The inherent variability of some environmental analytical methods hampers the circular economy of materials

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1. Supplementary Information

1.1 Part 1 Examples of skewed populations

Weight of objects to be reused in a civic amenity site (FR)

Citizens of the Pays d'Aix-en-Provence are invited to donate and freely reuse objects in a citizen waste recycling center called "donnerie" on the municipal waste recycling center of Meyreuil. For 5 months of 2021, the weight of the items or lots of items taken away was recorded. The distribution is shown in Figure SI 7 and the related Table (original data).

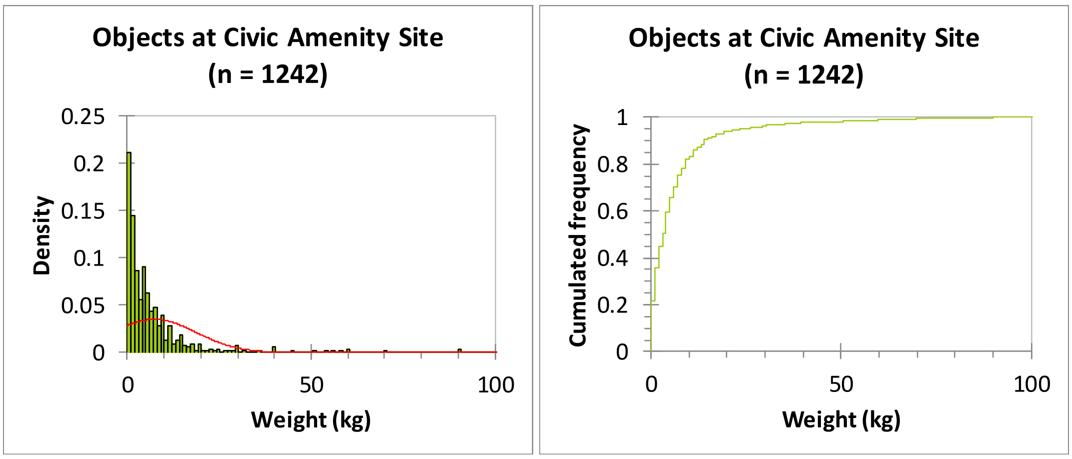


Figure SI 7: SI Distribution of populations – weight of objects that are reused at Civic Amenity Site (France). Red line: normal distribution with the same mean and standard deviation, clearly not fitting the data, with calculated negative values (these latter not shown)

Parameter	n	Minimum	Median	Mean	Maximum	CV	Normality
Mass (kg)	1242	0.03	3.3	7.4	100	1.54	No

Plastics prepared for solid recovered fuel (IT)

The mass and volume (projected horizontal area times width) of individual particles of plastics < 50 mm sorted to become a solid recovered fuel were measured to assess the form factor of this material for more precise sampling

Source: Pivato A, Beggio G, Hennebert P, Mensi C, Sisti M, Maggi L. 2022. Refining the calculation of the mass of solid waste samples: tentative estimation of the shape factor based on a large number of measurements of particles dimensions. SUM 2022 6th Symposium on circular economy and urban mining. Capri, Italy, 18-20 May 2022.)

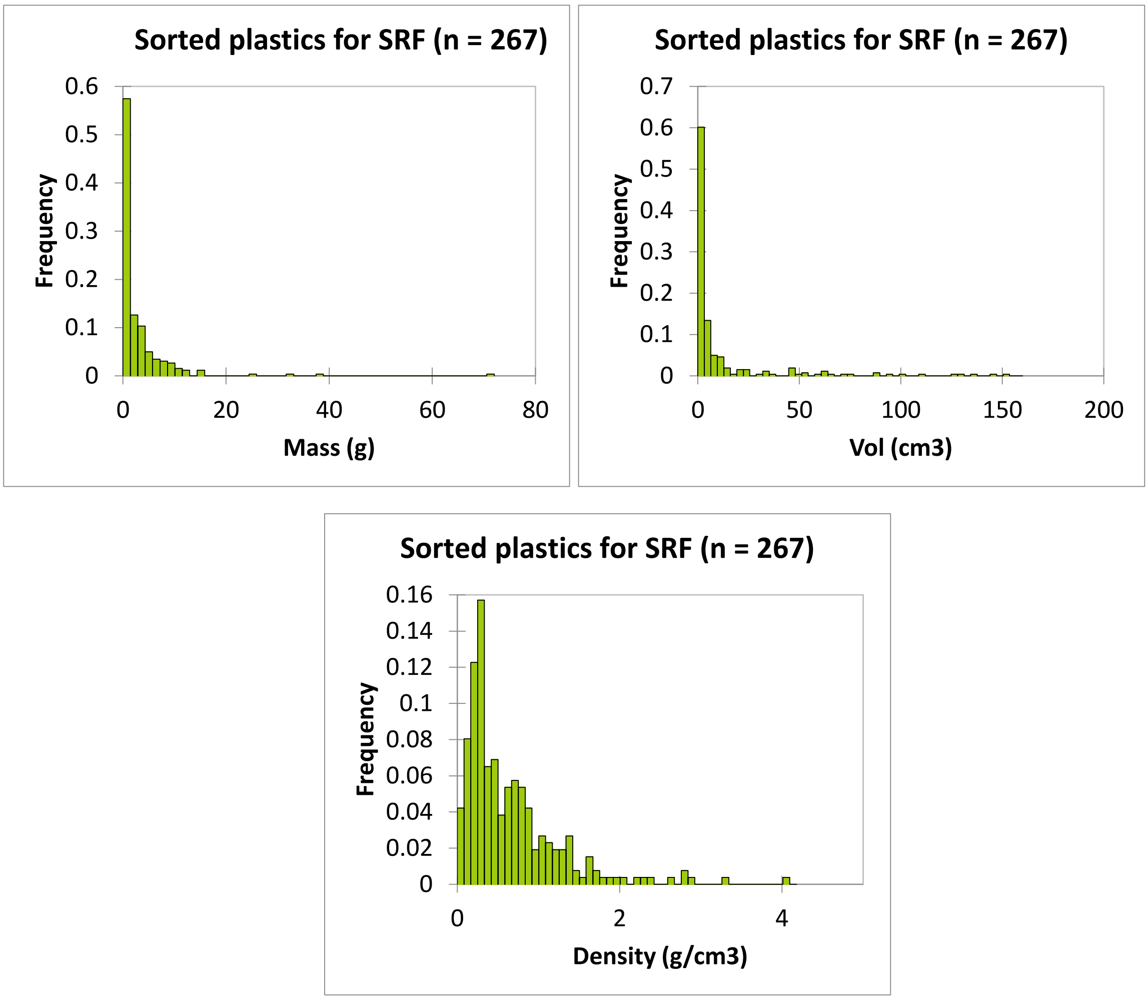


Figure SI 8: SI Distribution of population – volume, mass and density of plastic waste shreds (Italy)

Parameter	n	Minimum	Median	Mean	Maximum	CV	Normality
Volume (cm^3)	261	0.00	1.93	11.6	150.8	2.21	No
Mass (g)	261	0.010	1.000	2.99	71.00	2.05	No
Density (g / cm^3)	261	0.0211	0.440	0.656	4.080	0.92	No

Granulometry and chemical composition of marine sediments (FR)

From the French maritime ports monitoring network (REPOM) piloted by IFREMER and two sediment characterization and processing projects (PROPSED and SEDIMARD), Ineris has compiled a database of marine sediments (27,538 data for 818 samples, over a period from 1996 to 2008). Only 3 parameters out of 22 (particle size, TOC, TKN, 8 heavy metals, TPH, PAH, PCB, TBT) are normally distributed (n = 300 to 800). All CVs are > 0.50. Different distributions are shown in Figure SI 9. The same distribution patters were observed for fluvial sediments (not shown).

