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TECHNICAL STUDY NO. 12

Influence of the pretreatment of the samples during proficiency tests in solid matrices

This document is issued for information and is based on results and observations from A.G.L.A.E.'s proficiency tests.

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ABSTRACT

One of the main issue when implementing proficiency tests with a solid matrix is to obtain a sufficient batch homogeneity. AGLAE has implemented proficiency tests in raw solid matrices and in pretreated solid matrices for metals and organic micropollutants (PAHs) in order to check if the raw materials could be homogeneous enough to be employed during proficiency tests. The aim of these tests was also to evaluate the uncertainty of measurement component due to the pretreatment of the samples and to compare the analytical performances of the laboratories including or not the pretreatment part of the samples.

The batch heterogeneity is significantly higher in the raw batches, which may lead to exclude parameters from the test. The uncertainty of measurement component added by the pretreatment of the samples is negligible for the chemical analyses and metals but represents on average 17,5% of additional dispersion for the PAHs. The analytical biases are thus highlighted less precisely in a non-pretreated matrix because the additional dispersion makes the control less reliable (the acceptance limits are based on the data dispersion). Furthermore, the contents found are globally lower in the raw matrix.

Finally, these tests have shown that the check have to be mainly focused on the analytical part of the analysis and not on the pretreatment because the number of bad results attributed only to pretreatment is very low. The use of a pretreated matrix is recommended. However, the participation in proficiency tests in raw matrix, under the condition that the matrix is homogeneous enough, is recommended but at a lower frequency.

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PRESENTATION AND COMMENTS

1. INTRODUCTION

AGLAE has been providing proficiency tests for more than 20 years in solid matrices. The matrices sent to the participants of the proficiency tests are pretreated by AGLAE before the sending, in order to obtain a matrix as homogeneous as possible. Indeed, the main issue when implementing proficiency tests with solid matrix is to obtain a matrix which is homogeneous enough.
However, this implementation doesn't allow to include the "pretreatment of the sample" part in the quality control of the proficiency test.

In 2017, AGLAE implemented two proficiency tests in contaminated sites and soils with the aim:

- To evaluate the homogeneity of raw materials used during a proficiency test
- To evaluate the uncertainty of measurement component due to the pretreatment of the samples part
- To compare the analytical performances of the laboratories including or not the pretreatment of the samples part

The contents observed for each parameter on the pretreated and raw matrices have also been compared.
The first proficiency test was about chemical analyses and metals. The second one was about organic micropollutants (PAHs). The proficiency test about organic micropollutants was also the opportunity to test the influence of the spiking of the solid matrix on the content of the other parameters naturally in the matrix (not spiked).

2. PRESENTATION OF THE PROFICIENCY TESTS

The proficiency tests took place from October to December 2017 and gathered 18 participants for the test 17M43.1 "chemical analyses and metals in contaminated sites and soils" and 19 participants for the test 17M44.1 "organic micropollutants in contaminates sites and soils".

2.1. PREPARATION OF THE MATERIALS

The matrix used for the two tests is identical: soil from industrial wasteland. For each test, a batch of raw samples and a batch of samples pretreated by AGLAE were sent to the participants. For the test about organic micropollutants, an additional batch pretreated by AGLAE and spiked in PCBs was also sent. Note that this study has been carried out only on the parameters for which the matrix was naturally contaminated (no artificial spiking) so the PCBs aren't studied in this document.
The table below gathers the information about the materials preparation and the list of the parameters implemented.

Proficiency test	17M43.1		17M44.1		
Batch	**Batch 1 (pretreated batch)**	**Batch 2 (raw batch)**	**Batch 1 (Petreated and spiked batch)**	**Batch 2 (pretreated batch)**	**Batch 3 (raw batch)**
Parameters	TOC, dry matter(1), Al, As, Cd(1), Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Se(1), Zn	TOC, dry matter1), Al, As, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn	acenaphtene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3 - cd]pyrene, naphtalene, phenanthrene, pyrene, acenaphtylene, total hydrocarbons index(1), congener 28(1), congener 52(1), congener 101(1), congener 118(1), congener 138(1), congener 153(1), congener 180(1),	dry matter(1), acenaphtene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3 - cd]pyrene, naphtalene, phenanthrene, pyrene, acenaphtylene	dry matter(1), acenaphtene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3 - cd]pyrene, naphtalene, phenanthrene, pyrene, acenaphtylene
Matrix	soil from industrial wasteland				
Pretreatment	Dried crushed and sieved at 150µm	No pretreatment, raw matrix	Dried crushed and sieved at 150µm	Dried crushed and sieved at 150µm	No pretreatment, raw matrix
Spiking	Spiked in Cd and Se	-	Spiked for all the PCBs	-	-
Packaging	100mL polyethylene bottles (weight≈50g)	500mL polyethylene bottles (weight≈500g)	250mL yellow glass bottles (weight≈100g)	250mL yellow glass bottles (weight≈100g)	500mL yellow glass bottles (weight≈400g)
Fractionation	By quartering	By quartering	By quartering	By quartering	By quartering

