Environment and Health

Interlaboratory Study on the Analysis of Short-Chain Chlorinated Paraffins in Environmental Matrices

Phase IV

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Abbreviations and acronyms

AV	assigned value
CP	chlorinated paraffins
CV	coefficient of variation
ECD	electron capture detector
ECNI	electron capture negative ion
E&H	VU Dep. Environment and Health
EI	electron ionization
GC	gas chromatography
GC×GC	comprehensive two dimensional gas chromatography
HRMS	high resolution mass spectrometry
ILS	interlaboratory study
IVM	Institute for Environmental Studies
LRMS	low resolution mass spectrometry
MCCP	medium-chained chlorinated paraffin
MS	mass spectrometry
MS/MS	tandem mass spectrometry
POP	persistent organic pollutant
QUASIMEME	Quality Assurance of Information for Marine Environmental Monitoring in Europe
SCCP	short-chained chlorinated paraffin
TOF	time of flight
ww	weight

Summary

The fourth round of the QUASIMEME interlaboratory study (ILS) on SCCP analysis was carried out, which consisted of the determination of the sum concentrations of SCCPs in a test solution and three different naturally contaminated environmental extracts (dust, soil and biota).

In total, 12 laboratories participated of which eight were able to submit data. Participants analysed the test materials by the quantification standard provided and/or by their own quantification standards. They applied numerous instrumental and quantification techniques for determination. The GC-ECNI-LRMS was the most commonly applied instrument, while using the linear relationship between response factor and chlorine content was most commonly applied as quantification procedure. For the first time in the ILS rounds, the novel method on the TOF in combination with deconvolution was applied too.

The fish extract showed to be the most difficult extract with high within-laboratory and between-laboratory coefficients (CVs), probably due to the low SCCP levels. Apart from the fish extract, within-laboratory CVs were acceptable (1-19%). Between-laboratory CVs for the test materials were 23-50%, while the CVs for the extracts ranged from 47 to 72%. Using a standard with a similar chlorine content as the test solution or correcting for it showed to be essential for accuracy: the difference between the true value and the assigned value for the test solution increased with 18% when participants used the provided standard, a single mixture with a different chlorine content, compared to when they used their own (multiple) standard mixtures. Reported concentrations obtained by GC-ECNI-LRMS varied the most in all test materials and differed the most of the true value for the test solution.

Overall, the results of the fourth round of the present ILS indicate that the determination of SCCPs is still complex and further improvements are necessary. However, between-laboratory CVs of this ILS round are lower than those obtained in previous rounds of this ILS as well as in other ILS studies. We recommend to continue in monitoring laboratory agreements, with a focus on the quantification procedures and standards applied.

1 Introduction

Short-chain chlorinated paraffins (SCCPs) are industrial mixtures of polychlorinated *n*-alkanes with a carbon chain length between 10 and 13 and a chlorination degree of 30-70% by mass. Due to their high production volumes, persistency, bioaccumulative properties and toxicity potential, SCCPs are classified as persistent organic pollutants (POPs) with a few exemptions by the UNEP Stockholm Convention since May 2017. They are also listed as key compounds in several legislations or guidelines to be monitored in environmental matrices, including water by the European water framework directive. Therefore an increasing number of laboratories will need to provide comparable and reliable results.

The determination of SCCPs is very challenging, mainly because of their response on current detection systems and their complexity (>7500 and 46 theoretically possible positional isomers and congener groups, respectively). Although SCCPs have been analysed since the early 1980s, determination is only possible as the sum of all SCCPs and results between laboratories vary greatly. For example, the latest interlaboratory study (ILS) comprising different techniques with six participants [1], conducted eight years ago, reported concentrations in a soil test material that varied up to two orders of magnitude. To date, there are only two validated analytical procedures available for routine monitoring of CPs in environmental samples (e.g. ISO 12010 water and ISO 18635 sediment).

It was generally agreed during a workshop of QUASIMEME (Ostend, Belgium, March 2010) that an interlaboratory study (ILS) on SCCPs was needed, preferably designed in a step-wise way. VU Environment and Health (E&H, formerly IVM) has therefore organized, in cooperation with the proficiency testing scheme of QUASIMEME, four interlaboratory rounds on SCCPs, of which the results of round 1-3 have been published in previous reports. In brief, the results of the previous rounds indicate that SCCP analysis is still challenging, resulting in large differences in reported concentrations between laboratories. Nonetheless, interlaboratory CVs were found to decrease between the second (137%) and third round (80-86%), suggesting improvement. Using different cleanup methods did not seem to have a major effect on the variation. However, the choice of instrumental technique and quantification procedures might have had an effect, as many different instrumental techniques and quantification procedures were applied in the third round, and differences were found in results obtained by the different techniques.

This report focusses on the results of ILS round 4. By sending one test solution and three different naturally contaminated environmental extracts we have focussed on the analytical methods and quantification procedures applied.

2 Methods and materials

2.1 Study design

As the focus was mainly on the instrumental techniques and quantification procedures, uncertainties related to extraction and cleanup procedures were eliminated. Participants were asked to quantify, in triplicate, the total concentration of SCCPs in two ampoules per extract, using their own quantification standards, as well as the provided standard solution (ampoule A). They were also encouraged to provide additional information such as chlorination degrees and relative abundance of congener group (e.g. C_xCl_x) patterns. A short description of the analytical method used by the participants was also requested for a more in-depth analysis of the submitted data as well as performance characteristics. All the requested data was filled in report forms. The identification of the participating laboratory was primarily encoded and could be disclosed based on general consensus, after final evaluation of results. The first invitation for participation in the study was sent out in March 2016 and the samples were distributed in September 2016.

2.2 Material preparation

Samples were selected based on the similarity of the congener group abundance with the commercially available quantification mixtures, with very similar (test solution), semi-similar (dust > sediment) and different (biota). The test solution was a mixture of SCCP mixtures with a chlorine content of 63% Cl and 55.5% Cl 42:58 (w/w), resulting in a chlorine content of with 58.7% Cl. The house dust extract was a reference material from National Institute for Standards and Technology (NIST), coded SRM 2585, still uncertified for SCCPs. The soil extract was a reference material from Institute for Reference Materials and Measurements (IRMM), coded BCR 481, also uncertified for SCCPs. The fish extract was pooled eel from various locations in The Netherlands.

All the extracts were obtained by pressurized liquid extraction (PLE) and concentrated to ~1 mL by nitrogen. They were cleaned with 20 g acid silica (40% H_2SO_4 by weight) and preconditioned with 25 mL dichloromethane (DCM)/n-hexane 30:70 (v/v), by eluting with 80 mL DCM/*n*-hexane 30:70. After that extracts were concentrated to ~1 mL. Then a neutral silica gel column (1,6% deactivated with H_2O) was applied twice to fractionate SCCPs from most interfering compounds, eluting first with 14 mL of hexane (discarded) and 10 mL of diethyl ether/hexane (15:85 v/v). The eluents were blown to dryness by a gentle flow nitrogen and solvent exchanged to iso-octane. Test materials were screened for SCCPs and potential interfering compounds such as medium chained CPs (MCCPs) and toxaphenes. In the dust and biota extract MCCPs were present in higher concentrations than SCCPs (factor ~5 compared to assigned value, quantified using APCI-QToF-MS).

After preparation, extracts were ampouled in 1 mL glass vials. Each vial was filled with 200 ± 3 µL of the extract and flame sealed. No syringe or surrogate standards were added to the extracts.

Table 2-1 Solutions and extracts provided

	Ampoule	Amount (*n*)	Concentration SCCPs (µg/g iso-octane)	Concentration MCCPs (µg/g iso-octane)[a, b]
Quantification standard	A	1	64	NA
Test Solution	B	2	1.92[a, c]	N
Dust extract	C	2	unknown	3.1-3.4
Soil extract	D	2	unknown	<0.08
Biota extract	E	2	unknown	0.12-0.11

[a] Unknown to participants, [b] Determined by APCI-qTOF-MS [c] Target value

2.3 Analytical techniques applied

Details on the methods applied are found in the Annex I and summarized in Table 2.1. The number of participating laboratories is relatively small, therefore the following findings should be read with some caution.

2.3.1 Instrumental techniques

Most of the participants applied the GC-ECNI-LRMS technique. In contrast to previous rounds, the use of GC-EI-MS/MS remained unreported. Using the TOF became popular, especially the novel technique APCI-QToF-MS that was applied for the first time in the rounds.