Source: Padox J-M, Hennebert P. 2010. Qualité chimique des sédiments marins en France : Synthèse des bases de données disponibles. Rapport d'étude INERIS-DRC-10-105335-11618A. 12/08/2010. https://www.ineris.fr/fr/qualite-chimique-des-sediments-marins-en-france-synthese-des-bases-de-donnees-disponibles

Padox J-M, Hennebert P. 2010. Qualité chimique des sédiments fluviaux en France : Synthèse des bases de données disponibles. Rapport d'étude INERIS-DRC-10-105335-04971A. 03/06/2010. 101 p. https://www.ineris.fr/sites/ineris.fr/files/contribution/Documents/r-10-04971a-action22.pdf

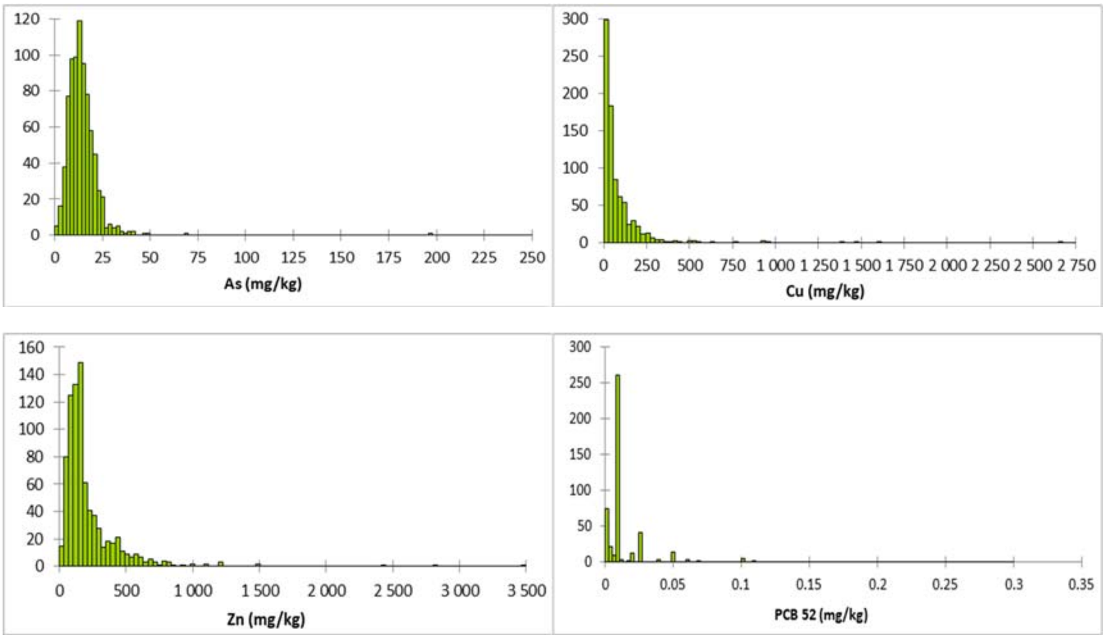


Figure SI 9: SI Distribution of populations – Total As, Cu, Zn and PCB 52 in marine sediments (France).

Parameter (mg/kg)	n	n ≤ LOQ (%)	Minimum	Median	Mean	Maximum	CVpopulation	Normal	Log-normal
As	791	0.25	0.09	13.0	13.85	196	0.666	Yes	No
Cu	817	0.73	2.00	41.3	85.2	2 651	1.88	No	Yes
Zn	813	-	1.54	150	219	3 493	1.137	No	No
PCB 52	107	70.1	1.00E-05	0.010	0.015	0.260	1.48	No	No

Other illustrated examples of skewed population are bromine in plastic scraps of waste of electrical and electronic equipment (WEEE) (Hennebert and Beggio 2021) printed circuit boards, fly ash, solid recovered fuel from municipal solid waste and tires (Beggio and Hennebert 2022, supplementary information).

Processed waste (fly ashes and bottom ashes)

a) <u>Chemical composition of municipal solid waste incinerator bottom ash (MSWI) fly ash (DK)</u>

A population of fly ash is presented in the validation data of Danish standard DS 3007 Horizontal sampling. Eight composite samples have been analysed for 26 parameters. The individual concentrations are not published in the validation data of the standard (and hence the distributions can not be presented), but well the mean concentration and their CV (sampling + analysis).

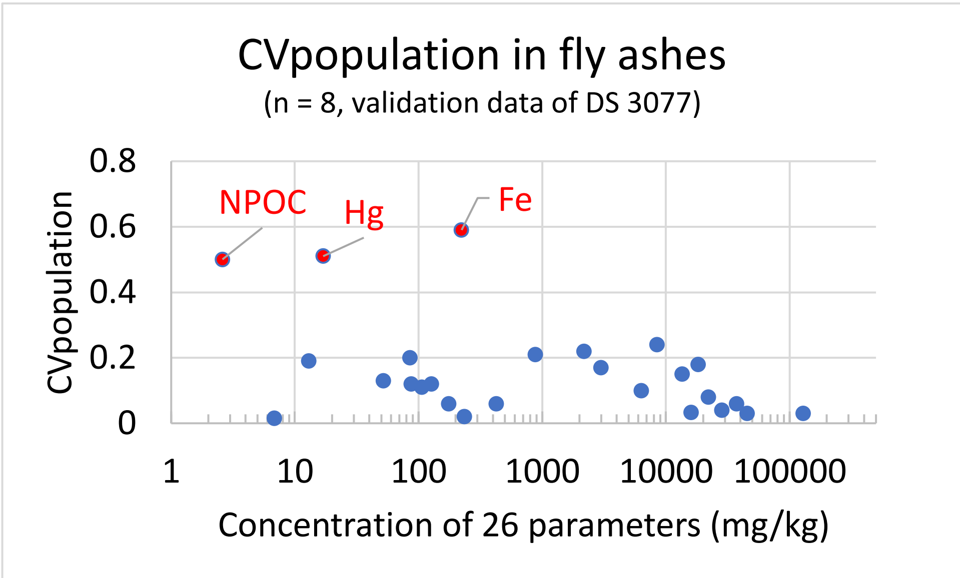


Figure SI 11: SI Distribution of populations – Total concentration of 26 parameters in 8 samples of MSWI fly ash of one incinerator (validation data of DS 3007) (Denmark). NPOC = non purgeable organic carbon.