(1) Parameters not studied in the document

2.2. EXPERIMENTAL DESIGN OF THE TESTS

For the two proficiency tests, each participant received two bottles of the batch pretreated by AGLAE and two bottles of the raw batch. For the test about organic micropollutants, they also received two bottles of a batch pretreated and spiked in PCBs.

Each bottle had to be analysed in replicate. The raw batches had to be pretreated before analysis by the participants. All the analyses had to be carried out in repeatability conditions for the raw batches and for the pretreated batches.

All the results have been expressed according to the mass of dry matter. The dry matter content of the test material had to be measured at (105 ± 5)°C in compliance with ISO 11465 (94) standard or any other standard currently applicable.

3. PRETREATMENT OF THE SAMPLES

The pretreatment of the matrices by AGLAE for the two proficiency tests has been carried out all at once.

The pretreatment of the matrix by AGLAE consisted in drying the matrix at a temperature <40°C in an oven. Then the matrix has been crushed and sieved at 150µm.

The modalities of pretreatment of the raw samples by the participants were collected in the results form. A little more than half of the participants have answered.
For the chemical analysis and the metals PT, the participants have mainly followed the ISO 11464 standard "pretreatment of samples for physico-chemical analysis" (NF or ISO versions) with a drying mainly carried out in an oven. The elements superior to 2mm have been crushed and added to the sampling for around half of the participants. The sub-sampling has been carried out manually by quartering.
For the organic micropollutants, the drying has been carried out in an oven or by freeze-drying (also a chemical drying with Na_2SO_4 and a drying at room temperature). The sampling has been carried out by quartering from the fraction <2mm only (one laboratory did it on the fraction <2mm+the crushing of the fraction >2mm).

The following tables present in details the answers of the laboratories to the questions asked about the pretreatment of the samples.

17M43.1 chemical analyses and metals	
normative reference for pretreatment	**Number of results**
1/ ISO 11464 (06)	2
2/ NF EN 16169 (12)	1
3/ NF ISO 11464 (06)	5
4/ Other	3
5/ No response	5
pretreatment - Drying modalities?	**Number of results**
1/ freeze-drying	3
2/ air drying	2
3/ oven drying	7
4/ other	1
5/ no response	3
elements removed	**Number of results**
1/ using a 2mm sieve	7
2/ by manual removal	0
3/ no response	9

17M43.1 chemical analyses and metals	
crushing of the fraction superior to 2mm ?	**Number of results**
1/ no	6
2/ yes	6
3/ no response	4
Sampling performed from:	**Number of results**
1/ the fraction<2mm + the crushing of the fraction>2mm	7
2/ the fraction<2mm only	4
3/ no response	5
Type of sub-sampling ?	**Number of results**
1/ static divider with splits	0
2/ spinning divider (rotary divider)	0
3/ by hand (quartering)	8
4/ other	2
5/ no response	6
Reduction of grain size distribution inferior to 2mm ?	**Number of results**
1/ no	6
2/ yes	6
3/ no response	4

17M44.1 organic micropollutants	
normative reference for pretreatment	**Number of results**
1/ NF EN 16169 (12)	0
2/ NF ISO 14507 (03)	2
3/ other	4
4/ no response	7
pretreatment - Drying modalities?	**Number of results**
1/ chemical in dry ice	0
2/ chemical in liquid nitrogen	0
3/ freeze-drying	3
4/ other	4
5/ no response	6
Sampling performed from:	**Number of results**
1/ the fraction<2mm + the crushing of the fraction>2mm	1
2/ the fraction<2mm only	7
3/ no response	5

