Final Report WG 14 Part F Field Tests Hoboken

CEN / TC 264/ WG14:

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

Minimum Validation Programme

Field Test Hoboken, 2001

VMM- CDVP IML –MEETNET ZWARE METALEN

PREPAIRED BY NATACHA CLAEYS
FINAL VERSION 05-03-02

FIELD TEST PERFORMED IN ASSISTANCE WITH ROLAND DE LATHOUWER (SAMPLING PART) AND ELKE ADRIAENSSENS (ANALYSIS PART)

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1. Introduction

This report is made by the VMM, department Networks and Research, Air Quality Group, for the Minimum Validation Programme (MVP) of CEN TC264/WG14. The MVP is funded by DGXI of the European Commission.

Results of the Minimum Validation Programme – Field Test – Antwerpen (Hoboken) - November – December 2001) are summarised.

2. Aim /MVP- Programme

2.1. MVP programme

The MVP includes
1) laboratory tests
2) preparation for the field tests
3) preliminary field tests and,
4) field tests.

A detailed overview of the MVP is provided in CEN/TC264/WG14 N95 – Description, of the Minimum Validation Programme. Additional documents provide details with respect to the preparation of the field tests 5CEN/TC264/WG14 N147 and PTN09) and the execution of the Preliminary Field Tests and Field Tests (CEN/TC264/WG14 N140 Rev5).

2.2. Field Tests – Field Test Hoboken

Field validation tests were carried out at four measurement sites (industrial sites and 2 urban sites). Field tests in Madrid (urban site) and Avonmouth (industrial site) were performed in spring and summer 2001. In autumn and winter 2001 field tests were performed in Berlin (urban site) and Hoboken (industrial site).

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 at each site. The sampling period at the site is 20 days. Daily 10 samples (8 real samples and 2 reserve samples) are collected. 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.

The following Table-1 provides a summary of the individual contributions of the participating laboratories :

Table-1 : Field test Berlin - Contributions of the participating laboratories (voluntary parts are shaded grey)

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

This report consists of the following parts :

- State and function tests of the CEN samplers in Hoboken
- Sampling site characteristics and sampling regime at the site Hoboken-Antwerpen
- Technical details of sample preparation and analysis in the participating labs.

3. Objectives

- Determine the performance characteristics (e.g. quantification limits, repeatability and reproducibility for Pb Cd, As and Ni measurements in ambient air) of the proposed reference method in accordance with EN 12341 with low Volume Sampler.
- Estimate the uncertainty budgets and expanded uncertainty of the complete method.

4. Field Test Belgium – Hoboken (A'pen)

4.1. Sampling site

4.1.1. Location – Set up

VMM performed the CEN field test at an industrial Flemish site.

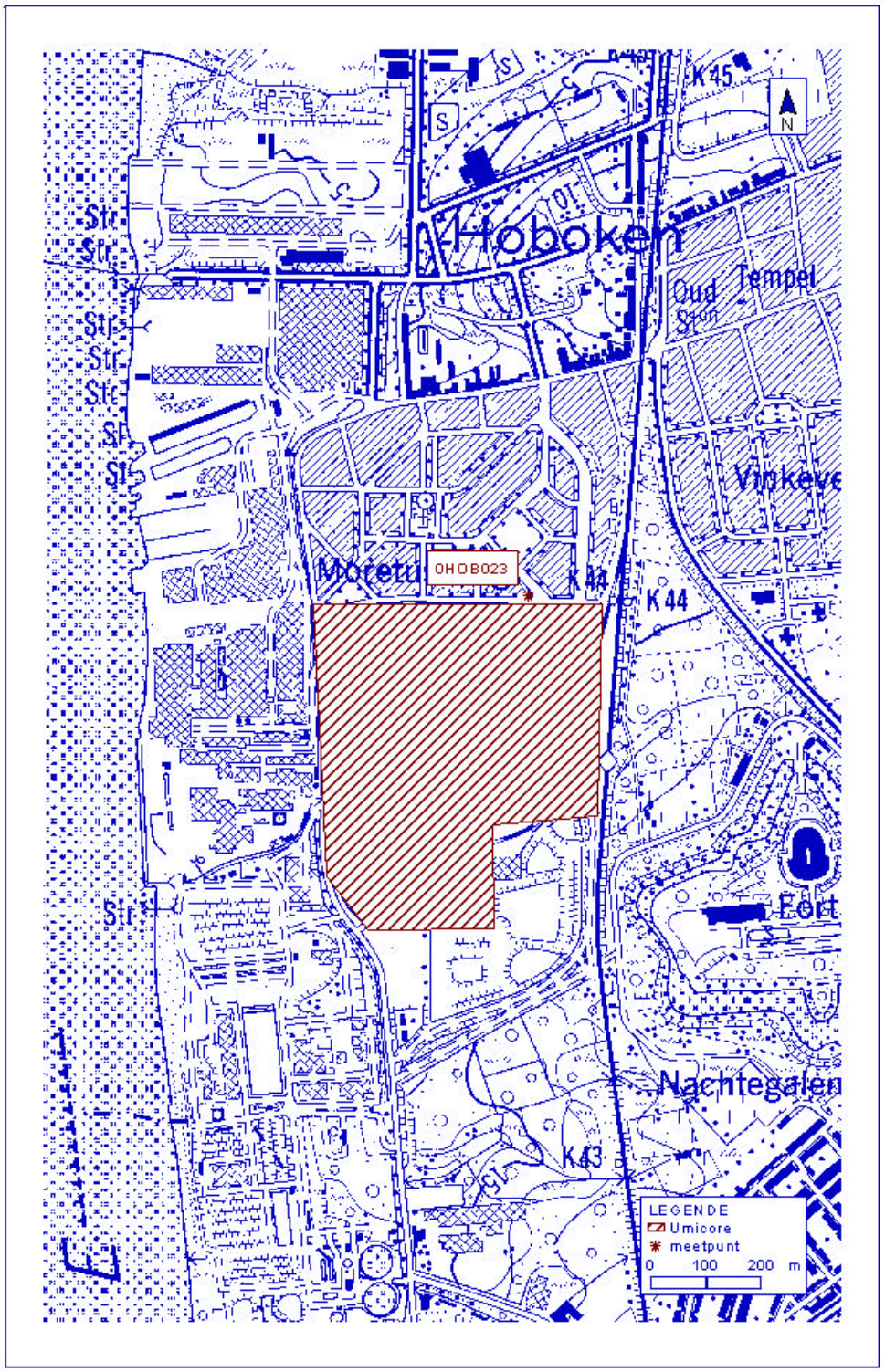
In the surrounding of the non-ferrous plant 'Union Miniere Hoboken ' VMM performs since the early eighties at several locations heavy metal measurements in ambient air. Recently the firm changed it's name to 'UMICORE'.

The CEN 10 KFG samplers were set up at the Hoboken site with internal code 0HOB23 which is located at the corner of two streets, Curiestraat and Standbeeldstraat. The site is located on the NNE side and only 10 m far away from the borderline of the plant. In the other wind directions the site is surrounded with residential houses.
The Lambert co-ordinates are 148059 and 206699.

Maps and pictures:

Figure 1: General map: Plant UMICORE and measuring site
Figure 2: Set up CEN Field Test: monitoring site and detailed map
Figure 3: General picture: direction Curiestraat – Chimney Umicore plant (1)
Figure 4: General picture: direction Curiestraat – Chimney Umicore plant (2)
Figure 5: General picture: corner Curiestraat – Standbeeldstraat (3)
Figure 6: General picture: direction Standbeeldstraat
Figure 7: Detail picture set up 10 KFG samplers
Figure 8: KFG LVS – Reference Sampler
Figure 9: KFG pump
Figure 10: KFG head: PM-10 inlet

Figuur 1.


K45
N
Hoboken
Oud Tempel
Vinkeve
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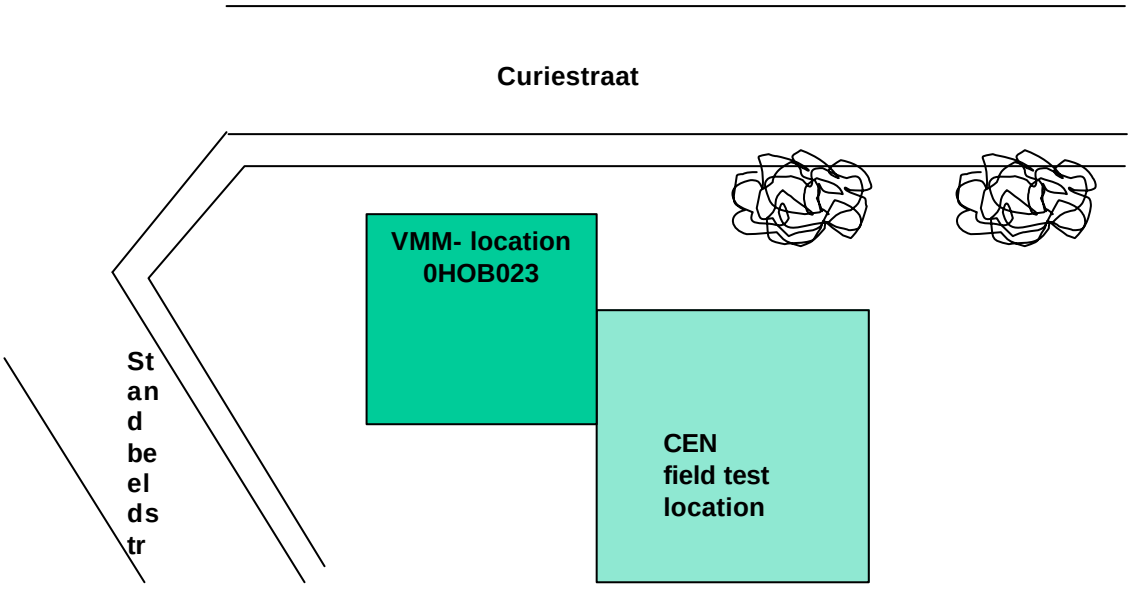
0HOB023
K44
K44
Fort
Nachtegalen
K43
LEGENDE
Umicore
meetpunt
0 100 200 m

Figure 2.

Monitoring site



Detailed Map :

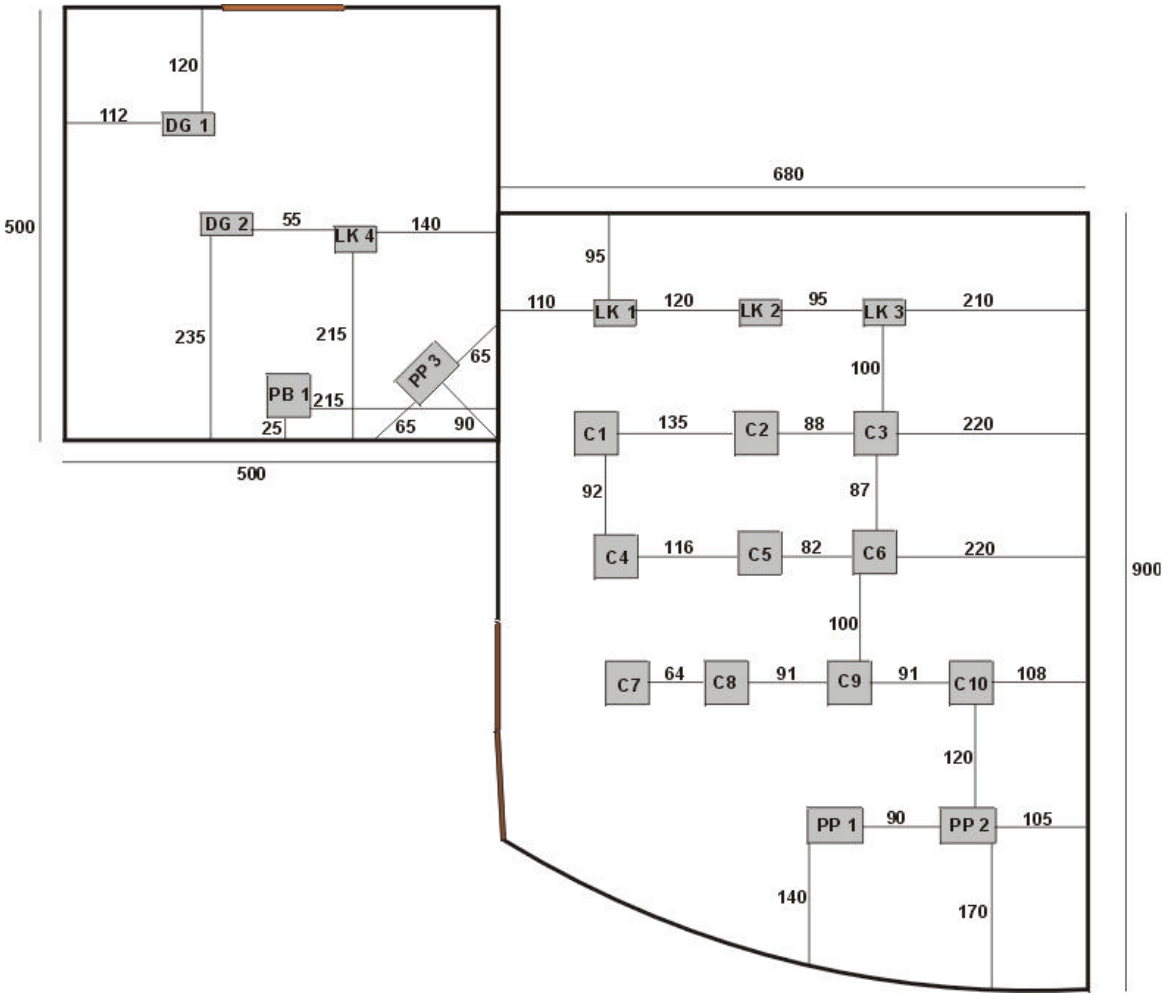


Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Figure 10.

4.1.2. Concentrations of heavy metals at the VMM HOBOKEN site.

Since 2000 heavy metal measurements in ambient air are performed at the 0HOB23 location. An overview is given in this chapter of the concentration levels, which were measured recently and in the past.

The VMM network is equipped with Pourbaix stations (+/-PM10 sampling - +/- 18m³/day air sampling). The analyses are performed with WD- XRF technique.

In 2002 the heavy metal network will be completely updated with new sequential PM-10 Leckel SEQ 47/50samplers. In 2000-2001 VMM performed some comparison measurements with a PM-10 Partisol Plus sampler and the standard Pourbaix stations.

For the long term analyses we report the nearby site 0HOB17 which is located at the Edisonstraat 20 and 100-m west from the plant. The Lambert co-ordinates are 147839-206699.

4.1.2.1. Current concentrations at 0HOB 23

The annual mean metal concentrations are based on daily measurements. In table 2 we have summarised for Pb, As, Cd and Ni the mean values at 0HOB23 for 2000 and 2001.

Table 2.

	Pb (µg/m³)	**Ni** (µg/m³)	**As** (µg/m³)	**Cd** (µg/m³)
Mean-2000**	**1,812**	**0,059**	**0,123**	**0,041**
Yearly Mean -2001	**1,032**	**0,031**	**0,044**	*****

*Not available
** period between 1-8-00 and 31-12-00

At the site 0HOB23 the yearly averages for Pb, Ni and As decreases in 2001 between 40 and 60% against 2000. However in 2000 the mean values covers only the period 1-8-2000 till 31-12-2000. The decrease can be explained by a sanitation measure installed by Umicore on the nearby Pb smelter.

The last 6 months of 2001 VMM has performed +/- PM10 (Pourbaix) and PM-10 (Partisol Plus) measurements simultaneously at the 0HOB23 location. In table 3 we have summarised for Pb, As and Ni the comparative results. At the moment the Cd results are not yet available.

Table 3.

6 months mean values	**Pb** (µg/m³)	**Ni** (µg/m³)	**As** (µg/m³)
2001- Pourbaix	**1,087**	**0,033**	**0,035**
2001- PM10- Partisol Plus	**0,828**	**0,022**	**0,037**

With exception for As the Partisol Plus PM10 - sampler measures lower Pb and Ni ambient air concentrations in comparison with the Pourbaix TSP sampler. No uniform correction factor for all the metals can be found.

4.1.2.2. Long term evolution at 0HOB 17 (comparable station)

Figures 11 till 14 show the running averages at 0HOB17 from 1990 till 2000. It reflects the long-term evolution of the heavy metal ambient air concentrations at Hoboken nearby the plant.

The implementation of new BBT techniques at the plant and a clean up programme shows that the last decade the ambient air concentrations of Pb, As and Cd decreases. For Ni the trend is slightly increasing.

Figure 11.

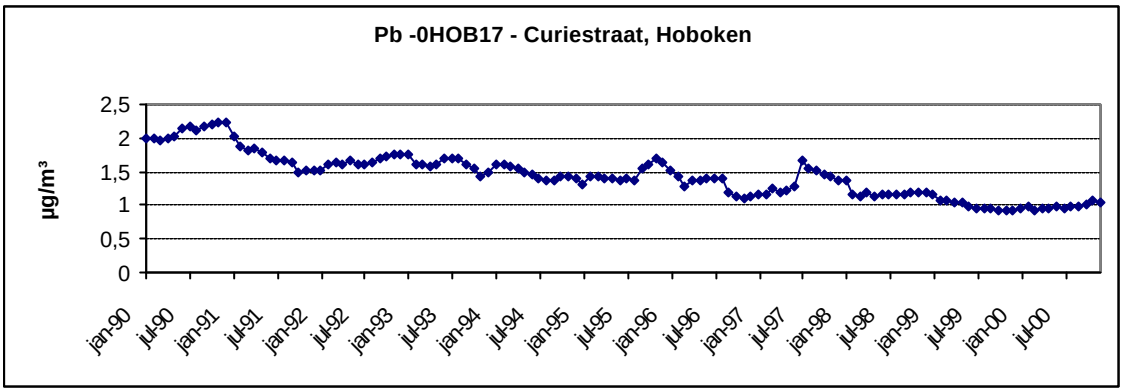


Figure 12.

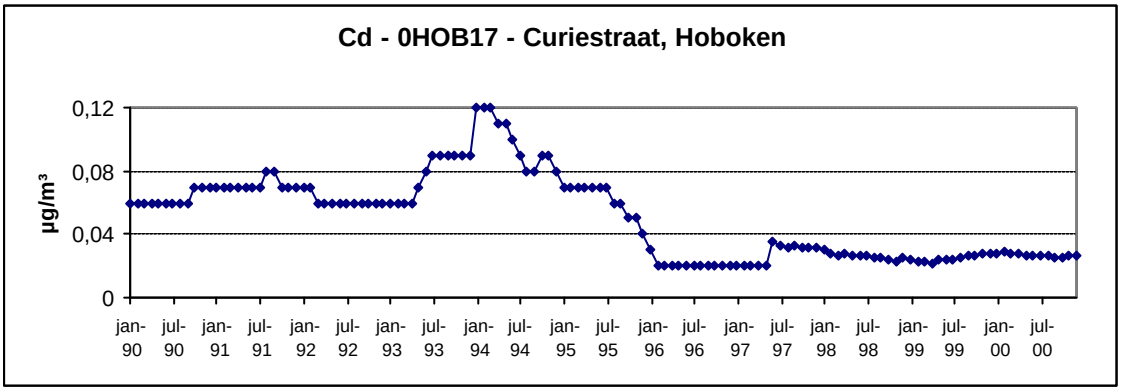


Figure 13.

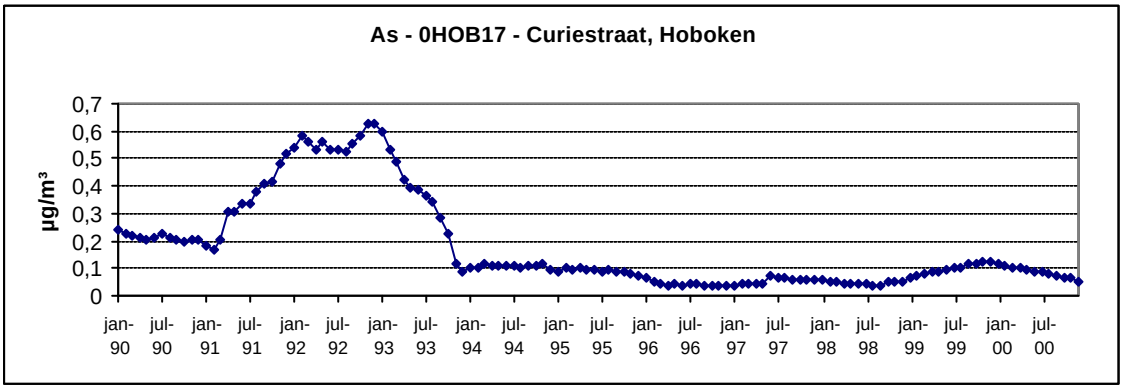
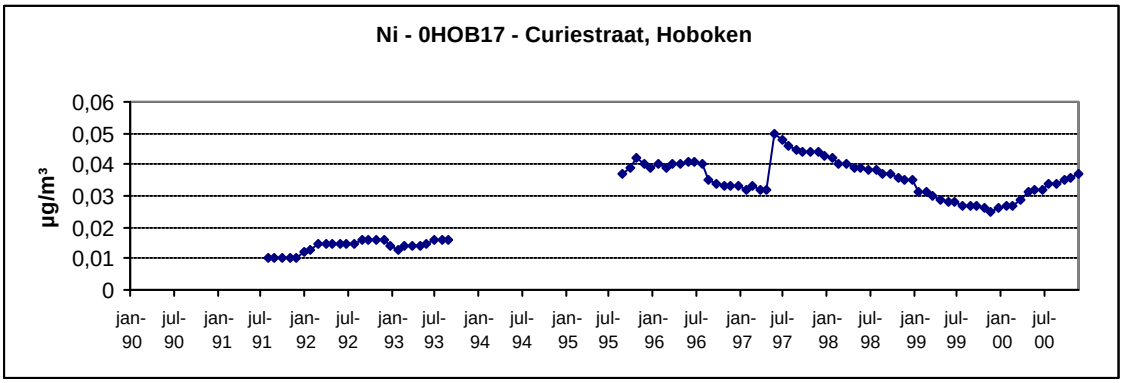


Figure 14.



4.2. Sampling Programme

4.2.1 Programme

4.2.1.1. Sampling at the site Hoboken – Antwerpen

Sampling at the site Hoboken (Antwerpen) was carried out using 10 CEN Low Volume PM10 Samplers (Kleinfiltergerät).

From the 5 th of November 2001 to the 18 th of December daily samples were taken. Sampling started each week on Monday at 9h30. The sampling period was 24 h.

One hour a day was used for changing filters, cleaning inlets and calibrating of the samplers. Five samplers were taken in one week. No sampling was performed during the weekend.

The daily filter exchanges were performed by several technicians from VMM in Antwerpen: Ms Inge Naveau , Ms Jacqueline Van Den Eede, Mr Roland De Lathouwer, Mr Paul Bruyndonckx ,Mr Jo Verbruggen and Mr. Dirk Frederickx (referred to as IN, JVDE,RDL, PB, JV and DF in the report forms included in Annex-1).

The samplers were calibrated and cleaned during the field campaign on 25/10; 9/11; 10/12 and 20/12/2001.

4.2.1.2. Gravimetric Measurements

Gravimetric measurements were performed to find out whether the sampling was not influenced by the position of the equipment on the field.
On two days during the field test, 30th of October 2001 and 12th of December2001, VMM performed an extra sampling period for gravimetric dust determinations.
VMM used cellulose nitrate filters, diameter 50 mm and pore size 3 µm, on all the 10 Kleinfiltergerät samplers during these 'dust' PM10 measurements. The filters were treated in accordance with EN12341 (conditioning at 20°C and 50% RH at least 48h).

4.2.2. Technical information

Detailed calibration data are shown in report forms included in Annex-2.

- Problems occurred quite often with the pumps of the samplers. Because of the high dust concentrations at the Hoboken site and periods of very high pollution (temperature inversion) samplers often stopped after 15,20 hours. Especially the samplers running with cellullose acetate filters had this problem. The 5 Kleinfiltergerät samplers that used quartz filters did not have this problem.For this reason VMM had to sample 27 days to have enough reliable filtersets.

General remark:

The ten Kleinfiltergerät samplers (2,3 m³/h) were equipped with the smaller pump (3 m³). If membrane filters (cellulose nitrate, cellulose acetate, teflon …) are used an important pressuredrop can occur. Especially if the sampling is performed in areas with a high dust concentration, the filter can be clogged. With unfavourable meteorological conditions (high humidity, temperature inversion) the pump is not able to deliver the necessary flow and the sampling stops after 10, 15, 20 hours…. The filter material is important for reliable sampling with high dust concentrations in combination with unfavourable meteorological conditions. With

membrane filters it is necessary to sample with a powerful pump (flow of 6 m³ for a PM10 inlet sampling on 2,3 m³/h) sampler. Teflon and cellulose acetate filters seem to give more difficulties than cellulose nitrate filters. Quartz filters always give good results, even with high dust concentrations and unfavourable meteorological conditions. But they are much more frible. Especially for weighing and gravimetrical determination of dust concentrations this is a major drawback.

- Other technical problems that occurred with the 10 Kleinfiltergerät samplers:
  ° The outer part of the PM10 inlet of sampler nr 5 was damaged during transportation. During the field-tests, it was replaced by a VMM-part.
  ° The wooden transportation boxes are too small. This caused damage to the mains, supply cables that had to be replaced.
  ° Sampler number 3 has an intermittent problem. A problem in the internal wiring of the sampler causes the sampler to shut down, especially during the programming of the sampler.
  ° Sampler nr. 9 was defective after 5 days and has been replaced by a Kleinfiltergerät of VMM (electronics and pump). The original inlet and suction pipe has been used. The exchange happened on the 13 th of November 2001.
  ° Programming of the Kleinfiltergerät samplers is time-consuming and not user-friendly. The new electronics are less user-friendly than the old ones.
  ° The temperature and pressure sensors are of a bad quality. For three of the samplers it was not possible to calibrate the ambient pressure. As a consequence in the field you find “strange” values for temperature (-53 °C !) and an important variation for ambient pressure values (1002 to 1025 mbar for the same sampling period !). This also means that the sampled volumes expressed in standard conditions are erroneous.
  ° Some inlets were not watertight, so several filters became wet during the sampling. Some of these filters had to be rejected during the validation.

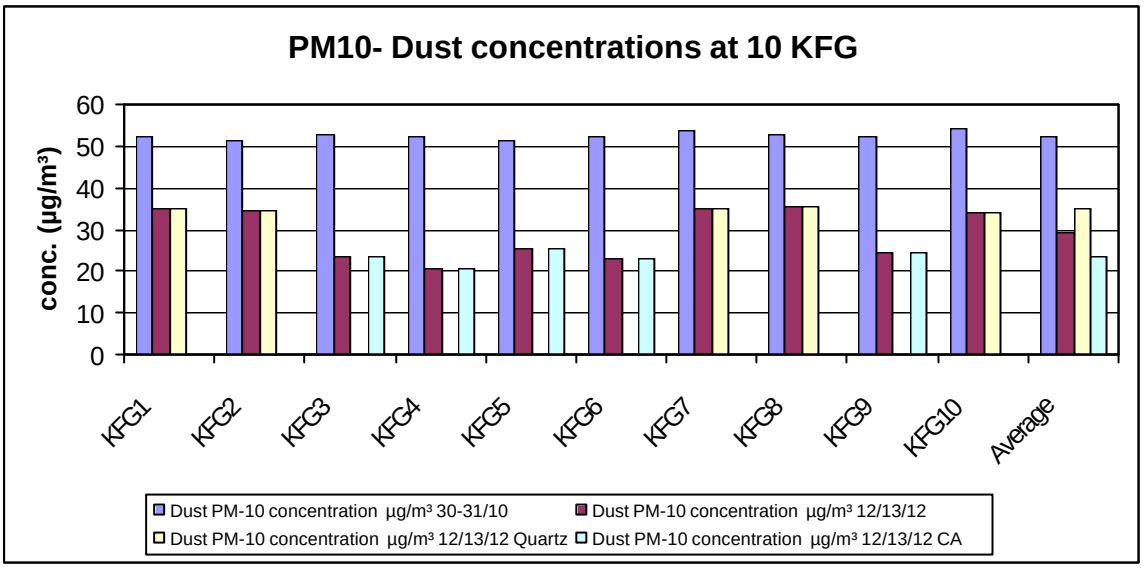
- The JRC-IES rotameter that was delivered with the 10 Kleinfiltergerät samplers showed a very unstable reading. The float was oscillating and moving between +/- 2 % of the value. The average of the rotameter reading was 9 % higher compared to our calibrated BIOS Dry Cal flowmeter. This instrument was calibrated against the National Primary Standard Brooks Vol-U meter at the Belgian Official Calibration Lab (IRCEL, Brussels).
- The reading of the Aalborg massflowmeter (from the Spanish lab - adapter owned by IND co) was erroneous compared to our calibrated BIOS Drycal flowmeter. It showed a value that was 22 % too high.

4.2.3. Results

Detailed sampling data is shown in report forms included in Annex-3.

Detailed gravimetric data is shown in Annex-4 A and B. Figure 15 below shows the results of the two measurements.

Figure 15.



On the 30 th of November 2001 a mean PM-10 dust concentration of 52,55 µg/m³ with a standard deviation of 0,90 µg/m³ or a relative standard deviation of 1.72% was measured with the 10 KFG's.

On the 12 the of December 2001 a mean PM-10 dust concentration of 29,18 µg/m³ with a standard deviation of 6,12 µg/m³ or a relative standard deviation of 20.96 % was measured with the 10 KFG's.

The first gravimetric test (30/31-10-2001) shows that the position of the samplers did not affect the dust concentration found on the filter.

The second gravimetric test (12/13-12-2001) shows a different result. The samplers with number 1,2,7,8 and 10 show equal values around 35µg/m³, while the other samplers with number 3,4,5,6 and 9 show a lower PM-10 dust concentration around 23 µg/m³).
Flowrates were once again checked but all the flows were within the 2% range. This means that samplers calibrated with cellulose acetate give a lower dust PM-10 concentration.

During the 'dust' PM-10 measurements VMM noticed also that some membrane filters, e.g. cellulose acetate filters, are not suitable for gravimetric measurements. Over a time scale of one month VMM experienced that these type of membrane filters looses 1,4 till 1.7% weight. Cellulose nitrate filters don't show this phenomena.
Figure 16 shows the mass stability of cellulose acetate en cellulose nitrate membrane blank filters.

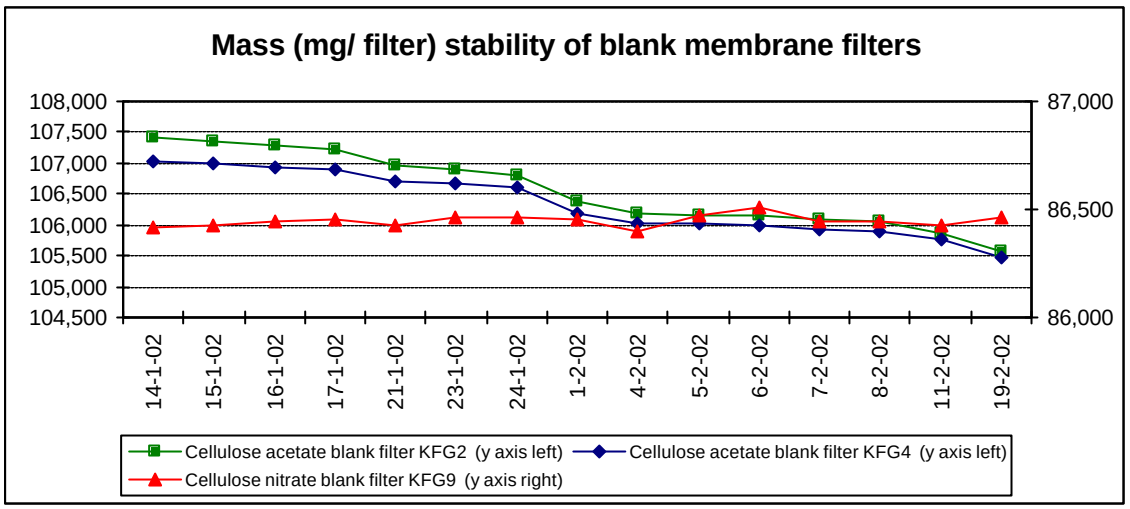


Figure 16.

4.2.4. Validation of the sampling results

Bad meteorological conditions and high dust loading caused severe technical sampling problems during the field test Hoboken. The technical problems occurred mainly because the samplers were installed with small pumps and while using membrane filters.
In six weeks VMM was able to sample 18 sample sets. In agreement with the secretary and convenor of CEN WG14 two extra days of which each time one filter has not sampled for 24 hours, but only 20h50 (29/11/01) and 20h29 (16/12/01), were distributed.

General remark:

For a correct evaluation of the sampling it would have been better to sample the dust concentration with an extra Kleinfiltergerät of whom the filters were weighed. So a relation with the average PM-10 dust concentration (in µg/m³ on the 24 hours sampling period) and the correct functioning of the samplers would have been possible. Even better evaluation would have been possible with monitoring equipment for wind direction and windspeed, relative humidity and temperature. Also a real-time dustmonitor (TEOM or FAG) could give good information as on when sampling stops.

4.3. Transport

After sampling the filters were put in plastic petri dishes. The dishes were labelled in the lab with the internal VMM lab code and on the top with the CEN-code.

On the 4th of January 2002 the filters and a distribution list were send off to labs: Lab A, Lab B and Lab D (UBA Vienna).

Detailed transport list is shown in Annex-5.

4.4. Sample Preparation and Analytical Methods

4.4.1. 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 closed microwave digestion in high pressure vessels using a mixture of 8 ml nitric acid and 2 ml 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

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

Lab B reported with sample C-3-6 a problem. After digestion it was noted that the vessel lid had leaked and solution appeared to be lost. The remaining extract was removed, combined with washing of the vessel and made up to 50 ml as per the standard procedure.

Lab C reported next additional information:
The digestions were carried out with the new and the old digestion units. In December new vent nuts for the old unit were delivered. Some tests were carried out, and no problems occurred during the digestion.
Five digestion runs were carried out. The digestion series 1 to 4 consisted of 1 reagent blank, 1 lab filter blank, 1 field filter blank, 1 NIST standard, 1 NIES standard and 7 real filters. In the 5th run only real filters were digested.
During the first and the second digestion, there were some problems caused by a damaged temperature sensor. No actions were needed, because the program stopped during the hold step. The other digestions were performed with another temperature sensor.

4.4.2. 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.

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 NIESNo.8 (Vehicle Exhaust Particulate Matter).

4.4.2.1. 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.

It is believed that when measuring arsenic and nickel, the NIES CRM excerts a significant matrix effect which results in low measured recoveries. To overcome this, a standard addition experiment was performed at two levels for NIES digests. This should reduce any matrix effects and enable more accurate measurement of the solution concentrations. 5µl aliquots of the digested sample were spiked with 5 and 10 µl of a 20 ng/ml stand giving spike levels of 6.00 and 13.3 ng/ml. The total volume for all measurements was 15 µl with any shortfall being made up with 16% nitric acid and 4% hydrogen peroxide. 16% nitric acid/4% hydrogen peroxide was used for the blank measurement.

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

Additional comments:

Sample dilutions: The filter, lab and reagent blanks were run without further dilution. The levels observed in the field samples were somewhat higher then those observed at previous field locations. This required a number of field samples to be diluted to ensure that measurement was undertaken within the calibration range. Secondary dilutions were typically 1 in 10 made up with 16% nitric acid so that solutions were analysed with the same acid concentrations.

NIES Reference material: the mean recovery of nickel for the NIES CRM was somewhat lower than had previously been measured. Replicate experiments, recalibration and dilution of the samples did not significantly improve the recovery. The recovery of the spiked addition standard was to be only 90% which might suggest the presence of some matrix effect for this element in this sample.

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 analytical conditions used are given below. As some samples contained In, this time, we used Y as internal standard for the elements As, Cd and Pb.

Analytical conditions :

Analysis performed : February 2002
Instrument : ICP/MS, type : Ultramass, producer : Varian

Masses monitored :

Y	89	Sc	45
As	75	Ni	60
Cd	111	Pb	208

Calibration :

The same calibration was used for samples, blanks and CRM-solutions, but solutions were diluted differently before analysis :

Blanks : dilution factor 2
Samples : dilution factor 2, 10, 20 (depending on element concentrations)
NIST 1648 : dilution factors 2 (for Cd, As and Ni) and 20 (for Pb)
NIES No.8 : dilution factors 2 (for Cd, As and Ni) and 4 (for Pb)

Internal standards : Y 20 µg/L (As, Cd, Pb),
Sc 10 µg/L (Ni)

External calibration standards :
-standard blank solution
-operating standard-1 solution (element conc. : 20 µg/L As, Pb, Cd, Ni)
-operating standard-2 solution (element conc. : 100 µg/L As, Pb, Cd, Ni)

- **RESULTS**
  - Blanks (lab A - D) – Pb, As, Ni, Cd
    The compete data set is included in Annex 6
  - QC's (lab A - D) – Pb, As, Ni, Cd
    The compete data set is included in Annex 7
  - Real samples (lab A - D) – Pb, As, Ni, Cd
    The compete data set is included in Annex 8

4.5. Ambient air concentrations

Figures 17 till 20 below show daily mean concentrations of Pb, Cd, As and Ni in ambient air as determined by the participating labs in the samples collected during the field test in Hoboken (Antwerpen). The complete data set with average and standard deviation calculations is included in Annex 9.

Figure 17.

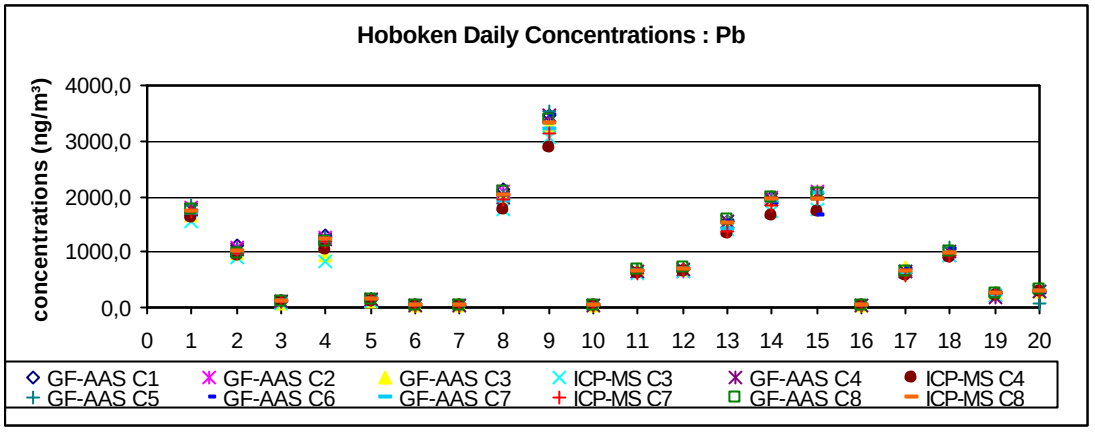


Figure 18.