According to their CV ≥ 0.5, non-purgeable organic carbon, mercury and iron are probably not normally distributed in the 8 composite samples. Hg is volatile and metallic iron is not crucible with classical laboratory equipment from the laboratory sample to the test portion. The other parameters with $CV_{population}$ ≤ 0.20 are probably normally distributed: no large values that increase the standard deviation are present.

b) <u>Shape of fine fractions of municipal solid waste incinerator bottom ash (MSWI BA) (IT)</u>

For sampling question, the shape of individual fine particles of MSWI BA (sample from Italy) has been individually analysed by an automated 3D imaging granulometer (Courtesy of Dr Thibault de Garidel-Thoron, CNRD, CEREGE Centre Européen de Recherche et d’Enseignement des Géosciences de l’Environnement, Aix-en-Provence, France). Some results of the ratio of 2D projected area of one particle by 2D calculated circle that includes that particle are presented in Figure SI 10:

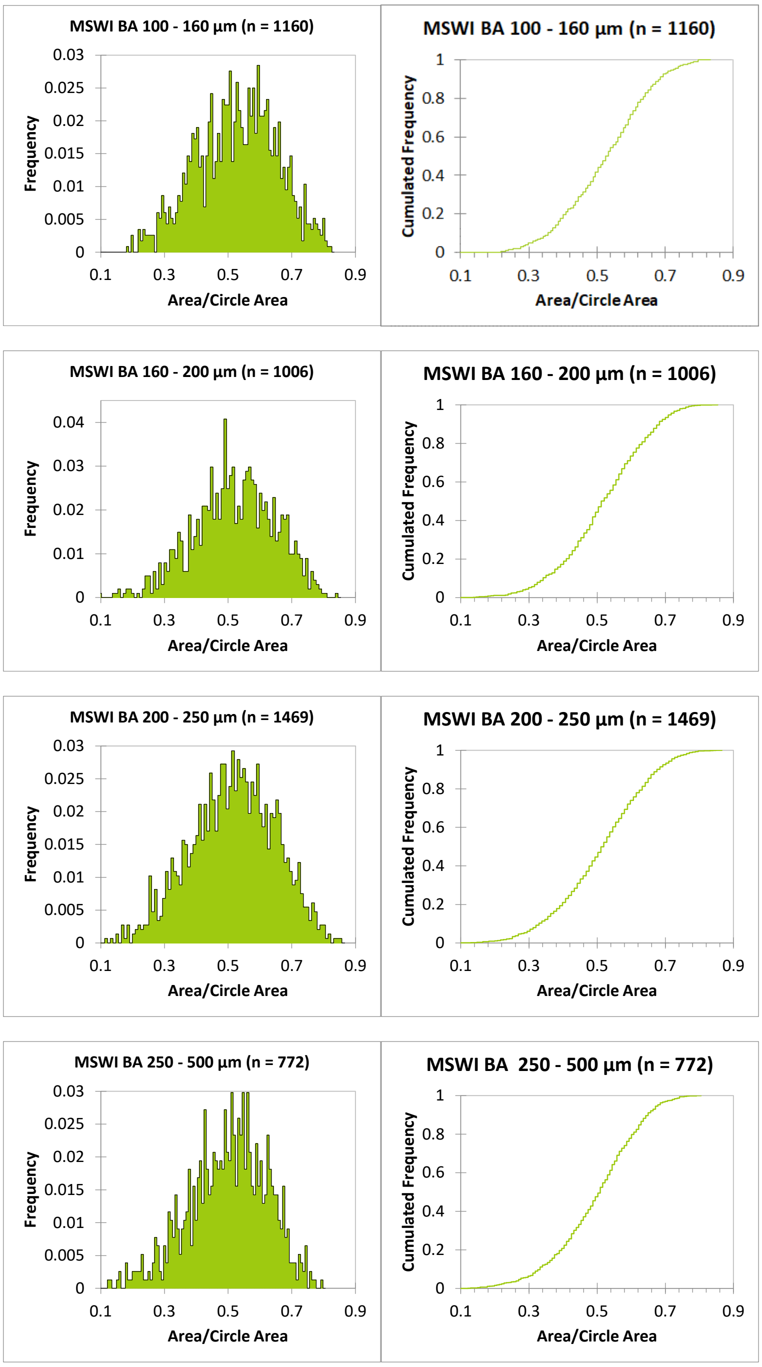


Figure SI 10: SI Distribution of populations – Ratio area/enclosing circle area of particles of different size in bottom ashes fine fractions (Italy).

Area/Enclosing circle area	n	Minimum	Median	Mean	Maximum	$CV_{population}$	Normality
100-160 µm	1160	0.181	0.532	0.527	0.823	0.239	Yes
160-200 µm	1006	0.094	0.520	0.521	0.844	0.243	Yes
200-250 µm	1469	0.050	0.520	0.515	0.856	0.257	Yes
250-500 µm	772	0.127	0.510	0.500	0.795	0.245	Yes

It can be suggested from these two cases that processed waste are more homogeneous and probably more frequently normal that unprocessed waste.

1.2 Part 2 The steps of representative sampling and analyses of waste

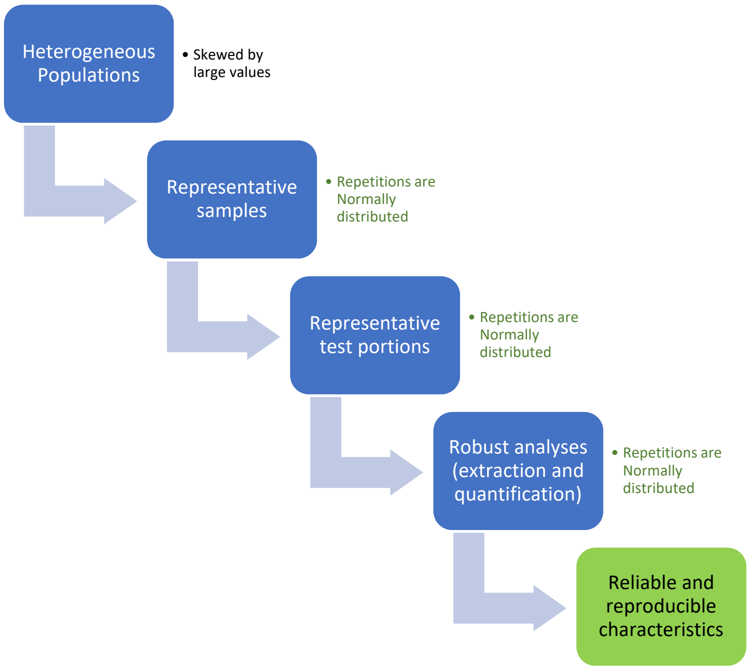


Figure SI 12: SI The steps from heterogeneous populations to reliable and reproducible characteristics

The total variance is the addition of the variance of each step.

This paper is dealing with the last step: Robust analyses (extraction and quantification) of homogeneous test portions.

1.3 Part 3 Reduction of variability by pretreatment of laboratory sample up to the test portion

Distribution of lead concentration in test portions from a same composite sample from a polluted site before and after pre-treatment is presented in Figure SI 13 (recalculated from Lamé et al. 2005). Before pretreatment, one test portion has a concentration of 125 000 mg Pb/kg.