17M44.1 organic micropollutants	
Type of sub-sampling ?	**Number of results**
1/ static divider with splits	0
2/ spinning divider (rotary divider)	0
3/ by hand (quartering)	6
4/ other	1
5/ no response	6
Reduction of grain size distribution inferior to 2mm ?	**Number of results**
1/ no	3
2/ yes	4
3/ no response	6
Did you prepare composite samples ?	**Number of results**
1/ no	8
2/ yes	0
3/ no response	5

4. RESULTS

The tables below present the assigned values (mean m) and the variation coefficients of reproducibility (CVR%) calculated for each parameter for the two tests.
The value assigned to the test material (mean m) and reproducibility values have been estimated with an improved version of algorithm A from ISO 13528 standard.
The stability of the materials is checked using the study of the laboratories' results distribution considering the date reported for the start of the sample treatment.
The results have shown that the materials were stable enough to be employed in the two proficiency tests.

17M43.1 chemical analyses and metals in contaminated sites and soils					
Parameter	**m pretreated batch**	**CVR (%) pretreated batch**	**m raw batch**	**CVR (%) raw batch**	Unit
TOC	38,68	27	31,9	38,5	g of C/kg of dry matter
dry matter	98,545	0,5	79,651	1	% in mass of raw matter
Al Population 1	13452,8	20	13205,9	35,5	mg/kg of dry matter
Al Population 2	**Insufficient number of results**				
As	9,94	11	9,45	9,5	mg/kg of dry matter
Cd	42,65	11,5	not analysed in the raw matrix		mg/kg of dry matter
Co	11,442	24	10,508	28	mg/kg of dry matter
Cr	46,516	30,5	27,665	33,5	mg/kg of dry matter
Cu	66,46	10	55,02	6,5	mg/kg of dry matter
Fe	21,799	9,5	20,484	17,5	g/kg of dry matter
Hg	0,35	11,5	0,366	7,5	mg/kg of dry matter
Mn	520,67	6,5	480,52	6,5	mg/kg of dry matter
Ni	26,523	24	23,313	24,5	mg/kg of dry matter
Pb	241,2	8	232,7	9	mg/kg of dry matter
Se	41,569	13	not analysed in the raw matrix		mg/kg of dry matter
Zn	0,183	5,5	0,162	6,5	g/kg of dry matter

Population 1 and 2 for Al: a double population was observed for Al on the raw material and on the pretreated material. A separate treatment was performed according to the dissolution method carried out. The results of the populations 2 which gathered the "total" dissolution method (hydrofluoric/perchloric etching, alkaline fusion / alkaline fluxes, microwave digestion Au + HF + HNO3) were excluded because of an insufficient number of results to carry out the statistical treatment.

17M44.1 organic micropollutants in contaminates sites and soils					
Parameter	m pretreated batch	CVR (%) pretreated batch	m raw batch	CVR (%) raw batch	Unit
dry matter	98,692	0,5	79,702	1	% in mass of raw matter
acenaphtene	21,43	32,5	15,02	64	µg/kg of dry matter
anthracene	83,12	27,5	76,52	56,5	µg/kg of dry matter
benzo[a]anthracene	343,18	18,5	332,85	28,5	µg/kg of dry matter
benzo[a]pyrene	262,77	19	257,97	28	µg/kg of dry matter
benzo[b]fluoranthene	486,34	19	457,09	25	µg/kg of dry matter
benzo[k]fluoranthene	163,74	23,5	157,03	36	µg/kg of dry matter
benzo[g,h,i]perylene	240,43	31,5	220,77	44,5	µg/kg of dry matter
chrysene	466,6	28	385,22	31	µg/kg of dry matter
dibenzo[a,h]anthracene	70,5	39,5	51,88	63	µg/kg of dry matter
fluoranthene	739,67	23	638,49	38,5	µg/kg of dry matter
fluorene	43,43	35	34,43	73,5	µg/kg of dry matter
indeno[1,2,3 - cd]pyrene	209,66	33	181,93	41,5	µg/kg of dry matter
naphtalene	73,41	38	53,42	69	µg/kg of dry matter
phenanthrene	689,13	28,5	432,41	53,5	µg/kg of dry matter
pyrene	594,05	26,5	478,02	37	µg/kg of dry matter
acenaphtylene	18,86	67,5	26,06	90	µg/kg of dry matter