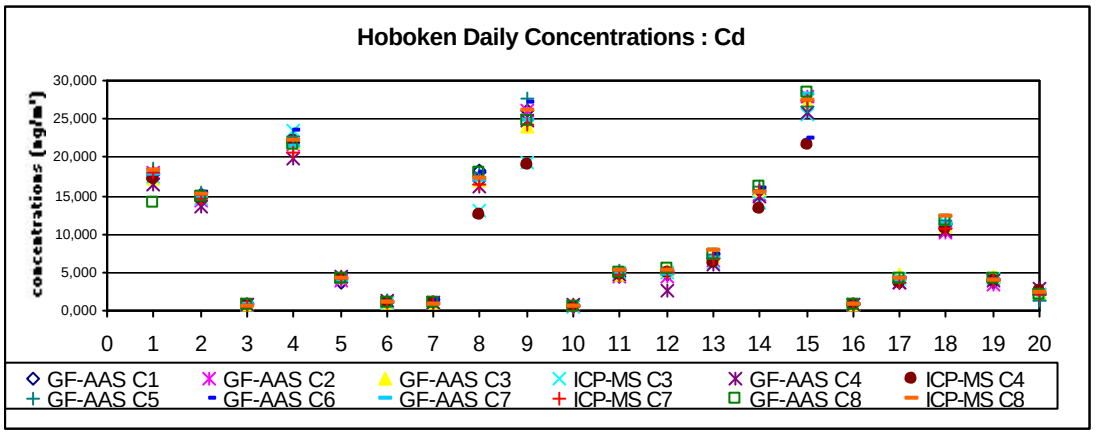


Figure 19.

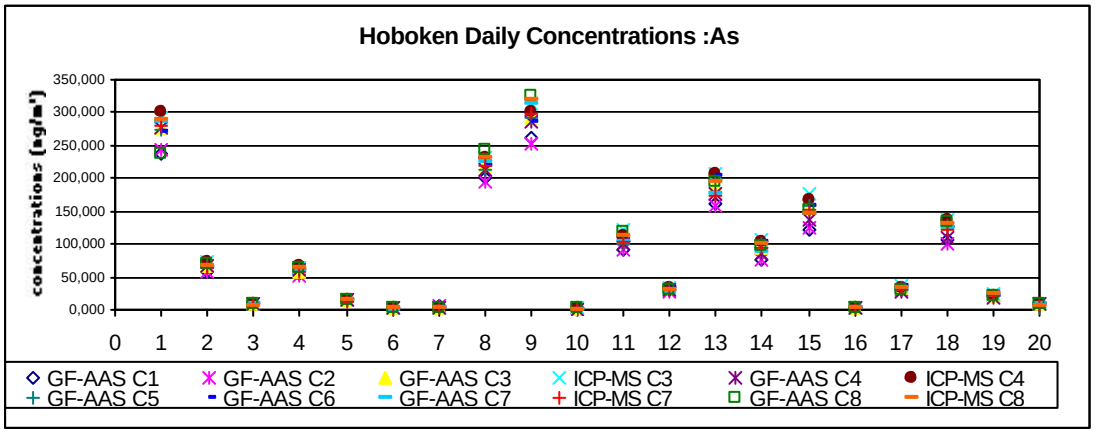
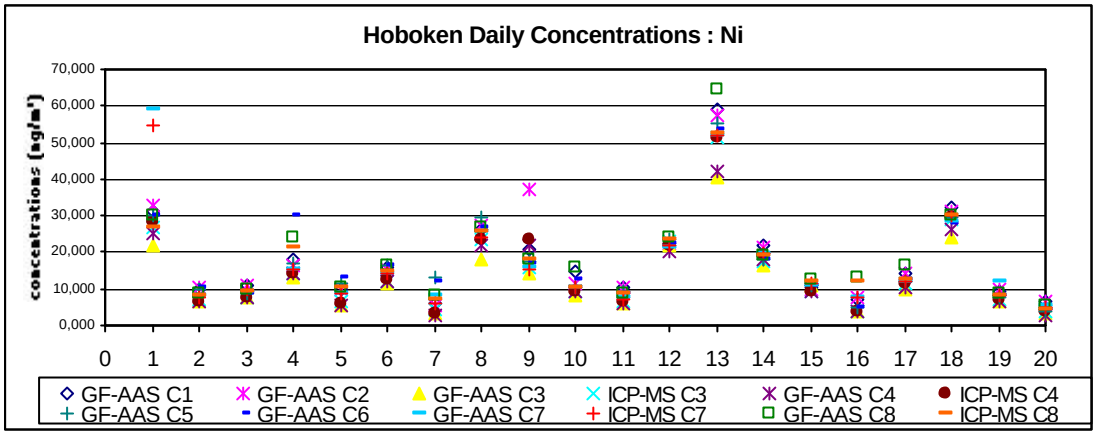


Figure 20.



All data reported were used in the figures.

However some data are assumed to be outlier or not valid:

Pb Lab B AAS C-*-4 (sampler 3&4 date 11/11/2001- reserve filter in C4 sampler)
Lab B ICP-MS C-*-4 (sampler 3&4 date 11 /11/2001- reserve filter in C4 sampler)
Lab C C-*-20 (sampler 5&6 date 16/12/2001 - reserve filter in C5 sampler)

Cd Lab B-AAS C-*-12 (sampler 3&4 date 26/11/2001)
Lab B-ICP-MS C-*-15 (sampler 3&4 date 29/11/2001) (reserve filter in C3 sampler)
Lab C C-*-20 (sampler 5&6 date 16/12/2001 - reserve filter in C5 sampler)
Lab C C-*-5 (sampler 5&6 date 12/11/2001 - reserve filter in C5 sampler)
Lab C C-*-4 (sampler 5&6 date 11/11/2001 - reserve filter in C4 sampler)
Lab D-AAS C-*-1(sampler 7&8 date 6/11/2001)

As Lab B-ICP-MS C-*-1 (sampler 3&4 date 6/11/2001) (reserve filter in C4 sampler)
Lab C C-*-20 (sampler 5&6 date 16/12/2001- reserve filter in C5 sampler)
Lab D-AAS C-*-1(sampler 7&8 date 6/11/2001)

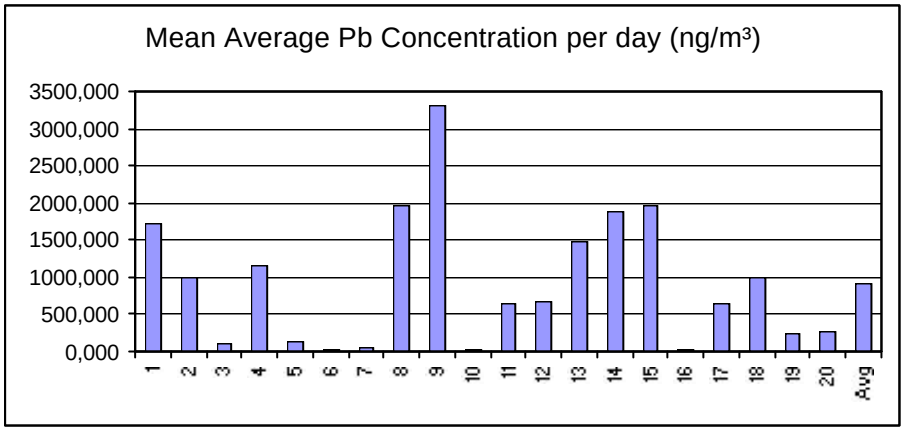
Ni Lab A-AAS C-*-9 (sampler 1&2 date 21/11/2001)
Lab B-AAS C-*-9 (sampler 3&4 date 21/11/2001) (reserve filter in C4 sampler)
Lab B-ICP-MS C-*-9 (sampler 3&4 date 21 /11/2001 - reserve filter in C4 sampler)
Lab C C-*-20 (Sampler 5&6 date 26/12/2001) (reserve filter in C5 sampler)
Lab C C-*-4 (Sampler 5&6 date 11/11/2001)
Lab D-AAS C-*-1(Sampler 7&8 date 6/11/2001)
Lab D-AAS C-*-13(Sampler 7&8 date 27/11/2001)
Lab D ICP-MS C-*-4 (Sampler 5&6 date 11/11/2001)
Lab D-ICP-MS C-*-1(Sampler 7&8 date 6/11/2001)
Lab D-ICP-MS C-*-13(Sampler 7&8 date 27/11/2001)

These data were traced out of the comparison figures made in Annex 11 till 13. The statistical evaluation will evaluate these data.

Beside some exceptions, daily mean concentrations for Pb, Cd and As show good agreement between all the CEN samplers. For Ni , daily mean concentrations show more variability between the samplers. Very near the sampling site there is probably a nickel source at low height, due to emission of a mechanic workplace of Umicore.

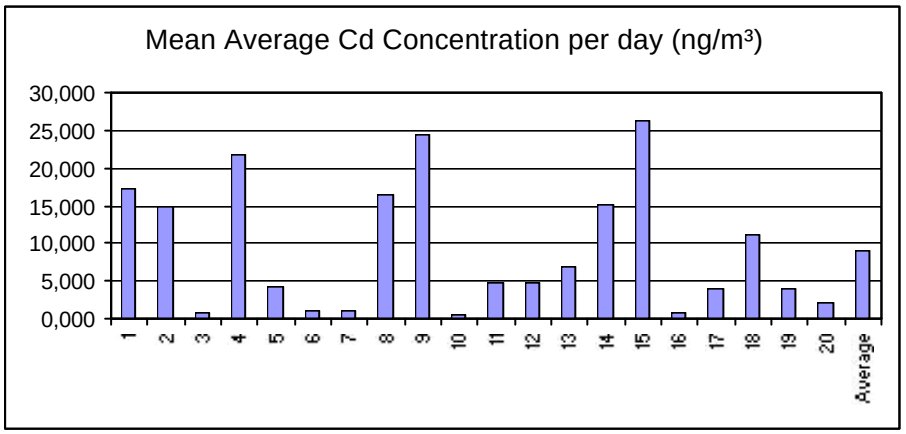
Figures 21 till24 below show daily mean concentrations of Pb, Cd, As and Ni in ambient air as determined per collecting day during the field test in Hoboken (Antwerpen).

Figure 21.



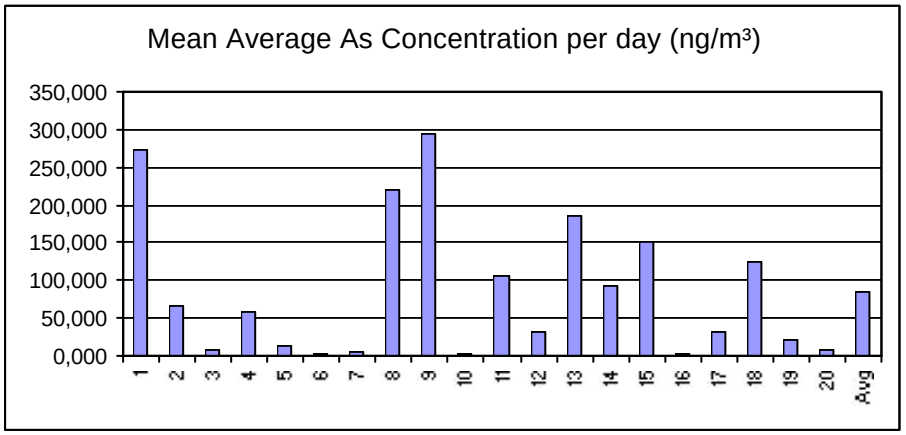
The average daily mean concentration of Pb is 914,8 ng/m³. The lowest and highest daily mean values are 22,24 ng/m³ and 3308 ng/m³.

Figure 22.



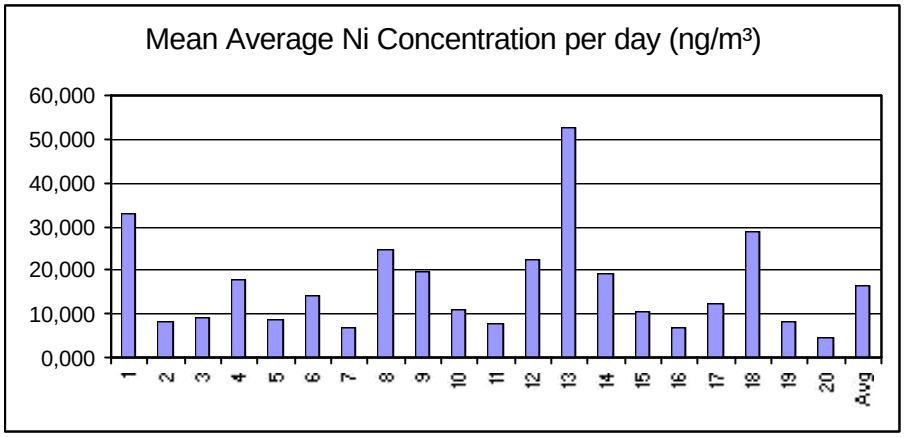
The average daily mean concentration of Cd is 9,135 ng/m³. The lowest and highest daily mean values are 0,591 ng/m³ and 26,34 ng/m³.

Figure 23.



The average mean concentration of As is 84,96 ng/m³. The lowest and highest daily mean values are 1,589 ng/m³ and 295,1 ng/m³.

Figure 24.



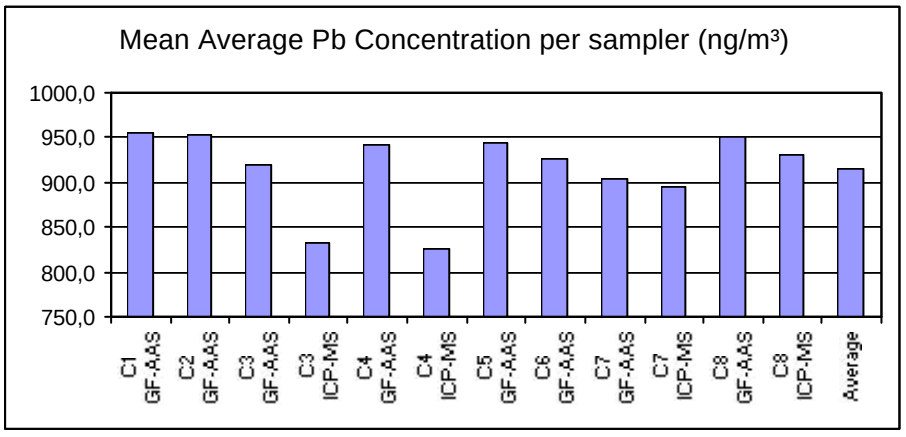
The average mean concentration of Ni is 16,36 ng/m³. The lowest and highest daily mean values are 4,609 ng/m³ and 52,58 ng/m³.

During the sampling period the highest Pb, Cd, As and Ni concentrations were found in the sample 9 (sampling date 21/ 11/2001),15 (sampling date 29/11/2001), 9 (sampling date 21/11/2001) and 13 (27/11/2001). These days the wind was coming from the SW direction.

During the sampling period the lowest Pb, Cd, As and Ni concentrations were found in the sample 6 (sampling date 13/ 11/2001 – windsector' N),10 (sampling date 22/11/2001 – windsector W), 10 (sampling date 22/11/2001) and 20 (16/12/2001 – windsector NE).

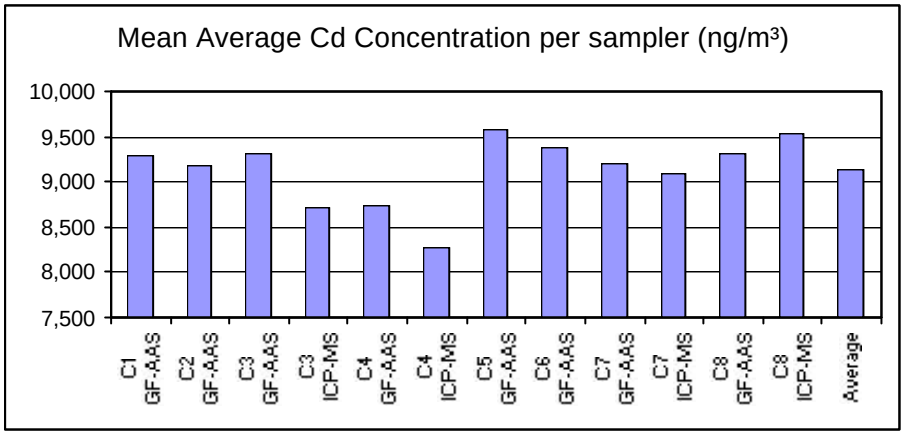
Figures 25 till 28 below show the average mean concentrations during the sampling period of 20 samples at each individual sampler. The abbreviations explained in the tables are used.

Figure 25.



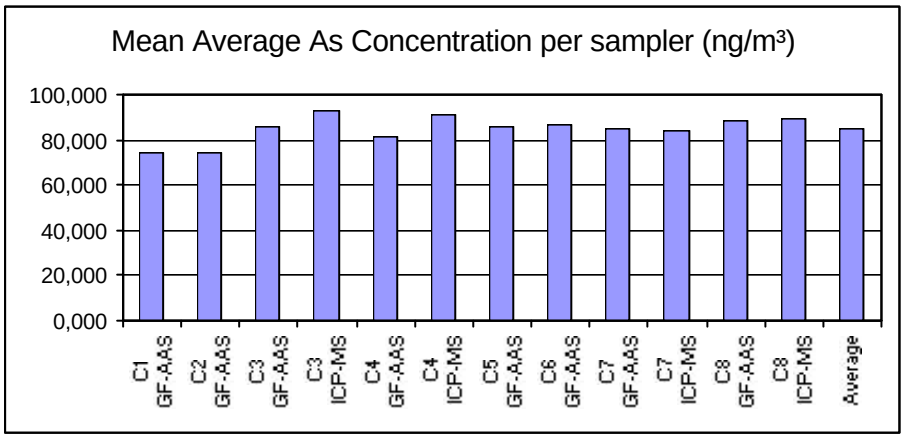
The average mean concentration of Pb is 914,8 ng/m³. The lowest and highest mean value, 824,9 ng/m³ (ICP-MS) and 955,0 ng/m³, is found with the sampler C4 and C1.

Figure 26.



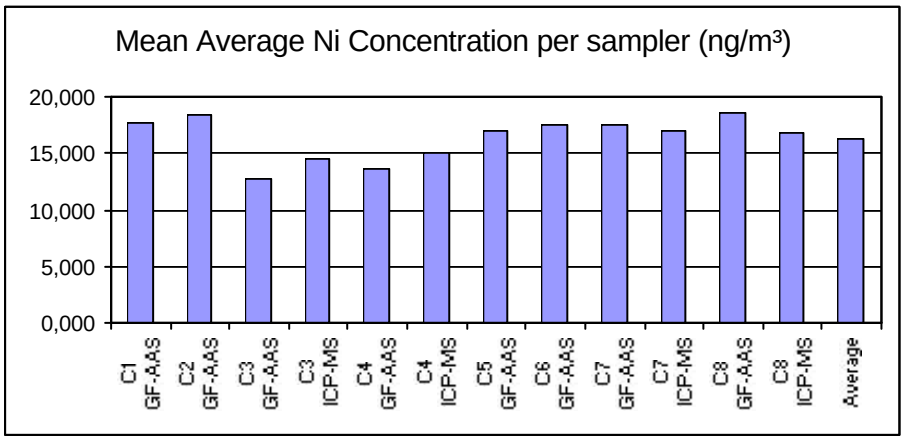
The average mean concentration of Cd is 9,135 ng/m³. The lowest and highest mean value, 8,285 (ICP-MS) ng/m³ and 9,580 ng/m³ , is found with the sampler C4 and C5.

Figure 27.



The average mean concentration of As is 84,96 ng/m³. The lowest and highest mean value, 74,01 ng/m³ and 92,93 ng/m³ (ICP-MS), is found with the sampler C2 and C3.

Figure 28.



The average mean concentration of Ni is 16,36 ng/m³. The lowest and highest mean value, 12,70 (GF-AAS) and 18,58 ng/m³ (GF-AAS), is found with the sampler C3 and C8.

4.6. Data calculations/ interpretation/ comparison of results

4.6.1. QA/QC results

4.6.1.1. Comparison blanks

Tables 5 till 7 below show concentrations of Pb, Cd, As and Ni in blanks as determined by the participating laboratories.

Table 5. Summary : Reagent Blanks

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	Quartz	GF-AAS	*0,568*	0,307	*0,025*	0,054	*0,000*	0,041	*0,725*	0,291
Lab-B	Membrane	GF-AAS	***-0,523***	0,269	***-0,088***	0,015	***0,000***	0,061	***-0,655***	0,080
Lab-C	Membrane	GF-AAS	***0,332***	0,121	***0,014***	0,007	***-0,072***	0,055	***0,436***	0,333
Lab-D	Quartz	GF-AAS	***0,121***	0,052	***0,001***	0,007	***-0,178***	0,053	***0,452***	0,338
Lab-B	Membrane	ICP-MS	0,120	0,100	0,009	0,010	***0,023***	0,031	0,051	0,065
Lab-D	Quartz	ICP-MS	0,253	0,082	0,016	0,012	***-0,320***	0,064	0,606	0,277

Table 6 : Summary : Filter Blanks

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	Quartz	GF-AAS	0,810	0,335	-0,040	0,034	-0,125	0,165	1,093	0,610
Lab-B	Membrane	GF-AAS	***0,132***	0,574	***-0,092***	0,051	***0,005***	0,144	***-0,386***	0,191
Lab-C	Membrane	GF-AAS	***0,345***	0,101	***0,022***	0,002	***-0,005***	0,054	***0,461***	0,167
Lab-D	Quartz	GF-AAS	***0,371***	0,035	***0,003***	0,009	***-0,162***	0,050	***0,909***	0,306
Lab-B	Membrane	ICP-MS	0,377	0,346	0,014	0,014	0,146	0,013	0,310	0,198
Lab-D	Quartz	ICP-MS	0,529	0,023	***0,012***	0,012	***-0,317***	0,071	1,080	0,172

Table 7: Summary : Field Filter Blanks

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	Quartz	GF-AAS	0,918	0,356	-0,070	0,032	-0,360	0,154	1,068	0,177
Lab-B	Membrane	GF-AAS	***0,705***	0,568	***-0,096***	0,017	***0,091***	0,074	***-0,032***	0,164
Lab-C	Membrane	GF-AAS	0,912	0,278	***0,024***	0,004	***-0,316***	0,211	1,458	1,267
Lab-D	Quartz	GF-AAS	1,176	0,465	***0,002***	0,010	***-0,057***	0,106	2,634	1,098
Lab-B	Membrane	ICP-MS	0,941	0,470	0,011	0,005	0,108	0,035	0,723	0,075
Lab-D	Quartz	ICP-MS	1,408	0,751	0,022	0,018	***0,091***	0,296	2,475	0,757

The Pb and Ni concentrations in the field blanks are sometimes higher then the AAS detection limits. The values reported from the ICP-MS analysis are mostly higher then the reported LOD's.

4.6.1.2. Comparison CRM's: NIST 1648 and NIES N°8

Looking to the individual data included in Annex 7 we see that the AAS recoveries from NIST 1648 set by CEN/TC264/WG14, i.e. within 90-110% for Pb and Cd and within 85-115% for As and Ni, are generally met. For Pb and Cd lab B and for Cd lab D reports some slightly higher individual data.
The targets are generally also met with the CRM NIES N°8. Except lab B reports one very high Cd result (NIES 2) with both techniques (AAS 156% and ICP 140%). Lab B and lab D report some As and Ni recoveries out of the range 85-115%.

Tables 8 and 9 show 'mean' recovery rates for the certified reference materials CRM's°.

Table 8:Summary : NIST 1684

Laboratory sampler	Filter material	Analytical technique	Determinant							
			Pb		Cd		As		Ni	
			6550 +/- 80 mg/kg		75 +/- 7 mg/kg		115 +/- 10 mg/kg		82 +/- 3 mg/kg	
			%	mg/kg	%	Mg/kg	%	mg/kg	%	mg/kg
Lab-A	Quartz	GF-AAS	97,9	6415,0	96,7	72,6	104,8	120,6	93,7	76,8
Lab-B	Membrane	GF-AAS	107,0	7011,0	106,8	80,1	105,2	121,0	97,0	79,6
Lab-C	Membrane	GF-AAS	99,6	6527,0	98,0	73,5	106,8	122,8	97,0	79,9
Lab-D	Quartz	GF-AAS	103,9	6804,0	103,3	77,5	109,0	125,3	99,5	81,6
Lab-B	Membrane	ICP-MS	100,3	6572,0	104,4	78,3	111,8	128,5	98,4	80,7
Lab-D	Quartz	ICP-MS	105,6	6914,0	105,0	78,7	109,3	125,7	101,0	82,8

The recovery rates for Pb, Cd, As and Ni in the certified reference material NIST 1648 are within the ranges, between 90-110% for Pb and Cd and 85-115% for As and Ni.

Table 9 :Summary : NIES N°8

Laboratory sampler	Filter material	Analytical technique	Determinant							
			Pb		Cd		As		Ni	
			219 +/- 9 mg/kg		1,1 +/- 0,1 mg/kg		2,6 +/- 0,2 mg/kg		18,5 +/- 1,5 mg/kg	
			%	mg/kg	%	Mg/kg	%	Mg/kg	%	mg/kg
Lab-A	Quartz	GF-AAS	103,0	226,0	96,6	1,1	107,8	2,8	93,7	17,3
Lab-B	Membrane	GF-AAS	102,1	224,0	110,3	1,2	85,4	2,2	88,1	16,3
Lab-C	Membrane	GF-AAS	100,2	219,0	92,5	1,0	110,9	2,9	98,2	18,2
Lab-D	Quartz	GF-AAS	101,3	222,0	91,1	1,0	**116,4**	3,0	86,0	15,9
Lab-B	Membrane	ICP-MS	100,3	220,0	100,6	1,1	111,9	2,9	83,7	15,5
Lab-D	Quartz	ICP-MS	104,0	228,0	100,0	1,1	**123,2**	3,2	87,1	16,1

The recovery rates for Pb, Cd, As and Ni in the certified reference material NIES N°8 are also within the ranges for NIST 1648. Only lab D-AAS and D- ICP-MS reported for As a slightly higher recovery.

4.6.2. Real samples

4.6.2.1. Comparison samplers (expressed in air concentrations (ng/m³))

- Comparison samplers lab A - Pb, As, Ni, Cd – Annex 10
- Comparison samplers lab B - Pb, As, Ni, Cd – Annex 11
- Comparison samplers lab C - Pb, As, Ni, Cd – Annex 12
- Comparison samplers lab D - Pb, As, Ni, Cd – Annex 13

The comparison of two parallel running samplers for one laboratory gives generally a good agreement. With exception of the Ni data set of laboratory D AAS and ICP-MS, the linear regressions show an agreement better then 10% and for the parameters As Pb and Cd most laboratories can reach the 5 % level.

4.6.2.2. Comparison of GF-AAS /ICP-MS data

- Pb, As, Ni, Cd - Annex 14 A B C and D

The comparison between AAS and ICP-MS for sampler 3 and 4 is within the 25 % range.
The comparison between AAS and ICP-MS for sampler 7 and 8 is within the 5 % range , with exception of sampler C8 Ni (y=0,84x+1.24).

The comparison between two individual samplers and the analytical techniques , performed by one laboratory, shows that generally the analytical method has the greatest 'uncertainty' budget.

Conclusions

During the twenty days field test of Hoboken a mean value of 915,8 ng/m³ for Pb , 9,135 ng/m³ for Cd, 84,96 ng/m³ for As and 16,36 ng/m³ for Ni was measured with the 8 Low Volume Reference Samplers.

According to other field tests some participating labs found with AAS detectable Ni and As blank values in the field filter blanks. All laboratories generally found recoveries for the NIST 1648 and NIES N°8 within the ranges set by the CEN WG14, e.g. between 90-110% for Pb and Cd and 85-115% for As and Ni.

Annexes from 1 to 14

ANNEXES

Final version 05-03-02

ANNEX 1

Calibration Samplers CEN-TESTS - 25 OCTOBER 2001											
	Act. Flow		Difference				After calibration		Difference		
Sampler	(l/min)	m³/h	(l/min)	(m³/h)	Dif. (%)		(l/min)	m³/h	(l/min)	(m³/h)	Dif. (%)
C1	37,42	2,25	-0,910	-0,055	-2,37%	*	37,91	2,27	-0,420	-0,025	-1,10%
C2	37,64	2,26	-0,690	-0,041	-1,80%	*	38,22	2,29	-0,110	-0,007	-0,29%
C3	38,09	2,29	-0,240	-0,014	-0,63%	OK					
C4	38,43	2,31	0,100	0,006	0,26%	OK					
C5	38,95	2,34	0,620	0,037	1,62%	*	38,82	2,33	0,490	0,029	1,28%
C6	38,77	2,33	0,440	0,026	1,15%	OK					
C7	38,42	2,31	0,090	0,005	0,23%	OK					
C8	38,1	2,29	-0,230	-0,014	-0,60%	OK					
C9	38,35	2,30	0,020	0,001	0,05%	OK					
C10	37,42	2,25	-0,910	-0,055	-2,37%	*	37,95	2,28	-0,380	-0,023	-0,99%
DG1	490	29,40	-10,000	-0,600	-2,00%	OK					
DG2	490	29,40	-10,000	-0,600	-2,00%	OK					
LK1	38,33	2,30	0,000	0,000	0,00%	OK					
LK2	38,41	2,30	0,080	0,005	0,21%	OK					
LK3	38,33	2,30	0,000	0,000	0,00%	OK					
LK4	38,41	2,30	0,080	0,005	0,21%	OK					
PP1	16,69	1,00	0,020	0,001	0,12%	OK					
PP2	16,63	1,00	-0,040	-0,002	-0,24%	OK					

FLOW-CHECK Samplers CEN-TESTS - 09 NOVEMBER 2001											
	Act. Flow		**Difference**				**After calibration**		**Difference**		
Sampler	**(l/min)**	**m³/h**	**(l/min)**	**(m³/h)**	**Dif. (%)**		**(l/min)**	**m³/h**	**(l/min)**	**(m³/h)**	**Dif. (%)**
C1	38,05	2,28	-0,280	-0,017	-0,73%	**OK**					
C2	38,58	2,31	0,250	0,015	0,65%	**OK**					
C3	38,1	2,29	-0,230	-0,014	-0,60%	**OK**					
C4	38,1	2,29	-0,230	-0,014	-0,60%	**OK**					
C5	38,35	2,30	0,020	0,001	0,05%	**OK**					
C6	38	2,28	-0,330	-0,020	-0,86%	**OK**					
C7	38,2	2,29	-0,130	-0,008	-0,34%	**OK**					
C8	39,16	2,35	0,830	0,050	2,17%	**OK**					
C9	38,54	2,31	0,210	0,013	0,55%	**OK**					
C10	38,83	2,33	0,500	0,030	1,30%	**OK**					
		0,00		0,000							
LK1	38,45	2,31	0,120	0,007	0,31%	**OK**					
LK2	38,3	2,30	-0,030	-0,002	-0,08%	**OK**					
LK3	38,07	2,28	-0,260	-0,016	-0,68%	**OK**					
		0,00		0,000							
PP1	17,31	1,04	0,640	0,038	3,84%	*	16,65	1,00	-0,020	-0,001	-0,12%
PP2	17,31	1,04	0,640	0,038	3,84%	*	16,63	1,00	-0,040	-0,002	-0,24%

FLOW-CHECK Samplers CEN-TESTS - 10 DECEMBER 2001

	Act. Flow		Difference				After calibration		Difference			
Sampler	(l/min)	m³/h	(l/min)	(m³/h)	Dif. (%)		(l/min)	m³/h	(l/min)	(m³/h)	Dif. (%)	
C1	37,14	2,23	-1,190	-0,071	-3,10%	*	37,95	2,28	-0,380	-0,023	-0,99%	
C2	37,54	2,25	-0,790	-0,047	-2,06%	OK						
C3	36,59	2,20	-1,740	-0,104	-4,54%	*	37,89	2,27	-0,440	-0,026	-1,15%	
C4	36,31	2,18	-2,020	-0,121	-5,27%	*	37,96	2,28	-0,370	-0,022	-0,97%	
C5	36,6	2,20	-1,730	-0,104	-4,51%	*	38,15	2,29	-0,180	-0,011	-0,47%	
C6	37,3	2,24	-1,030	-0,062	-2,69%		37,96	2,28	-0,370	-0,022	-0,97%	
C7	37,14	2,23	-1,190	-0,071	-3,10%	*	37,2	2,23	-1,130	-0,068	-2,95%	
C8	36,9	2,21	-1,430	-0,086	-3,73%	*	38,19	2,29	-0,140	-0,008	-0,37%	
C9	38,05	2,28	-0,280	-0,017	-0,73%	OK						
C10	37,43	2,25	-0,900	-0,054	-2,35%	*	38,23	2,29	-0,100	-0,006	-0,26%	
DG1	500	30,00	-30,000	-1,800	-5,66%	OK						
DG2	500	30,00	-30,000	-1,800	-5,66%	OK						
LK1	41,2	2,47	2,870	0,172	7,49%	*	38,36	2,30	0,030	0,002	0,08%	
LK2	41,4	2,48	3,070	0,184	8,01%	*	38,29	2,30	-0,040	-0,002	-0,10%	
LK3	39,8	2,39	1,470	0,088	3,84%	*	38,4	2,30	0,070	0,004	0,18%	

FLOW-CHECK Samplers CEN-TESTS - 20 DECEMBER 2001

	Act. Flow		Difference				After calibration		Difference			
Toestel	**(l/min)**	**m³/h**	**(l/min)**	**(m³/h)**	**Dif. (%)**		**(l/min)**	**m³/h**	**(l/min)**	**(m³/h)**	**Dif. (%)**	
C1	39,35	2,36	1,020	0,061	2,66%	*	38,35	2,30	0,020	0,001	0,05%	
C2	38,71	2,32	0,380	0,023	0,99%	OK						
C3	38,9	2,33	0,570	0,034	1,49%	OK						
C4	38,54	2,31	0,210	0,013	0,55%	OK						
C5	39,07	2,34	0,740	0,044	1,93%	OK						
C6	39,04	2,34	0,710	0,043	1,85%	OK						
C7	38,35	2,30	0,020	0,001	0,05%	OK						
C8	39,38	2,36	1,050	0,063	2,74%	*	38,53	2,31	0,200	0,012	0,52%	
C9	38,94	2,34	0,610	0,037	1,59%	OK						
C10	39,29	2,36	0,960	0,058	2,50%	*	38,19	2,29	-0,140	-0,008	-0,37%	
DG1	500	30,00	-35,000	-2,100	-6,54%	OK						
DG2	500	30,00	-30,000	-1,800	-5,66%	OK						
LK1	36	2,16	-2,330	-0,140	-6,08%	*	38,42	2,31	0,090	0,005	0,23%	
LK2	35,71	2,14	-2,620	-0,157	-6,84%	*	38,35	2,30	0,020	0,001	0,05%	
LK3	36,47	2,19	-1,860	-0,112	-4,85%	*	38,4	2,30	0,070	0,004	0,18%	
PP2	16,3	0,98	-0,370	-0,022	-2,22%	*	16,8	1,01	0,130	0,008	0,78%	
PP3	16,96	1,02	0,290	0,017	1,74%	OK						

ANNEX 2

			WG14 - Field Validation Programme					
			Meteorological Conditions					
Sampling Site:	Madrid (A)	Antwerp (C)						
	Bristol (B)	Berlin (D)						
	Preliminary Field Tests (P)							
Date	T min	T max	Mean T	Atm Pre	Wind	Wind Sector	Rain, Snow, Fog	Comments
	(°C)	(°C)	(°C)	(hPa)	(m/s)	(N/E/S/W)	(R), (S), (F)	
6-11-01	7,6	13,0	10,5	1012,8	5,6	SW	R	
7-11-01	9,2	12,3	11,1	1007,1	5,2	W	R	
8-11-01	4,0	10,5	7,5	995,7	5,9	NW	R	
11-11-01	3,1	7,7	5,7	1024,5	3,0	SW	0	
12-11-01	7,9	11,7	9,9	1014,9	2,7	W	R	
13-11-01	3,9	9,4	6,4	1019,5	3,9	N	R	
18-11-01	3,2	8,5	5,6	1024,7	2,5	NE	0	
20-11-01	3,4	9,9	7,4	1030,4	2,5	SW	0	
21-11-01	7,9	10,4	8,9	1027,8	7,0	SW	0	
22-11-01	4,6	11,0	8,1	1017,7	6,1	W	R	
25-11-01	10,2	12,5	11,0	1016,6	3,7	SW	R	
26-11-01	1,8	9,8	6,9	1013,2	1,8	N	R	
27-11-01	0,5	7,8	5,2	1010,5	3,9	SW	R	
28-11-01	6,3	9,7	7,6	1015,8	4,3	W	0	
29-11-01	6,5	11,3	9,0	1014,6	5,9	SW	R	
2-12-01	4,5	9,3	7,0	1025,0	2,0	NE	R	
3-12-01	7,6	10,4	9,1	1021,1	2,3	SE	R	
4-12-01	8,3	11,8	10,1	1013,5	6,0	SW	R	
5-12-01	6,9	12,8	9,2	1016,3	6,5	SW	R	
16-12-01	-3,4	2,4	0,0	1038,5	3,7	NE	0	

		QA/QC Volume /Flow - Registration				
	Sampling Site:	Madrid (A)	Antwerp (C)	Operator:	PB - IN - RDL	
		Bristol (B)	Berlin (D)			
		Preliminary Field Tests (P)				
	Sampler - No.:	1				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,27	-0,025	-1,10%	yes
	2	09-11-01	2,28	-0,017	-0,73%	no
	3	10-12-01	2,28	-0,023	-0,99%	yes
	4	20-12-01	2,30	0,000	0,00%	yes
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
	Sampler - No.:	2				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,29	-0,007	-0,29%	yes
	2	09-11-01	2,31	0,015	0,65%	no
	3	10-12-01	2,25	-0,047	-2,06%	no
	4	20-12-01	2,32	0,023	0,99%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
		N° 3 (10-12-01) : no better adjusment was possible.				

