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Development of particulate matter certified reference materials (PM_{10} CRMs) Final report

Administrative Arrangement no. 070402/2006/438490/MAR/C3 "Feasibility study for the production of certified reference materials for the selected PAH compounds and heavy metals in the PM10 matrix"

E. Perez Przyk, A. Held, J. Charoud-Got

EUR 23244 EN - 2008

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Contact information
Address: E. Perez Przyk
E-mail: elzbieta.perez-przyk@ec.europa.eu
Tel.: 014/571 612
Fax: 014-571 548

http://irmm.jrc.ec.europa.eu/
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EUR 23244 EN
ISBN 978-92-79-08347-1
ISSN 1018-5593
DOI 10.2787/21226

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Summary

The present report summarises the work carried out within the feasibility study devoted to the development of particulate matter certified reference materials (PM_{10} CRM) at the RM Unit of IRMM. At present there is no suitable PM_{10} RM certified for elements and/or PAHs. Therefore, this project was aimed at developing a CRM, which will play an active tool in the implementation of the Air Quality Framework Directive and its 1st and 4th Daughter Directives.
In order to establish the target characteristics for the future PM_{10} CRM, a meeting with experts in the field of air quality was organised. This report includes decisions made during that meeting.
Five candidate materials have been selected for the feasibility study on air quality CRM development. These are two existing CRMs, BCR-605 (urban dust certified for trimethyllead) and BCR-723 (a road dust certified for Pd, Pt and Rh), and three materials specifically collected for this purpose, a tunnel dust, a winter filter dust and a summer filter dust. An evaluation of the suitability of these materials for the future air quality CRM was performed.
As dust contains coarse particles (up to 500 µm) the first challenging step was the development of a suitable approach towards particle size reduction. This was obtained by means of a jet mill. After milling, 90 vol.% of the materials were below 25 µm.
The test materials were analysed with respect to the content of selected elements and PAHs. The analyte contents in the test materials reflected the real environmental conditions and it was in agreement with the requirements for the future PM_{10} CRM. All elements and PAHs of interest were easy to detect. In general, all test materials were easy in handling and did not pose any problems during the sample preparation.
Furthermore, a homogeneity study for tunnel dust, summer filter dust and winter filter dust was carried out. The homogeneity uncertainty of the determination of elements and PAHs in all materials was lower than 1.5 %. The exception was tunnel dust, for which the obtained values of the uncertainty for PAH determinations were comparatively higher (between 1.5 % and 7.8 %). However, this can be improved by a better material homogenisation. A minimum sample intake for all test materials with respect to As, Cd, Ni, Pb and benzo[*a*]pyrene has also been defined. The minimum sample intakes obtained for As, Cd, Ni, Pb and benzo[*a*]pyrene in all test materials (excluding Ni in summer filter dust) were below or equal to 50 mg.

The short-term stability has been tested to establish dispatch conditions for tunnel dust, summer filter dust and winter filter dust. The materials intended for the determination of the element content can be transported at ambient temperature for up to four weeks. Alternatively, if the materials are intended for the determination of PAHs, a temperature of 4 °C should be used to transport winter filter dust and 18 °C for both tunnel dust and summer filter dust.

It was shown that it is feasible to produce CRMs for particulate matter that have the required properties and sufficiently mimic PM_{10} in the analytical process. After the feasibility study including commutability study it was concluded that suitable candidate materials for the PM_{10} CRM are tunnel dust for elements and tunnel dust or the filter materials for the PAHs.

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Glossary

ANOVA	Analysis of variance
Ant	Anthracene
ASE	Accelerated Solvent Extraction
BaA	Benzo[*a*]anthracene
BaP	Benzo[*a*]pyrene
BbF	Benzo[*b*]fluoranthene
BghiP	Benzo[*ghi*]perylene
BjF	Benzo[*j*]fluoranthene
BkF	Benzo[*k*]fluoranthene
BCR	Community Bureau of Reference
CRM	Certified Reference Material
EC	European Communities
DahA	Dibenzo[*a,h*]anthracene
DD	Daughter Directive
DG ENV	Directorate General for the Environment
ERM	European Reference Material
Flu	Fluoranthene
GC-MS	Gas Chromatograph coupled to a Mass Selective Detector
HCL	Hollow Cathode Lamp
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometer
IRMM	Institute for Reference Materials and Measurements
ISO	International Organization for Standardization
I123P	Indeno[123-*cd*]pyrene
κ'	Factor for two-sided tolerance limits for normal distribution
m	Average Sample Mass
M	Minimum Sample Intake
MS_{among}	Mean square among bottles from an ANOVA
MS_{within}	Mean square within a bottle from an ANOVA
NIST	National Institute of Standards and Technology
PAH	Polycyclic Aromatic Hydrocarbon
Ph	Phenanthrene
PM	Particulate Matter
$PM_{2.5}$	Particulate Matter of 2.5 µm and less aerodynamic diameter
PM_{10}	Particulate Matter of 10 µm and less aerodynamic diameter
PSA	Particle Size Analysis
RF	Radio Frequency
RM	Reference Material
RM Unit	Reference Materials Unit
RSD	Relative Standard Deviation
$Q_{10,\ 16,\ 50,\ 84,\ 90,\ \text{and}\ 100}$	Cumulative distribution equals 10 vol.%, 16 vol.%, 50 vol.%, 84 vol.%, 90 vol.% and 100 vol.%, respectively
s	Standard deviation
s_{bb}	Between-unit variability
s_{wb}	Standard deviation within a bottle
SRM	Standard Reference Material
S-HCL	Super Hollow Cathode Lamp
SS-GFAAS	Solid Sampling Graphite Furnace Atomic Absorption Spectrometer
TSP	Total Suspended Particulate
UNC	Target uncertainty for microhomogeneity
u_{bb}	Uncertainty related to a possible between-bottle heterogeneity
u^*_{bb}	Maximum heterogeneity that could be hidden by method repeatability
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

Definitions [1]

Reference material (RM):	material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process. Note 1: RM is a generic term. Note 2: The properties can be quantitative or qualitative, e.g., identity of substances or species. Note 3: Uses may include the calibration of a measurement system, assessment of a measurement procedure, assigning values to other materials, and quality control. Note 4: A RM can only be used for a single purpose in a given measurement.
Certified Reference Material (CRM):	reference material, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability. Note 1: The concept of value includes qualitative attributes such as identity or sequence. Uncertainties for such attributes may be expressed as probabilities. Note 2: Metrologically valid procedures for the production and certification of reference materials are given in, among others, ISO Guides 34 and 35. Note 3: ISO Guide 31 gives guidance on the contents of certificates.

1. Introduction

The reduction of exposure to airborne pollutants is one of the most important environmental and health issues that have recently been brought up in Europe. Several EC Directives in the field of air quality have been introduced. In 1996, the European Council adopted the Air Quality Framework Directive 96/62/EC on ambient air quality assessment and management. Four Daughter Directives (DDs) followed the Framework Directive. The first (1999/30/EC) and fourth (2004/107/EC) DDs relate to limit values for PM_{10}, Cd, Pb, Ni, As and several PAHs in ambient air. Laboratories in the Member States have to transpose the Directives and set up their monitoring strategies. However, implementation of the Directives requires certified reference materials (CRMs) to ensure the quality of measurement data. Currently, there are no CRMs available which are certified for the content of the above-mentioned compounds in the PM_{10} matrix. SRM 1648 (NIST), which has been used so far, is currently out of stock. Furthermore, it is considered as unsuitable because of its very high lead content and too large particle size. In addition, it is not certified for PAHs.

The aim of this project is to verify the feasibility of the development of PM_{10} CRMs certified for their content of selected PAHs and elements. Successful results of the feasibility study will enable IRMM to start a second part of the project, i.e. production and certification of air quality CRMs for routine analyses recommended by EC Directives. Furthermore, it can be possible to provide reference materials for interlaboratory comparisons (proficiency tests) at the European and national level.

2. Target characteristics of the final reference materials

Before the start of this project, target characteristics for the future CRMs had to be established. For that purpose, a questionnaire was sent to European expert laboratories. The questionnaire covered issues such as the properties of the starting material and approaches to obtain them, target values and uncertainties of certified analytes, sample intake, and packing of the CRMs. A few months later, a meeting with experts on air quality monitoring and emission legislation was organised, i.e. with representatives of the AQUILA network (national air quality reference laboratories), the Directorate General for the Environment (DG ENV) and others. The objective of that meeting was to discuss and to agree on the requirements for the future air quality CRMs. The following was envisaged:

a. Matrix – PM_{10}

Taking into account the purpose of the use of CRMs (e.g. checking of digestion step and/or accuracy of results from an individual laboratory) an exact PM_{10} matrix is not required. However, a particle size distribution close to PM_{10} would be a big advantage.

There is no reason to go into the direction of smaller particle size ($PM_{2.5}$) as the legislation on the content of elements and PAHs in $PM_{2.5}$ is not foreseen in the near future, and PM_{10} regulations will be retained.

b. Source of PM_{10}

Sampling PM_{10} on a filter is not a good approach to obtain the raw material because it takes a long time to collect the required amount (about 10 kg) of starting material. Long-term sampling will be subject to seasonal variations and does not assure a highly homogenous material. Moreover, monitoring labs routinely use very different types of filters. An introduction of filter-based CRMs would thus force the laboratories to use only that particular type of filters or the CRM producer would have to provide PM_{10} CRMs for multiple filter types. The second option is not feasible due to the high costs of producing multiple CRMs.

Another disadvantage of the sampling PM_{10} on filters is that the PM_{10} cannot be mechanically removed from the filters. Therefore, the use of TSP (Total Suspended Particulate) was considered as an acceptable approach on the condition that the starting material is representative for PM_{10} in Europe. It should also have low silica content. A high content of silica would cause difficulties with element determinations when hydrofluoric acid is not used during the digestion step.
The possibility of using existing BCR CRMs was considered. These CRMs are BCR-605 (an urban dust certified for trimethyllead) and BCR-723 (a road dust certified for Pd, Pt and Rh).

c. Single or two different CRMs
From both the CRM production and the application point of view there is a preference towards the production of two different CRMs; one for organic and another for inorganic analyses. The difference between the volatility of elements and PAHs might require different approaches during CRM production, storage and dispatching. The sample preparation procedures for organic and inorganic measurements are also different. If both types of parameters would be certified in one material, compromise conditions would have to be chosen. This, in turn, could deteriorate the quality of the CRMs.

d. Elements
All elements covered by the 1st and 4th DDs (As, Cd, Ni and Pb) excluding Hg should be certified. The 4th DD does not contain a target value for the content of Hg in the PM_{10}. There is only a requirement for the measurement of Hg, which does not allow to derive a target value for Hg. The list of certified elements can be expanded by elements of high importance from ambient air quality and emission legislation point of view, if feasible. The following elements could be considered: B, Be, Co, Cr, Cu, Fe, K, La, Pt-group elements, Sb, Sn, Te, Tl, V and Zn.

e. PAHs
All PAHs covered by the 4th DD and possibly a few additional ones should be certified. The following PAHs are covered by the 4th DD: benzo[*a*]anthracene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene. The PAHs that could further be considered are naphthalene, fluoranthene, coronene and phenanthrene.

f. Target values
There was a large data scatter among the target values for the content of elements and benzo[*a*]pyrene proposed by the laboratories (see Figure 1). A list of the additional PAHs with their corresponding target values suggested by one laboratory is presented in Table 1. It was proposed that the target values should reflect the limit values given in the DDs (see Table 2) and should be useful for both low and high volume sampling. It is more convenient to have CRMs with higher target value of analytes as it gives the possibility to decrease an analyte concentration by e.g. dilution or using smaller sample in-weight.

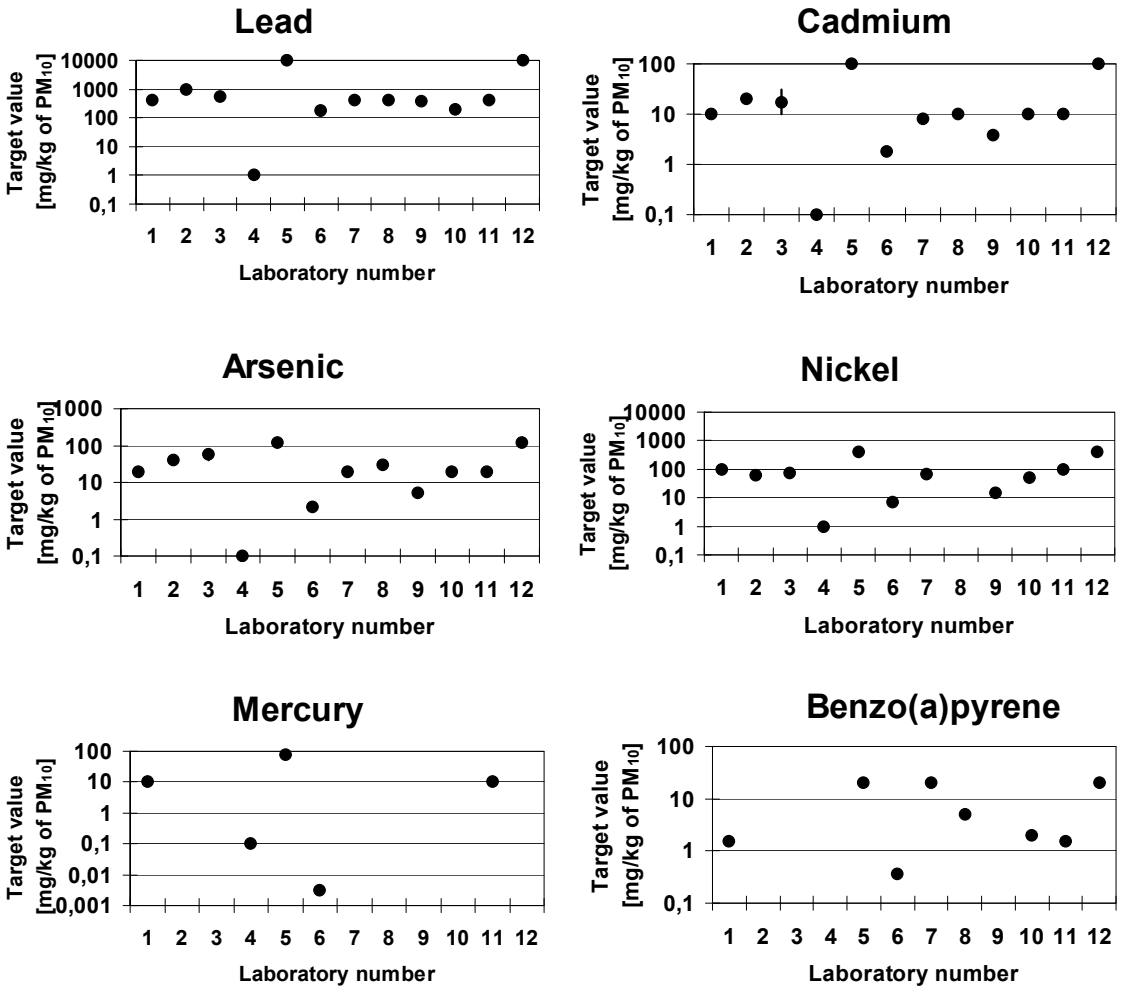


Figure 1: Target values for the content of elements and benzo[*a*]pyrene in a PM_{10} CRM, which are of interest to the expert laboratories.

Table 1: Target values for the content of PAHs in a PM_{10} CRM proposed by one laboratory

Compound	**Target value [mg/kg of PM_{10}]**
Benzo[*e*]pyrene	5
Phenanthrene	10 - 20
Fluoranthene	10 - 20
Benzo[*b*]fluoranthene	5
Benzo[*k*]fluoranthene	5
Indeno[1,2,3-*cd*]pyrene	5
Benzo[*ghi*]perylene	5

For benzo[*a*]pyrene see Figure 1

Table 2: Target values for Pb, As, Cd, Ni and benzo[*a*]pyrene in ambient air (averaged over a calendar year)

Pollutant	**Target value**	
Pb[a]	0.5	µg/m^3
As[a]	6	ng/m^3
Cd[b]	5	ng/m^3
Ni[b]	20	ng/m^3
Benzo[*a*]pyrene[b]	1	ng/m^3

[a]: Refers to the limit value in Annex IV of the1st DD
[b]: Refers to the target value in Annex I of the 4th DD

g. Uncertainty

The ranges for the target uncertainties proposed by IRMM that include all uncertainty components for a CRM property value according to ISO Guide 35, were 10 – 15 % and 15 – 20 % for elements and PAHs, respectively. These target uncertainties are based on the experience from the certification of similar parameters in other matrix Reference Materials. These values were considered as too high by most laboratories. It was proposed that the uncertainties should be about ¼ of the target measurement uncertainties of the 1st and 4th DD or less (see Table 3). However, it is very unlikely that these low uncertainties can be achieved within a reasonable budget and timeframe.

Table 3: Values of uncertainty for fixed and indicative measurements of benzo[*a*]pyrene and elements in PM_{10} CRMs

Compound	**Uncertainty [%]** proposed in the DDs	**Target uncertainty for CRM [%]** 1/4 of measurement uncertainty
Benzo[*a*]pyrene	50	12.5
As	40	10
Cd	40	10
Ni	40	10
Pb	not given	-

h. Homogeneity

The homogeneity of the material should be sufficient to allow minimum sample intakes in the low milligram range, between 5 and 50 mg.

3. Sources of the test materials

Within the frame of this project, the following materials have been evaluated in order to determine whether they are suitable for the production of the future air quality CRMs:

a. BCR-723

The material is a road dust certified for Pd, Pt and Rh and is available from IRMM.

b. BCR-605

The material is an urban road dust certified for trimethyllead and is available from IRMM. However, the number of units that are at the IRMM's disposal is not sufficient for the CRM production. Thus, the material is not considered as a potential candidate for the certification process.

c. Winter and summer filter dust (TSP collected from the ventilation systems of IRMM buildings)

The matrix is a rural dust, which has been collected onto ventilation filters for 6 - 8 months at an air speed of 10 - 15 m/s. Only the dust from filters (class F8 filters, *Profil b.v.b.a.*, Merelbeke, Belgium) which stop particles larger than 10 µm has been taken. It was impossible to draw TSP out of the third and farther filtration layers; fine dust particles went too deeply into the filter material. Two sampling campaigns in March and September 2006 have been performed. The collection time was strictly dependent on the scheduled time for filters exchange in the buildings. The dust was collected using a vacuum cleaner. Finally, about 2 kg of the TSP from each campaign ("winter filter dust" collected in March and "summer filter dust" collected in September) have been collected. The collected materials have been separated from the coarse particles by sieving (0.5 mm sieve) and stored at 4 ^{o}C to avoid losses of volatile analytes.

d. Tunnel dust (TSP collected from the walls of the road tunnel “Wislostrada” in Warsaw, Poland)

The matrix is an urban road dust that was collected mainly from the tunnel walls and partially from the tunnel sidewalks inaccessible to people. The tunnel is approximately 900 m in length and is a major traffic route through Warsaw. The walls are coated with a layer of a chemically inert substance, which gives the high probability of obtaining a pure TSP, i.e. without fractions of building materials. About 25 kg (13 kg from the walls and 12 kg from the sidewalks) of the material has been collected from May to October 2006 using industrial vacuum cleaners. For the feasibility study only the material collected form the tunnel walls was used. This material has been separated from the coarse particles by sieving (0.5 mm sieve) and stored at 4 ^{o}C to avoid losses of volatile analytes.

The dust collection took a long time owing to difficult working conditions in the tunnel and the unfavourable weather. Early in spring the tunnel walls were still frozen, and the rainy summer resulted in wet walls in the tunnel and further delayed the dust collection.

4. Feasibility study

The aim of the feasibility study is to determine whether a CRM production is possible. It also helps to evaluate and select the most appropriate matrix and to locate an appropriate site for the collection of the starting material. The following activities have been carried out:

- measurement of the particle size distribution and evaluation of the microhomogeneity; development of a suitable approach for processing of the materials, i.e. towards particle size reduction, e.g. through grinding and sieving of TSP, etc.,
- determination of the analyte content, stability and homogeneity of the test materials,
- evaluation of the suitability of the test materials as a possible PM_{10} CRM with respect to its behaviour in the analytical process (especially according to the standard method EN 14902 and a future draft standard method for PAHs). This was done in cooperation with voluntary laboratories of the AQUILA group.

4.1. Particle size distribution

All test materials (BCR-605, BCR-723, road dust, winter filter dust and summer filter dust) were evaluated with respect to particle size distribution. Microscopy and particle size measurements were performed in the PSA laboratory of the RM Unit, IRMM.

Measurement methods:

- Particle size measurements were performed using a laser light diffraction technique, device: SYMPATEC Helos equipped with 50 mL cuvette, dispersant: 2-propanol, measurement time: 10 s, stirrer rate: 1200 revolutions per minute.
- Micrographs were taken using a Zeiss microscope Stemi 2000-C, dispersant: 2-propanol.

Results:

a)

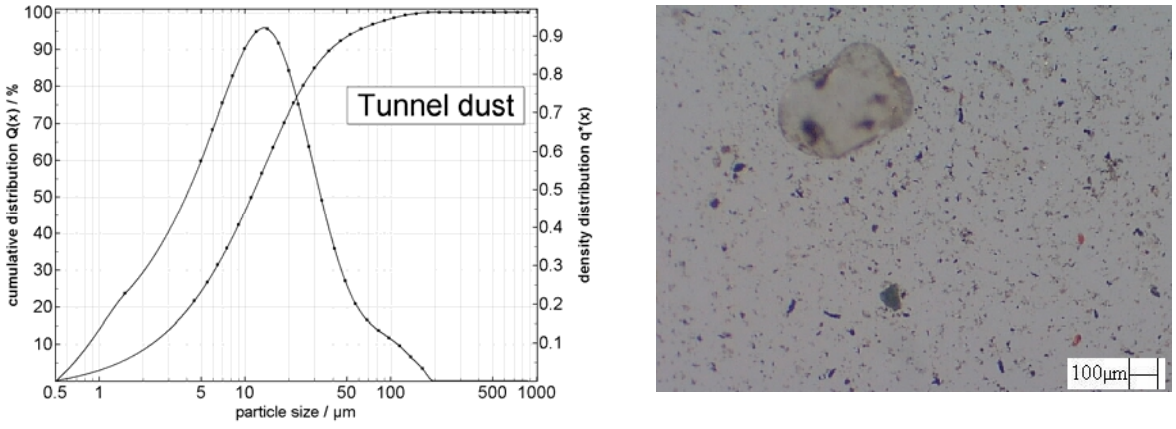
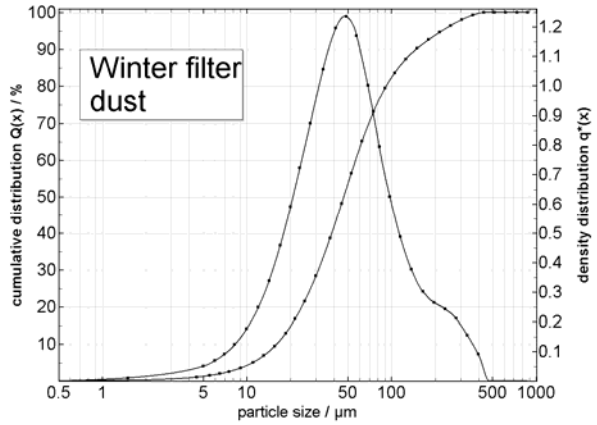
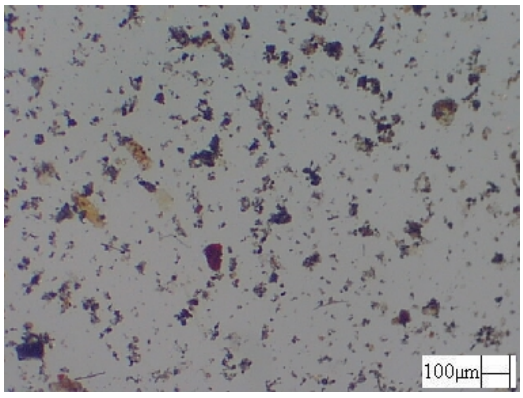


Figure 2: Particle size distribution (in vol.%) and micrograph obtained for a) tunnel dust after sieving through a 500 µm mesh.

b)





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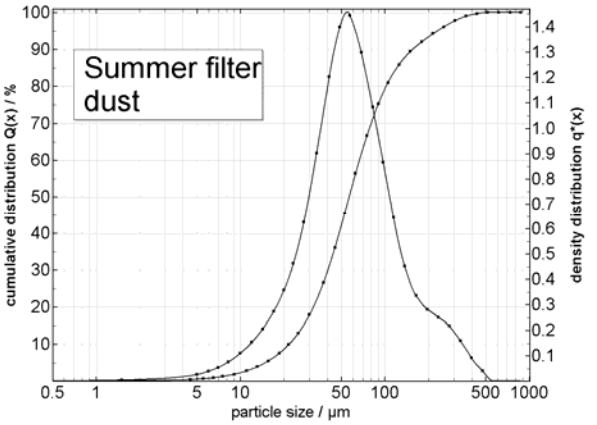

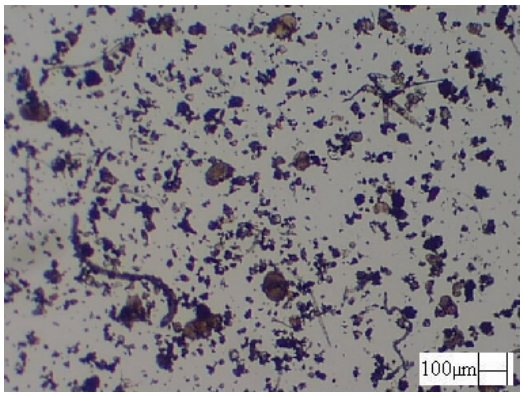

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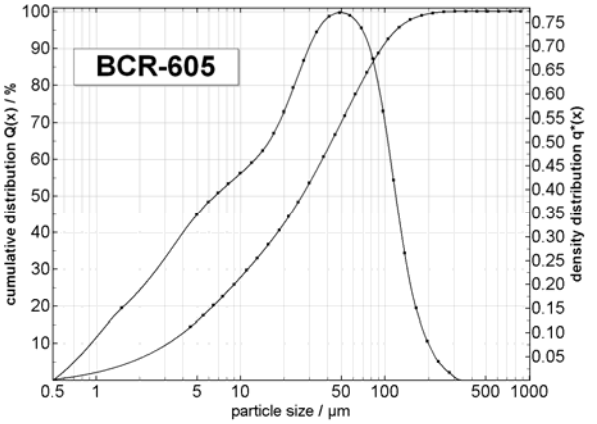
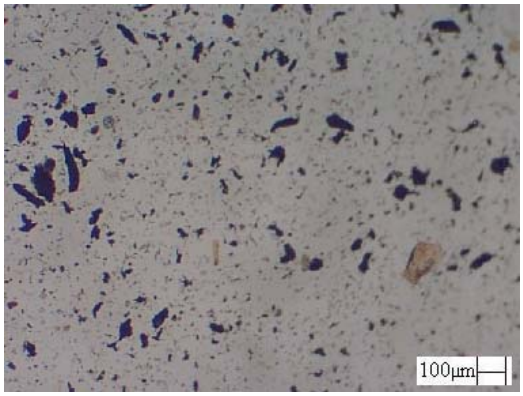
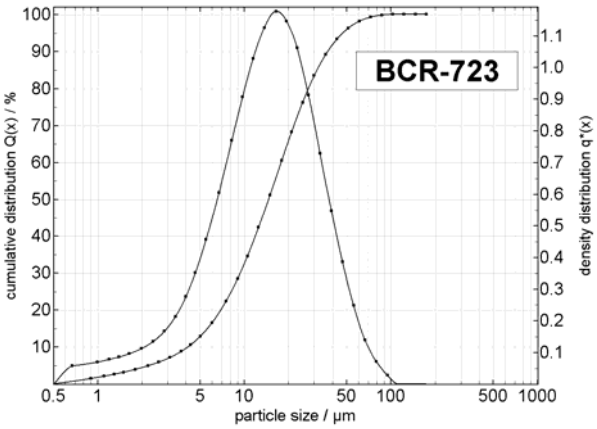




e)



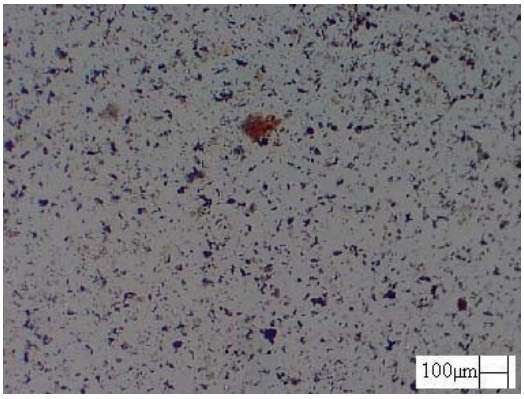


Figure 2 continuation: Particle size distribution (in vol.%) and micrograph obtained for b) winter filter dust and c) summer filter dust after sieving through a 500 µm mesh, and for d) BCR-605 and e) BCR-723, without sieving

Among all tested materials, BCR-723 and the tunnel dust had the smallest median particle size (about 12 µm). However, their top particle size was about 100 µm for BCR-723 and 180 µm for the tunnel dust. This can be explained by the presence of a few large particles (see Fig 2a, e) that widened the particle size range. In case of the filter materials, both median and top particle size were significantly larger than 10 µm. A median particle size of 47 µm and 57 µm for winter and summer filter dust, respectively, and a top particle size of 435 µm and 515 µm for the winter and summer filter dust, respectively, were measured. For BCR-605 a median particle size of 27 µm and a top particle size of 305 µm were measured. A fraction of bigger and irregular shape particles is present in these materials (see Fig 2b, c and d). Based on these results it was concluded that further processing of the materials was needed in order to reduce the particle size to the required level. For that purpose, the following processing techniques were tested:

- **a.** ball milling gave an opposite effect, i.e. aggregation of particles was observed (see Fig 3).
- **b.** fractional sieving using different type of sieves (nylon and metallic). This technique had a very low efficiency, i.e. for the material containing about 85 vol.% of particles smaller than 30 µm, only 19 %, 37 %, 23 % and less than 1 % of the material went through 125 µm, 63 µm, 45 µm and 30 µm mesh, respectively. This can be the result of a electrostatic charging of very fine particles, which blocked the sieves.
- **c.** jet milling allowed to obtain a very fine material (90 vol.% of particles below 25 µm, see Table 4), and was considered as the best solution.

Three materials (tunnel dust, summer filter dust and winter filter dust) were ground in this way. Before the milling, the materials were dried at 29 ^{o}C to decrease the water content (measured with Karl-Fischer titration, KFT) below 5 %. Additionally, (also before the jet milling) the tunnel dust was sieved through 245 µm sieve in order to separate the raw dust from possible sand particles (during rainy days sand from the tunnel road/sidewalks could be spread over its walls). The fraction > 245 µm, about 10 % of the raw material, was rejected.
The principle of the jet milling is based on the acceleration of the material particles by multiple jets of air in the mill chamber. The particle size reduction is the result of the high-velocity collisions between the material particles. Both the acceleration and collisions cause continuous mixing of the material during milling. Therefore, no additional operations towards the material homogenisation were performed. However, for the future CRM production and certification campaign, the influence of the material homogenisation in the Turbula mixer on the particle size distribution was studied. The test was performed on a small portion of the material, about 1 kg. No difference in the size distribution before and after homogenisation for 15 min was observed, see Annex A. However, it is worth noting that as the test was carried out using a limited quantity of the material, the particle size distribution during a real production process will not be necessarily the same. For that reason, it is recommended to perform the material homogenisation before the milling step.

After the jet milling, the materials were bottled into 0.5 g units under nitrogen, closed with a rubber stopper and a metal cap. The two existing CRMs (BCR-605 and BCR-723) were rebottled in the same way (without any processing steps). It was also verified whether the automated filling causes aggregation. No significant changes were observed, (see Annex A). The bottled materials were stored at the temperature appropriate for each step of the feasibility study (details in the corresponding sections of this report). The processing and final particle size distribution of all test materials is summarised in Table 4.