5. COMPARISON OF THE RESULTS IN THE PRETREATED MATICES AND THE RAW MATRICES

5.1. COMPARISON OF THE HOMOGENEITY OF BOTH BATCHES

The objective of these tests was to check whether raw materials made possible to ensure sufficient homogeneity of the materials to be used in a proficiency test.
For this, the heterogeneity of the prepared batches was estimated from the measurement of the deviations between two bottles from the same batch and analysed under repeatability conditions. This batch heterogeneity was compared to the interlaboratory error to check if it was problematic for the implementation of a proficiency test.
For the chemical analyses and metals test, the materials were homogeneous enough for the batch pretreated by AGLAE. On the other hand, for the raw batch they were not homogeneous enough for Cu and especially for Hg. For Pb, the deviations between bottles appear non-negligible compared to the interlaboratory error, but the batch heterogeneity remains minor for this parameter. Note also that if only one bottle had been sent, the heterogeneity of Pb on the raw batch would have been considered major. Indeed, the sending of two bottles of

the same batch to each participant makes it possible to limit the impact of the batch heterogeneity in the evaluation of the analytical performances.
For the organic micropollutants test, both raw and pretreated materials were found to be homogeneous enough to be used in the test. No significant batch heterogeneity was found unlike the chemical analyses and metals test.

The batch heterogeneity observed on the pretreated batch (batch 1) was compared to that of the raw batch (batch 2) expressed as the coefficient of variation CVu in order to check if there is an overall trend to have the raw matrix more heterogeneous or if it remains a problem specific to some parameters.

17M43.1 chemical analyses and metals in contaminated sites and soils			17M44.1 organic micropollutants in contaminates sites and soils		
Parameter	CVu (%) batch 1 (pretreated)	CVu (%) batch 2 (raw)	Parameter	CVu (%) batch 2 (pretreated)	CVu (%) batch 3 (raw)
TOC	0,67	1,96	acenaphtene	5,46	24,14
Al Population 1	2,26	3,20	anthracene	0 (Not significant)	13,21
As	0 (Not significant)	1,20	benzo[a]anthracene	0 (Not significant)	7,55
Co	0,32	0 (Not significant)	benzo[a]pyrene	3,48	7,06
Cr	0 (Not significant)	2,13	benzo[b]fluoranthene	0 (Not significant)	5,36
Cu	0,77	3,56	benzo[k]fluoranthene	0,48	5,99
Fe	0,56	1,76	benzo[g,h,i]perylene	3,25	4,87
Hg	1,35	9,46	chrysene	0 (Not significant)	6,04
Mn	1,19	0,49	dibenzo[a,h]anthracene	2,02	8,02
Ni	0 (Not significant)	1,20	fluoranthene	0 (Not significant)	9,90
Pb	0,76	5,68	fluorene	0 (Not significant)	14,92
Zn	1,35	1,11	indeno[1,2,3 - cd]pyrene	0 (Not significant)	7,89
			naphtalene	0 (Not significant)	13,04
			phenanthrene	0 (Not significant)	3,78
			pyrene	0 (Not significant)	8,40
			acenaphtylene	2,55	3,32

A hypothesis test (signed ranks test) shoows that, overall, the batch heterogeneities observed on the raw batch (batch 2) are higher than those of the pretreated batch (batch 1) for each test. For the 17M43.1 test, the highest relative batch heterogeneity is observed for Hg. For this parameter, **the deviations between bottles were even higher than the deviations between laboratories.**
For organic micropollutants, the CVu is not significantly different from zero for most of the parameters on the pretreated batch while it is on the raw batch.