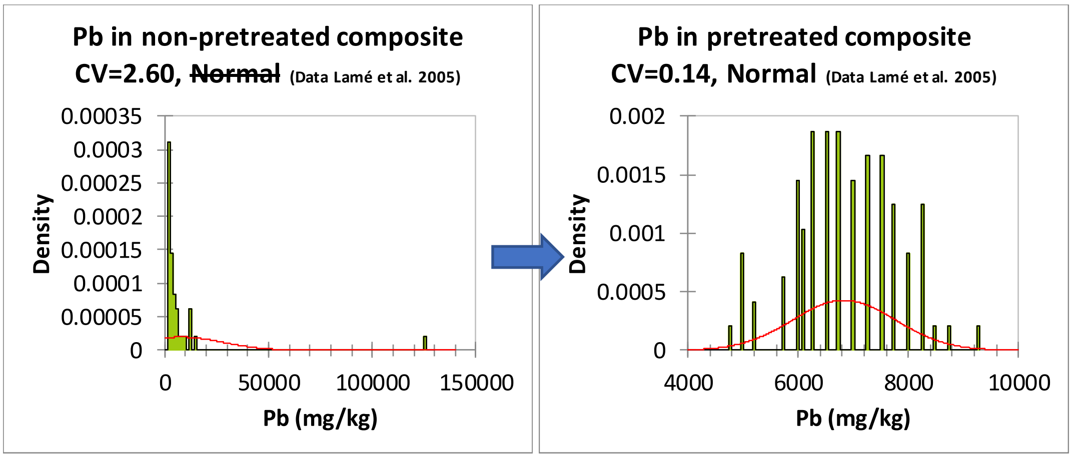


Figure SI 13: SI From heterogeneous sample to representative sample (at the scale of the test portion)

Variable	n	Minimum	Maximum	Mean	SD	CV	Normality (4 tests)
Non-pretreated Composite	37	1750	125000	7743	20124	2.60	No (4/4)
Pretreated Composite	91	4750	9250	6832	935	0.14	Yes (4/4)

The pretreatment homogenises the material at the test portion scale and dissipates the variability. Repetitions are normally distributed in a narrow range of concentration: $CV_{analysis}$ is reduced from 2.60 to 0.14.

Source: Lamé F, Honders T, Derksen G, Gadella M. 2005. Validated sampling strategy for assessing contaminants in soil stockpiles. Environmental Pollution 134 (2005) 5–11.

1.4 Part 4 Variability of normal (gaussian) distribution

The Figure SI 14 shows the spreading of a normal distribution with increasing CV from 0.20 to 0.50, illustrating that a limit to the variability must be set for analytical methods. The part of the values that are included in the very large interval [zero – two times the mean] is indicated: 100% for CV = 0.20, 95.4% for CV = 0.50. For CV = 0.60, 1.00 and 1.50, the parts of the values that lie within [0 x; 2 x] are 90.4%, 68.3% and 49.5%, respectively (not shown).

For the accelerated percolation test prEN 16637-3 (see main document), the elements have a mean CV = 0.57, meaning that if they were normally distributed, 92.1% of the values would lie within [0 x; 2 x]. For the organics, the mean CV = 0.79 and only 79.4% of the values would lie within [0 x; 2 x].

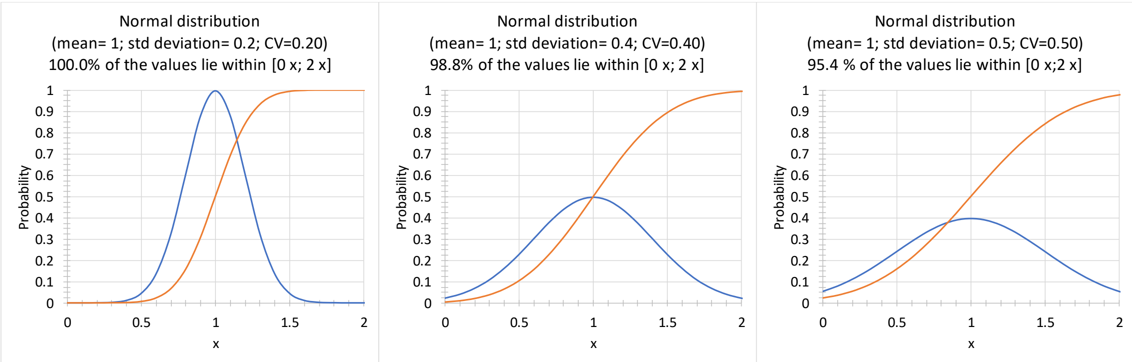


Figure SI 14: SI The normal distribution with mean = 1 and coefficients of variation CV = 0.2, 0.4 and 0.5 (blue line: probability density; red line: cumulated frequency)

1.5 Part 5 Literature evidence of the presence of a colloidal fraction in different leaching tests (literature data)

Table SI3: SI Literature data on colloidal fraction of different leaching tests (not only EN 12457 series)

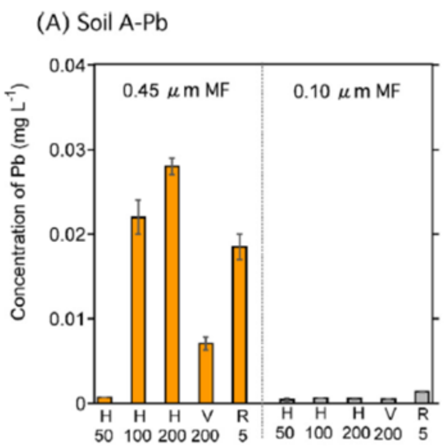
Literature data on colloidal fraction of elements and PAHs and PCBs of leaching tests (EN 12457 series and others)

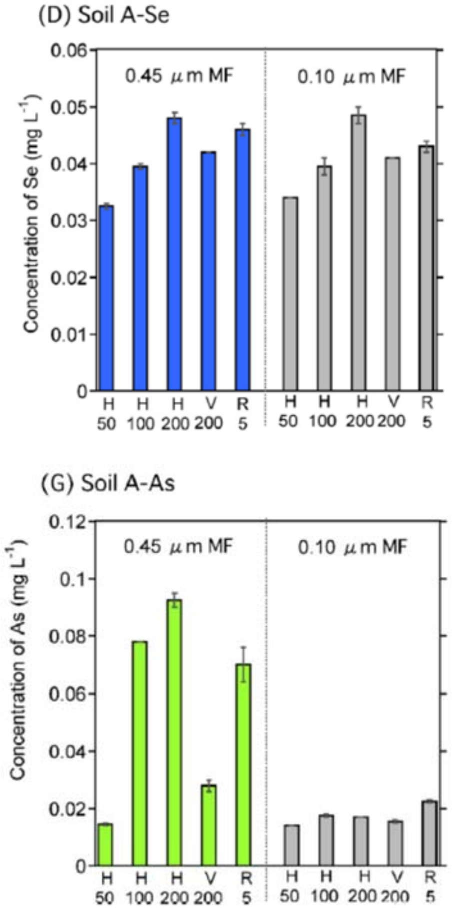
Ref n°1: Agitation mode (horizontal shaking, vertical shaking, rotation, speed) influences the 0.45 µm- and the 0.10 µm-filtered leachate concentration

Ref n°2 to 4: Of 134 waste leachates, there is always at least one element that is colloidal (0.45 µm-cc > 1.5 x 0.003 µm-cc), up to 100% of the 0.45 µm-cc

Ref n°5, 6: The colloidal fraction of PAHs and PCBs are respectively >20 times and > 100 times higher than the soluble fraction in 5 sediments

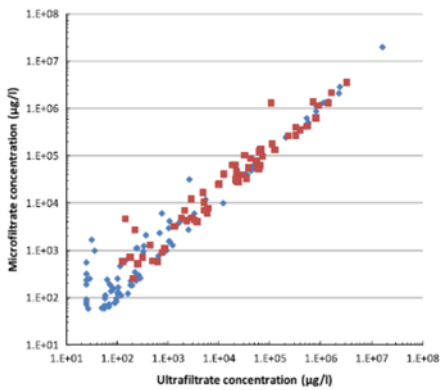
Ref n°7 to 10: The colloidal organic carbon (called dissolved organic carbon – DOM in LeachXS) is a major vector of elements, especially at pH > 10