		QA/QC Volume /Flow - Registration				
	Sampling Site:	Madrid (A)	Antwerp (C)	Operator:	PB - IN - RDL	
		Bristol (B)	Berlin (D)			
		Preliminary Field Tests (P)				
	Sampler - No.:	3				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,29	-0,014	-0,63%	no
	2	09-11-01	2,29	-0,014	-0,60%	no
	3	10-12-01	2,27	-0,026	-1,15%	yes
	4	20-12-01	2,33	0,034	1,49%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
	Sampler - No.:	4				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,31	0,006	0,26%	no
	2	09-11-01	2,29	-0,014	-0,60%	no
	3	10-12-01	2,18	-0,022	-0,27%	yes
	4	20-12-01	2,31	0,013	0,55%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					

		QA/QC Volume /Flow - Registration				
	Sampling Site:	Madrid (A)	Antwerp (C)	Operator:	PB - IN - RDL	
		Bristol (B)	Berlin (D)			
		Preliminary Field Tests (P)				
	Sampler - No.:	5				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,33	0,029	1,28%	yes
	2	09-11-01	2,30	0,000	0,00%	no
	3	10-12-01	2,29	-0,011	-0,47%	yes
	4	20-12-01	2,34	0,044	1,93%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
	Sampler - No.:	6				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,33	0,026	1,15%	no
	2	09-11-01	2,28	-0,020	-0,86%	no
	3	10-12-01	2,28	-0,022	-0,97%	yes
	4	20-12-01	2,34	0,043	1,85%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					

		QA/QC Volume /Flow - Registration				
	Sampling Site:	Madrid (A)	Antwerp (C)	Operator:	PB - IN - RDL	
		Bristol (B)	Berlin (D)			
		Preliminary Field Tests (P)				
	Sampler - No.:	7				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,31	0,005	0,23%	no
	2	09-11-01	2,29	-0,008	-0,34%	no
	3	10-12-01	2,23	-0,068	-2,95%	yes
	4	20-12-01	2,30	0,000	0,00%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
		N° 3 (10-12-01) : no better adjusment was possible.				
	Sampler - No.:	8				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,29	-0,014	-0,60%	no
	2	09-11-01	2,35	0,050	2,17%	no
	3	10-12-01	2,29	-0,008	-0,37%	yes
	4	20-12-01	2,31	0,012	0,52%	yes
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
		N° 2 (09-11-01) : no better adjustment was possible				

		QA/QC Volume /Flow - Registration				
	Sampling Site:	Madrid (A)	Antwerp (C)	Operator:	PB - IN - RDL	
		Bristol (B)	Berlin (D)			
		Preliminary Field Tests (P)				
	Sampler - No.:	9				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,30	0,000	0,00%	no
	2	09-11-01	2,31	0,013	0,55%	no
	3	10-12-01	2,28	-0,017	-0,73%	no
	4	20-12-01	2,34	0,037	1,59%	no
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					
	Sampler - No.:	10				
	Required Air Flow:	2.30 m³/h		Date:	10-01-02	
Flow Check (Rotameter):						
	No.	Date	Actual flow	Difference	Difference	Adjusted
		(dd/mm/yy)	(m³/h)	(m³/h)	(%)	yes / no
	1	25-10-01	2,28	-0,023	-0,99%	yes
	2	09-11-01	2,33	0,030	1,30%	no
	3	10-12-01	2,29	-0,006	-0,26%	yes
	4	20-12-01	2,29	-0,008	-0,37%	yes
	Remark: The air flow has to be checked, if the difference is > 0.046 m³/h					

ANNEX 3

			WG14 - Field Validation Programme									
				Sampling form								
Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C	Technique		AAS	
	Bristol (B)	Berlin (D)					B	D			ICP-MS	
	Preliminary Field Tests (P)											
Sampler No.:	1					Filter Material:		Membrane	Quartz			

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-1-1	C-10-1	06-11-01	9:30	55,20	52,82	RDL-PB	Filter C-1-1 damaged, replaced by C-10-1
C-1-2	C-1-2	07-11-01	10:30	55,04	52,25	PB-IN	
C-1-3	C-1-3	08-11-01	11:30	55,14	53,66	PB-RDL	
C-1-4	C-1-4	11-11-01	9:30	54,07	52,18	PB-IN	
C-1-5	C-1-5	12-11-01	10:30	55,18	53,42	RDL-PB-IN	
C-1-6	C-1-6	13-11-01	11:30	55,14	54,54	PB-RDL-DF	
C-1-7	C-1-7	18-11-01	9:30	55,16	54,35	JV-RDL-IN	
C-1-8	C-1-9	20-11-01	11:30	55,18	54,40	IN-JV-RDL	
C-1-9	C-1-10	21-11-01	12:30	55,13	53,71	IN-JV	
C-1-10	C-1-11	22-11-01	13:30	55,03	54,38	PB-RDL-DF	
C-1-11	C-1-12	25-11-01	9:30	55,12	53,17	PB-IN	
C-1-12	C-1-13	26-11-01	10:30	55,07	54,23	RDL-PB-DF	
C-1-13	C-1-14	27-11-01	11:30	55,15	53,63	RDL-PB-IN	
C-1-14	C-1-15	28-11-01	12:30	55,21	54,04	PB-IN	
C-1-15	C-1-16	29-11-01	13:30	55,10	52,72	PB-IN	
C-1-16	C-1-17	02-12-01	9:30	55,10	54,20	PB-IN-DF	
C-1-17	C-1-18	03-12-01	10:30	55,00	53,17	PB-RDL-DF	
C-1-18	C-1-19	04-12-01	11:30	55,25	53,81	PB-RDL-DF	
C-1-19	C-1-20	05-12-01	12:30	55,18	53,55	PB-RDL-DF	
C-1-20	C-1-25	16-12-01	9:30	55,09	56,48	PB-IN-DF	

			WG14 - Field Validation Programme								
				Sampling form							
Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C	Technique	AAS	
	Bristol (B)	Berlin (D)					B	D		ICP-MS	
	Preliminary Field Tests (P)										
Sampler No.:	2					Filter Material:		Membrane	Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-2-1	C-2-1	06-11-01	9:30	55,12	52,97	RDL-PB	
C-2-2	C-2-2	07-11-01	10:30	55,05	52,46	PB-IN	
C-2-3	C-2-3	08-11-01	11:30	55,26	54,05	PB-RDL	
C-2-4	C-2-4	11-11-01	9:30	55,00	54,16	PB-IN	
C-2-5	C-2-5	12-11-01	10:30	55,19	53,61	RDL-PB-IN	
C-2-6	C-2-6	13-11-01	11:30	55,21	54,77	PB-RDL-DF	
C-2-7	C-2-7	18-11-01	9:30	55,08	54,46	JV-RDL-IN	
C-2-8	C-2-9	20-11-01	11:30	55,12	54,57	IN-JV-RDL	
C-2-9	C-2-10	21-11-01	12:30	54,98	53,78	IN-JV	
C-2-10	C-2-11	22-11-01	13:30	55,14	54,71	PB-RDL-DF	
C-2-11	C-2-12	25-11-01	9:30	55,13	53,36	PB-IN	
C-2-12	C-2-13	26-11-01	10:30	55,16	54,60	RDL-PB-DF	
C-2-13	C-2-14	27-11-01	11:30	55,05	53,68	RDL-PB-IN	
C-2-14	C-2-15	28-11-01	12:30	54,99	53,96	PB-IN	
C-2-15	C-2-16	29-11-01	13:30	55,06	52,79	PB-IN	
C-2-16	C-2-17	02-12-01	9:30	55,02	54,28	PB-IN-DF	
C-2-17	C-2-18	03-12-01	10:30	55,06	53,45	PB-RDL-DF	
C-2-18	C-2-19	04-12-01	11:30	55,17	53,86	PB-RDL-DF	
C-2-19	C-2-20	05-12-01	12:30	55,18	53,73	PB-RDL-DF	
C-2-20	C-2-25	16-12-01	9:30	55,18	56,76	PB-IN-DF	

WG14 - Field Validation Programme

Sampling form

Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C	Technique	AAS	
	Bristol (B)	Berlin (D)					B	D		ICP-MS	
	Preliminary Field Tests (P)										
Sampler No.:	3					Filter Material:		Membrane	Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-3-1	C-3-1	06-11-01	9:30	55,15	52,64	RDL-PB	
C-3-2	C-3-2	07-11-01	10:30	55,13	52,30	PB-IN	
C-3-3	C-3-3	08-11-01	11:30	55,20	53,43	PB-RDL	
C-3-4	C-3-4	11-11-01	9:30	55,04	54,03	PB-IN	
C-3-5	C-3-5	12-11-01	10:30	55,16	52,94	RDL-PB-IN	
C-3-6	C-3-6	13-11-01	11:30	55,16	53,72	PB-RDL-DF	
C-3-7	C-3-7	18-11-01	9:30	55,11	55,46	JV-RDL-IN	
C-3-8	C-3-9	20-11-01	11:30	55,15	53,62	IN-JV-RDL	
C-3-9	C-3-10	21-11-01	12:30	55,14	53,08	IN-JV	
C-3-10	C-3-11	22-11-01	13:30	55,15	53,76	PB-RDL-DF	
C-3-11	C-9-12	25-11-01	9:30	55,17	52,92	PB-IN	Filter C-3-12 sampled only 9h47, replaced by C-9-12
C-3-12	C-3-13	26-11-01	10:30	55,04	53,61	RDL-PB-DF	
C-3-13	C-3-14	27-11-01	11:30	55,12	52,92	RDL-PB-IN	
C-3-14	C-3-15	28-11-01	12:30	55,06	53,14	PB-IN	
C-3-15	C-3-16	29-11-01	13:30	47,77	45,21	PB-IN	Filter C-3-16 sampled only 20h50, filter C-9-16 was wet
C-3-16	C-3-17	02-12-01	9:30	55,11	53,20	PB-IN-DF	
C-3-17	C-3-18	03-12-01	10:30	55,08	52,65	PB-RDL-DF	
C-3-18	C-9-19	04-12-01	11:30	55,17	53,41	PB-RDL-DF	Filter C-3-19 sampled only 21h05, replaced by C-9-19
C-3-19	C-3-20	05-12-01	12:30	55,25	52,86	PB-RDL-DF	
C-3-20	C-3-25	16-12-01	9:30	55,09	55,05	PB-IN-DF	

Filter Code: Site - Sampler No. - Filter

				WG14 - Field Validation Programme								
					Sampling form							
Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C		Technique	AAS	
	Bristol (B)	Berlin (D)					B	D			ICP-MS	
	Preliminary Field Tests (P)											
Sampler No.:	4					Filter Material:		Membrane		Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-4-1	C-4-1	06-11-01	9:30	55,18	53,05	RDL-PB	
C-4-2	C-4-2	07-11-01	10:30	55,14	52,45	PB-IN	
C-4-3	C-4-3	08-11-01	11:30	55,2	53,91	PB-RDL	
C-4-4	C-4-4	11-11-01	9:30	54,95	53,9	PB-IN	Filter C-4-4 sampled only 12h05, replaced by C-9-4
C-4-5	C-4-5	12-11-01	10:30	55,15	53,51	RDL-PB-IN	
C-4-6	C-4-6	13-11-01	11:30	55,16	54,66	PB-RDL-DF	
C-4-7	C-4-7	18-11-01	9:30	55,09	54,44	JV-RDL-IN	
C-4-8	C-4-9	20-11-01	11:30	55,14	54,54	IN-JV-RDL	
C-4-9	C-9-10	21-11-01	12:30	55,16	53,42	IN-JV	Filter C-4-10 was wet, replaced by C-9-10
C-4-10	C-9-11	22-11-01	13:30	55,16	54,22	PB-RDL-DF	Filter C-4-11 was wet, replaced by C-9-11
C-4-11	C-4-12	25-11-01	9:30	55,10	53,28	PB-IN	
C-4-12	C-4-13	26-11-01	10:30	55,09	54,46	RDL-PB-DF	
C-4-13	C-4-14	27-11-01	11:30	55,14	53,74	RDL-PB-IN	
C-4-14	C-4-15	28-11-01	12:30	55,04	53,95	PB-IN	
C-4-15	C-4-16	29-11-01	13:30	55,04	52,73	PB-IN	
C-4-16	C-4-17	02-12-01	9:30	55,10	54,28	PB-IN-DF	
C-4-17	C-4-18	03-12-01	10:30	55,08	53,41	PB-RDL-DF	
C-4-18	C-4-19	04-12-01	11:30	55,16	53,82	PB-RDL-DF	
C-4-19	C-4-20	05-12-01	12:30	55,20	53,70	PB-RDL-DF	
C-4-20	C-4-25	16-12-01	9:30	55,01	56,49	PB-IN-DF	

			WG14 - Field Validation Programme								
				Sampling form							
Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C	Technique	AAS	
	Bristol (B)	Berlin (D)					B	D		ICP-MS	
	Preliminary Field Tests (P)										
Sampler No.:	5					Filter Material:		Membrane	Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-5-1	C-5-1	06-11-01	9:30	55,12	52,83	RDL-PB	
C-5-2	C-5-2	07-11-01	10:30	55,17	52,35	PB-IN	
C-5-3	C-5-3	08-11-01	11:30	55,19	53,75	PB-RDL	
C-5-4	C-5-4	11-11-01	9:30	55,01	53,92	PB-IN	
C-5-5	C-5-5	12-11-01	10:30	55,16	53,34	RDL-PB-IN	Filter C-5-5 wet, filter C-9-5 not sampled
C-5-6	C-5-6	13-11-01	11:30	55,17	54,52	PB-RDL-DF	
C-5-7	C-5-7	18-11-01	9:30	55,11	54,24	JV-RDL-IN	
C-5-8	C-5-9	20-11-01	11:30	55,10	54,30	IN-JV-RDL	
C-5-9	C-5-10	21-11-01	12:30	55,04	53,60	IN-JV	
C-5-10	C-5-11	22-11-01	13:30	55,10	54,44	PB-RDL-DF	
C-5-11	C-5-12	25-11-01	9:30	55,10	53,10	PB-IN	
C-5-12	C-5-13	26-11-01	10:30	55,07	54,19	RDL-PB-DF	
C-5-13	C-5-14	27-11-01	11:30	55,11	53,56	RDL-PB-IN	
C-5-14	C-5-15	28-11-01	12:30	54,99	53,80	PB-IN	
C-5-15	C-5-16	29-11-01	13:30	55,06	52,60	PB-IN	
C-5-16	C-5-17	02-12-01	9:30	55,07	54,15	PB-IN-DF	
C-5-17	C-5-18	03-12-01	10:30	55,13	53,27	PB-RDL-DF	
C-5-18	C-5-19	04-12-01	11:30	55,04	53,60	PB-RDL-DF	
C-5-19	C-5-20	05-12-01	12:30	55,26	53,63	PB-RDL-DF	
C-5-20	C-9-25	16-12-01	9:30	47,08	47,89	PB-IN-DF	Sampler C5 did not start, filter C-9-25 only sampled 20h29

			WG14 - Field Validation Programme									
				Sampling form								
Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C		Technique	AAS	
	Bristol (B)	Berlin (D)					B	D			ICP-MS	
	Preliminary Field Tests (P)											
Sampler No.:	6					Filter Material:		Membrane		Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m³)	(m³) Std.Cond.		
C-6-1	C-6-1	06-11-01	9:30	55,17	53,69	RDL-PB	
C-6-2	C-6-2	07-11-01	10:30	55,12	53,11	PB-IN	
C-6-3	C-6-3	08-11-01	11:30	55,17	54,27	PB-RDL	
C-6-4	C-6-4	11-11-01	9:30	55,12	54,19	PB-IN	
C-6-5	C-6-5	12-11-01	10:30	55,14	53,56	RDL-PB-IN	
C-6-6	C-6-6	13-11-01	11:30	55,20	54,85	PB-RDL-DF	
C-6-7	C-9-7	18-11-01	9:30	55,15	54,08	JV-RDL-IN	Filter C-6-7 sampled only 13h07, replaced by C-9-7
C-6-8	C-6-9	20-11-01	11:30	55,16	54,44	IN-JV-RDL	
C-6-9	C-6-10	21-11-01	12:30	55,15	53,96	IN-JV	
C-6-10	C-6-11	22-11-01	13:30	55,19	54,84	PB-RDL-DF	
C-6-11	C-6-12	25-11-01	9:30	55,11	53,32	PB-IN	
C-6-12	C-6-13	26-11-01	10:30	55,10	54,50	RDL-PB-DF	
C-6-13	C-6-14	27-11-01	11:30	55,14	53,83	RDL-PB-IN	
C-6-14	C-6-15	28-11-01	12:30	55,17	54,22	PB-IN	
C-6-15	C-6-16	29-11-01	13:30	55,07	52,99	PB-IN	
C-6-16	C-6-17	02-12-01	9:30	55,12	54,66	PB-IN-DF	
C-6-17	C-6-18	03-12-01	10:30	55,08	53,88	PB-RDL-DF	
C-6-18	C-6-19	04-12-01	11:30	55,18	54,07	PB-RDL-DF	
C-6-19	C-6-20	05-12-01	12:30	55,17	53,92	PB-RDL-DF	
C-6-20	C-6-25	16-12-01	9:30	55,14	56,77	PB-IN-DF	

			WG14 - Field Validation Programme									
				Sampling form								
Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	A	C	Technique		AAS	
	Bristol (B)	Berlin (D)					B	D			ICP-MS	
	Preliminary Field Tests (P)											
Sampler No.:	7					Filter Material:		Membrane		Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-7-1	C-7-1	06-11-01	9:30	55,18	52,08	RDL-PB	
C-7-2	C-7-2	07-11-01	10:30	55,16	51,56	PB-IN	
C-7-3	C-7-3	08-11-01	11:30	54,18	52,90	PB-RDL	
C-7-4	C-7-4	11-11-01	9:30	55,20	53,27	PB-IN	
C-7-5	C-7-5	12-11-01	10:30	55,18	52,64	RDL-PB-IN	
C-7-6	C-7-6	13-11-01	11:30	55,12	53,61	PB-RDL-DF	
C-7-7	C-7-7	18-11-01	9:30	55,12	53,47	JV-RDL-IN	
C-7-8	C-7-9	20-11-01	11:30	55,16	53,44	IN-JV-RDL	
C-7-9	C-7-10	21-11-01	12:30	55,15	52,86	IN-JV	
C-7-10	C-7-11	22-11-01	13:30	55,12	53,60	PB-RDL-DF	
C-7-11	C-7-12	25-11-01	9:30	55,19	52,50	PB-IN	
C-7-12	C-7-13	26-11-01	10:30	55,19	53,51	RDL-PB-DF	
C-7-13	C-7-14	27-11-01	11:30	55,17	52,79	RDL-PB-IN	
C-7-14	C-7-15	28-11-01	12:30	55,15	53,08	PB-IN	
C-7-15	C-7-16	29-11-01	13:30	55,21	52,05	PB-IN	
C-7-16	C-7-17	02-12-01	9:30	55,16	53,32	PB-IN-DF	
C-7-17	C-7-18	03-12-01	10:30	55,16	52,47	PB-RDL-DF	
C-7-18	C-7-19	04-12-01	11:30	55,13	52,80	PB-RDL-DF	
C-7-19	C-7-20	05-12-01	12:30	55,14	52,63	PB-RDL-DF	
C-7-20	C-7-25	16-12-01	9:30	55,15	55,65	PB-IN-DF	

WG14 - Field Validation Programme

Sampling form

Sampling Site:	Madrid (A)	Antwerp (C)				Laboratory:	C	Technique	AAS	
	Bristol (B)	Berlin (D)					D		ICP-MS	
	Preliminary Field Tests (P)									
Sampler No.:	8					Filter Material:	Membrane	Quartz		

Filter - Code	Internal	Start Date	Start Time	Volume	Volume	Operator	Remark
	Lab Code	(dd/mm/yy)	(h:min)	(m^3)	(m^3) Std.Cond.		
C-8-1	C-8-1	06-11-01	9:30	55,17	52,67	RDL-PB	
C-8-2	C-8-2	07-11-01	10:30	55,08	52,29	PB-IN	
C-8-3	C-8-3	08-11-01	11:30	55,18	53,66	PB-RDL	
C-8-4	C-8-4	11-11-01	9:30	55,12	53,58	PB-IN	
C-8-5	C-8-5	12-11-01	10:30	55,18	53,03	RDL-PB-IN	
C-8-6	C-8-6	13-11-01	11:30	55,20	54,01	PB-RDL-DF	
C-8-7	C-8-7	18-11-01	9:30	55,12	53,71	JV-RDL-IN	
C-8-8	C-8-9	20-11-01	11:30	55,12	53,57	IN-JV-RDL	
C-8-9	C-8-10	21-11-01	12:30	55,09	53,09	IN-JV	
C-8-10	C-8-11	22-11-01	13:30	55,17	53,99	PB-RDL-DF	
C-8-11	C-8-12	25-11-01	9:30	55,15	52,79	PB-IN	
C-8-12	C-8-13	26-11-01	10:30	55,11	53,96	RDL-PB-DF	
C-8-13	C-8-14	27-11-01	11:30	55,18	53,35	RDL-PB-IN	
C-8-14	C-8-15	28-11-01	12:30	55,19	53,54	PB-IN	
C-8-15	C-8-16	29-11-01	13:30	55,13	52,42	PB-IN	
C-8-16	C-8-17	02-12-01	9:30	55,17	53,57	PB-IN-DF	
C-8-17	C-8-18	03-12-01	10:30	55,16	52,89	PB-RDL-DF	
C-8-18	C-8-19	04-12-01	11:30	55,18	53,29	PB-RDL-DF	
C-8-19	C-8-20	05-12-01	12:30	55,19	53,03	PB-RDL-DF	
C-8-20	C-8-25	16-12-01	9:30	55,17	55,85	PB-IN-DF	

ANNEX 4

ANNEX A

CEN fieldtests Hoboken - gravimetric sampling (30/31 october 2001)

Dustconcentrations (samplingperiod : Tuesday 30 october 14h30 to Wednesday 31 october 14h30)

Sampler	Filtertype	Mass blanc filter (in g)	Mass sampled filter (in g)	Mass on filter (in µg)	Sampled volume (in m³)	Dustconcentration (in µg/m³)	Difference (in µg/m³) compared with mean value 10 KFG	Difference (in %) compared with mean value 10 KFG	Remarks
KFG1	CN Sartorius 3 µm - 50 mm	0,08179	0,08468	2890	55,157	52,40	-0,16	-0,30	
KFG2	CN Sartorius 3 µm - 50 mm	0,08186	0,08468	2820	55,126	51,16	-1,40	-2,66	
KFG3	CN Sartorius 3 µm - 50 mm	0,08212	0,08503	2910	55,162	52,75	0,20	0,39	
KFG4	CN Sartorius 3 µm - 50 mm	0,08210	0,08498	2880	55,111	52,26	-0,29	-0,56	
KFG5	CN Sartorius 3 µm - 50 mm	0,08219	0,08503	2840	55,065	51,58	-0,98	-1,86	
KFG6	CN Sartorius 3 µm - 50 mm	0,08202	0,08491	2890	55,149	52,40	-0,15	-0,28	
KFG7	CN Sartorius 3 µm - 50 mm	0,08179	0,08475	2960	55,199	53,62	1,07	2,04	
KFG8	CN Sartorius 3 µm - 50 mm	0,08175	0,08467	2920	55,101	52,99	0,44	0,84	
KFG9	CN Sartorius 3 µm - 50 mm	0,08179	0,08466	2870	55,052	52,13	-0,42	-0,80	
KFG10	CN Sartorius 3 µm - 50 mm	0,08183	0,08482	2990	55,145	54,22	1,67	3,18	
			Mean value 10 KFG :	**2897**	**55,13**	**52,55**			
			MIN value:	**2820**	**55,05**	**51,16**			
			MAX value	**2990**	**55,20**	**54,22**			
			Difference (MAX-MIN):	**170**	**0,15**	**3,06**			
			Std. Deviation:	**51,22**	**0,05**	**0,91**			

ANNEX B

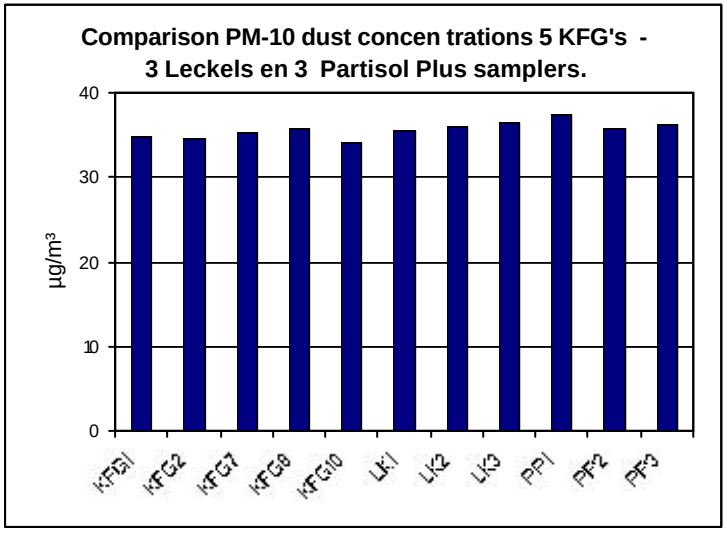
CEN fieldtests Hoboken - gravimetric sampling (12/13 december 2001)

Dustconcentrations (period : Wednesday 12 th of December 13h30 to Thursday 13th of December 12h30)

Sampler	Filtertype	Mass blanc filter (in g)	Mass sampled filter (in g)	Mass on filter (in µg)	Sampled volume (in m³)	Dustconcentration (in µg/m³)	Difference (in µg/m³) compared with mean value 10 KFG	Difference (in %) compared with mean value 10 KFG	Remarks
KFG1	CN 3 µm - 50 mm	0,17731	0,17923	1920	55,058	34,87	5,69	19,50	
KFG2	CN 3 µm - 50 mm	0,18284	0,18474	1900	55,097	34,48	5,30	18,17	
KFG3	CN 3 µm - 50 mm	0,11665	0,11794	1290	55,167	23,38	-5,80	-19,87	
KFG4	CN 3 µm - 50 mm	0,11612	0,11727	1150	55,091	20,87	-8,31	-28,47	
KFG5	CN 3 µm - 50 mm	0,11723	0,11864	1410	55,155	25,56	-3,62	-12,40	
KFG6	CN 3 µm - 50 mm	0,11743	0,11871	1280	55,157	23,21	-5,98	-20,48	
KFG7	CN 3 µm - 50 mm	0,18684	0,18878	1940	55,165	35,17	5,98	20,51	
KFG8	CN 3 µm - 50 mm	0,18656	0,18853	1970	55,149	35,72	6,54	22,41	
KFG9	CN 3 µm - 50 mm	0,11684	0,11819	1350	55,160	24,47	-4,71	-16,13	
KFG10	CN 3 µm - 50 mm	0,15985	0,16173	1880	55,165	34,08	4,90	16,78	
			Mean value 10 KFG :		**55,14**	**29,18**			
			MIN:		**55,06**	**20,87**			
			MAX:		**55,17**	**35,72**			
			Difference (MAX-MIN)		**0,11**	**14,85**			
LK1	CN 3µm - 50 mm	0,08449	0,08644	1950	55,02	35,44	6,26		Filterringen va UBA
LK2	CN 3µm - 50 mm	0,08429	0,08628	1990	55,33	35,97	6,78		Filterringen va UBA
LK3	CN 3µm - 47 mm	0,06888	0,07089	2010	55,12	36,47	7,28		Filterringen va VMM
LK4	CN 3µm - 47 mm	/	/	/	/	/	/		Toestel gestop
PP1	CN 0,8 µm - 47 mm	0,05902	0,05992	900	24,10	37,34	8,16		
PP2	CN 0,8 µm - 47 mm	0,05891	0,05977	860	24,00	35,83	6,65		
PP3	CN 0,8 µm - 47 mm	0,05887	0,05979	920	25,40	36,22	7,04		
DG1	Quartz Schleicher & Schuell 150 mm	1,54274	1,56634	23600	740,022	31,89	2,71		
DG2	Quartz Schleicher & Schuell 150 mm	1,54253	1,56575	23220	741,531	31,31	2,13		

Comparison with KFG with quartz filters (KFG 1, 2, 7,8,10) and Leckel and Partisol Plus (cellulose nitrate filters)

Sampler	Dustconcentration (in µg/m³)
KFG1	34,87
KFG2	34,48
KFG7	35,17
KFG8	35,72
KFG10	34,08
LK1	35,44
LK2	35,97
LK3	36,47
PP1	37,34
PP2	35,83
PP3	36,22
Mean	**35,60**
MIN	**34,08**
MAX	**37,34**
Difference	**3,26**



ANNEX 5

CEN-CODE			1	2	3			4	5	6					7	/	8	9	10			11	12	13	14	15			16	17	18	19	/			/	/	/	/				20	/	/
			Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday
			6-nov	7-nov	8-nov	##	##	11-nov	12-nov	13-nov	##	##	##	##	18-nov	19-nov	20-nov	21-nov	22-nov	##	##	25-nov	26-nov	27-nov	28-nov	29-nov	##	##	2-dec	3-dec	4-dec	5-dec	6-dec	##	##	9-dec	10-dec	11-dec	12-dec	##	##	##	16-dec	17-dec	18-dec
C1	lab A	Q	Filter teared apart																														GRAVIMETRY											
C2	lab A	Q																																											
C3	Lab B	CA														15h07 sampled						09h47 sampled				20h50 sampled				to less sampled		17h43 sampled			21h23 sampled	14h05 sampled	07h16 sampled					12h48 sampled	08h47 sampled
C4	lab B	CA						12h05 sampled										filter became wet	filter became wet													17h53 sampled			19h01 sampled	13h55 sampled	07h04 sampled					12h15 sampled	08h34 sampled
C5	lab C	CA							filter became wet							13h47 sampled																17h22 sampled			20h27 bemonsterd	14h05 sampled	06h30 sampled				not started	11h29 sampled	08h16 sampled
C6	lab C	CA													13h07sampled	15h59 sampled																18h55 sampled			20h24 sampled	15h00 sampled	07h01 sampled					11h46 sampled	09h52 sampled
C7	lab D	Q																																										
C8	lab D	Q																																			filter teared apart							
C9	reserve	CA						reserve filter for C4	not started	not started, replaced by VMM KFC					reserve filter for C6	13h10sampled	07h16 bemonsterd	filter became wet	filter became wet			reserve filter for C3				filter became wet				reserve filter for C3			14h35 sampled			18h23 sampled	12h14 sampled	03h22 sampled				reserve filter for C5 only sampled 20h29	10h01 sampled	06h03 sampled
C10	reserve	Q	reserve filter for C1					Filter teared apart	Filter teared apart																												filter teared apart							08h12 sampled
PP1	ecole doaui	PTFE						19h22 sampled																						15h22 sampled							22h15 sampled						05h13 sampled
PP2	airparif	PTFE		22h49 sampled				0h01 sampled							00h01sampled	09h43 sampled	not started (no filter)						16h23 sampled		11h18 sampled				10h30 sampled														
PP3		PTFE																																		07h36 sampled					not started		02h52 sampled
LK1	UBA Germany	CN																																										
LK2	UBA Germany	CN																																										
LK3	VMM	CN																																		11h34 sampled					00h05 sampled		
LK4	VMM	CN	no data																sampler taken away																										
DG1	UBA Germany	Q													not started																														
DG2	UBA Germany	Q																																										
internal	VMM lab code		1	2	3			4	5	6					7	8	9	10	11			12	13	14	15	16			17	18	19	20	21			22	23	24					25	26	27

ANNEX 6

LAB A								
Sample	Pb		Cd		As		Ni	
description	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Reagent Blank 1	0,73	0,66	-0,02	-0,02	0,07	0,06	0,70	0,64
Reagent Blank 2	1,05	0,96	0,02	-0,02	-0,02	-0,02	0,96	0,87
Reagent Blank 3	0,40	0,36	0,06	0,05	-0,30	-0,03	1,14	1,03
Reagent Blank 4	0,32	0,29	0,10	0,09	-0,01	-0,01	0,40	0,36
Lab Filter Blank 1	0,84	0,76	-0,02	-0,02	-0,22	-0,20	1,10	1,00
Lab Filter Blank 2	1,23	1,12	-0,02	-0,02	-0,34	-0,31	2,16	1,97
Lab Filter Blank 3	1,10	1,0	-0,03	-0,03	0,08	0,07	0,64	0,58
Lab Filter Blank 4	0,40	0,36	-0,01	-0,09	-0,07	-0,06	0,90	0,82
Field Filter Blank 1	1,40	1,27	-0,03	-0,03	-0,43	-0,39	0,94	0,86
Field Filter Blank 2	1,29	1,17	-0,07	-0,06	-0,17	-0,15	1,10	1,00
Field Filter Blank 3	0,75	0,68	-0,10	-0,09	-0,42	-0,38	1,40	1,27
Field Filter Blank 4	0,60	0,55	-0,11	-0,1	-0,57	-0,52	1,25	1,14

LAB B (AAS)								
Sample	Pb		Cd		As		Ni	
description	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Reagent Blank 1	***-0,560***	***-0,509***	***-0,094***	***-0,085***	***0,040***	***0,036***	***-0,820***	***-0,745***
Reagent Blank 2	***-0,920***	***-0,836***	***-0,114***	***-0,104***	***-0,100***	***-0,091***	***-0,680***	***-0,618***
Reagent Blank 3	***-0,620***	***-0,564***	***-0,076***	***-0,069***	***0,040***	***0,036***	***-0,760***	***-0,691***
Reagent Blank 4	***-0,200***	***-0,182***	***-0,104***	***-0,095***	***0,020***	***0,018***	***-0,620***	***-0,564***
Lab Filter Blank 1	***0,880***	***0,800***	***-0,046***	***-0,042***	***-0,080***	***-0,073***	***-0,140***	***-0,127***
Lab Filter Blank 2	***0,460***	***0,418***	***-0,060***	***-0,055***	***0,200***	***0,182***	***-0,620***	***-0,564***
Lab Filter Blank 3	***-0,440***	***-0,400***	***-0,150***	***-0,136***	***-0,160***	***-0,145***	***-0,540***	***-0,491***
Lab Filter Blank 4	***-0,320***	***-0,291***	***-0,150***	***-0,136***	***0,060***	***0,055***	***-0,400***	***-0,364***
Field Filter Blank 1	***0,460***	***0,418***	***-0,134***	***-0,122***	***0,120***	***0,109***	***0,080***	***0,073***
Field Filter Blank 2	***1,600***	***1,455***	***-0,096***	***-0,087***	***0,160***	***0,145***	***0,120***	***0,109***
Field Filter Blank 3	***0,160***	***0,145***	***-0,096***	***-0,087***	***0,140***	***0,127***	***-0,280***	***-0,255***
Field Filter Blank 4	***0,880***	***0,800***	***-0,096***	***-0,087***	***-0,020***	***-0,018***	***-0,060***	***-0,055***

LAB B (ICP)								
Sample	Pb		Cd		As		Ni	
description	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Reagent Blank 1	0,112	0,102	***0,004***	***0,004***	***0,001***	***0,001***	0,075	0,068
Reagent Blank 2	***0,061***	***0,056***	***0,000***	***0,000***	***0,034***	***0,031***	***-0,008***	***-0,007***
Reagent Blank 3	0,293	0,267	0,014	0,013	***-0,005***	***-0,005***	0,148	0,135
Reagent Blank 4	***0,063***	***0,057***	0,023	0,021	***0,070***	***0,063***	***0,009***	***0,008***
Lab Filter Blank 1	0,962	0,875	0,024	0,021	0,166	0,151	0,659	0,599
Lab Filter Blank 2	0,385	0,350	0,032	0,029	0,143	0,130	0,249	0,226
Lab Filter Blank 3	0,156	0,142	***0,000***	***0,000***	0,176	0,160	0,171	0,155
Lab Filter Blank 4	0,157	0,142	***0,005***	***0,004***	0,159	0,145	0,284	0,258
Field Filter Blank 1	0,663	0,603	0,012	0,011	0,102	0,093	0,786	0,714
Field Filter Blank 2	1,722	1,565	0,020	0,018	0,164	0,149	0,905	0,822
Field Filter Blank 3	0,612	0,556	0,011	0,010	***0,074***	***0,068***	0,705	0,641
Field Filter Blank 4	1,144	1,040	0,006	0,005	0,135	0,123	0,784	0,713

LAB C								
Sample	Pb		Cd		As		Ni	
description	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Reagent Blank 1	***0,192***	***0,175***	***0,007***	***0,006***	***-0,009***	***-0,008***	***0,301***	***0,274***
Reagent Blank 2	***0,367***	***0,334***	***0,024***	***0,022***	***-0,058***	***-0,053***	***0,197***	***0,179***
Reagent Blank 3	***0,517***	***0,470***	***0,018***	***0,016***	***-0,097***	***-0,088***	1,014	0,922
Reagent Blank 4	***0,383***	***0,348***	***0,011***	***0,010***	***-0,151***	***-0,137***	***0,408***	***0,371***
Lab Filter Blank 1	***0,312***	***0,284***	***0,026***	***0,024***	***-0,053***	***-0,048***	***0,438***	***0,398***
Lab Filter Blank 2	***0,413***	***0,375***	***0,026***	***0,024***	***0,03***	***0,027***	***0,326***	***0,296***
Lab Filter Blank 3	***0,271***	***0,246***	***0,022***	***0,020***	***0,058***	***0,053***	***0,504***	***0,458***
Lab Filter Blank 4	***0,52***	***0,473***	***0,024***	***0,022***	***-0,059***	***-0,054***	0,759	0,690
Field Filter Blank 1	***0,569***	***0,517***	***0,028***	***0,025***	***-0,425***	***-0,386***	1,088	0,989
Field Filter Blank 2	1,266	*1,151*	***0,031***	***0,028***	***-0,396***	***-0,360***	3,681	3,346
Field Filter Blank 3	1,023	0,930	***0,024***	***0,022***	***-0,554***	***-0,504***	0,933	0,848
Field Filter Blank 4	1,155	*1,050*	***0,021***	***0,019***	***-0,014***	***-0,013***	0,713	0,648