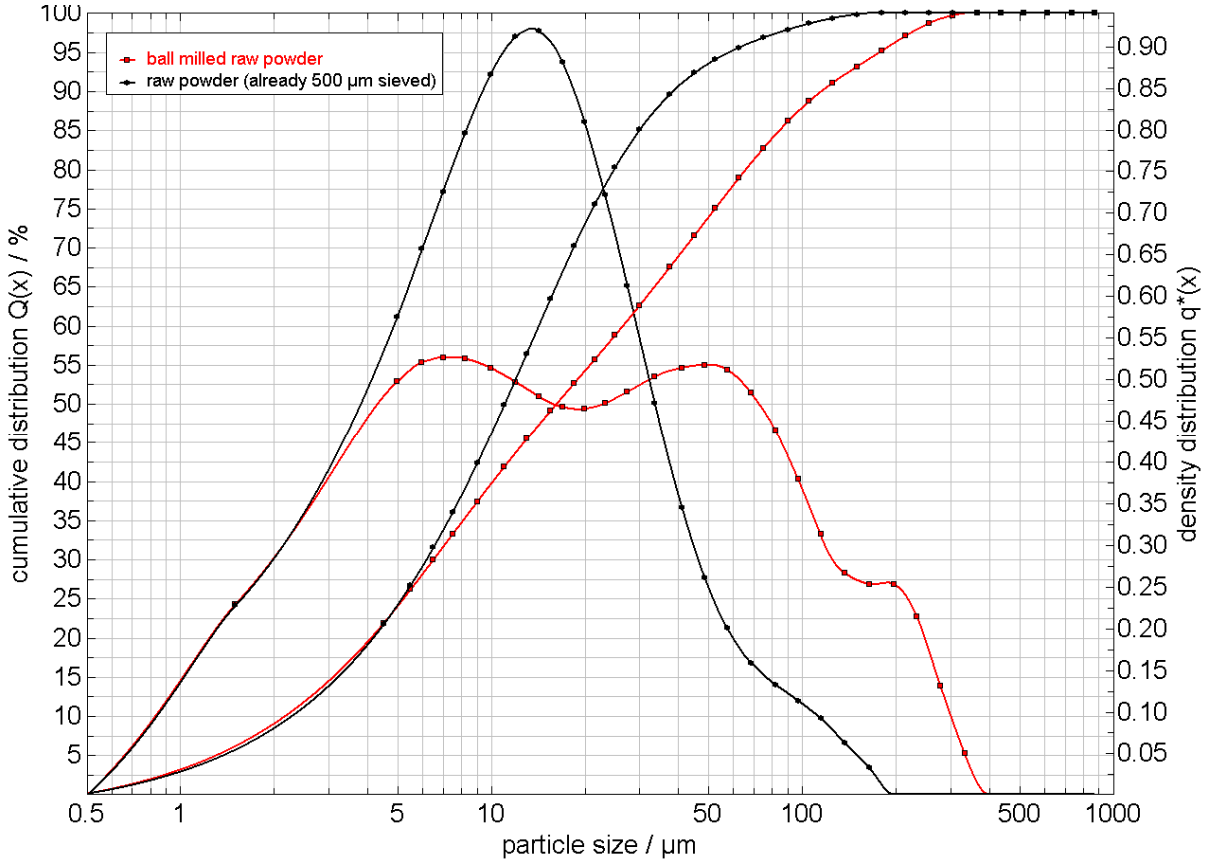


Figure 3: Comparison of the particle size distribution of tunnel dust before and after the ball milling for 30 min.

Table 4: Final particle size distribution of all test materials obtained after the processing

Material	Particle size ± expanded uncertainty[a] [µm ± %]						Processing steps[b]				
	Q_{10}[c]	Q_{16}[c]	Q_{50}[c]	Q_{84}[c]	Q_{90}[c]	Q_{100}[c]	1	2	3	4	5
Tunnel dust	1.77 ± 4.9	2.52 ± 4.2	7.62 ± 4.3	14.93 ± 4.8	17.45 ± 4.8	61	✓	✓	✓	✓	✓
Winter filter dust	1.99 ± 4.9	2.92 ± 4.2	6.90 ± 4.3	13.07 ± 4.8	16.30 ± 4.8	51	✓		✓	✓	✓
Summer filter dust	2.20 ± 4.9	3.19 ± 4.2	8.04 ± 4.3	18.44 ± 4.8	24.31± 4.8	87	✓		✓	✓	✓
BCR-605	3.29 ± 4.9	5.04 ± 4.2	26.69 ± 4.3	76.69 ± 4.8	95.05 ± 4.8	305					✓
BCR-723	4.11 ± 4.9	5.87 ± 4.2	14.67 ± 4.3	30.60 ± 4.8	37.35 ± 4.8	103					✓

[a]: with a coverage factor k = 2 corresponding to a level of confidence of about 95 %
[b]: Processing steps:
1. sieving through 0.5 mm mesh, 2. sieving through 0.245 mm mesh, 3. drying, 4. jet milling and 5. bottling.
✓: was carried out
[c]: $Q_{10, 16, 50, 84, 90, \text{and } 100}$ – cumulative distribution equals 10 vol.%, 16 vol.%, 50 vol.%, 84 vol.%, 90 vol.% and 100 vol.%, respectively

4.2. Content of elements

All test materials were screened for the presence of the following elements: As, B, Be, Cd, Co, Cr, Cu, Fe, Ni, Pb, Te, Tl and Zn. The measurements were performed before the material processing (described in section 4.1.) in the element analysis laboratory of the RM Unit, IRMM.

Sample preparation:

5 mL HNO_3 65 % and 1 mL H_2O_2 3 % were added to about 0.3 g sample. After minimum 30 min the samples were digested in a microwave system (Ultraclave, Milestone, IT) using the following temperature-controlled program: heating from room temperature to 220 ^oC in 25 min, 220 ^oC was maintained constant for 25 min, then cooled down to room temperature. The starting pressure was 45 bars. After the digestion, the samples were diluted with deionised water to 25 mL.

Analytical method:

The measurements were performed by means of ICP-OES (Thermo IRIS Intrepid II) in axial view using a cyclonic spray chamber with the following conditions: RF Power: 1150 W; Nebulizer flow: 0.87 L/min; auxiliary gas: 0.5 L/min.

Results:

Table 5: Results of screening measurements on the content of selected elements in all test materials

Element	Mass fraction [mg/kg]				
	BCR-723	BCR-605	Tunnel dust	Winter filter dust	Summer filter dust
As	27	38	25	38	37
B	28	50	49	49	55
Be	0.19	0.58	0.51	0.78	0.74
Cd	5.4	9.2	4.8	20	13
Co	28	12	14	19	16
Cr	286	111	149	141	102
Cu	270	392	516	519	674
Fe	20875	21875	24380	21970	22145
Ni	172	78	66	101	65
Pb	817	1382	149	503	362
Zn	1472	1472	1093	11422	6542

As shown in Table 5, the elements covered by the DDs, i.e. As, Cd, Ni and Pb were detected in all materials. Their content matches the values proposed by most of the expert laboratories (see Figure 1). The content of Te and Tl was below the quantification limit of the analytical method. No uncertainty was estimated for these determinations as the purpose of the analyses was screening only.

4.3. Content of PAHs

All test materials were screened for the presence of PAHs. The measurement were performed before the material processing, see section 4.1. The measurements were carried out in the organic analysis laboratory of the RM Unit, IRMM.

Sample preparation:

About 0.5 g sample was extracted with dichloromethane using an ASE system. An aliquot (about 0.5 mL) of the obtained extracts was cleaned using Florisil disposable cartridges; SPE elution agents: n-hexane : dichloromethane (1 : 1).

Analytical method:

The measurements were performed by means of GC-MS: SIM mode, DB5-MS column (J&W Scientific; 30 m x 0.25 mm x 0.25 µm), temperature program: 60 °C for 2 min, 140 °C (25 °C/min) for 1 min, 320 °C (10 °C/min) for 10 min.

Results:

Table 6: Results of screening measurements of the content of PAHs

Compound	Mass fraction [mg/kg]				
	BCR-605	BCR-723	Tunnel dust	Winter filter dust	Summer filter dust
Naphtalene	1.3	0.8	0.9	0.8	0.6
Acenaphthylene	0.3	0.2	0.2	0.2	0.1
Acenaphtene	0.2	0.1	0.1	0.1	0.1
Fluorene	0.9	0.2	-	-	-
Phenenthrene	10.0	6.6	2.4	2.3	1.1
Anthracene	1.6	0.4	0.5	0.3	0.1
Fluoranthene	17.9	0.3	5.4	3.5	1.5
Pyrene	22.8	6.1	5.1	2.5	1.1
Benzo[*a*]anthracene	2.8	1.0	0.9	1.8	0.5
Chrysene	5.7	2.7	1.6	3.6	1.2
Benzo[*b*]fluoranthene	3.8	1.7	2.0	4.9	1.6
Benzo[*k*]fluoranthene	1.0	0.4	0.6	1.4	0.4
Benzo[*a*]pyrene	1.3	0.7	0.6	1.9	1.2
Indeno[1,2,3-*cd*]pyrene	3.1	1.5	1.3	2.9	1.2
Dibenzo[*a,h*]anthracene	0.4	0.3	0.2	0.5	0.2
Benzo[*ghi*]perylene	4.7	3.3	1.8	2.7	1.2

As shown in Table 6, all PAHs excluding benzo[*j*]fluoranthene and coronene, which have to be certified (see *Target characteristics of the final reference* materials) were detected in both materials. Benzo[*j*]fluoranthene and coronene were not measured because they were not included in the set-up of the analytical method. Some interferences were present for acenaphtene and chrysene in the chromatograms for both samples. No uncertainty was estimated for these determinations, as the purpose of the analyses was screening only. Based on the determination of the content of PAHs, it can be concluded that all tested materials fulfil the recommendations established by the expert laboratories (see Figure 1 and Table 1) for the future PM_{10} CRM.

4.4. Homogeneity study: elements

4.4.1. Between-unit homogeneity

The between-bottle homogeneity is tested to ensure that the certified values of the CRM are valid for all bottles of the material, within the stated uncertainty.

The between-unit homogeneity test was performed for three materials (tunnel dust, winter filter dust and summer filter dust). Ten bottles of each material were selected using a random stratified sampling scheme and analysed with respect to the content of As, Cd, Ni and Pb. The measurements were carried out in the element analysis laboratory of the RM Unit, IRMM. From each bottle, three samples were prepared and analysed in a randomised manner to be able to separate a potential analytical drift from a trend in the filling sequence. Before analysis, the bottles were stored at 4 ^{o}C. Water content was not determined. The results of these measurements were evaluated using a method described by Linsinger *et al*. [2] as described below.

Sample preparation:

Each bottle was shaken for 10 min before opening. 5 mL HNO_3 65 % and 1 mL H_2O_2 30 % were added to about 0.15 g sample. The sample was left for at least 30 min and then digested in a microwave system (Ultraclave, Milestone, IT) using the following temperature-controlled program: heating from room temperature to 220 ^{o}C in 55 min, 220 ^{o}C was maintained for 30 min, then cooled down to room temperature. The starting pressure was 40 bars. After the digestion, the samples were diluted with deionised water to 25 mL. Before the analysis, the sample was centrifuged for about 5 min to separate the solution from the material residues.

Analytical method:

- The measurements of all elements, excluding Cd in Tunnel dust were performed by means of ICP-OES (Thermo IRIS Intrepid II) in axial view using a cyclonic spray chamber with the following conditions: RF Power: 1150 W; Nebulizer flow: 0.87 L/min; auxiliary gas: 0.5 L/min.
- Because of the low content of Cd in Tunnel dust the measurements were performed using GF-AAS (Analytik Jena) with the conditions described in Table 7 and 8.

Table 7: Optical and magnetic field parameters selected for determinations of Cd using AAS

Parameter	**Value**
Wavelength [nm]	228.8
Spectra slit [nm]	1.2
Lamp type	HCL
Lamp current [mA]	3.5
Magnet field mode	2-field
Integration mode	peak area
Integration time [s]	6.0

Table 8: Temperature program used for determinations of Cd using AAS

Step	Temp. [°C]	Hold [s]
1st Drying	80	20
2nd Drying	95	20
3rd Drying	110	10
Pyrolysis	650	10
Atomisation	1150	5
Cleanout	2300	4

4.4.1.1. Descriptive evaluation

Grubbs-tests were performed to detect potentially outlying individual results as well as outlying bottle averages.

For Tunnel dust, one outlying individual result was found for As. No outlying bottle averages were found.

For summer filter dust, neither outlying individual results nor outlying bottle averages were found.

For winter filter dust, some outlying individual results and one outlying bottle average were found for As, Ni and Pb.

As no technical reason for the outliers could be found all the data were retained for statistical analysis.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence.

Some trends in the analytical sequence were visible (see Table 9), pointing at instability of the analytical system. A drift correction was applied.

In tunnel dust, the mass fraction of Cd and Pb increased with increasing bottle numbers. These trends were significant on a 95 %, but not on a 99 % confidence level. In summer filter dust, the mass fraction of As, Ni and Pb decreased with increasing bottle numbers. These trends were only significant on a 95 % confidence level for Ni and Pb. For As it was also significant on a 99 % level. All data were retained. The uncertainty contribution deduced from the homogeneity study is very low (see Table 10), despite the fact that any potential trends are reflected in this uncertainty.

It was furthermore checked whether the individual data and bottle averages follow a normal distribution using normal probability plots and whether the individual data are unimodally distributed using histograms.

For all materials, all individual results and bottle means follow normal distributions. Individual results and most of the bottle means are unimodally distributed for all elements. An exception is summer filter dust for which the unimodal distribution of bottle means was found only for Cd.

The results of the descriptive evaluation are given in Table 9.

Table 9: Results of the descriptive evaluation of the homogeneity study for the content of elements in tunnel dust, winter filter dust and summer filter dust

For individual values with indication of outliers, see Annex B

	Outliers		Significant trends (95 % confidence)		Distribution of individuals results		Distribution of bottle means	
	Individual values	Bottle average	Analytical sequence	Filling sequence	Normal	Unimodal	Normal	Unimodal
Tunnel dust								
As	1	no	no[a]	no	yes	yes	yes	approx.
Cd	no	no	no[a]	yes	yes	yes	yes	yes
Pb	no	no	no	yes	yes	yes	yes	approx.
Ni	no	no	no[a]	no	yes	yes	yes	yes
Winter filter dust								
As	1	1	no[a]	no	yes	yes	yes	yes
Cd	no	no	no[a]	no	yes	yes	yes	approx.
Pb	1[b]	1[b]	no	no	yes	yes	yes	approx.
Ni	1	1	no	no	yes	yes	yes	hint of bimodal
Summer filter dust								
As	no	no	no	yes[b]	yes	yes	approx.	no
Cd	no	no	no[a]	no	yes	yes	yes	yes
Pb	no	no	no[a]	yes	yes	approx.	yes	no
Ni	no	no	no	yes	yes	yes	yes	no

[a]: drift correction applied
[b]: significant on 99 % confidence level

4.4.1.2. Variation between bottles

The aim was to evaluate whether the variation between bottles would significantly influence the certified uncertainty of the future PM_{10} CRMs. As all individual values followed unimodal distributions, the results could be evaluated using ANOVA. The standard deviations within bottles (s_{wb}) and between bottles (s_{bb}) as well as the maximum heterogeneity that could be hidden by the method repeatability (u^*_{bb}) were calculated. The s_{wb} is equivalent to the analytical variation if the individual subsamples were representative for the whole bottle. The s_{bb} expressed as a relative standard deviation is given by the following equation:

$$s_{bb} = \frac{\sqrt{\frac{MS_{among} - MS_{within}}{n}}}{\bar{y}}$$

MS_{among}: mean square among bottles from an ANOVA
MS_{within}: mean square within a bottle from an ANOVA
n: average number of replicates per bottle
$\bar{y}$: average of all results of the homogeneity study

The u^*_{bb} is defined as follows:

$$u^*_{bb} = \frac{RSD_{method}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}}$$

$\nu_{MSwithin}$: degrees of freedom of MS_{within}

The larger value of s_{bb} or u_{bb}^{*} are used as uncertainty contribution for homogeneity, u_{bb}.

The results of the evaluation of the between-unit variation are summarised in Table 10.

Table 10: Results of the homogeneity studies for the content of elements in tunnel dust, winter filter dust and summer filter dust

	Average [mg/kg]	s_{wb}		s_{bb}		u^{*}_{bb}	
		[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]
Tunnel dust							
As	6.29	0.308	4.9	0.078	1.2	0.100	1.6
Cd	0.856	0.018	2.1	n.c.	n.c.	0.006	0.7
Pb	102.2	1.375	1.35	n.c.	n.c.	0.446	0.44
Ni	49.7	0.718	1.4	n.c.	n.c.	0.233	0.5
Winter filter dust							
As	29.0	0.321	1.1	0.332	1.1	0.104	0.4
Cd	13.7	0.179	1.3	0.139	1.0	0.058	0.4
Pb	475.2	7.61	1.6	3.552	0.7	2.471	0.5
Ni	90.6	1.38	1.5	0.479	0.5	0.450	0.5
Summer filter dust							
As	27.1	0.739	2.7	0.425	1.6	0.240	0.9
Cd	8.37	0.085	1.0	0.037	0.4	0.028	0.3
Pb	300.1	2.851	1.0	3.086	1.0	0.926	0.3
Ni	57.8	0.961	1.7	0.809	1.4	0.312	0.5

n.c. = cannot be calculate as $MS_{among} < MS_{within}$

As shown in Table 10, the uncertainty of homogeneity is very low, i.e. below 1 %. However, only for As in Tunnel dust it is slightly higher (1.6 %). This can be attributed to the low content of As, which is close to the quantification limit of the method used.

4.4.2. Minimum sample intake

The typical PM_{10} sample mass collected on filters by laboratories is about 1 - 30 mg, depending on the sample collection time. Thus, future air quality CRMs have to be homogenous at that low milligram range. For this, the minimum sample intake is included in the material evaluation. The minimum sample intake provides information about the minimum sample mass of a solid CRM for which a certified uncertainty is valid. As it is related to the certified parameters (values and corresponding uncertainties), it is an essential part of CRM certificates. For minimum sample intake determinations with respect to elements, solid sampling atomic absorption spectrometry (SS-AAS) is a very efficient technique because a very low (about 0.05 – 5 mg) sample intake can be used. At these small sample intakes the analytical variation becomes negligible in comparison to the variation due to microheterogeneity. The observed standard deviation can therefore be used to estimate a minimum sample amount necessary for a given measurement repeatability, as described by Pauwels et al [3, 4]. Another advantage of this technique is that a large number of measurements can be performed in a short time. In addition, sample pretreatment is not required, hence, analyte loss and contamination is avoided.

All test materials were evaluated with respect to the minimum sample intake for As, Cd, Ni and Pb in the element analysis laboratory of the RM Unit, IRMM. One bottle per material was

analysed. About thirty measurements were performed for each element (exception: 15 measurements for As in summer filter dust). Sample mass of 0.051 mg to 0.479 mg were used. The samples were stored at room temperature before analysis. The results of the minimum sample intake determinations for the uncertainty of 2 % are summarised Table 13.

Instrument:

Zeeman SS-GFAAS, Zeenit 60, Analytik Jena

Experimental conditions:

Even though the materials are of the same matrix type (dust), their different origin induces a variation in the element contents and the chemical compositions. This might explain the different behaviour of the materials in the measurement process. For that reason, the analytical method was adjusted accordingly. The experimental conditions are summarised in Tables 11 and 12.

Table 11: Optical and magnetic field parameters selected for microhomogeneity determinations using SS-AAS

Parameter	Cd	Pb	As	Ni
Wavelength [nm]	228.8 326.1[2, 3]	261.4 283.3[1 - 3]	197.2 193.7[1-3]	234.6
Spectra slit [nm]	0.8	0.8	0.8	0.2
Lamp type	HCL	HCL	S-HCL	HCL
Lamp current [mA]	3.5	4.0	12.0	4.0
Boost current	-	-	18	-
Magnet field mode	3-field 2-field[1 - 3]	3-field	2-field	2-field
Integration mode	peak area	peak area	peak area	peak area
Integration time [s]	4.0	4.0	4.0	7.0

[1]: Tunnel dust
[2]: Winter filter dust
[3]: Summer filter dust

Table 12: Temperature program used for microhomogeneity determinations using SS-AAS

Step	Cd		Pb		As		Ni	
	Temp. [°C]	Hold [s]	Temp. [°C]	Hold [s]	Temp. [°C]	Hold [s]	Temp. [°C]	Hold [s]
1st Drying	90	30	105	5	80	10	80	5
2nd Drying	200	15	200	20	190	20	200	10
Pyrolysis	700	40	700	25	950 1000[1 -3]	30	1350	25
Atomisation	1900	4	2000	3	2300 2350[1 - 3]	4	2600	6
Cleanout	2400	4	2400	3	2400	4	2650	3

[1]: Tunnel dust
[2]: Winter filter dust
[3]: Summer filter dust

Calibrants:

- BCR-144R: sewage sludge from domestic origin, Pb: 106 ± 4 mg/kg, Cd: 1.82 ± 0.10 mg/kg
- BCR-145R: sewage sludge, Pb: 286 ± 5 mg/kg, Cd: 3.50 ± 0.15 mg/kg
- BCR-146R: sewage sludge from industrial origin, Pb: 609 ± 14 mg/kg, Cd: 18.8 ± 0.5 mg/kg, Ni: 69.7 ± 4.0 mg/kg
- BCR-277R: estuarine sediment, As: 18.3 ± 1.8 mg/kg

Results:

The minimum sample intake was calculated using the following equation [3, 4]:

$$M = \left(\frac{\kappa' \cdot s}{UNC} \right)^2 \cdot m .$$

Where:

M	minimum sample intake [mg],
κ'	factor for two-sided tolerance limits for normal distribution, chosen for *n* number of measurements and 95 % confidence level [5],
s	standard deviation [%],
m	average sample mass [mg],
UNC	target uncertainty for microhomogeneity [%]; 2 % uncertainty was assumed.

Table 13: Minimum sample intake (M) determined for As, Cd, Ni and Pb in all test materials with the assumption of 2 % uncertainty

Material	Element	*M* [mg]
Tunnel dust	As	45
	Cd	40
	Ni	31
	Pb	9
Winter filter dust	As	16
	Cd	30
	Ni	8
	Pb	30
Summer filter dust	As	39
	Cd	35
	Ni	33
	Pb	36
CRM 605	As	30
	Cd	45
	Ni	130
	Pb	46
BCR-723	As	30
	Cd	23
	Ni	28
	Pb	18

As shown in Table 13, the minimum sample intakes obtained for all elements in all test materials (excluding Ni in summer filter dust) are within the range proposed by the AQUILA group for the future PM_{10} CRM (5 to 50 mg).

4.5. Homogeneity study: PAHs

4.5.1. Between-unit homogeneity

The between-unit homogeneity test was carried out for three materials (tunnel dust, winter filter dust and summer filter dust). Ten bottles of each material were selected using a random stratified sampling scheme and analysed with respect to the content of selected PAHs: benzo[*a*]anthracene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, fluoranthene, anthracene and phenanthrene. The measurements were carried out in the organic analysis laboratory of RM Unit, IRMM. From each bottle, two samples were prepared. Before analysis, the bottles were stored at 4 ^{o}C. No water content was determined.

Sample preparation:

The bottles were shaken for about 10 min before opening. About 0.15 g sample was extracted with dichloromethane using an ASE system. The obtained extracts were cleaned using aminopropylsilane SPE cartridges; elution agents: n-hexane : dichloromethane (1 : 1).

Analytical method:

The measurements were performed by means of a GC-MS: SIM mode, DB-17HT column (J&W Scientific; 30 m x 0.32 mm x 0.15 µm) using the following temperature program: 60 ^{o}C for 2 min, 140 ^{o}C (25 ^{o}C/min) for 1 min, 320 ^{o}C (10 ^{o}C/min) for 10 min.

4.5.1.1. Descriptive evaluation

Grubbs-tests were performed to detect potentially outlying individual results as well as outlying bottle averages.

For all materials dust, some outlying individual results and bottle averages were found. As no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the filling sequence.

Some trends in the analytical sequence were visible for all PAHs excluding phenanthrene in winter filter dust (see Table 14), pointing at instability of the analytical system. A drift correction was applied.

In winter filter dust the mass fraction of bezo[*a*]pyrene decreased with increasing bottle numbers. This trend was significant on a 99 % confidence level. The observed trend is most likely due to the time that it took to prepare the samples (two days instead of one). The removal of the last four samples (prepared in the second day) makes the trend not significant. Nevertheless, all data were retained. The uncertainty of the homogeneity study is very low (see Table 14), even though any potential trends are reflected in this uncertainty.

For tunnel dust and summer filter dust, trends in either the analytical or the filling sequence were not found.

The individual data and bottle averages were evaluated using normal probability plots to determine whether they follow a normal distribution and, using histograms to determine whether the individual data are unimodally distributed.

For all PAHs in all test materials, excluding phenanthrene in tunnel dust, all individual results and bottle means follow normal distributions.

The individual results and most of the bottle means are unimodally distributed for all PAHs in tunnel dust.

A hint of non-unimodal distribution of the individual results was found for anthracene, fluoranthene and dibenzo[*a,h*]anthracene in winter filter dust. In this material a non-unimodal distribution of the bottle means was found for benzo[*b*]fluoranthene, indeno[123-*cd*]pyrene and dibenzo[*a,h*]anthracene.

A normal distribution for both the individual results and the bottle means was found in summer filter dust only for phenanthrene and anthracene. For the rest of PAHs the distributions were non-unimodal. This can be attributed to the particle size distribution of the material, in which a fraction of bigger particle is clearly visible (see Annex A) and the two maxima in the distributions are of a very similar population (see Fig 4).

Representative plots of the non-unimodal distribution of the individual results in summer filter dust and winter filter dust are shown in Figure 4.

The results of the descriptive evaluation are summarised in Table 14.

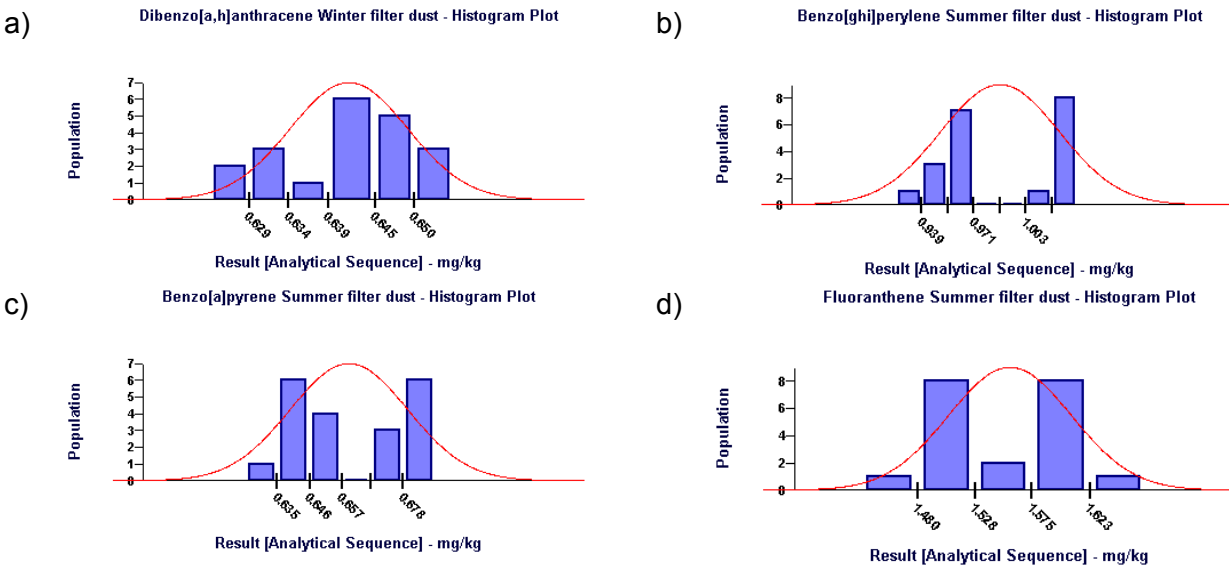


Figure 4: Distribution of the individual results obtained from the determination of a) dibenzo[*a,h*]anthracene in winter filter dust and, b) benzo[*ghi*]perylene , c) benzo[*a*]pyrene and d) fluoranthene in summer filter dust

Table 14: Results of the homogeneity study for the content of PAHs in tunnel dust, winter filter dust and summer filter dust

For individual values with indication of outliers, see Annex B

	Outliers		Significant trends (95 % confidence)		Distribution of individuals results		Distribution of bottle means	
	Individual values	Bottle average	Analytical sequence	Filling sequence	Normal	Unimodal	Normal	Unimodal
Tunnel dust								
Ph	1[a]	1[a]	no	no	no	yes	no	yes
Ant	1[a]	1[a]	no	no	approx.	yes	yes	yes
Flu	1[a]	1	no	no	approx.	yes	yes	yes
BaA	1	2	no	no	yes	yes	yes	yes
BbF	1[a]	2	no	no	approx.	approx.	yes	yes
BkF	1	no	no	no	approx.	yes	yes	approx.
BaP	1	2	no	no	yes	yes	yes	yes
I123P	1	no	no	no	approx.	yes	yes	yes
DahA	1	2	no	no	approx.	yes	yes	approx.
BghiP	1	no	no	no	approx.	approx.	yes	hint of bimodal
Winter filter dust								
Ph	1[a]	1	no	no	yes	yes	yes	yes
Ant	no	no	no	no	yes	hint of bimodal	yes	yes
Flu	no	no	no	no	yes	hint of bimodal	yes	hint of bimodal
BaA	no	1	no	no	yes	yes	yes	yes
BbF	no	no	no	no	yes	yes	yes	no
BkF	no	no	no	no	yes	yes	yes	yes
BaP	no	1	yes[a]	yes	yes	hint of bimodal	yes	yes
I123P	no	1[a]	no	no	yes	yes	approx.	no
DahA	no	no	no	no	yes	hint of bimodal	yes	no
BghiP	no	2	yes[a]	no	yes	yes	yes	hint of bimodal
Summer filter dust								
Ph	1[a]	1	no	no	yes	yes	yes	yes
Ant	1	no	no	no	yes	yes	yes	yes
Flu	no	no	no	no	yes	no	yes	no
BaA	no	no	no	no	yes	no	yes	no
BbF	no	no	yes	no	yes	no	yes	no
BkF	no	no	no	no	yes	no	yes	no
BaP	no	no	no	no	no	no	yes	no
I123P	no	no	no	no	approx	no	yes	no
DahA	no	no	no	no	yes	no	yes	no
BghiP	no	no	yes	no	approx	no	approx	no

[a]: significant on a 99 % confidence level

4.5.1.2. Variation between bottles

In general, the results can be evaluated using ANOVA when the data follow a unimodal distribution. This was not the case for the results obtained for summer filter dust (see section 4.5.1.1.). However, the obtained individual values were in a very narrow range (see Annex B and Fig 4); therefore, it was decided to use ANOVA. The standard deviations within bottles (s_{wb}) and between bottles (s_{bb}) as well as the maximum heterogeneity that could be hidden by the method repeatability (u^*_{bb}) were calculated. The results of the evaluation of the between-unit variation are summarised in Table 15.