N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
1	Contaminated soils	Demineralized water L/S 10 l/kg Different agitation methods and time, Settling 15 min, Centrifuged 1700 g (3000 rpm) for 20 min, filtration 0.45 µm or 0.10 µm, analysis	*However, agitating certain types of soil and then passing the solution through a membrane filter with 0.45-mm pores yields filtrates that have been colored by the colloidal particles. These colloids might affect the results of the inorganic substances obtained in the batch tests.... The As and Pb concentrations in the leachates of some types of soil were*		(Yasutaka et al., 2017) Yasutaka, T., Imoto, Y., Kurosawa, A., Someya, M., Higashino, K., Kalbe, U., Sakanakura, H., 2017. Effects of colloidal particles on the results and reproducibility of batch leaching tests for heavy metal-contaminated soil. Soils Found. 57, 861–871. https://doi.org/10.1016/j.sandf.2017.08.014

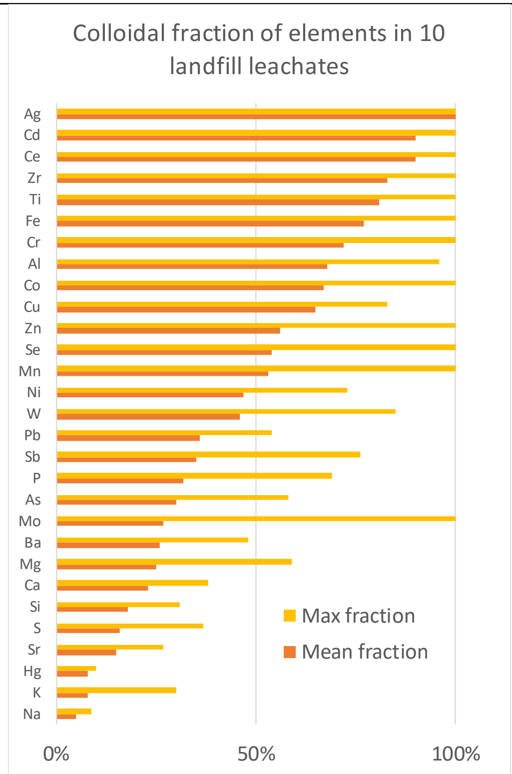
N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
			clearly affected by the amount of colloidal particles with a diameter of 0.10–0.45 mm and by the agitation method used. This was probably because As and Pb were present mainly in the particulate form in the leachate that had been passed through a membrane filter with 0.45-mm pores. This is not the case for every type of soil. The results of batch leaching tests showed that not only dissolved but also colloidal forms with a diameter of 0.10–0.45 mm might be included and that the existence of colloidal particles in the leachate decreases the batch leaching test reproducibility. *Batch tests are used as compliance tests in several countries, and the results are compared with*	 *Fig. 3. Pb, Se and As concentrations in the extracts of soils A, B, and C when different agitation methods and membrane filter (MF) pore diameters were used. x-axis labels H, V and R mean horizontal shaking,*	

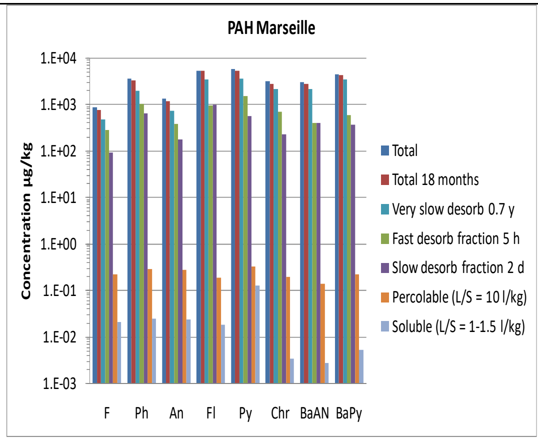
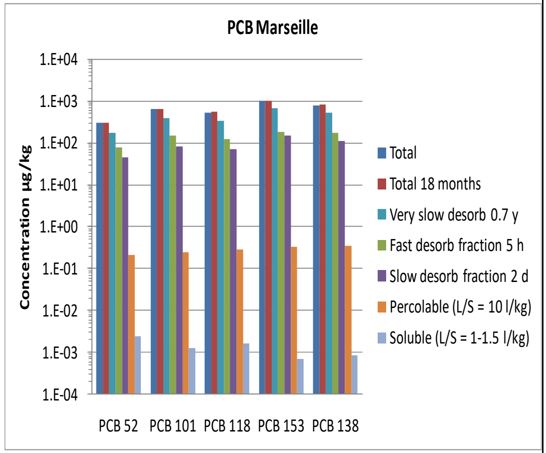
N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
			threshold values to assess the environmental impacts. The results of batch tests used in this way need to be very reproducible and reliable for all types of soil. The results of this study and other studies indicate that the reproducibility of a batch test will be affected by the amount of colloidal particles in the filtrate and that the amount of colloidal particles present will be controlled not only by the soil type, but also by the agitation method (i.e., agitation time, frequency, method and direction). *The results of batch leaching tests showed that not only dissolved but also colloidal forms with a diameter of 0.10–0.45 mm might be included and that the existence of colloidal*	*vertical shaking and rotation, respectively, and the numbers below them indicate the speed of the shaking/rotation in rpm.*	

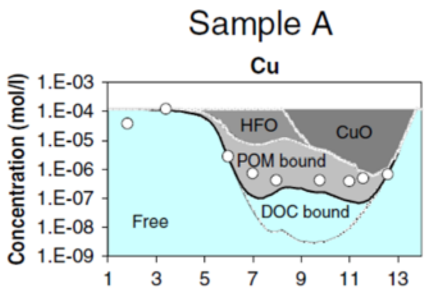
N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
			particles in the leachate decreases the batch leaching test reproducibility. Note 1: The difference between the 0.45µm-filtered fraction and the 0.10 µm-filtered fraction is a colloidal fraction Note 2: - Agitation mode: H horizontal, V vertical, R rotating - Energy: 50, 100, 200, 200, 5 indicates the speed of shaking/rotation in rpm.		

N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
2	25 waste leachates MSWI APC residue, fly ash, bottom ash, industrial APC residue, bottom ash, steel slag, metallic dust, bauxite residue, waste packaging, compost, sediments, soils, landfill leachate	EN 12457-2, settling 15 min, cascade microfiltration 0.45 µm and ultrafiltration 3 KDa.	*Mn, As, Co, Pb, Sn, Zn had always a colloidal form (MF concentration/UF concentration > 1.5) and total organic carbon (TOC), Fe, P, Ba, Cr, Cu, Ni are partly colloidal for more than half of the samples. Nearly all the micro-pollutants (As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V and Zn) were found at least once in colloidal form greater than 100 µg/L. In particular, the colloidal forms of Zn were always by far more concentrated than its dissolved form… All the waste had at least one element detected as colloidal. The solid waste leachates contained significant amount of colloids different in elemental composition from natural ones. … Standardized cross-filtration method could*		(Hennebert et al., 2013) Hennebert, P., Avellan, A., Yan, J., Aguerre-Chariol, O., 2013. Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. Waste Manag. 33. https://doi.org/10.1016/j.wasman.2013.04.014