LAB D AAS								
Sample	Pb		Cd		As		Ni	
description	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Reagent Blank 1	***0,190***	***0,173***	***0,011***	***0,010***	***-0,216***	***-0,196***	***0,256***	***0,233***
Reagent Blank 2	***0,056***	***0,051***	***-0,003***	***-0,003***	***-0,269***	***-0,244***	***0,736***	***0,669***
Reagent Blank 3	***0,155***	***0,141***	***-0,006***	***-0,005***	***-0,150***	***-0,137***	***0,111***	***0,101***
Reagent Blank 4	***0,130***	***0,118***	***0,003***	***0,003***	***-0,148***	***-0,135***	***0,885***	***0,805***
Lab Filter Blank 1	***0,424***	***0,386***	***0,001***	***0,000***	***-0,117***	***-0,107***	1,127	1,025
Lab Filter Blank 2	***0,373***	***0,339***	***0,013***	***0,012***	***-0,195***	***-0,178***	***0,652***	***0,593***
Lab Filter Blank 3	***0,381***	***0,346***	***0,009***	***0,009***	***-0,157***	***-0,142***	***0,811***	***0,737***
Lab Filter Blank 4	***0,456***	***0,415***	***-0,009***	***-0,008***	***-0,245***	***-0,223***	1,409	1,281
Field Filter Blank 1	1,500	1,364	***0,004***	***0,003***	***-0,186***	***-0,169***	3,959	3,599
Field Filter Blank 2	1,920	1,745	***0,017***	***0,015***	***-0,130***	***-0,118***	3,796	3,451
Field Filter Blank 3	*0,843*	*0,767*	***-0,005***	***-0,004***	***0,066***	***0,060***	1,409	1,281
Field Filter Blank 4	*0,909*	*0,826*	***-0,007***	***-0,007***	***0,002***	***0,001***	2,423	2,203

LAB D ICP								
Sample	Pb		Cd		As		Ni	
description	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Reagent Blank 1	0,206	0,375	0,0183	0,0333	***-0,212***	***-0,386***	0,289	0,525
Reagent Blank 2	0,119	0,217	***0,0058***	***0,0105***	***-0,137***	***-0,250***	0,554	1,007
Reagent Blank 3	0,120	0,218	***0,0036***	***0,0065***	***-0,199***	***-0,361***	0,204	0,371
Reagent Blank 4	0,110	0,200	***0,0079***	***0,0144***	***-0,156***	***-0,283***	0,287	0,521
Lab Filter Blank 1	0,283	0,515	***0,0053***	***0,0096***	***-0,179***	***-0,326***	0,668	1,214
Lab Filter Blank 2	0,294	0,535	***0,0074***	***0,0135***	***-0,213***	***-0,388***	0,472	0,858
Lab Filter Blank 3	0,279	0,507	***0,0082***	***0,0149***	***-0,120***	***-0,218***	0,568	1,033
Lab Filter Blank 4	0,307	0,559	***0,0063***	***0,0115***	***-0,184***	***-0,335***	0,669	1,216
Field Filter Blank 1	0,778	1,415	***0,0126***	***0,0229***	***-0,083***	***-0,151***	1,653	3,005
Field Filter Blank 2	1,356	2,466	0,0262	0,0476	0,282	0,513	1,675	3,045
Field Filter Blank 3	0,459	0,834	***0,0051***	***0,0093***	***0,041***	***0,075***	0,782	1,421
Field Filter Blank 4	0,505	0,917	***0,0048***	***0,0087***	***-0,040***	***-0,073***	1,336	2,429

Repotred LOD's	Pb		Cd		As		Ni	
Lab	µg/l	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*	(µg/l)	(ng/m³)*
Lab A - AAS	not reported	not reported	not reported	not reported	not reported	not reported	not reported	not reported
Lab B - AAS	2,000	1,818	0,100	0,091	0,300	0,273	1,000	0,909
Lab C - AAS	0,655	0,6	0,052	0,047	0,468	0,430	0,632	0,58
Lab D - AAS	not reported	0,91	not reported	0,091	not reported	0,91	not reported	0,91
Lab B - ICP-MS	0,102	0,093	0,006	0,005	0,080	0,073	0,020	0,018
Lab D - ICP-MS	0,078	0,141	0,013	0,023	0,067	0,122	0,172	0,313

ANNEX 7

LAB A									
		Pb		Cd		As		Ni	
certified value (mg/kg)		6550 +/- 80		75 +/- 7		115 +/-10		82 +/- 3	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIST/1	10	6520	99,5	73,7	98,2	119,1	103,6	77,8	94,9
NIST/2	10	6490	99,1	71,9	95,9	125,2	108,8	77,2	94,1
NIST/3	11	6290	96,0	72,5	96,7	116,1	101,0	75,8	92,4
NIST/4	11	6358	97,1	72,1	96,1	121,8	105,9	76,4	93,2
Mean		6415	97,9	72,6	96,7	120,6	104,8	76,8	93,7
SD		109	1,7	0,8	1,0	3,9	3,3	0,9	1,1
RSD (%)		2	1,7	1,1	1,1	3,2	3,2	1,1	1,2
certified value (mg/kg)		219 +/- 9		1.1 +/- 0.1		2.6 +/- 0.2		18.5 +/- 1.5	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIES/1	80	226	103,2	1,1	98,2	2,6	101,2	17,5	94,6
NIES/2	80	231	105,5	1,1	96,4	2,8	106,9	17,8	96,2
NIES/3	80	220	100,5	1,1	95,5	2,9	111,5	16,9	91,4
NIES/4	82	225	102,7	1,1	96,4	2,9	111,5	17,1	92,4
Mean		226	103,0	1,1	96,6	2,8	107,8	17,3	93,7
SD		5	2,1	0,0	1,1	0,1	4,9	0,4	2,2
RSD (%)		2	2,0	1,2	1,2	4,6	4,5	2,3	2,3
LAB B AAS									
		Pb		Cd		As		Ni	
Certified value (mg/kg)		6550 +/- 80		75 +/- 7		115 +/-10		82 +/- 3	
Description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIST/1	11,9	7224	110,3	83,0	110,7	126,1	109,6	83,2	101,5
NIST/2	9,5	6769	103,3	74,7	99,6	118,3	102,9	71,3	86,9
NIST/3	9,6	7262	**110,9**	83,6	**111,5**	125,8	109,4	82,4	100,5
NIST/4	11,2	6789	103,6	79,1	105,5	113,9	99,1	81,4	99,3
Mean		7011	107,0	80,1	106,8	121,0	105,2	79,6	97,0
SD		269	4,1	4,1	5,5	5,9	5,2	5,6	6,8
RSD (%)		4	3,8	5,1	5,1	4,9	4,9	7,0	7,0
Certified value (mg/kg)		219 +/- 9		1.1 +/- 0.1		2.6 +/- 0.2		18.5 +/- 1.5	
Description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIES/1	84	220	100,5	1,1	98,1	2,4	92,0	16,5	89,3
NIES/2	82,5	221	101,0	1,7	**153,2**	2,0	**76,5**	17,2	93,0
NIES/3	82,5	229	104,4	1,1	98,3	2,2	**84,4**	15,6	**84,5**
NIES/4	79,5	225	102,7	1,0	91,7	2,3	88,5	15,8	85,6
Mean		224	102,1	1,2	110,3	2,2	85,4	16,3	88,1
SD		4	1,8	0,3	28,7	0,2	6,7	0,7	3,9
RSD (%)		2	1,7	26,1	26,1	7,9	7,9	4,4	4,4

LAB B ICP									
		Pb		Cd		As		Ni	
certified value (mg/kg)		6550 +/- 80		75 +/- 7		115 +/-10		82 +/- 3	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIST/1	11,9	6861	104,8	81,6	108,8	134,4	116,8	82,1	100,1
NIST/2	9,5	6287	96,0	73,3	97,8	124,6	108,4	78,3	95,5
NIST/3	9,6	6739	102,9	82,3	109,7	131,1	114,0	83,4	101,7
NIST/4	11,2	6399	97,7	75,9	101,3	124,0	107,8	79,0	96,3
mean		6572	100,3	78,3	104,4	128,5	111,8	80,7	98,4
SD		272	4,2	4,4	5,8	5,0	4,4	2,4	3,0
RSD (%)		4	4,1	5,6	5,6	3,9	3,9	3,0	3,0
certified value (mg/kg)		219 +/- 9		1.1 +/- 0.1		2.6 +/- 0.2		18.5 +/- 1.5	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIES/1	84,0	218	99,4	1,0	89,2	2,8	108,0	15,6	84,2
NIES/2	82,5	218	99,7	1,5	**140,6**	3,0	**115,8**	16,4	88,8
NIES/3	82,5	221	101,1	1,0	90,1	3,0	114,5	15,6	**84,1**
NIES/4	79,5	221	100,9	0,9	82,6	2,8	109,2	14,3	77,5
mean		220	100,3	1,1	100,6	2,9	111,9	15,5	83,7
SD		2	0,8	0,3	26,9	0,1	3,9	0,9	4,7
RSD (%)		1	0,8	26,7	26,7	3,4	3,4	5,6	5,6

LAB C									
		Pb		Cd		As		Ni	
certified value (mg/kg)		6550 +/- 80		75 +/- 7		115 +/-10		82 +/- 3	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIST/1	10,6	6712	102,5	75,5	100,7	120,1	104,4	83,6	102,0
NIST/2	10,9	6642	101,4	73,4	97,8	125,5	109,1	78,4	95,6
NIST/3	9,6	6172	94,2	70,7	94,3	122,8	106,8	78,1	95,2
NIST/4	11,3	6580	100,5	74,3	99,0	122,8	106,8	79,5	97,0
mean		6527	99,6	73,5	98,0	122,8	106,8	79,9	97,4
SD		243	3,7	2,0	2,7	2,2	1,9	2,6	3,1
RSD (%)		4	3,7	2,8	2,8	1,8	1,8	3,2	3,2
certified value (mg/kg)		219 +/- 9		1.1 +/- 0.1		2.6 +/- 0.2		18.5 +/- 1.5	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIES/1	99,9	221	101,1	1,0	91,8	2,9	112,3	17,8	96,4
NIES/2	79,6	231	105,6	1,0	90,9	2,8	108,8	20,2	108,9
NIES/3	77,9	227	103,6	1,0	90,0	2,8	108,5	16,6	89,7
NIES/4	79,7	199	90,6	1,1	97,3	3,0	113,8	18,1	97,6
mean		219	100,2	1,0	92,5	2,9	110,9	18,2	98,2
SD		15	6,6	0,0	3,3	0,1	2,6	1,5	8,0
RSD (%)		6,6	6,6	3,5	3,5	2,4	2,4	8,1	8,1

LAB D AAS									
		Pb		Cd		As		Ni	
certified value (mg/kg)		6550 +/- 80		75 +/- 7		115 +/-10		82 +/- 3	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIST/1	10,1	6946	106,1	85,2	**113,6**	125,8	109,4	80,3	98,0
NIST/2	10,4	6699	102,3	77,6	103,5	124,9	108,6	85,2	103,9
NIST/3	10	6441	98,3	70,4	93,9	119,2	103,7	73,0	89,1
NIST/4	10,5	7129	108,8	76,7	102,2	131,4	114,3	87,7	107,0
mean	10,3	6804	103,9	77,5	103,3	125,3	109,0	81,6	99,5
SD	0,2	299	4,6	6,1	8,1	5,0	4,4	6,5	7,9
RSD (%)	2,3	4	4,4	7,8	7,8	4,0	4,0	7,9	7,9
certified value (mg/kg)		219 +/- 9		1.1 +/- 0.1		2.6 +/- 0.2		18.5 +/- 1.5	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIES/1	80,5	218	99,7	1,0	92,6	2,9	112,8	14,4	**77,7**
NIES/2	81	224	102,5	1,0	**87,8**	3,3	**128,1**	17,7	95,8
NIES/3	80,9	217	99,3	1,0	92,1	2,7	105,5	14,3	**77,3**
NIES/4	79,7	227	103,5	1,0	91,8	3,1	**119,2**	17,2	93,0
mean	80,5	222	101,3	1,0	91,1	3,0	116,4	15,9	86,0
SD	0,6	5	2,1	0,0	2,2	0,2	9,6	1,8	9,9
RSD (%)	0,7	2	2,0	2,4	2,4	8,2	8,2	11,5	11,5

LAB D ICP									
		Pb		Cd		As		Ni	
certified value (mg/kg)		6550 +/- 80		75 +/- 7		115 +/-10		82 +/- 3	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIST/1	10,1	7257	110,8	88,1	117,5	132,1	114,9	89,4	109,0
NIST/2	10,4	6913	105,5	76,2	101,6	125,6	109,2	80,9	98,6
NIST/3	10	6886	105,1	75,5	100,6	123,4	107,3	81,8	99,7
NIST/4	11,5	6601	100,8	75,1	100,2	121,6	105,7	79,2	96,6
mean		6914	105,6	78,7	105,0	125,7	109,3	82,8	101,0
SD		269	4,1	6,3	8,4	4,6	4,0	4,5	5,5
RSD (%)		4	3,9	8,0	8,0	3,6	3,6	5,4	5,4
certified value (mg/kg)		219 +/- 9		1.1 +/- 0.1		2.6 +/- 0.2		18.5 +/- 1.5	
description/replicate	weight (mg)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)	(mg/kg)	recovery (%)
NIES/1	80,5	228	104,2	1,1	104,3	3,3	125,1	15,5	83,7
NIES/2	81	229	104,4	1,0	95,4	3,1	119,0	16,4	88,8
NIES/3	80,9	231	105,7	1,1	99,7	3,3	127,8	15,6	84,2
NIES/4	79,7	223	101,8	1,1	100,5	3,1	120,9	17,0	91,9
mean		228	104,0	1,1	100,0	3,2	**123,2**	16,1	87,1
SD		4	1,6	0,0	3,7	0,1	4,0	0,7	3,9
RSD (%)		2	1,5	3,7	3,7	3,2	3,2	4,5	4,5

ANNEX 8

			WG14 - Field Validation Programme Analytical Results									
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	1			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m³)		µg/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³
C-1-1	6-11-01	55,2	Filter C-1-1 damaged, replaced by C-10-1		94190	1706,3	985	17,84	13088	237,10	1706	30,91
C-1-2	7-11-01	55,04			61320	1114,1	830	15,08	3199	58,10	533,5	9,69
C-1-3	8-11-01	55,14			5876	106,6	39	0,70	501	9,09	598	10,85
C-1-4	11-11-01	54,07			70650	1306,6	1184	21,90	2882	53,30	961,5	17,78
C-1-5	12-11-01	55,18			7915	143,4	208	3,77	823	14,91	537	9,73
C-1-6	13-11-01	55,14			1176	21,3	59	1,07	96	1,73	862,5	15,64
C-1-7	18-11-01	55,16			2342	42,4	56,5	1,02	305	5,52	331,5	6,01
C-1-8	20-11-01	55,18			117640	2131,9	1005	18,21	11146	201,99	1436	26,01
C-1-9	21-11-01	55,13			190720	3459,5	1444	26,19	14458	262,25	1141	20,70
C-1-10	22-11-01	55,03			1502	27,3	31	0,55	117	2,12	810	14,72
C-1-11	25-11-01	55,12			36080	654,6	247	4,48	5000	90,71	582	10,56
C-1-12	26-11-01	55,07			37190	675,3	262	4,76	1596	28,98	1248	22,66
C-1-13	27-11-01	55,15			86030	1559,9	378	6,85	8904	161,45	3248	58,89
C-1-14	28-11-01	55,21			108440	1964,1	834	15,11	4178	75,67	1207	21,86
C-1-15	29-11-01	55,1			113580	2061,3	1508	27,37	6686	121,34	559	10,15
C-1-16	2-12-01	55,1			1456	26,4	45	0,81	164	2,97	403,5	7,32
C-1-17	3-12-01	55			33455	608,3	204	3,70	1737	31,58	775	14,09
C-1-18	4-12-01	55,25			52450	949,3	594	10,75	5848	105,85	1785	32,31
C-1-19	5-12-01	55,18			13305	241,1	195	3,53	1195	21,66	508	9,21
C-1-20	16-12-01	55,09			16500	299,5	116	2,10	500	9,07	348	6,32

WG14 - Field Validation Programme

Analytical Results

Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	2			Filter Material:	Membrane		Quartz					

Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-2-1	6-11-01	55,12			98500	1787,0	995	18,05	13366	242,49	1823	33,07
C-2-2	7-11-01	55,05			58690	1066,1	796	14,46	3130	56,85	562	10,21
C-2-3	8-11-01	55,26			5617	101,6	40	0,71	452,5	8,19	594	10,75
C-2-4	11-11-01	55			69700	1267,3	1184	21,53	2874	52,25	908	16,51
C-2-5	12-11-01	55,19			7682	139,2	209	3,79	827	14,98	530	9,60
C-2-6	13-11-01	55,21			1266	22,9	60	1,08	99	1,79	835	15,12
C-2-7	18-11-01	55,08			2285	41,5	52	0,94	287	5,21	311	5,65
C-2-8	20-11-01	55,12			115460	2094,7	948	17,19	10780	195,57	1511	27,40
C-2-9	21-11-01	54,98			191060	3475,1	1432	26,05	13942	253,58	2051	37,30
C-2-10	22-11-01	55,14			1399,5	25,4	29	0,52	104	1,89	635	11,52
C-2-11	25-11-01	55,13			35305	640,4	249	4,51	4983	90,39	561	10,18
C-2-12	26-11-01	55,16			35705	647,3	250	4,53	1563	28,34	1238	22,44
C-2-13	27-11-01	55,05			84900	1542,2	360	6,54	8741	158,78	3150	57,22
C-2-14	28-11-01	54,99			108300	1969,4	835	15,18	4174	75,90	1186	21,57
C-2-15	29-11-01	55,06			115120	2090,8	1544	28,04	6947	126,17	551	10,00
C-2-16	2-12-01	55,02			1452,5	26,4	44	0,79	137	2,49	424	7,71
C-2-17	3-12-01	55,06			35910	652,2	204	3,70	1756	31,88	774	14,05
C-2-18	4-12-01	55,17			52150	945,3	568	10,30	5622	101,90	1717	31,12
C-2-19	5-12-01	55,18			12892	233,6	194	3,51	1211	21,94	539	9,76
C-2-20	16-12-01	55,18			16482	298,7	122	2,20	528	9,56	364	6,60

			WG14 - Field Validation Programme Analytical Results									
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	3			Filter Material:	Membrane		Quartz					

Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m³)		µg/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³
C-3-1	6-11-01	55,15			91159	1653	950	17,23	15258	276,7	1210	21,94
C-3-2	7-11-01	55,13			54146	982,2	813	14,75	3693	66,99	354	6,421
C-3-3	8-11-01	55,2			4510	81,7	42,7	0,774	497	9,004	413	7,482
C-3-4	11-11-01	55,04			51564	936,8	1205	21,89	3159	57,39	734	13,34
C-3-5	12-11-01	55,16			5944	107,8	248	4,496	840	15,23	316	5,729
C-3-6	13-11-01	55,16			1151	20,87	62,2	1,128	88	1,595	637	11,55
C-3-7	18-11-01	55,11			2244	40,72	57,7	1,047	251	4,555	195	3,538
C-3-8	20-11-01	55,15			1E+05	1972	939	17,03	12037	218,36	1003	18,19
C-3-9	21-11-01	55,14			2E+05	3287	1320	23,94	16132	292,6	769	13,95
C-3-10	22-11-01	55,15			1568	28,43	38,2	0,693	69	1,251	466	8,45
C-3-11	25-11-01	55,17	Filter C-3-12 sampled only 9h47, replaced by C-9-12		37218	674,6	263	4,767	6265	113,6	325	5,891
C-3-12	26-11-01	55,04			38653	702,3	294	5,342	1805	32,79	1212	22,02
C-3-13	27-11-01	55,12			85707	1555	389	7,057	10394	188,6	2225	40,37
C-3-14	28-11-01	55,06			1E+05	1944	862	15,66	5227	94,93	912	16,56
C-3-15	29-11-01	47,77	Filter C-3-16 sampled only 20h50, filter C-9-16 was wet		98331	2058	1301	27,23	7454	156	530	11,09
C-3-16	2-12-01	55,11			1439	26,11	43,4	0,788	111	2,014	197	3,575
C-3-17	3-12-01	55,08			40088	727,8	256	4,648	1823	33,1	547	9,931
C-3-18	4-12-01	55,17	Filter C-3-19 sampled only 21h05, replaced by C-9-19		57302	1039	608	11,02	7225	131	1330	24,11
C-3-19	5-12-01	55,25			14839	268,6	248	4,489	1124	20,34	368	6,661
C-3-20	16-12-01	55,09			16560	300,6	134	2,432	481	8,731	178	3,231

			WG14 - Field Validation Programme Analytical Results									
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	4			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-4-1	6-11-01	55,18			97471	1766	901	16,33	15206	275,6	1380	25,01
C-4-2	7-11-01	55,14			57589	1044	745	13,51	3636	65,94	359	6,511
C-4-3	8-11-01	55,2			5371	97,3	46,4	0,841	467	8,46	437	7,917
C-4-4	11-11-01	54,95	Filter C-4-4 sampled only 12h05, replaced by C-9-4		67631	1231	1093	19,89	3318	60,38	773	14,07
C-4-5	12-11-01	55,15			7379	133,8	249	4,515	768	13,93	292	5,295
C-4-6	13-11-01	55,16			1237	22,43	69,5	1,26	88	1,595	655	11,87
C-4-7	18-11-01	55,09			2258	40,99	58,9	1,069	224	4,066	155	2,814
C-4-8	20-11-01	55,14			1E+05	1986	890	16,14	11816	214,3	1203	21,82
C-4-9	21-11-01	55,16	Filter C-4-10 was wet, replaced by C-9-10		2E+05	3468	1369	24,82	15702	284,7	1203	21,81
C-4-10	22-11-01	55,16	Filter C-4-11 was wet, replaced by C-9-11		1697	30,77	41	0,743	60	1,088	523	9,482
C-4-11	25-11-01	55,1			36250	657,9	260	4,719	5519	100,2	332	6,025
C-4-12	26-11-01	55,09			38263	694,6	139	2,523	1612	29,26	1122	20,37
C-4-13	27-11-01	55,14			85148	1544	333	6,039	9768	177,1	2322	42,11
C-4-14	28-11-01	55,04			1E+05	1934	813	14,77	4768	86,63	1005	18,26
C-4-15	29-11-01	55,04			1E+05	2070	1427	25,93	7525	136,7	498	9,048
C-4-16	2-12-01	55,1			1482	26,9	39,8	0,722	102	1,851	198	3,593
C-4-17	3-12-01	55,08			35387	642,5	206	3,74	1542	28	585	10,62
C-4-18	4-12-01	55,16			54946	996,1	580	10,51	6030	109,3	1444	26,18
C-4-19	5-12-01	55,2			10363	187,7	211	3,822	970	17,57	368	6,667
C-4-20	16-12-01	55,01			14965	272	160	2,909	420	7,635	155	2,818

			WG14 - Field Validation Programme									
				Analytical Results								
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	3			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-3-1	6-11-01	55,15			85900	1557,6	962,8	17,5	16170	293,2	1487	27,0
C-3-2	7-11-01	55,13			49990	906,8	812,1	14,7	3993	72,4	380	6,9
C-3-3	8-11-01	55,2			4827	87,4	40,05	0,7	447,3	8,1	426,6	7,7
C-3-4	11-11-01	55,04			46370	842,5	1288	23,4	3452	62,7	776,7	14,1
C-3-5	12-11-01	55,16			5283	95,8	242	4,4	809,3	14,7	351,4	6,4
C-3-6	13-11-01	55,16			1144	20,7	59,78	1,1	105,5	1,9	675,7	12,2
C-3-7	18-11-01	55,11			2173	39,4	54,66	1,0	234,9	4,3	226,3	4,1
C-3-8	20-11-01	55,15			97350	1765,2	717,2	13,0	12720	230,6	1311	23,8
C-3-9	21-11-01	55,14			2E+05	3054,0	1068	19,4	17260	313,0	860,8	15,6
C-3-10	22-11-01	55,15			1642	29,8	33,83	0,6	108,4	2,0	516,3	9,4
C-3-11	25-11-01	55,17	Filter C-3-12 sampled only 9h47, replaced by C-9-12		34610	627,3	274,1	5,0	6709	121,6	365	6,6
C-3-12	26-11-01	55,04			34970	635,4	268,2	4,9	1823	33,1	1264	23,0
C-3-13	27-11-01	55,12			77410	1404,4	348,1	6,3	11430	207,4	2829	51,3
C-3-14	28-11-01	55,06			94310	1712,9	782,7	14,2	5918	107,5	968,9	17,6
C-3-15	29-11-01	47,77	Filter C-3-16 sampled only 20h50, filter C-9-16 was wet		84500	1768,9	1224	25,6	8394	175,7	448,3	9,4
C-3-16	2-12-01	55,11			1456	26,4	37,84	0,7	138	2,5	224,8	4,1
C-3-17	3-12-01	55,08			34860	632,9	224,4	4,1	2057	37,3	622	11,3
C-3-18	4-12-01	55,17	Filter C-3-19 sampled only 21h05, replaced by C-9-19		50970	923,9	627,7	11,4	7635	138,4	1587	28,8
C-3-19	5-12-01	55,25			12060	218,3	224,6	4,1	1302	23,6	384,3	7,0
C-3-20	16-12-01	55,09			15970	289,9	119,6	2,2	469,1	8,5	219,6	4,0

			WG14 - Field Validation Programme									
				Analytical Results								
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	4			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-4-1	6-11-01	55,18			89240	1617	950,1	17,22	16630	301,4	1560	28,27
C-4-2	7-11-01	55,14			50930	923,6	806,6	14,63	4042	73,3	372,4	6,754
C-4-3	8-11-01	55,2			5051	91,5	39,49	0,715	456,3	8,266	434,9	7,879
C-4-4	11-11-01	54,95	Filter C-4-4 sampled only 12h05, replaced by C-9-4		57270	1042	1219	22,18	3641	66,26	795,7	14,48
C-4-5	12-11-01	55,15			5390	97,73	233,6	4,236	794	14,4	326,7	5,924
C-4-6	13-11-01	55,16			1230	22,3	58,49	1,06	95,98	1,74	687,2	12,46
C-4-7	18-11-01	55,09			2300	41,75	51,33	0,932	232,4	4,219	187,1	3,396
C-4-8	20-11-01	55,14			97180	1762	696,9	12,64	12690	230,1	1303	23,63
C-4-9	21-11-01	55,16	Filter C-4-10 was wet, replaced by C-9-10		2E+05	2901	1057	19,16	16610	301,1	1310	23,75
C-4-10	22-11-01	55,16	Filter C-4-11 was wet, replaced by C-9-11		1725	31,27	35,23	0,639	114,2	2,07	508,1	9,211
C-4-11	25-11-01	55,1			32880	596,7	259,3	4,706	6142	111,5	360,9	6,55
C-4-12	26-11-01	55,09			35450	643,5	268,6	4,876	1773	32,18	1213	22,02
C-4-13	27-11-01	55,14			74510	1351	341,7	6,197	11350	205,8	2820	51,14
C-4-14	28-11-01	55,04			90420	1643	732,6	13,31	5672	103,1	1050	19,08
C-4-15	29-11-01	55,04			95760	1740	1189	21,6	9191	167	517,4	9,4
C-4-16	2-12-01	55,1			1532	27,8	37,63	0,683	137	2,486	221,9	4,027
C-4-17	3-12-01	55,08			31330	568,8	205,4	3,729	1893	34,37	628,5	11,41
C-4-18	4-12-01	55,16			49690	900,8	584,8	10,6	7499	135,9	1634	29,62
C-4-19	5-12-01	55,2			11180	202,5	222,5	4,031	1234	22,36	400,8	7,261
C-4-20	16-12-01	55,01			16080	292,3	139,9	2,543	472,5	8,589	219,4	3,988

			WG14 - Field Validation Programme									
				Analytical Results								
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	5			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m³)		µg/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³
C-5-1	6-11-01	55,12			102150	1853,2	1019	18,478	15160	275,04	1649	29,907
C-5-2	7-11-01	55,17			57300	1038,6	851	15,425	3685	66,78	532	9,643
C-5-3	8-11-01	55,19			5640	102,2	43,1	0,781	442,3	8,01	477	8,642
C-5-4	11-11-01	55,01			68600	1247,0	1251	22,741	3294	59,87	942	17,124
C-5-5	12-11-01	55,16	Filter C-5-5 wet, filter C-9-5 not sampled		8145	147,7	234,3	4,248	777	14,09	636,5	11,539
C-5-6	13-11-01	55,17			1266,5	23,0	66,8	1,211	77,4	1,40	891	16,150
C-5-7	18-11-01	55,11			2384,5	43,3	59,2	1,074	250,7	4,55	711	12,901
C-5-8	20-11-01	55,1			111700	2027,2	985	17,877	11810	214,34	1627	29,528
C-5-9	21-11-01	55,04			194300	3530,2	1518	27,580	16055	291,70	951,5	17,287
C-5-10	22-11-01	55,1			1369,5	24,9	30,85	0,560	62,25	1,13	558,5	10,136
C-5-11	25-11-01	55,1			37890	687,7	288,4	5,233	5590	101,45	520	9,437
C-5-12	26-11-01	55,07			38155	692,8	271,2	4,925	1876	34,07	1285	23,334
C-5-13	27-11-01	55,11			85050	1543,3	395,9	7,184	10875	197,33	3035	55,072
C-5-14	28-11-01	54,99			107450	1954,0	885	16,094	5590	101,65	1003	18,240
C-5-15	29-11-01	55,06			107550	1953,3	1460	26,507	8760	159,10	603	10,952
C-5-16	2-12-01	55,07			1395	25,3	39	0,708	131,5	2,39	278,2	5,051
C-5-17	3-12-01	55,13			33485	607,4	227,6	4,128	1923	34,87	677	12,280
C-5-18	4-12-01	55,04			59900	1088,3	639,5	11,619	7070	128,45	1620	29,424
C-5-19	5-12-01	55,26			13465	243,7	218	3,944	1225	22,17	438	7,926
C-5-20	16-12-01	47,08	Sampler C5 did not start, filter C-9-25 only sampled 20h29		2805,5	59,6	60,8	1,291	117,9	2,50	177,4	3,768

			WG14 - Field Validation Programme									
				Analytical Results								
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	6			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-6-1	6-11-01	55,17			95250	1726,5	985	17,854	14965	271,25	1670	30,261
C-6-2	7-11-01	55,12			54550	989,7	842,5	15,285	3542	64,26	586	10,631
C-6-3	8-11-01	55,17			5575	101,1	42,2	0,765	426,5	7,73	482	8,737
C-6-4	11-11-01	55,12			70200	1273,6	1294	23,476	3397	61,62	1651	29,944
C-6-5	12-11-01	55,14			7675	139,2	233,7	4,237	822,5	14,92	717	13,003
C-6-6	13-11-01	55,2			1233	22,3	64,05	1,160	78,7	1,43	915	16,576
C-6-7	18-11-01	55,15	Filter C-6-7 sampled only 13h07, replaced by C-9-7		2525	45,8	66,8	1,211	245,3	4,45	665	12,058
C-6-8	20-11-01	55,16			111300	2017,8	991,5	17,975	12115	219,63	1474	26,722
C-6-9	21-11-01	55,15			191400	3470,5	1493	27,063	15730	285,22	930,5	16,872
C-6-10	22-11-01	55,19			1429	25,9	33,3	0,603	71,2	1,29	680	12,321
C-6-11	25-11-01	55,11			35565	645,3	292,2	5,301	5780	104,88	481	8,727
C-6-12	26-11-01	55,1			37935	688,5	271,5	4,926	1854	33,65	1245	22,586
C-6-13	27-11-01	55,14			85750	1555,1	399,9	7,252	11165	202,48	2968	53,818
C-6-14	28-11-01	55,17			104000	1885,1	873	15,824	5710	103,50	983	17,818
C-6-15	29-11-01	55,07			90300	1639,7	1230	22,335	8670	157,44	604	10,968
C-6-16	2-12-01	55,12			1387,5	25,2	36,65	0,665	124,1	2,25	262,7	4,766
C-6-17	3-12-01	55,08			37580	682,3	236	4,285	1973	35,82	680	12,346
C-6-18	4-12-01	55,18			58550	1061,1	620,5	11,245	6830	123,78	1554	28,162
C-6-19	5-12-01	55,17			13405	243,0	218,8	3,965	1228	22,26	441,5	8,002
C-6-20	16-12-01	55,14			14895	270,1	117,7	2,135	496	9,00	251,1	4,553
Filter Code: Site - Sampler No. - Filter No.				*Voluntary								

			WG14 - Field Validation Programme									
				Analytical Results								
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	7			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m³)		µg/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³
C-7-1	6-11-01	55,18			94362	1710	981,2	17,78	15869	287,6	3257	59,02
C-7-2	7-11-01	55,16			54480	987,7	802,1	14,54	3536	64,1	455,2	8,253
C-7-3	8-11-01	54,18			5278	97,4	38,5	0,711	415,7	7,673	510	9,414
C-7-4	11-11-01	55,2			64830	1174	1176	21,3	3151	57,08	844,3	15,3
C-7-5	12-11-01	55,18			7368	133,5	222	4,023	712,5	12,91	473,6	8,583
C-7-6	13-11-01	55,12			1249	22,7	56,16	1,019	77,57	1,407	768,8	13,95
C-7-7	18-11-01	55,12			2257	40,9	49,91	0,905	190	3,446	449,8	8,161
C-7-8	20-11-01	55,16			105354	1910	933,4	16,92	12431	225,4	1417	25,69
C-7-9	21-11-01	55,15			177171	3213	1361	24,69	17262	313	887,1	16,09
C-7-10	22-11-01	55,12			1374	24,9	28,24	0,512	83,87	1,522	587,2	10,65
C-7-11	25-11-01	55,19			35347	640,5	257,3	4,662	5686	103	419,6	7,603
C-7-12	26-11-01	55,19			37441	678,4	256,6	4,649	1591	28,83	1167	21,14
C-7-13	27-11-01	55,17			76998	1396	374,1	6,781	9762	176,9	2866	51,95
C-7-14	28-11-01	55,15			105201	1908	853,3	15,47	4861	88,14	1074	19,47
C-7-15	29-11-01	55,21			112764	2042	1561	28,28	8096	146,6	614,8	11,14
C-7-16	2-12-01	55,16			1587	28,77	43,71	0,792	127,1	2,304	425,6	7,715
C-7-17	3-12-01	55,16			34018	616,7	215,2	3,901	1612	29,22	653,8	11,85
C-7-18	4-12-01	55,13			52832	958,3	621,6	11,27	6796	123,3	1555	28,21
C-7-19	5-12-01	55,14			12697	230,3	212,4	3,852	1134	20,57	652,5	11,83
C-7-20	16-12-01	55,15			15678	284,3	113,2	2,052	449,8	8,156	296,7	5,38
Filter Code: Site - Sampler No. - Filter No.				*Voluntary	**Detection limits [ng/m³]: Pb: 0.91; Cd: 0.091; As: 0.91; Ni: 0.91**							

WG14 - Field Validation Programme

Analytical Results

Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	8			Filter Material:	Membrane		Quartz					
Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m³)		µg/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³	ng/filter	ng/m³
C-8-1	6-11-01	55,17			97455	1766,4	776,6	14,08	13054	236,6	1668	30,23
C-8-2	7-11-01	55,08			53828	977,3	818,9	14,87	3820	69,36	468,1	8,498
C-8-3	8-11-01	55,18			5344	96,9	37,07	0,672	477,8	8,659	533,2	9,664
C-8-4	11-11-01	55,12			65593	1190,0	1197	21,71	3498	63,47	1313	23,83
C-8-5	12-11-01	55,18			7750	140,4	226,4	4,102	823,2	14,92	577	10,46
C-8-6	13-11-01	55,2			1258	22,8	55,86	1,012	106	1,92	915,2	16,58
C-8-7	18-11-01	55,12			2338	42,4	52	0,943	242,6	4,401	457,4	8,298
C-8-8	20-11-01	55,12			114339	2074,4	997,4	18,09	13466	244,3	1473	26,73
C-8-9	21-11-01	55,09			185825	3373,1	1370	24,87	17894	324,8	989,9	17,97
C-8-10	22-11-01	55,17			1370	24,8	30,6	0,555	102,2	1,852	876,8	15,89
C-8-11	25-11-01	55,15			38203	692,7	274,6	4,978	6524	118,3	480,5	8,713
C-8-12	26-11-01	55,11			39609	718,7	297,2	5,392	1736	31,5	1336	24,24
C-8-13	27-11-01	55,18			86597	1569,4	408,8	7,408	10771	195,2	3567	64,64
C-8-14	28-11-01	55,19			110052	1994,1	898,5	16,28	5343	96,82	1045	18,93
C-8-15	29-11-01	55,13			113588	2060,4	1567	28,42	8457	153,4	705,4	12,8
C-8-16	2-12-01	55,17			1448	26,2	38,14	0,691	129,5	2,347	734,5	13,31
C-8-17	3-12-01	55,16			36409	660,1	226,4	4,105	1700	30,82	890,3	16,14
C-8-18	4-12-01	55,18			55958	1014,1	649,8	11,78	7370	133,6	1664	30,15
C-8-19	5-12-01	55,19			14009	253,8	227,5	4,123	1201	21,76	487,5	8,833
C-8-20	16-12-01	55,17			16949	307,2	121	2,194	467,2	8,468	307,7	5,578

			WG14 - Field Validation Programme: Analytical Results									
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	7			Filter Material:	Membrane		Quartz					

Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-7-1	6-11-01	55,18			96295	1745	994	18,02	15488	280,7	3027	54,9
C-7-2	7-11-01	55,16			54662	991	808	14,65	3489	63,2	427	7,7
C-7-3	8-11-01	54,18			5455	101	37	0,68	437	8,1	526	9,7
C-7-4	11-11-01	55,20			65315	1183	1135	20,57	3127	56,7	837	15,2
C-7-5	12-11-01	55,18			7659	139	226	4,09	749	13,6	490	8,9
C-7-6	13-11-01	55,12			1264	23	59	1,07	100	1,8	793	14,4
C-7-7	18-11-01	55,12			2307	42	54	0,98	220	4,0	325	5,9
C-7-8	20-11-01	55,16			107249	1944	909	16,48	12096	219,3	1319	23,9
C-7-9	21-11-01	55,15			173279	3142	1342	24,34	16435	298,0	837	15,2
C-7-10	22-11-01	55,12			1378	25	31	0,55	80	1,5	579	10,5
C-7-11	25-11-01	55,19			34637	628	264	4,78	5793	105,0	386	7,0
C-7-12	26-11-01	55,19			36985	670	267	4,84	1759	31,9	1192	21,6
C-7-13	27-11-01	55,17			75075	1361	372	6,74	9524	172,6	2859	51,8
C-7-14	28-11-01	55,15			101358	1838	862	15,63	5120	92,8	1099	19,9
C-7-15	29-11-01	55,21			109311	1980	1506	27,28	8384	151,9	625	11,3
C-7-16	2-12-01	55,16			1453	26	41	0,74	135	2,5	410	7,4
C-7-17	3-12-01	55,16			32256	585	205	3,72	1703	30,9	663	12,0
C-7-18	4-12-01	55,13			51951	942	587	10,65	6659	120,8	1660	30,1
C-7-19	5-12-01	55,14			13092	237	216	3,91	1167	21,2	453	8,2
C-7-20	16-12-01	55,15			16159	293	117	2,13	386	7,0	261	4,7