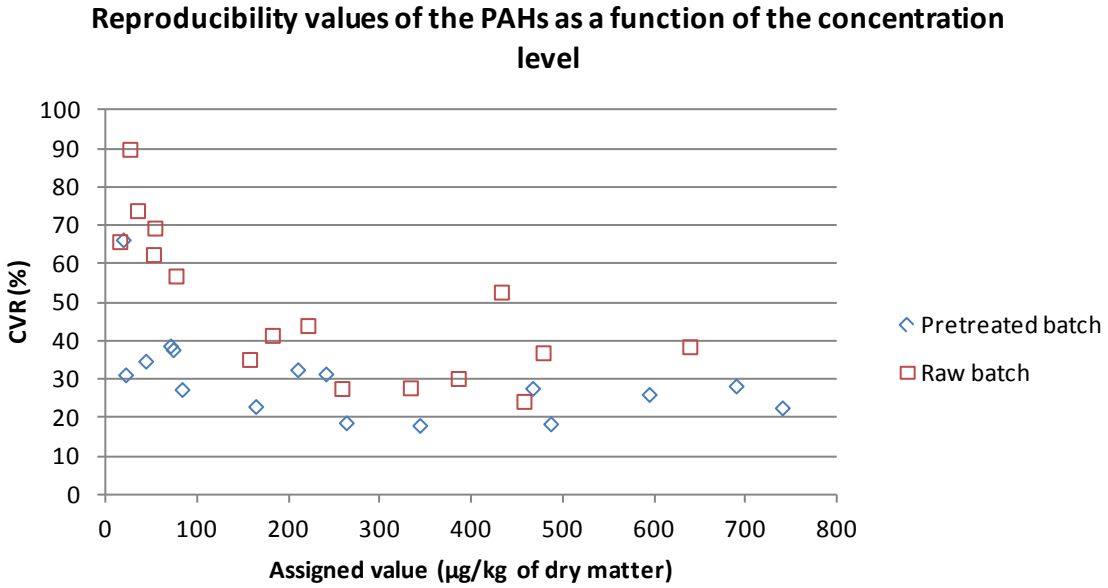
5.2. COMPARISON OF THE REPRODUCIBILITY ON BOTH BATCHES

An estimation of the uncertainty of measurement component due to the pretreatment of the samples part has been carried out.
The reproducibility observed on both batches expressed as coefficient of variation CVR was compared. Note that reproducibility does not include the batch heterogeneity component, it is only the analytical error. For pretreated batches, this is only the "analytical" part of the error, while for the raw batches there is also the part due to the pretreatment. The deviation between the CVRs obtained for the two batches therefore represents the additional uncertainty (expressed in the form of a coefficient of variation) brought into the results by the pretreatment.

17M43.1 chemical analyses and metals in contaminated sites and soils			17M44.1 organic micropollutants in contaminates sites and soils		
Parameter	CVR (%) batch 1 (pretreated)	CVu (%) batch 2 (raw)	Parameter	CVR (%) batch 2 (pretreated)	CVR (%) batch 3 (raw)
TOC	27,0	38,2	acenaphtene	31,20	65,85
Al population 1	19,8	35,7	anthracene	27,38	56,92
As	11,0	8,90	benzo[a]anthracene	18,03	27,82
Co	24,0	27,8	benzo[a]pyrene	18,73	27,64
Cr	30,2	33,7	benzo[b]fluoranthene	18,44	24,29
Cu	9,54	6,14	benzo[k]fluoranthene	22,96	35,20
Fe	9,59	17,4	benzo[g,h,i]perylene	31,43	44,02
Hg	10,4	9,78	chrysene	27,68	30,25
Mn	6,70	6,24	dibenzo[a,h]anthracene	38,72	62,49
Ni	23,6	24,2	fluoranthene	22,60	38,51
Pb	7,43	9,63	fluorene	34,75	73,92
Zn	4,88	5,91	indeno[1,2,3 - cd]pyrene	32,53	41,47
			naphtalene	37,73	69,39
			phenanthrene	28,29	52,73
			pyrene	26,10	36,94
			acenaphtylene	66,33	89,88

A signed rank test was carried out and has shown that overall there is no significant deviation between the CVRs observed for pretreated and raw batches for chemicals analyses and metals, even if there is a trend to have CVRs rather higher for the raw batch than for the pretreated one. The uncertainty component brought by the pretreatment therefore seems negligible compared to the analytical error alone.

For organic micropollutants, the reproducibility observed for the raw matrix is globally significantly lower than that observed on the pretreated matrix, with on average CVRs higher of 17.5%, which corresponds to the random error component of the uncertainty of measurement only due to pretreatment.
For PAHs, the reproducibility is lower for the lowest contents (see graph below). This is especially true for the raw batch. Also, the deviation between the CVRs of the raw batch and those of the pretreated batch is higher for the lowest concentrations.



Note that for the raw batch, it is the very high dispersion of results from one laboratory to another that makes the batch appears sufficiently homogeneous. In fact, for a batch to be considered as sufficiently homogeneous, the deviations between bottles are compared to the interlaboratory error. With a high interlaboratory error, even high deviations between bottles may be considered satisfactory for the implementation of a proficiency test.

5.3. COMPARISON OF THE ANALYTICAL PERFORMANCES ON BOTH BATCHES

The analytical performances of the laboratories were also compared for both batches to see, on the one hand, if obtaining bad results could be due only to the "pretreatment" part of the analysis, and on the other hand, to see if the quality of the control, that is, its ability to highlight analytical errors, was the same for a raw material and a pretreated material.