All columns used for single GC and as first column for GC×xGC were non-polar, with dimethyl- or penhyylmethylpolysiloxane stationary phases. As second column for GCxGC a semi-polar column was applied. LC was used only to introduce the analytes to the TOF-MS, and therefore no-columns were installed. Helium was used as carrier gas while methane was used for reagent gas for GC-MS. Different ions were monitored (Table 2.1), ranging from non-specific to ion congener group-specific monitoring, for which the number of monitored congener groups varied.

2.3.2 Calibration and quantification procedures

Calibration and quantification procedures varied and usually depends on the instrumental technique applied. Most participants gave information on their quantification procedures for the data obtained by participants' own standards. When GC-ECNI-LRMS was applied, the majority of the participants used the linear relationship between the chlorine content of the commercially available quantification mixtures and the response factor, developed by Reth et al. [2]. Other quantification procedures used with GC-ECNI-MS included the method of Tomy et al. [4] and the use of multiple linear regression (ISO 18635). When the TOF was used, the novel deconvolution method by Bogdal et al. [3] was most applied.

Table 2-2 Analytical techniques applied

Lab code	Analytical technique	R[a]	Column Type	Dimensions[b]	Injection	Temperatures (°C) Oven program[c]	MS source	Monitored SCCPs[d]	Calibration & Quantification method[e]
001	Magnetic Sector GC-ECNI-HRMS	8000	HP-Ultra 2	20 x 0.2 x 0.11	1 x 1 µL	90°C (1min)[c], 20°C/min to 245°C, 50°C/min to 300°C (5min)	140	C10Cl5-10 C11Cl5-10 C12Cl6-10 C13Cl7-9	Internal, Tomy et al. [4]
008	GC-ECNI- LRMS	1000	Rtx-5SiMS	30 x 0.25 x 0.25	3 x 2 µL	105°C (1min), 34°C/min to 190°C (1min), 8°C/min to 250°C, 40°C/min to 290°C (8min)	200	Non-specific: $[Cl_2]^-$ and $[HCl_2]^-$ ions	Internal, Castells et al. [5]
015a	GC-ECNI- LRMS	1000	DB-1	50 x 0.25 x 0.25	4 x 1 µL	90ºC (2min), 30ºC/min to 290ºC, 15ºC/min to 325ºC (7min)	200	C10Cl5-10 C11Cl5-10 C12Cl5-10 C13Cl5-10	Internal, linear RF and Cl% by Reth et al. [2]
015b	GCxC-ECD	NA	HP-5MS ZB-50	15 x 0.25 x 0.1 5 x 0.25 x 0.25	1 x 1 µL	90ºC (2min), 10ºC/min to 180ºC (2min), 1.5ºC/min to 280ºC, 30°C/min to 320°C (10min)	300[f]	Non-specific	Internal, linear RF and Cl% by Reth et al. [2]
016	GC-ECNI- LRMS	1000	DB-5MS	15 x 0.25 x 0.1	1 x 2 µL	80°C (2min), 70°C/min to 280°C (2min), 70°C/min to 300°C (2min)	150	4 specific ions	ISO 18635 [6]
023	GC-ECNI- LRMS	1000	DB-1MS	15 x 0.25 x 0.25	1 x 2 µL	110°C (1min), 15°C/min to 330°C	150	C10Cl5-10 C11Cl5-10 C12Cl5-9 C13Cl5-9	External, NA

Table 2-2 Analytical techniques applied (continued)

Lab code	Analytical technique	R[a]	Column Type	Dimensions[b]	Injection	Temperatures (°C) Oven program[c]	MS source	Monitored SCCPs[d]	Calibration & Quantification method[e]
031	LC-APCI-QToF-MS	8200	No column	NA	1 x 5 µL	NA	NA	C9Cl6-9 C10Cl3-10 C11Cl3-11 C12Cl3-12 C13Cl3-13	Internal, deconvolution [3]
035	GC-ECNI-TOF-MS	7500-12500	HP-5MS	15 x 0.25 x 0.1	1 x 5 µL	90°C (1min), 25°C/min to 290 °C (3min)	150	C9Cl7-9 C10Cl4-10 C11Cl4-11 C12Cl4-12 C13Cl4-13	External, linear RF and Cl% [7]
036a	LC-APCI-QToF-MS	10000	No column	NA	1 x 5 µL	NA	NA	C10Cl3-10 C11Cl3-11 C12Cl3-12 C13Cl3-13	Internal, deconvolution [3]
036b	LC-APCI-QToF-MS	10000	No column	NA	1 x 5 µL	NA	NA	C10Cl3-10 C11Cl3-11 C12Cl3-12 C13Cl3-13	Internal, linear RF and Cl% [2]

R Resolution; RF Response factor; NA Not available

[a] Approximate full width at half maximum (FWHM)

[b] in length m x i.d. mm x film µm

[c] Hold time in brackets

[d] Congener groups expressed as CxClx, without number of H atoms

[e] When using participants owns standards

[f] Temperature of ECD

2.4 Data assessment

The data assessment was carried out according to the principles employed in the data assessment of the QUASIMEME proficiency testing organisation (www.quasimeme.org). All data received from the participants were entered into an excel database and assessed using a standard procedure enabling direct comparison between participants. The assigned value (AV), the between-laboratory CV values and the laboratory assessment using z-scores were calculated with the Cofino Model (Cofino *et al.*, 2000). In Table 3-1 the so-called 'Inclusion rate' is shown. This value is a percentage that reflects how many datapoints are included in the 'Between-lab CV', shown in the column left from the Inclusion rate column. The higher the inclusion rate, the lower the number of outliers. A higher inclusion rate tells that the between-laboratory CV is more representative for the entire group of participants that produced that specific matrix-determinand combination.

The Cofino model provides a highly reliable estimate of the measurement relating to the method. It is generally acknowledged that robust statistics cannot cope with more than 10 % extreme values, particularly with a skewed distribution. The Cofino model is able to routinely cope with these types of distribution and provide the best estimate of the consensus value, which may be used as the AV.

The details of the Cofino Model are provided elsewhere [8], but in summary the approach is as follows:

All data is included in the assessment

No data is trimmed or down weighted

AV is based on Cofino NDA model

All left censored values (LCV)[1] are also included, provided certain criteria are met (Chapter 2.4.11).

The performance of the laboratories in this assessment is illustrated in the z-score histogram. Where the AV for a determinand is indicative, the values are plotted as their original reported concentrations. The rules for confirming whether the consensus value should be an AV or an indicative value are given in the Assessment Rules for the Evaluation of the QUASIMEME LP Studies Data (Wells and Scurfield, 2004) with relevant examples.

Normally, four plots are given for each determinand (Figure 2.1). The upper left plot provides an impression of the probability density function (PDF) model for all data (black) and for the first mode (PMF1) model of the data (blue dotted). Superimposed on these PDFs is a histogram of the individual measurements (grey bars). This plot shows the distribution of the data as a whole, and of the data in the main mode (PMF1) model on which the AV is based (inclusion rate in Table 3-1).

The "Kilt Plot" (Overlap Matrix; upper right plot) provides an overview of the degree of overlap of each pair of data. It gives a clear indication of the degree of homogeneity of the data. As a key, the white areas indicate maximum overlap of the PDFs and, therefore, highest agreement (an overlap of one implies that the two laboratories of the pair report exactly the same results), while the black area show the pairs in poor agreement.

The lower left plot is a ranked overview of all data with an error bar of ± 2 SD. The numerical values are given in blue and the LCVs are given in red.