N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
			be amended for the presence of colloids in waste leachates. Note: the colloidal fraction is represented as the difference between the “microfiltrate” (MF) and the “ultrafiltrate” (UF) concentrations, on log scale		
3, 4	MSWI BA, Sunscreens, Paints, Construction and Demolition waste, Landfill leachates	EN 12457-2, settling 15 min, cascade microfiltration 0.45 µm and ultrafiltration 3 KDa.	*Paints, concrete and particularly cosmetics proved to be sources of ENPs. Colloidal forms of elements or ENPs were found in leachate obtained from paint (Si), in cosmetics leachates (Al, Si, Ti and Zn), and in one demolition concrete (Ti). In non-hazardous landfill leachates, all elements have a colloidal fraction (Figure).* Note: laboratory leachates of solid landfill leachate sludge		(Hennebert et al., 2017) Hennebert, P., Merdy, P., 2017. Mineral Colloids and Nanoparticles in Municipal Solid Waste Incinerator Bottom Ashes and Sunscreens, in: Sardinia 2017 – 16th International Waste Management and Landfill Symposium. Hennebert P, Anderson A, Merdy P. 2017. Mineral nanoparticles in waste: potential sources, occurrence in some engineered nanomaterials leachates, municipal sewage sludges and municipal landfill sludges. J Biotechnol Biomater 2017, 7:2. 12 p.

N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
			(produced by filtration or decantation in ponds), or liquid leachates of landfill (in decantation ponds)	 Max fraction = maximum colloidal fraction observed per element among 10 landfill leachates Mean fraction = mean colloidal fraction observed per element among 10 landfill leachates	

N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
5, 6	5 marine and fluvial sediments		*Percolated PAHs are correlated with DOC and humic acids, and PCBs with neutral hydrophobic carbon.* Note: the colloidal fraction is represented as the difference between the "percolable" and the "soluble" fraction, on log scale.	 	(Charrasse et al. 2013), (Hennebert et al. 2014) Charrasse B, Tixier C, Hennebert P, Doumenq P. 2013. Polyethylene passive samplers to determine sediment–pore water distribution coefficients of persistent organic pollutants in five heavily contaminated dredged sediments. Sci Total Environ (2013), http://dx.doi.org/10.1016/j.scitotenv.2013.10.125 Hennebert P, Charrasse B, Doumenq P, Tixier C. 2014. Biodegradable, labile, leachable, dissolved, colloidal and calculated fractions of hydrophobic organic contaminants of five sediments. 4th International Symposium on Sediment Management (I2SM). Ferrara (Italy). 17/09/2014. 9 p.

N	Matrix	Leaching test	Citation on colloidal fraction in leachate	Example	Reference; yellow: members of WG1 Leaching tests of CEN TC 444
7	Construction debris, concrete pavement	pH dependent batch leaching test CEN/TS 14429	*The importance of complexation to humic substances was also shown in samples derived from construction debris.* Note: the colloidal fraction is represented as "DOC bound" in the figure, on log scale		(López Meza et al., 2010) López Meza, S., Kalbe, U., Berger, W., Simon, F.G., 2010. Effect of contact time on the release of contaminants from granular waste materials during column leaching experiments. Waste Manag. 30, 565–571. https://doi.org/10.1016/j.wasman.2009.11.022

1.6 Part 6 Experimental evidence of colloids and nanoparticles in leachates and effect on parameter concentrations

Material and method

Number and size of particles

An experiment conducted at the University of Toulon (France) assessed the influence of the centrifugation step on the number and the size of particles passing through the filtration membrane (Table 1). The number and size of particles were assessed by a Nanoparticle Track Analyzer immediately after filtration of the different (fraction) volumes.

Table SI 1: Experimental design for the number and size of particles

Sample	Dredged canal contaminated waste sediment (north of France), air dried	Experiment by Patricia Merdy, University of Toulon (FR)
Leaching	EN 12457-2: sieving < 4 mm, 24 h rotary tumbler, L/S= 10 L deionised water	
Solid/liquid separation	*Decantation-Centrifugation-Filtration (C)* Annex E of EN 12457	*Decantation- Filtration (NC)*
	1. Decantation 15 min	1. Decantation 15 min
	2. Centrifugation 30 min 2000 g	2. - no centrifugation
	3. Front Filtration 0.45 µm membrane vacuum	3. Front Filtration 0.45 µm membrane vacuum

Turbidity and concentration of elements

An experiment conducted at Eurofins lab in Saverne (France) is described in Table 2, to assess the influence of the centrifugation step on the leachates' turbidity and concentration for the EU landfill acceptance parameters.

Twenty-seven samples were used in different batches and their leachate analysed for 20 parameters:

- Turbidity and physico-chemical parameters (electrochemistry and titration analyzers)
- dry residue (gravimetry)
- anions (TOC-meter, spectrophotometry)
- inorganic elements (12 heavy metals by ICPMS)

The experimental design is presented in Table 2.

Twenty parameters for landfill acceptance of waste were measured. The values lower than the limit of quantification for centrifugated or non-centrifugated fraction or both were NOT used, as done for the assessment of validation trials.

Table SI 2: Experimental design and result

Samples (27)	Waste (4), Sludge (2), Sediment (6), Soil (15)	
Leaching	**EN 12457-2: sieving < 4 mm, 24 h rotary tumbler 10 rpm, L/S= 10 L deionised water, filtration 0.45 µm membrane**	
	Test 1	Test 2
Solid/liquid separation	*Decantation-Centrifugation-Filtration (C)* Annex E of EN 12457	*Decantation- Filtration (NC)*
	1. Decantation 15 min	1. Decantation 15 min
	2. Centrifugation 4min 3500 g /	2. no centrifugation

	3. Turbidity measurement (12 samples)	**3. Turbidity measurement (12 samples)**
	4. Front Filtration 0.45 µm membrane (automated high-pressure filter) of 300 ml	4. Front Filtration 0.45 µm membrane (automated high-pressure filter) of 300 ml
	5. Turbidity measurement (12 samples)	**5. Turbidity measurement (12 samples)**
	6. Parameters and elements analysis (27 samples)	6. Parameters and elements analysis (sampoles)

It must be noted that 300 ml, so not all the volume of the leachate has been filtered. The volume for the analyses is about 150 ml.

Results

<u>Size and number of colloids and (nano)particles in a leachate of sediment</u>

The results are presented in Table 3 and Figure 15.

Table SI 3: Particles in leachates with or without centrifugation

Solid/liquid separation	**Decantation-Centrifugation-Filtration (Annex E of EN 12457) (C)**	**Decantation-Filtration (NC)**	**C / NC**
Filter cake (g) after 100 ml	0.002	2.128	*0.001*
Number of particles (n/ml)			
0 - 50 ml	1.1E+08	4.2E+07	*2.5*
50 - 100 ml	1.9E+08	3.8E+07	*4.8*
Size of particles (D_{50} nm)			
0 - 50 ml	157	141	*1.1*
50 - 100 ml	143	121	*1.2*
Size of particles (D_{90} nm)			
0 - 50 ml	243	207	*1.2*
50 - 100 ml	234	212	*1.1*

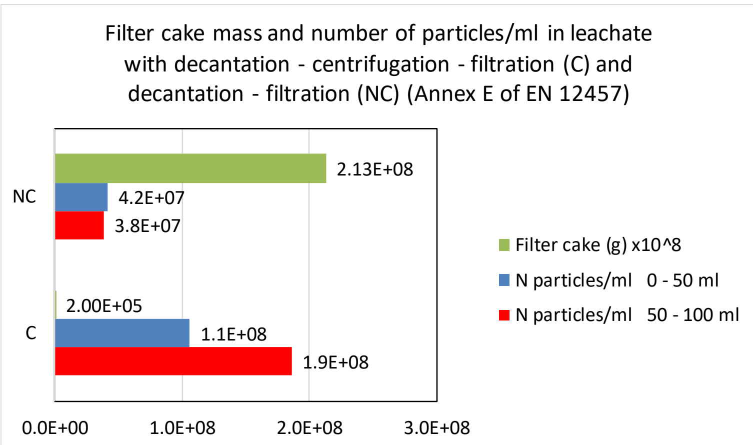


Figure SI 15: Filter cake and number of particles of a sediment leachate after decantation, centrifugation and filtration (C) and decantation and filtration (NC)

The results show that:

- There is practically no filter cake after preliminary centrifugation (2 mg vs 2 g);
- All particles have a size < 0.45 µm, indicating that there are no leaks in the filter membranes;
- There are more and larger particles with centrifugation;
- The difference in number of particles increases as the filtered volume increases.