For this, a verification of the presence of an analytical bias only on the raw batch was carried out; in which case, it can be considered that the laboratory has a bad result only because of the pretreatment part. For chemical analyses and metals, for the laboratories evaluated as "questionable" or "unsatisfactory" on a parameter, in 84% of the cases, the bad result was due to an analytical problem and not to the pretreatment part. That is to say that in 84% of cases, the laboratory has a bad result on both matrices. For organic micropollutants, it is in 78% of the cases.

The percentage of satisfactory z-scores between the pretreated batch and the raw batch was also compared.

17M43.1 chemical analyses and metals in contaminated sites and soils				17M44.1 organic micropollutants in contaminates sites and soils			
Parameter	% of satisfactory z-scores pretreated batch	% of satisfactory z-scores raw batch	deviation in %	Parameter	% of satisfactory z-scores pretreated batch	% of satisfactory z-scores raw batch	deviation in %
TOC	92,3	92,3	0,0	acenaphtene	92,3	100,0	+8,3
Al population 1	77,8	77,8	0,0	anthracene	84,6	92,3	+9,1
As	87,5	75,0	-14,3	benzo[a]anthracene	78,6	85,7	+9,1
Co	86,7	93,3	+7,7	benzo[a]pyrene	76,9	92,3	+20,0
Cr	93,8	93,8	0,0	benzo[b]fluoranthene	84,6	84,6	0,0
Cu	81,3	68,8	-15,4	benzo[k]fluoranthene	91,7	91,7	0,0
Fe	83,3	100,0	+20,0	benzo[g,h,i]perylene	92,9	92,9	0,0
Hg	53,8	61,5	+14,3	chrysene	85,7	92,9	+8,3
Mn	66,7	83,3	+25,0	dibenzo[a,h]anthracene	92,3	92,3	0,0
Ni	93,8	93,8	0,0	fluoranthene	84,6	84,6	0,0
Pb	87,5	68,8	-21,4	fluorene	84,6	92,3	+9,1
Zn	50,0	68,8	+37,5	indeno[1,2,3 - cd]pyrene	92,9	92,9	0,0
				naphtalene	92,3	92,3	0,0
				phenanthrene	92,9	92,9	0,0
				pyrene	85,7	92,9	+8,3
				acenaphtylene	100,0	100,0	0,0

For chemical analyses and metals, the percentage of satisfactory z-scores is generally higher for the raw batch, except for As, Cu and Pb, showing that analytical biases have globally been highlighted more times on the pretreated matrix than on the raw matrix.

This is explained by the fact that there are few bad results only due to the pretreatment but also because of the higher dispersion of the results for the raw batch. The standard deviation for proficiency assessment is therefore wider on the raw batch than on the pretreated batch and the resulting acceptance limits are also wider. This additional dispersion is due to the additional error caused by the pretreatment but also because of higher batch heterogeneity of the raw batch.

For organic micropollutants, the percentage of satisfactory z-scores is the same or higher for the raw batch. Analytical biases are therefore potentially more likely not to be highlighted on the raw matrix. This high rate of satisfactory z-scores is partly explained by the significantly higher reproducibility of the raw batch but also the batch heterogeneity; as a consequence, the acceptance limits are wider.

5.4. COMPARISON OF THE CONTENTS OBSERVED ON THE PRETREATED AND RAW SAMPLES

The means m obtained for the pretreated material (batch 1) and those for the raw material (batch 2) were compared using a hypothesis test on paired series (signed rank test), in order to see if there was an overall trend (all parameters combined for each test) to obtain significantly different contents on both batches. The deviation between the two batches was calculated. The means obtained by each participant on both batches were then compared, parameter by parameter, using a hypothesis test on paired series (signed rank test or Student's test according to the normality or not of the distribution) (see column "significantly different means ?" in the table below).