Table 15: Results of the homogeneity studies for the content of PAHs in tunnel dust, winter filter dust and summer filter dust

	Average [mg/kg]	**s_{wb}**		**s_{bb}**		**u^*_{bb}**	
		[mg/kg]	[%]	[mg/kg]	[%]	[mg/kg]	[%]
Tunnel dust							
Ph	2.69	0.442	16.5	n.c.	n.c.	0.209	7.8
Ant	0.350	0.033	9.4	n.c.	n.c.	0.015	4.4
Flu	5.08	0.266	5.2	n.c.	n.c.	0.126	2.5
BaA	0.945	0.040	4.3	n.c.	n.c.	0.019	2.0
BbF	1.66	0.057	3.4	n.c.	n.c.	0.027	1.6
BkF	0.769	0.025	3.2	n.c.	n.c.	0.012	1.5
BaP	0.771	0.027	3.5	n.c.	n.c.	0.013	1.7
I123P	1.37	0.050	3.7	n.c.	n.c.	0.024	1.7
DahA	0.315	0.012	3.7	n.c.	n.c.	0.006	1.8
BghiP	1.88	0.067	3.5	n.c.	n.c.	0.031	1.7
Winter filter dust							
Ph	2.48	0.035	1.4	0.014	0.6	0.017	0.7
Ant	0.196	0.006	3.3	0.001	0.6	0.003	1.5
Flu	3.28	0.020	0.6	n.c.	n.c.	0.009	0.3
BaA	1.41	0.008	0.6	0.005	0.3	0.004	0.3
BbF	4.11	0.029	0.7	0.021	0.5	0.014	0.3
BkF	1.59	0.009	0.6	0.006	0.4	0.004	0.3
BaP	1.46	0.009	0.6	0.012	0.8	0.004	0.3
I123P	3.11	0.020	0.7	0.014	0.4	0.010	0.3
DahA	0.642	0.005	0.8	0.006	0.9	0.002	0.4
BghiP	2.79	0.019	0.7	0.019	0.7	0.009	0.3
Summer filter dust							
Ph	1.07	0.058	5.5	0.019	1.8	0.028	2.6
Ant	0.094	0.003	2.8	0.004	4.3	0.001	1.3
Flu	1.56	0.027	1.7	0.045	2.9	0.013	0.8
BaA	0.505	0.007	1.4	0.014	2.7	0.003	0.7
BbF	1.28	0.023	1.8	0.042	3.3	0.011	0.8
BkF	0.505	0.009	1.9	0.019	3.7	0.004	0.9
BaP	0.659	0.010	1.5	0.018	2.7	0.005	0.7
I123P	0.969	0.021	2.2	0.029	3.0	0.010	1.0
DahA	0.219	0.004	1.9	0.007	3.3	0.002	0.9
BghiP	0.987	0.020	2.1	0.031	3.2	0.010	1.0

n.c. = cannot be calculated as $MS_{among} < MS_{within}$

As indicated by the data in Table 15, the uncertainty of homogeneity obtained for summer filter dust and winter filter dust is very low (below 1.5 %) except for phenanthrene in summer filter dust for which the uncertainty was 2.6 %. However, the uncertainties obtained for summer filter dust can be underestimated because of the non-unimodal distribution of the individual results. For tunnel dust, the uncertainty of homogeneity is comparatively higher, (between 1.5 % and 7.8 %). This can be attributed to the material heterogeneity, as the concentration of PAHs along the tunnel may not be constant. If this is the case, a longer material homogenisation (milling and/or mixing) should be applied during the processing of the final CRM. The high values obtained for phenanthrene and anthracene can be attributed to both the outlying individual value and the outlying bottle mean. Both outliers were significant on a 99 % confidence level, and were found in the same sample prepared from the same bottle.

4.5.2. Minimum sample intake

The minimum sample intake for the determination of PAHs was derived from the commutability study (see section 4.7.). It was based on the assumption that the within-bottle variation must be better than the experimental standard deviation of any other measurement technique. The relative standard deviations of the measurements of benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*ghi*]perylene and indeno[123-*cd*]perylene performed on different sample masses (10 - 35 mg, ~50 mg and ~100 mg) by four different laboratories were compared.
The obtained results are summarised in Figure 5.

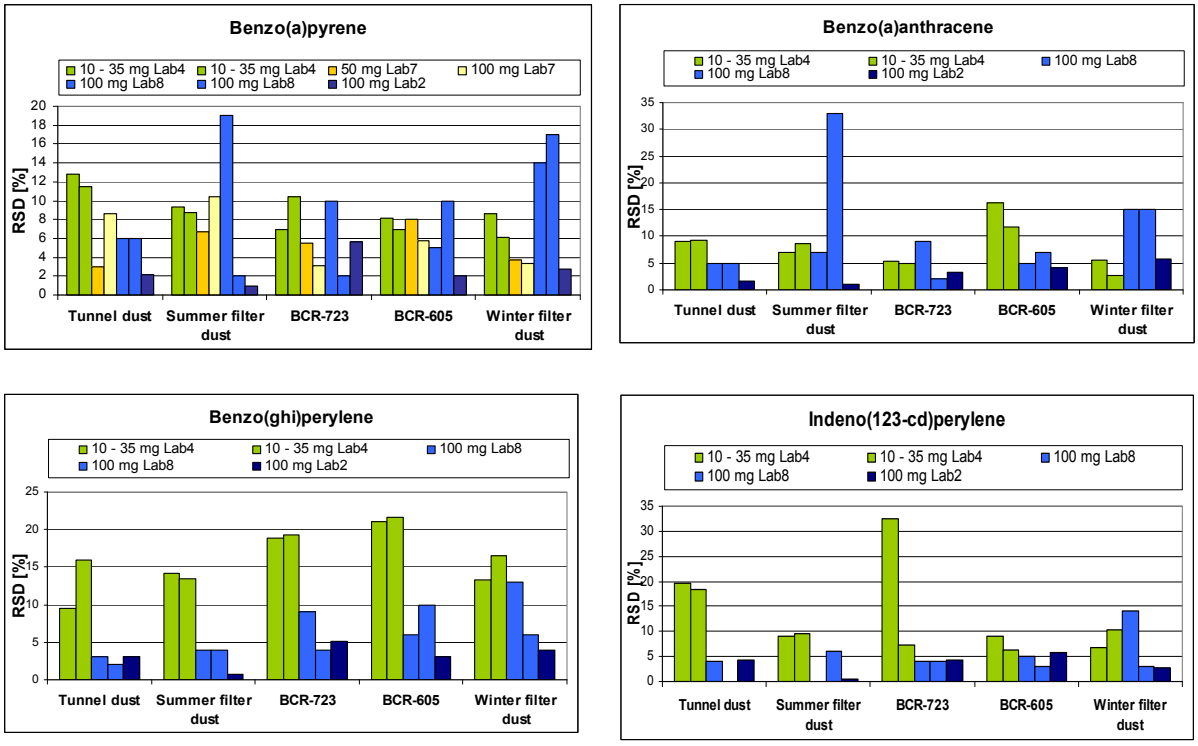


Figure 5: Results of determinations of benzo[*a*]pyrene, benzo[*a*]anthracene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]perylene in all test materials performed by the laboratories of the AQILA group.

As shown in Figure 5 there is no significant difference among the RSD values obtained for 100 mg and 50 mg samples. As the measurement reproducibility for the 50 mg sample does not differ significantly from that obtained for the 100 mg it was concluded that the minimum sample intake for benzo[*a*]pyrene is 50 mg. For the other PAHs there is no clear trend

towards increasing RSD values with decreasing sample masses. Hence, it is possible that for other PAHs the same value applies; however, additional measurements should be performed to verify this and to check whether the test materials are homogeneous within the range 35 – 50 mg sample mass.

4.6. Stability study

In order to asses the stability of the test materials, two types of the stability studies are carried out:

- Long-term stability study and,
- Short-term stability study.

The long-term stability study evaluates a material stability at the storage conditions, and typically covers a storage period of two years. This study is essential to assess possible instability and assign a shelf life to the test materials.

The short-term stability study aims at determining an appropriate transport temperature of both the test material and the future PM_{10} CRMs. During the transport especially in summer time, quite high temperatures can be reached. Thus, the short-term stability study allows determining whether special transport conditions should be provided to avoid any degradation of the material.

The material stability is evaluated using measurements based on "isochronous" storage design: samples stored at predetermined temperature for set time periods are shifted after the respective storage time to the reference temperature. At the end of the study all samples are analysed in one run under repeatability conditions. Because all measurements are done at the same time this approach minimise over/under estimation of the material stability caused by an analytical variation [6].

Both short- and long-term stability study have been performed for three test materials: tunnel dust, winter filter dust and summer filter dust.

As the long-term study has been scheduled for one and two years (see Table 14), the results cannot be presented in this report. The results of this study will be used during the production of PM_{10} CRMs. The test temperatures for the long-term stability study are 4 ^{o}C and 18 ^{o}C for elements and PAHs, and the reference temperature is - 20 ^{o}C.

Table 14: Time schedule for the continuation of the feasibility study

Action	2007								2008		2009	
	1	2	3	4	5	6	7	8 - 12	1 - 6	7 - 12	1 - 6	7 - 12
1 year long-term stability study												
2 years long-term stability study												

4.6.1. Short-term stability: elements

The samples were stored for 0, 1, 2 and 4 weeks at 18 ^{o}C and 60 ^{o}C according to the isochronous study. The reference temperature was – 20 ^{o}C. Based on common knowledge the material stability with respect to the content of elements is very high at room temperature. Therefore, as a first approach the material stability was evaluated at the highest temperature (60 ^{o}C). Two samples per each storage time were selected using a random stratified sampling scheme and analysed with the respect of the content of As, Cd, Ni and Pb in the element analysis laboratory of the RM Unit, IRMM. The bottles were kept at room temperature for at least one hour before opening to reach the equilibrium temperature. From

each bottle, three samples were prepared and analysed in a randomised manner as described in section 4.4.1. Water content was not determined.
The results were screened for outlying values. No outliers were found.
The data points obtained were plotted against storage time at the test temperature and the regression line calculated. The slope of the regression line was then tested for statistical significance. Only for winter filter dust the slopes for As, Pb and Ni were found significant on a 95 %, but not on a 99 % confidence level. This is the result of one data point (that corresponds to four weeks storage time), which is higher in comparison to the other storage times (see Annex C). The higher values observed for four weeks storage time can be attributed to the decrease of the water content during the longer sample storage at 60 °C. The removal of that data point makes the slope not significant.
The results of the short-term stability study are summarised in Table 15.

Table 15: Results of the short-term stability study for the content of elements in tunnel dust, winter filter dust and summer filter dust.
Test temperature: 60 °C; reference temperature: - 20 °C.

	Average ± s [mg/kg]	**Slope** [mg/kg/week]	**Slope significant (95 % confidence)**
Tunnel dust			
As	8.214 ± 0.313	0.037	no
Cd	0.870 ± 0.024	0.004	no
Pb	104.346 ± 1.184	0.017	no
Ni	49.725 ± 0.619	-0.034	no
Winter filter dust			
As	30.456 ± 0.610	0.217	yes
Cd	14.875 ± 0.410	0.063	no
Pb	472.354 ± 9.182	2.469	yes
Ni	89.570 ± 1.519	0.488	yes
Summer filter dust			
As	27.278 ± 1.363	0.178	no
Cd	8.250 ± 0.646	0.064	no
Pb	300.975 ± 14.185	1.511	no
Ni	56.231 ± 2.626	0.305	no

s: standard deviation

As indicated by the data in Table 15 the test materials are stable for at least 2 weeks at 60 °C. It allows assuming that the stability of those materials at lower temperature for the same or even longer time is sufficient for the material dispatch. Therefore, no stability study for 18 °C was carried out. Moreover, the determined content of all elements (excluding As in tunnel dust) is in agreement with the values obtained during the homogeneity study (see Table10). The difference in As determinations can be explained by the low content of As in Tunnel dust, which is close to the quantification limit of the used method.

The samples can be safely dispatched at ambient temperature on the condition that it does not exceed 60 °C for up to 2 weeks.

4.6.2. Short-term stability: PAHs

Samples were stored for 0, 1, 2 and 4 weeks at 4 °C and 18 °C according to the isochronous study. The reference temperature was – 20 °C. Two samples per each storage time (exception: three samples for Tunnel dust for 0 week storage time) were selected using a random stratified sampling scheme and analysed with the respect of the content of selected PAHs. The analyses were carried out in the organic analysis laboratory of RM Unit, IRMM. The bottles were kept at room temperature for at least one hour before opening to reach the temperature equilibrium. From each bottle, two samples were prepared and analysed as described in section 4.5.1. No water content was determined.

The results were screened for outlying values.
For summer filter dust, outliers were found for a sum of phenanthrene and anthracene, fluoranthene, benzo[*a*]pyrene and benzo[*ghi*]perylene for 4 °C storage temperature. The outlying values were significant on a 95 % but not on a 99 % confidence level. The ones for fluoranthene, benzo[*a*]pyrene and benzo[*ghi*]perylene were found after applying a double Grubbs test. No outliers were found for 18 °C storage temperature.
For winter filter dust, outlying values were found for dibenzo[*a,h*]anthracene and a sum of phenanthrene and anthracene for 4 °C and 18 °C storage temperature, respectively. The one for dibenzo[*a,h*]anthracene was significant on a 95 % but not on a 99 % confidence level. The outlier for a sum of phenanthrene and anthracene was also significant on a 99 % confidence level.
For tunnel dust, outliers were found for benzo[*b*]fluoranthene and benzo[*ghi*]perylene, and dibenzo[*a,h*]anthracene and indeno[123-*cd*]pyrene for 4 °C and 18 °C storage temperature, respectively. The one for indeno[123-*cd*]pyrene was significant on a 95 % but not on a 99 % confidence level. The others were significant also on a 99 % confidence level.

Furthermore, the regression lines were calculated and tested for significance. Only for winter filter dust, the slopes for fluoranthene and a sum of phenanthrene and anthracene at 18 °C storage temperature were found significant on a 99 % confidence level. This is the result of one data point (that corresponds to four weeks storage time), which is lower in comparison to the other storage times (see Annex C). The results of the short-term stability study are summarised in Table 16 and 17.

As indicated by the data in Table 18, tunnel dust and summer dust are stable at 18 °C up to 4 weeks. Winter filter dust is stable at 4 °C up to 4 weeks. Hence, tunnel dust and summer dust can be safely dispatched at 18 °C, and winter filter dust at 4 °C for up to 4 weeks.

The determined content of all PAHs in agreement with the values obtained during the homogeneity study (see Table15).

Table 16: Results of the short-term stability study for the content of PAHs in tunnel dust, winter filter dust and summer filter dust.
Test temperature: 4 °C; reference temperature: - 20 °C.

	Average ± s [mg/kg]	**Slope** [mg/kg/week]	**Slope significant (95 % confidence)**
Tunnel dust			
Ph + Ant	2.863 ± 0.040	- 0.004	no
Flu	4.937 ± 0.051	0.003	no
BaA	0.913 ± 0.008	- 0.001	no
BbF	1.862 ± 0.067	- 0.016	no
BkF	0.722 ± 0.017	- 0.001	no
BaP	0.756 ± 0.011	- 0.002	no
I123P	1.120 ± 0.016	- 0.002	no
DahA	0.242 ± 0.048	- 0.004	no
BghiP	1.833 ± 0.015	- 0.003	no
Winter filter dust			
Ph + Ant	2.482 ± 0.037	- 0.009	no
Flu	3.268 ± 0.021	0.000	no
BaA	1.422 ± 0.012	0.000	no
BbF	5.303 ± 0.125	- 0.001	no
BkF	1.405 ± 0.017	0.003	no
BaP	1.472 ± 0.017	0.002	no
I123P	2.639 ± 0.026	0.005	no
DahA	0.628 ± 0.020	- 0.001	no
BghiP	2.880 ± 0.021	0.006	no
Summer filter dust			
Ph + Ant	1.150 ± 0.035	0.008	no
Flu	1.585 ± 0.041	0.009	no
BaA	0.520 ± 0.014	0.002	no
BbF	1.452 ± 0.038	0.005	no
BkF	0.489 ± 0.030	0.001	no
BaP	0.620 ± 0.022	0.001	no
I123P	0.786 ± 0.022	0.005	no
DahA	0.216 ± 0.007	0.000	no
BghiP	1.013 ± 0.027	0.004	no

s: standard deviation

Table 17: Results of the short-term stability study for the content of PAHs in tunnel dust, winter filter dust and summer filter dust.
Test temperature: 18 °C; reference temperature: - 20 °C.

	Average ± s [mg/kg]	**Slope** [mg/kg/week]	**Slope significant (95 % confidence)**
Tunnel dust			
Ph + Ant	2.884 ± 0.046	- 0.005	no
Flu	4.935 ± 0.083	- 0.003	no
BaA	0.915 ± 0.011	- 0.001	no
BbF	1.927 ± 0.088	0.005	no
BkF	0.719 ± 0.016	- 0.002	no
BaP	0.754 ± 0.011	- 0.001	no
I123P	1.118 ± 0.020	- 0.004	no
DahA	0.276 ± 0.034	0.007	no
BghiP	1.837 ± 0.017	- 0.003	no
Winter filter dust			
Ph + Ant	2.450 ± 0.054	- 0.024	yes[a]
Flu	3.230 ± 0.037	- 0.019	yes[a]
BaA	1.401 ± 0.015	- 0.004	no
BbF	5.279 ± 0.121	0.004	no
BkF	1.395 ± 0.023	- 0.001	no
BaP	1.449 ± 0.018	- 0.005	no
I123P	2.620 ± 0.015	- 0.001	no
DahA	0.633 ± 0.015	0.003	no
BghiP	2.854 ± 0.019	- 0.001	no
Summer filter dust			
Ph + Ant	1.132 ± 0.049	- 0.001	no
Flu	1.569 ± 0.056	0.005	no
BaA	0.516 ± 0.019	0.001	no
BbF	1.450 ± 0.065	0.005	no
BkF	0.485 ± 0.029	0.001	no
BaP	0.612 ± 0.024	- 0.001	no
I123P	0.781 ± 0.033	0.002	no
DahA	0.218 ± 0.008	0.001	no
BghiP	1.003 ± 0.045	0.002	no

s: standard deviation
[a]: significant on a 99 % confidence level

4.7. Commutability study

The aim of this study is to evaluate the test materials with respect to their behaviour in the analytical process, and to compare the materials with real PM_{10} samples in term of handling, analyte content and matrix composition. It was done in cooperation with voluntary laboratories of the AQUILA group. Ten laboratories participated in this study. Each laboratory received two bottles of each material for the determination of elements and/or two additional bottles for the determination of PAHs. The test materials were labelled as Dust No 1 to 5 corresponding to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively. Additionally, each bottle was numbered to be distinguished within one material. Together with the samples the laboratories received the screening results of the content of

selected elements and PAHs performed before the material processing at IRMM, see Table 5 and 6. The laboratories were asked to analyse each bottle in three replicates (three samples from each bottle) and provide the results together with the measurement RSD or/and uncertainty, and a short description of the method used including the sample preparation. They were also asked to answer the following questions:

1. Have you studied different digestion approaches to element determinations before? If so, have you noticed any difference in using different digestion mixtures, e.g. nitric acid with hydrogen peroxide vs. nitric acid with hydrofluoric acid?
2. Give us your opinion about the presence of the compounds of your interest. Could you detect all of them?
3. Assess the concentration levels of the compounds of your interest in the materials. Would they fit your needs for a CRM?
4. Did you evaluate the chemical composition of the matrices, e.g. carbon content or particle size of the material? Do you have any comments on the matrix?
5. Did you notice any differences between the PM10 you usually analyse and our materials regarding handling, digestion, analysis etc.? Please elaborate.
6. Which of those materials would you consider the most appropriate as a PM10 CRM and why?
7. Other comments?

Eight out of ten laboratories sent the results with the questionnaire to IRMM. The outcome of this study is described below.
The answers for the questions 3 to 7 are summarised in Annex D.
A description of the methods used for the determination of elements and PAHs, and additional comments on the dust materials analysis are provided in Annex E.

4.7.1. Results of the determination of elements and PAHs

Most of the laboratories determined As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn, benzo[*a*]anthracene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, fluoranthene, anthracene and phenanthrene. The results for these elements and PAHs received from the laboratories were compared to those obtained at the IRMM. The results are illustrated in Annex F. Additional information about the content of other elements and PAHs is summarised in Annex G.

Comparison of the content of elements
All laboratories excluding Lab 7 and IRMM provided two values per element. Lab 7 analysed four bottles and provided four values per element. The results given by IRMM were taken from the homogeneity study described in this report. IRMM provided only one value which corresponds to an average of 30 determinations (10 bottles in three replicates).
As can be seen in Annex F in most cases the results within each laboratory and among the laboratories are in good agreement. The largest scatter among the results was observed for Zn and Fe in tunnel dust, Cu, Cr and V in BCR-723, Cr, As and V in winter filter dust. The observed differences can be attributed to the dry mass correction, which was not done.

Comparison of the content of PAHs
All laboratories excluding Lab 2, Lab 7 and IRMM provided two values per compound. Lab 2 and IRMM gave one and Lab 7 four values. The results given by IRMM were taken from the homogeneity study described in this report. IRMM provided only one value which corresponds to an average of 20 determinations (10 bottles in two replicates).
As can be seen in Annex F in most cases the results within each laboratory and among the laboratories are in good agreement. The largest scatter among the results was observed for phenanthrene and fluoranthene in all test materials. As most of the laboratories did not

provide the RSD and/or uncertainty of the results, a more accurate evaluation of the results is impossible. Similarly to the element determinations, the observed differences can be attributed to the dry mass correction, which was not done.

4.7.2. Material evaluation

In general, all laboratories could easily detect all elements and PAHs of their interest.
With regard to the concentration level of analytes there were two opinions. For some laboratories the content of both elements and PAHs in all test materials was suitable, and similar to the real PM_{10} samples or CRMs used. On the other hand, for others, a high variability of the analyte contents in one material requires the application of different dilution factors. In addition, the analysis of Cd was more difficult owing to its low level as compared to other elements in tunnel dust and BCR-723.

None of the laboratories evaluated the chemical composition of the matrices.

In general, all test materials were easy in handling and did not pose any problems during the sample preparation. For one laboratory, BCR-605 was difficult to weigh owing to its high electrostatic charge. In PAH analyses the test materials seemed to be more difficult to clean-up as compared to real samples.

4.7.3. A suitable candidate for PM_{10} CRM

The materials indicated by the laboratories as appropriate for the production of the air quality CRM are summarised in Table 18.

In summary, the commutability study indicates that in general all test materials are suitable as a PM_{10} CRM in terms of the analyte contents and material handling. In addition, in most cases the results of the material determination with respect to the content of elements and PAHs are in agreement among laboratories. However, the best candidate pointed out by the laboratories as a PM_{10} CRM is tunnel dust for the element determination and tunnel dust or summer filter dust for PAHs.

Table 18: Candidates for PM_{10} CRM selected by the laboratories of the AQUILA group

Laboratory #	Selected materials	Justification
Determination of elements		
1	Tunnel dust	The concentration of elements of interest are almost in the same range than our samples
3	No answer	
4	Tunnel dust, Summer filter dust	They fit well for our purposes as they are urban and traffic originating PM10 particles
6	Tunnel dust	The low concentration of the analysed elements means that it is not necessary to perform excessive dilution procedures, and the percentage RSD of the three repeats from each vial was the lowest of the five dusts
7	Tunnel dust BCR-605	No justification
8	No opinion	
Determination of PAHs		
1	No answer	
2	Summer filter dust	The lowest concentrations
4	Tunnel dust Winter filter dust	We were able to detect all the compounds of major interest from that material. Winter filter dust was also almost as good (anthracene was missing). The compounds with the lowest boiling points were difficult to analyse overall
5	No answer	
7	Tunnel dust Summer filter dust BCR-723	The concentrations of the components are in the range of real samples.
8	Tunnel dust Summer filter dust	They are relevant to the types of samples we would normally analyse

4.8. Conclusions

The feasibility study has shown that the production of air quality CRMs is possible. In particular, it has been demonstrated that with regard to the:

a. Particle size distribution: it was possible to decrease the particle size in the raw material down to the required level, i.e. close to PM_{10} (90 % of dust particles were below 25 µm). This was obtained by means of a jet mill. The particle size distribution was not affected by either the automated filling or the material homogenisation in the Turbula mixer. It is recommended to first homogenise the material followed by milling when using large (more than 1 kg) quantities of the material.

b. Content of analytes: in general all test materials were suitable as a PM_{10} CRM in terms of the content of analytes (elements and PAHs). The analyte contents in the test materials reflected the real environmental conditions, which is an advantage. However, a high variability of the analyte contents in the material required an application of different dilution factors, which made the analysis more laborious. In general the results of the material determination with respect to the content of elements and PAHs were in agreement among laboratories which participated in the material evaluation study.

c. Homogeneity: the uncertainty of homogeneity with respect to elements and PAHs obtained for summer filter dust and winter filter dust (BCR-605 and BCR-723 were not evaluated) was lower than 1.5 %. The exception was tunnel dust, for which the obtained values of the uncertainty for PAH determinations were comparatively higher (between 1.5 % and 7.8 %). This observation is probably the result of a not constant concentration of PAHs along the tunnel, where the material was collected, and of the possibility that the material was not fully homogenised during the selected processing conditions, i.e. jet milling (see section 4.1.).

It is worth noting that the amount of tunnel and filter dust processed in the jet milling was ~13 kg and ~ 2 kg, respectively. Thus, the lower “mixing” efficiency of the jet milling for tunnel dust as compared to filter dust can be explained by the difference in quantity of the processed materials.

To improve homogeneity a Turbula mixer should be employed for the material homogenisation as described in section 4.1.

The minimum sample intakes obtained for As, Cd, Ni, Pb and benzo[*a*]pyrene in all test materials (excluding Ni in summer filter dust) were 50 mg or below.

BCR-605 was considered to be homogeneous with respect to the content of trimethyllead at a level of 1 g and above, see certification report [7]. During the certification of BCR-723, the minimum sample intake for the determinations of Pd, Pt and Rh was determined to be 100 mg [8].

d. Short-term stability: the materials intended for the determination of the element content can be transported at ambient temperature for up to 4 weeks. Alternatively, if the materials are intended for the determination of PAHs, a temperature of 4 °C should be used to transport winter filter dust and 18 °C for both tunnel dust and summer filter dust.

For the future CRM productions suitable candidates are the tunnel dust material for elements and the tunnel dust or the filter dust materials for PAHs. There is still sufficient material available of the tunnel dust to allow CRM production while for the filter dust additional material would need to be collected.

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Acknowledgments

The collaboration of the AQUILA group and the expert laboratories participating in the commutability study is appreciated.

The financial support by DG Environment (Administrative Arrangement no. 070402/2006/438490/MAR/C3 "Feasibility study for the production of certified reference materials for the selected PAH compounds and heavy metals in the PM10 matrix") is gratefully acknowledged.

The finalisation of the feasibility study would not have been possible without cooperation, support and advice of
M. Moynihan and other colleagues from the Infrastructure and Site Management Unit, IRMM,
A. Oostra, A. Bau, P. Conneely, H. Emteborg and other colleagues from the Material Processing Sector, RM Unit, IRMM,
O. Bercaru, C. Contreras Lopez, G. Kerckhove, B. Sejeroe-Olsen and G. Van Britsom from RM Unit, IRMM.

The authors would like to thank G. Roebben (RM Unit, IRMM) for the reviewing of the report.

Annexes

Annex A: Particle size distribution
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Annex F: Commutability study: results of the determination of elements and PAHs
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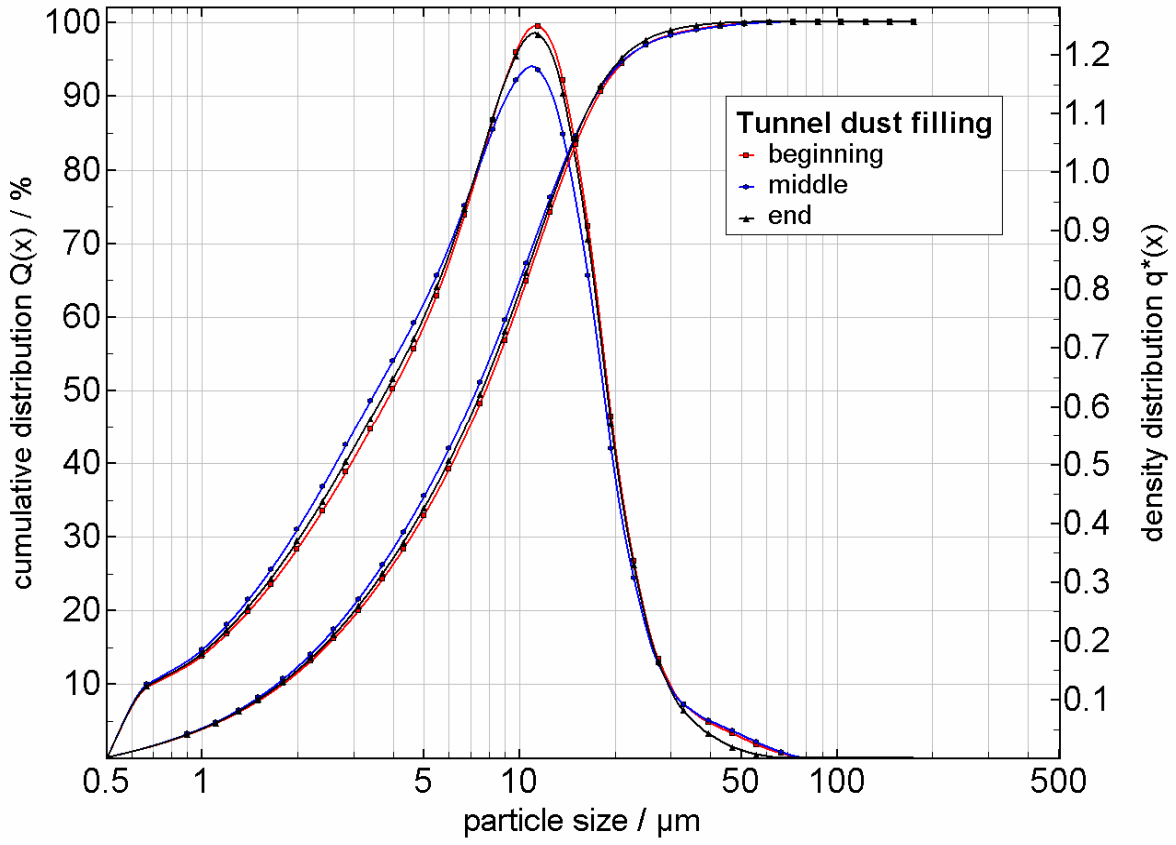
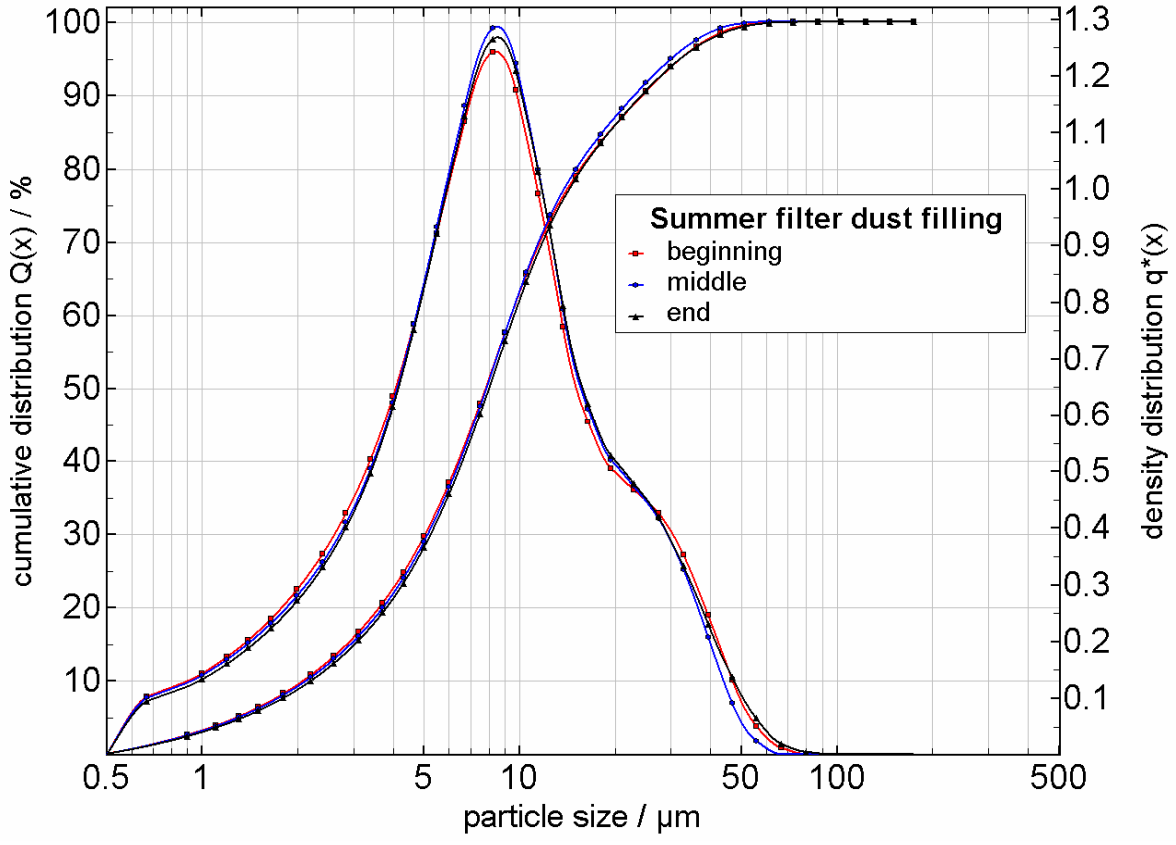
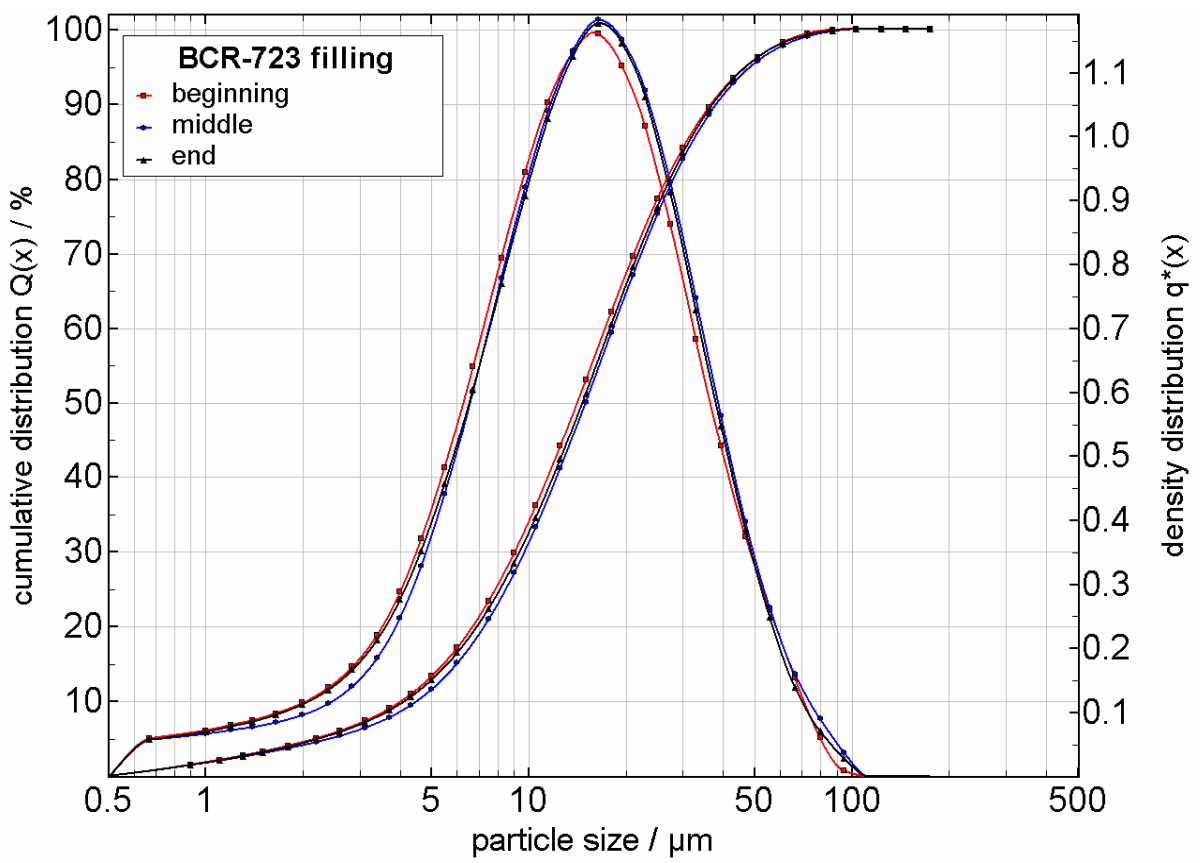
ANNEX A: Particle size distribution

