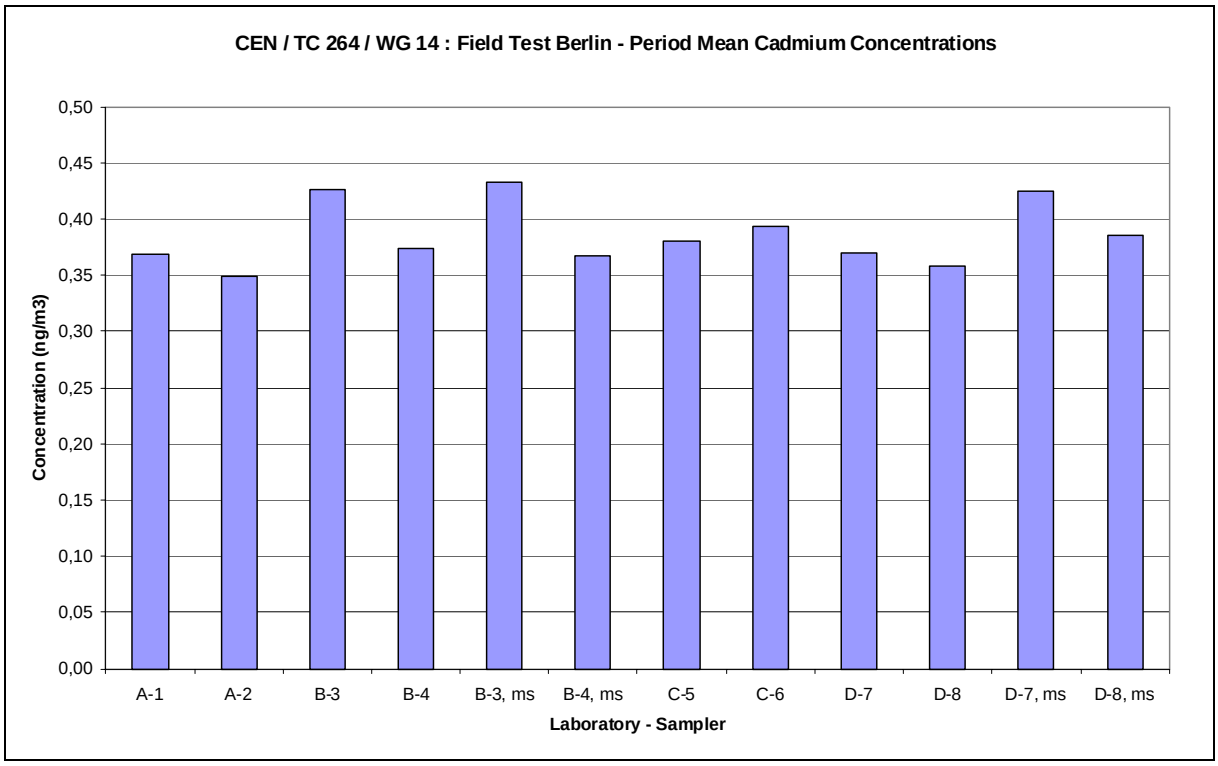


Figure 9 : Field Test Berlin - Period Mean Arsenic Concentrations (CEN PM10 LVS)