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[1] *Left Censored Values* is the correct nomenclature for "less than" values

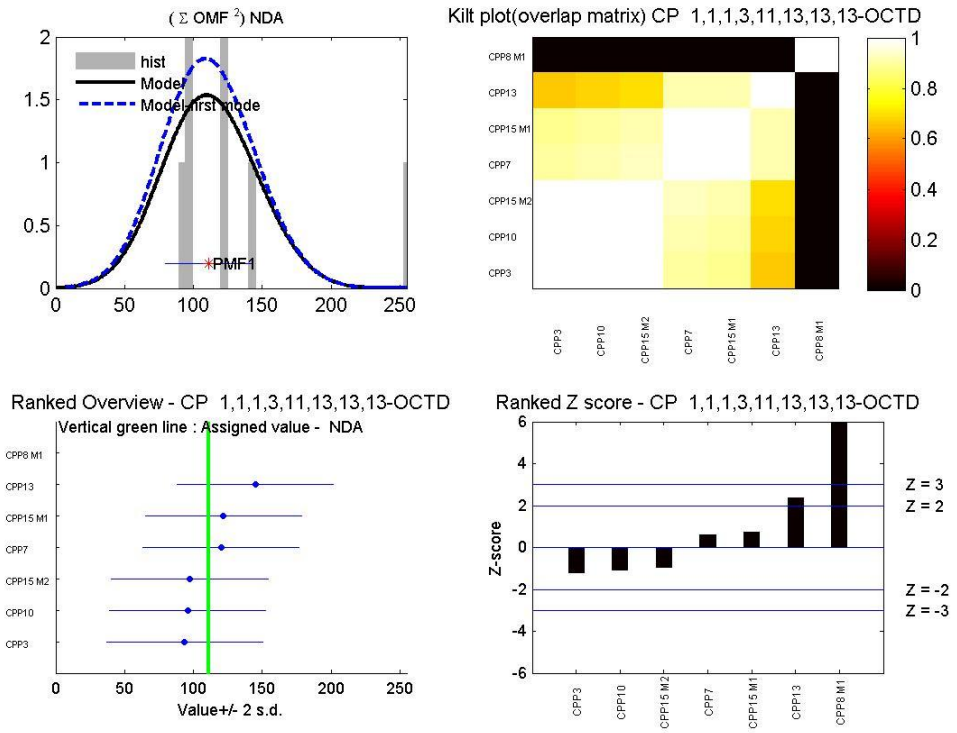

Figure 2.1 Examples of the graphical output of the Cofino Model statistics.

The ranked z-score plot (lower right) is based on the mean of the data, which is normally also the AV. However, if there is any adjustment required to the AV as a result of the assessment, *e.g.*, use of the nominal concentration or a trimmed value, then the final z-score given in the z-score histograms will reflect these changes. In this assessment, no such adjustments are made and therefore, the z-score plot (lower right) is the definite plot for obtaining the individual lab z-scores.

For each matrix-determinand combination a set of these four graphs is available. They can be found in Annex G.

2.4.1 The assigned values and indicative values

The AV is obtained from the main mode model of the data using the Cofino Model (blue dotted line in upper left panel in Figure 2.1, and is centred around the highest density of values. Unless otherwise stated, the AV is based on this consensus value of *all* data. Although *all* data are included in the assessment, those values that lie some distance from AV contribute less to the mean than values which occur at or near the mean.

In some instances it is not possible to set an AV, and an indicative value is given. No assessment of laboratory performance is given where an indicative value is set. An overview of the assessment, with explanation, decision flowcharts and examples, is given in the paper *Assessment Rules for the evaluation of the QUASIMEME Laboratory Performance Studies Data*, available on the QUASIMEME website (www.quasimeme.org). A summary of the categories is given below:

Category 1

For data with the number of numerical observations ≥ 7

An AV is based on the mean when ≥ 25% of values have a z-score of |Z| < 2. Where < 25% of the data has |Z| < 2 the value is indicative. *i.e.* at least 25% must be in good agreement.

Category 2

For data with the number of numerical observations > 3 and < 7

An AV is based on the mean when ≥ 70% of values have a z-score of |Z| < 3 and a minimum of 4 observations have |Z| < 2. Otherwise the value is indicative. i.e. for small datasets, n > 3 and n < 7, there need to be very good agreement and a maximum of one extreme value before an AV can be given.

Category 3

For data with the number of numerical observations < 4

No AV is given. Normally the median value is given as an indicative value.

Category 4

For data with the high Total Error% >100% in combination with bad performance

No AV is given.

2.4.2 The Z-score Assessment

A z-score (Thompson and Wood, 1993) is calculated for each participant's data for each matrix / determinand combination which is given an AV. The z-score is calculated as follows:

$$z\text{-}score = \frac{\text{Mean from Laboratory} - \text{Assigned Value}}{\text{Total Error}}$$

It is emphasized that in many ILSs the between laboratory standard deviation obtained from the statistical evaluation of the assessment is used as 'total error' in the formula above. In the QUASIMEME data assessment, the total error is estimated independently taking the needs of present-day international monitoring programs as starting point. For each determinand in a particular matrix, a proportional error (PE) and a constant error (CE) have been defined. The total error depends on the magnitudes of these errors and on the AV:

$$\text{Total Error} = \frac{\text{Assigned Value} \times \text{Proportional Error (\%)}}{100} + 0.5 \times \text{Constant Error}$$

The values for the PE and CE were developed by QUASIMEME. The values are based on the following criteria:

- Consistency of the required standard of performance to enable participating laboratories to monitor their assessment over time.

- Achievable targets in relation to the current state of the art and the level of performance needed for national and international monitoring programmes.

The assessment is based on ISO 43 and z-scores. The QUASIMEME model is designed to provide a consistent interpretation over the whole range of concentration of analytes provided, including an assessment where LCVs are reported.

The PE in this assessment was set at 12.5 %. The CE has been set for each determinand or determinand group. This value was initially set to reflect the limit of determination, but is at present more closely related to the overall laboratory performance. The magnitude of the CE is set to provide a constant assessment in terms of z-score regardless of concentration. Therefore, at low concentrations the level of accuracy required to obtain a satisfactory z-score is less stringent than at a high concentrations.

Following usual practices *e.g.* ISO 43, the z-scores can be interpreted as follows to assure the quality of their data:

$\|Z\| < 2$	Satisfactory performance
$2 < \|Z\| < 3$	Questionable performance
$\|Z\| > 3$	Unsatisfactory performance
$\|Z\| > 6$	Frequently points to gross errors (mistakes with units during reporting, calculation or dilution errors, etc.).

Figure 2.2 illustrates the interpretation of the z-scores:

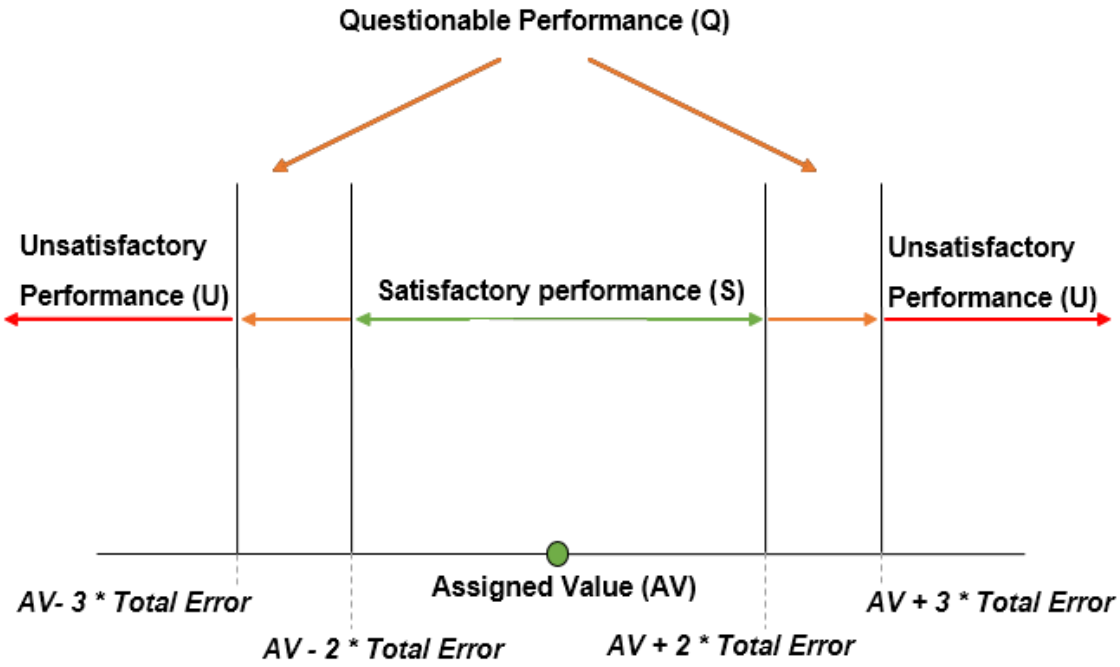

Figure 2.2 Interpretation of z-scores.

It is not possible to calculate a z-score for LCVs as LCVs represent a cut-off value rather than continuous data. However, Quasimeme provides a simple quality criterion:

LCV/2 < (concentration corresponding to |z|=3): LCV consistent with AV.

LCV/2 > (concentration corresponding to |z|=3): LCV inconsistent with AV, i.e. LCV reported by laboratory much higher than numerical values reported by other laboratories.