			WG14 - Field Validation Programme : Analytical Results									
Sampling Site:	Madrid (A)	Antwerp (C)		Laboratory:	A	C		Technique		AAS		
	Bristol (B)	Berlin (D)			B	D				ICP-MS		
	Preliminary Field Tests (P)											
Sampler No.:	8			Filter Material:	Membrane		Quartz					

Filter - Code	Start Date	Volume	Remark	PM-10 Conc.*	Pb		Cd		As		Ni	
	(dd/mm/yy)	(m^3)		µg/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3	ng/filter	ng/m^3
C-8-1	6-11-01	55,17			95299	1727	1006	18,23	16004	290,1	1479	26,8
C-8-2	7-11-01	55,08			54995	998	836	15,18	3684	66,9	440	8,0
C-8-3	8-11-01	55,18			4982	90	34	0,62	384	7,0	508	9,2
C-8-4	11-11-01	55,12			67585	1226	1222	22,17	3531	64,1	1175	21,3
C-8-5	12-11-01	55,18			7610	138	225	4,08	780	14,1	576	10,4
C-8-6	13-11-01	55,20			1252	23	57	1,04	101	1,8	818	14,8
C-8-7	18-11-01	55,12			2264	41	50	0,90	236	4,3	399	7,2
C-8-8	20-11-01	55,12			112216	2036	950	17,24	12833	232,8	1404	25,5
C-8-9	21-11-01	55,09			183174	3325	1444	26,21	17668	320,7	984	17,9
C-8-10	22-11-01	55,17			1344	24	30	0,55	80	1,4	585	10,6
C-8-11	25-11-01	55,15			36702	665	281	5,09	6196	112,4	482	8,7
C-8-12	26-11-01	55,11			37709	684	293	5,31	1701	30,9	1297	23,5
C-8-13	27-11-01	55,18			83437	1512	435	7,88	10677	193,5	2900	52,6
C-8-14	28-11-01	55,19			107097	1941	843	15,28	5609	101,6	1062	19,2
C-8-15	29-11-01	55,13			108126	1961	1511	27,40	8124	147,4	651	11,8
C-8-16	2-12-01	55,17			1509	27	44	0,80	152	2,8	650	11,8
C-8-17	3-12-01	55,16			35501	644	232	4,21	1862	33,8	699	12,7
C-8-18	4-12-01	55,18			54267	983	671	12,16	7221	130,9	1663	30,1
C-8-19	5-12-01	55,19			14016	254	222	4,02	1272	23,0	467	8,5
C-8-20	16-12-01	55,17			16507	299	123	2,23	397	7,2	241	4,4

ANNEX 9

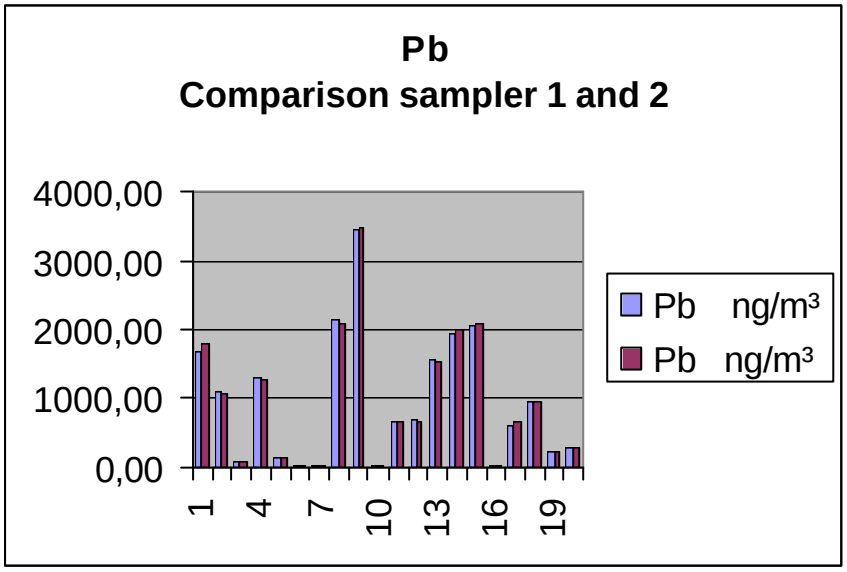
Pb															
	sampler 1	sampler 2	sampler 3	sampler 3	sampler 4	sampler 4	sampler 5	sampler 6	sampler 7	sampler 7	sampler 8	sampler 8			
	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8			
Filtertype	quartz	quartz	membrane	membrane	membrane	membrane	membrane	membrane	quartz	quartz	quartz	quartz			
Analytical method	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS			
Sample number	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8	Average	STD	RSD
	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	%
1	1706,3	1787,0	1652,9	1557,6	1766,4	1617,3	1853,2	1726,5	1710,1	1745,1	1766,4	1727,4	1718,019	79,176	4,61
2	1114,1	1066,1	982,2	906,8	1044,4	923,6	1038,6	989,7	987,7	991,0	977,3	998,5	1001,653	57,620	5,75
3	106,6	101,6	81,7	87,4	97,3	91,5	102,2	101,1	97,4	100,7	96,9	90,3	96,220	7,157	7,44
4	1306,6	1267,3	936,8	842,5	1230,8	1042,2	1247,0	1273,6	1174,5	1183,2	1190,0	1226,1	1160,058	144,289	12,44
5	143,4	139,2	107,8	95,8	133,8	97,7	147,7	139,2	133,5	138,8	140,4	137,9	129,603	18,198	14,04
6	21,3	22,9	20,9	20,7	22,4	22,3	23,0	22,3	22,7	22,9	22,8	22,7	22,244	0,806	3,62
7	42,4	41,5	40,7	39,4	41,0	41,7	43,3	45,8	40,9	41,8	42,4	41,1	41,846	1,585	3,79
8	2131,9	2094,7	1971,7	1765,2	1986,2	1762,4	2027,2	2017,8	1910,0	1944,3	2074,4	2035,9	1976,812	117,384	5,94
9	3459,5	3475,1	3287,1	3054,0	3468,4	2900,7	3530,2	3470,5	3212,5	3142,0	3373,1	3325,0	3308,169	196,430	5,94
10	27,3	25,4	28,4	29,8	30,8	31,3	24,9	25,9	24,9	25,0	24,8	24,4	26,898	2,532	9,41
11	654,6	640,4	674,6	627,3	657,9	596,7	687,7	645,3	640,5	627,6	692,7	665,5	650,899	27,334	4,20
12	675,3	647,3	702,3	635,4	694,6	643,5	692,8	688,5	678,4	670,1	718,7	684,3	677,595	25,064	3,70
13	1559,9	1542,2	1554,9	1404,4	1544,2	1351,3	1543,3	1555,1	1395,6	1360,8	1569,4	1512,1	1491,105	85,702	5,75
14	1964,1	1969,4	1943,6	1712,9	1933,9	1642,8	1954,0	1885,1	1907,5	1837,9	1994,1	1940,5	1890,484	108,551	5,74
15	2061,3	2090,8	2058,4	1768,9	2069,7	1739,8	1953,3	1639,7	2042,5	1979,9	2060,4	1961,3	1952,177	151,737	7,77
16	26,4	26,4	26,1	26,4	26,9	27,8	25,3	25,2	28,8	26,3	26,2	27,3	26,605	0,999	3,76
17	608,3	652,2	727,8	632,9	642,5	568,8	607,4	682,3	616,7	584,8	660,1	643,6	635,606	43,294	6,81
18	949,3	945,3	1038,6	923,9	996,1	900,8	1088,3	1061,1	958,3	942,3	1014,1	983,4	983,469	57,592	5,86
19	241,1	233,6	268,6	218,3	187,7	202,5	243,7	243,0	230,3	237,4	253,8	254,0	234,501	22,588	9,63
20	299,5	298,7	300,6	289,9	272,0	292,3	59,6	270,1	284,3	293,0	307,2	299,2	272,204	67,898	24,94
Avg	955,0	953,4	920,3	832,0	942,4	824,9	944,6	925,4	904,9	894,8	950,3	930,016	914,808	44,550	4,87
Standard deviation	946,3	950,8	903,3	820,7	940,6	797,1	957,3	914,2	887,5	872,6	930,4	910,8	901,3		
Minimum value															
Maximum value															

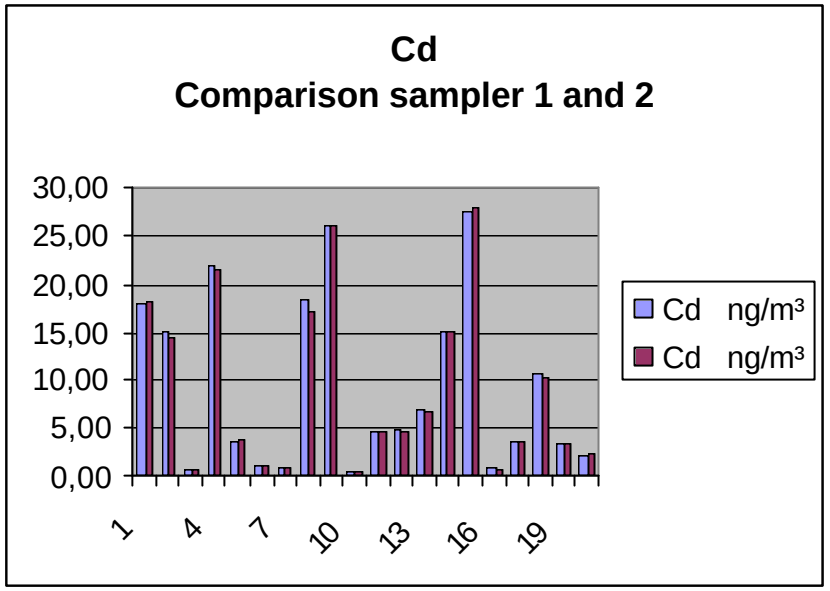
Cd															
	sampler 1	sampler 2	sampler 3	sampler 3	sampler 4	sampler 4	sampler 5	sampler 6	sampler 7	sampler 7	sampler 8	sampler 8			
	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8			
Filtertype	quartz	quartz	membrane	membrane	membrane	membrane	membrane	membrane	quartz	quartz	quartz	quartz			
Analytical method	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS			
Sample number	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8	Average	STD	RSD
	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	%
1	17,844	18,052	17,226	17,458	16,328	17,218	18,478	17,854	17,782	18,021	14,077	18,227	17,380	1,186	6,82
2	15,080	14,460	14,747	14,731	13,511	14,628	15,425	15,285	14,541	14,655	14,868	15,179	14,759	0,499	3,38
3	0,698	0,715	0,774	0,726	0,841	0,715	0,781	0,765	0,711	0,685	0,672	0,623	0,725	0,058	7,93
4	21,898	21,527	21,893	23,401	19,891	22,184	22,741	23,476	21,296	20,569	21,709	22,173	21,897	1,042	4,76
5	3,769	3,787	4,496	4,387	4,515	4,236	4,248	4,237	4,023	4,093	4,102	4,079	4,164	0,240	5,77
6	1,070	1,078	1,128	1,084	1,260	1,060	1,211	1,160	1,019	1,073	1,012	1,035	1,099	0,077	6,98
7	1,024	0,940	1,047	0,992	1,069	0,932	1,074	1,211	0,905	0,985	0,943	0,903	1,002	0,089	8,91
8	18,213	17,190	17,026	13,005	16,141	12,639	17,877	17,975	16,921	16,485	18,095	17,237	16,567	1,864	11,25
9	26,193	26,046	23,939	19,369	24,819	19,162	27,580	27,063	24,687	24,335	24,873	26,212	24,523	2,691	10,97
10	0,554	0,517	0,693	0,613	0,743	0,639	0,560	0,603	0,512	0,554	0,555	0,550	0,591	0,071	11,95
11	4,481	4,508	4,767	4,968	4,719	4,706	5,233	5,301	4,662	4,776	4,978	5,092	4,849	0,266	5,49
12	4,758	4,532	5,342	4,873	2,523	4,876	4,925	4,926	4,649	4,844	5,392	5,310	4,746	0,750	15,81
13	6,854	6,540	7,057	6,315	6,039	6,197	7,184	7,252	6,781	6,736	7,408	7,880	6,854	0,537	7,83
14	15,106	15,185	15,656	14,215	14,771	13,310	16,094	15,824	15,473	15,634	16,281	15,276	15,235	0,828	5,44
15	27,368	28,042	27,235	25,623	25,927	21,602	26,507	22,335	28,278	27,278	28,417	27,403	26,335	2,216	8,42
16	0,808	0,791	0,788	0,687	0,722	0,683	0,708	0,665	0,792	0,745	0,691	0,799	0,740	0,053	7,19
17	3,700	3,696	4,648	4,074	3,740	3,729	4,128	4,285	3,901	3,725	4,105	4,213	3,995	0,300	7,50
18	10,751	10,295	11,020	11,378	10,515	10,602	11,619	11,245	11,274	10,653	11,777	12,162	11,108	0,568	5,11
19	3,534	3,507	4,489	4,065	3,822	4,031	3,944	3,965	3,852	3,914	4,123	4,022	3,939	0,259	6,59
20	2,097	2,202	2,432	2,171	2,909	2,543	1,291	2,135	2,052	2,129	2,194	2,226	2,198	0,375	17,04
Average	9,290	9,180	9,320	8,707	8,740	8,285	9,580	9,378	9,206	9,094	9,314	9,530	9,135	0,378	4,14
Standard deviation	9,026	9,008	8,585	8,061	8,340	7,453	9,169	8,710	8,859	8,645	8,827	8,971	8,601		
Minimum value															
Maximum value															

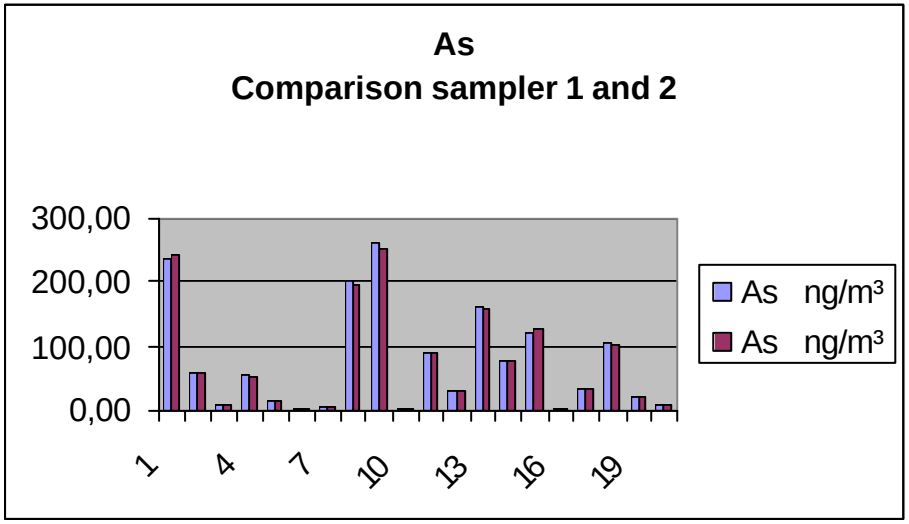
As															
	sampler 1	sampler 2	sampler 3	sampler 3	sampler 4	sampler 4	sampler 5	sampler 6	sampler 7	sampler 7	sampler 8	sampler 8			
	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8			
Filtertype	quartz	quartz	membrane	membrane	membrane	membrane	membrane	membrane	quartz	quartz	quartz	quartz			
Analytical method	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS			
Sample number	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8	Average	STD	RSD
	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	%
1	237,101	242,489	276,664	293,200	275,571	301,377	275,036	271,252	287,584	280,678	236,620	290,082	272,305	22,036	8,09
2	58,103	56,848	66,987	72,429	65,941	73,304	66,784	64,260	64,103	63,247	69,357	66,892	65,688	4,931	7,51
3	9,086	8,189	9,004	8,103	8,460	8,266	8,013	7,731	7,673	8,073	8,659	6,961	8,185	0,588	7,18
4	53,301	52,245	57,395	62,718	60,382	66,260	59,871	61,620	57,082	56,654	63,467	64,060	59,588	4,342	7,29
5	14,906	14,976	15,228	14,672	13,926	14,397	14,086	14,917	12,912	13,573	14,919	14,131	14,387	0,686	4,77
6	1,732	1,793	1,595	1,913	1,595	1,740	1,403	1,426	1,407	1,813	1,920	1,834	1,681	0,191	11,38
7	5,520	5,211	4,555	4,262	4,066	4,219	4,548	4,448	3,446	3,996	4,401	4,283	4,413	0,540	12,24
8	201,993	195,573	218,359	230,644	214,291	230,141	214,338	219,634	225,363	219,280	244,304	232,817	220,561	13,433	6,09
9	262,253	253,583	292,564	313,021	284,663	301,124	291,697	285,222	313,009	298,007	324,823	320,704	295,056	21,852	7,41
10	2,117	1,886	1,251	1,966	1,088	2,070	1,130	1,290	1,522	1,453	1,852	1,444	1,589	0,372	23,39
11	90,711	90,386	113,558	121,606	100,163	111,470	101,452	104,881	103,021	104,962	118,293	112,354	106,072	9,842	9,28
12	28,981	28,336	32,794	33,121	29,261	32,184	34,066	33,648	28,834	31,880	31,503	30,856	31,289	2,011	6,43
13	161,451	158,783	188,570	207,366	177,149	205,840	197,333	202,485	176,943	172,634	195,201	193,496	186,437	16,727	8,97
14	75,675	75,905	94,933	107,483	86,628	103,052	101,655	103,498	88,140	92,843	96,819	101,623	94,021	10,586	11,26
15	121,343	126,171	156,039	175,717	136,719	166,988	159,099	157,436	146,644	151,862	153,403	147,363	149,899	15,734	10,50
16	2,967	2,490	2,014	2,504	1,851	2,486	2,387	2,251	2,304	2,456	2,347	2,760	2,402	0,296	12,33
17	31,582	31,883	33,097	37,346	27,996	34,368	34,872	35,821	29,216	30,867	30,818	33,760	32,635	2,749	8,42
18	105,846	101,903	130,959	138,390	109,318	135,950	128,452	123,777	123,274	120,789	133,569	130,858	123,590	12,057	9,76
19	21,656	21,937	20,344	23,566	17,572	22,355	22,168	22,258	20,573	21,169	21,759	23,047	21,534	1,550	7,20
20	9,067	9,560	8,731	8,515	7,635	8,589	2,503	8,995	8,156	7,005	8,468	7,193	7,868	1,852	23,54
Avg	74,770	74,007	86,232	92,927	81,214	91,309	86,045	86,342	85,060	84,162	88,125	89,326	84,960	5,847	6,88
Standard deviation	82,363	81,416	94,826	101,675	92,004	100,621	94,921	94,065	98,126	94,883	97,431	100,625	94,263		
Minimum value															
Maximum value															

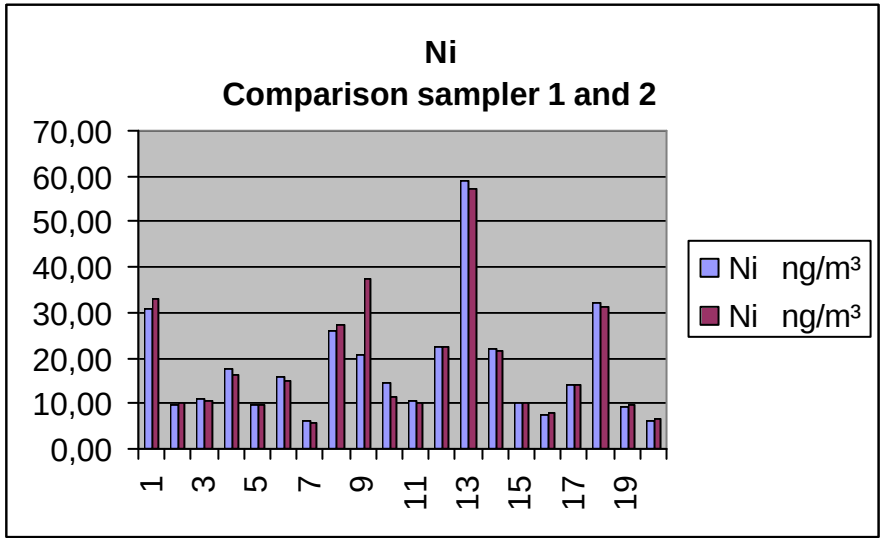
Ni															
	sampler 1	sampler 2	sampler 3	sampler 3	sampler 4	sampler 4	sampler 5	sampler 6	sampler 7	sampler 7	sampler 8	sampler 8			
	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8			
Filtertype	quartz	quartz	membrane	membrane	membrane	membrane	membrane	membrane	quartz	quartz	quartz	quartz			
Analytical method	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS	GF-AAS	GF-AAS	GF-AAS	ICP-MS	GF-AAS	ICP-MS			
Sample number	C1	C2	C3	C3	C4	C4	C5	C6	C7	C7	C8	C8	Average	STD	RSD
	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	conc (ng/m³)	%
1	30,906	33,073	21,940	26,963	25,009	28,271	29,907	30,261	59,024	54,851	30,232	26,804	33,104	11,549	34,89
2	9,693	10,209	6,421	6,893	6,511	6,754	9,643	10,631	8,253	7,732	8,498	7,991	8,269	1,489	18,00
3	10,845	10,749	7,482	7,728	7,917	7,879	8,642	8,737	9,414	9,709	9,664	9,210	8,998	1,135	12,62
4	17,783	16,509	13,336	14,112	14,067	14,480	17,124	29,944	15,295	15,158	23,826	21,323	17,746	4,955	27,92
5	9,732	9,603	5,729	6,371	5,295	5,924	11,539	13,003	8,583	8,877	10,456	10,430	8,795	2,487	28,28
6	15,642	15,115	11,548	12,250	11,875	12,458	16,150	16,576	13,948	14,391	16,579	14,816	14,279	1,851	12,97
7	6,010	5,646	3,538	4,106	2,814	3,396	12,901	12,058	8,161	5,894	8,298	7,239	6,672	3,263	48,91
8	26,015	27,404	18,187	23,772	21,817	23,631	29,528	26,722	25,692	23,905	26,732	25,470	24,906	2,939	11,80
9	20,697	37,304	13,946	15,611	21,809	23,749	17,287	16,872	16,085	15,177	17,969	17,865	19,531	6,288	32,20
10	14,719	11,516	8,450	9,362	9,482	9,211	10,136	12,321	10,653	10,503	15,893	10,597	11,070	2,250	20,33
11	10,559	10,176	5,891	6,616	6,025	6,550	9,437	8,727	7,603	6,985	8,713	8,741	8,002	1,609	20,11
12	22,662	22,444	22,020	22,965	20,367	22,019	23,334	22,586	21,142	21,604	24,241	23,541	22,410	1,072	4,78
13	58,894	57,221	40,366	51,324	42,111	51,143	55,072	53,818	51,953	51,827	64,640	52,559	52,577	6,592	12,54
14	21,862	21,568	16,564	17,597	18,259	19,077	18,240	17,818	19,469	19,933	18,929	19,234	19,046	1,547	8,13
15	10,145	9,998	11,095	9,385	9,048	9,400	10,952	10,968	11,136	11,322	12,795	11,814	10,672	1,105	10,36
16	7,323	7,706	3,575	4,079	3,593	4,027	5,051	4,766	7,715	7,442	13,313	11,790	6,698	3,198	47,75
17	14,091	14,048	9,931	11,293	10,621	11,411	12,280	12,346	11,853	12,024	16,140	12,679	12,393	1,694	13,67
18	32,308	31,122	24,107	28,766	26,178	29,623	29,424	28,162	28,210	30,109	30,148	30,137	29,024	2,198	7,57
19	9,206	9,759	6,661	6,956	6,667	7,261	7,926	8,002	11,833	8,220	8,833	8,468	8,316	1,484	17,84
20	6,317	6,597	3,231	3,986	2,818	3,988	3,768	4,553	5,380	4,729	5,578	4,367	4,609	1,170	25,39
Avg	17,770	18,388	12,701	14,507	13,614	15,013	16,917	17,444	17,570	17,020	18,574	16,754	16,356	1,924	11,76
Standard deviation	12,481	13,103	9,175	11,624	10,113	11,935	11,929	11,764	14,399	14,059	13,199	11,169	11,694		
Minimum value															
Maximum value															

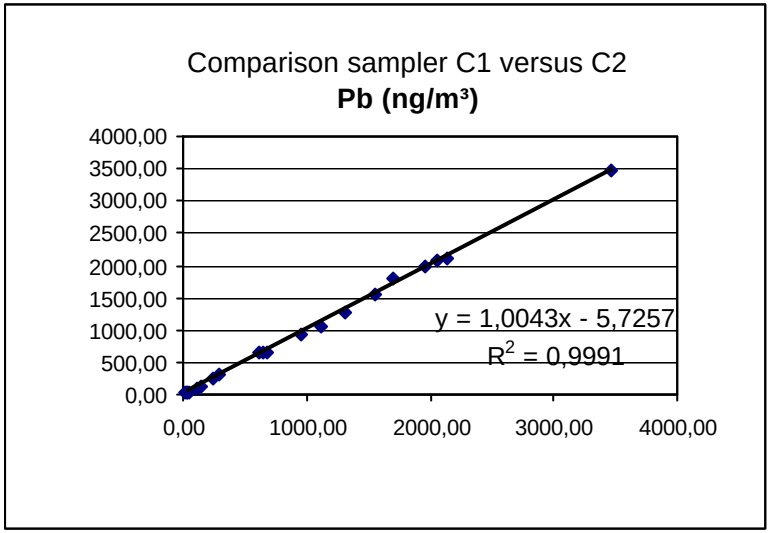
ANNEX 10

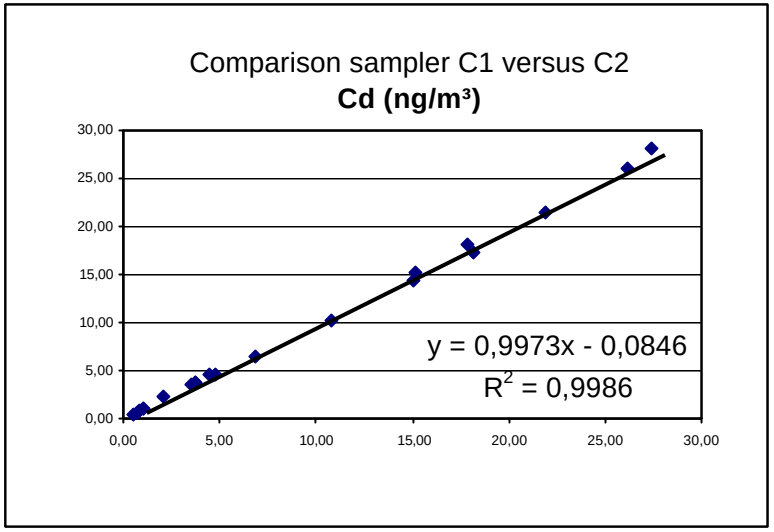

Pb
Comparison sampler 1 and 2
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

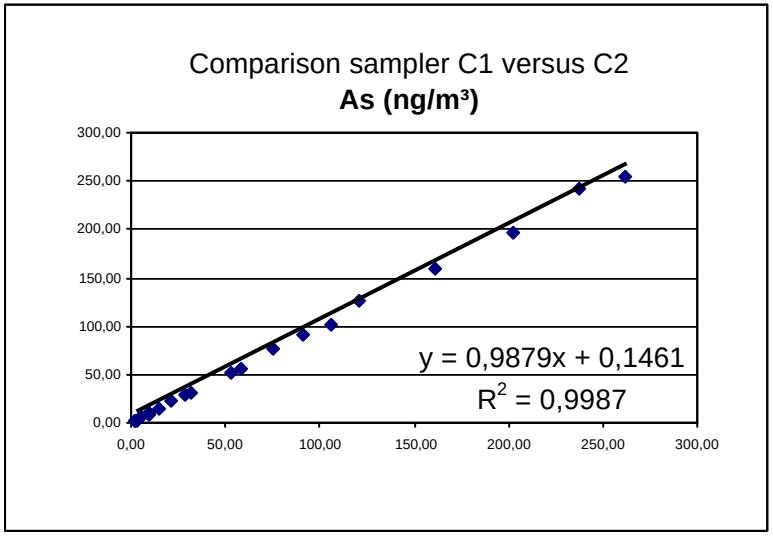

Cd
Comparison sampler 1 and 2
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

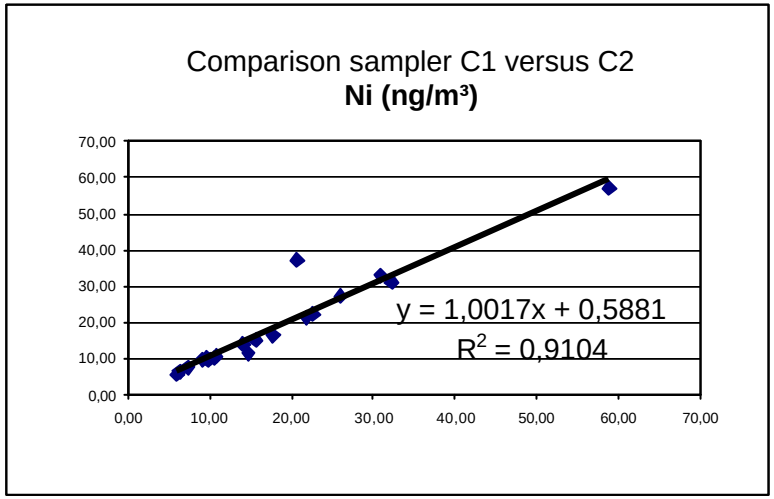

As
Comparison sampler 1 and 2
300,00
200,00
100,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison sampler 1 and 2
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
3
5
7
9
11
13
15
17
19
Ni ng/m³
Ni ng/m³

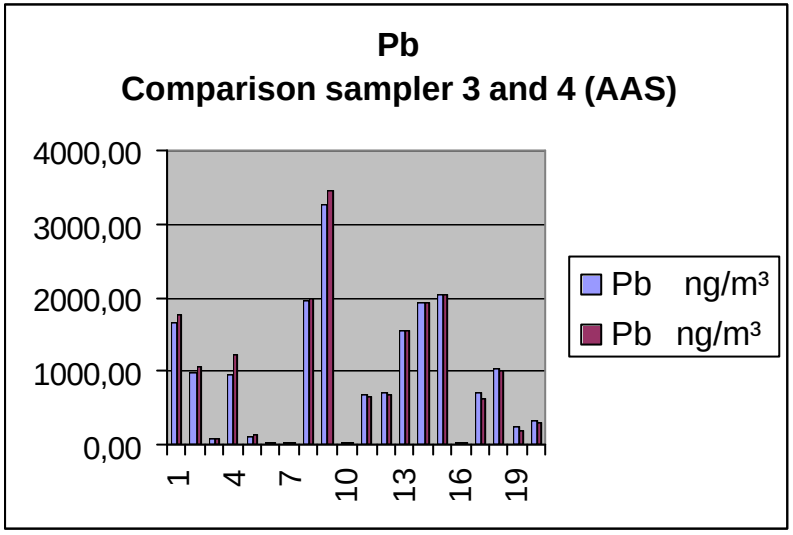

Comparison sampler C1 versus C2
Pb (ng/m³)
4000,00
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 1,0043x - 5,7257
R2 = 0,9991

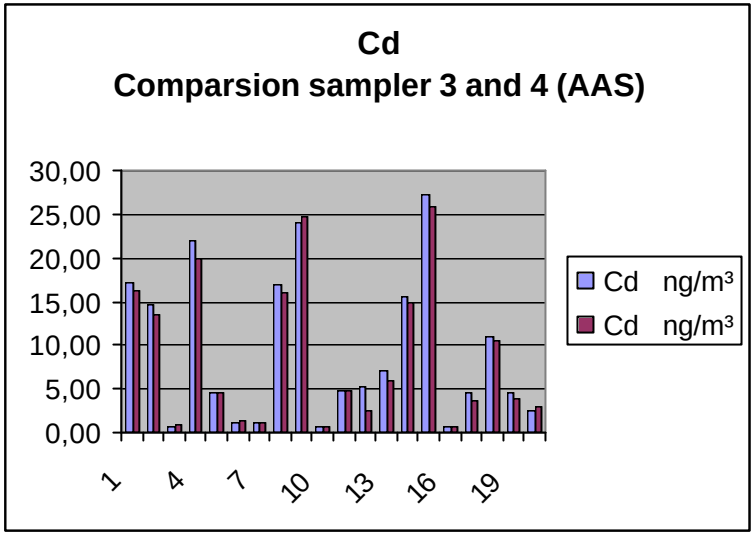

Comparison sampler C1 versus C2
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,9973x - 0,0846
R2 = 0,9986

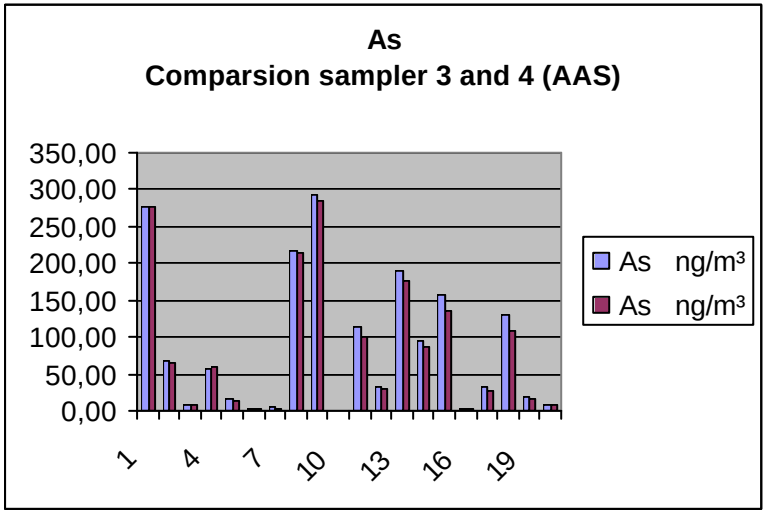

Comparison sampler C1 versus C2
As (ng/m³)
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
y = 0,9879x + 0,1461
R2 = 0,9987

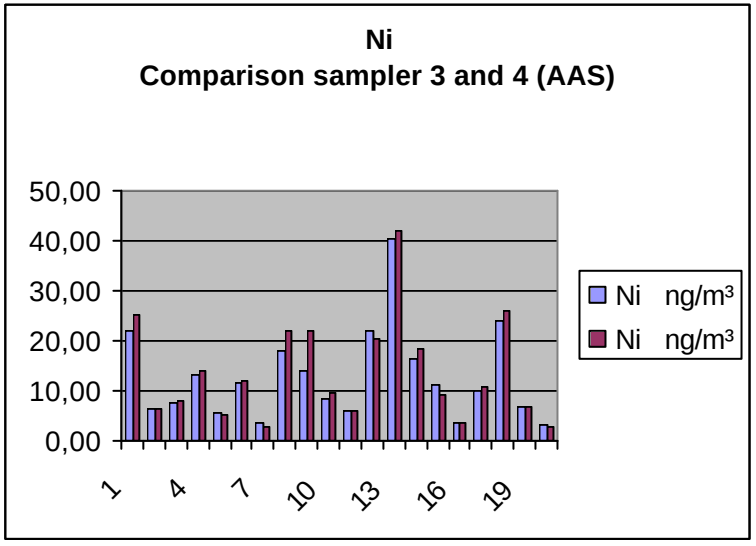

Comparison sampler C1 versus C2
Ni (ng/m³)
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
y = 1,0017x + 0,5881
R2 = 0,9104

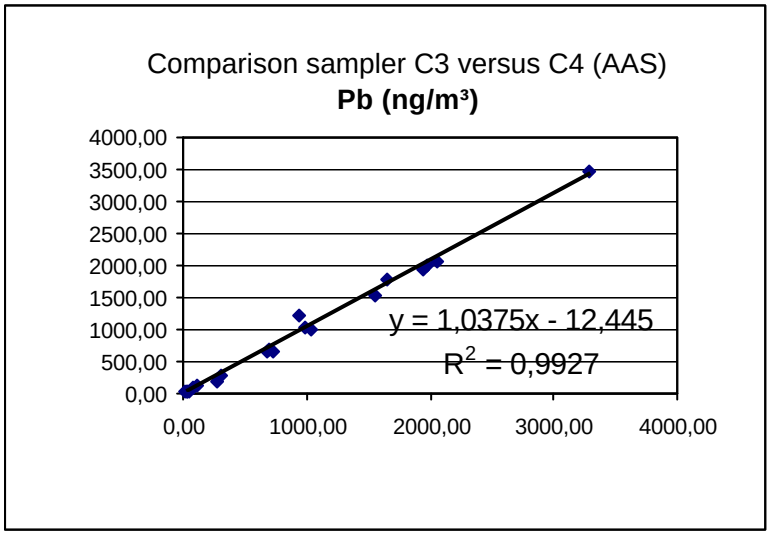
ANNEX 11

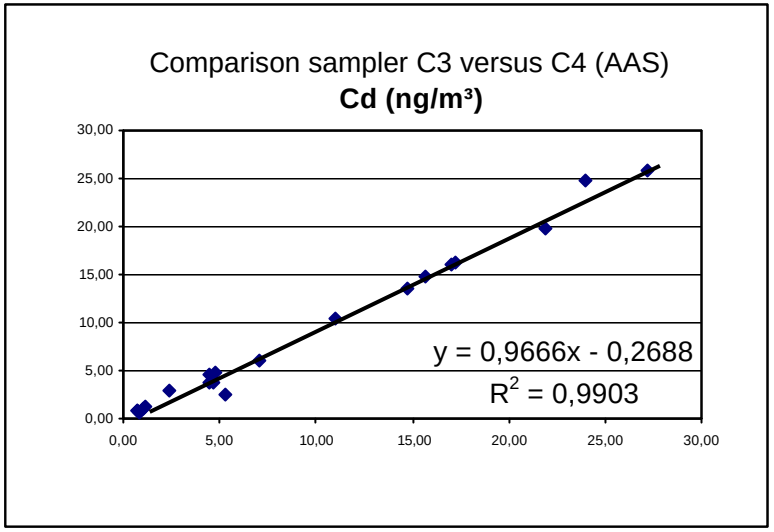

Pb
Comparison sampler 3 and 4 (AAS)
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