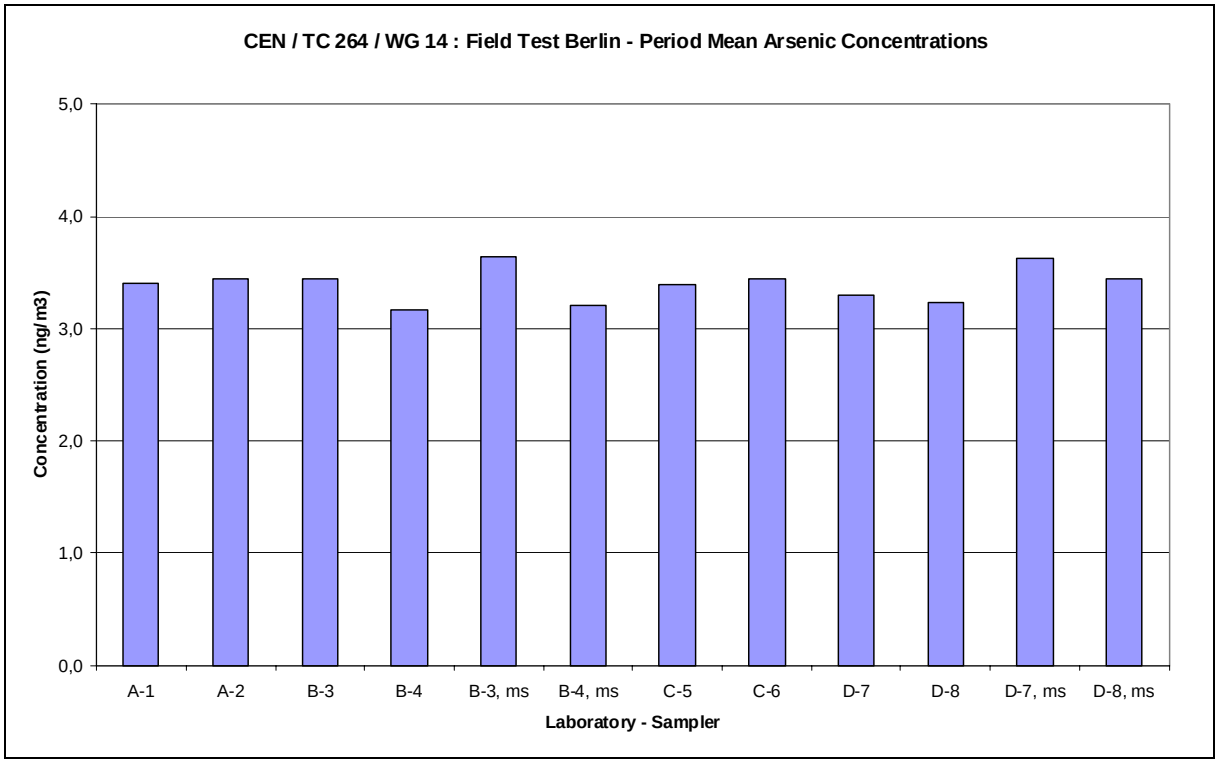
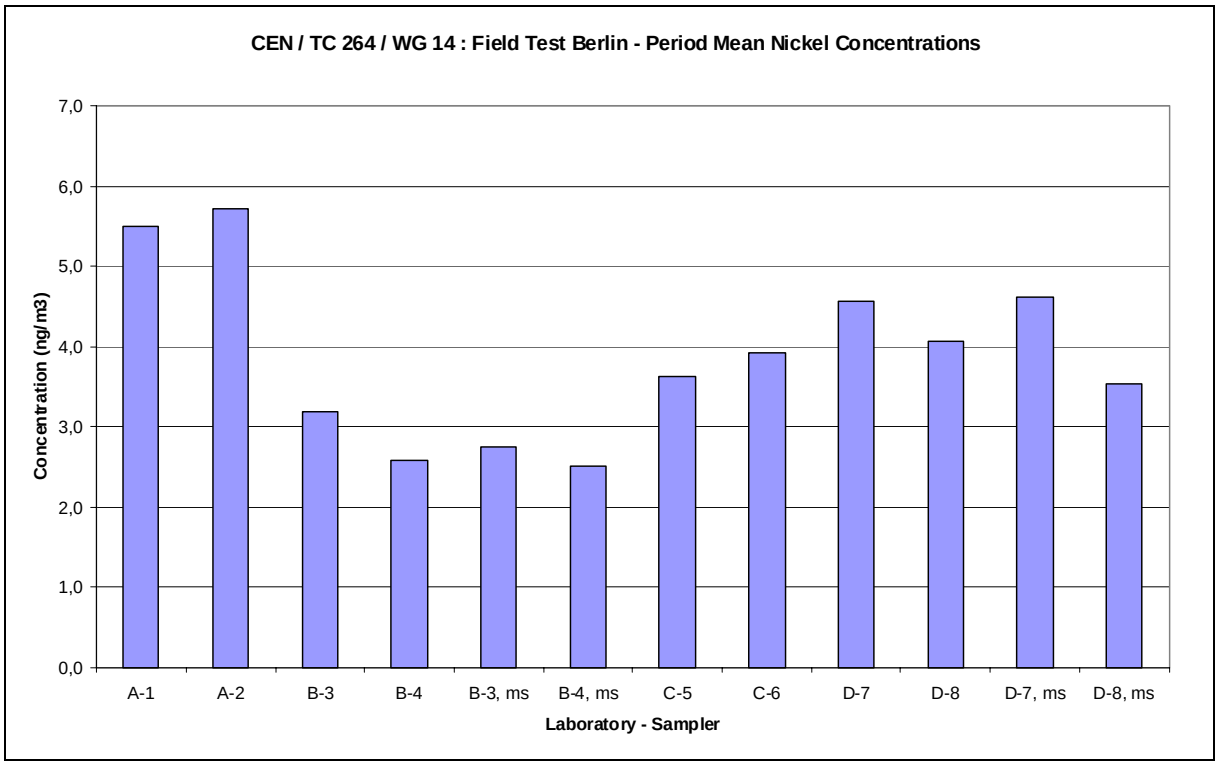


Figure 10 : Field Test Berlin - Period Mean Nickel Concentrations (CEN PM10 LVS)



Results of the samples collected with additional samplers (sequential low volume samplers and sequential high volume samplers) provided by Lab D (UBA-DE) as a voluntary contribution are summarized in Annexes 3 - 4.

Annexes

Annex-1 : Data summaries provided by the participating laboratories

Sampling details (meteorological conditions, flow rates etc.) as well as individual data summaries for each participating laboratory are provided as MS Excel files using the report forms supplied by CEN/TC264/WG14.

Annex-2 : Analytical reports provided by the participating laboratories

Annex-3 : Results of the voluntary measurements (additional samplers)

Annex-4 : Data summaries for additional samplers (voluntary measurements)

Individual data summaries for additional samplers (sequential low volume samplers and sequential high volume samplers) are provided as MS Excel files using report forms comparable to those supplied by CEN/TC264/WG14.

Umweltbundesamt
Federal Environmental Agency

CEN / TC 264 / WG 14 :
Reference Method for the Measurement of Pb/Cd/As/Ni in Ambient Air, Minimum Validation Programme – Field Test Berlin, 2001

Annex-3 :
Results of the Voluntary Measurements (Additional Samplers)

Report for CEN / TC 264 / WG 14,
Prepared by

Elke Bieber
Umweltbundesamt
Paul-Ehrlich-Straße 29
D-63263 Langen
Germany

Langen, January 2002

Results of the Voluntary Measurements

Lab D (UBA-DE) provided additional samplers for the Berlin campaign. These samplers belong to the air pollution monitoring network of the German Federal Environmental Agency and are used there usually to monitor long range transboundary air pollution. The following instruments were provided :
3 sequential Low Volume PM10 Sampler (sLVS-1 - sLVS-3) : Leckel SEQ 47/50 (sampler sLVS-2 was treated as reserve instrument)
2 sequential High Volume PM10 Sampler (sHVS-1 and sHVS-2) : Digitel DHA 80

Technical details of sampling, sample preparation, analysis as well as blank values and CRM recovery rates are included in the main report. This annex gives results for field samples, in comparison to the samples collected with the CEN PM10 Low Volume Sampler (Kleinfiltergerät).

Field samples : Pb/Cd/As/Ni Concentrations in Air

Figures A1 - A4 below show daily mean concentrations of Pb, Cd, As and Ni in air as determined by the participating labs in the samples collected during the field test in Berlin. Since concentrations of Pb and As were rather high on 30/09/01 and 15/10/01 (compared to the other days) two different scales were chosen for presentation of data. The complete data set is included in Annex-1 and Annex-4.