Results of the particle size measurements during the material filling



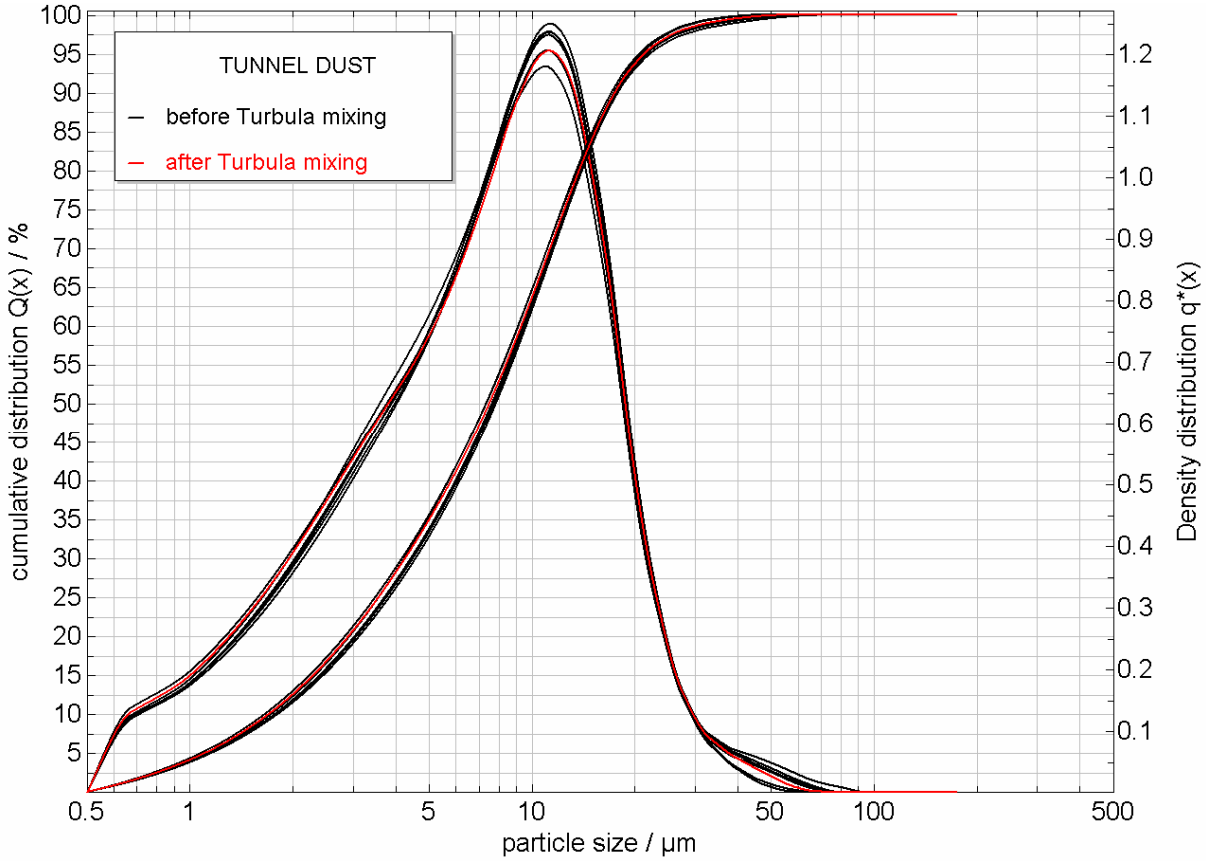


ANNEX A: Particle size distribution



ANNEX A: Particle size distribution

Results of the particle size measurements before and after the Turbula mixing



ANNEX B: Results of the homogeneity studies

Tunnel dust, As

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6141	1	6.20	2	6.39	3	6.03
6142	4	6.66	5	6.20	6	5.99
6143	7	6.02	8	6.00	9	6.36
6144	10	6.67	11	6.16	12	6.40
6145	13	6.49	14	6.59	15	6.63
6146	16	6.38	17	6.53	18	6.39
6147	19	6.09	20	5.40[a]	21	6.13
6148	22	6.64	23	6.15	24	6.39
6149	25	6.05	26	6.56	27	6.11
6150	28	6.78	29	6.62	30	5.66

[a]: Outlier on a 95 % confidence level

Tunnel dust, Cd

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6141	8	0.826	18	0.874	29	0.856
6142	6	0.845	13	0.837	26	0.861
6143	3	0.850	16	0.867	24	0.856
6144	1	0.881	11	0.829	25	0.855
6145	9	0.855	19	0.849	28	0.858
6146	10	0.879	15	0.832	22	0.857
6147	7	0.862	12	0.830	23	0.857
6148	2	0.861	20	0.862	21	0.864
6149	4	0.866	17	0.856	30	0.864
6150	5	0.887	14	0.825	27	0.870

Tunnel dust, Ni

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6141	1	49.2	2	50.1	3	50.5
6142	4	50.9	5	50.0	6	50.6
6143	7	49.5	8	49.6	9	49.1
6144	10	49.7	11	48.7	12	49.7
6145	13	50.1	14	49.0	15	48.0
6146	16	50.2	17	49.6	18	48.9
6147	19	50.8	20	49.9	21	48.7
6148	22	49.9	23	49.8	24	49.5
6149	25	49.8	26	49.7	27	50.5
6150	28	49.7	29	49.0	30	51.2

ANNEX B: Results of the homogeneity studies

Tunnel dust, Pb

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6141	1	100.7	2	102.3	3	103.8
6142	4	101.1	5	101.0	6	103.7
6143	7	102.2	8	102.2	9	101.6
6144	10	101.9	11	101.0	12	101.2
6145	13	103.8	14	102.6	15	99.77
6146	16	103.5	17	102.3	18	101.2
6147	19	103.2	20	103.8	21	100.8
6148	22	102.4	23	102.3	24	102.1
6149	25	102.5	26	102.4	27	104.0
6150	28	102.4	29	100.5	30	104.9

Winter filter dust, As

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6131[a]	8	30.4[a]	17	29.7	23	29.5
6132	5	29.2	19	29.1	22	29.6
6133	4	29.0	12	28.9	30	28.4
6134	2	28.3	15	29.3	25	28.5
6135	6	29.2	11	28.9	21	29.1
6136	3	29.1	18	29.0	26	28.5
6137	1	28.5	16	28.4	24	28.7
6138	9	28.6	13	29.0	27	29.0
6139	10	29.2	20	29.4	29	28.8
6140	7	29.2	14	28.7	28	29.1

[a]: Outlier on a 95 % confidence level

Winter filter dust, Cd

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6131	8	14.1	17	14.0	23	14.0
6132	5	13.8	19	13.9	22	13.8
6133	4	13.7	12	13.6	30	13.9
6134	2	13.3	15	14.0	25	13.6
6135	6	13.8	11	13.6	21	13.4
6136	3	13.8	18	13.7	26	13.3
6137	1	13.4	16	13.5	24	13.6
6138	9	13.6	13	13.6	27	13.5
6139	10	13.8	20	13.9	29	14.0
6140	7	13.7	14	13.7	28	13.4

ANNEX B: Results of the homogeneity studies

Winter filter dust, Ni

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6131[a]	8	95.5[b]	17	91.4	23	91.3
6132	5	92.8	19	91.2	22	90.3
6133	4	92.0	12	90.6	30	88.0
6134	2	90.6	15	89.9	25	88.8
6135	6	90.0	11	90.8	21	90.4
6136	3	91.0	18	90.8	26	88.7
6137	1	91.1	16	89.2	24	89.0
6138	9	90.1	13	89.3	27	91.0
6139	10	91.3	20	92.5	29	90.4
6140	7	89.3	14	89.9	28	91.8

[a]: Outlier on a 95 % confidence level [b]: Outlier on a 99 % confidence level

Winter filter dust, Pb

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6131[a]	8	508.9[a]	17	479.6	23	479.8
6132	5	483.1	19	475.7	22	471.9
6133	4	483.0	12	475.2	30	461.5
6134	2	474.8	15	474.2	25	467.0
6135	6	474.1	11	475.2	21	476.3
6136	3	474.5	18	474.3	26	464.9
6137	1	477.2	16	466.6	24	467.5
6138	9	473.1	13	470.0	27	474.9
6139	10	480.4	20	484.2	29	474.1
6140	7	468.5	14	472.2	28	478.8

[a]: Outlier on a 99 % confidence level

Summer filter dust, As

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6121	7	27.1	12	28.5	27	27.4
6122	6	26.8	18	28.3	22	27.1
6123	10	27.3	20	28.4	30	27.7
6124	1	26.8	13	28.8	23	27.4
6125	9	27.1	16	28.4	29	27.5
6126	3	25.8	19	27.3	26	26.4
6127	2	25.6	17	27.2	25	26.6
6128	5	25.7	14	27.0	24	26.6
6129	4	26.2	11	27.4	28	26.5
6130	8	26.1	15	27.2	21	26.3

ANNEX B: Results of the homogeneity studies

Summer filter dust, Cd

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6121	1	8.33	2	8.36	3	8.47
6122	4	8.30	5	8.39	6	8.28
6123	7	8.41	8	8.33	9	8.36
6124	10	8.28	11	8.26	12	8.30
6125	13	8.40	14	8.36	15	8.44
6126	16	8.53	17	8.51	18	8.36
6127	19	8.39	20	8.59	21	8.40
6128	22	8.51	23	8.43	24	8.24
6129	25	8.38	26	8.37	27	8.33
6130	28	8.39	29	8.36	30	8.15

Summer filter dust, Ni

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6121	7	58.1	12	60.1	27	56.5
6122	6	57.9	18	58.8	22	58.9
6123	10	58.9	20	60.0	30	59.4
6124	1	57.6	13	59.5	23	58.3
6125	9	58.4	16	59.0	29	58.2
6126	3	55.3	19	57.9	26	56.7
6127	2	56.3	17	56.7	25	57.0
6128	5	56.0	14	58.5	24	57.9
6129	4	56.5	11	58.0	28	56.2
6130	8	56.8	15	57.1	21	57.1

Summer filter dust, Pb

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2		Replicate 3	
	Sequence number	Result	Sequence number	Result	Sequence number	Result
6121	7	304.8	12	307.3	27	294.4
6122	6	301.8	18	301.8	22	302.8
6123	10	305.5	20	304.3	30	307.8
6124	1	300.5	13	303.4	23	301.0
6125	9	304.9	16	302.9	29	303.0
6126	3	293.9	19	297.9	26	296.4
6127	2	296.4	17	295.8	25	297.0
6128	5	297.0	14	302.0	24	300.4
6129	4	298.2	11	298.5	28	294.4
6130	8	299.6	15	293.2	21	296.3

ANNEX B: Results of the homogeneity studies

Tunnel dust, Phenanthrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	2.50	2	2.56
5803	3	2.55	4	2.57
5804	5	2.70	6	2.56
5805	7	2.57	8	3.06
5806[a]	9	2.54	10	4.43[a]
5807	11	2.64	12	2.46
5808	13	2.51	14	2.65
5809	15	2.56	16	2.54
5810	17	2.52	18	2.60
5811	19	2.66	20	2.55

[a]: Outlier on a 99 % confidence level

Tunnel dust, Anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	0.327	2	0.339
5803	3	0.339	4	0.343
5804	5	0.344	6	0.336
5805	7	0.337	8	0.390
5806[a]	9	0.335	10	0.467[a]
5807	11	0.348	12	0.321
5808	13	0.344	14	0.357
5809	15	0.343	16	0.338
5810	17	0.344	18	0.353
5811	19	0.345	20	0.340

[a]: Outlier on a 99 % confidence level

Tunnel dust, Fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	4.91	2	5.01
5803	3	4.98	4	5.03
5804	5	5.01	6	5.01
5805	7	4.99	8	5.60
5806[a]	9	4.97	10	5.90[b]
5807	11	5.16	12	4.86
5808	13	4.98	14	5.23
5809	15	5.05	16	4.98
5810	17	5.02	18	5.05
5811	19	4.92	20	5.01

[a]: Outlier on a 95 % confidence level [b]: Outlier on a 99 % confidence level

ANNEX B: Results of the homogeneity studies

Tunnel dust, Benzo[*a*]anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	0.910	2	0.932
5803	3	0.933	4	0.946
5804	5	0.941	6	0.940
5805[a]	7	0.932	8	1.036
5806[a]	9	0.932	10	1.046[a]
5807	11	0.976	12	0.907
5808	13	0.921	14	0.975
5809	15	0.939	16	0.932
5810	17	0.924	18	0.936
5811	19	0.915	20	0.924

[a]: Outlier on a 95 % confidence level

Tunnel dust, Benzo[*b*]fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	1.65	2	1.66
5803	3	1.64	4	1.65
5804	5	1.63	6	1.68
5805[a]	7	1.64	8	1.83[b]
5806[a]	9	1.66	10	1.79
5807	11	1.71	12	1.63
5808	13	1.66	14	1.69
5809	15	1.65	16	1.64
5810	17	1.63	18	1.63
5811	19	1.60	20	1.63

[a]: Outlier on a 95 % confidence level [b]: Outlier on a 99 % confidence level

Tunnel dust, Benzo[*k*]fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	0.760	2	0.772
5803	3	0.760	4	0.766
5804	5	0.760	6	0.781
5805	7	0.759	8	0.838[a]
5806	9	0.764	10	0.822
5807	11	0.793	12	0.752
5808	13	0.765	14	0.782
5809	15	0.767	16	0.758
5810	17	0.752	18	0.745
5811	19	0.738	20	0.744

[a]: Outlier on a 95 % confidence level

ANNEX B: Results of the homogeneity studies

Tunnel dust, Benzo[*a*]pyrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	0.747	2	0.759
5803	3	0.764	4	0.767
5804	5	0.763	6	0.784
5805[a]	7	0.764	8	0.840[a]
5806[a]	9	0.764	10	0.832
5807	11	0.795	12	0.745
5808	13	0.756	14	0.789
5809	15	0.766	16	0.761
5810	17	0.758	18	0.759
5811	19	0.747	20	0.750

[a]: Outlier on a 95 % confidence level

Tunnel dust, Indeno[1,2,3-*cd*]pyrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	1.30	2	1.34
5803	3	1.34	4	1.36
5804	5	1.36	6	1.39
5805	7	1.35	8	1.50[a]
5806	9	1.36	10	1.48
5807	11	1.40	12	1.31
5808	13	1.36	14	1.40
5809	15	1.36	16	1.35
5810	17	1.37	18	1.37
5811	19	1.33	20	1.36

[a]: Outlier on a 95 % confidence level

Tunnel dust, Dibenzo[*a,h*]anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	0.301	2	0.308
5803	3	0.308	4	0.315
5804	5	0.310	6	0.321
5805[a]	7	0.314	8	0.347[a]
5806[a]	9	0.311	10	0.341
5807	11	0.323	12	0.305
5808	13	0.311	14	0.323
5809	15	0.313	16	0.311
5810	17	0.312	18	0.314
5811	19	0.305	20	0.313

[a]: Outlier on a 95 % confidence level

ANNEX B: Results of the homogeneity studies

Tunnel dust, Benzo[*ghi*]perylene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5802	1	1.83	2	1.86
5803	3	1.86	4	1.87
5804	5	1.86	6	1.93
5805	7	1.86	8	2.06[a]
5806	9	1.86	10	2.01
5807	11	1.93	12	1.81
5808	13	1.85	14	1.91
5809	15	1.86	16	1.84
5810	17	1.85	18	1.84
5811	19	1.79	20	1.83

[a]: Outlier on a 95 % confidence level

Summer filter dust, Phenanthrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	1.04	2	1.05
5813	3	1.07	4	1.08
5814	5	1.09	6	1.06
5815	7	1.09	8	1.08
5816[a]	9	1.28[b]	10	1.06
5817	11	1.08	12	1.10
5818	13	1.02	14	1.02
5819	15	1.02	16	1.00
5820	17	1.01	18	1.07
5821	19	1.03	20	1.15

[a]: Outlier on a 95 % confidence level [b]: Outlier on a 99 % confidence level

Summer filter dust, Anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.092	2	0.093
5813	3	0.098	4	0.094
5814	5	0.097	6	0.096
5815	7	0.090	8	0.093
5816	9	0.107[a]	10	0.099
5817	11	0.096	12	0.098
5818	13	0.092	14	0.087
5819	15	0.087	16	0.087
5820	17	0.091	18	0.095
5821	19	0.092	20	0.094

[a]: Outlier on a 95 % confidence level

ANNEX B: Results of the homogeneity studies

Summer filter dust, Fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	1.52	2	1.51
5813	3	1.58	4	1.59
5814	5	1.60	6	1.58
5815	7	1.61	8	1.60
5816	9	1.67	10	1.57
5817	11	1.59	12	1.61
5818	13	1.50	14	1.51
5819	15	1.51	16	1.48
5820	17	1.50	18	1.51
5821	19	1.52	20	1.57

Summer filter dust, Benzo[*a*]anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.495	2	0.488
5813	3	0.515	4	0.518
5814	5	0.523	6	0.509
5815	7	0.520	8	0.521
5816	9	0.525	10	0.502
5817	11	0.522	12	0.530
5818	13	0.488	14	0.494
5819	15	0.495	16	0.485
5820	17	0.488	18	0.490
5821	19	0.502	20	0.496

Summer filter dust, Benzo[*b*]fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	1.25	2	1.24
5813	3	1.31	4	1.32
5814	5	1.35	6	1.33
5815	7	1.35	8	1.33
5816	9	1.33	10	1.25
5817	11	1.32	12	1.34
5818	13	1.23	14	1.24
5819	15	1.26	16	1.22
5820	17	1.23	18	1.24
5821	19	1.27	20	1.24

ANNEX B: Results of the homogeneity studies

Summer filter dust, Benzo[*k*]fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.492	2	0.486
5813	3	0.511	4	0.518
5814	5	0.535	6	0.522
5815	7	0.531	8	0.530
5816	9	0.529	10	0.495
5817	11	0.524	12	0.528
5818	13	0.478	14	0.482
5819	15	0.491	16	0.482
5820	17	0.476	18	0.490
5821	19	0.501	20	0.492

Summer filter dust, Benzo[*a*]pyrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.650	2	0.643
5813	3	0.671	4	0.669
5814	5	0.680	6	0.672
5815	7	0.686	8	0.689
5816	9	0.679	10	0.636
5817	11	0.687	12	0.685
5818	13	0.642	14	0.647
5819	15	0.639	16	0.635
5820	17	0.637	18	0.637
5821	19	0.656	20	0.648

Summer filter dust, Indeno[1,2,3-cd]pyrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.929	2	0.935
5813	3	0.995	4	0.996
5814	5	1.016	6	0.996
5815	7	1.018	8	1.007
5816	9	1.016	10	0.932
5817	11	0.999	12	1.009
5818	13	0.934	14	0.938
5819	15	0.950	16	0.931
5820	17	0.933	18	0.943
5821	19	0.964	20	0.936

ANNEX B: Results of the homogeneity studies

Summer filter dust, Dibenzo[*a,h*]anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.211	2	0.210
5813	3	0.226	4	0.226
5814	5	0.228	6	0.225
5815	7	0.229	8	0.225
5816	9	0.229	10	0.213
5817	11	0.228	12	0.229
5818	13	0.210	14	0.210
5819	15	0.213	16	0.207
5820	17	0.211	18	0.212
5821	19	0.219	20	0.213

Summer filter dust, Benzo[*ghi*]perylene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5812	1	0.962	2	0.960
5813	3	1.025	4	1.017
5814	5	1.029	6	1.020
5815	7	1.030	8	1.024
5816	9	1.024	10	0.939
5817	11	1.026	12	1.035
5818	13	0.952	14	0.961
5819	15	0.963	16	0.944
5820	17	0.945	18	0.956
5821	19	0.970	20	0.957

Winter filter dust, Phenanthrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	2.48	2	2.53
5823	3	2.49	4	2.48
5824	5	2.47	6	2.47
5825[a]	7	2.60[b]	8	2.50
5826	9	2.46	10	2.48
5827	11	2.45	12	2.49
5828	13	2.46	14	2.43
5829	15	2.54	16	2.46
5830	17	2.47	18	2.48
5831	19	2.50	20	2.45

[a]: Outlier on a 95 % confidence level [b]: Outlier on a 99 % confidence level

ANNEX B: Results of the homogeneity studies

Winter filter dust, Anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	0.195	2	0.202
5823	3	0.206	4	0.194
5824	5	0.184	6	0.202
5825	7	0.195	8	0.200
5826	9	0.192	10	0.195
5827	11	0.200	12	0.193
5828	13	0.183	14	0.193
5829	15	0.204	16	0.194
5830	17	0.189	18	0.191
5831	19	0.201	20	0.205

Winter filter dust, Fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	3.28	2	3.28
5823	3	3.29	4	3.27
5824	5	3.25	6	3.27
5825	7	3.31	8	3.29
5826	9	3.27	10	3.28
5827	11	3.25	12	3.28
5828	13	3.29	14	3.25
5829	15	3.31	16	3.25
5830	17	3.26	18	3.27
5831	19	3.29	20	3.27

Winter filter dust, Benzo[*a*]anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	1.42	2	1.41
5823[a]	3	1.43	4	1.42
5824	5	1.40	6	1.41
5825	7	1.41	8	1.41
5826	9	1.40	10	1.41
5827	11	1.40	12	1.40
5828	13	1.41	14	1.39
5829	15	1.42	16	1.40
5830	17	1.41	18	1.40
5831	19	1.41	20	1.41

[a]: Outlier on a 95 % confidence level

ANNEX B: Results of the homogeneity studies

Winter filter dust, Benzo[*b*]fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	4.06	2	4.09
5823	3	4.13	4	4.15
5824	5	4.10	6	4.13
5825	7	4.12	8	4.14
5826	9	4.09	10	4.13
5827	11	4.04	12	4.10
5828	13	4.16	14	4.08
5829	15	4.08	16	4.03
5830	17	4.13	18	4.11
5831	19	4.13	20	4.13

Winter filter dust, Benzo[*k*]fluoranthene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	1.59	2	1.59
5823	3	1.60	4	1.60
5824	5	1.58	6	1.59
5825	7	1.59	8	1.60
5826	9	1.58	10	1.58
5827	11	1.57	12	1.58
5828	13	1.60	14	1.57
5829	15	1.58	16	1.56
5830	17	1.59	18	1.58
5831	19	1.59	20	1.59

Winter filter dust, Benzo[*a*]pyrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	1.49	2	1.47
5823[a]	3	1.50	4	1.49
5824	5	1.47	6	1.46
5825	7	1.47	8	1.47
5826	9	1.45	10	1.46
5827	11	1.45	12	1.47
5828	13	1.46	14	1.45
5829	15	1.45	16	1.46
5830	17	1.46	18	1.44
5831	19	1.46	20	1.46

[a]: Outlier on a 95 % confidence level

ANNEX B: Results of the homogeneity studies

Winter filter dust, Indeno[1,2,3-*cd*]pyrene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	3.09	2	3.10
5823[a]	3	3.15	4	3.17
5824	5	3.10	6	3.11
5825	7	3.11	8	3.13
5826	9	3.10	10	3.13
5827	11	3.07	12	3.12
5828	13	3.12	14	3.07
5829	15	3.11	16	3.08
5830	17	3.11	18	3.10
5831	19	3.10	20	3.12

[a]: Outlier on a 99 % confidence level

Winter filter dust, Dibenzo[*a,h*]anthracene

Mass fractions in mg/kg

Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822	1	0.629	2	0.633
5823	3	0.641	4	0.645
5824	5	0.644	6	0.650
5825	7	0.649	8	0.655
5826	9	0.647	10	0.651
5827	11	0.641	12	0.642
5828	13	0.640	14	0.629
5829	15	0.634	16	0.635
5830	17	0.647	18	0.633
5831	19	0.647	20	0.641

Winter filter dust, Benzo[*ghi*]perylene

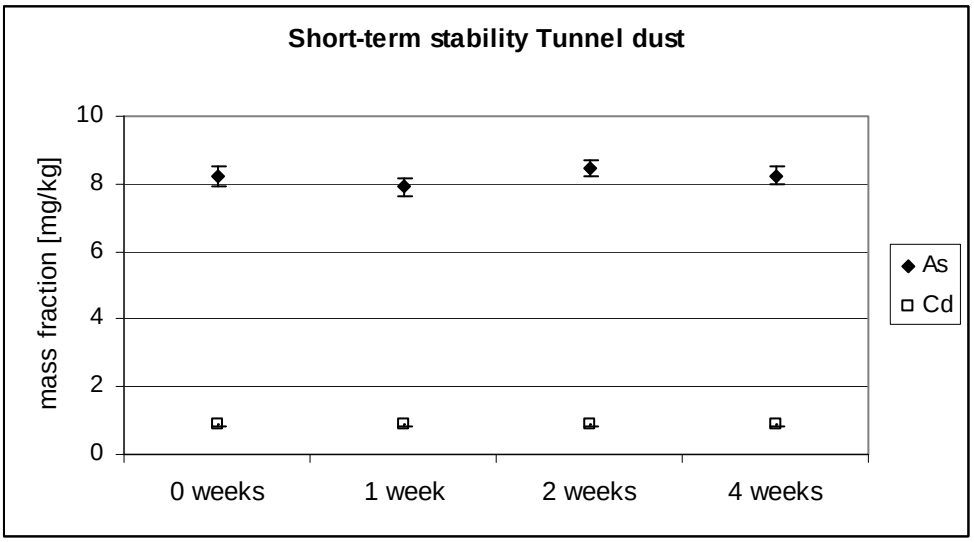
Mass fractions in mg/kg

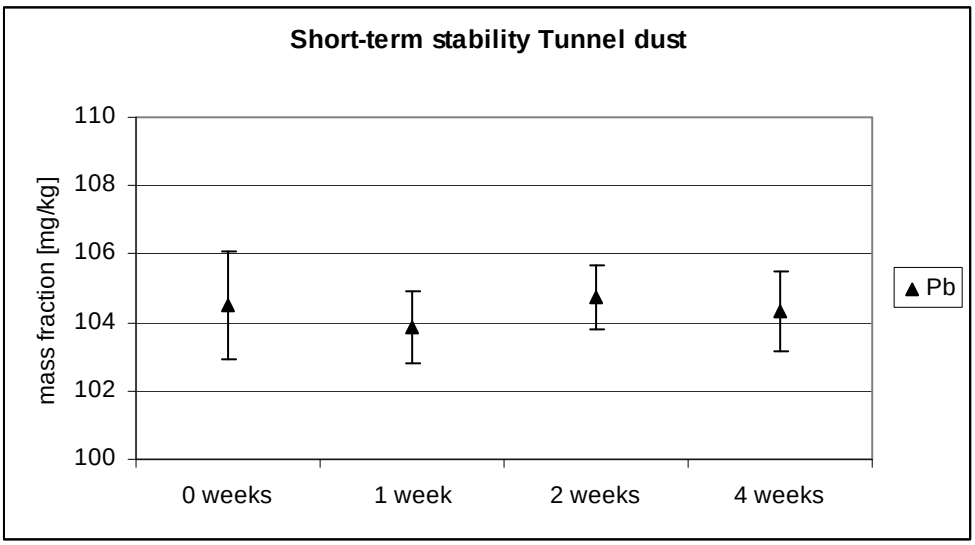
Sample number	Replicate 1		Replicate 2	
	Sequence number	Result	Sequence number	Result
5822[a]	1	2.85	2	2.80
5823[a]	3	2.84	4	2.83
5824	5	2.78	6	2.78
5825	7	2.79	8	2.79
5826	9	2.78	10	2.79
5827	11	2.77	12	2.78
5828	13	2.79	14	2.76
5829	15	2.80	16	2.76
5830	17	2.78	18	2.74
5831	19	2.81	20	2.79