Z-score key:	S – Satisfactory
	Q – Questionable
	U – Unsatisfactory
LCV key:	C – Consistent
	I – Inconsistent
No data:	B - Blank

3 Results

Submitted results have been statistically evaluated and as all the data met the criteria, described in Chapter 2, an AV was established. Z-scores were calculated based on the AV. Summary statistics are presented in Table 3-1. A summary of the AVs and the percentage of satisfactory to unsatisfactory z-scores are presented in Table 3-2 and Figure 3.1. Whenever less than values (LCV) were submitted, the percentage of consistent and inconsistent LCVs with the AV is given. Because of the low levels in the fish extract the CE was set to 0.005 instead of 0.025.

Every laboratory submitted results in triplicate for two ampoules and within-laboratory variation could be calculated (Table 3-2).

The submitted data is presented in Annex B. Tables with individual z-scores are presented in Annex C-D, consistencies of the individual results are presented in Annex E-F and z-score plots in Annex G-H.

Table 3-1 Results of reported ΣSCCPs concentrations

Determinand	Assigned Value (µg/g)	Model mean (µg/g)	Median	Min[a] (µg/g)	Max[b] (µg/g)	Model Between-lab CV	Inclusion rate	n > LOQ
ΣSCCPs, determined with provided standard								
Test solution	1.01	1.01	1.01	0.19	3.08	23%	65%	42
Dust	0.34	0.34	0.28	0.05	1.08	68%	72%	42
Soil	1.05	1.05	1.01	0.47	2.20	47%	69%	35
Fish	0.02	0.02	0.02	0.004	0.07	86%	71%	25
ΣSCCPs, determined with participant's standards								
Test solution	1.34	1.34	1.41	0.31	4.06	50%	72%	60
Dust	0.68	0.68	0.68	0.16	1.44	72%	82%	60
Soil	1.47	1.47	1.38	0.30	2.49	47%	80%	53
Fish	0.02	0.02	0.02	0.002	0.60	50%	53%	43

[a] Min: lowest value submitted > LOQ
[b] Max: highest value submitted > LOQ
N.A. Not available

Table 3-2 Summary of laboratory performance

Determinand	Within-laboratory variation	z-scores |Z|<2 S[a]	z-scores 3>|Z|>2 Q[a]	z-scores 6>|Z|>3 U[a]	z-scores |Z|>6 E[a]	Consis-tent LCV	Inconsis-tent LCV
ΣSCCPs, determined with provided standard							
Test solution	5-10%	71%	0%	14%	14%	-	-
Dust	1-18%	52%	5%	19%	24%	-	-
Soil	1-11%	49%	3%	37%	11%	-	-
Fish	3-24%	39%	26%	3%	13%	9%	18%
ΣSCCPs, determined with participant's standards							
Test solution	5-10%	45%	5%	40%	10%	-	-
Dust	1-19%	42%	5%	38%	15%	-	-
Soil	1-11%	43%	19%	38%	0%	-	-
Fish	6-46%	42%	6%	12%	23%	6%	12%

[a] S Satisfactory Q Questionable U Unsatisfactory E Extreme

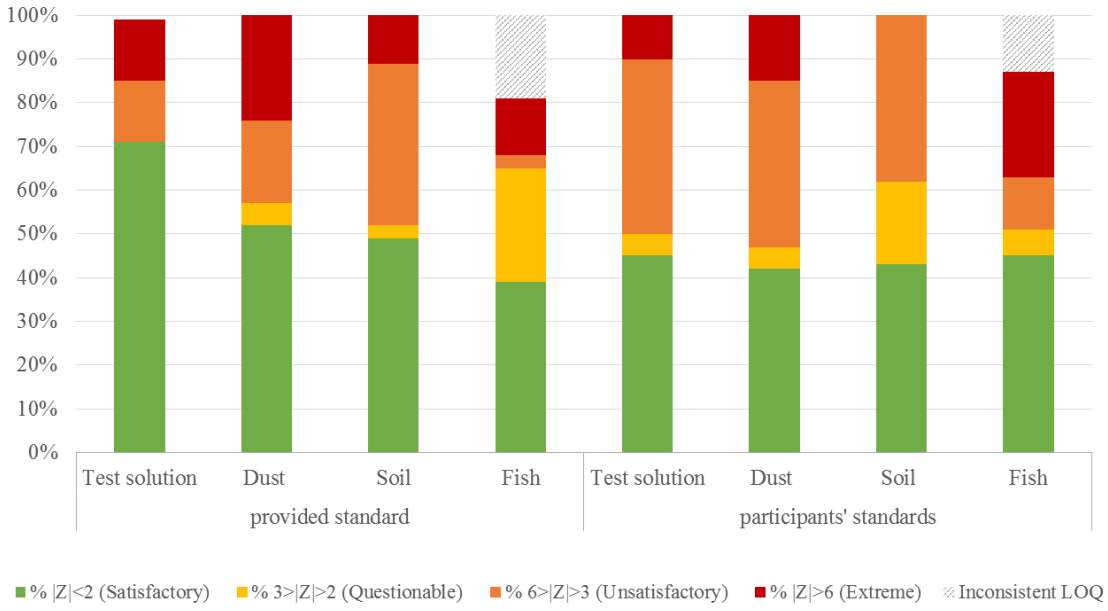

Figure 3.1 Percentage of laboratory performances, expressed in z-scores

4 Discussion

As described in a flow diagram in Figure 4.1, in total twelve laboratories signed up in this round, of which eight submitted data (completion rate of 67%). Four participating laboratories were unable to submit data due to restructuring or instrumental issues. Because of the techniques used, three participating laboratories only submitted data that was quantified with their own standards. Two laboratories submitted two data sets, either obtained by two different instruments (CPP-15) or two different quantification methods (CPP-36). One participant reported distorted signals for the soil extract and was therefore unable to submit data for that extract. SCCP levels in the biota extract were very low and for some participants lower than their limit of quantification.

Reported relative abundancies were dependent on the technique used, as different abundancies were reported per technique (Figure 4.2).

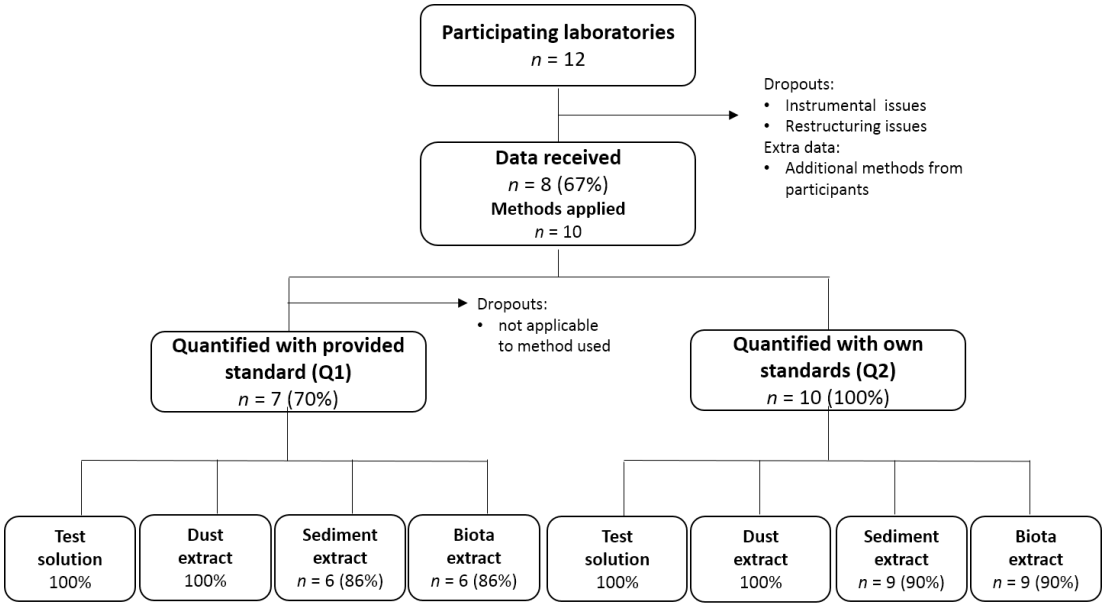

Figure 4.1 Flow diagram of number of participants and submitted results

4.1 Laboratory performance

The fish extract showed to be the most difficult extract to analyse, probably because of the low concentration (AV 0.02 µg/g), which was lower than some of the LOQs of the participants (0.2 µg/g).