A few samples of the additional samplers were missing :
sampler sLVS-3 : sample of 11/10/01
sampler sHVS-1 : samples of 13/09/01 and 03/10/01
sampler sHVS-2 : sample of 03/10/01

Figure A1a : Field Test Berlin - Daily Mean Lead Concentrations (all samplers)

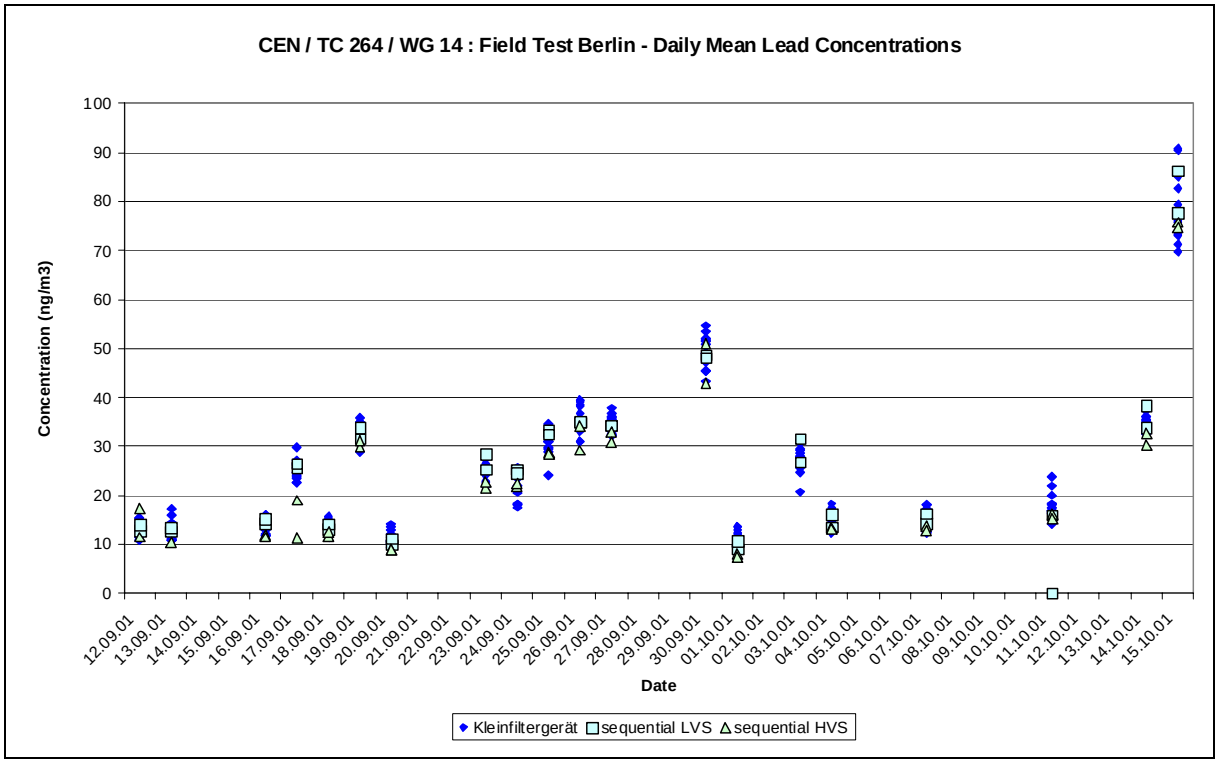


Figure A1b : Field Test Berlin - Daily Mean Lead Concentrations (all samplers)

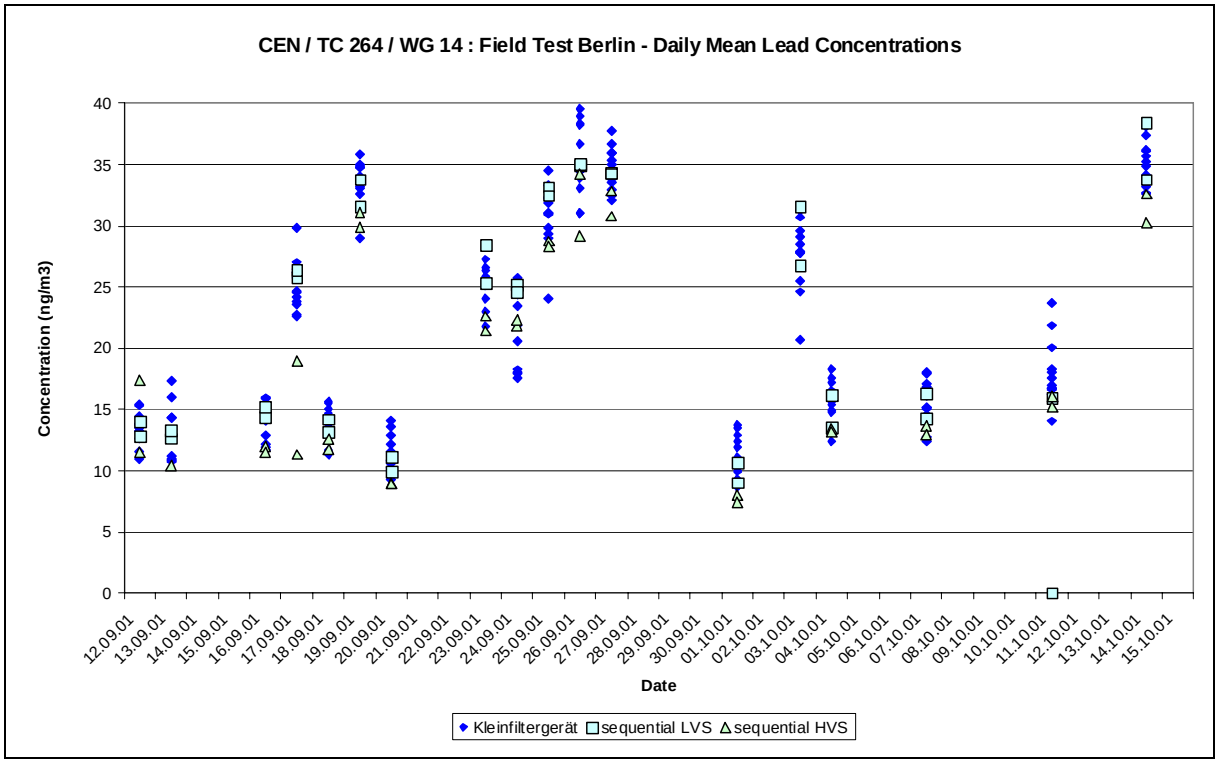


Figure A2 : Field Test Berlin - Daily Mean Cadmium Concentrations (all samplers)