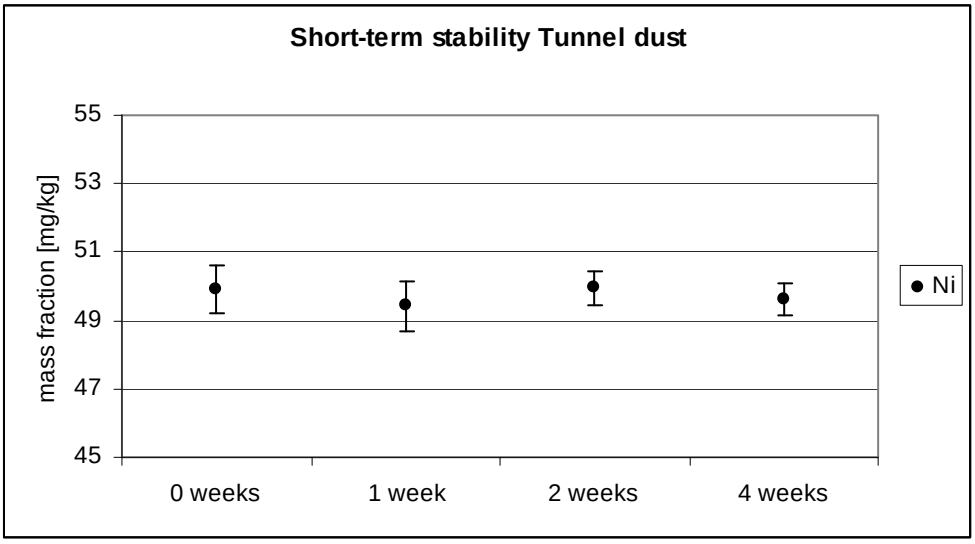
[a]: Outlier on a 95 % confidence level

ANNEX C: Results of the short-term stability studies

Error bars represent standard deviations







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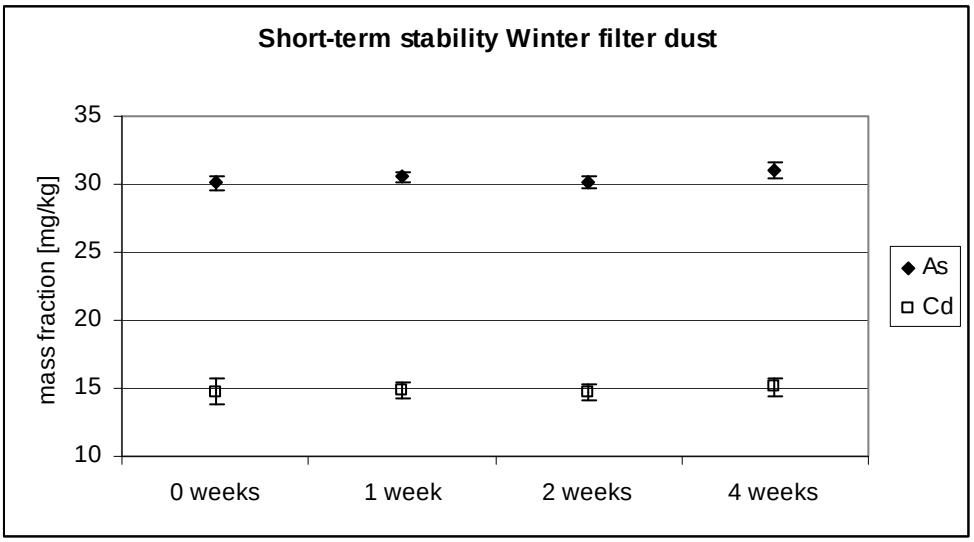
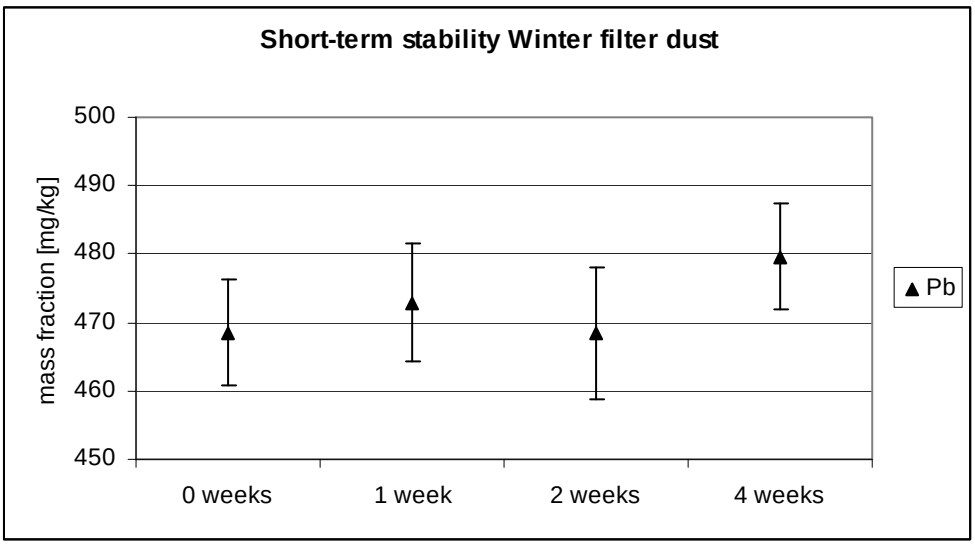
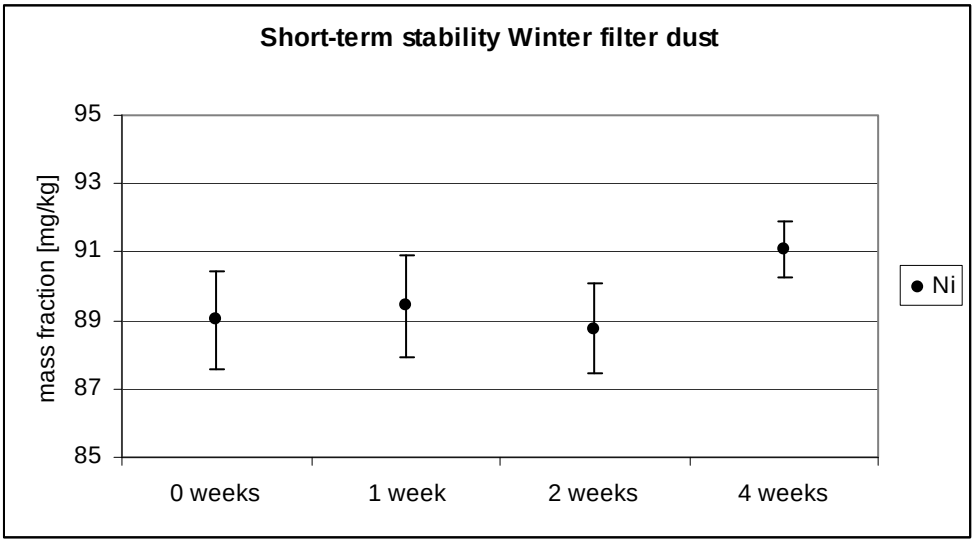
Error bars represent standard deviations







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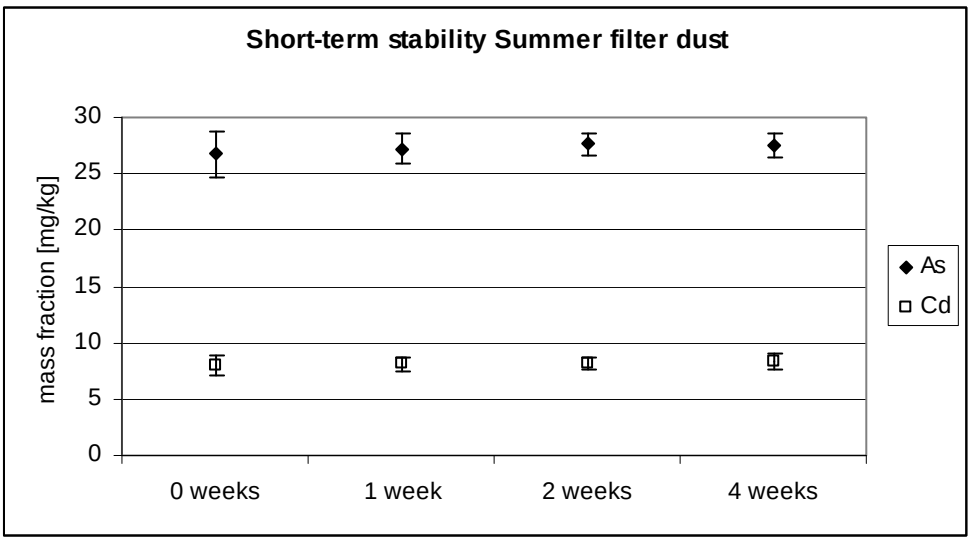

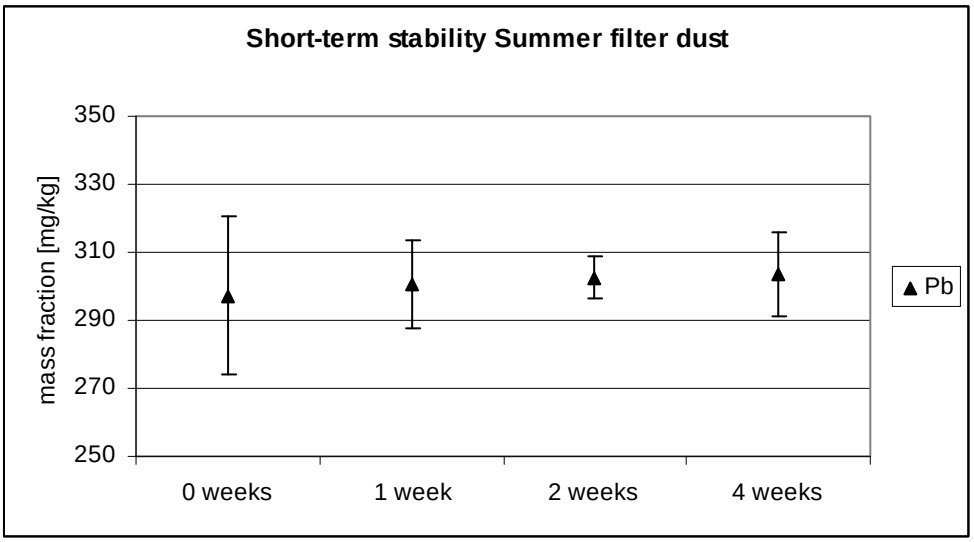

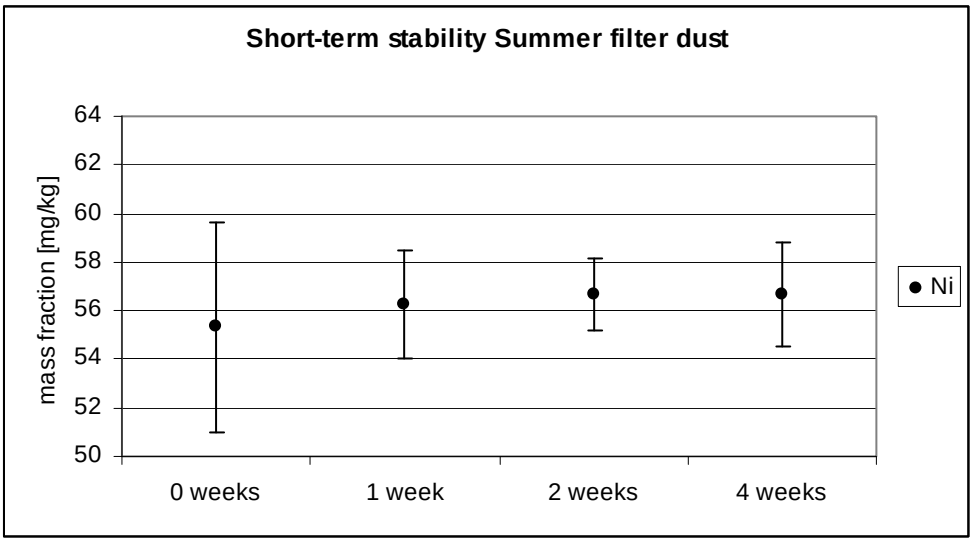

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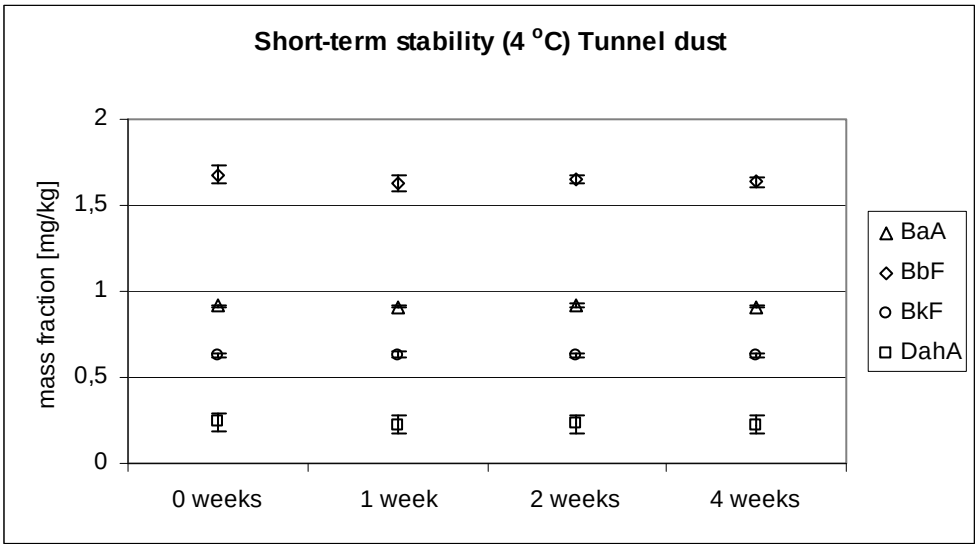

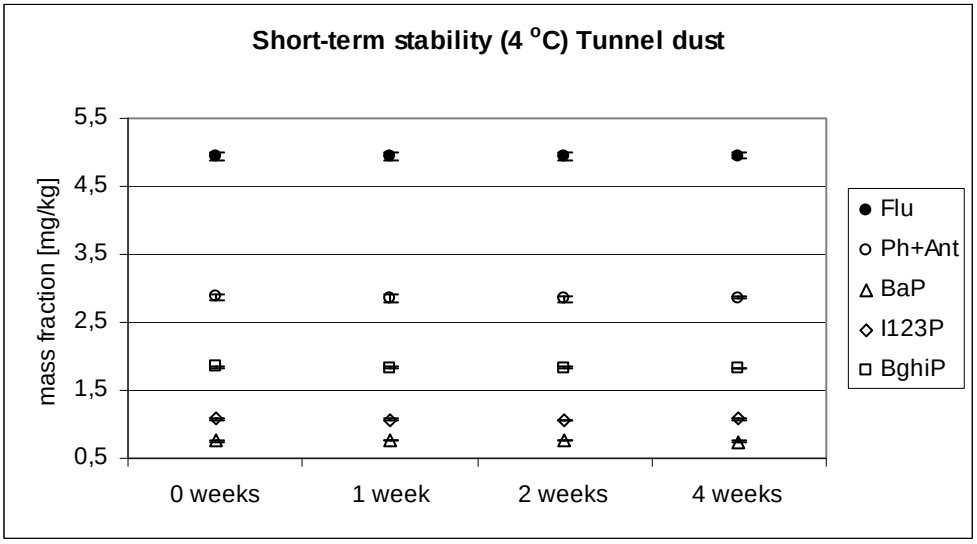

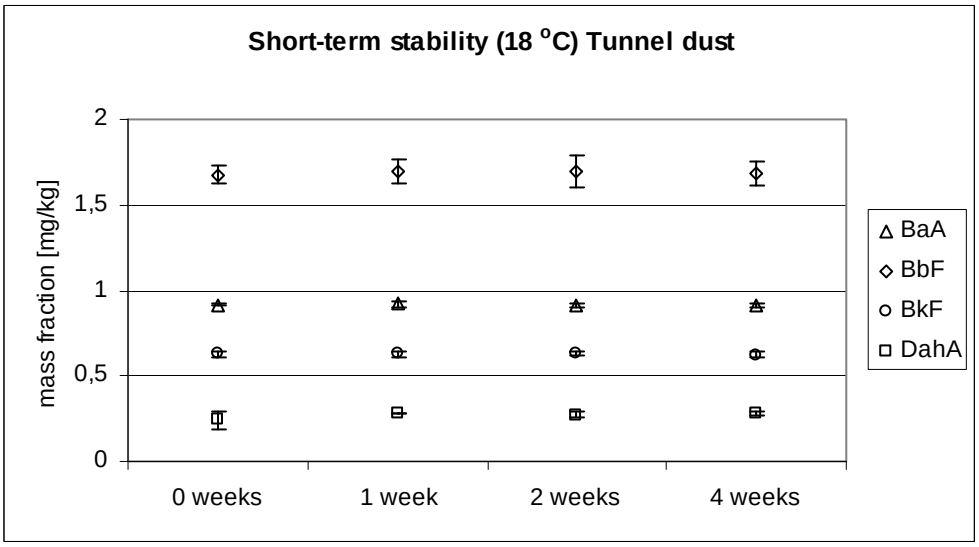

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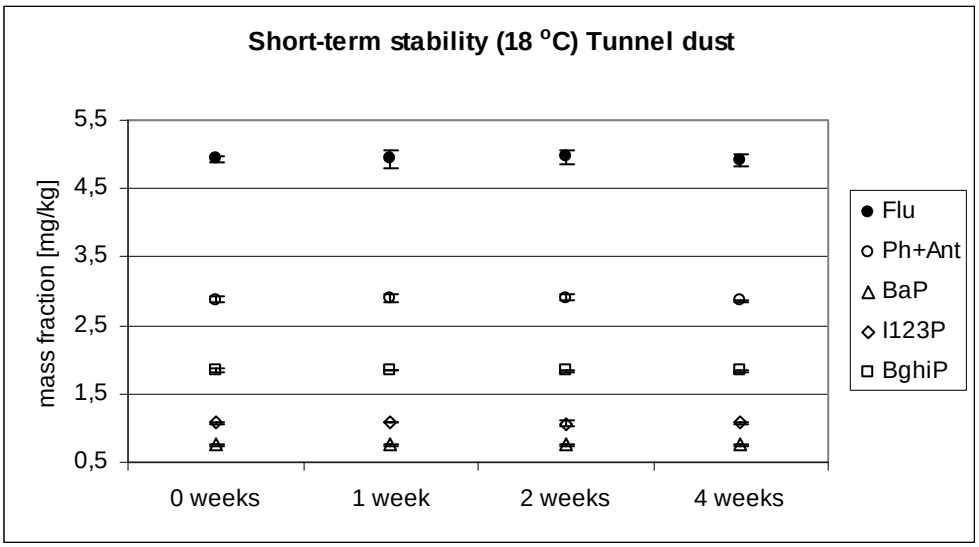

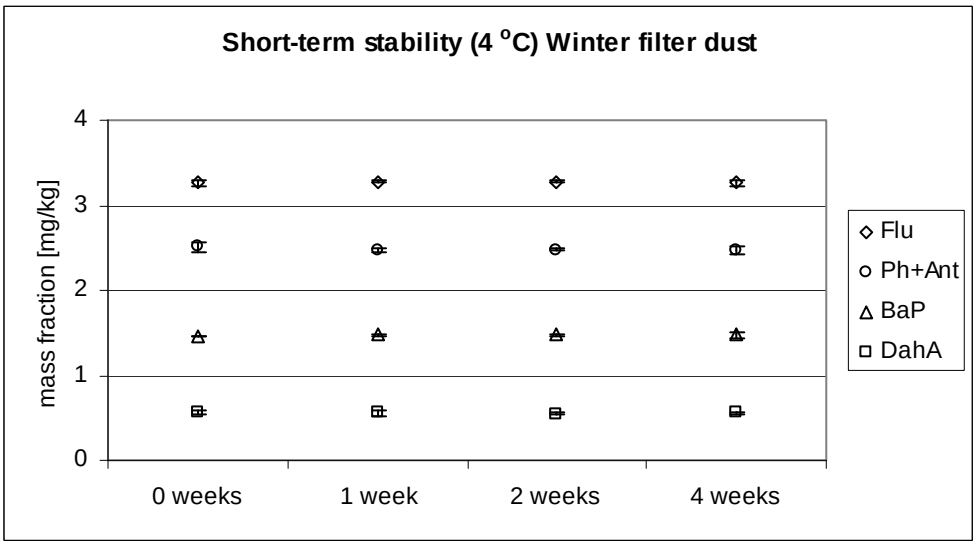

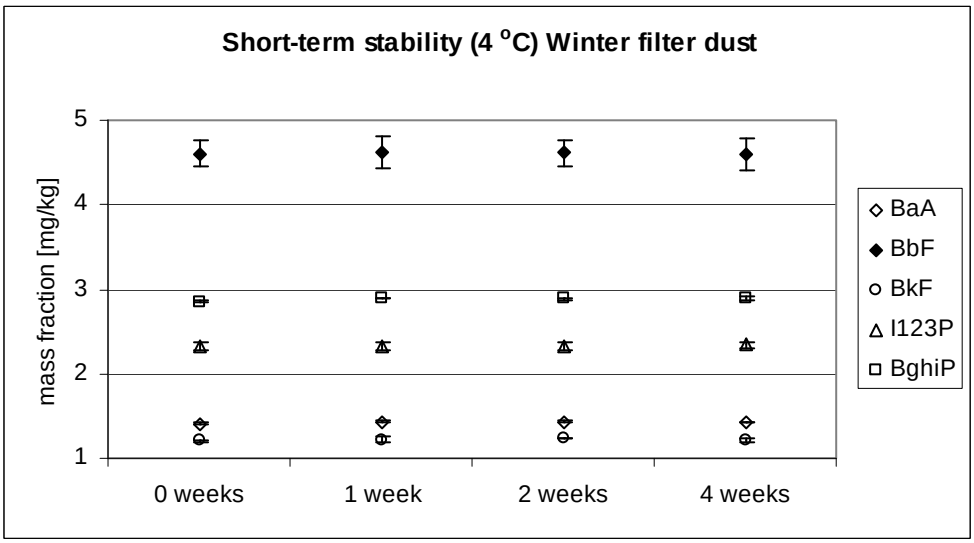

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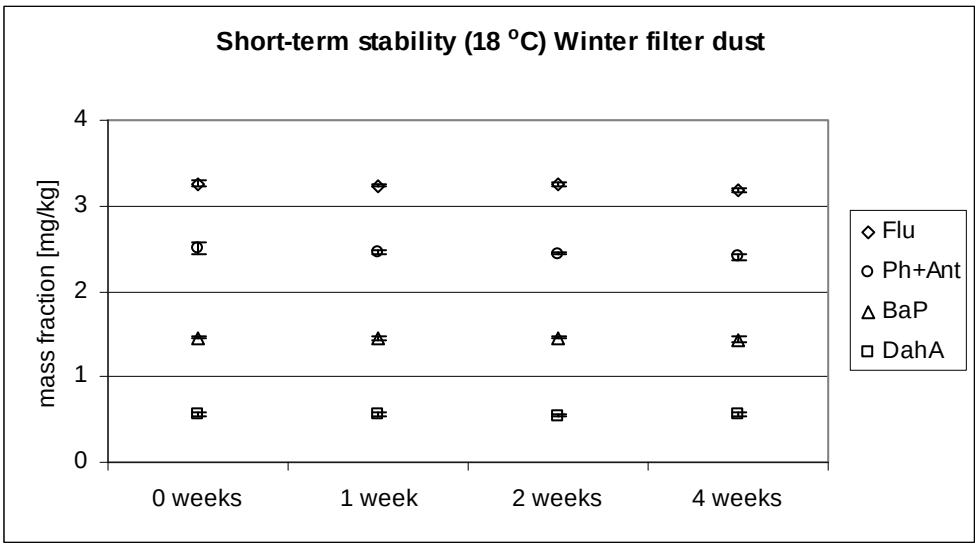

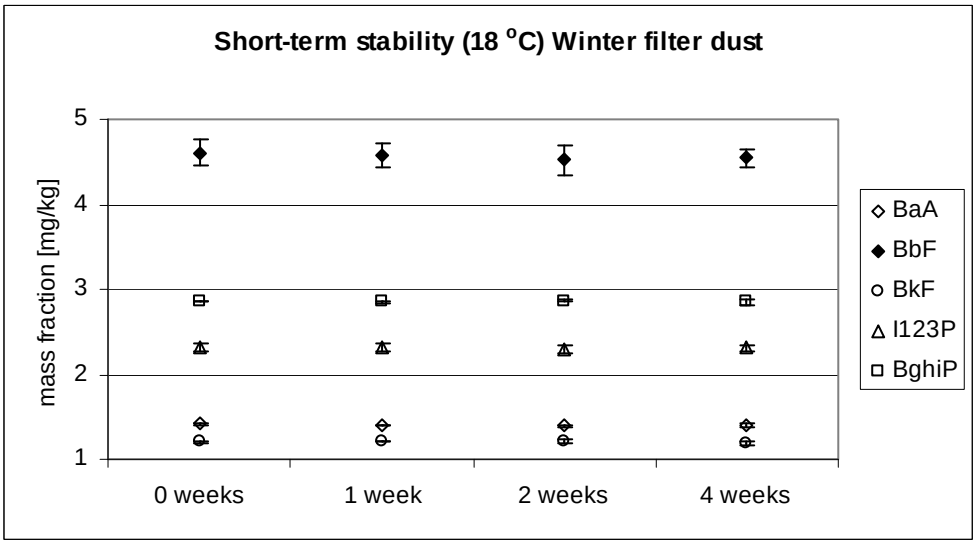

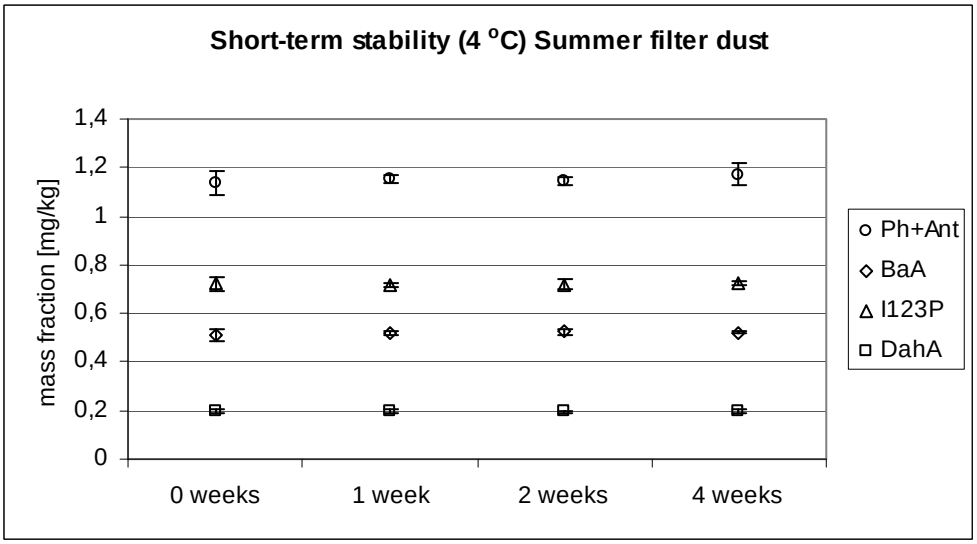

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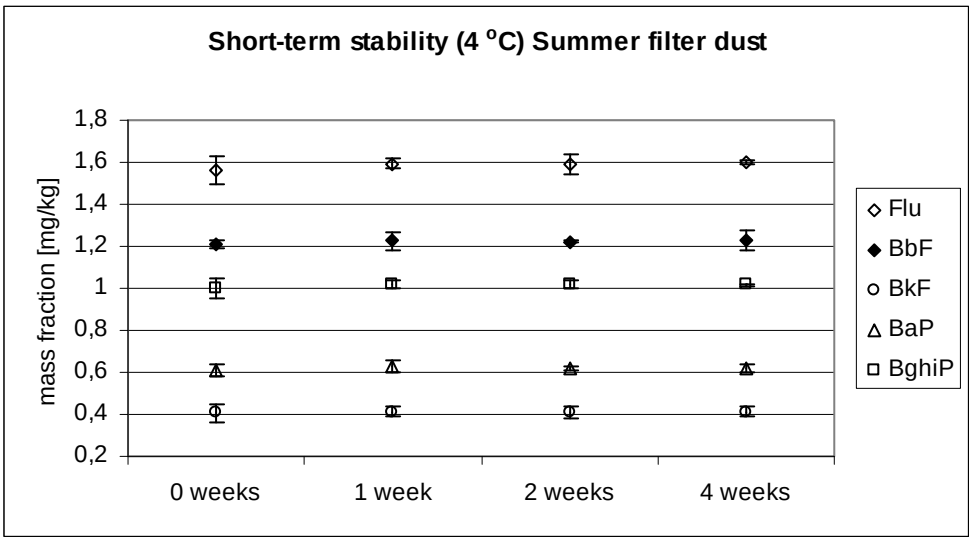
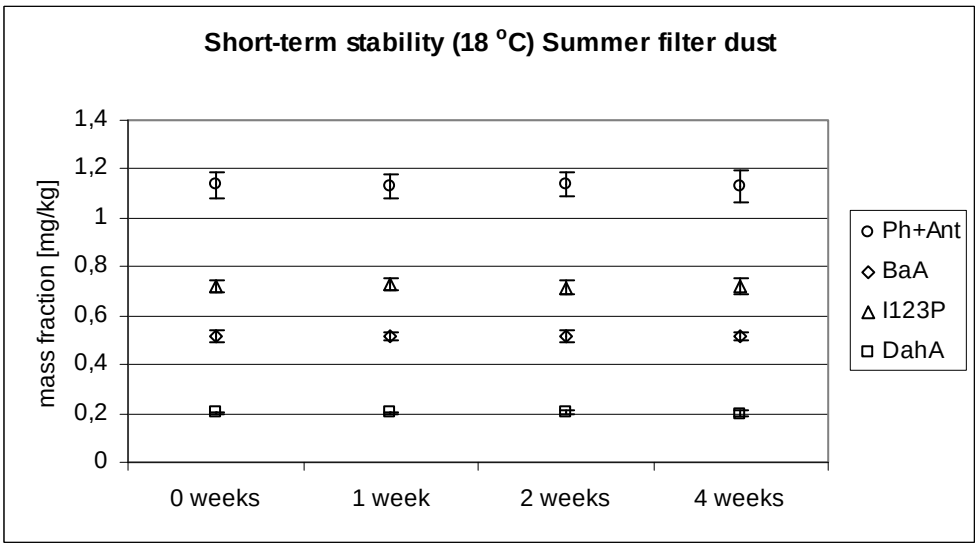
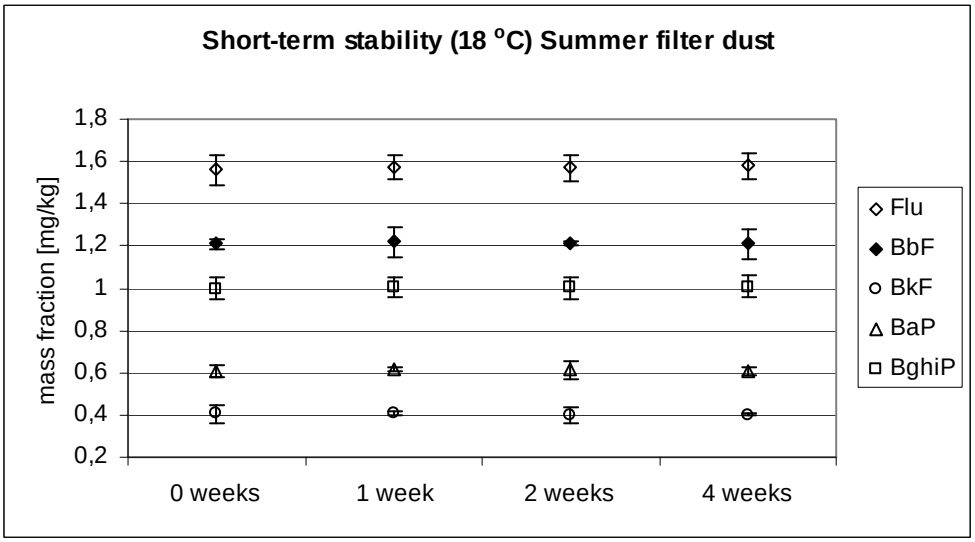






ANNEX D: Commutability study: questionnaire

Questions:

1. Give us your opinion about the presence of the compounds of your interest. Could you detect all of them?
2. Assess the concentration levels of the compounds of your interest in the materials. Would they fit your needs for a CRM?
3. Did you evaluate the chemical composition of the matrices, e.g. carbon content or particle size of the material? Do you have any comments on the matrix?
4. Did you notice any differences between the PM10 you usually analyse and our materials regarding handling, digestion, analysis etc.? Please elaborate.
5. Which of those materials would you consider the most appropriate as a PM10 CRM and why?