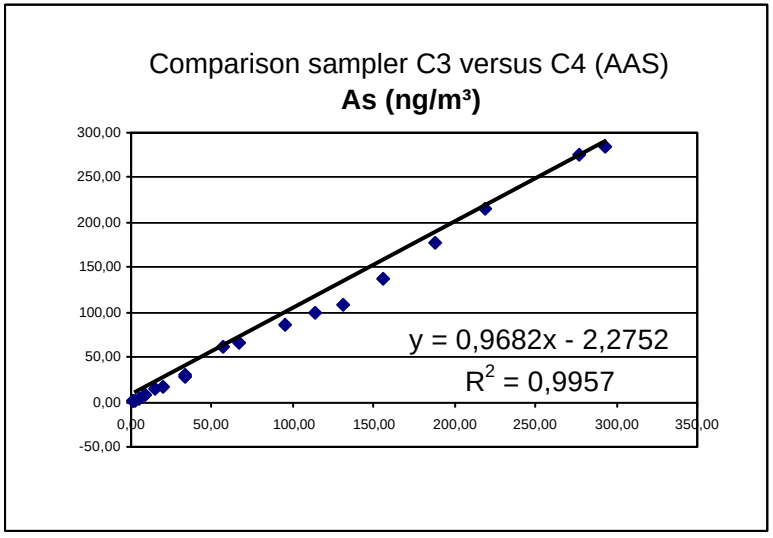

Cd
Comparsion sampler 3 and 4 (AAS)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

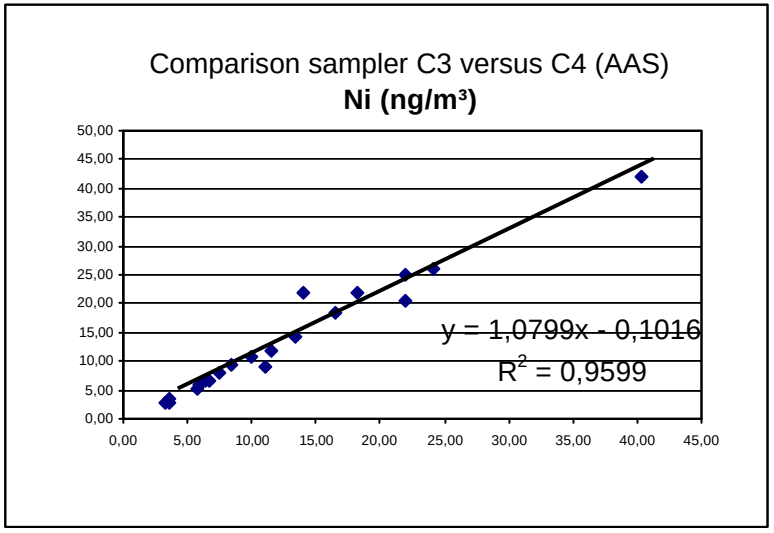

As
Comparsion sampler 3 and 4 (AAS)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³

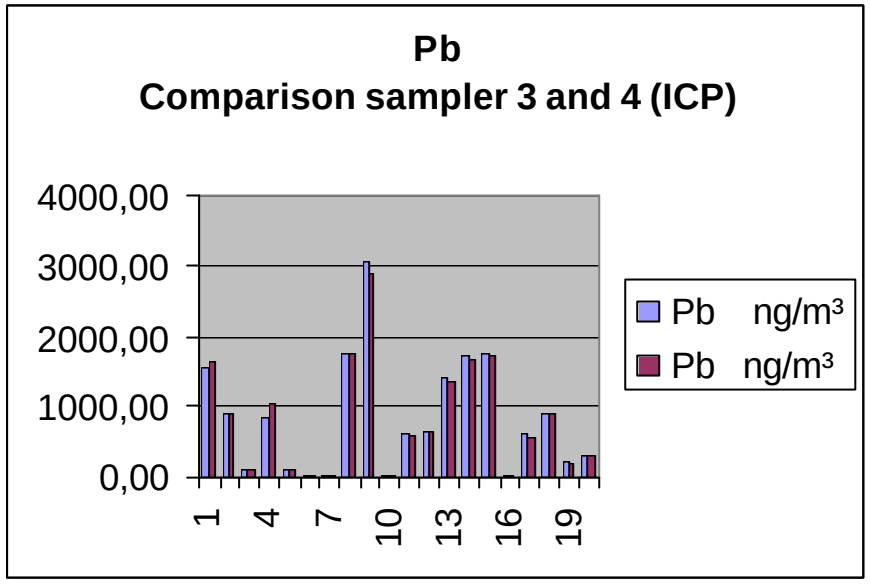

Ni
Comparison sampler 3 and 4 (AAS)
50,00
40,00
30,00
20,00
10,00
0,00
1
4
7
10
13
16
19
Ni ng/m³
Ni ng/m³

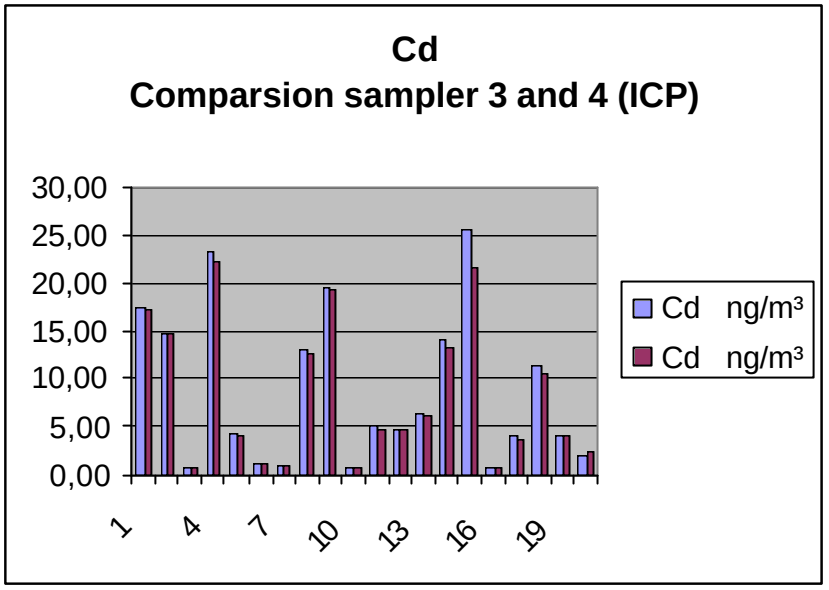

Comparison sampler C3 versus C4 (AAS)
Pb (ng/m³)
4000,00
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 1,0375x - 12,445
R2 = 0,9927

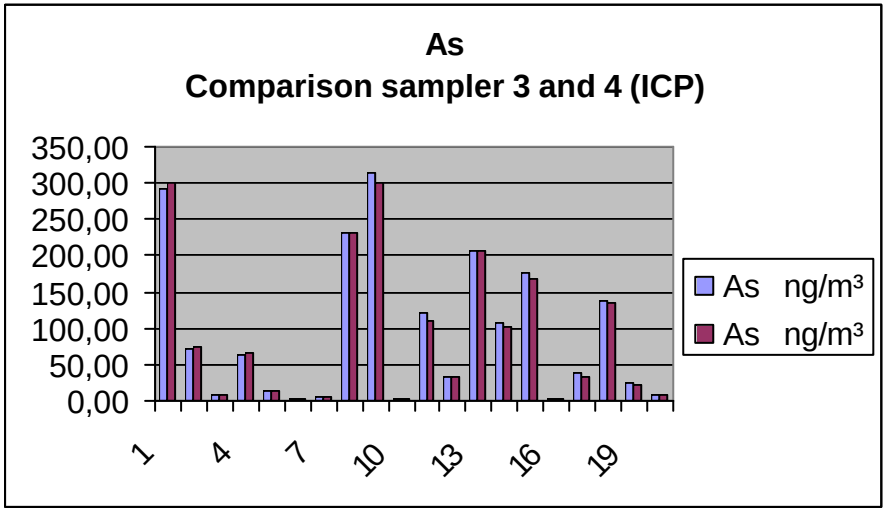

Comparison sampler C3 versus C4 (AAS)
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,9666x - 0,2688
R2 = 0,9903

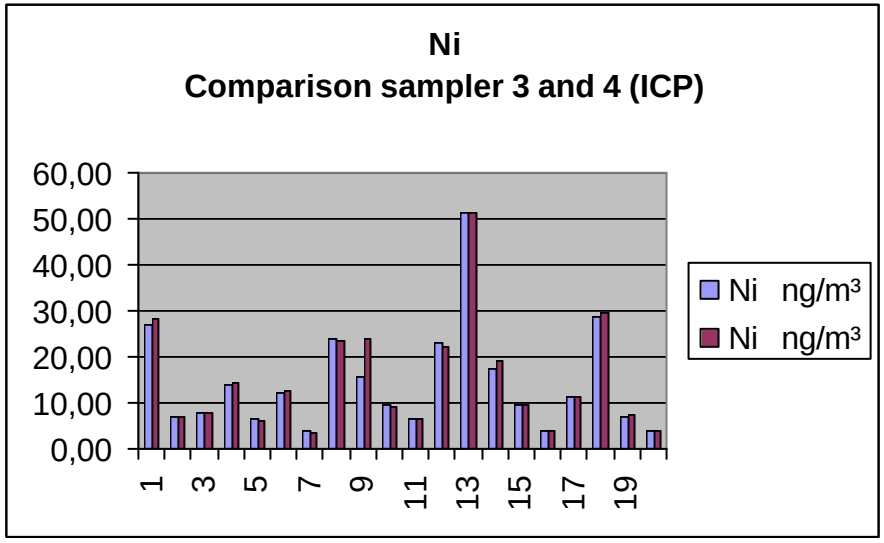

Comparison sampler C3 versus C4 (AAS)
As (ng/m³)
300,00
250,00
200,00
150,00
100,00
50,00
0,00
-50,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 0,9682x - 2,2752
R2 = 0,9957

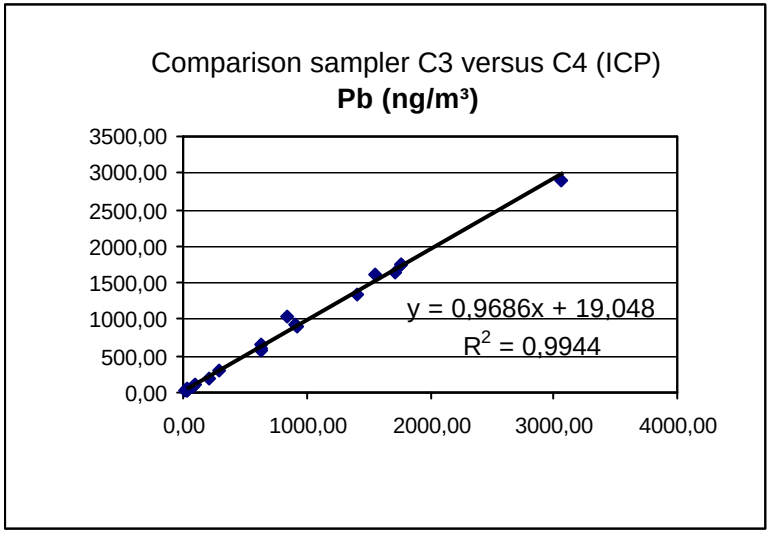

Comparison sampler C3 versus C4 (AAS)
Ni (ng/m³)
50,00
45,00
40,00
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
35,00
40,00
45,00
y = 1,0799x - 0,1016
R2 = 0,9599

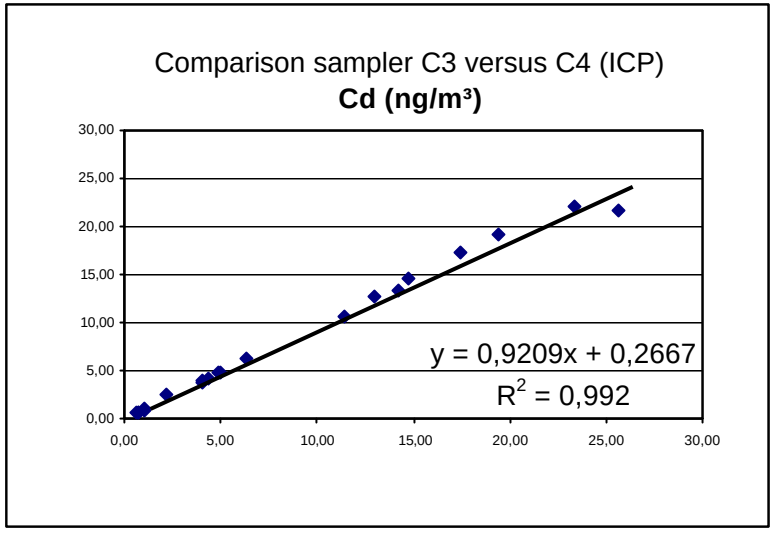

Pb
Comparison sampler 3 and 4 (ICP)
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

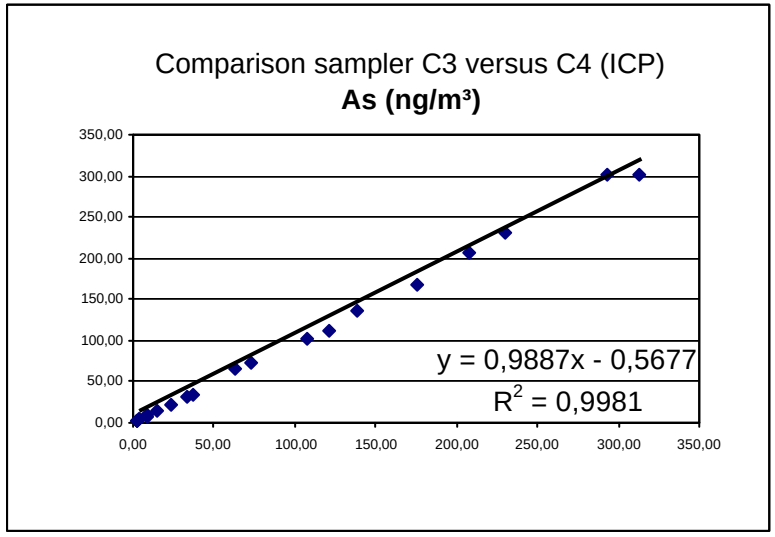

Cd
Comparsion sampler 3 and 4 (ICP)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

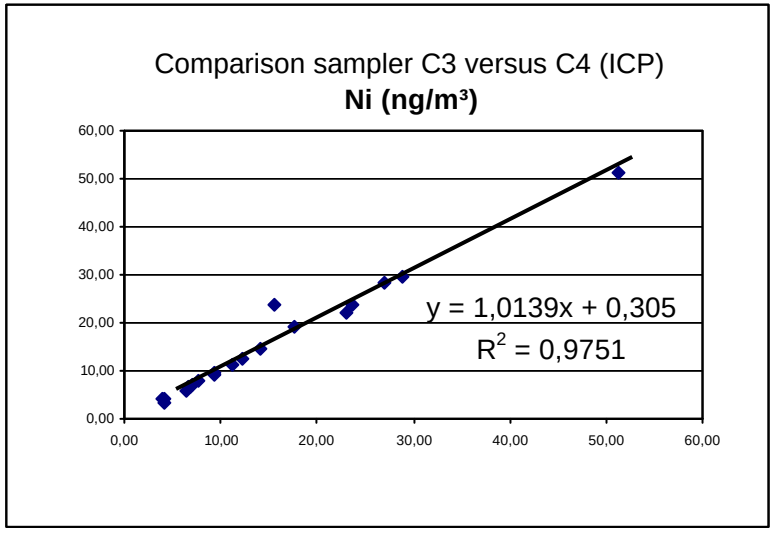

As
Comparison sampler 3 and 4 (ICP)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison sampler 3 and 4 (ICP)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
3
5
7
9
11
13
15
17
19
Ni ng/m³
Ni ng/m³

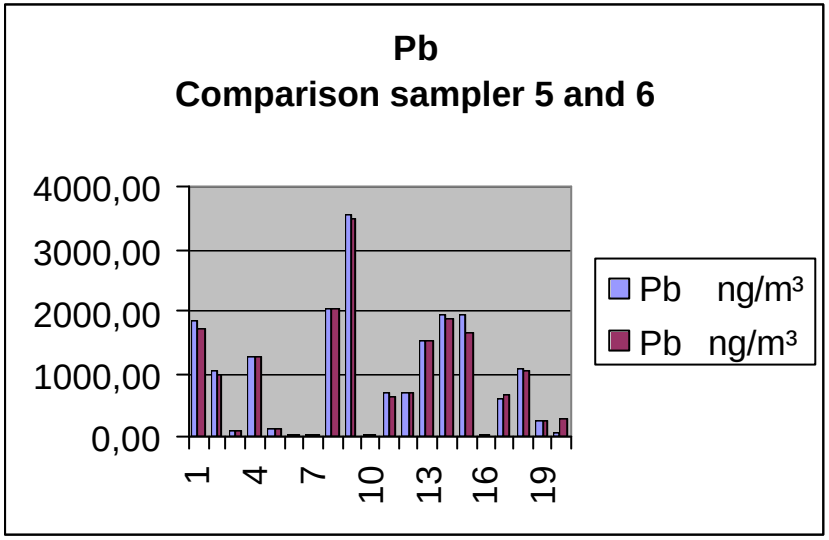

Comparison sampler C3 versus C4 (ICP)
Pb (ng/m³)
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 0,9686x + 19,048
R2 = 0,9944

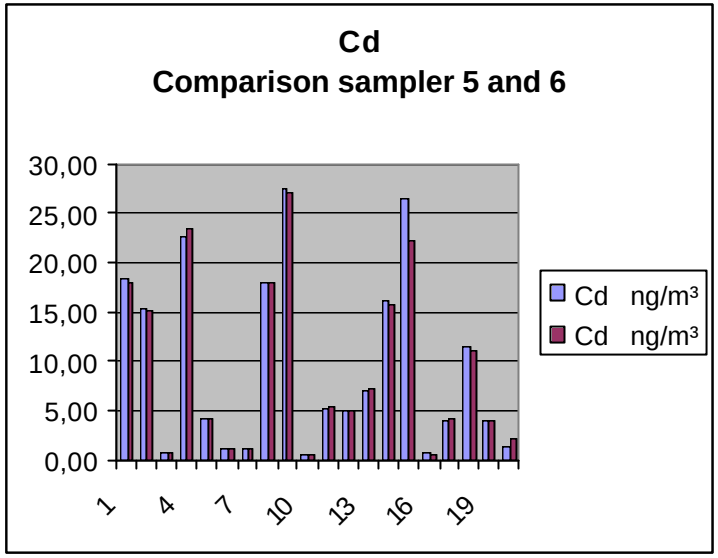

Comparison sampler C3 versus C4 (ICP)
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,9209x + 0,2667
R2 = 0,992

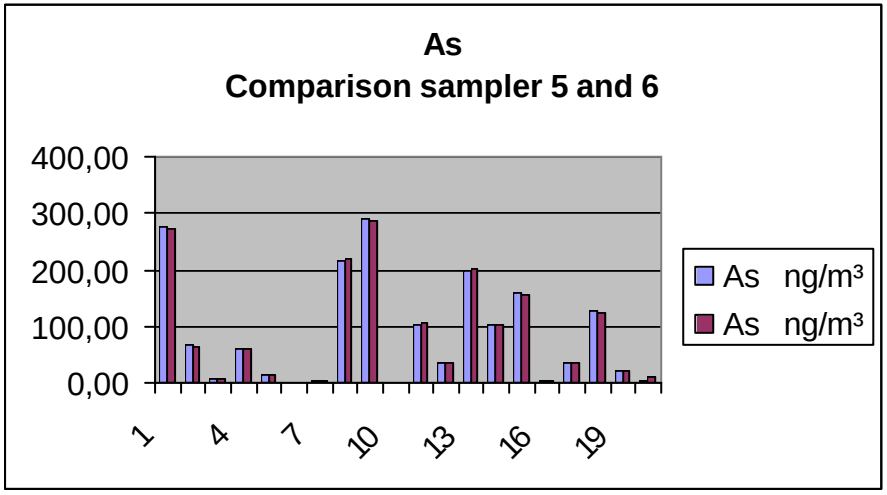

Comparison sampler C3 versus C4 (ICP)
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 0,9887x - 0,5677
R2 = 0,9981

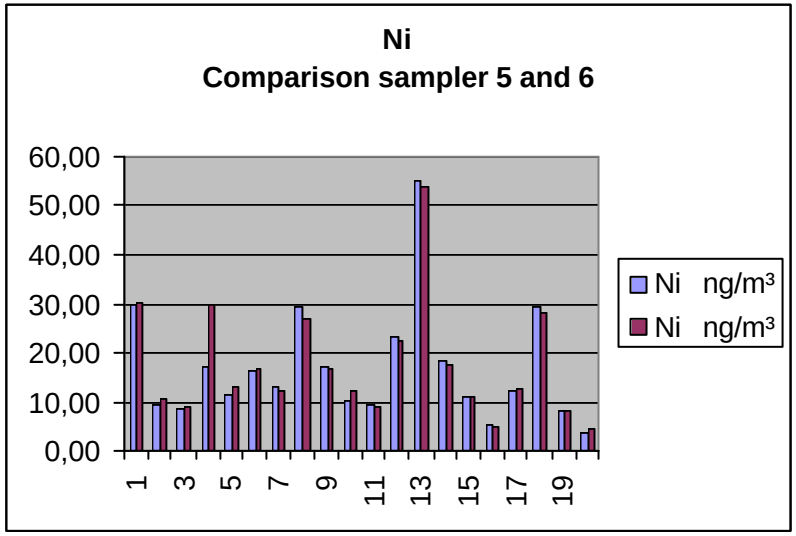

Comparison sampler C3 versus C4 (ICP)
Ni (ng/m³)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
y = 1,0139x + 0,305
R2 = 0,9751

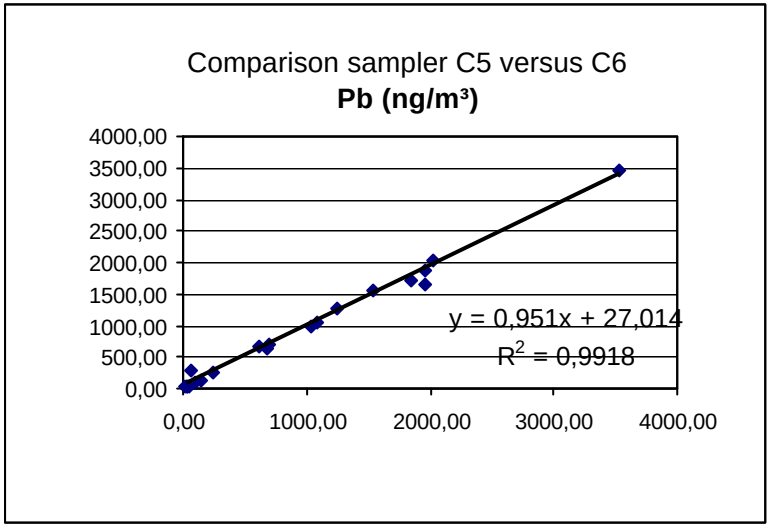
ANNEX 12

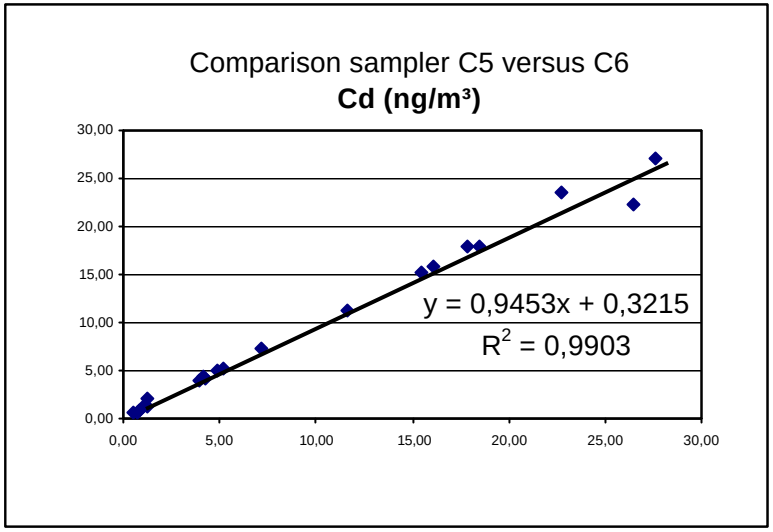

Pb
Comparison sampler 5 and 6
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

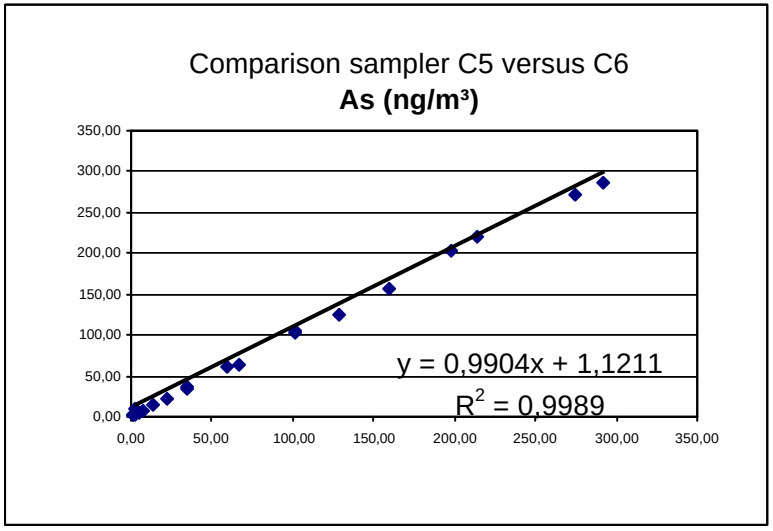

Cd
Comparison sampler 5 and 6
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

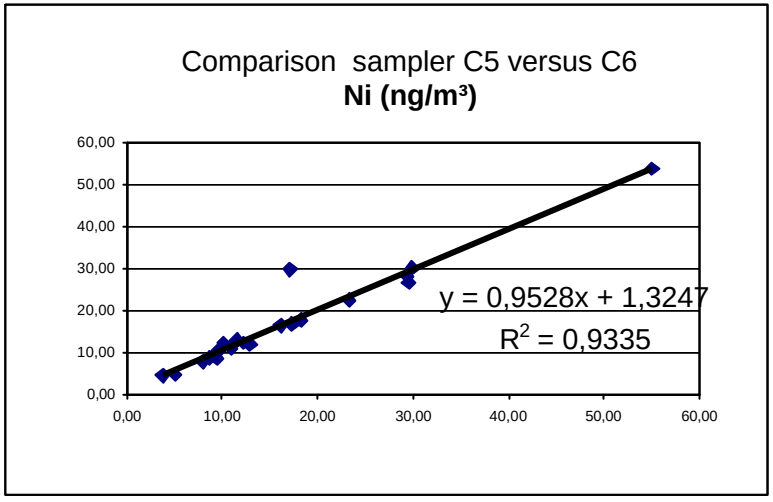

As
Comparison sampler 5 and 6
400,00
300,00
200,00
100,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison sampler 5 and 6
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
3
5
7
9
11
13
15
17
19
Ni ng/m³
Ni ng/m³

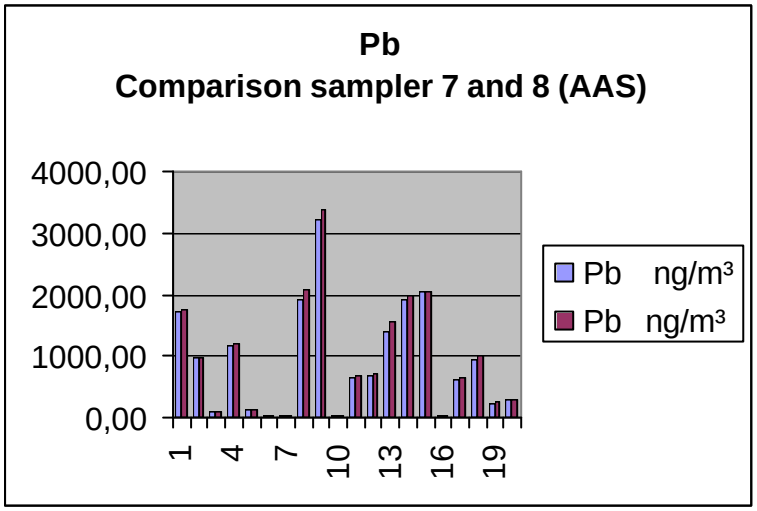

Comparison sampler C5 versus C6
Pb (ng/m³)
4000,00
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 0,951x + 27,014
R2 = 0,9918

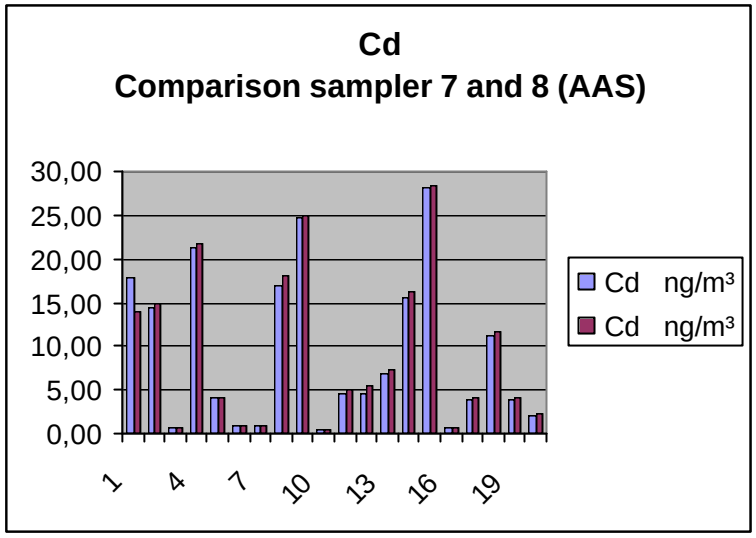

Comparison sampler C5 versus C6
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,9453x + 0,3215
R2 = 0,9903

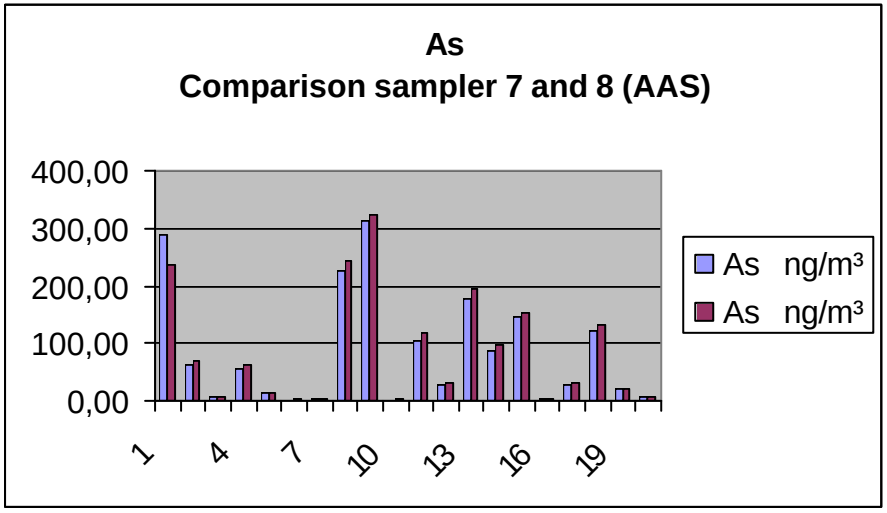

Comparison sampler C5 versus C6
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 0,9904x + 1,1211
R2 = 0,9989

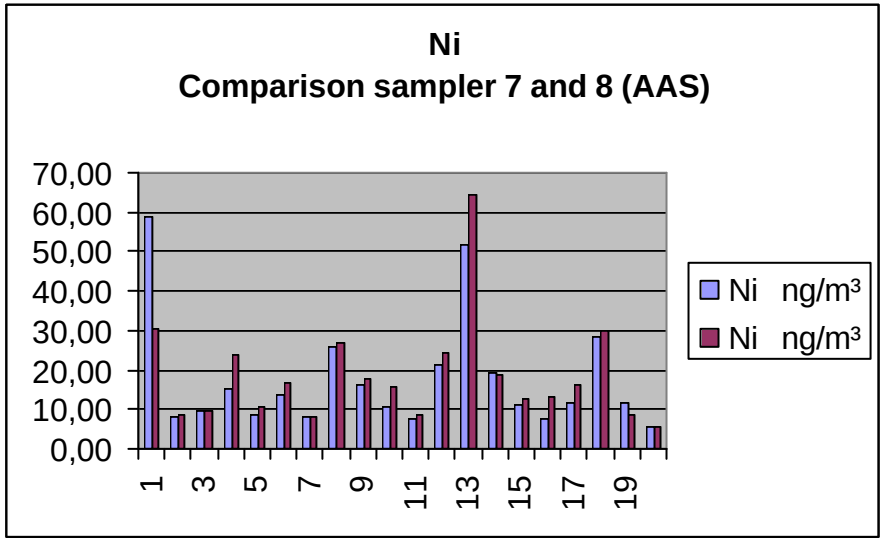

Comparison sampler C5 versus C6
Ni (ng/m³)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
y = 0,9528x + 1,3247
R2 = 0,9335

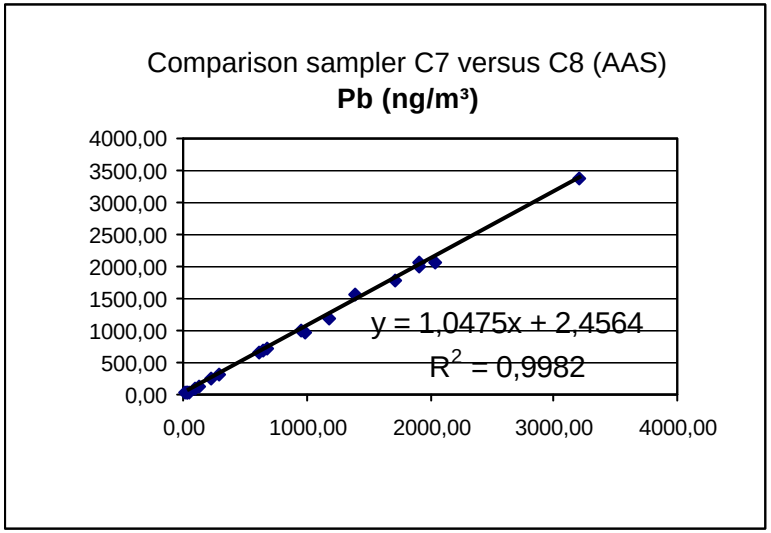
ANNEX 13

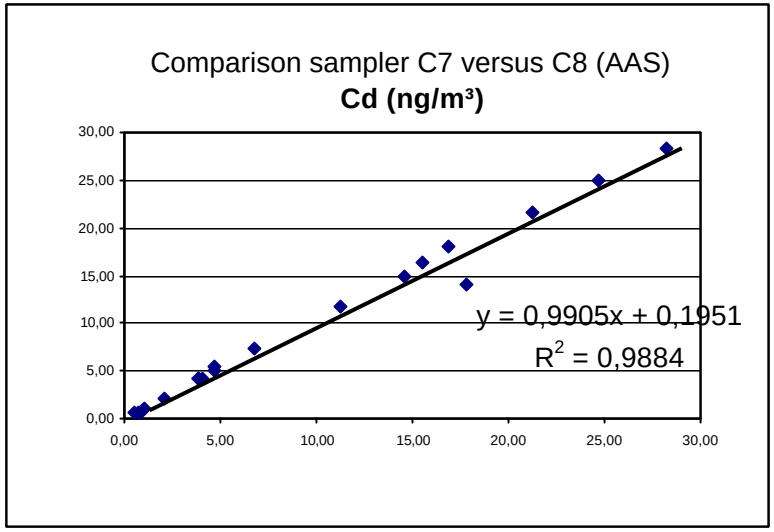

Pb
Comparison sampler 7 and 8 (AAS)
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

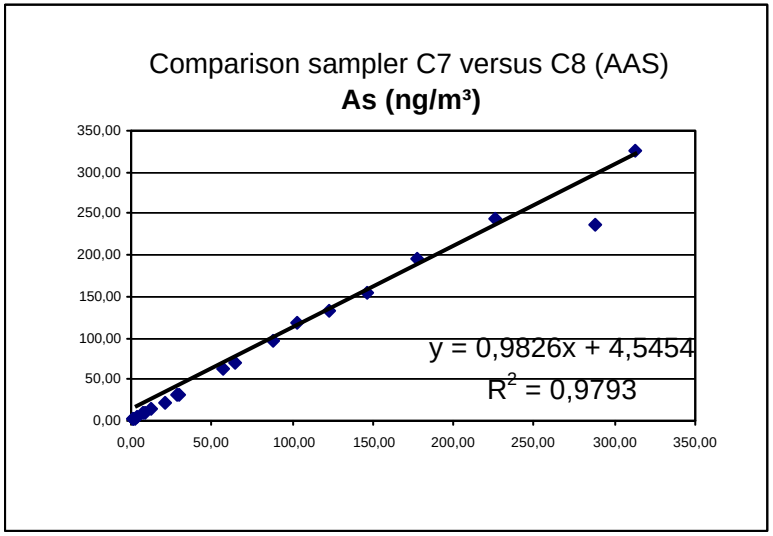

Cd
Comparison sampler 7 and 8 (AAS)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

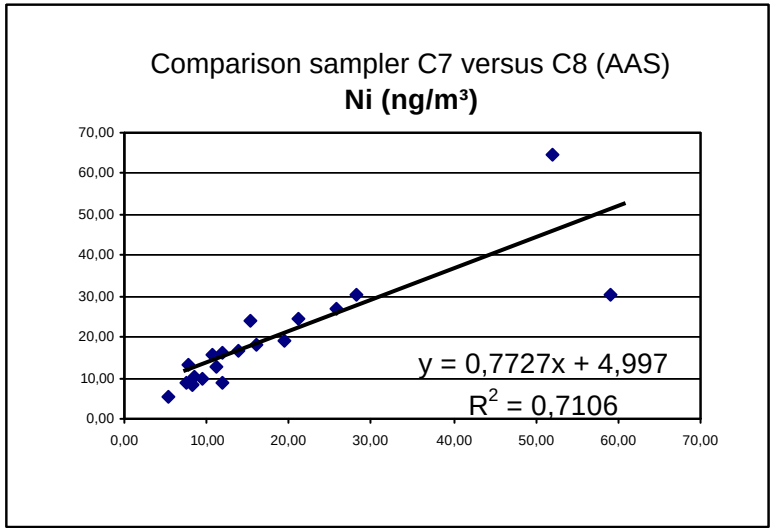

As
Comparison sampler 7 and 8 (AAS)
400,00
300,00
200,00
100,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³