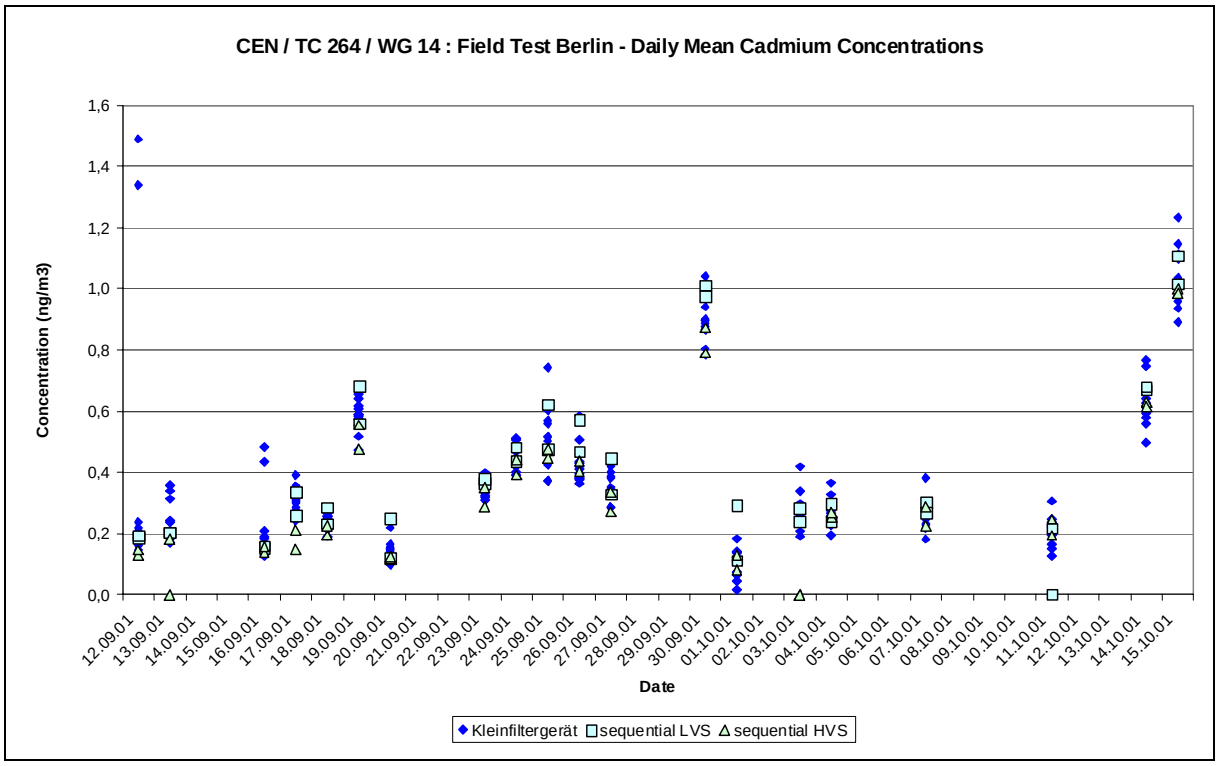


Figure A3a : Field Test Berlin - Daily Mean Arsenic Concentrations (all samplers)