The content of elements

Answers for the questions	
Lab 1	
question 1	We are interested in As, Cd, Ni and Pb. In all five samples we were able to detect them, even not always in the concentrations of your screening.
question 2	Yes, they did.
question 3	No, we did not evaluate the chemical composition of the matrices.
question 4	For PM10 we use NIST 1648 as reference material. In handling digestion and analysis we did not notice differences
question 5	Dust No 1 would be the most appropriate reference material for our investigations, cause the concentration of elements of interest are almost in the same range than our samples.
Lab 3	
question 1	All elements are detectable but very low content of Cd make it more difficult to analyse in DUST 1 and DUST 3. It is especially the case when large differences of contents are encountered between elements of interest (i.e. Zn versus Cd or Co). In such cases, different dilution factor has to be applied if one does not allow introduction of samples presenting very high concentrations in the system in order to avoid cross contamination and memory effect.
question 2	The concentration level depends on the amount of material weighted. Because aerosols are usually scarse and difficult to collect, very small amount of natural material (below 1 mg) is generally mineralized and analyzed. As we try to mimic as close as possible the samples when processing the SRM, highly homogeneous material with significant concentrations should be preferred in order to weigh as little as possible. However, grinding gross dust may reduce the interest in producing a PM10 natural particle sample. Another important factor is the ratio between the metals of interest as it should be as close as possible of the one uncountered in airborne particles. However, this may differ from one site to another (industrial versus rural for example). Finally, the amount of organic matter may have some impact on the digestion process and on the analytical interferences depending on the analytical technique employed.

The content of elements (continuation)

Lab 3	
question 3	No matrix analyses were performed.
question 4	We did observed high amount of organic material in sample DUST 3 and moderately in DUST 5 inducing yellow solution in the final acid digestion mixture, which is not usually the case when manipulating the NIST 1648 but often the case with the NIES 8. In addition, small black particles were still visible in DUST 3 solution after mineralisation that we attributed to black carbon residue.
question 5	DUST 4 and 5 could be good candidates but Zn concentrations are too high in my opinion in DUST 5.
Lab 4	
question 1	Yes, we could easily detect all of them. We would appreciate having a reference material certified for Al and V, too.
question 2	The concentration levels were suitable for our purposes and they fit for our needs for a CRM.
question 3	No, we did not evaluate the chemical composition of the matrices. It would be useful to have more information on the CRM matrix in order to evaluate the possible interferences in analysis.
question 4	Dust No 4 was difficult to weigh because of its electrostatic charge.
question 5	Dust No 1 and Dust No 2 fit well for our purposes as they are urban and traffic originating PM10 particles.
Lab 6	
question 1	We have provided results for Ni, As, Cd and Pb. These elements were easily detected in all 5 dusts. Additionally, we analysed for the following elements successfully: V, Cr, Mn, Fe, Cu and Zn.
question 2	For the given elements the concentration levels were acceptable in each dust.
question 3	No analysis was undertaken on the chemical composition of the matrices.
question 4	Each of the dusts was easy to handle and did not cause any problems during the preparation and digestion of the samples.
question 5	We recommend that dust No. 1 is the most appropriate as a PM10 CRM. The low concentration of the analysed elements means that it is not necessary to perform excessive dilution procedures, and the percentage RSD of the three repeats from each vial was the lowest of the five dusts.

The content of elements (continuation)

Lab 7	
question 1	We.are interested in the determination of Cr, Fe, Zn, Benzo(a)anthracen, Benzo(j)fluoranthen*, Benzo(e)pyren*, Benzo(b)fluoranthen, Benzo(k)fluoranthen, Dibenzo(a,h)anthracen, Indeno(1,2,3-c,d)pyren. We are able to detect all of them except those marked – here a method is being developed.
question 2	-
question 3	No
question 4	We did not notice any differences.
question 5	For determination of metals components with ICP-OES we remark Dust No. 1 and 4 as appropriate.
Lab 8	
question 1	We usually report to 2 significant figures if the level is >10 times the limit of detection. Some Cd levels were a little low (LOD 0.1 µg/g)- but all metals results have been reported to 2 decimal places here. Pb was a little high for ICP-MS at the dilution used, and a little low for Cd
question 2	The levels were not dissimilar to the CRM we use
question 3	We were able to get a complete digestion using our new Anton Parr 16 rota microwave system (2^{nd} and 3^{rd} digests). However the first digest using an older microwave resulted in black soot remaining. Nevertheless the results were much the same
question 4	No
question 5	-

The content of PAHs

Answers for the questions	
Lab 1	
question 1	-
question 2	Yes, they did.
question 3	No, we did not evaluate the chemical composition of the matrices.
question 4	PM10 samples seem to be more contaminated.
question 5	-
Lab 2	
question 1	Yes. Recoveries of naphthalene were unsatisfactory and therefore the results for this compound are not reported.
question 2	The concentration of the compounds is much too high for our purposes. A factor 10 less will be preferable.
question 3	No
question 4	We usually analyze PM collected on quartz fibre filters.
question 5	The one with the lowest concentrations (Dust No. 2)
Lab 4	
question 1	We could reliably analyze almost all of those compounds. We had problems only with benzo(k)- and benzo(b)-fluoranthene (and benzo(j)fluoranthene). We cannot firmly separate those from each other, so we have decided to analyze all those 2-3 peaks as one compound (benzo(k,b,j)-fluoranthene).
question 2	The concentration levels varied, so we tried to make parallel samples with different masses. Concentration variability within a sample seemed to be smallest in dust No 1 and 5.
question 3	Samples were quite dirty, as CRMs usually are. Our column got dirty quite fast with the samples. Dust No 4 was most difficult to handle. Compared to other urban dust CRM-material, there was not significant difference in matrix.
question 4	Normally we analyze air samples and mainly from background areas, so the samples were pretty dirty and concentrations were usually high compared to the normal sample material.
question 5	Dust No 1 seems to be most suitable for PAHs because we were able to detect all the compounds of major interest. Dust No 5 were also almost as good, (anthracene was missing). The compounds with lowest boiling points were difficult to analyze overall.
Lab 5	
question 1	Yes
question 2	No opinion
question 3	No
question 4	-
question 5	-

The content of PAHs (continuation)

Lab 7	
question 1	We are interested in the determination of Cr, Fe, Zn, Benzo(a)anthracen, Benzo(j)fluoranthen*, Benzo(e)pyren*, Benzo(b)fluoranthen, Benzo(k)fluoranthen, Dibenzo(a,h)anthracen, Indeno(1,2,3-c,d)pyren. We are able to detect all of them except those marked – here a method is being developed.
question 2	-
question 3	No
question 4	We did not notice any differences.
question 5	For BaP measured by HPLC we remark Dust No. 1, 2 and 3 as appropriate. Reason for this is that the concentrations of the components are in the range of real samples.
Lab 8	
question 1	No but generally those compounds of research rather than routine analytical intrest.
question 2	Yes
question 3	No
question 4	No
question 5	Dust No 1 or 2 are relevant to the types of samples we would normally analyse.

The determination of elements

Lab #	Method short description	Other comments
1	Sample preparation: About 100 mg of the dust were digested with 8 ml HNO3 65% subboiled and 2 ml H2O2 30% pa in a µ-wave oven (Multiwave, Anton Paar). Further preparation steps: dilution to 50 ml in calibrated quartz flusks with MilliQ; then filtration through 150 mm folded filters in 50 ml PE flasks. Then samples were measured with ICP-MS (PE Elan DRC II) against working curve, using matrix matched aqueous standards (Baker Instra Analyzed ICP standards).	We tried to use different acid ratios as well as different temperature programmes. Higher temperature and pressure leads to better recoveries of the reference materials. For a complete digestion a temperature of at least 220 °C for a period of at least 90 minutes show complete digestion for most elements with HNO3/H2O2 (except: Cr, Ti, Sb…) With HNO3/HF acid mixtures complete digestion of most elements can be observed with a digestion time of 40 minutes at 220 °C (except Cr). In our routine working procedures we use a digestion with HNO3/H2O2. We do not reach a full digestion of all elements compared to digestion procedures with HNO3/HF, but for the elements of our interest (As,Ni,Cd,Pb) it is sufficient. Further the lab ware and instrument spare parts are made of quartz and this is not suitable for the use of HF in higher concentrations.
3	About 10 mg of each dust sample (between 9.6 to 12.6 mg) have been weighted in a clean lab (class 100) with a precision balance (0.01 mg). No drying step was undertaken before weighting. Samples were then digested with a microwave ETHOS temperature controlled oven using the EN14902 protocol (mixture of 8ml suprapure HNO3 and 2 ml suprapure H2O2. After digestion, solutions were completed with Milli-Q water to 50 ml and sub-samples were transferred into vials for dilution (by a factor 5), matrix acid correction and addition of internal standard (In at 1 ppb). ICP-MS (PE 6100 DRC) analyses were then performed on triplicates during one analytical session. Commercially available 1000 ppm mono-elemental standards traceable to NIST were used for calibration curves while digestion blanks, analytical blanks and Quality Control solutions traceable to the NIST were analyzed repeatedly. About 2 samples of 10 mg of NIST 1648 were mineralized and analysed simultaneously to the dust samples. No correction was applied based on the SRM results but the bias was taken into account in the calculation of uncertainty. In the table, Mass fraction is the mean of 3 replicates and the RSD is the standard deviation divided by the mean value. The expanded uncertainty (k = 2) is based on the GUM by combining the repeatability (on 3 replicates) and the bias from SRM 1648 dust samples. We applied a tolerance of plus or minus 10% for the SRM and rectangular distribution is assumed, therefore the semirange is divided by the square root of 3.	Zn was analyzed in all the samples but we expect a significant inaccuracy in our data for sample 3 and 5 as concentrations found were much higher than our calibration range. A first try with only 3 to 5 mg of dust samples was performed but shown a lower reproducibility which may either indicates some heterogeneity in the samples or some difficulties in weighting small amount of dust (hydroscopic effect?). Our experience in digestion procedure, applying the EN 14902 or other techniques seems to confirm that both mixture are equivalent in terms of recovery for Ni, Cd, As and Pb. However, high temperatures suggested by the EN14902 may be difficult to be sustained for some Teflon reactors. For other elements such as Cr, recoveries may be low if HCl is not used in the acid mixture which is why we did not include any data for this element.

The determination of elements (continuation)

Lab #	Method short description	Other comments
4	The samples were digested in three replicates in microwave oven according to the standard EN 14902 (8 ml HNO_3 + 2 ml H_2O_2) with the exception that the temperature program of our microwave oven ends to 180 ºC. That is the max temperature we can reach at the moment. Each digested sample was analysed in three replicates by ICP-MS using the standard method ASTM D 5673-96. Before analysis the digested samples were diluted to concentrations matching with the measurement range of the analysis method. Indium was used as an internal standard. The sample weight was in the range 70 -110 mg and most typically 80 -90 mg. The results (mass fraction mg/kg) are the arithmetic averages of nine determinations and RSD % is the relative standard deviation of the nine results, respectively. In every microwave digestion batch certified reference material (NIES-8) was digested together with the Dust-samples. The NIES-8 samples were analysed in the same analysis batches as the Dust-samples. We got really good recovery rates for the NIES-8 material for all elements analysed on the contrary to the Dust-samples for which we got quite low recovery rates for Cd and As when comparing with the concentrations given in Table 2 (Results of screening measurements provided by IRMM).	We have tested other digestion methods, too. We used only nitric acid in MW-digestion and the recovery rates were very good for certified urban particulate matter. Thank you for arranging this very important study!
6	Samples were stored in the original containers in a refrigerator until analysis. Each sample vial was shaken thoroughly to mix the contents, and then dried overnight in an oven at 100 ^{o}C. Approximately 40mg of each sample was weighed accurately into a digestion vessel and digested in 8ml nitric acid (70%) and 2ml hydrogen peroxide (30%) in a microwave at elevated temperature (up to 200^{o}C) and pressure. The digested samples were diluted gravimetrically with ultrapure deionised water to approximately 50g. A further gravimetric dilution was then performed. Three sub-samples were taken from each supplied vial. Each sample was analysed by ICP-MS using a range of calibration standards traceable to NIST elemental standards. The method included the use of internal standards and a drift correction. Calibration curves were generated using a generalised least squares method	We routinely use a nitric acid and hydrochloric acid digestion procedure for certain elements in particulate matter, but this is not appropriate for the given elements Ni, As, Cd and Pb. HF has not been used in any digestions of ambient particulate matter. Uncertainties are quoted with a 95% confidence level. The uncertainties do not include a component for the extraction efficiency or extraction variability of the digestion process, as we do not have previous experience with these dusts. No uncertainty is included for the matrix interference effects on the arsenic results, for the same reason (previous experience with some CRMs has shown that a high carbon content or presence of certain polyatomic species in the sample may interfere with the arsenic signal and artificially increase the calculated concentration).

The determination of elements (continuation)

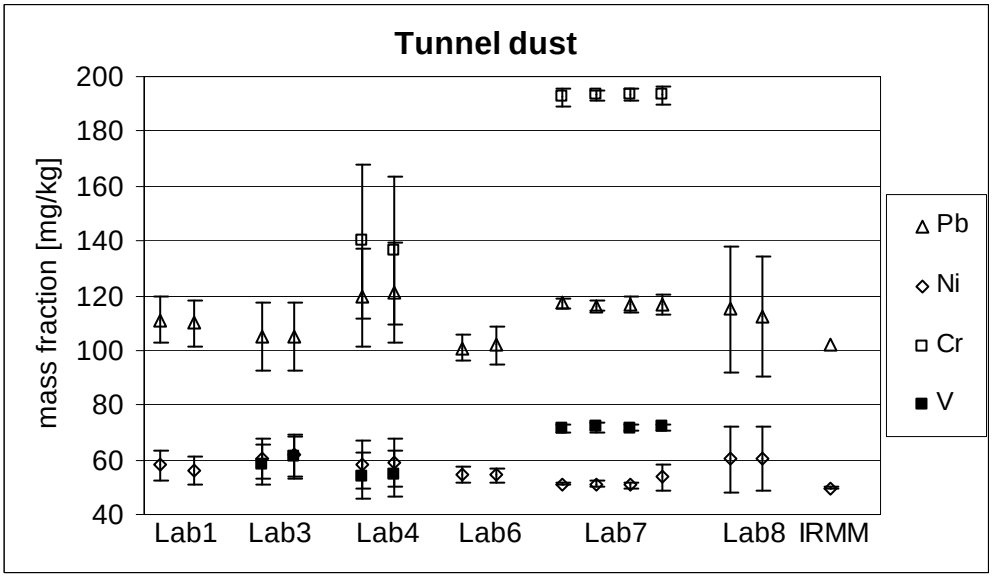
Lab #	Method short description	Other comments
7	Pressure-digestion system (not microwave)-oven temperature is about 170 °C. Each sample weight is about 40 mg, solutions used: 5 ml HNO_3 ≈ 65 %, 2 ml H_2O_2 ≈ 30 %, 3 ml HF ≈ 40 %. This sample solution is dried then it is diluted to 50 ml with 1 % HNO_3. All elements of the samples have been measured by ICP-OES with cross-flow nebulizer and for "As" we used the "Apex nebulizer" (this system dries the sample before nebulizing).	We realized that open digestion of Urban Particulate Matter NIST 1648 without HF leads to lower results of about 10 % for Ni. For Cr minor results of 30 % are detected if not measured by a pressure system.
8	Microwave digestion with HNO_3/HF acids ICP-MS analysis: As 75, Cd 111, Pb 208, Ni 60 The sample weights ranged between 100 and 200 mg	We consider HNO_3/H_2O_2 a leach rather than a full digestion, although for many metals/ sample types it seems to make little difference. We use TH-2 (harbour sediment) from Environment Canada at the moment, and obtained recoveries of: As 112% (~9 µg/g) Cd 115% (~5 µg/g) Pb 99% (~190 µg/g) Ni 106% (~43 µg/g) on this run.
IRMM	See section 4.4.	

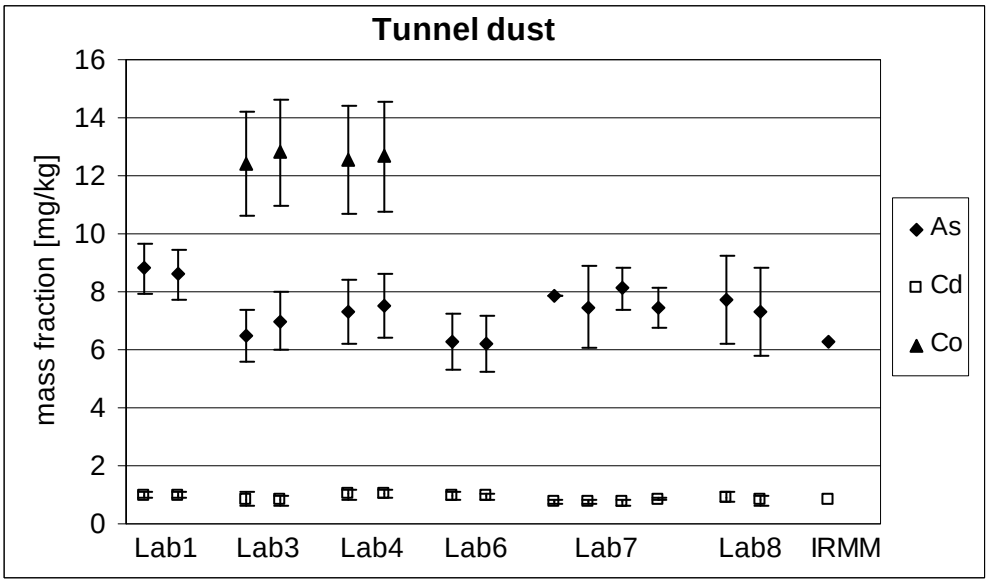
ANNEX E: Commutability study: description of the analytical methods

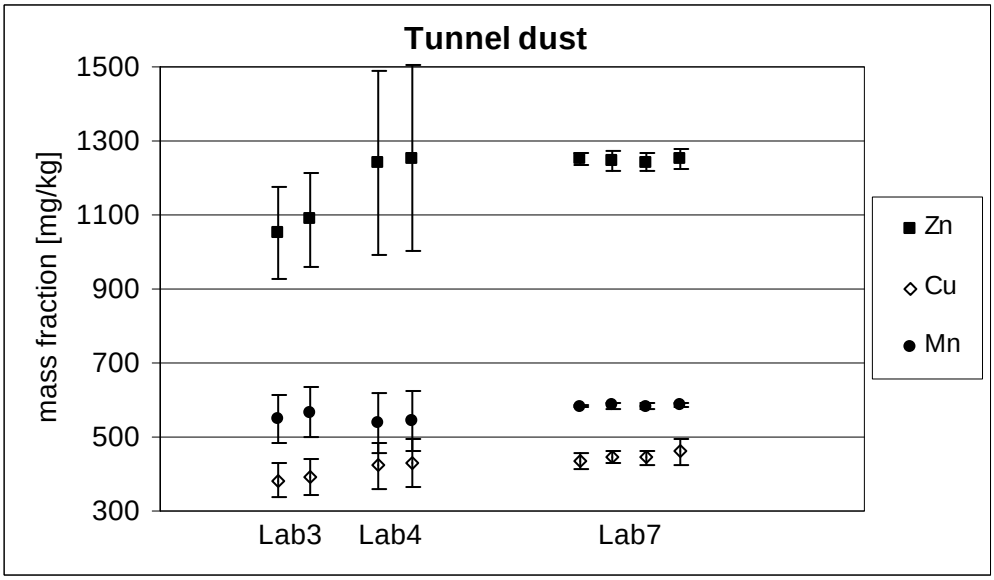
The determination of PAHs

Lab #	Method short description	Other comments
1	Sample preparation: After addition of a surrogate standard (d-BaA, d-BkF, d-BaP, d-DBA, d-Ind over night) about 100 mg of the dust were extracted with n-hexane – diethylether (9:1) in a Soxhlet apparatus. The clean up for the extracts were performed with silica gel. An aliquot was injected into a HPLC system and the analytes were determined by Fluorescence detection.	-
2	Extraction with Pressurized Liquid Extraction followed by silica cleanup. Analysis with GC-MS. Calculation of analyte recoveries with deuterium-labelled standard. The sample weight was in about 100 mg. The results for chrysene are the sum of chrysene and triphenylene, as the two compounds are not resolved in the chromatogram.	-
4	Analysis is based on a standard prEN 15549, also the standard ISO 12884:2000 has been used when developing this method. About 10 to 35 mg of a sample was weighted on the filter. Soxhlet-extraction: 16 hrs in 60 ml of CH2Cl2 w. ISTD. Sample concentration into ~3 ml, drying w. Na2SO4, then concentration into ~1ml under N2. Filtering sample into GC-vial. GC-SIM-MS-analysis. Blanks are subtracted from the results.	We have tried ultrasonic-extraction for the PAHs but yields were better with soxhlet extraction.
5	Accelerated solvent extraction with dichloromethane	
7	15 minute-ultrasonic extraction with toluene. Afterwards the samples are stored for 24 hours in the dark. Then the toluene is evaporated, the PAHs dissolved by acetonitrile and measured by HPLC. We have proceeded two extractions. The first of it has a sample weight of 50 mg, for the second extraction the weight is 100 mg.	
8	Soxhlet extraction in DCM followed by analysis on GCMS (SIM) using deuterated internal standards. The sample weights were about 100 mg.	Several different methods of extraction were tried in the past before settling on dichloromethane
IRMM	See section 4.5.	

The names tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust correspond to the sample label Dust No 1 to 5, respectively.
Error bars represent uncertainties







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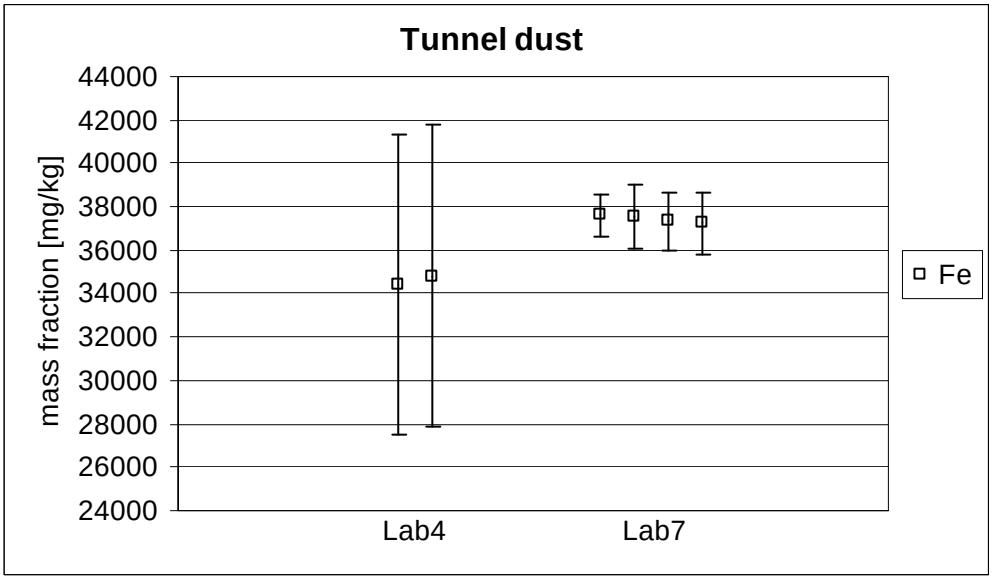

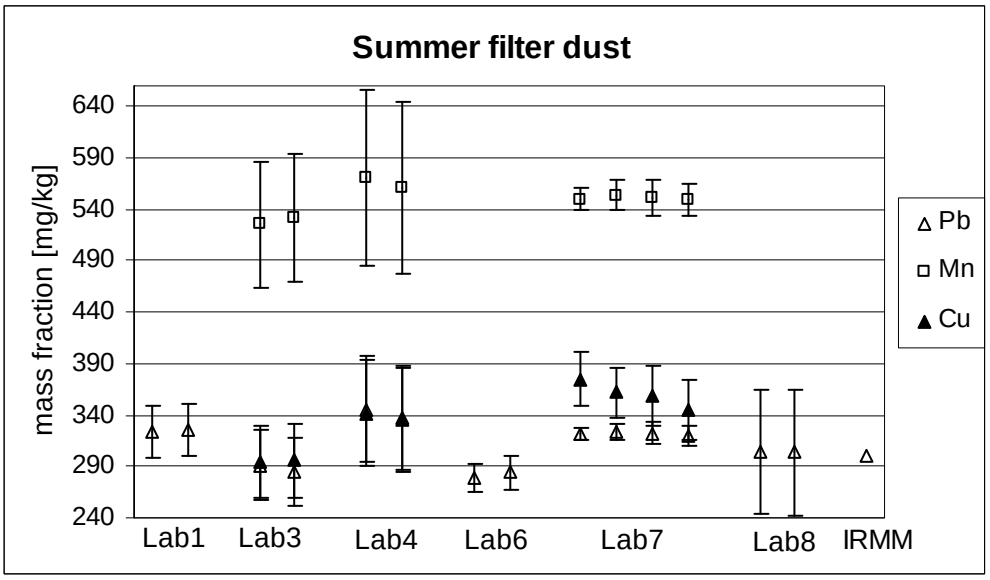

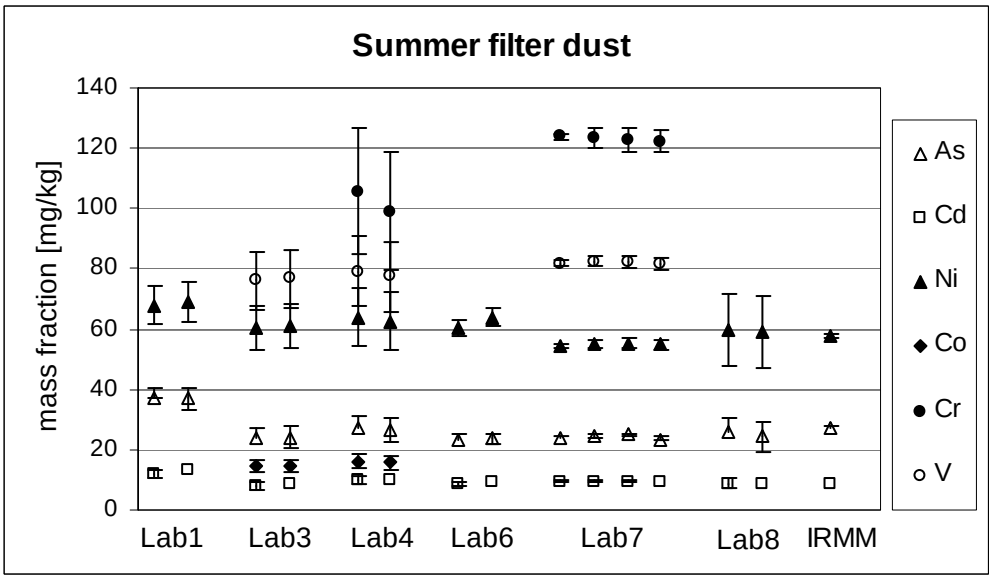

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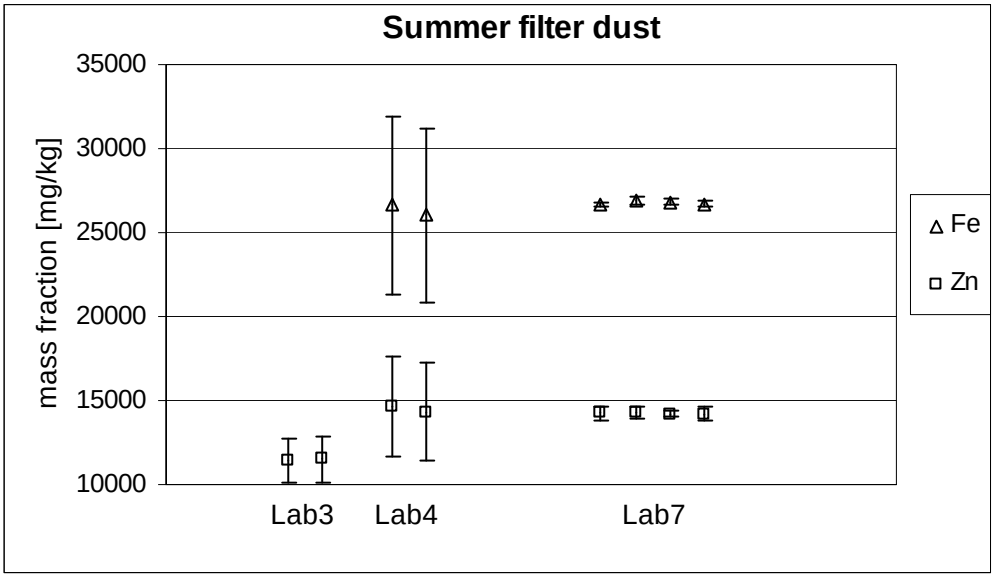

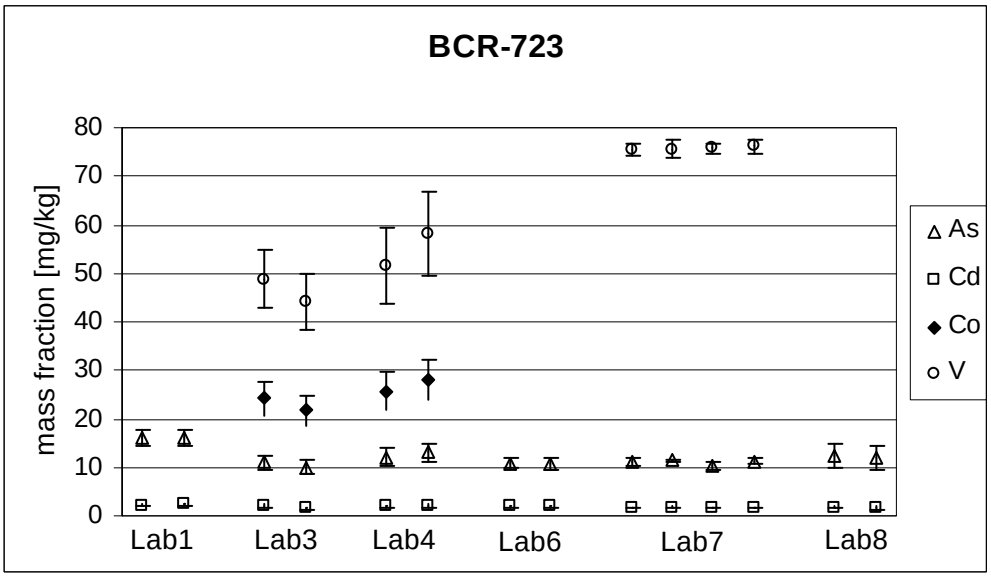

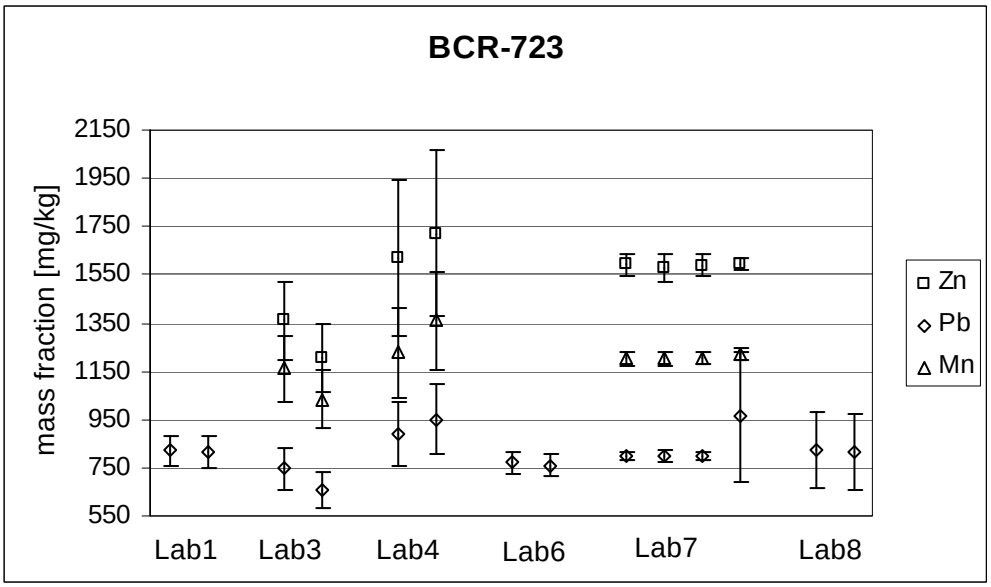

Annex F: Commutability study: results of the determination of elements and PAHs

The names tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust correspond to the sample label Dust No 1 to 5, respectively.
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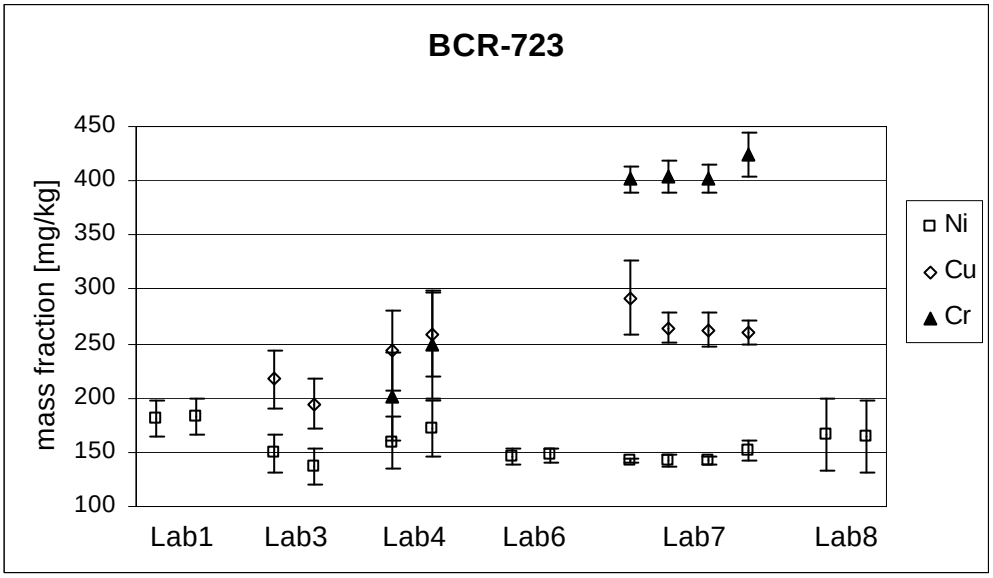