Apart from the fish extract, acceptable within-laboratory performances were obtained (1-19%). Acceptable between-laboratory CVs were obtained for the test solution quantified with provided standard according to criterion of QUASIMEME proficiency scheme testing (<25%). CVs for the environmental extracts was substantial.

Apart from the test solution, between-laboratory CVs were similar when the provided standard or the participant's own standards was used for quantification. The CV doubled for the results of the test solution obtained by participants using their own standards. The largest difference in results was found between the participants that used LRMS (Figure 4.2). In general, the difference in

reported concentrations between the participants that used TOF was smaller than between the participants using LRMS.

Many laboratories (71%) had satisfactory z-scores for the test solutions quantified with the provided standard (Figure 3.1 and Table 3-2). Around half of the participants (39-52%) had satisfactory z-scores for the rest of the test materials.

Accuracy and precision of the assigned value could be evaluated in some degree for the test solution, because the concentration was known (Figure 4.3). The difference between the assigned value (1.34 µg/g, marked with purple line in graph E) for the results quantified by the participants' own standards and the true concentration for the test solution (1.92 µg/g; 'target value' marked with green line in graph E) was 18% lower than when the provided standard was used. This is probably because of the difference in chlorine content between the test solution (58.7%) and provided standard (63%), indicating how essential it is to have a similar chlorine content between the standards and the sample and/or using multiple standards and correct for the chlorine difference.

The levels in all test materials obtained by most LRMS were higher compared to that obtained by HRMS (Figure 4.3). However, the presence of MCCPs in the dust and biota extracts did not lead to substantially higher reported concentrations by LRMS compared to HRMS.

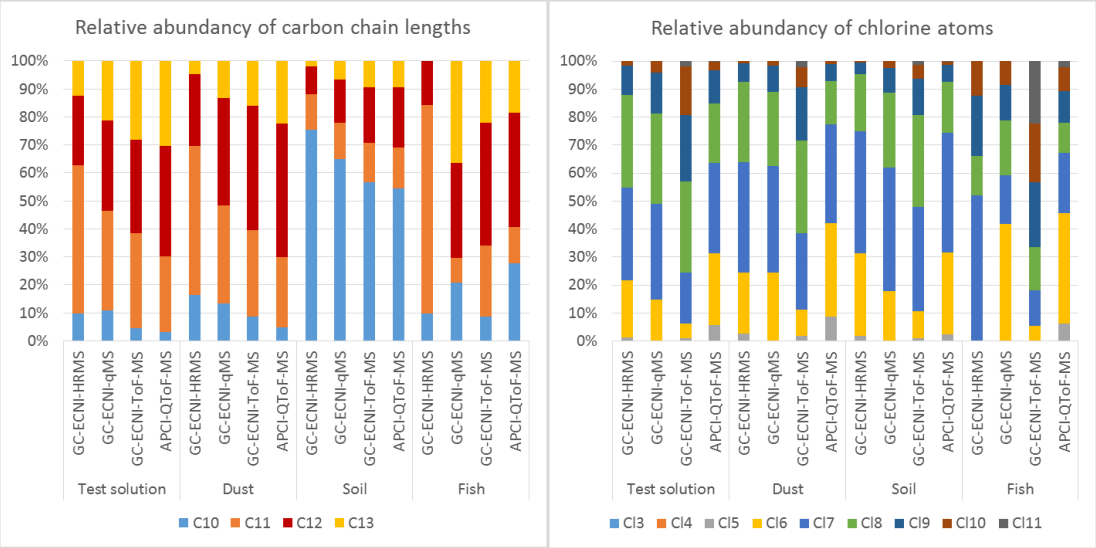

Figure 4.2 Reported Relative Abundancy of the test materials.

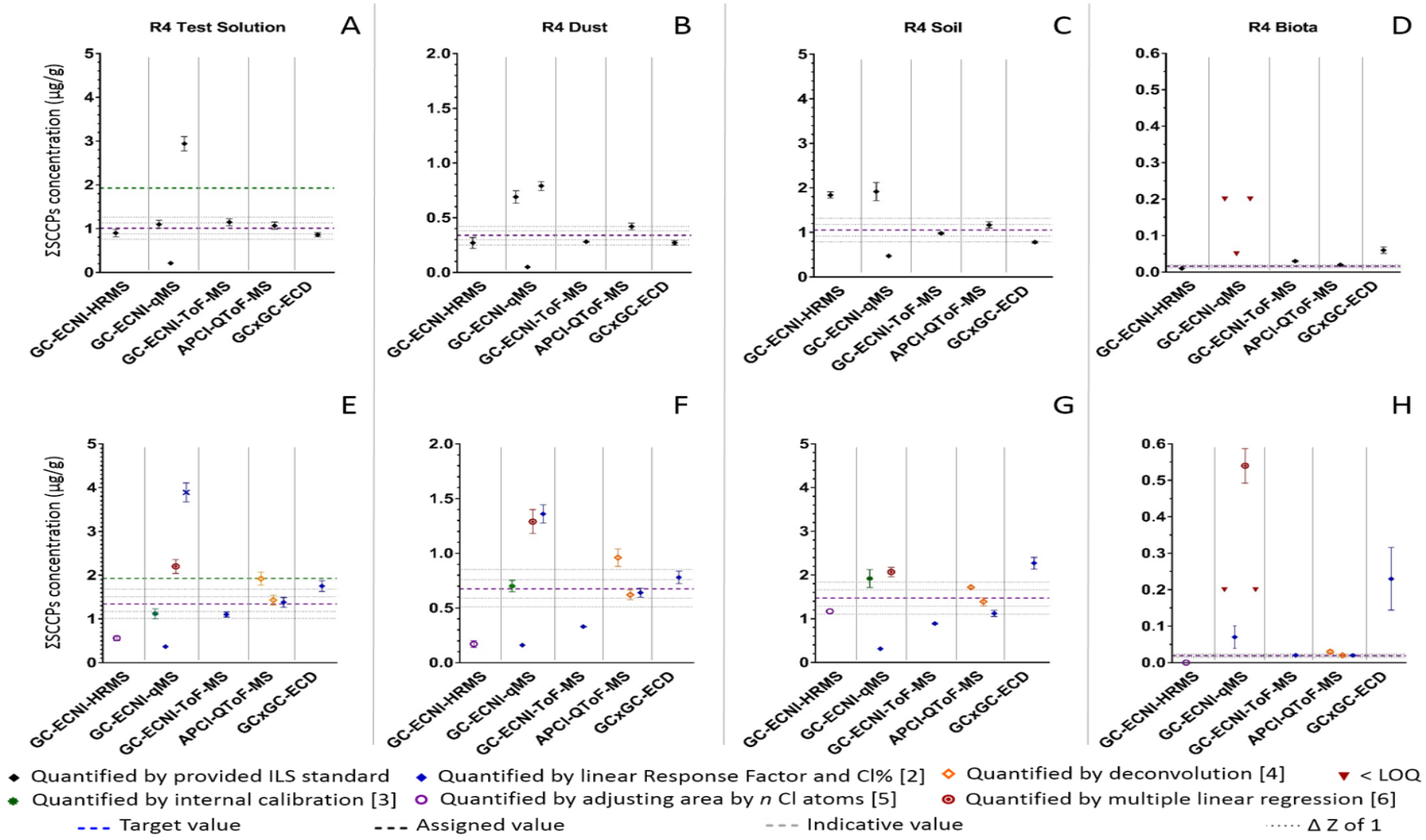

Figure 4.3 Reported concentrations of the test materials sorted per instrument technique applied and either quantified by provided ILS standard (A-D) or by participants' own standards (E-H).

4.2 Comparison with previous rounds and other interlaboratory studies

When compared to previous rounds and other interlaboratory studies, the results of this round suggest improvement in agreement; all between-laboratory CVs of this round were lower compared to previous rounds (Figure 4.4).

To our knowledge, only two interlaboratory studies exist that assessed the variability associated between laboratories with different acquisition and quantification techniques; one comprising a test solution as well as a fish extract, conducted by Tomy et al. in 1998 [9], and one with a soil extract conducted by Pellizato et al. in 2009 [1]. Compared to the CV for the test mixture solution of the study of Tomy et al. (44%) [9], the CVs for the test solution of this study were about equal or lower (23-50%). The CVs obtained for the fish extract in this study (50-86%), with eight participants, was comparable to the CV (47%) for the results for the fish extract of Tomy et al. [9] that had fewer participants (n = 6). Tomy et al. reported another CV for the fish extract, which was lower (27%), but this CV was only based on results of three participants.