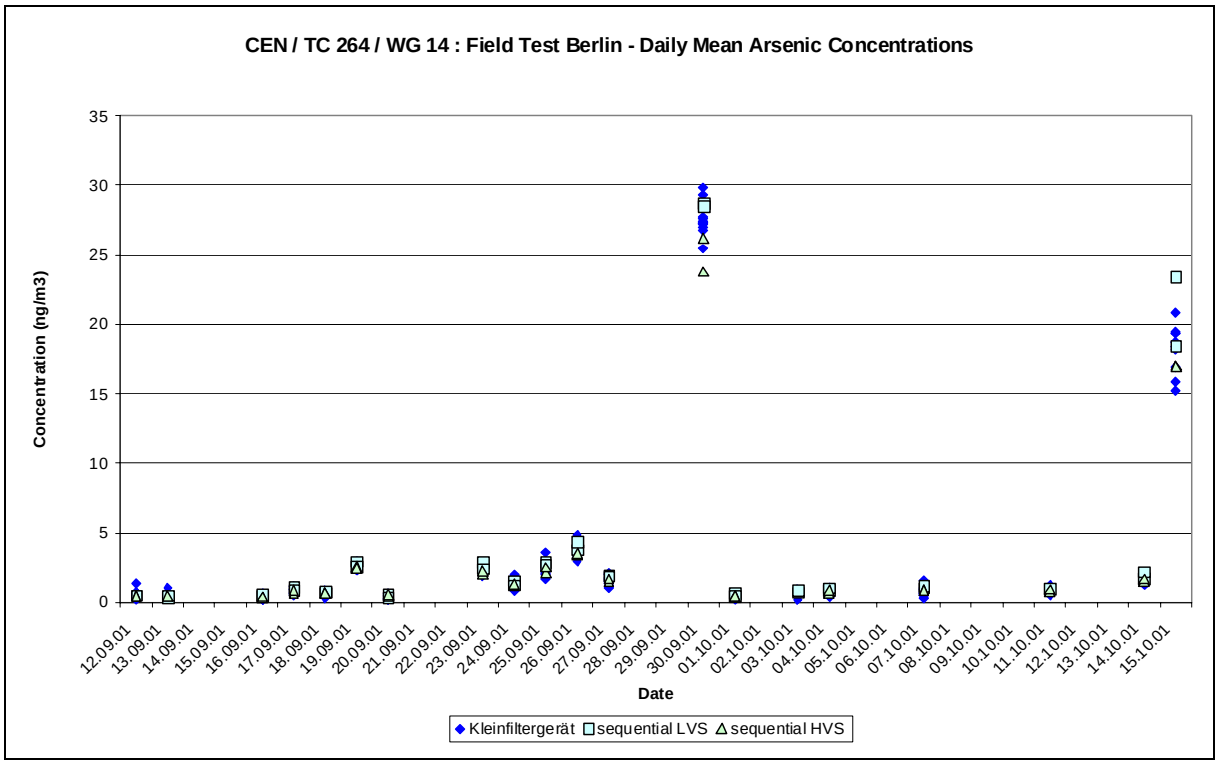


Figure A3b : Field Test Berlin - Daily Mean Arsenic Concentrations (all samplers)

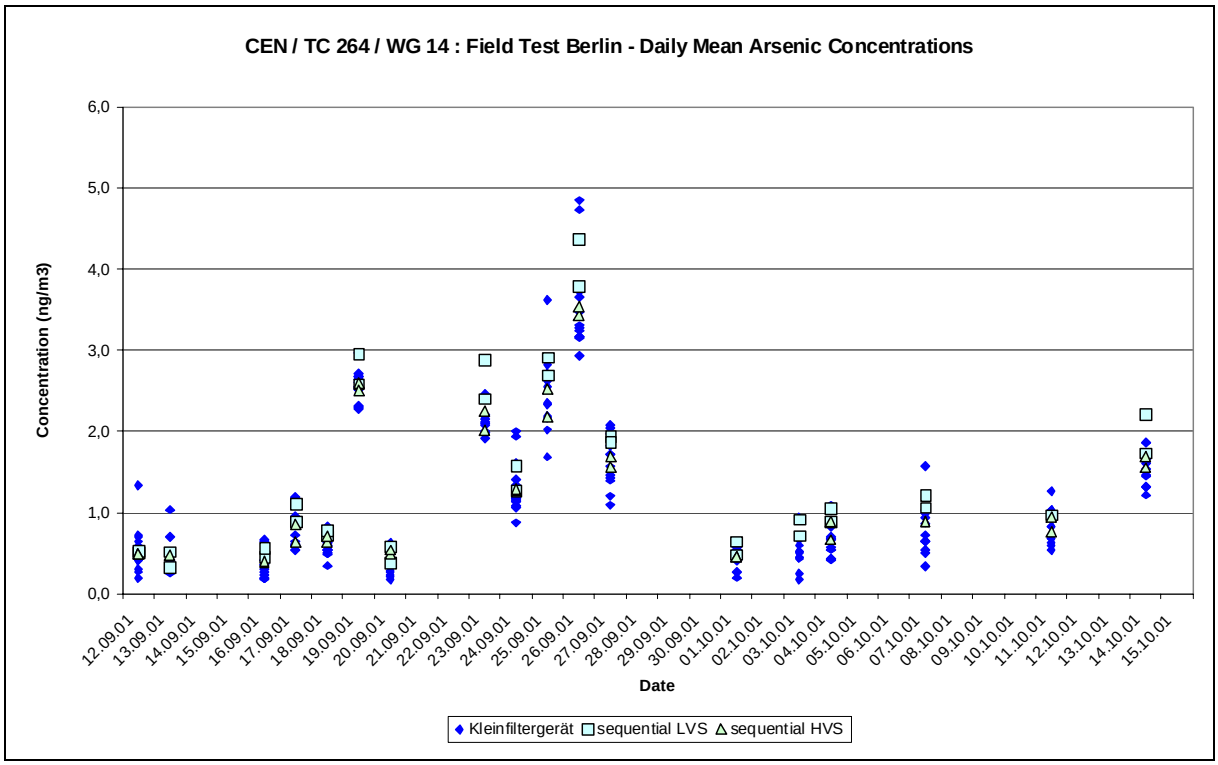
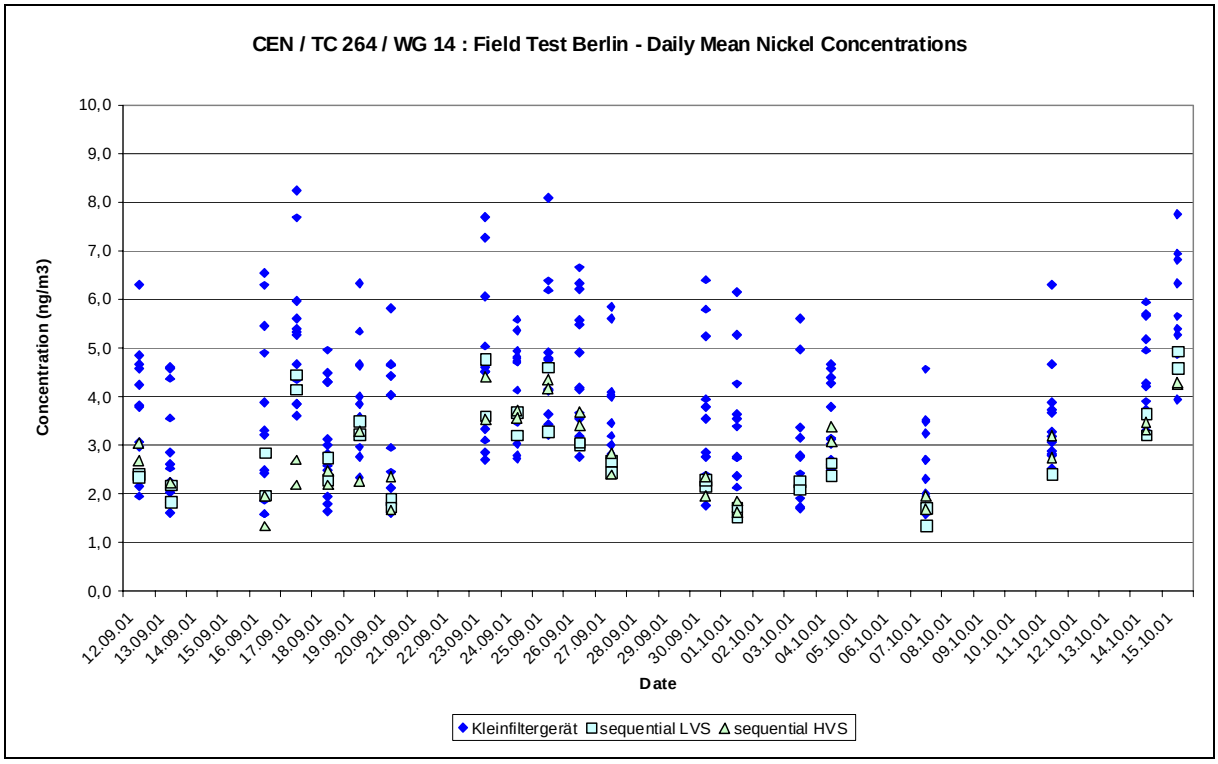