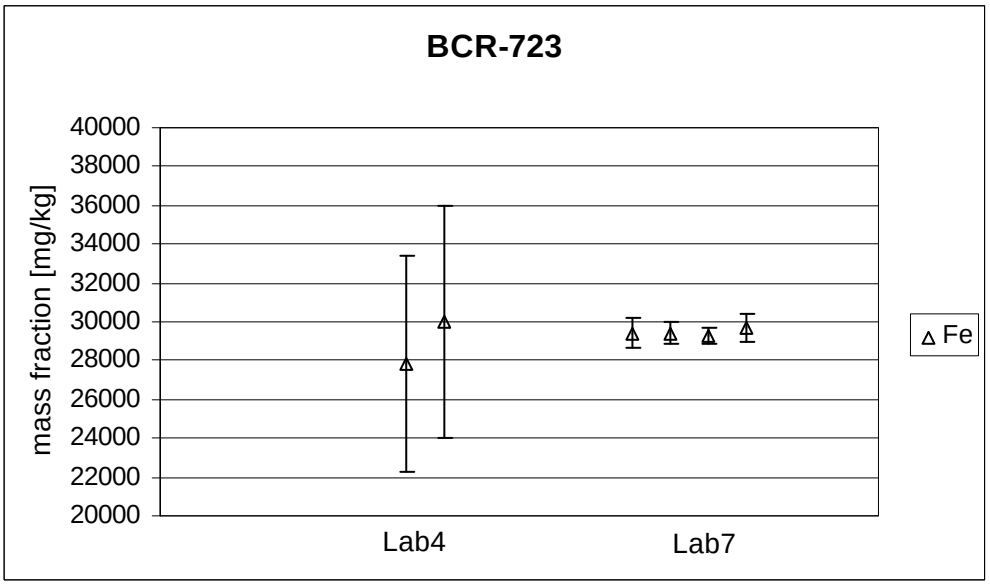

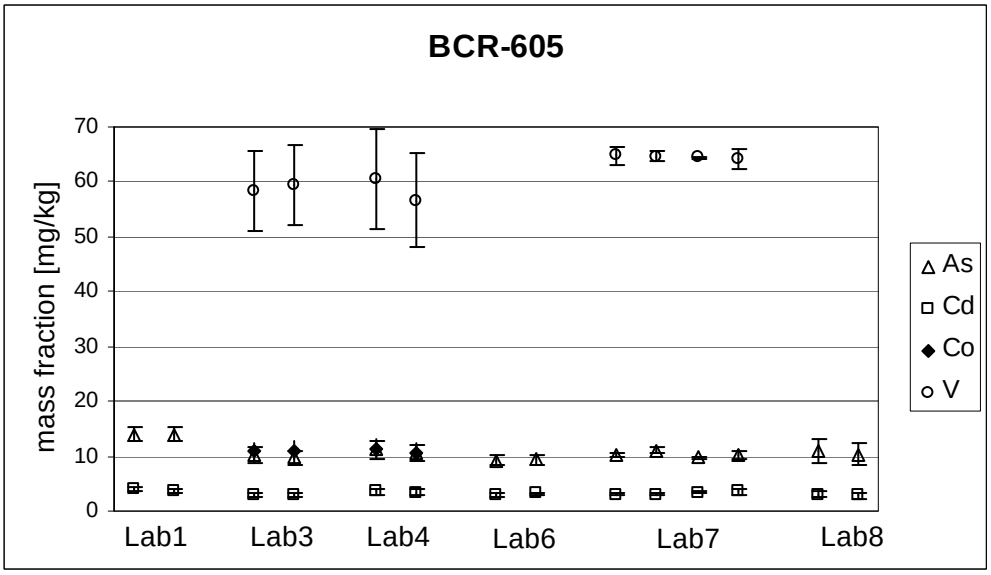

Annex F: Commutability study: results of the determination of elements and PAHs

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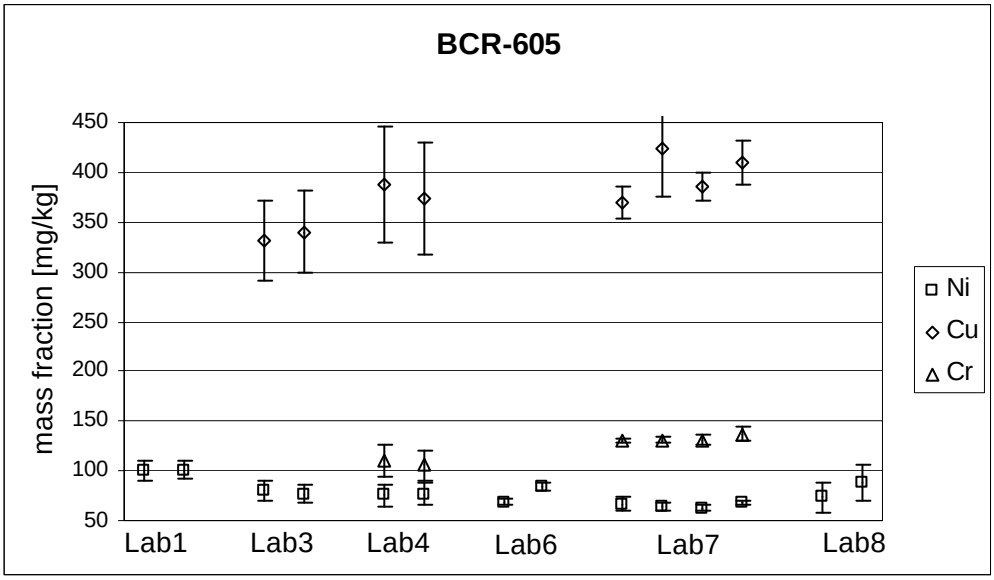

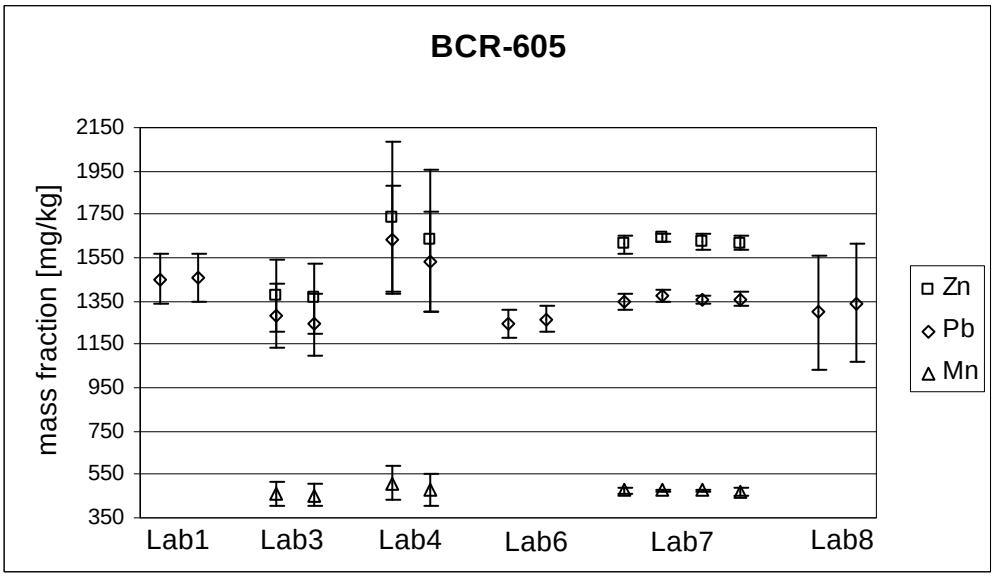

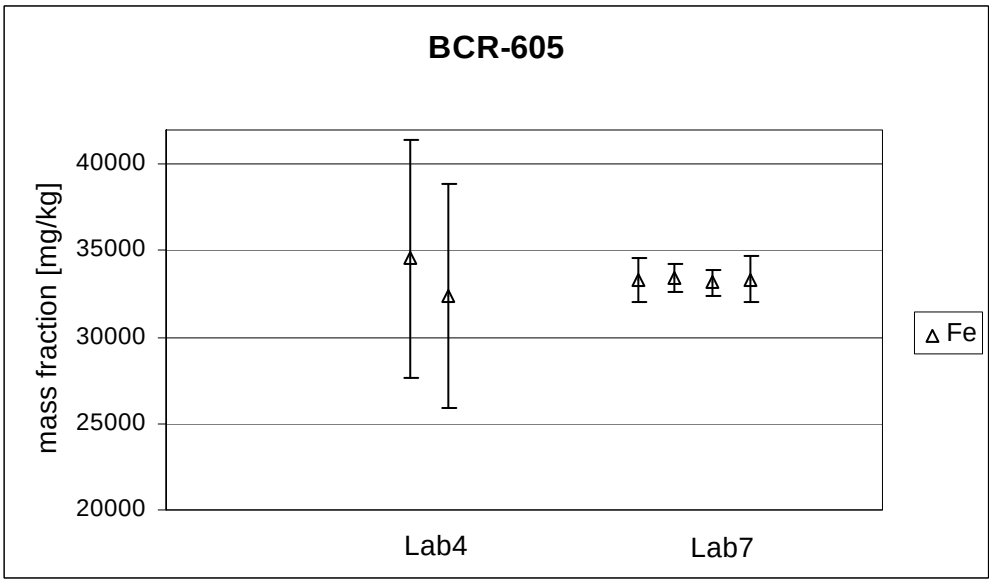

Annex F: Commutability study: results of the determination of elements and PAHs

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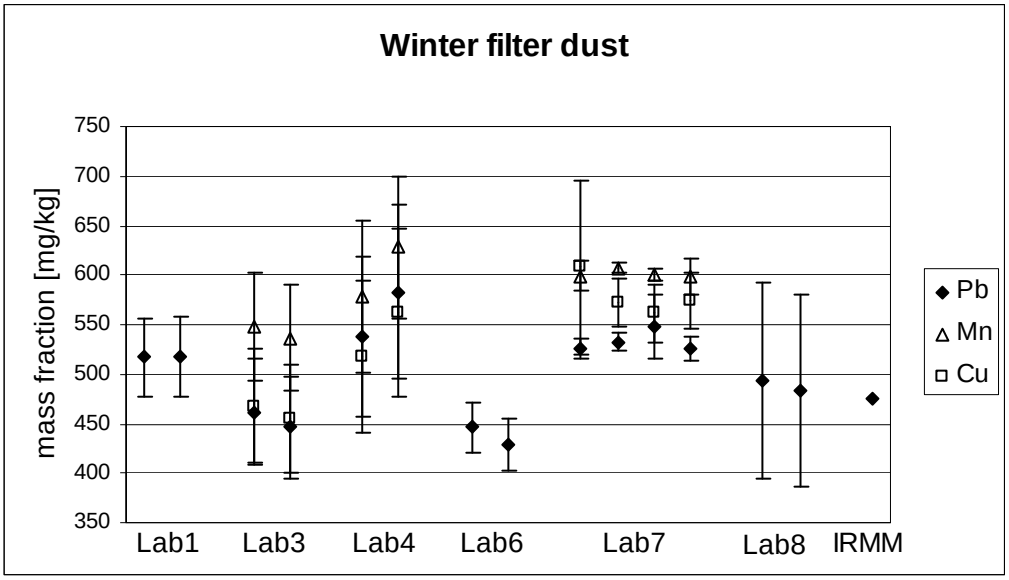

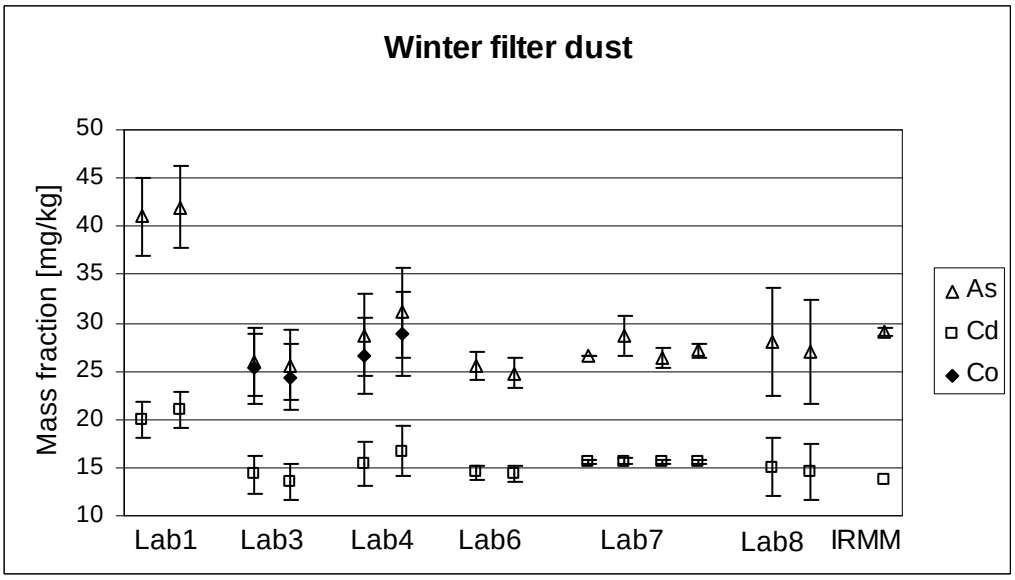

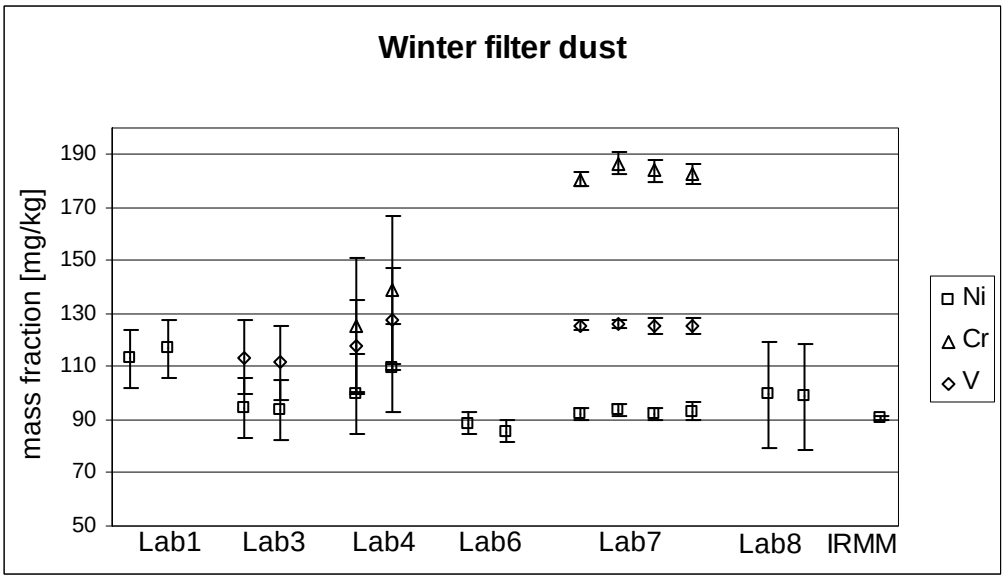

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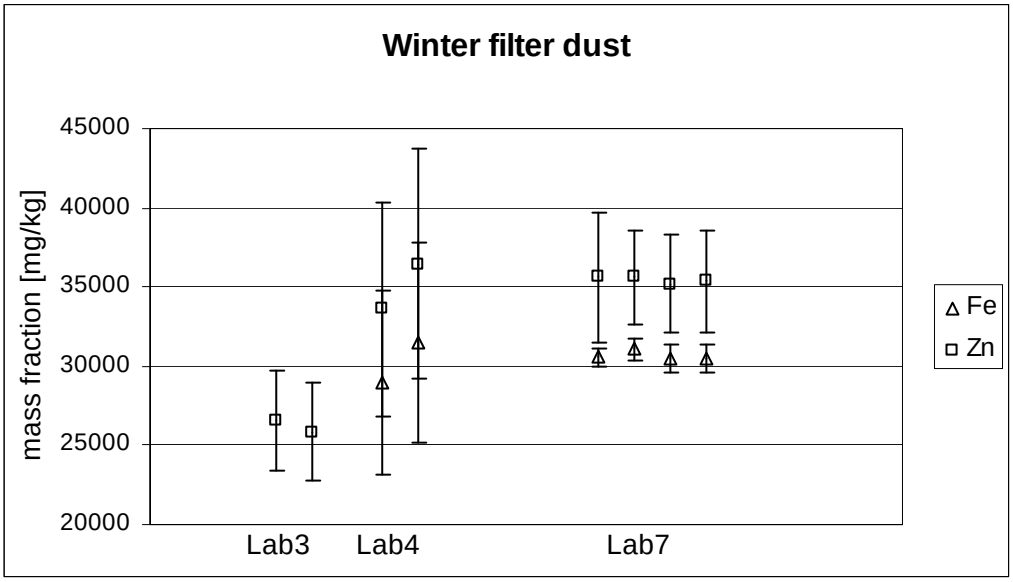

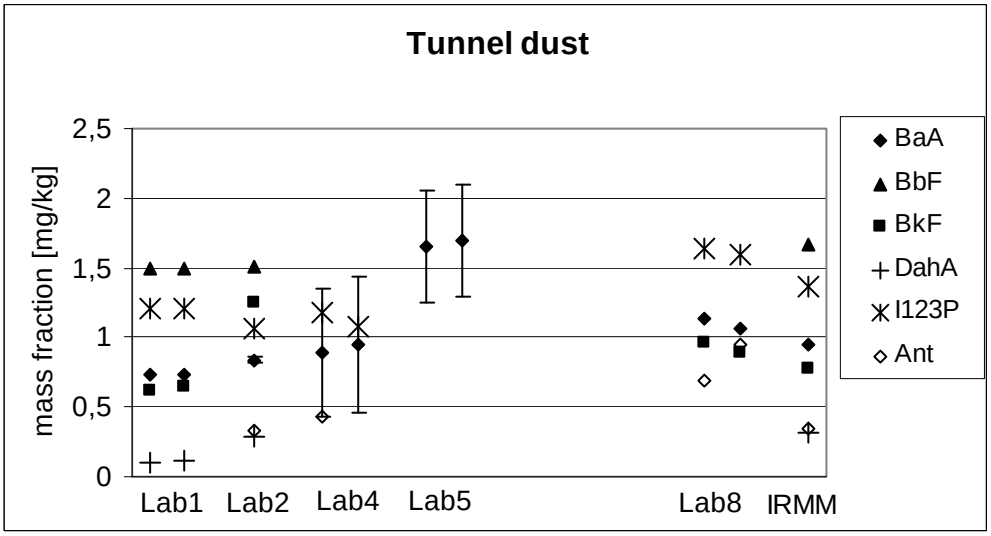

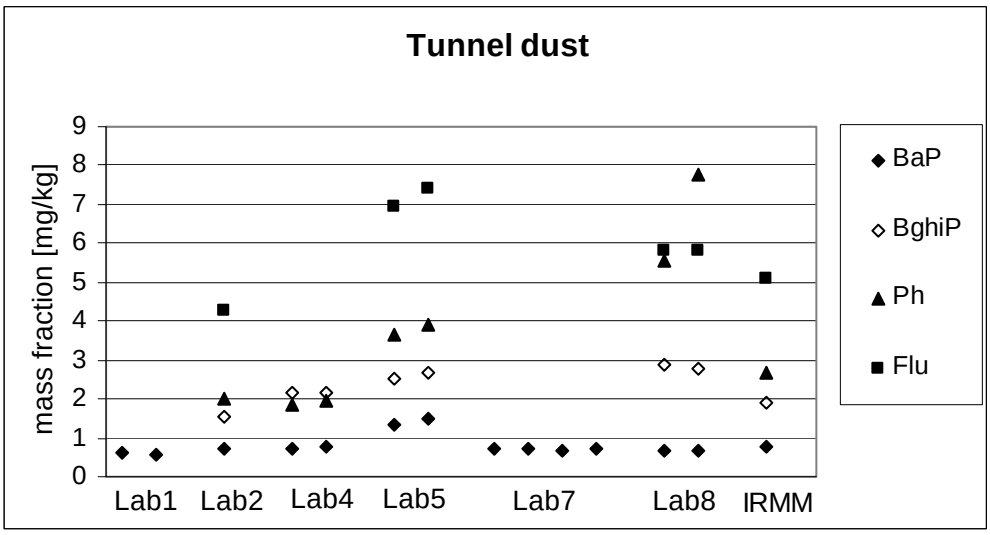

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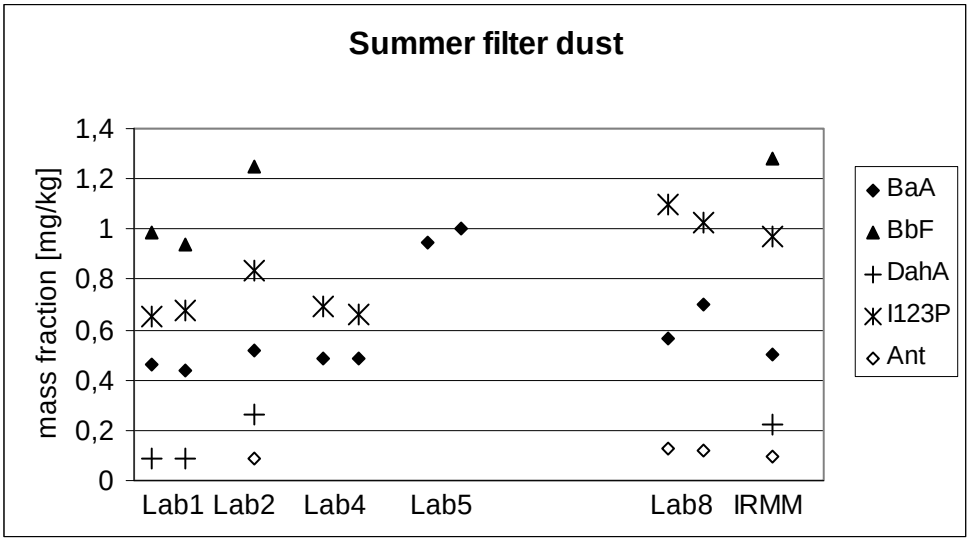

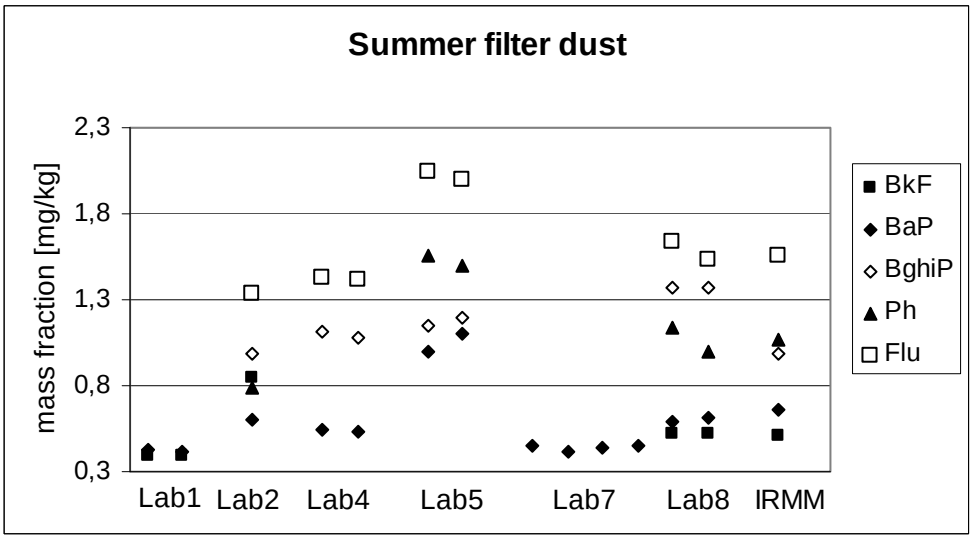

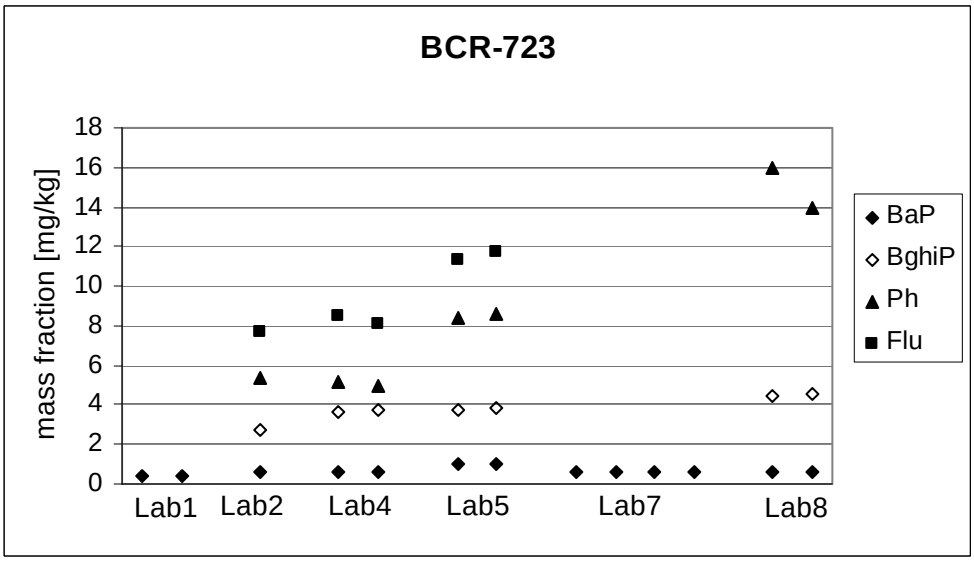

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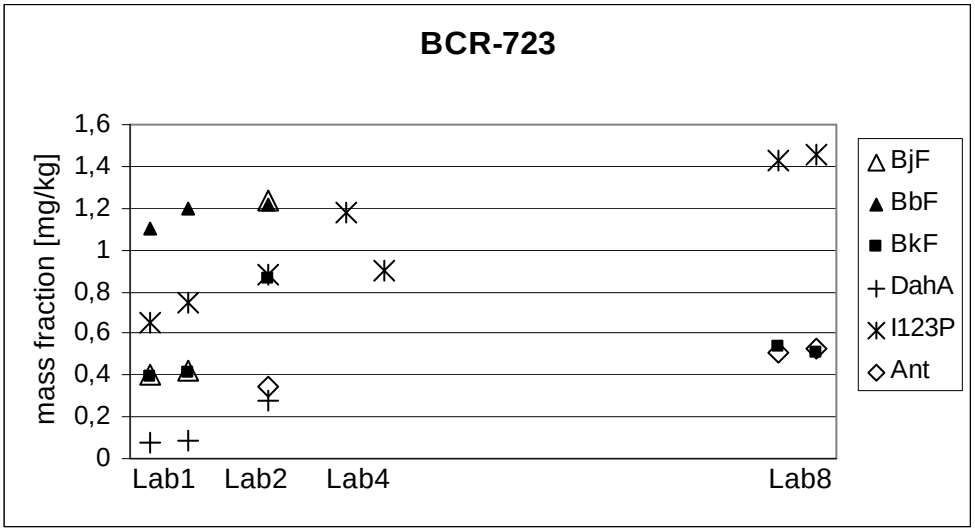