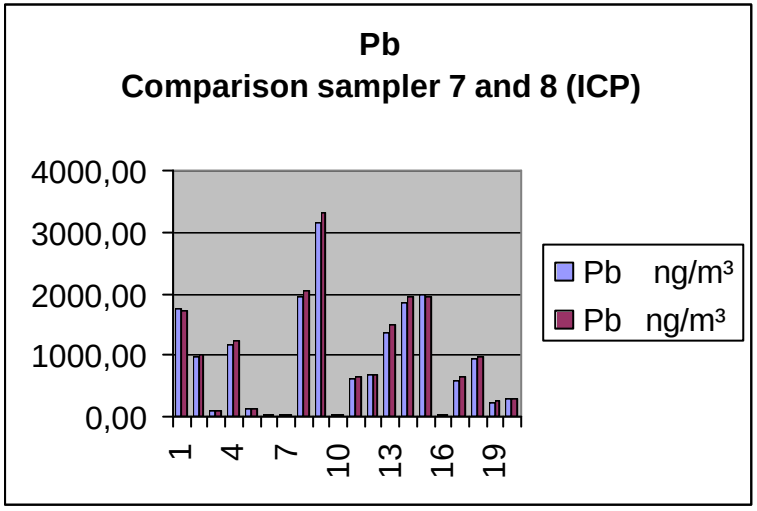

Ni
Comparison sampler 7 and 8 (AAS)
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
3
5
7
9
11
13
15
17
19
Ni ng/m³
Ni ng/m³

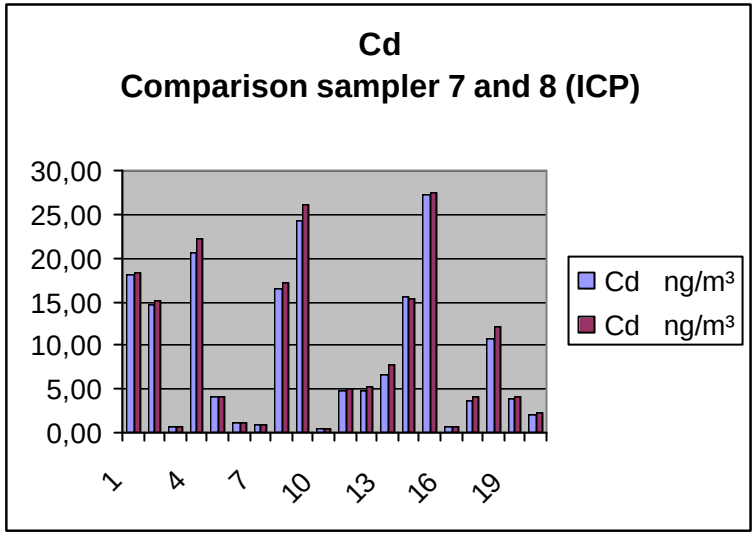

Comparison sampler C7 versus C8 (AAS)
Pb (ng/m³)
4000,00
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 1,0475x + 2,4564
R2 = 0,9982

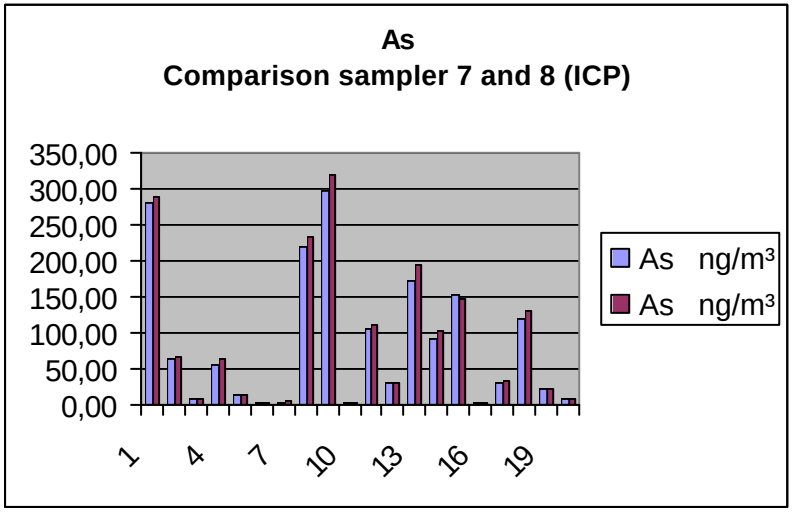

Comparison sampler C7 versus C8 (AAS)
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,9905x + 0,1951
R2 = 0,9884

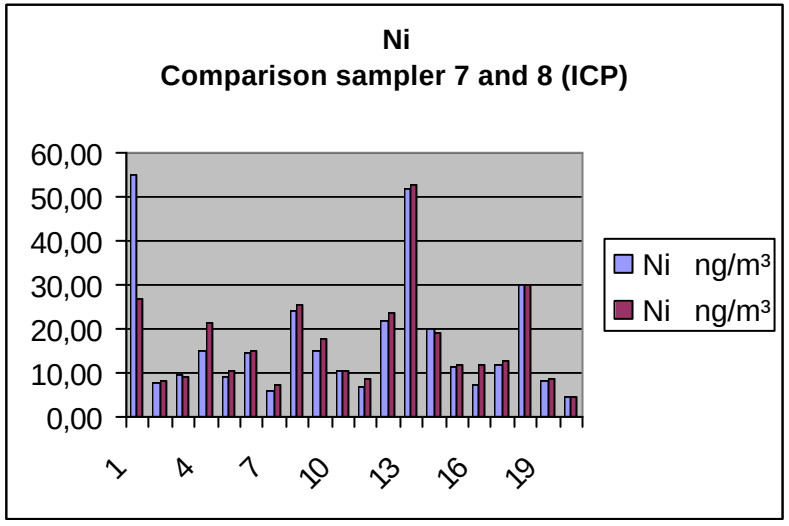

Comparison sampler C7 versus C8 (AAS)
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 0,9826x + 4,5454
R2 = 0,9793

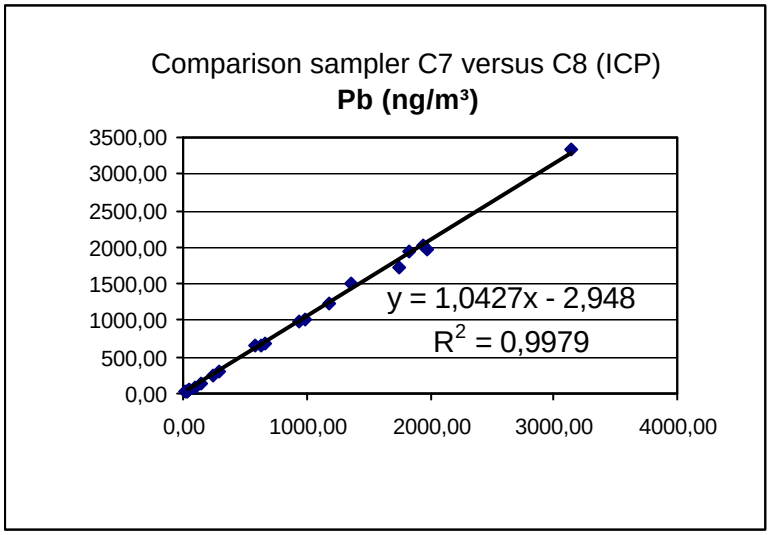

Comparison sampler C7 versus C8 (AAS)
Ni (ng/m³)
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
y = 0,7727x + 4,997
R2 = 0,7106

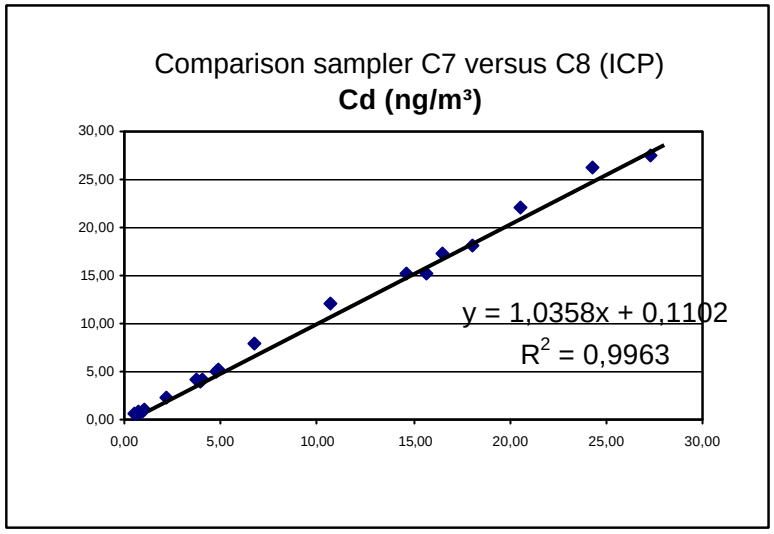

Pb
Comparison sampler 7 and 8 (ICP)
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

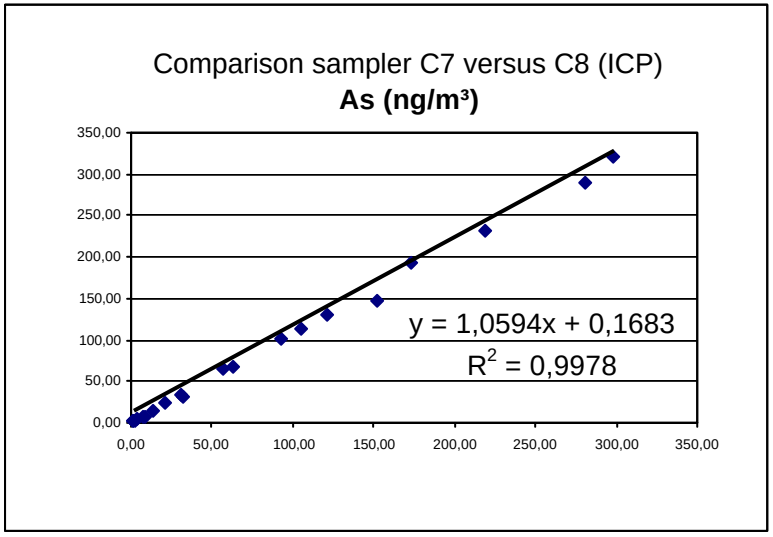

Cd
Comparison sampler 7 and 8 (ICP)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

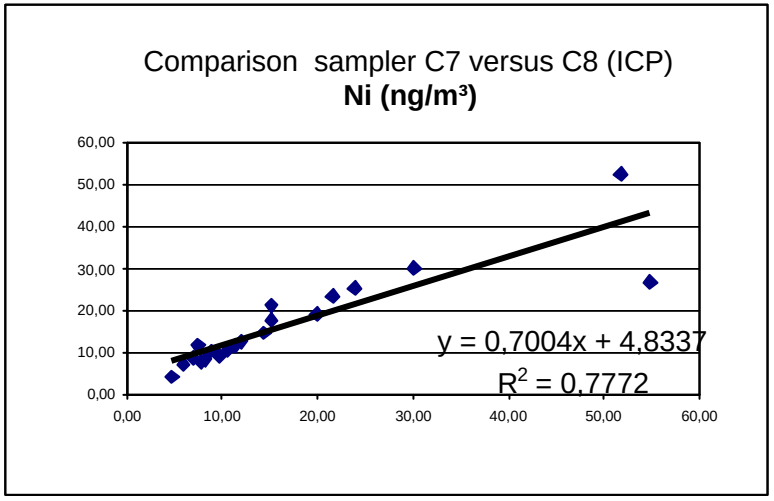

As
Comparison sampler 7 and 8 (ICP)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison sampler 7 and 8 (ICP)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
4
7
10
13
16
19
Ni ng/m³
Ni ng/m³

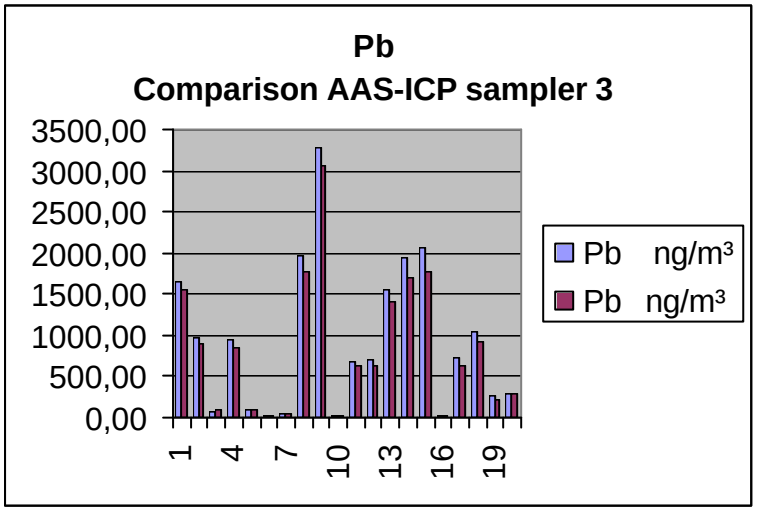

Comparison sampler C7 versus C8 (ICP)
Pb (ng/m³)
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 1,0427x - 2,948
R2 = 0,9979

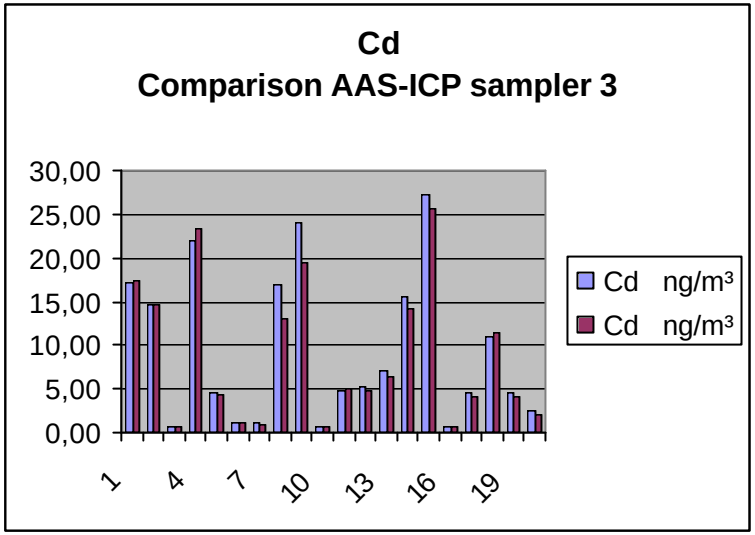

Comparison sampler C7 versus C8 (ICP)
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 1,0358x + 0,1102
R2 = 0,9963

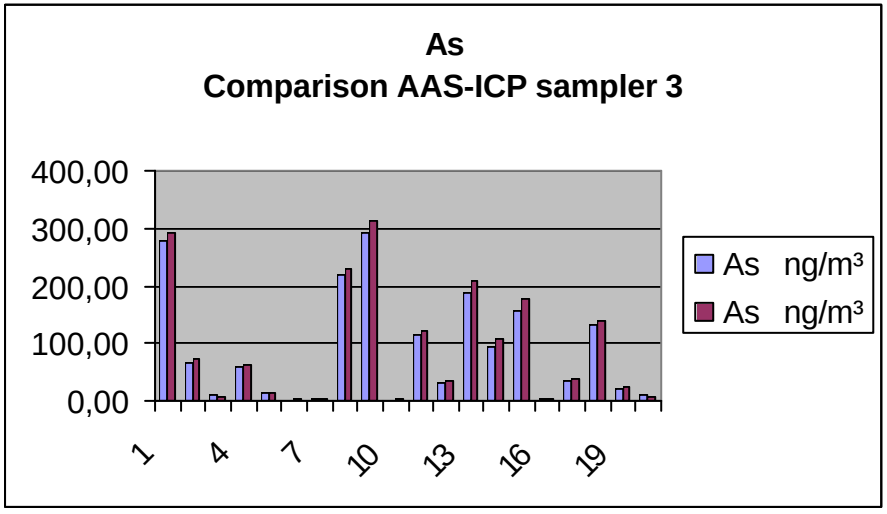

Comparison sampler C7 versus C8 (ICP)
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 1,0594x + 0,1683
R2 = 0,9978

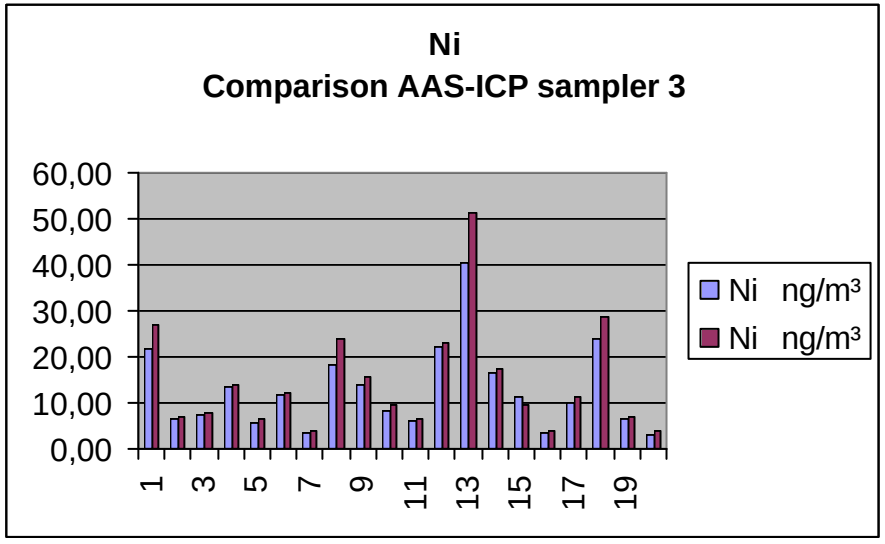

Comparison sampler C7 versus C8 (ICP)
Ni (ng/m³)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
y = 0,7004x + 4,8337
R2 = 0,7772

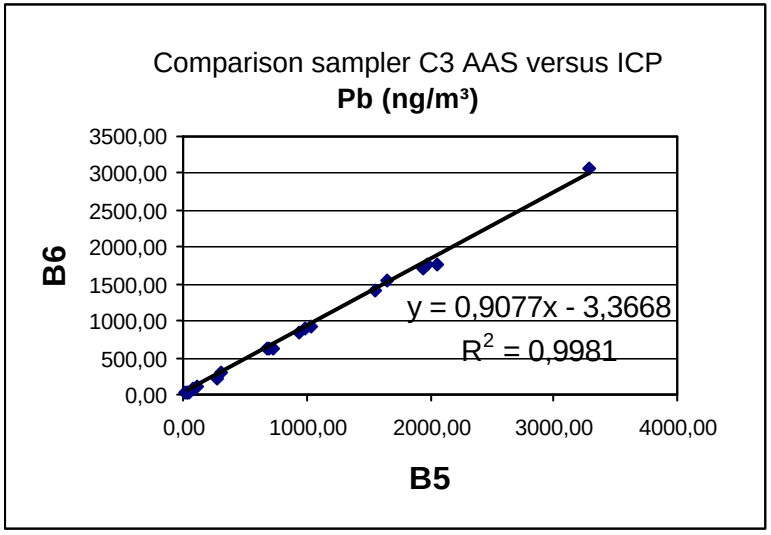
ANNEX 14 A

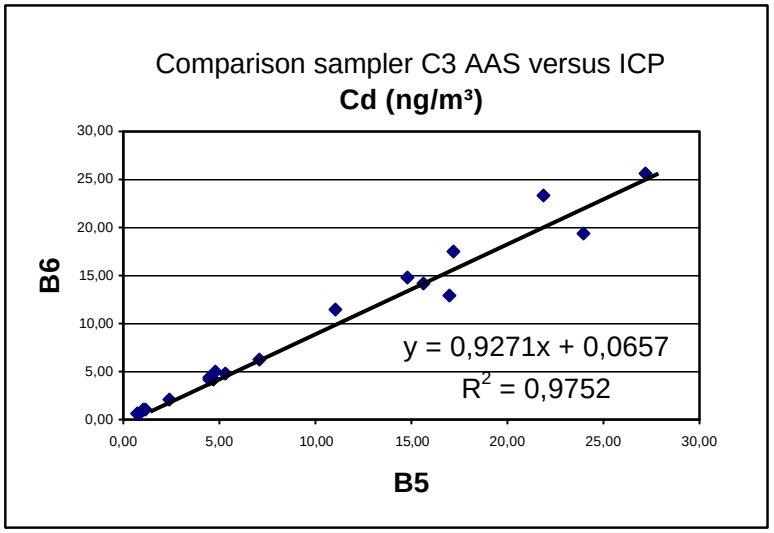

Pb
Comparison AAS-ICP sampler 3
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

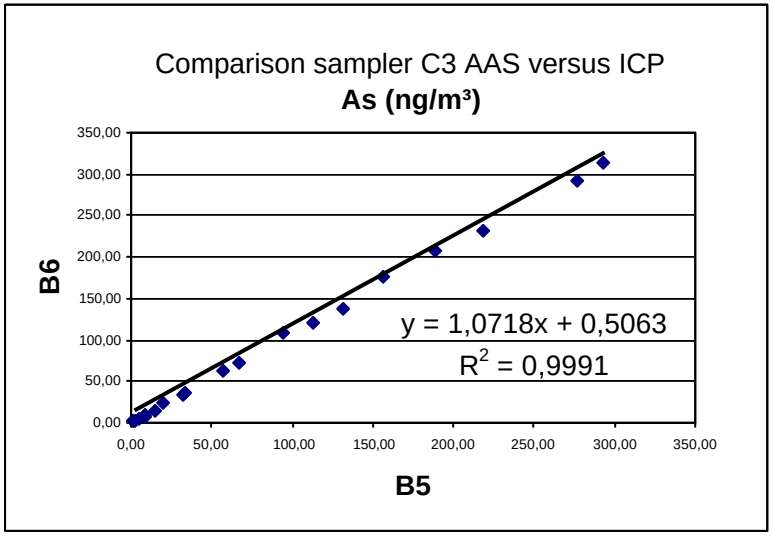

Cd
Comparison AAS-ICP sampler 3
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

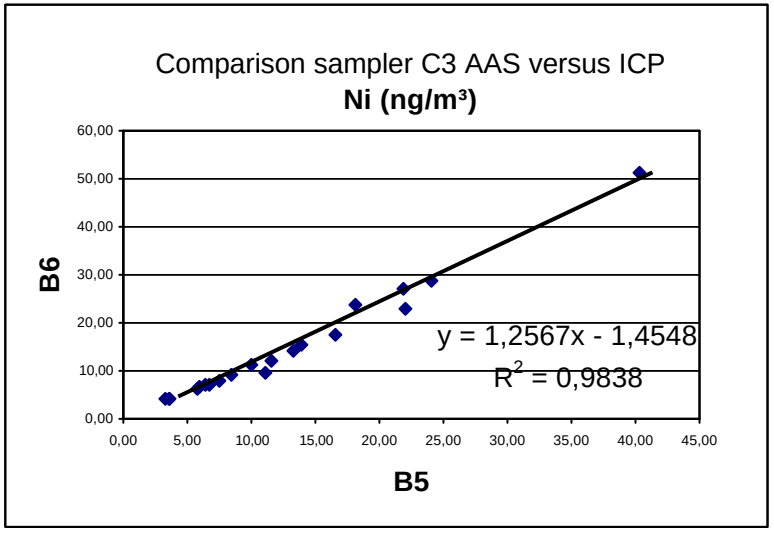

As
Comparison AAS-ICP sampler 3
400,00
300,00
200,00
100,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison AAS-ICP sampler 3
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
3
5
7
9
11
13
15
17
19
Ni ng/m³
Ni ng/m³

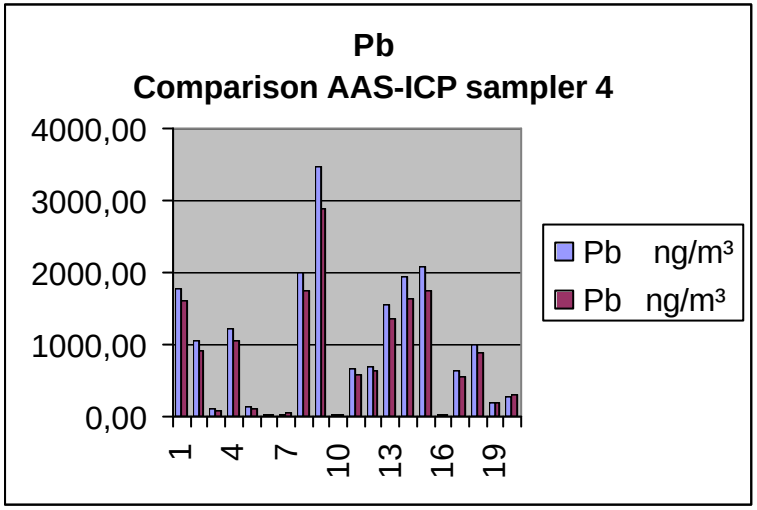

Comparison sampler C3 AAS versus ICP
Pb (ng/m³)
B6
B5
y = 0,9077x - 3,3668
R2 = 0,9981
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00

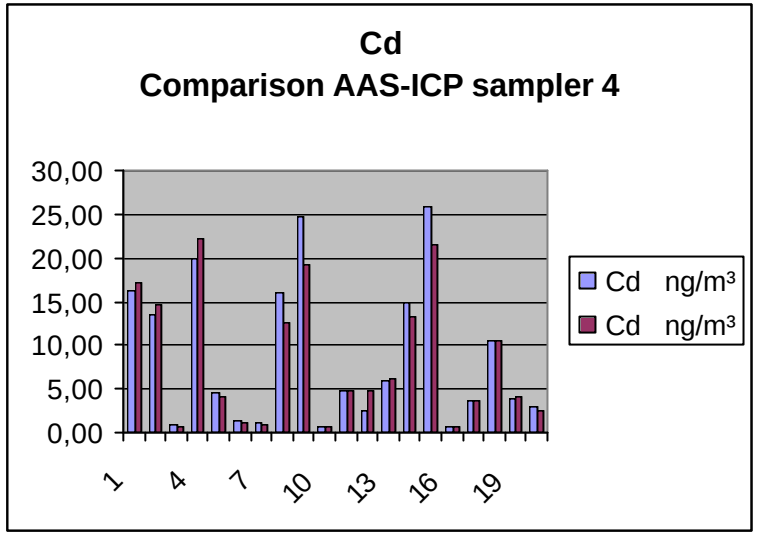

Comparison sampler C3 AAS versus ICP
Cd (ng/m³)
B6
B5
y = 0,9271x + 0,0657
R2 = 0,9752
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00

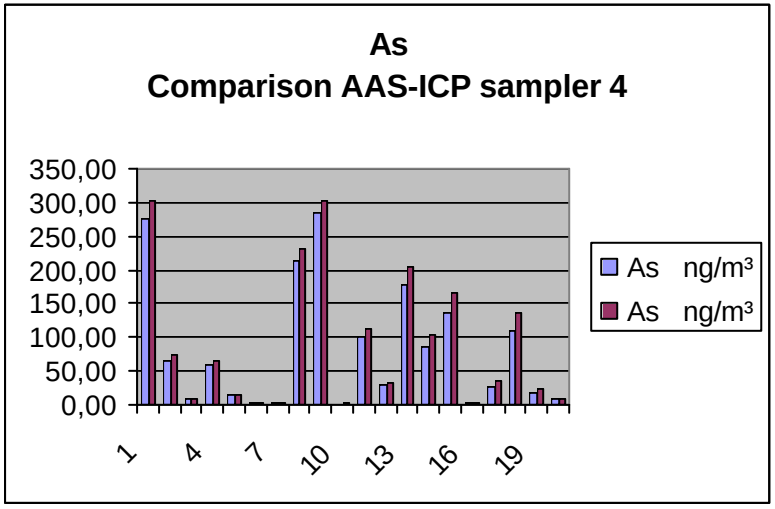

Comparison sampler C3 AAS versus ICP
As (ng/m³)
B6
B5
y = 1,0718x + 0,5063
R2 = 0,9991
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00

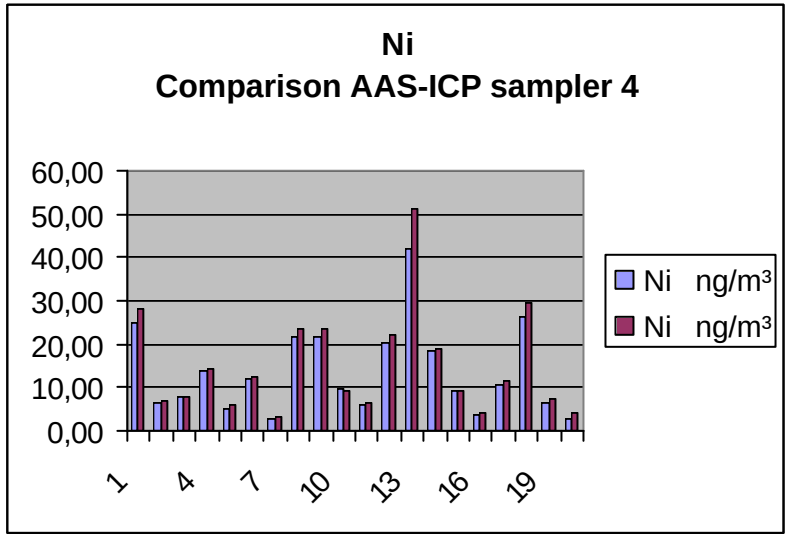

Comparison sampler C3 AAS versus ICP
Ni (ng/m³)
B6
B5
y = 1,2567x - 1,4548
R2 = 0,9838
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
35,00
40,00
45,00

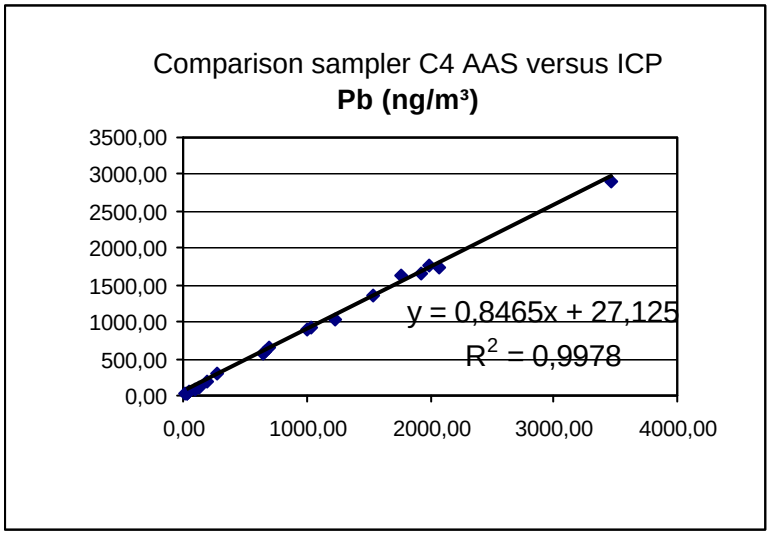
ANNEX 14 B

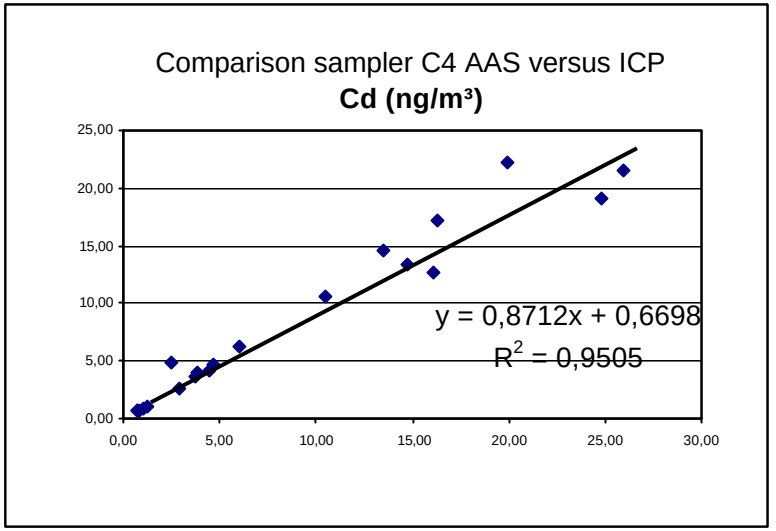

Pb
Comparison AAS-ICP sampler 4
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

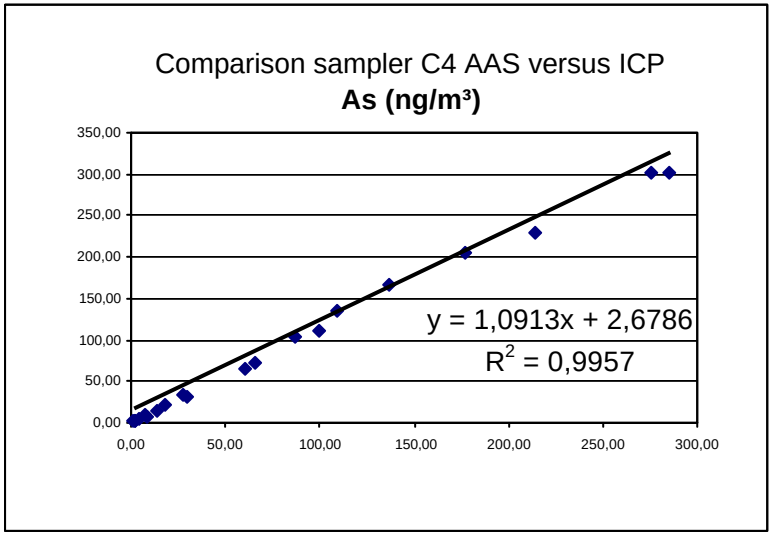

Cd
Comparison AAS-ICP sampler 4
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

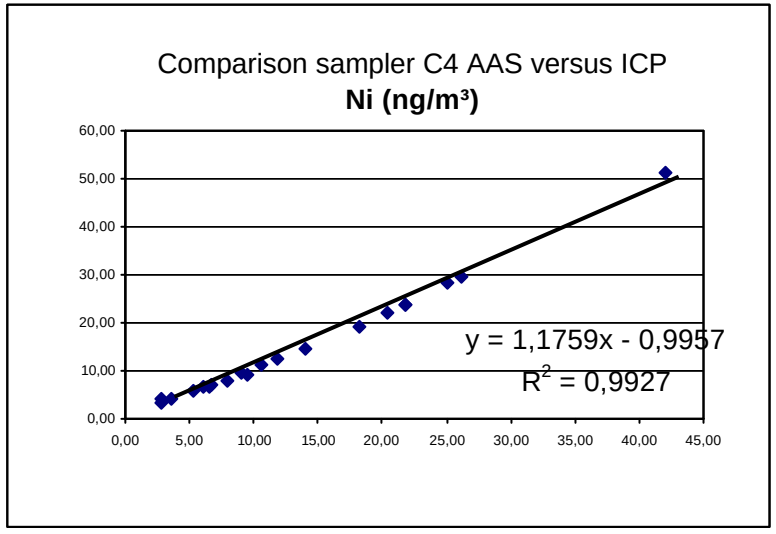

As
Comparison AAS-ICP sampler 4
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison AAS-ICP sampler 4
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
4
7
10
13
16
19
Ni ng/m³
Ni ng/m³

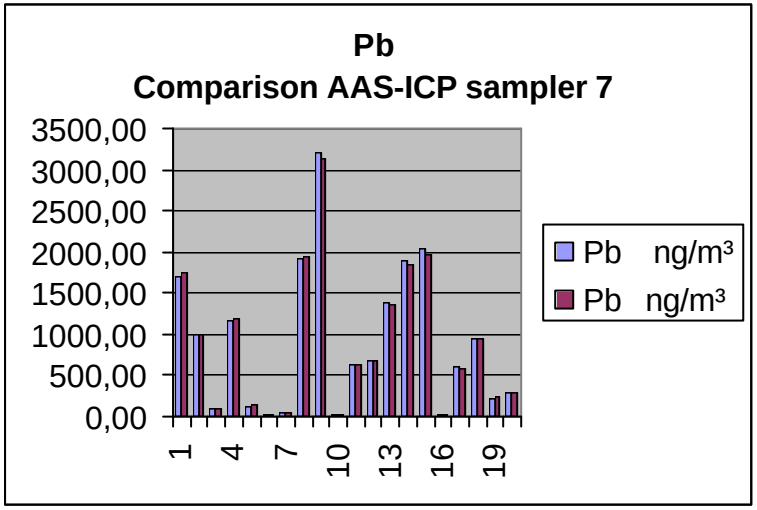

Comparison sampler C4 AAS versus ICP
Pb (ng/m³)
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 0,8465x + 27,125
R2 = 0,9978

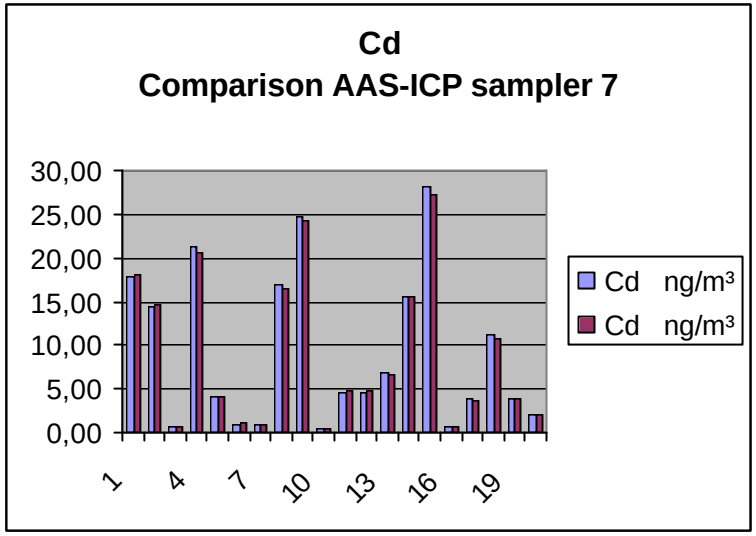

Comparison sampler C4 AAS versus ICP
Cd (ng/m³)
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,8712x + 0,6698
R2 = 0,9505

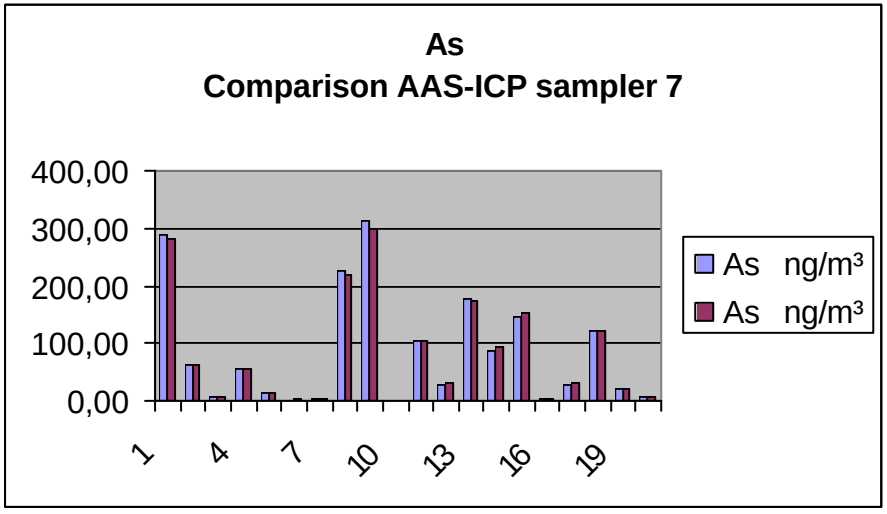

Comparison sampler C4 AAS versus ICP
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
y = 1,0913x + 2,6786
R2 = 0,9957