Figure A4 : Field Test Berlin - Daily Mean Nickel Concentrations (all samplers)



All data reported for lead were used for the generation of Figure-3 and Figure-7. However some data were excluded for the generation of Figures 4 – 6 and 8 –10 :

Cd : Lab B, Sampler 4 : 1 value excluded (assumed outlier)
Lab D, Sampler 7 : 1 value excluded (assumed outlier)
As : Lab C, Sampler 5 : 1 value excluded (negative concentration value)
Lab C, Sampler 6 : 1 value excluded (negative concentration value)
Ni : Lab D, Sampler 8 : 1 value excluded (ICP/MS only; contamination).

Besides these exceptions, daily mean concentrations for Pb, Cd and As show rather good agreement between all CEN PM10 Samplers and the additional sequential samplers. However for Ni, daily mean concentrations show much more variability between the samplers.

Figures A5 – A8 below show period mean concentrations of Pb, Cd, As and Ni in air as determined by the participating labs in all samples collected during the field test in Berlin. The following abbreviations are used :

Table-A1 : Abbreviations

Code	Lab	Sampler	Analytical Technique	Code	Lab	Sampler	Analytical Technique
A 1	A	CEN-1	GF-AAS	A 2	A	CEN-2	GF-AAS
B 3	B	CEN-3	GF-AAS	B 4	B	CEN-4	GF-AAS
B 3, ms	B	CEN-3	ICP/MS	B 4, ms	B	CEN-4	ICP/MS
C 5	C	CEN-5	GF-AAS	C 6	C	CEN-6	GF-AAS
D 7	D	CEN-7	GF-AAS	D 8	D	CEN-8	GF-AAS
D 7, ms	D	CEN-7	ICP/MS	D 8, ms	D	CEN-8	ICP/MS
D sLVS 1	D	sLVS-1	ICP/MS	D sLVS 3	D	sLVS-3	ICP/MS
D sHVS 1	D	sHVS-1	ICP/MS	D sHVS 2	D	sHVS-2	ICP/MS

Figure A5 : Field Test Berlin - Period Mean Lead Concentrations (all samplers)

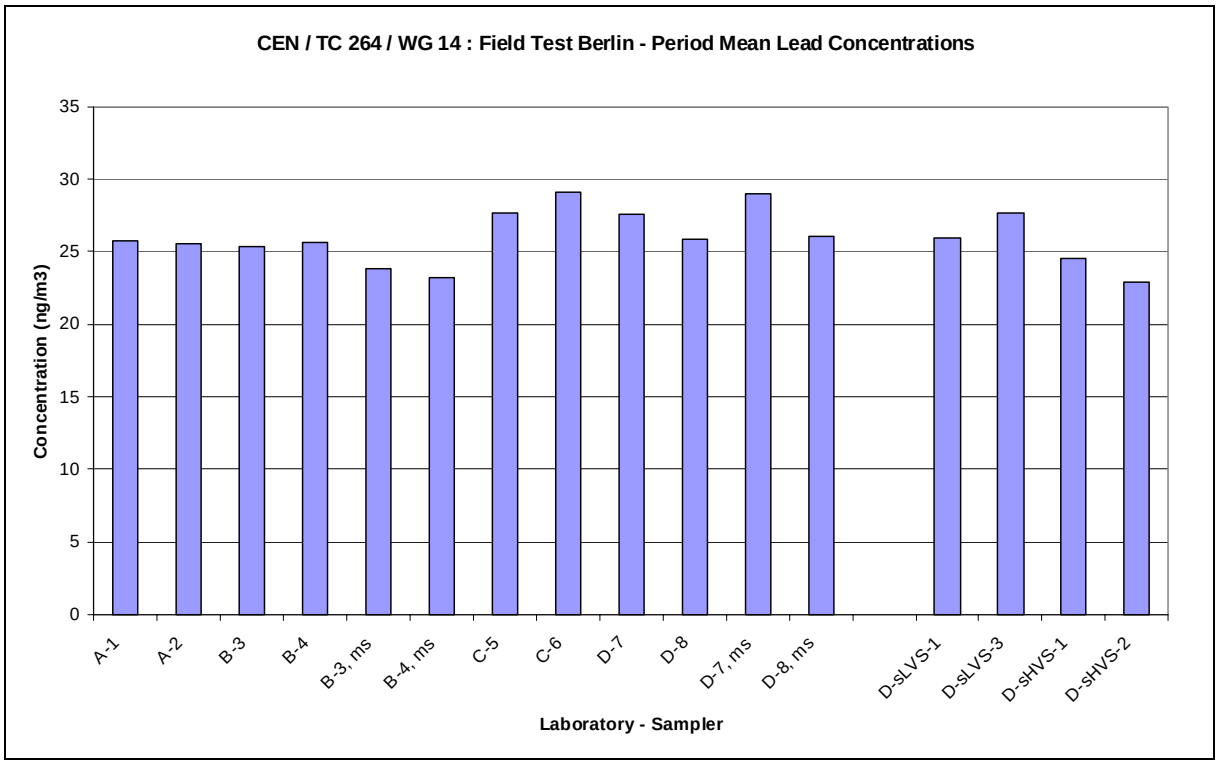


Figure A6 : Field Test Berlin - Period Mean Cadmium Concentrations (all samplers)