Conclusion:

- There are particles in leachates filtered < 0.45 µm
- The centrifugation prior to filtration counter-intuitively increases the number and the size of particles in the leachate

<u>Turbidity</u>

Turbidity before filtration

The turbidity after decantation and centrifugation is available for 12 samples and is 15% of the turbidity after decantation (without centrifugation).

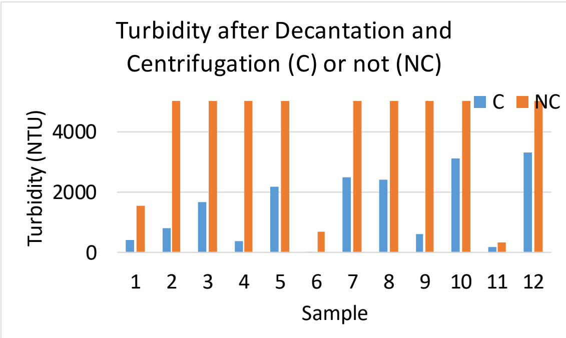


Figure SI 16: Turbidity after decantation for 12 samples

Turbidity after filtration

The turbidity after decantation, centrifugation and filtration is available for 12 samples and is in mean equal to the turbidity after decantation and filtration (lower for some samples and higher for others).

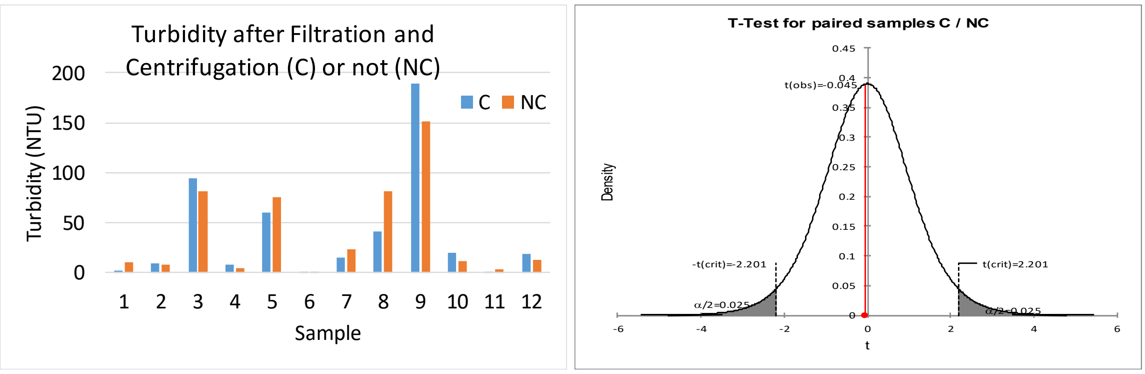


Figure SI 17: Turbidity after filtration for 12 samples

Conclusion on turbidity:

- as the centrifugation has no influence of the turbidity after filtration, the turbidity (after decantation) cannot be used as an indicator of the need of centrifugation of the leachate;
- the turbidity (after decantation) could be an indicator of the thickness of the filtration cake (that acts as a second filter) but that thickness (after 300 ml) has not been measured.
-

<u>Parameters and elements</u>

With 287 pairs of data (where C and/or NC are > LOQ), the distribution of the ratio [concentration C (centrifugation + filtration) / concentration NC (no centrifugation + filtration)] and its statistical analysis are presented in Figure 5 and Table 4.

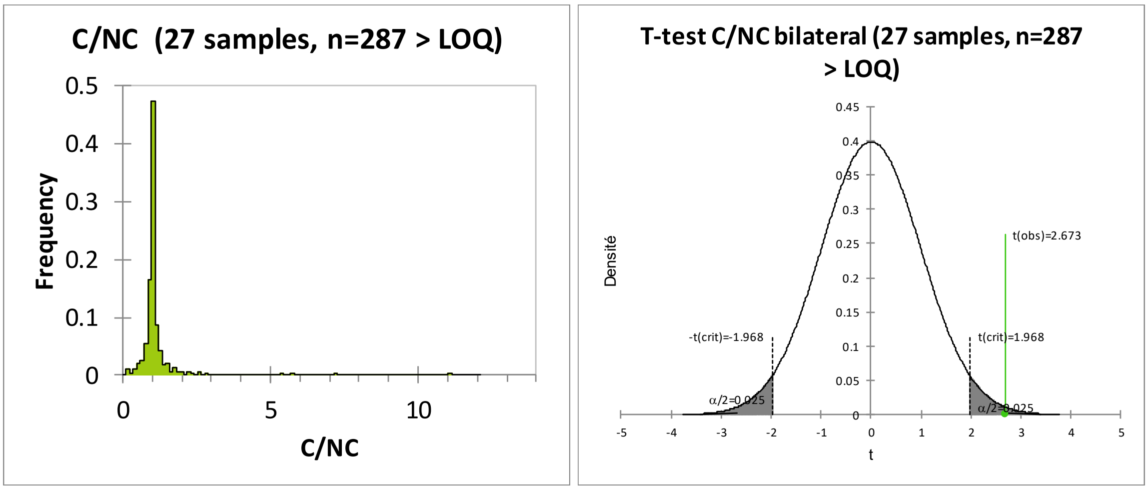


Figure SI 18: The mean centrifugated concentration is higher than the mean non-centrifugated concentration (the ratio (C/NC) is significantly higher than 1) (pair of data C/NC) (p = 0.008)

Table SI 4: Statistical analysis of the centrifugated/non centrifugated (C/NC) ratios of concentration T-test for one sample (bilateral).

Variable	Observations (paired samples)	Minimum	Maximum	Mean	Standard deviation
C/NC	287	0.150	11.098	1.134	0.850

Difference	0.134
t observed	2.673
|t| (Critical value)	1.968
DF	286
p-value (bilateral)	0.008
alpha	0.05

The 95% confidence interval of the mean C/NC ratio is [1.035 ; 1.233].