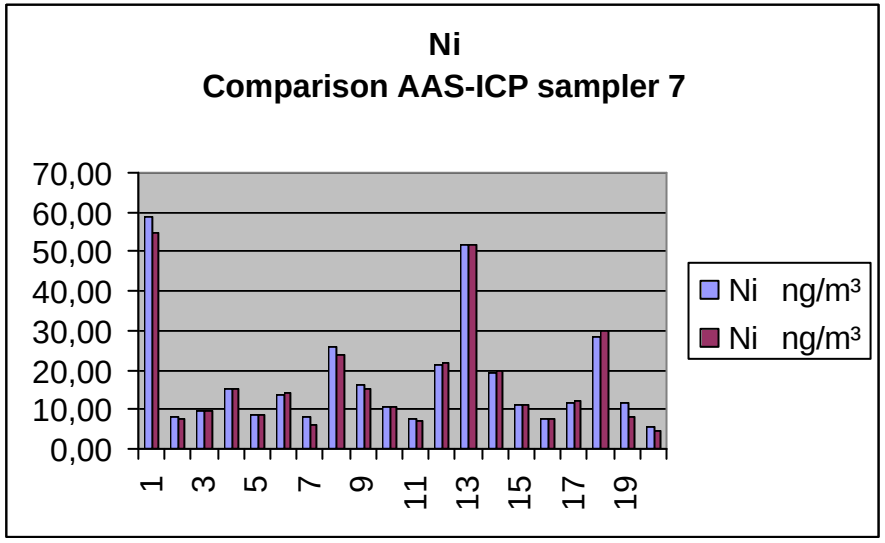

Comparison sampler C4 AAS versus ICP
Ni (ng/m³)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
35,00
40,00
45,00
y = 1,1759x - 0,9957
R2 = 0,9927

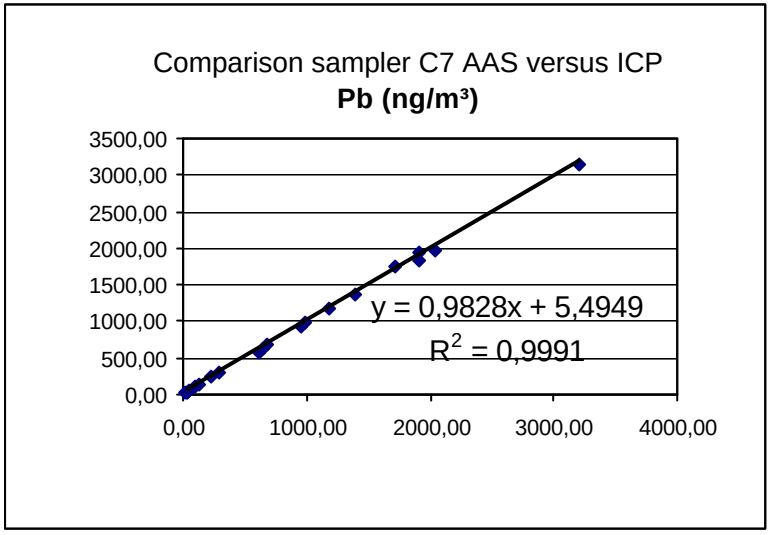
ANNEX 14 C

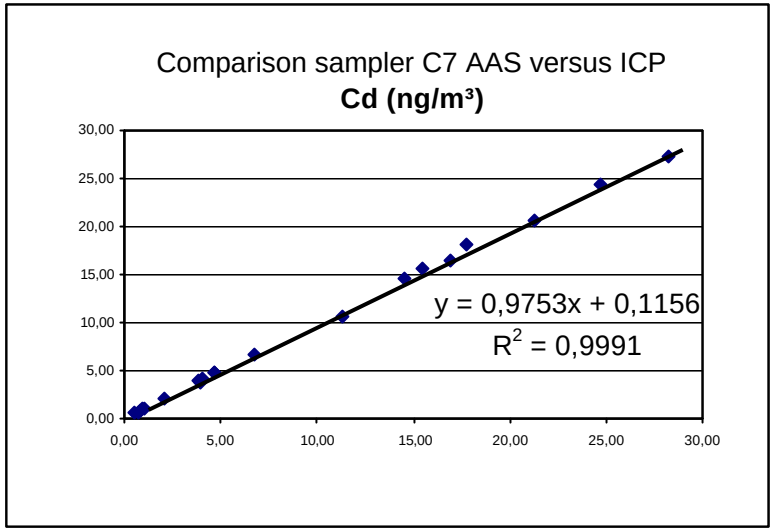

Pb
Comparison AAS-ICP sampler 7
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

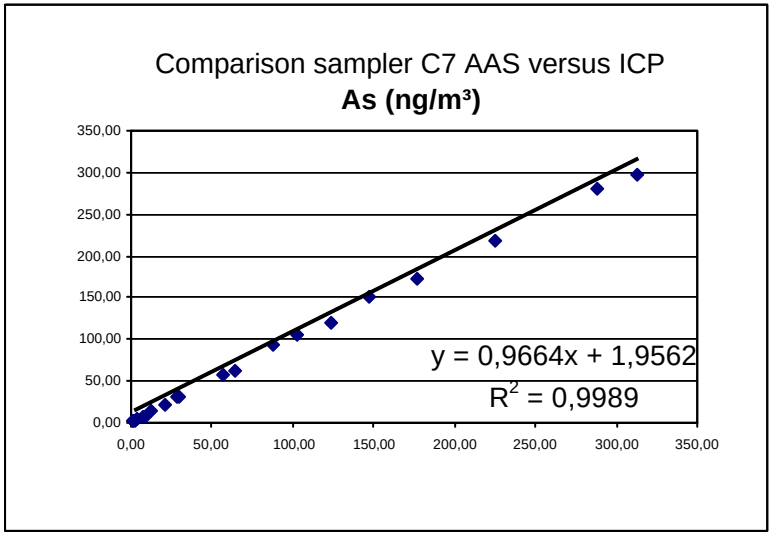

Cd
Comparison AAS-ICP sampler 7
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

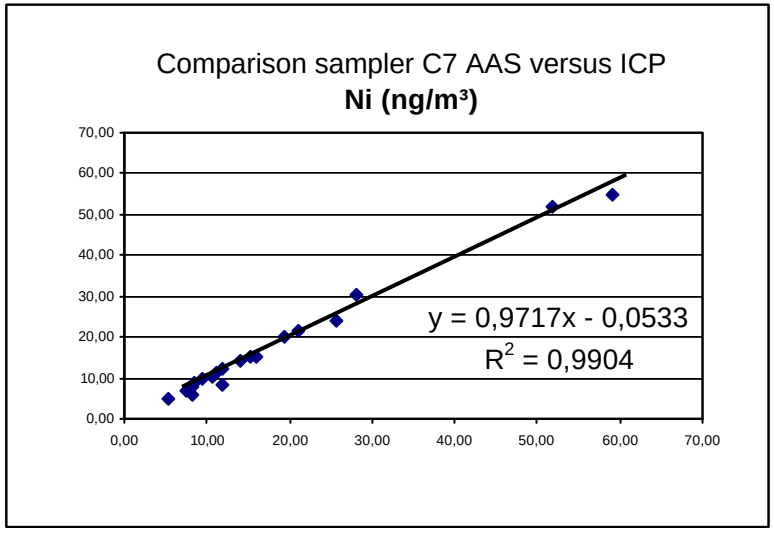

As
Comparison AAS-ICP sampler 7
400,00
300,00
200,00
100,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison AAS-ICP sampler 7
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
3
5
7
9
11
13
15
17
19
Ni ng/m³
Ni ng/m³

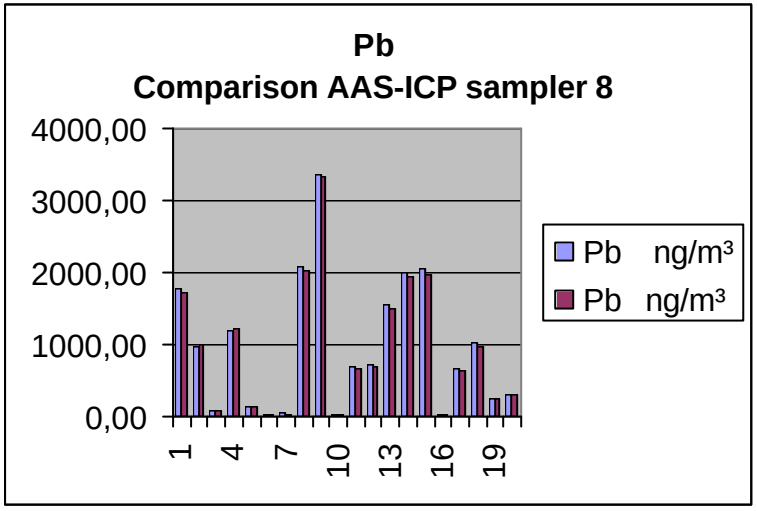

Comparison sampler C7 AAS versus ICP
Pb (ng/m³)
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 0,9828x + 5,4949
R2 = 0,9991

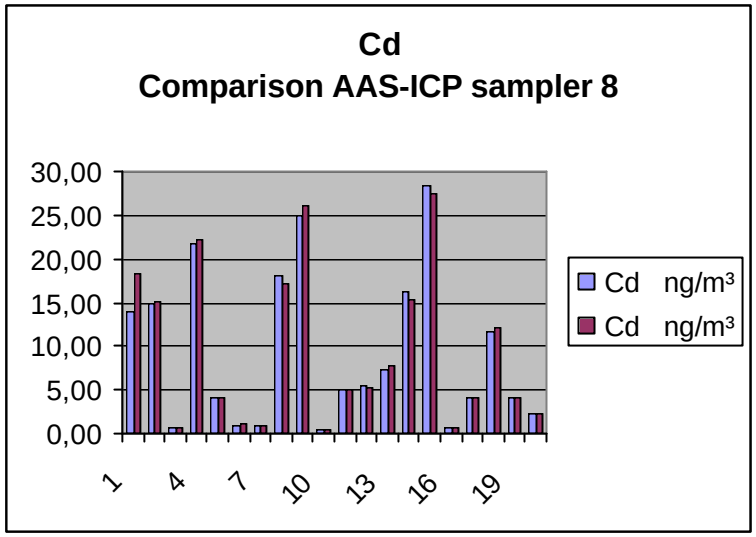

Comparison sampler C7 AAS versus ICP
Cd (ng/m³)
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 0,9753x + 0,1156
R2 = 0,9991

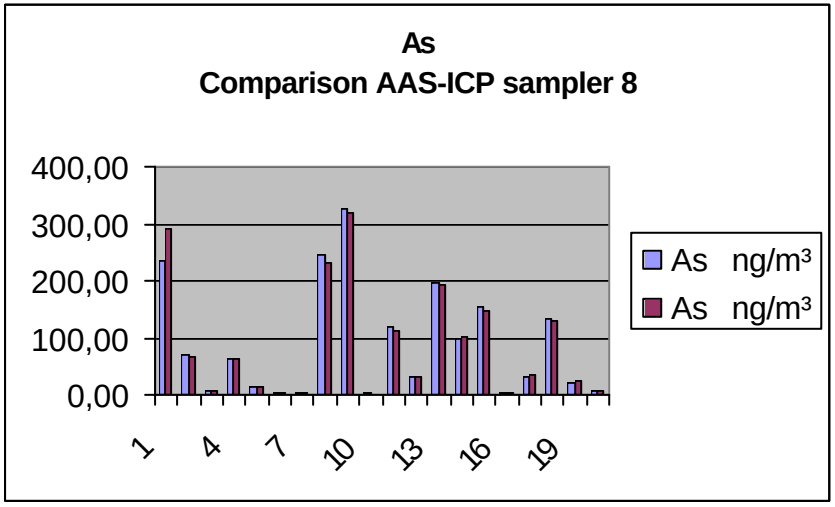

Comparison sampler C7 AAS versus ICP
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 0,9664x + 1,9562
R2 = 0,9989

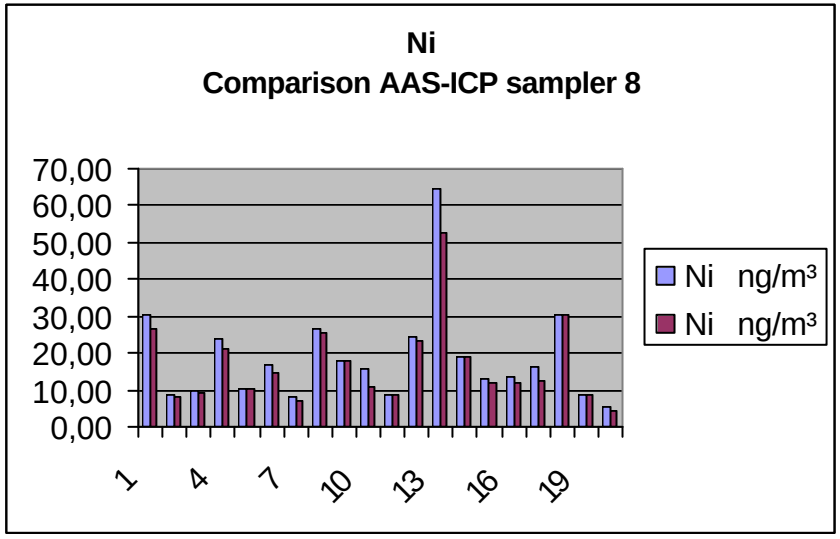

Comparison sampler C7 AAS versus ICP
Ni (ng/m³)
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
y = 0,9717x - 0,0533
R2 = 0,9904

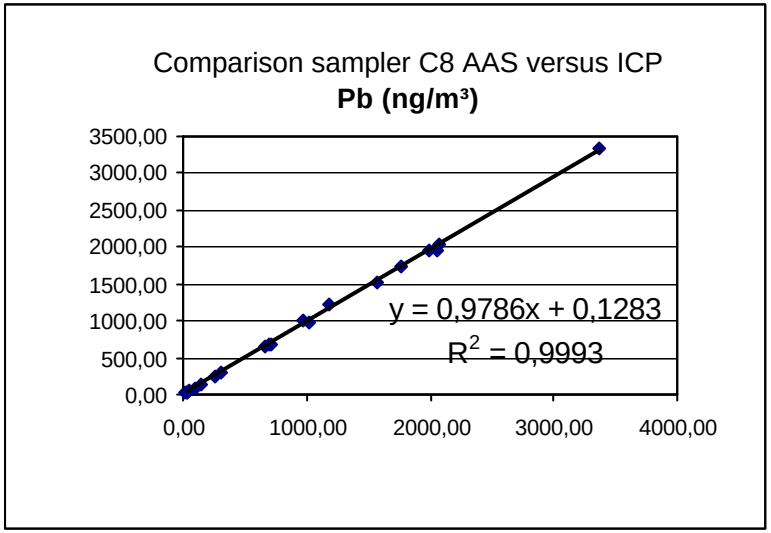
ANNEX 14 D

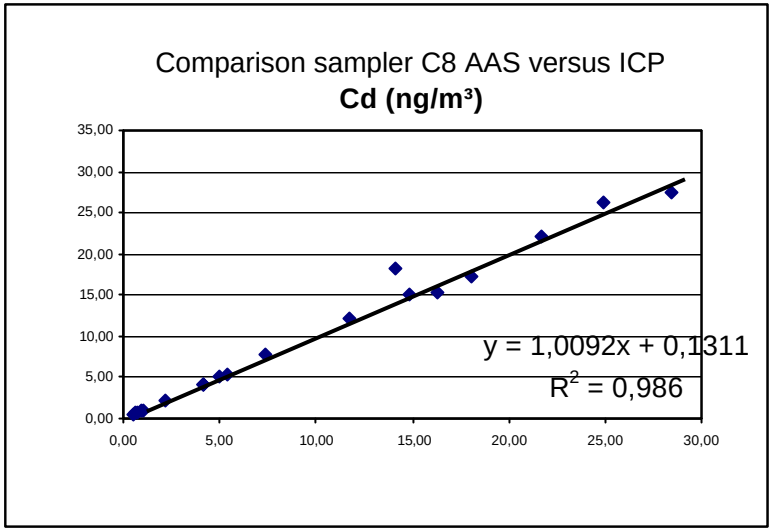

Pb
Comparison AAS-ICP sampler 8
4000,00
3000,00
2000,00
1000,00
0,00
1
4
7
10
13
16
19
Pb ng/m³
Pb ng/m³

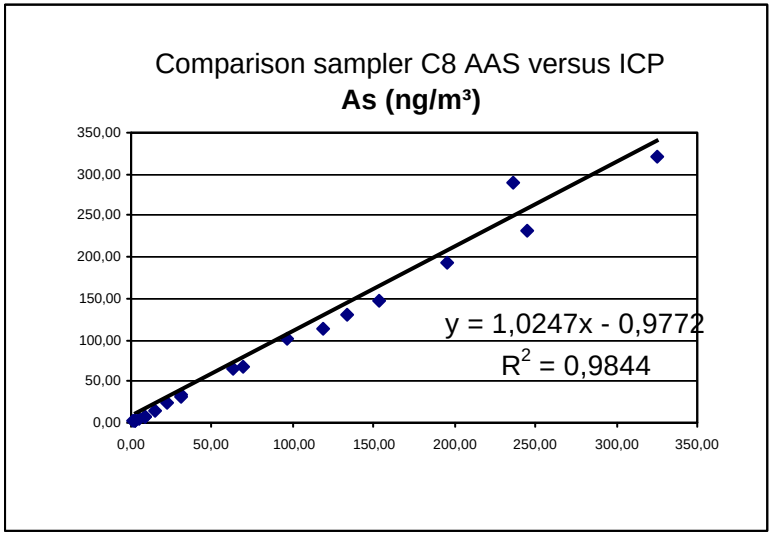

Cd
Comparison AAS-ICP sampler 8
30,00
25,00
20,00
15,00
10,00
5,00
0,00
1
4
7
10
13
16
19
Cd ng/m³
Cd ng/m³

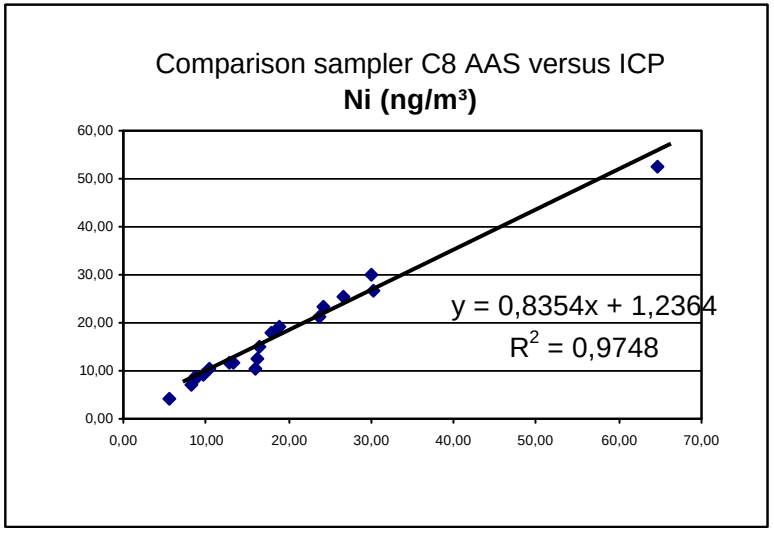

As
Comparison AAS-ICP sampler 8
400,00
300,00
200,00
100,00
0,00
1
4
7
10
13
16
19
As ng/m³
As ng/m³


Ni
Comparison AAS-ICP sampler 8
70,00
60,00
50,00
40,00
30,00
20,00
10,00
0,00
1
4
7
10
13
16
19
Ni ng/m³
Ni ng/m³


Comparison sampler C8 AAS versus ICP
Pb (ng/m³)
3500,00
3000,00
2500,00
2000,00
1500,00
1000,00
500,00
0,00
0,00
1000,00
2000,00
3000,00
4000,00
y = 0,9786x + 0,1283
R2 = 0,9993


Comparison sampler C8 AAS versus ICP
Cd (ng/m³)
35,00
30,00
25,00
20,00
15,00
10,00
5,00
0,00
0,00
5,00
10,00
15,00
20,00
25,00
30,00
y = 1,0092x + 0,1311
R2 = 0,986


Comparison sampler C8 AAS versus ICP
As (ng/m³)
350,00
300,00
250,00
200,00
150,00
100,00
50,00
0,00
0,00
50,00
100,00
150,00
200,00
250,00
300,00
350,00
y = 1,0247x - 0,9772
R2 = 0,9844


Comparison sampler C8 AAS versus ICP
Ni (ng/m³)
60,00
50,00
40,00
30,00
20,00
10,00
0,00
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
y = 0,8354x + 1,2364
R2 = 0,9748

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D-63225 Langen
Germany

Langen, 27 February 2002

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Fax : 0049 6103 704 147
email : elke.bieber@uba.de

Short Report on the

Field Test in Antwerpen of the Minimum Validation Programme for a "Reference Method for the Measurement of Pb, Cd, As and Ni in Ambient Air" (CEN / TC 264 / WG 14)

Voluntary contribution, performed by Lab. D, UBA-Germany

1 Samples collected with CEN Low Volume PM10 Samplers 7 and 8

The samples (digested and previously analysed using AAS by Lab D, UBA-Austria) were reanalysed in our lab using ICP/MS-technique. Before analysis, the samples were diluted with deionised H_2O 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 analytical conditions used are given below. As some samples contained In, this time, we used Y as internal standard for the elements As, Cd and Pb.

Analytical conditions :

Analysis performed : February 2002
Instrument : ICP/MS, type : Ultramass, producer : Varian

Masses monitored :

Y	89	Sc	45
As	75	Ni	60
Cd	111	Pb	208

Calibration :

The same calibration was used for samples, blanks and CRM-solutions, but solutions were diluted differently before analysis :

Blanks : dilution factor 2
Samples : dilution factor 2, 10, 20 (depending on element concentrations)
NIST 1648 : dilution factors 2 (for Cd, As and Ni) and 20 (for Pb)
NIES No.8 : dilution factors 2 (for Cd, As and Ni) and 4 (for Pb)

Internal standards : Y 20 µg/L (As, Cd, Pb),
Sc 10 µg/L (Ni)

External calibration standards :
-standard blank solution
-operating standard-1 solution (element conc. : 20 µg/L As, Pb, Cd, Ni)
-operating standard-2 solution (element conc. : 100 µg/L As, Pb, Cd, Ni)

2 Samples collected with additional sequential PM10 samplers

Lab D (UBA-DE) provided additional samplers for the **Antwerpen** 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 :

2 sequential Low Volume PM10 Sampler : Leckel SEQ 47/50
2 sequential High Volume PM10 Sampler : Digitel DHA 80

2.1 Sequential Low Volume PM10 Samplers

Membrane filters (Sartorius cellulose **nitrate**, pore size : 3 µm) were used with the sequential low volume samplers. Before digestion, filters were cut to pieces using ceramic scissors and transferred into the digestion vessels. 8 mL conc. HNO3 (subboiled in our lab) and 2 mL H2O2 (30 %, ultrapure quality) were added. Microwave digestion in closed vessels was performed using a temperature controlled microwave device.

Instrument : CEM Mars 5 with XP1500 vessels Volume 100ml

Temperature programme :

Ramp Time (min)	Temperature (°C)	Hold Time (min)	Temperature (°C)
3	140	3	140
20	220	25	220

Subsequently samples were cooled to room temperature.

Digestion solutions were transferred to 100 mL flasks, 100 µL of the internal standard solution (20 mg/L Y and 10 mg/L Sc) were added, and diluted with deionised water. Blank values presented in the report forms as **[µg/L]** are referring to these solutions. Thus only values calculated as **[ng/m3]** are directly comparable to the results of other laboratories.

Analytical conditions :

Analysis performed : January 2002
Instrument : ICP/MS, type : Ultramass, producer : Varian

Masses monitored :

Y	89	Sc	45
As	75	Ni	60
Cd	111	Pb	208

Calibration :

The same calibration was used for samples, blanks and CRM-solutions, but samples and CRM solutions were diluted before analysis of Pb

Samples : dilution factors 10 / 20 (for Pb and As)

NIST 1648 : dilution factor 20 (for Pb)
NIES No.8 : dilution factor 5 (for Pb)

Internal standards : Y 20 µg/L (As, Cd, Pb),
Sc 10 µg/L (Ni)

External calibration standards :

-standard blank solution
-operating standard-1 solution (element conc. : 20 µg/L As, Pb, Cd, Ni)
-operating standard-2 solution (element conc. : 100 µg/L As, Pb, Cd, Ni)

2.2 Sequential High Volume PM10 Samplers

Quartz filters (Munktell MK360, diameter 150 mm) were used with the sequential high volume samplers. Only part of the filter was used for analysis (circular punchings; diameter 40 mm). Before digestion, punched filter parts were cut to small pieces using ceramic scissors and transferred into the digestion vessels. 8 mL conc. HNO3 (subboiled in our lab) and 2 mL H2O2 (30 %, ultrapure quality) were added. Microwave digestion in closed vessels was performed using a temperature controlled microwave device.

Instrument : CEM Mars 5 with XP1500 vessels Volume 100ml

Temperature programme :

Ramp Time (min)	Temperature (°C)	Hold Time (min)	Temperature (°C)
3	140	3	140
20	220	25	220

Subsequently samples were cooled to room temperature.

The content of the digestion vessel was transferred to a 100 mL flask, 100 µL of the internal standard solution (20 mg/L Y and 10 mg/L Sc) were added, and diluted with deionised water. Filter residues were separated from the solution by centrifugation. Blank values presented in the report forms as **[µg/L]** are referring to these solutions. Thus only values calculated as **[ng/m3]** are directly comparable to the results of other laboratories.

Analytical conditions :

Analysis performed : January 2002
Instrument : ICP/MS, type : Ultramass, producer : Varian

Masses monitored :

Y	89	Sc	45
As	75	Ni	60
Cd	111	Pb	208

Calibration :

The same calibration was used for samples, blanks and CRM-solutions, but samples and CRM solutions were diluted before analysis of Pb

Samples : dilution factors 10 / 20 (for Pb and As)
NIST 1648 : dilution factor 20 (for Pb)
NIES No.8 : dilution factor 5 (for Pb)

Internal standards : Y 20 µg/L (As, Cd, Pb),
Sc 10 µg/L (Ni)

External calibration standards :

-standard blank solution
-operating standard-1 solution (element conc. : 20 µg/L As, Pb, Cd, Ni)
-operating standard-2 solution (element conc. : 100 µg/L As, Pb, Cd, Ni)

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CEN TC 264 / WG 14
Minimum Validation Programme
Field Tests - Hoboken
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1. Background

This report is made by the Department of Chemistry and Environment of the Ecole des Mines de Douai (France) that has participated to a part of the Minimum Validation Programme (MVP) of CEN/TC264/WG14. This work has been done on a voluntary basis.

2. Aim/Overview

The MVP is a programme for the validation of the reference method proposed by the workgroup CEN/TC264/WG14 for the analysis of As, Cd, Ni and Pb in atmospheric particles. This programme includes field tests on four European sampling sites.
This report presents additional work that has been carried out by the Ecole des Mines de Douai on the site of Hoboken. The objective of this work is to bring additional information to those obtained with the MVP. Some slightly differences have been introduced to the method used during the MVP :

- the sampler was a Partisol Plus 2025 from Rupprecht and Pataschnick. It is a LVS sampler with a 1 m^3/h flow rate,
- membranes used for particle collection were Teflon filters,
- digestion was carried out using nitric acid only.

3. Materials

Filter Material :
Zefluor membrane (Gelman), Teflon filters, 2-µm pore size, 47mm diameter.

Reagents :
Nitric Acid (65 %), Suprapur from Merck
Ultrapure water, USF Ionpure (Resistivity : 18,2 MΩ)

Reference material :
NIST 1648 Urban Particulate Matter

4. Digestion procedure

The samples were digested with a microwave oven Ethos TC from Milestone. An HPR-1000/10S segmented rotor was used. It contains ten 100-mL TFM vessels that operate at pressures up to 100 bar.

Contrary to what is recommended by WG14 documents, washing-up of the TFM vessels were carried out by soaking in a 5% nitric acid solution. This procedure has the advantage of washing parts of the vessels that would not be during a microwave programme (especially the space between the body and the cap of the vessel).

The digestion matrix was 8 mL concentrated nitric acid. Digestion was achieved using a temperature-controlled programme as follows.

Microwave temperature-controlled programme

Step	Temperature (°C)	Time (mn)	Max. power (W)
1	Ramp from 25 to 220	20	1000
2	220	25	1000

After cooling the contents of the vessels were transferred to 50 mL volumetric flasks and made up to volume with ultrapure water.

5. ICP-MS Analysis

Standards were prepared from single element 1 g/l certified solutions (Titrisol - Merck). Calibration standards were prepared in 2% nitric acid solutions at 1, 2, 3, 4 and 5 µg/L for As, Cd and Ni ; at 5, 10, 15, 20 and 25 µg/L for Pb.

Before analysis sample solutions were diluted from 8 to 100 times depending on their metals content. Final solutions contained 2% of nitric acid.
An internal standard (1µg/l of Rh) was added in each standard/sample solution.

An Elan DRC Plus ICP-MS (Perkin Elmer) was used. Operating conditions were :

RF Generator	1050 W
Plasma gas flow	15 L/min
Auxiliary gas flow	1.2 L/mn
Nebuliser gas flow	0.95 L/mn
Dwell time	50 ms
Sweeps	20

For Ni analysis, the Dynamic Reaction Cell (DRC), that is a system for reduction of interferences, was used with following parameters :

Reaction gas	NH_3
Gas flow	0.3 mL/mn
DRC quadrupole parameters	a = 0.05 ; q = 0.7

All masses of interest were monitored for As, Cd, Ni and Pb. The data reported are for masses Ni60, Cd114, As75, Pb206

6. ICP-AES Analysis

Only Cd, Ni and Pb were analysed with this technique. The objective was to compare the results with those from the ICP-MS. Final results in the tables are those from ICP-MS.

Standards were prepared from single element 1 g/l certified solutions (Titrisol - Merck). Calibration standards were prepared in 16 % nitric acid solutions at 5, 10 and 15 µg/L for Cd ; 10, 20 and 30 µg/L for Ni ; at 200, 400 and 600 µg/L for Pb.

Sample solutions have been analysed as produced by the digestion step.

A JY24 ICP-AES (Jobin Yvon) instrument was used. Samples were introduced with an ultrasonic nebuliser (Cetac). Operating conditions were :

RF Generator	1000 W
Plasma gas flow	12 L/min
Auxiliary gas flow	0.2 L/mn
Nebuliser gas flow	0.7 L/mn
Integration	7 points measured for 0,5 s around the target wavelength and fitted by a normal law

Elements were measured at the following wavelengths 214.438 for Cd, 220.353 for Pb and 231.604 for Ni.

7. Results

We analysed the samples produced by a sampler Partisol Plus that was located near the MVP samplers in Hoboken. The results as well as those of the QA/QC samples are presented in the following.

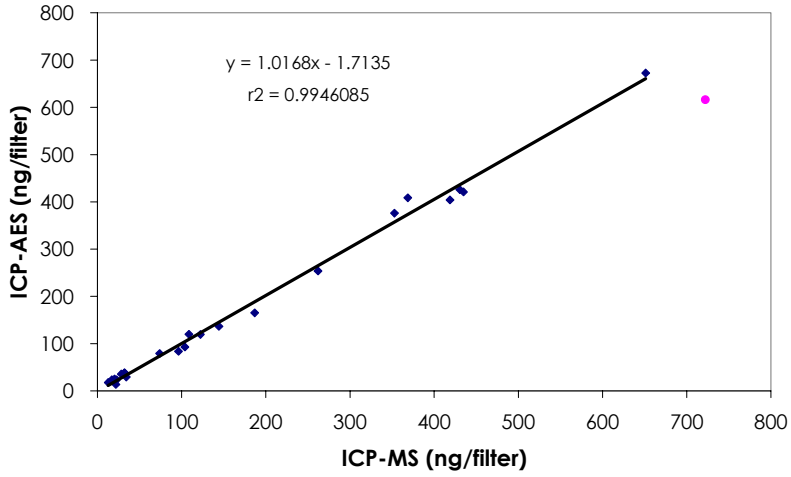
7.1 Field samples

We received 27 samples (Internal lab code from PP1-1 to PP1-27) from Hoboken. Two of them were cellulose nitrate filters and have not been analysed (Filter Code PP1-19 and PP1-20). Only 20 filters have been kept for the MVP. Nevertheless all filters were analysed. The results retained for the MVP are presented in the joined Excel worksheet (Monsterneming sampler french - Partisol 1 and 2 _Antwerp_15012002s (1).xls). The other ones are presented in the following table.

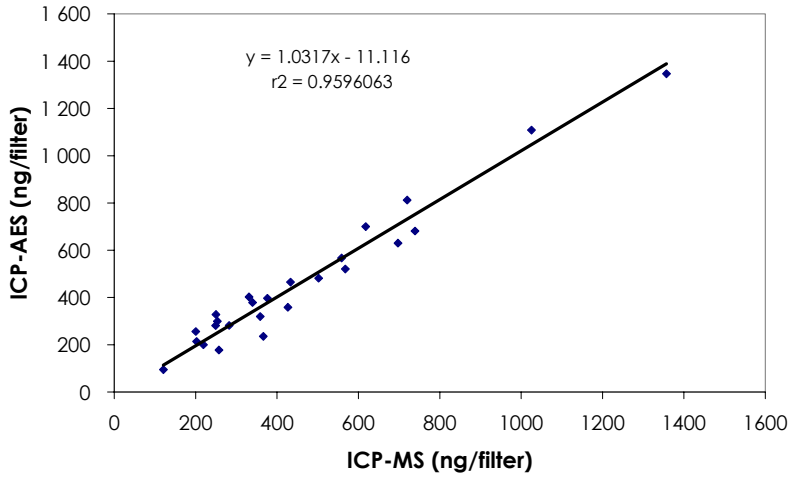
Field samples ruled out for MVP

Internal Lab Code	Start Date	As (ng/filter)	Cd (ng/filter)	Ni (ng/filter)	Pb (ng/filter)
8_1	19/11/01	863.2	144.4	1025.6	20835
21_1	06/12/01	109.6	32	376.4	1691.6
22_1	09/12/01	131.6	32.4	426.8	2177.2
23_1	10/12/01	273.2	74	358.8	3524.8
24_1	11/12/01	82	20.4	697.2	1148.8
27_1	18/12/01	53.6	22	433.2	1253.6

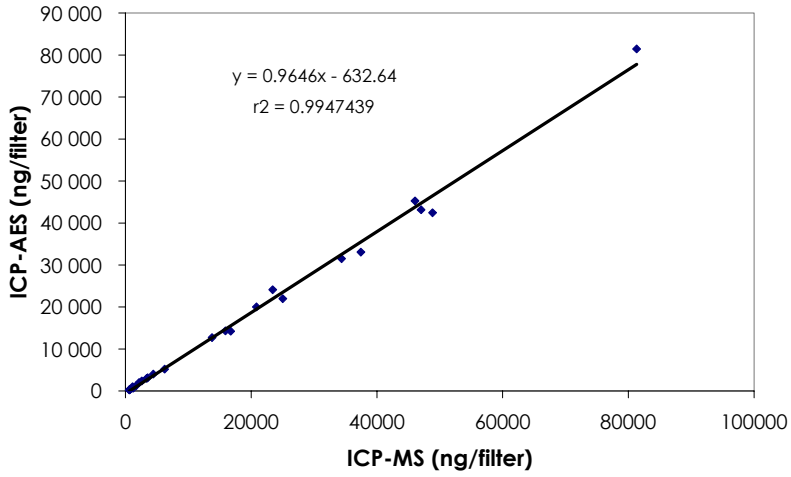
ICP-MS results have been compared to those of ICP-AES. The comparison is presented by the three following figures.



ICP-AES vs ICP-MS : Cd



ICP-AES vs ICP-MS : Ni



ICP-AES vs ICP-MS : Pb

Correlations between ICP-AES and ICP-MS results are good. Slopes are around 1. For Cd a point (the pink one) have been discarded for the regression. As it was analysed twice by ICP-MS in two different diluted solutions and gave the same result, we suspect that a trouble occurred during the ICP-AES analysis.

7.2 QA/QC

Three types of QA/QC solutions were prepared and analysed with field samples batches :

- four solutions from reference material NIST 1648,
- two field filter blank solutions,
- two reagent blank solutions.

NIST 1648

Four NIST 1648 samples were put down on Teflon filters and weighed. Masses ranged from 0.72 to 1.95 mg. Results are presented as recoveries in the following table.

NIST 1648 samples (recoveries)

	nist1	nist2	nist3	nist4
As	1.01	1.01	0.91	0.90
Cd	1.03	2.13	0.95	0.91
Ni	1.43	1.26	1.48	1.19
Pb	1.02	1.03	0.87	1.03

Mean recoveries are within the 0.95 - 1.05 range for Pb and As. For Cd the nist2 sample has a quite high value. If we rule out this sample, the mean recovery is within the 0.95 - 1.05 range. Ni presents high recoveries values that we could not explain, but it seems that this trouble is recurrent since it occurs every time we analyse NIST 1648 samples.

Reagent blank solutions

The concentrations of the two reagent blank solutions are shown in the following table expressed as equivalent ng/filter.

Reagent blank solutions (ng/filter)

	Blank1	Blank2
As	2.6	1
Cd	0.8	0
Ni	23	30
Pb	16.4	21.2

Results of the field samples are raw data. No blank value was subtracted.

Field filter blank

The concentration values from the field filter blanks of Hoboken are shown in the following table expressed as ng/filter.

Field filter blanks (ng/filter)

	Filter1	Filter2
As	19.6	3.4
Cd	3	1.4
Ni	176.2	646.8
Pb	176.6	80

We were really surprised by these field filter blank values that do not reflect the values we usually measure in Teflon filters. As an exemple of what is usually found, the following table shows the results for the analysis of three lab blank filters.

Lab filter blanks (ng/filter)

	Filter1	Filter2	Filter3
As	< 1	< 1	< 1
Cd	1	< 1	< 1
Ni	5.75	10.25	6
Pb	1.25	1.25	1.25