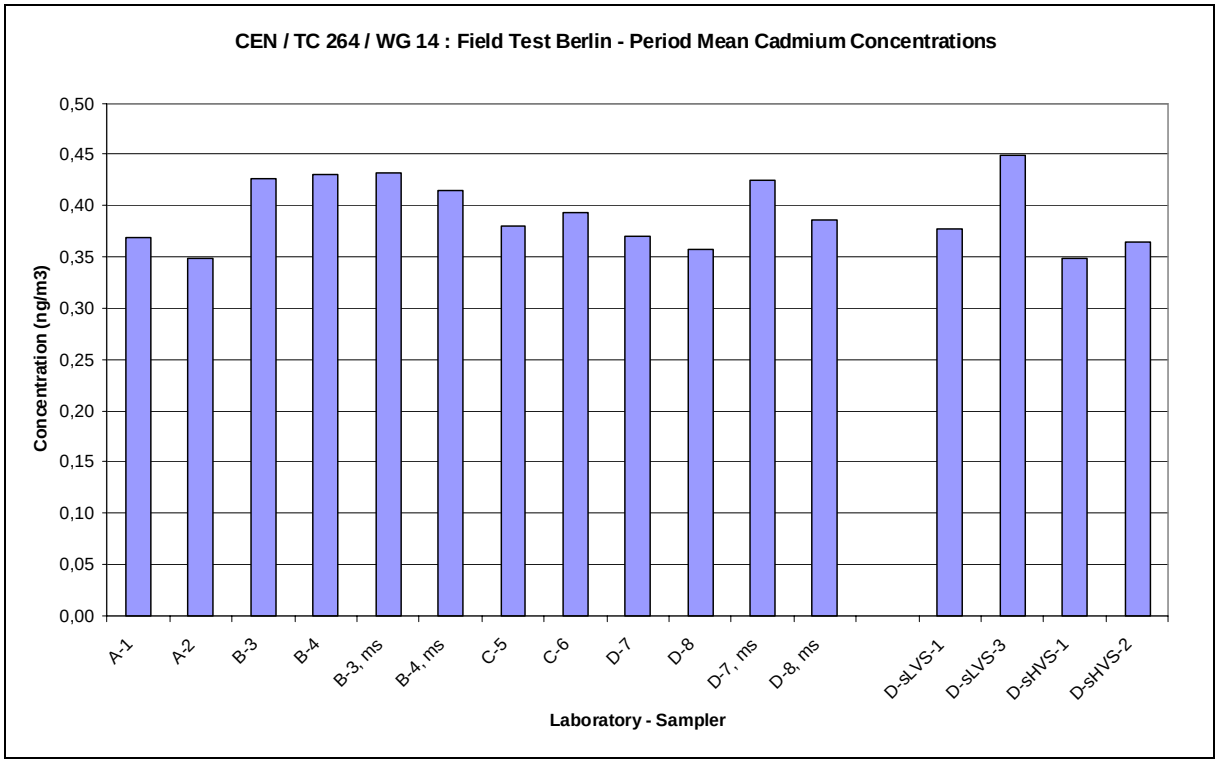


Figure A7 : Field Test Berlin - Period Mean Arsenic Concentrations (all samplers)