All CVs for the results for the environmental extracts of this study were substantially lower than the CV for the soil extract of the interlaboratory study by Pellizzato et al. (209%) [1]. Both soil extracts were from the identical soil sample type (CRM-481), and while the final concentration of this round was twice as low, the CV was a factor 4 lower.

In terms of precision, the difference between the assigned value (1.01-1.34 µg/g) and the true concentration (1.92 µg/g; 'target value' in graphs A and E in Figure 4.3) for the test solution (30-48%) was smaller than the difference found in round 1 (54%), and than that of the interlaboratory study of Tomy et al. (from -30 to + 310%) [9], suggesting improvement.

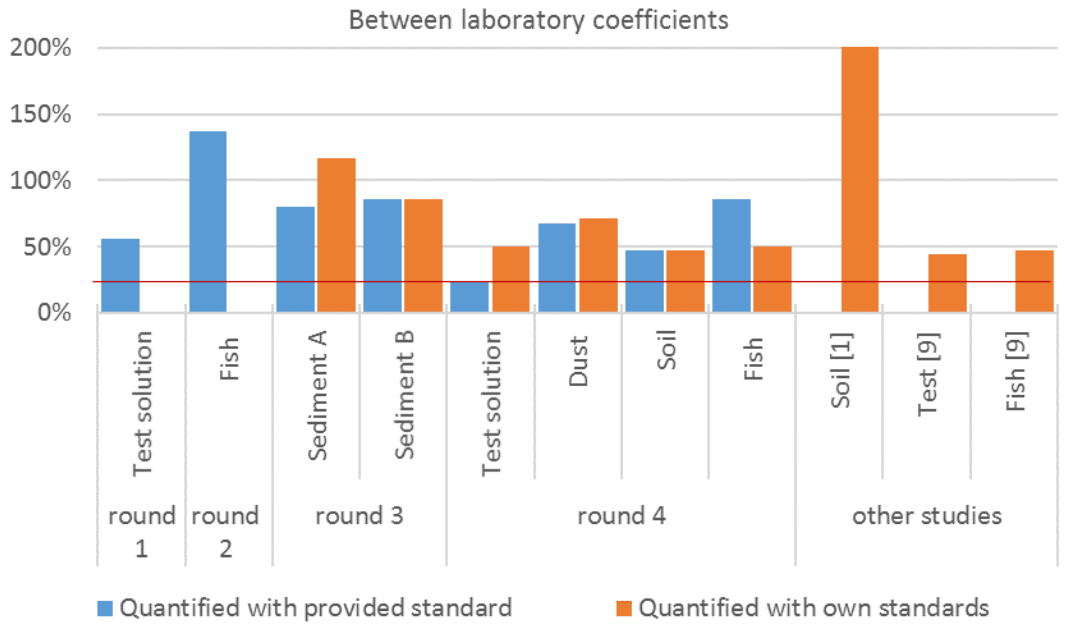

Figure 4.4 Criterion of QUASIMEME proficiency scheme testing (<25%, red line) and between-laboratory coefficients (CVs) of the results of this round, other rounds and other interlaboratory studies on SCCPs.

Conclusion

Eight laboratories provided data for the fourth round of the QUASIMEME interlaboratory study on SCCP analysis, which included a test solution and three different naturally contaminated environmental extracts. A number of different instrumental and quantification techniques were used for the determination of the sum of SCCPs. Overall, differences in reported concentrations in the environmental extracts between the laboratories are still substantial (between-laboratory CVs 23-86%). Nonetheless, the results have improved compared to previous rounds of this ILS and other interlaboratory studies. The differences are most likely due to the choice of instrument and/or quantification procedures used. The largest differences in reported concentrations were found when GC-ECNI-LRMS was used. Using participants' own standards for quantification did not increase the CV for the environmental extracts. Using a standard that had a similar chlorine content or a quantification procedure that corrects for this is obviously essential.

More interlaboratory comparison exercises are recommended to monitor laboratory agreements, with a focus on quantification procedures and standards applied. We suggest that for a possible future interlaboratory comparison providing quantification standards is no longer needed.

Acknowledgements

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Appendices

A. List of participants.

B. Reported concentrations and graphical output

C. Numerical z-score values per matrix quantified with provided standard

D. Numerical z-score values with participants' own standards

E. Consistency of data quantified with provided standard

F. Consistency of data quantified with participants' own standards

G. Graphical output Cofino Statistics of results quantified with provided ILS standard

H. Graphical output Cofino Statistics of results quantified with participants' own standards

I. Additional method information

Appendix A List of participants

Laboratory	Contact person	Delivery address	Postal code and City	Country	E-mail
ALS Environmental Burlington	Magdalena Kulig	1435 Norjohn Court, Unit 1	L7L 0E6, Ontario	Canada	quality.burlington@alsglobal.com
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Landesamt fuer Umwelt Bayern	Benjamin Schweinfurther	Bürgermeister-Ulrich-Straße 160, Referat 75	86179 Augsburg	Germany	Benjamin.Schweinfurther@lfu.bayern.de

Laboratory	Contact person	Delivery address	City and postal code	Country	E-mail
NILU - Norwegian Institute for Air Research	Stine M. Bjørneby	Instituttveien 18	2007 Kjeller	Norway	smb@nilu.no
QAEHS – University of Queensland	Jake O'Brien	39 Kessels road	4108 Brisbane	Australia	j.obrien2@uq.edu.au
WESSLING GmbH	Andrea Kaiser	Am Umweltpark 1	44793 Bochum	Germany	andrea.kaiser@wessling.de

Appendix B Reported concentrations

ΣSCCPs (µg/g)	Assigned value	Model Mean	Median	Min	Max	Model Between-lab CV%	Model percentage in PMF1	n>LOQ
Quantified with provided provided standard								
Test solution	1.01	1.01	1.01	0.19	3.08	23%	65%	42
Dust extract	0.34	0.34	0.28	0.05	1.08	68%	72%	42
Soil extract	1.05	1.05	1.01	0.47	2.20	47%	69%	35
Biota extract	0.02	0.02	0.02	0.004	0.07	86%	71%	25
Quantified with participants' own standards								
Test solution	1.34	1.34	1.41	0.31	4.06	50%	72%	60
Dust extract	0.68	0.68	0.68	0.16	1.44	72%	82%	60
Soil extract	1.47	1.47	1.38	0.30	2.49	47%	80%	53
Biota extract	0.02	0.02	0.02	0.002	0.60	50%	53%	43