Parameter	Mean m pretreated batch	Mean m raw batch	deviation in %	significantly different means ?	Unit
17M43.1 chemical analyses and metals in contaminated sites and soils					
Cr	46,516	27,665	-40,53	YES	mg/kg of dry matter
TOC	38,68	31,9	-17,52	NO	g of C/kg of dry matter
Cu	66,46	55,02	-17,21	YES	mg/kg of dry matter
Ni	26,523	23,313	-12,1	YES	mg/kg of dry matter
Zn	0,183	0,162	-11,55	YES	mg/kg of dry matter
Co	11,442	10,508	-8,16	YES	mg/kg of dry matter
Mn	520,67	480,52	-7,71	YES	mg/kg of dry matter
Fe	21,799	20,484	-6,04	YES	mg/kg of dry matter
As	9,94	9,45	-4,94	YES	mg/kg of dry matter
Pb	241,2	232,7	-3,52	NO	mg/kg of dry matter
Al Population 1	13452,8	13205,9	-1,84	NO	mg/kg of dry matter
Hg	0,35	0,366	+4,83	NO	g/kg of dry matter
17M44.1 organic micropollutants in contaminates sites and soils					
phenanthrene	689,13	432,41	-37,25	YES	µg/kg of dry matter
acenaphtene	21,43	15,02	-29,92	NO	µg/kg of dry matter
naphtalene	73,41	53,42	-27,22	NO	µg/kg of dry matter
dibenzo[a,h]anthracene	70,5	51,88	-26,4	YES	µg/kg of dry matter
fluorene	43,43	34,43	-20,72	NO	µg/kg of dry matter
pyrene	594,05	478,02	-19,53	YES	µg/kg of dry matter
chrysene	466,6	385,22	-17,44	YES	µg/kg of dry matter
fluoranthene	739,67	638,49	-13,68	NO	µg/kg of dry matter
indeno[1,2,3 - cd]pyrene	209,66	181,93	-13,23	YES	µg/kg of dry matter
benzo[g,h,i]perylene	240,43	220,77	-8,18	YES	µg/kg of dry matter
anthracene	83,12	76,52	-7,93	NO	µg/kg of dry matter

Parameter	Mean m pretreated batch	Mean m raw batch	deviation in %	significantly different means ?	Unit
benzo[b]fluoranthene	486,34	457,09	-6,02	YES	µg/kg of dry matter
benzo[k]fluoranthene	163,74	157,03	-4,1	NO	µg/kg of dry matter
benzo[a]anthracene	343,18	332,85	-3,01	YES	µg/kg of dry matter
benzo[a]pyrene	262,77	257,97	-1,83	YES	µg/kg of dry matter
acenaphtylene	18,86	26,06	+38,16	NO	µg/kg of dry matter

For both tests, overall, the contents observed on pretreated and raw batches are statistically different with a trend to have higher contents on the pretreated batch, except for acenaphthylene and Hg.

For the test on chemical analyses and metals, except for TOC, these deviations appear statistically significant when they reach 5% (for As). For the TOC, even with a deviation of 17.5% it is not statistically significant given the high dispersion of results. Note also the case of Cr, for which the deviation is particularly high with results on average higher than 40.5% on the pretreated batch.

For PAHs, the deviations observed ranged from 1.83% for benzo[a]pyrene to 38.16% for acenaphthylene.
The deviation is statistically significant for benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[g, h, i]perylene, chrysene, dibenzo[a, h]anthracene , indeno[1,2,3 - cd]pyrene, phenanthrene and pyrene, which correspond mostly to the heaviest PAHs. Conversely, for most PAHs which are lighter (acenaphthene, anthracene, benzo[k]fluoranthene, fluoranthene, fluorene, naphthalene and acephatylene), the means observed on the pretreated batch and the raw batch are not significantly different.

6. COMPARISON OF THE RESULTS BETWEEN A SPIKED MATRIX AND A NON-SPIKED MATRIX

For the organic micropollutants test (17M44.1), three batches have been prepared (see table below)
- batch 1 pretreated and spiked with PCBs
- batch 2 pretreated and not spiked
-batch 3 raw (to pretreat by laboratories) and not spiked

PT	17M44.1		
Batch	**Batch 1 (batch pretreated and spiked)**	**Batch 2 (batch pretreated)**	**Batch 3 (raw batch)**
Parameters	acenaphtene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3 - cd]pyrene, naphtalene, phenanthrene, pyrene, total hydrocarbons index, congener 28, congener 52, congener 101, congener 118, congener 138, congener 153, congener 180, acenaphtylene	dry matter, acenaphtene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3 - cd]pyrene, naphtalene, phenanthrene, pyrene, acenaphtylene	dry matter, acenaphtene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3 - cd]pyrene, naphtalene, phenanthrene, pyrene, acenaphtylene
Matrix used	soil from industrial wasteland		
Treatment	Dried crushed and sieved at 150µm	Dried crushed and sieved at 150µm	No pretreatment, raw matrix
Spiking	Spiked for all PCBs	no spiking	no spiking