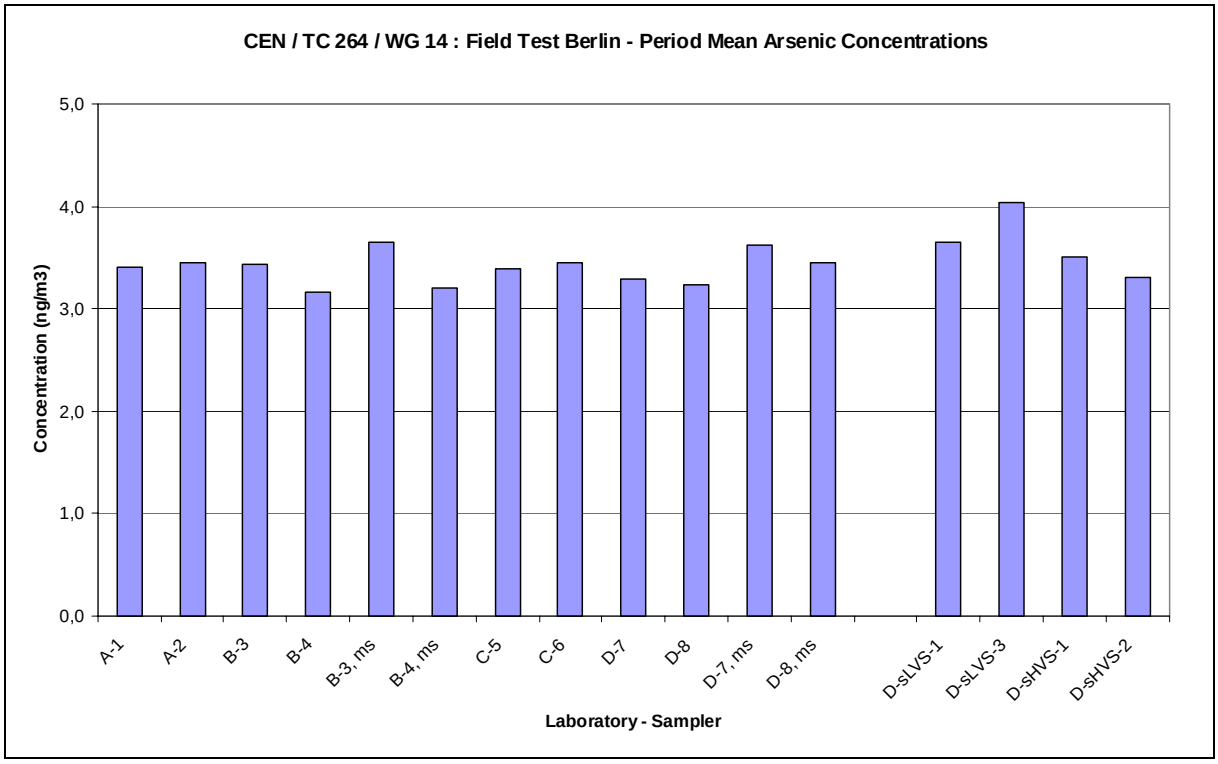
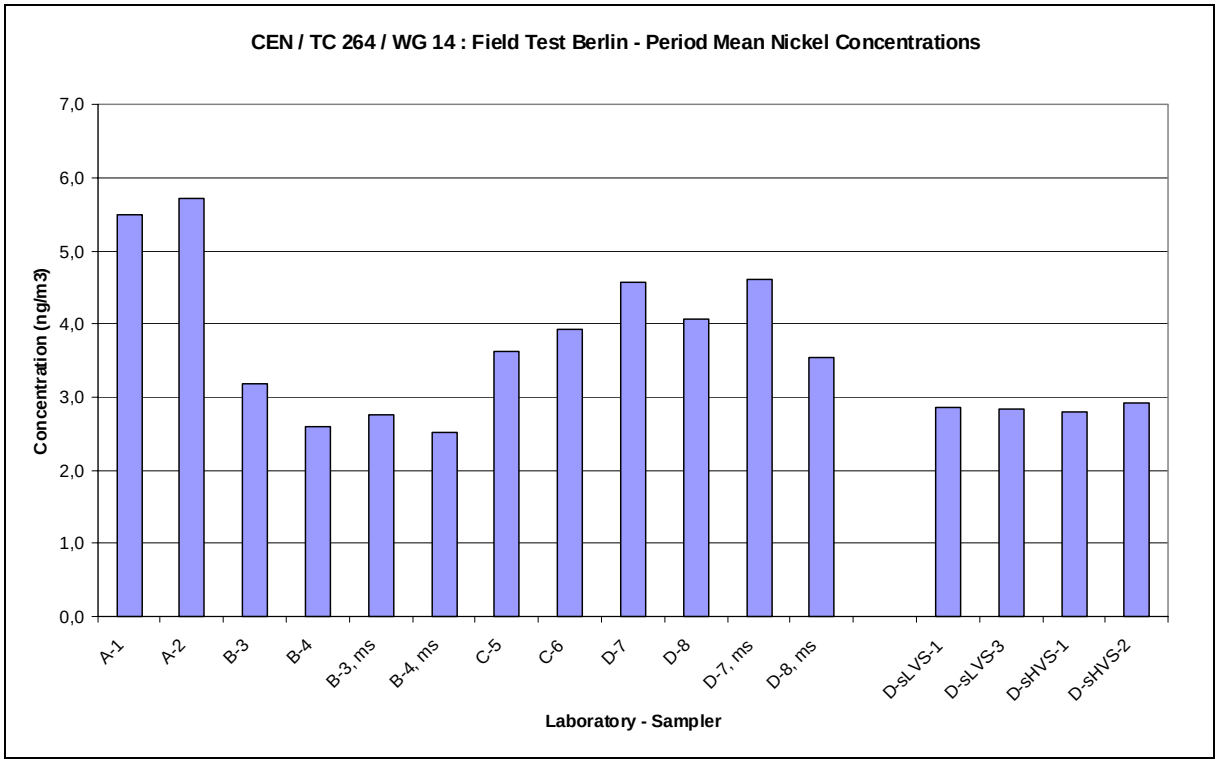


Figure A8 : Field Test Berlin - Period Mean Nickel Concentrations (all samplers)



Field Samples : PM10 Mass

During the period 08/10/01 – 10/10/01 voluntary PM10 mass measurements were performed. Quartz filter were used with all samplers. The results are presented in Table-A1 and Figure-A9 (the results of the reserve samplers CEN-9, CEN-10 and sLVS-2 are included) :

Table-A1 : PM10 Mass

Sampler No.	Sampler Type	Filter Material	PM10 Mass		
			08/10/2001	09/10/2001	10/10/2001
			µg/m³	µg/m³	µg/m³
CEN-1	KFG	quartz	**25,1**	**26,3**	**26,1**
CEN-2	KFG	quartz	**25,1**	**25,5**	**26,0**
CEN-3	KFG	quartz	**29,1**	**29,1**	**28,3**
CEN-4	KFG	quartz	**26,3**	**27,2**	**26,5**
CEN-5	KFG	quartz	**22,1**	**24,1**	**24,4**
CEN-6	KFG	quartz	**28,8**	**29,3**	**28,6**
CEN-7	KFG	quartz	**28,4**	**30,6**	**29,2**
CEN-8	KFG	quartz	**22,2**	**23,9**	**24,8**
CEN-9	KFG	quartz	**24,9**	**24,5**	**25,7**
CEN-10	KFG	quartz	**28,3**	**29,9**	**27,5**
sLVS-1	sLVS	quartz	**22,0**	**22,9**	**24,3**
sLVS-2	sLVS	quartz	**25,5**	**26,2**	**27,4**
sLVS-3	sLVS	quartz	**26,0**	**25,4**	**26,1**
sHVS-1	sHVS	quartz	**18,8**	**20,4**	**22,0**
sHVS-2	sHVS	quartz	**19,7**	**21,0**	**22,7**

Although there is some variability in PM10 mass concentrations between all samplers, the sequential High Volume Samplers seem to show systematically the lowest PM10 mass concentrations.

Figure-A9 : Field Test Berlin – Period Mean PM10 Concentrations (all samplers)
(Period : 08/10/01 – 10/10/01)