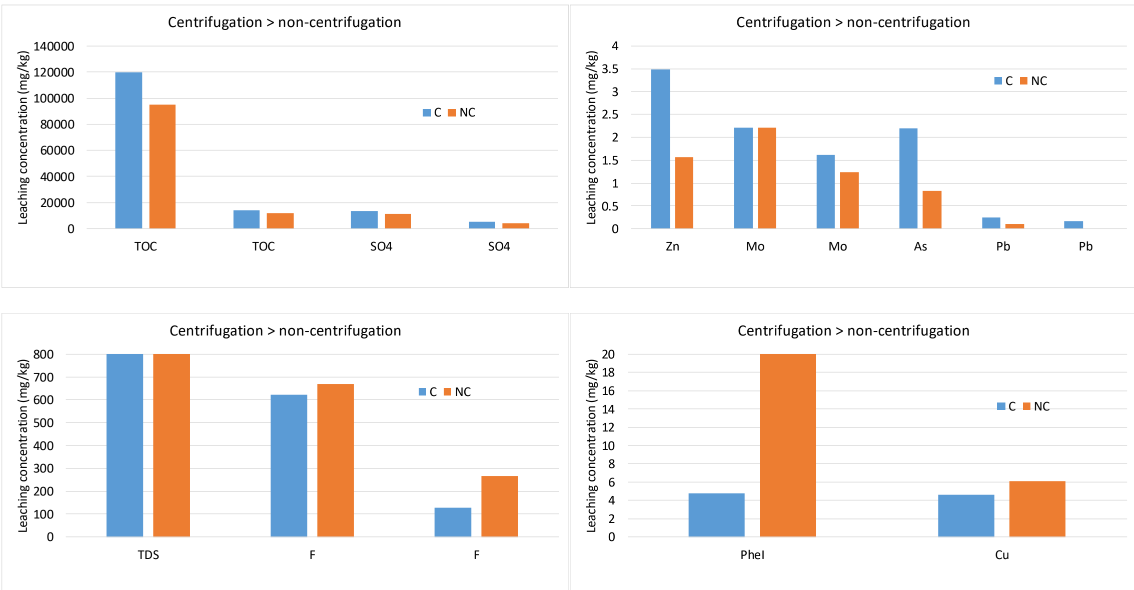
This set of 287 paired data from 27 samples confirms what was found by the number of particles. A leachate that is centrifuged and then filtered is counter-intuitively 13% MORE concentrated than a leachate that is only filtered.

Parameters with high concentration

For high concentrations, the effect of centrifugation depends on the parameters or elements. When the element is present in the leachate in significant concentration (the concentration is > 1 mg/kg for TDS, TOC, SO4, F, Zn, Ni, Phenol Index, Cu, Ba, Zn, Mo, As, as observed here, and the concentration is > LOQ for Pb, Cr and Cd), the centrifugation prior to filtration increases or decrease the value or concentration of the parameters or elements (results with 12 samples). Four types of effect can be distinguished (Table 5, Figure 6). The effect of centrifugation cannot be predicted.

Table SI 5: Effect of centrifugation on ratios of parameters (data of 12 samples)

Parameters	**Concentration (with centrifugation) > Concentration (without centrifugation) C > NC**	**C < NC**	**C < or > NC (depending on samples)**	**C = NC**
Physico-chemical	-	EC (2 samples) TDS (1 sample)	-	pH
Organics	TOC (2 samples)	Phenol Index (1 sample)	-	
Anions	SO4 (2 samples)	F (2 samples)	-	Cl
Heavy metals	As (1 sample) Cd (1 sample) Mo (1 sample) Pb (4 samples) Zn (2 samples)	Cu (1 sample)	Ba (2 samples) Cr (2 samples) Ni (4 samples)	Hg Sb Se



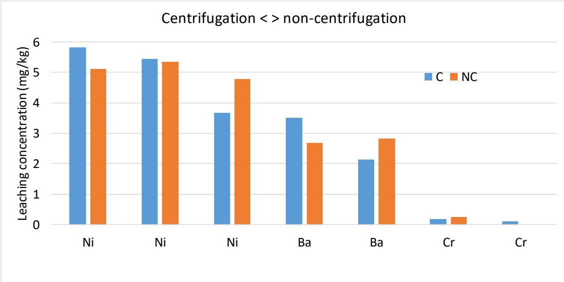


Figure SI 19: The effect of centrifugation for the highest concentrations depends on the parameters

Conclusion

The build-up of a filter cake generates an uncontrolled additional filtration. Preliminary centrifugation avoids the build-up of that filter cake. With the accumulation of a filter cake (without a centrifugation step), fewer particles are present in the leachate and they are smaller (all < 0.45 µm, reduction of 63% in number, and reduction of 13% in size). As these particles contain elements (shown in 100 waste leachates, Hennebert et al. 2013, 2017), it is expected that the concentration of the elements in the leachate will be lower without centrifugation.

In a set of 27 samples and 20 parameters, with 287 paired values higher than the limit of quantification,

- the turbidity (after decantation) cannot be used as an indicator of the need of centrifugation of the leachate;
- the concentrations in the centrifugated leachates are in mean 13% higher;
- the effect of centrifugation on concentration of one element for one sample with "high" concentration is not predictable.

Therefore, the variability and reduction of concentration created by the filter cake should be fixed. More reproducible (intra- and interlaboratory) leach test results could be obtained with a fixed and well defined solid / liquid separation (in accordance with Annex E of the EN 12457 series, without any additive).

References

Hennebert P, Avellan A, Yan J, Aguerre-Chariol O. 2013. Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. Waste Management 33 (2013) 1870–1881.

Hennebert P, Anderson A, Merdy P. 2017. Mineral nanoparticles in waste: potential sources, occurrence in some engineered nanomaterials leachates, municipal sewage sludges and municipal landfill sludges. J Biotechnol Biomater 2017, 7:2. 12 p.

ISO 2016. Document ISO/TC 147/SC 2 N 1567. Date: 2016-02-08. Guidance document on designing an interlaboratory trial for validation of analytical methods within ISO/TC 147/SC 2

1.7 Part 7: Characterisation of analyses by their intensity of extraction

Table SI 6 : SI Characterisation of analyses with partial extraction, mild extraction, total extraction

Extraction	Partial	Mild	Total
Extracted fraction	Soluble	Partial - Available - Bio-available	Pseudo total - Total
Domain	Environment (short-term)	Agriculture - Biology - Risk assessment	Environment (long-term) - Geology
Grain size	Minimal modification	Ground	Finely ground < 150 µm
Mass of test portion (typical)	> 100 g	100 - 10 g	< 10 g
Extraction liquid	Deionised water	Diluted extractants solutions	Strong acids or bases
Temperature	20°C	up to 100°C	> 100°C
Agitation energy	Low	Medium	High, Thermal
Time	24 h - 1 week	1 h	1 h to some minutes
Solid/liquid separation procedure	Critical	Critical	Particles are dissolved, Decantation
Presence of particles, and colloids in the filtrate	Presence, Critical	Presence, Critical	No presence
Part of total content	<1%	<1 - 50% ?	>90%
Tests	Leaching tests (EN 12457)	pH-dependence test (EN 14997)	Total dissolution (HF, Alkaline attack)
	Percolation tests (EN 14405)	(Bio)available fraction tests	Pseudo-total dissolution (Aqua Regia)
	Ecotox tests (EN ISO 11348-3, EN ISO 8692, ISO 18187, ISO 17512-1)	Extractible fraction (CN-, Phenols)	Total organics: PAH, PCB, PCDD/F
Intra-laboratory variability CVr and inter-laboratory variability CVR	**High**	**Medium**	**Low**
Reported mean CVr and CVR (validation data of standards)	**0.17 / 0.36** **(leaching tests)**	**0.20 / 0.25 (ecotox tests, no extraction)**	**0.10 / 0.24 (total elements and organics)**