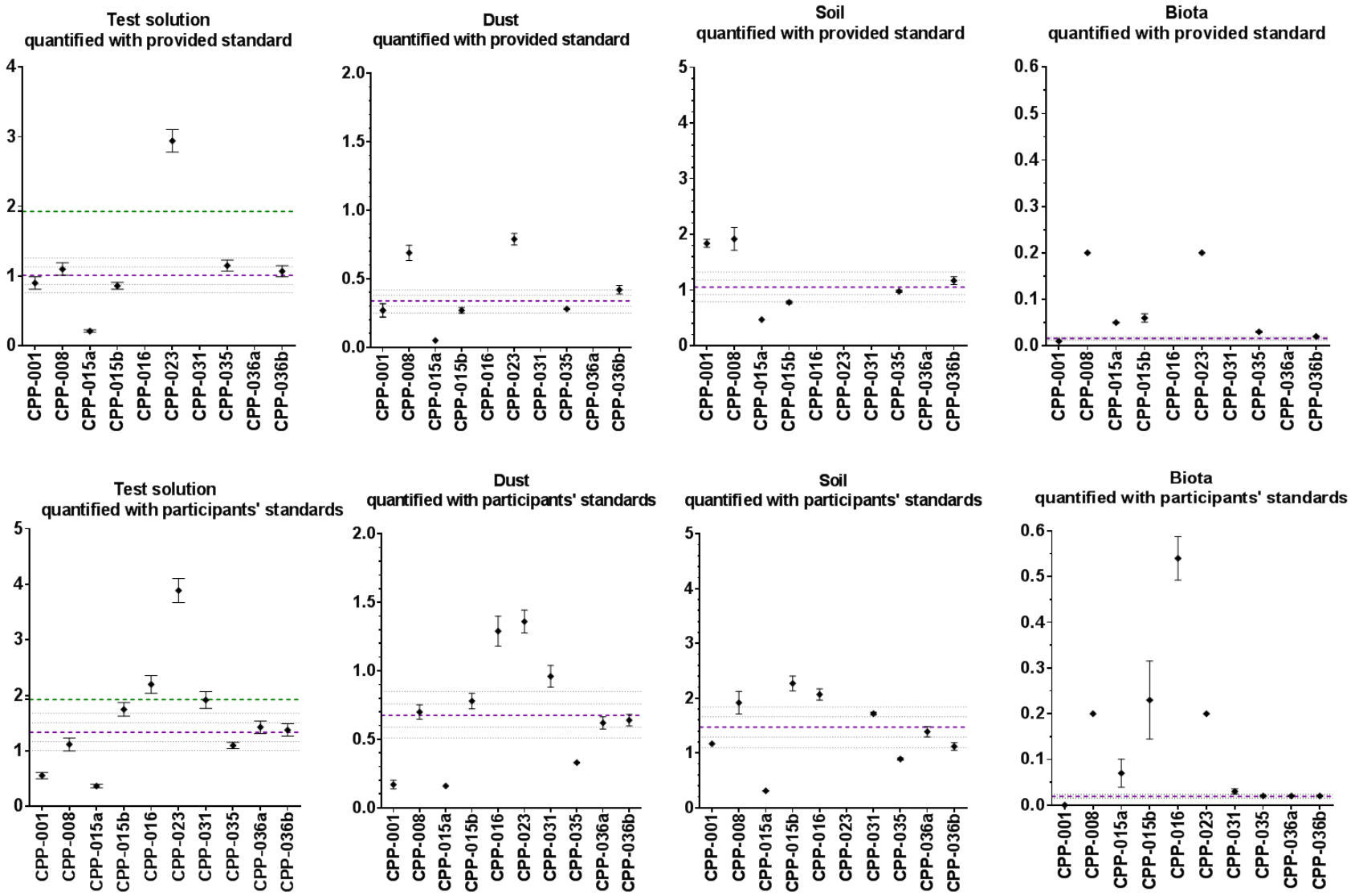
Participant code	CPP-001						CPP-008					
Concentration in µg/g	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution quantified with provided standard	0.840	0.790	0.830	0.950	1.010	0.960	1.100	1.100	1.000	1.000	1.200	1.200
Test solution quantified with participants' own standards	0.520	0.49	0.51	0.59	0.63	0.59	1.1	1.1	1	1	1.2	1.3
Dust extract quantified with provided standard	0.240	0.210	0.240	0.280	0.350	0.270	0.770	0.700	0.720	0.620	0.680	0.630
Dust extract quantified with participants' own standards	0.150	0.130	0.150	0.180	0.220	0.170	0.780	0.700	0.720	0.620	0.680	0.680
Soil extract quantified with provided standard	1.940	1.850	1.810	1.840	NA	1.740	1.900	1.600	1.800	2.200	2.000	2.000
Soil extract quantified with participants' own standards	1.240	1.180	1.150	1.110	NA	1.170	1.900	1.600	1.800	2.200	2.000	2.000
Biota extract quantified with provided standard	0.006	0.007	0.008	0.004	0.005	0.007	-0.200	-0.200	-0.200	-0.200	-0.200	-0.200
Biota extract quantified with participants' own standards	0.005	0.004	0.004	0.002	0.003	0.005	-0.200	-0.200	-0.200	-0.200	-0.200	-0.200

Participant code	CPP-015a						CPP-015b					
Concentration in µg/g	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution quantified with provided standard	0.209	0.207	0.238	0.223	0.185	0.213	0.947	0.827	0.873	0.803	0.865	0.844
Test solution quantified with participants' own standards	0.366	0.377	0.404	0.386	0.313	0.368	1.554	1.763	1.895	1.670	1.835	1.792
Dust extract quantified with provided standard	0.051	0.054	0.051	0.058	0.057	0.054	0.269	0.265	0.305	0.266	0.250	0.248
Dust extract quantified with participants' own standards	0.149	0.159	0.153	0.187	0.173	0.161	0.753	0.838	0.864	0.790	0.731	0.730
Soil extract quantified with provided standard	0.484	0.485	0.470	0.475	0.466	0.466	0.790	0.780	0.808	0.793	0.782	0.738
Soil extract quantified with participants' own standards	0.323	0.324	0.310	0.311	0.309	0.305	2.180	2.140	2.270	2.490	2.360	2.270
Biota extract quantified with provided standard	0.011	-0.010	-0.010	0.013	-0.010	0.013	0.050	0.049	NA	NA	0.053	0.069
Biota extract quantified with participants' own standards	0.049	-0.010	-0.010	0.050	-0.010	0.102	0.208	0.180	NA	NA	0.184	0.360

Participant code	CPP-016						CPP-023					
Concentration in µg/g	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution quantified with provided standard	NA	NA	NA	NA	NA	NA	3.049	2.955	2.802	3.075	3.073	2.689
Test solution quantified with participants' own standards	2.03	1.99	2.4	2.24	2.29	2.26	4.048	3.924	3.697	4.057	4.054	3.548
Dust extract quantified with provided standard	NA	NA	NA	NA	NA	NA	0.798	0.831	0.750	0.820	0.795	0.722
Dust extract quantified with participants' own standards	1.210	1.110	1.360	1.280	1.380	1.380	1.385	1.439	1.280	1.424	1.376	1.233
Soil extract quantified with provided standard	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Soil extract quantified with participants' own standards	1.870	2.100	2.080	2.090	2.180	2.100	NA	NA	NA	NA	NA	NA
Biota extract quantified with provided standard	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Biota extract quantified with participants' own standards	0.500	0.590	0.600	0.480	0.540	0.540	NA	NA	NA	NA	NA	NA

Participant code *Concentration in µg/g*	CPP-031						CPP-035					
	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution quantified with provided standard	NA	NA	NA	NA	NA	NA	1.213	1.174	1.160	1.203	1.160	0.995
Test solution quantified with participants' own standards	2.05	2.01	1.94	1.63	1.93	1.96	1.112	1.105	1.074	1.167	1.128	0.999
Dust extract quantified with provided standard	NA	NA	NA	NA	NA	NA	0.279	0.278	0.274	0.274	0.280	0.270
Dust extract quantified with participants' own standards	0.984	0.837	0.966	1.08	0.945	0.923	0.338	0.335	0.329	0.335	0.338	0.330
Soil extract quantified with provided standard	NA	NA	NA	NA	NA	NA	1.006	0.998	0.956	0.978	0.998	0.958
Soil extract quantified with participants' own standards	1.69	1.75	1.71	1.7	1.73	1.75	0.910	0.903	0.866	0.884	0.900	0.863
Biota extract quantified with provided standard	NA	NA	NA	NA	NA	NA	0.030	0.028	0.028	0.026	0.026	0.026
Biota extract quantified with participants' own standards	0.0412	0.0291	0.0274	0.0303	0.027	0.0283	0.022	0.020	0.020	0.019	0.019	0.018

Participant code	CPP-036a						CPP-036b					
Concentration in µg/g	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution quantified with provided standard	NA	NA	NA	NA	NA	NA	1.024	0.953	1.189	1.090	1.114	1.050
Test solution quantified with participants' own standards	1.363	1.265	1.583	1.453	1.508	1.420	1.291	1.204	1.503	1.409	1.469	1.380
Dust extract quantified with provided standard	NA	NA	NA	NA	NA	NA	0.369	0.422	0.411	0.430	0.436	0.461
Dust extract quantified with participants' own standards	0.546	0.623	0.609	0.634	0.643	0.678	0.564	0.646	0.634	0.658	0.663	0.687
Soil extract quantified with provided standard	NA	NA	NA	NA	NA	NA	1.108	1.131	1.188	1.302	1.155	1.127
Soil extract quantified with participants' own standards	1.311	1.335	1.394	1.571	1.379	1.351	1.055	1.076	1.128	1.251	1.115	1.085
Biota extract quantified with provided standard	NA	NA	NA	NA	NA	NA	0.016	0.017	0.016	0.016	0.015	0.016
Biota extract quantified with participants' own standards	0.021	0.025	0.023	0.022	0.020	0.022	0.018	0.020	0.019	0.019	0.016	0.018


Test solution
quantified with provided standard
Dust
quantified with provided standard
Soil
quantified with provided standard
Biota
quantified with provided standard
Test solution
quantified with participants' standards
Dust
quantified with participants' standards
Soil
quantified with participants' standards
Biota
quantified with participants' standards
CPP-001
CPP-008
CPP-015a
CPP-015b
CPP-016
CPP-023
CPP-031
CPP-035
CPP-036a
CPP-036b