In order to know the influence of the spiking carried out by AGLAE on the pretreated matrix, the results obtained on batches 1 and 2 were compared.

parameter	m batch 1 (pretreated and spiked in PCBs batch)	m batch 2 (pretreated batch)	Deviation in %	significantly different means ?	unit
acenaphtene	21,93	21,43	+2,34	NO	µg/kg of dry matter
anthracene	80,63	83,12	-2,99	NO	µg/kg of dry matter
benzo[a]anthracene	339,12	343,18	-1,18	YES	µg/kg of dry matter
benzo[a]pyrene	277,49	262,77	+5,60	NO	µg/kg of dry matter
benzo[b]fluoranthene	509,44	486,34	+4,75	NO	µg/kg of dry matter

parameter	m batch 1 (pretreated and spiked in PCBs batch)	m batch 2 (pretreated batch)	Deviation in %	significantly different means ?	unit
benzo[k]fluoranthene	168,58	163,74	+2,96	NO	µg/kg of dry matter
benzo[g,h,i]perylene	248,14	240,43	+3,21	NO	µg/kg of dry matter
chrysene	466,56	466,60	-0,01	NO	µg/kg of dry matter
dibenzo[a,h]anthracene	76,66	70,50	+8,75	NO	µg/kg of dry matter
fluoranthene	750,17	739,67	+1,42	NO	µg/kg of dry matter
fluorene	43,32	43,43	-0,26	NO	µg/kg of dry matter
indeno[1,2,3 - cd]pyrene	211,90	209,66	+1,07	NO	µg/kg of dry matter
naphtalene	75,15	73,41	+2,38	NO	µg/kg of dry matter
phenanthrene	696,43	689,13	+1,06	NO	µg/kg of dry matter
pyrene	562,81	594,05	-5,26	NO	µg/kg of dry matter
acenaphtylene	18,30	18,86	-2,97	NO	µg/kg of dry matter

The deviations observed between the raw and the pretreated batches are quite small (between 0.01% for chrysene and 8.75% for dibenzo[a,h]anthracene). A hypothesis test (signed rank test) was performed and showed that overall the means between the raw and the pretreated batches were not significantly different. For each parameter taken individually, the means are also not statistically different except for benzo [a] anthracene but the difference between the spiked and non-spiked batches remains very small (1.18%).
The spiking of the matrix had no impact on the analysis of the other parameters.

7. DISCUSSION AND CONCLUSION

These tests showed that the batch heterogeneity was significantly higher for the raw batches, which led to exclude two parameters on the raw batch during the chemical analyses and metals test. In the PAHs test the batch heterogeneity was also important on the raw batch, even up to 24% of coefficient of variation against 5.5% maximum on the pretreated batch.
The reproducibility of the results also tends to be higher on the raw batch for both tests. For PAHs, this trend is statistically significant and represents on average an additional dispersion of 17.5%.

These additional dispersion sources (interlaboratory error and batch heterogeneity) make the control less reliable because the acceptance limits of the results are based on the dispersion of the data. Analytical biases will be highlighted in a less precise way on a non-pretreated matrix upstream. It will therefore be necessary to implement more tests before being able to detect them. In addition, the majority of the bad results highlighted

are due to the "analysis" part and not to the pretreatment of the sample. These observations show that it is important to control the "analysis" part and therefore it is preferable to carry out proficiency tests on pretreated solid matrices than on raw matrices. The ideal is to be able to make controls on raw matrices, but may be with a lower frequency, but with the risk of not obtaining sufficiently homogeneous materials on the raw matrix.
It was also found that for both tests (chemical analyses and metals, and PAHs), the contents found by the participants tend to be lower on the raw batches than on the batches pretreated by AGLAE. They are even significantly lower on the raw batch for more than half of the parameters in both tests. The origin of this difference is probably due to the fact that AGLAE crushes and sieves the matrix at 150 µm, i.e. at a smaller particle size than that recommended in the standards (<250 µm). The laboratories therefore have access to a larger proportion of the compounds on the pretreated matrix than on that which they have themselves pretreated.

Finally, the fact of spiking the pretreated matrix has no impact on the analysis of other unspiked parameters present in the matrix; it does not lead to observe significantly different results.