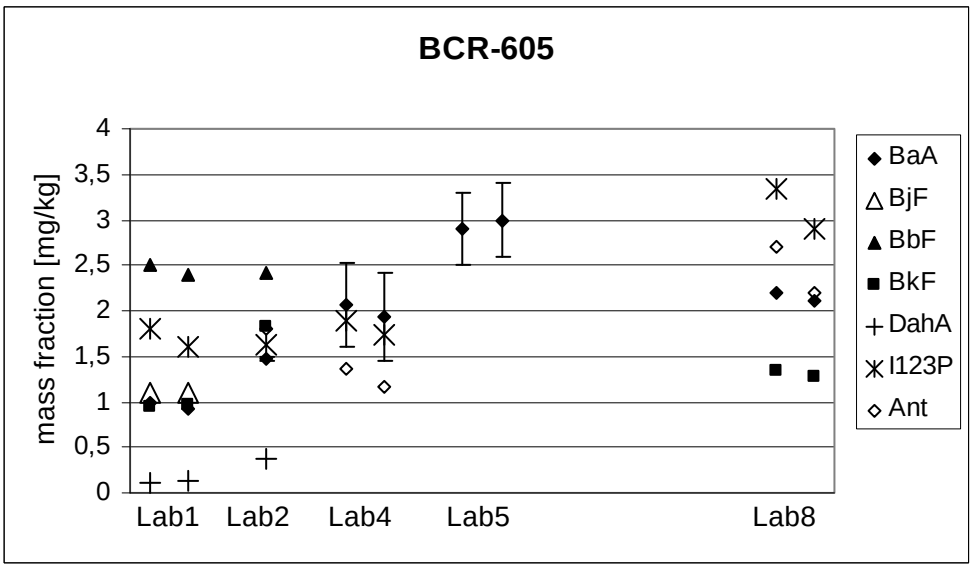

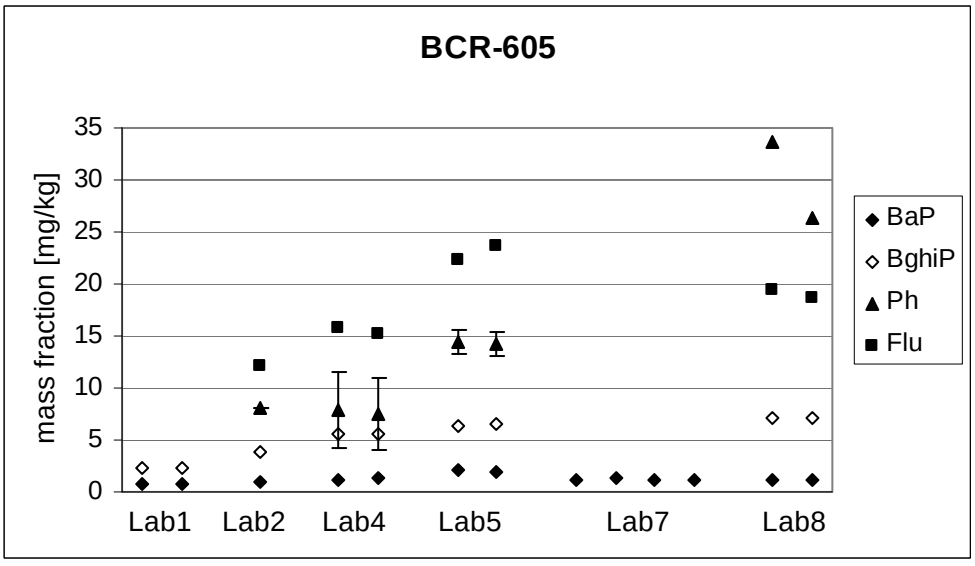

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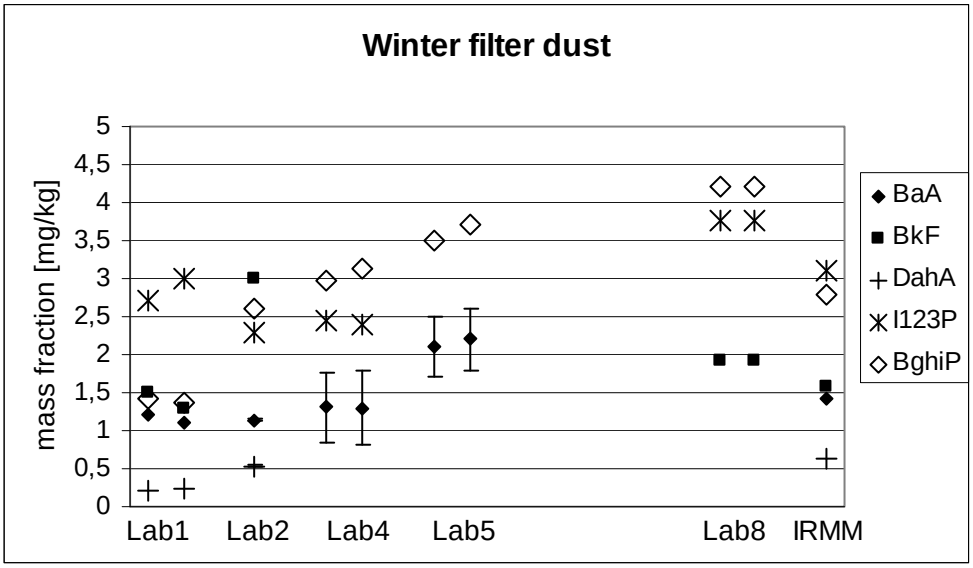

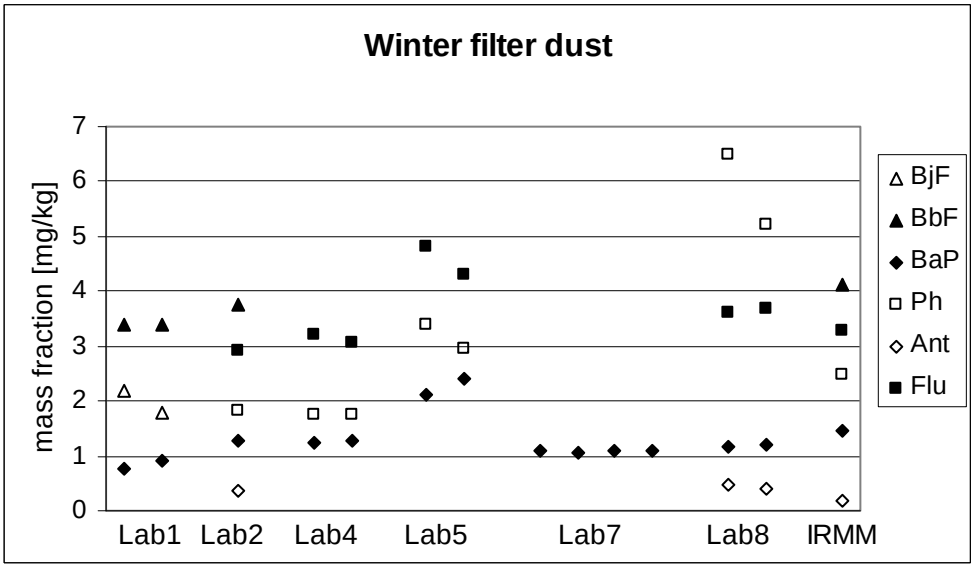

ANNEX G: Commutability study: results of the determination of other PAHs

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 1

Compound	Sample No	Mass fraction [mg/kg]
Dust No 1		
Benzo(j)fluoranthene	069	0.64
	095	0.63
Dust No 2		
Benzo(j)fluoranthene	040	0.39
	075	0.46
Dust No 3		
Benzo(j)fluoranthene	021	0.40
	084	0.42
Dust No 4		
Benzo(j)fluoranthene	012	1.1
	032	1.1
Dust No 5		
Benzo(j)fluoranthene	019	2.2
	067	1.8

ANNEX G: Commutability study: results of the determination of other PAHs

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 2

Compound	Sample No	Mass fraction [mg/kg]	RSD [%]
Dust No 1			
Acenaphthylene	1	117	10.0
	2	132	
	3	143	
Acenaphtene	1	78	15.6
	2	88	
	3	106	
Fluorene	1	172	6.9
	2	187	
	3	197	
Pyrene	1	4313	0.9
	2	4236	
	3	4297	
Chrysene	1	1792	2.6
	2	1700	
	3	1752	
Dust No 2			
Acenaphthylene	1	94	3.8
	2	87	
	3	89	4.1
Acenaphtene	1	82	
	2	81	
	3	76	
Fluorene	1	145	1.4
	2	145	
	3	142	
Pyrene	1	1109	0.8
	2	1094	
	3	1095	
Chrysene	1	1323	1.2
	2	1333	
	3	1301	
Dust No 3			
Acenaphthylene	1	129	0.9
	2	130	
	3	131	
Acenaphtene	1	80	10.4
	2	85	
	3	69	
Fluorene	1	203	1.7
	2	210	
	3	206	
Pyrene	1	4828	2.2
	2	4902	
	3	5042	

ANNEX G: Commutability study: results of the determination of other PAHs

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 2 continuation

Chrysene	1	2223	0.9
	2	2198	
	3	2184	
Dust No 4			
Acenaphthylene	1	205	7.4
	2	236	
	3	215	
Acenaphtene	1	139	7.7
	2	162	
	3	151	
Fluorene	1	737	0.7
	2	745	
	3	746	
Pyrene	1	15206	0.4
	2	15169	
	3	15089	
Chrysene	1	3884	4.1
	2	3931	
	3	3640	
Dust No 5			
Acenaphthylene	1	167	3.5
	2	156	
	3	161	
Acenaphtene	1	96	4.6
	2	88	
	3	91	
Fluorene	1	238	3.3
	2	223	
	3	234	
Pyrene	1	2247	1.3
	2	2211	
	3	2190	
Chrysene	1	2520	5.9
	2	2749	
	3	2826	

ANNEX G: Commutability study: results of the determination of other PAHs

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 4

Compound	Mass fraction [mg/kg]	RSD [%]	Uncertainty [mg/kg]
Dust No 1			
naphtalene	0.47	5.3	0.02
	0.47	6.9	0.02
fluorene	0.20	16.9	0.04
	0.21	19.3	0.04
pyrene	4.63	14.9	1.99
	4.60	6.1	1.97
chrycene/trifenyleeni?	1.86	6.3	0.31
	1.94	3.1	0.32
benzo(k+b+)fluoranthene	2.57	6.2	0.34
	2.73	2.2	0.36
dibenz(a,h+a,c)anthracene	0.20	11.0	0.07
	-	-	-
Dust No 2			
naphtalene	0.28	19.3	0.01
	0.28	14.8	0.01
fluorene	0.16	10.5	0.03
	0.16	13.2	0.03
pyrene	1.28	36.2	0.55
	1.19	33.7	0.51
chrycene/trifenyleeni?	1.23	13.8	0.21
	1.29	20.7	0.21
benzo(k+b+)fluoranthene	2.07	10.8	0.27
	2.17	15.1	0.28
Dust No 3			
naphtalene	0.59	10,1	0,03
	0.51	9,6	0,02
fluorene	0.18	7,2	0,03
	0.16	8,2	0,03
pyrene	5.55	10,3	2,38
	5.16	7,5	2,22
chrycene/trifenyleeni?	2.64	5,9	0,44
	2.54	4,0	0,42
benzo(k+b+)fluoranthene	2.25	3,9	0,29
	2.13	5,5	0,28
dibenz(a,h+a,c)anthracene	0.24	11,9	0,09
	0.24	-	0,09

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 4 continuation

Dust No 4			
naphtalene	0.83	9.4	0.04
	0.71	7.2	0.03
acenaphtylene	0.29	2.4	0.05
	0.26	4.9	0.04
acenphtene	0.12	0.7	0.01
	0.15	20.8	0.02
fluorene	0.66	9.6	0.12
	0.62	9.0	0.11
chrycene/trifenyleeni?	5.51	6.2	0.92
	5.25	5.4	0.88
benzo(k+b+)fluoranthene	4.65	4.8	0.61
	4.62	5.4	0.61
dibenz(a,h+a,c)anthracene	0.34	11.2	0.13
	0.35	13.1	0.13
Dust No 5			
naphtalene	0.48	26.0	0.02
	0.44	4.9	0.02
fluorene	0.24	21.3	0.04
	0.23	5.5	0.04
pyrene	2.53	11.8	1.08
	2.28	4.2	0.98
chrycene/trifenyleeni?	3.11	8.3	0.52
	3.00	3.3	0.50
benzo(k+b+)fluoranthene	6.46	3.8	0.85
	6.32	2.9	0.83
dibenz(a,h+a,c)anthracene	0.76	60.4	0.28
	0.60	29.6	0.22

ANNEX G: Commutability study: results of the determination of other PAHs

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8

Compound	Sample No	Mass fraction [mg/kg]			RSD [%]
Dust No 1					
Napthalene	Green -76	3.3	14	1.1	113
	Green -98	3.2	3	5.6	37
2-Methyl Napthalene	Green –76	0.32	0.89	0.33	64
	Green –98	0.71	0.64	0.74	7
1-Methyl Napthalene	Green –76	<0.2	0.49	<0.2	-
	Green –98	0.39	0.36	0.4	5
Biphenyl	Green –76	<0.9	<0.9	<0.9	-
	Green –98	<0.9	<0.9	<0.9	-
Acenapthylene	Green –76	0.22	0.47	0.24	45
	Green –98	0.41	0.36	0.45	11
Acenapthene	Green –76	<0.07	0.2	0.075	64
	Green –98	0.18	0.15	0.19	12
Fluorene	Green –76	0.22	0.51	0.25	49
	Green –98	0.46	0.42	0.48	7
2-Methyl Phenanthrene	Green –76	1.1	2.5	1.3	46
	Green –98	2.3	2.1	2.4	7
2-Methyl Anthracene	Green –76	<0.2	0.24	<0.2	-
	Green –98	0.33	0.23	0.32	19
1-Methyl Anthracene	Green –76	<0.008	<0.008	<0.008	-
	Green –98	<0.008	<0.008	<0.008	
1-Methyl Phenanthrene	Green –76	0.65	1.6	0.95	48
	Green –98	1.5	1.4	1.5	5
9-Methyl Anthracene	Green -76	<0.09	<0.09	<0.09	-
	Green –98	<0.09	<0.09	<0.09	-
4,5-Methylene Phenanthrene	Green –76	0.46	1.1	0.55	49
	Green –98	0.98	0.95	1	3
Pyrene	Green –76	5.7	6.4	6	6
	Green –98	5.9	5.8	5.8	1
Retene	Green –76	0.32	0.35	0.36	6
	Green –98	0.33	0.31	0.36	8
Benzo(c)phenanthrene	Green –76	0.32	0.35	0.44	17
	Green –98	0.32	0.3	0.41	17
Chrysene	Green –76	2	2	2.1	3
	Green –98	2.2	2	2.1	5
Cyclopenta(c,d)pyrene	Green –76	0.073	0.075	0.08	5
	Green –98	0.076	0.09	0.092	10
Benzo(b)naph(2,1-d)thiophene	Green –76	0.056	0.091	0.064	26
	Green –98	0.067	0.056	0.07	11
5-Methyl Chrysene	Green –76	<0.1	<0.1	<0.1	-
	Green –98	<0.1	<0.1	<0.1	-
Benzo(b+j)fluoranthene	Green –76	2.9	3.1	3.3	6
	Green –98	2.9	2.8	2.9	2
Cholanthrene	Green -76	0.046	0.048	0.053	7
	Green -98	0.051	0.049	0.047	4

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8 continuation

Benzo(e)pyrene	Green -76	4.9	1.5	1.6	71
	Green –98	1.4	1.3	1.4	4
Perylene	Green –76	0.17	0.17	0.22	15
	Green –98	0.2	0.18	0.21	8
Dibenzo(ah/ac)anthracene	Green –76	0.27	0.27	0.31	8
	Green –98	0.29	0.28	0.29	2
Dibenzo(al)pyrene	Green –76	<1	<1	<1	-
	Green –98	<1	<1	<1	-
Dibenzo(ae)pyrene	Green –76	0.28	0.42	0.5	28
	Green –98	0.42	0.48	0.47	7
Dibenzo(ai)pyrene	Green –76	0.042	0.052	0.056	14
	Green –98	0.069	0.073	0.066	6
Coronene	Green –76	1.1	1.1	1.2	5
	Green -98	1.1	1.1	1.2	5
Dust No 2					
Napthalene	Red-03	0.76	<0.4	0.46	35
	Red-37	<0.4	<0.4	0.52	-
2-Methyl Napthalene	Red-03	<0.3	<0.3	<0.3	-
	Red-37	<0.3	<0.3	<0.3	-
1-Methyl Napthalene	Red-03	<0.2	<0.2	<0.2	-
	Red-37	<0.2	<0.2	<0.2	-
Biphenyl	Red-03	<0.9	<0.9	<0.9	-
	Red-37	<0.9	<0.9	<0.9	-
Acenapthylene	Red-03	0.089	0.092	0.092	2
	Red-37	0.084	0.084	0.08	3
Acenapthene	Red-03	<0.07	<0.07	<0.07	-
	Red-37	<0.07	<0.07	<0.07	-
Fluorene	Red-03	<0.1	<0.1	<0.1	-
	Red-37	<0.1	<0.1	<0.1	-
2-Methyl Phenanthrene	Red-03	0.23	0.24	0.23	2
	Red-37	0.23	<0.2	<0.2	-
2-Methyl Anthracene	Red-03	<0.2	<0.2	<0.2	-
	Red-37	<0.2	<0.2	<0.2	-
1-Methyl Anthracene	Red-03	<0.008	<0.008	<0.008	-
	Red-37	<0.008	<0.008	<0.008	-
1-Methyl Phenanthrene	Red-03	0.13	0.16	0.13	12
	Red-37	0.13	0.15	0.12	11
9-Methyl Anthracene	Red-03	<0.09	<0.09	<0.09	-
	Red-37	<0.09	<0.09	<0.09	-
4,5-Methylene Phenanthrene	Red-03	0.12	0.12	0.13	5
	Red-37	0.12	0.1	0.11	9
Pyrene	Red-03	1.3	1.4	1.3	4
	Red-37	1.2	1.2	1.3	5
Retene	Red-03	0.49	0.54	0.49	6
	Red-37	0.48	0.46	0.46	2
Benzo(c)phenanthrene	Red-03	0.13	0.3	0.12	55
	Red-37	0.11	0.11	0.11	0

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8 continuation

Chrysene	Red-03	1.1	1.1	1	5
	Red-37	0.95	0.93	0.91	2
Cyclopenta(c,d)pyrene	Red-03	0.047	0.078	0.072	25
	Red-37	0.068	0.068	0.075	6
Benzo(b)naph(2,1-d)thiophene	Red-03	0.05	0.047	<0.04	4
	Red-37	<0.04	<0.04	<0.04	-
5-Methyl Chrysene	Red-03	<0.1	<0.1	<0.1	-
	Red-37	<0.1	<0.1	<0.1	-
Benzo(b+j)fluoranthene	Red-03	2.1	2	2	3
	Red-37	2	1.9	1.9	3
Cholanthrene	Red-03	0.031	0.029	0.036	11
	Red-37	0.032	0.03	0.031	3
Benzo(e)pyrene	Red-03	0.91	0.82	0.88	5
	Red-37	0.85	0.78	0.82	4
Perylene	Red-03	0.1	0.14	0.14	18
	Red-37	0.13	0.13	0.13	0
Dibenzo(ah/ac)anthracene	Red-03	0.23	0.23	0.24	2
	Red-37	0.23	0.23	0.23	0
Anthanthrene	Red-03	0.031	0.061	0.061	34
	Red-37	0.06	0.076	0.073	12
Dibenzo(al)pyrene	Red-03	<1	<1	<1	-
	Red-37	<1	<1	<1	-
Dibenzo(ae)pyrene	Red-03	0.3	0.29	0.28	3
	Red-37	0.34	0.27	0.3	12
Dibenzo(ai)pyrene	Red-03	0.045	0.041	0.045	5
	Red-37	0.046	0.042	0.046	5
Coronene	Red-03	0.41	0.43	0.52	13
	Red-37	0.5	0.41	0.39	14
Dust No 3					
Napthalene	Purple-85	1.5	0.6	0.48	65
	Purple-41	0.55	0.77	0.55	20
2-Methyl Napthalene	Purple-85	0.93	0.38	0.57	45
	Purple-41	0.6	0.58	0.35	27
1-Methyl Napthalene	Purple-85	0.33	<0.2	<0.2	-
	Purple-41	<0.2	<0.2	<0.2	-
Biphenyl	Purple-85	<0.9	<0.9	<0.9	-
	Purple-41	<0.9	<0.9	<0.9	
Acenapthylene	Purple-85	0.35	0.18	0.23	34
	Purple-41	0.25	0.25	0.15	27
Acenapthene	Purple-85	0.11	<0.07	0.074	28
	Purple-41	0.082	0.071	<0.07	10
Fluorene	Purple-85	0.43	0.23	0.31	31
	Purple-41	0.32	0.28	0.2	23
2-Methyl Phenanthrene	Purple-85	11	6.7	8.6	25
	Purple-41	8.4	7.6	5.9	17
2-Methyl Anthracene	Purple-85	<0.2	<0.2	<0.2	-
	Purple-41	<0.2	<0.2	<0.2	-

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8 continuation

1-Methyl Anthracene	Purple-85	<0.008	<0.008	<0.008	-
	Purple-41	<0.008	<0.008	<0.008	-
1-Methyl Phenanthrene	Purple-85	6.4	4.1	5.1	22
	Purple-41	4.9	4.2	3.5	17
9-Methyl Anthracene	Purple-85	<0.09	<0.09	<0.09	-
	Purple-41	<0.09	<0.09	<0.09	-
4,5-Methylene Phenanthrene	Purple-85	1.1	0.72	0.88	21
	Purple-41	0.94	0.86	0.64	19
Pyrene	Purple-85	6.5	7.8	6.4	11
	Purple-41	7	6.6	7.8	9
Retene	Purple-85	0.21	0.26	0.26	12
	Purple-41	0.27	0.25	0.25	6
Benzo(c)phenanthrene	Purple-85	0.46	0.55	0.55	10
	Purple-41	0.57	0.51	0.57	6
Chrysene	Purple-85	2	2.2	2.4	9
	Purple-41	2.4	2.2	2.2	5
Cyclopenta(c,d)pyrene	Purple-85	0.13	0.17	0.12	19
	Purple-41	0.14	0.17	0.17	11
Benzo(b)naph(2,1-d)thiophene	Purple-85	0.11	0.13	0.13	9
	Purple-41	0.13	0.12	0.12	5
5-Methyl Chrysene	Purple-85	<0.1	<0.1	<0.1	-
	Purple-41	<0.1	<0.1	<0.1	-
Benzo(b+j)fluoranthene	Purple-85	1.8	2.1	2	8
	Purple-41	2.1	2	2.2	5
Cholanthrene	Purple-85	<0.004	<0.004	<0.004	-
	Purple-41	<0.004	0.0062	<0.004	-
Benzo(e)pyrene	Purple-85	1.4	1.5	1.5	4
	Purple-41	1.6	1.5	1.6	4
Perylene	Purple-85	0.097	0.11	0.11	7
	Purple-41	0.13	0.013	0.12	5
Dibenzo(ah/ac)anthracene	Purple-85	0.18	0.23	0.22	13
	Purple-41	0.23	0.24	0.25	4
Anthanthrene	Purple-85	0.072	0.081	0.067	10
	Purple-41	0.1	0.11	0.094	8
Dibenzo(al)pyrene	Purple-85	<1	<1	<1	-
	Purple-41	<1	<1	<1	-
Dibenzo(ae)pyrene	Purple-85	0.19	0.26	0.26	17
	Purple-41	0.26	0.23	0.24	6
Dibenzo(ai)pyrene	Purple-85	<0.02	<0.02	<0.02	-
	Purple-41	<0.02	<0.02	<0.02	-
Coronene	Purple-85	2.4	2.9	2.6	10
	Purple-41	2.9	2.6	2.8	6

ANNEX G: Commutability study: results of the determination of other PAHs

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8 continuation

Dust No 4					
Napthalene	Blue-63	1.6	0.94	2.3	42
	Blue-03	9.4	2.3	4.5	67
2-Methyl Napthalene	Blue-63	2.9	1.3	2.3	37
	Blue-03	3	1.2	2.3	42
1-Methyl Napthalene	Blue-63	1.1	1.2	1.6	20
	Blue-03	1.4	0.56	1.1	42
Biphenyl	Blue-63	<0.9	<0.9	<0.9	-
	Blue-03	<0.9	<0.9	<0.9	-
Acenapthylene	Blue-63	0.57	0.66	0.74	13
	Blue-03	0.74	0.43	0.55	27
Acenapthene	Blue-63	0.31	0.41	0.43	17
	Blue-03	0.38	0.19	0.38	35
Fluorene	Blue-63	1.8	2.2	2.3	13
	Blue-03	2.1	1.1	1.7	31
2-Methyl Phenanthrene	Blue-63	21	29	29	18
	Blue-03	27	15	21	29
2-Methyl Anthracene	Blue-63	1.6	1.2	1.2	17
	Blue-03	1.1	0.87	0.8	17
1-Methyl Anthracene	Blue-63	<0.008	<0.008	<0.008	-
	Blue-03	<0.008	<0.008	<0.008	-
1-Methyl Phenanthrene	Blue-63	13	17	18	17
	Blue-03	15	8.6	12	27
9-Methyl Anthracene	Blue-63	<0.09	<0.09	<0.09	-
	Blue-03	<0.09	<0.09	<0.09	-
4,5-Methylene Phenanthrene	Blue-63	3.2	4.4	4.4	17
	Blue-03	3.8	2	3.1	31
Pyrene	Blue-63	24	26	23	2
	Blue-03	23	23	22	3
Retene	Blue-63	1.8	1.8	1.8	0
	Blue-03	1.8	1.8	1.7	3
Benzo(c)phenanthrene	Blue-63	1	1.1	1.1	5
	Blue-03	1	1.1	0.95	8
Chrysene	Blue-63	4.8	5.5	5.5	8
	Blue-03	5.6	5.2	4.7	9
Cyclopenta(c,d)pyrene	Blue-63	0.3	0.26	0.17	27
	Blue-03	0.22	0.21	0.2	5
Benzo(b)naph(2,1-d)thiophene	Blue-63	0.37	0.4	0.4	4
	Blue-03	0.39	0.39	0.34	8
5-Methyl Chrysene	Blue-63	<0.1	<0.1	<0.1	-
	Blue-03	<0.1	<0.1	<0.1	-
Benzo(b+j)fluoranthene	Blue-63	5.1	5.4	5.2	3
	Blue-03	4.9	5.2	4.8	4
Cholanthrene	Blue-63	<0.004	<0.004	<0.004	-
	Blue-03	0.097	0.13	0.036	54
Benzo(e)pyrene	Blue-63	2.9	3.1	3.0	3
	Blue-03	10	12	10	11

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8 continuation

Perylene	Blue-63	0.33	0.34	0.33	2
	Blue-03	0.32	0.33	0.28	9
Dibenzo(ah/ac)anthracene	Blue-63	0.4	0.46	0.44	7
	Blue-03	0.47	0.49	0.47	2
Anthanthrene	Blue-63	0.16	0.19	0.17	9
	Blue-03	0.11	0.11	0.078	19
Dibenzo(al)pyrene	Blue-63	<1	<1	<1	-
	Blue-03	<1	<1	<1	-
Dibenzo(ae)pyrene	Blue-63	0.58	0.51	0.51	8
	Blue-03	0.44	0.45	0.46	2
Dibenzo(ai)pyrene	Blue-63	<0.02	<0.02	<0.02	-
	Blue-03	0.068	0.07	0.077	7
Coronene	Blue-63	3.9	4.2	4	4
	Blue-03	3.8	3.9	3.6	4
Dust No 5					
Napthalene	Gold-46	3.5	2.6	2.3	22
	Gold-98	1.6	5.4	8.6	67
2-Methyl Napthalene	Gold-46	0.84	0.76	0.69	10
	Gold-98	0.33	1	0.53	55
1-Methyl Napthalene	Gold-46	0.45	0.39	0.37	10
	Gold-98	<0.2	0.53	0.28	44
Biphenyl	Gold-46	<0.9	<0.9	<0.9	-
	Gold-98	<0.9	<0.9	<0.9	-
Acenapthylene	Gold-46	0.5	0.42	0.4	12
	Gold-98	0.23	0.54	0.29	47
Acenapthene	Gold-46	0.16	0.13	0.14	11
	Gold-98	<0.07	0.22	0.1	53
Fluorene	Gold-46	0.58	0.5	0.5	9
	Gold-98	0.23	0.67	0.37	53
2-Methyl Phenanthrene	Gold-46	1.2	1.0	1.1	9
	Gold-98	0.62	1.4	0.81	43
2-Methyl Anthracene	Gold-46	<0.2	<0.2	<0.2	-
	Gold-98	<0.2	<0.2	<0.2	-
1-Methyl Anthracene	Gold-46	<0.008	<0.008	<0.008	-
	Gold-98	<0.008	<0.008	<0.008	-
1-Methyl Phenanthrene	Gold-46	0.75	0.63	0.71	9
	Gold-98	0.33	0.84	0.48	48
9-Methyl Anthracene	Gold-46	<0.09	<0.09	<0.09	-
	Gold-98	<0.09	<0.09	<0.09	-
4,5-Methylene Phenanthrene	Gold-46	0.62	0.52	0.57	9
	Gold-98	0.31	0.69	0.39	43
Pyrene	Gold-46	2.7	2.9	2.3	12
	Gold-98	2.7	2.6	2.7	2
Retene	Gold-46	0.68	0.69	0.56	11
	Gold-98	0.74	0.61	0.71	10

Dust No 1 to 5 correspond to tunnel dust, summer filter dust, BCR-723, BCR-605 and winter filter dust, respectively.

Lab 8 continuation

Benzo(c)phenanthrene	Gold-46	0.4	0.42	0.32	14
	Gold-98	0.5	0.37	0.41	16
Chrysene	Gold-46	3.4	3.4	2.5	17
	Gold-98	3.5	3.2	3.2	5
Cyclopenta(c,d)pyrene	Gold-46	0.16	0.18	0.14	13
	Gold-98	0.14	0.12	0.13	8
Benzo(b)naph(2,1-d)thiophene	Gold-46	0.089	0.089	0.071	13
	Gold-98	0.094	0.077	0.08	11
5-Methyl Chrysene	Gold-46	<0.1	<0.1	<0.1	-
	Gold-98	<0.1	<0.1	<0.1	-
Benzo(b+j)fluoranthene	Gold-46	7.5	8.1	6.5	11
	Gold-98	7.6	7.2	7.1	4
Cholanthrene	Gold-46	0.1	0.11	0.082	15
	Gold-98	0.091	0.015	0.095	67
Benzo(e)pyrene	Gold-46	11	12	9.4	12
	Gold-98	11	11	11	0
Perylene	Gold-46	0.25	0.28	0.32	12
	Gold-98	0.29	0.22	0.25	14
Dibenzo(ah/ac)anthracene	Gold-46	0.71	0.76	0.55	16
	Gold-98	0.72	0.64	0.53	15
Anthanthrene	Gold-46	0.037	0.042	0.051	16
	Gold-98	0.048	0.031	0.054	27
Dibenzo(al)pyrene	Gold-46	<1	<1	<1	-
	Gold-98	<1	<1	<1	-
Dibenzo(ae)pyrene	Gold-46	0.55	0.63	0.46	16
	Gold-98	0.54	0.54	0.39	18
Dibenzo(ai)pyrene	Gold-46	0.056	0.063	0.062	6
	Gold-98	0.068	0.059	0.059	8
Coronene	Gold-46	1.4	1.5	1.2	11
	Gold-98	1.4	1.3	1.2	8

European Commission

EUR 23244 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Development of particulate matter certified reference materials (PM_{10} CRMs)
Author(s): E. Perez Przyk, A. Held, J. Charoud-Got
Luxembourg: Office for Official Publications of the European Communities
2008 – 93 pp. – 21.0 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-08347-1
DOI 10.2787/21226

Abstract

The present report summarises the work carried out within the feasibility study devoted to the development of particulate matter certified reference materials (PM_{10} CRM) at the RM Unit of IRMM. At present there is no suitable PM_{10} RM certified for elements and/or PAHs. Therefore, this project was aimed at developing a CRM, which will play an active tool in the implementation of the Air Quality Framework Directive and its 1st and 4th Daughter Directives.
In order to establish the target characteristics for the future PM_{10} CRM, a meeting with experts in the field of air quality was organised. This report includes decisions made during that meeting.
Five candidate materials have been selected for the feasibility study on air quality CRM development. These are two existing CRMs, BCR-605 (urban dust certified for trimethyllead) and BCR-723 (a road dust certified for Pd, Pt and Rh), and three materials specifically collected for this purpose, a tunnel dust, a winter filter dust and a summer filter dust. An evaluation of the suitability of these materials for the future air quality CRM was performed.
As dust contains coarse particles (up to 500 µm) the first challenging step was the development of a suitable approach towards particle size reduction. This was obtained by means of a jet mill. After milling, 90 vol.% of the materials were below 25 µm.
The test materials were analysed with respect to the content of selected elements and PAHs. The analyte contents in the test materials reflected the real environmental conditions and it was in agreement with the requirements for the future PM_{10} CRM. All elements and PAHs of interest were easy to detect. In general, all test materials were easy in handling and did not pose any problems during the sample preparation.
Furthermore, a homogeneity study for tunnel dust, summer filter dust and winter filter dust was carried out. The homogeneity uncertainty of the determination of elements and PAHs in all materials was lower than 1.5 %. The exception was tunnel dust, for which the obtained values of the uncertainty for PAH determinations were comparatively higher (between 1.5 % and 7.8 %). However, this can be improved by a better material homogenisation. A minimum sample intake for all test materials with respect to As, Cd, Ni, Pb and benzo[*a*]pyrene has also been defined. The minimum sample intakes obtained for As, Cd, Ni, Pb and benzo[*a*]pyrene in all test materials (excluding Ni in summer filter dust) were below or equal to 50 mg.

The short-term stability has been tested to establish dispatch conditions for tunnel dust, summer filter dust and winter filter dust. The materials intended for the determination of the element content can be transported at ambient temperature for up to four weeks. Alternatively, if the materials are intended for the determination of PAHs, a temperature of 4 °C should be used to transport winter filter dust and 18 °C for both tunnel dust and summer filter dust.

It was shown that it is feasible to produce CRMs for particulate matter that have the required properties and sufficiently mimic PM_{10} in the analytical process. After the feasibility study including commutability study it was concluded that suitable candidate materials for the PM_{10} CRM are tunnel dust for elements and tunnel dust or the filter materials for the PAHs.

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LA-NA-23244-EN-C

ISBN 978-92-79-08347-1