Appendix C Numerical z-score values per matrix quantified with provided standard

	CPP-001						CPP-008						CPP-015a					
Matrix	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution	-1.21	-1.57	-1.28	-0.42	0.02	-0.34	0.67	0.67	-0.05	-0.05	1.39	1.39	-5.77	-5.78	-5.56	-5.67	-5.94	-5.74
Dust extract	-1.80	-2.35	-1.80	-1.07	0.20	-1.25	7.86	6.59	6.95	5.13	6.22	5.31	-5.24	-5.19	-5.25	-5.11	-5.14	-5.20
Soil extract	6.16	5.53	5.25	5.46	NA	4.77	5.88	3.80	5.18	7.96	6.57	6.57	-3.95	-3.94	-4.04	-4.01	-4.07	-4.08
Fish extract	-2.18	-1.95	-1.73	-2.62	-2.40	-1.95	NA	NA	NA	NA	NA	NA	-1.12	NA	NA	-0.68	NA	-0.60

	CPP-015b						CPP-016	CPP-023						CPP-031
Matrix	1-1	1-2	1-3	2-1	2-2	2-3		1-1	1-2	1-3	2-1	2-2	2-3	
Test solution	-0.44	-1.30	-0.97	-1.48	-1.03	-1.18	NA	14.74	14.07	12.97	14.94	14.92	12.15	NA
Dust extract	-1.27	-1.34	-0.61	-1.32	-1.61	-1.66	NA	8.37	8.98	7.50	8.78	8.32	6.99	NA
Soil extract	-1.82	-1.89	-1.70	-1.80	-1.88	-2.19	NA	NA	NA	NA	NA	NA	NA	NA
Fish extract	7.66	7.51	NA	NA	8.40	11.85	NA	NA	NA	NA	NA	NA	NA	NA

Matrix	CPP-035						CPP-036a	CPP-036b					
	1-1	1-2	1-3	2-1	2-2	2-3		1-1	1-2	1-3	2-1	2-2	2-3
Test solution	1.48	1.20	1.10	1.41	1.10	-0.09	NA	0.12	-0.39	1.31	0.59	0.77	0.31
Dust extract	-1.08	-1.10	-1.18	-1.18	-1.08	-1.26	NA	0.55	1.52	1.32	1.67	1.78	2.23
Soil extract	-0.33	-0.38	-0.67	-0.52	-0.38	-0.66	NA	0.38	0.55	0.94	1.73	0.71	0.51
Fish extract	3.22	2.74	2.75	2.27	2.38	2.29	NA	-0.03	0.40	0.10	0.09	-0.23	-0.01

NA Not available (Data not submitted)

Appendix D Numerical z-score values per matrix quantified with participants' own standard

	CPP-001						CPP-008					
Matrix	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution	-4.56	-4.73	-4.61	-4.17	-3.95	-4.17	-1.34	-1.34	-1.89	-1.89	-0.78	-0.23
Dust extract	-5.42	-5.63	-5.42	-5.11	-4.70	-5.22	1.07	0.24	0.45	-0.58	0.04	0.04
Soil extract	-1.18	-1.49	-1.64	-1.84	NA	-1.54	2.18	0.65	1.67	3.71	2.69	2.69
Fish extract	-2.93	-3.14	-3.14	-3.54	-3.34	-2.93	NA	NA	NA	NA	NA	NA

	CPP-015a						CPP-015b					
Matrix	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution	-5.41	-5.35	-5.20	-5.30	-5.71	-5.40	1.18	2.34	3.07	1.82	2.74	2.50
Dust extract	-5.43	-5.34	-5.40	-5.04	-5.19	-5.31	0.79	1.67	1.93	1.17	0.56	0.56
Soil extract	-5.85	-5.84	-5.91	-5.91	-5.92	-5.94	3.60	3.40	4.06	5.18	4.52	4.06
Fish extract	5.89	NA	NA	6.25	NA	16.82	38.13	32.47	NA	NA	33.38	69.00

Matrix	CPP-016						CPP-023					
	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution	3.82	3.60	5.88	4.99	5.26	5.10	15.02	14.33	13.07	15.07	15.05	12.25
Dust extract	5.50	4.47	7.04	6.22	7.25	7.25	7.30	7.86	6.22	7.71	7.21	5.73
Soil extract	2.03	3.20	3.10	3.15	3.60	3.20	NA	NA	NA	NA	NA	NA
Fish extract	97.38	115.61	117.64	93.32	105.48	105.48	NA	NA	NA	NA	NA	NA

Matrix	CPP-031						CPP-035					
	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution	3.93	3.71	3.32	1.60	3.27	3.43	-1.27	-1.31	-1.48	-0.97	-1.18	-1.90
Dust extract	3.17	1.65	2.98	4.16	2.77	2.54	-3.49	-3.52	-3.58	-3.52	-3.48	-3.57
Soil extract	1.11	1.42	1.21	1.16	1.31	1.42	-2.86	-2.90	-3.08	-2.99	-2.91	-3.10
Fish extract	4.40	1.95	1.61	2.19	1.52	1.79	0.46	0.15	0.15	-0.11	-0.13	-0.21

Matrix	CPP-036a						CPP-036b					
	1-1	1-2	1-3	2-1	2-2	2-3	1-1	1-2	1-3	2-1	2-2	2-3
Test solution	0.12	-0.42	1.34	0.62	0.92	0.44	-0.28	-0.76	0.90	0.37	0.71	0.21
Dust extract	-1.35	-0.55	-0.69	-0.44	-0.34	0.02	-1.16	-0.32	-0.44	-0.19	-0.14	0.11
Soil extract	-0.82	-0.70	-0.39	0.50	-0.47	-0.61	-2.12	-2.02	-1.75	-1.12	-1.82	-1.97
Fish extract	0.40	1.07	0.69	0.59	0.13	0.53	-0.39	0.17	-0.10	-0.19	-0.61	-0.34

Appendix E Consistency of the data quantified with provided standard

Matrix	CPP-001	CPP-008	CPP-015a	CPP-015b	CPP-016
Test solution	S-S-S-S-S-S	S-S-S-S-S-S	U-U-U-U-U-U	S-S-S-S-S-S	B-B-B-B-B-B
Dust extract	S-Q-S-S-S-S	U-U-U-U-U-U	U-U-U-U-U-U	S-S-S-S-S-S	B-B-B-B-B-B
Soil extract	U-U-U-U-B-U	U-U-U-U-U-U	U-U-U-U-U-U	S-S-S-S-S-Q	B-B-B-B-B-B
Fish extract	Q-S-S-Q-Q-S	I-I-I-I-I-I	S-C-C-S-C-S	U-U-B-B-U-U	B-B-B-B-B-B

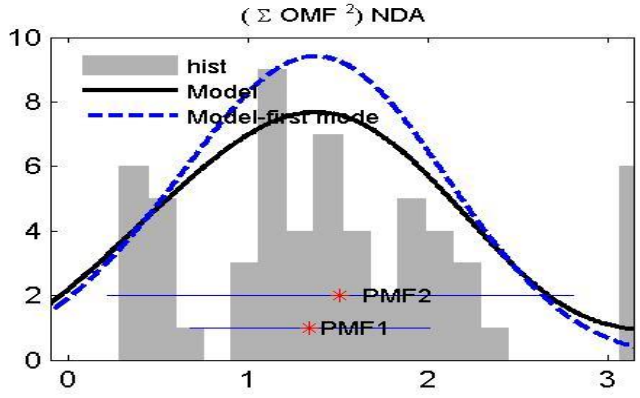
Matrix	CPP-023	CPP-031	CPP-035	CPP-036a	CPP-036b
Test solution	U-U-U-U-U-U	B-B-B-B-B-B	S-S-S-S-S-S	B-B-B-B-B-B	S-S-S-S-S-S
Dust extract	U-U-U-U-U-U	B-B-B-B-B-B	S-S-S-S-S-S	B-B-B-B-B-B	S-S-S-S-S-Q
Soil extract	B-B-B-B-B-B	B-B-B-B-B-B	S-S-S-S-S-S	B-B-B-B-B-B	S-S-S-S-S-S
Fish extract	B-B-B-B-B-B	B-B-B-B-B-B	U-Q-Q-Q-Q-Q	B-B-B-B-B-B	S-S-S-S-S-S

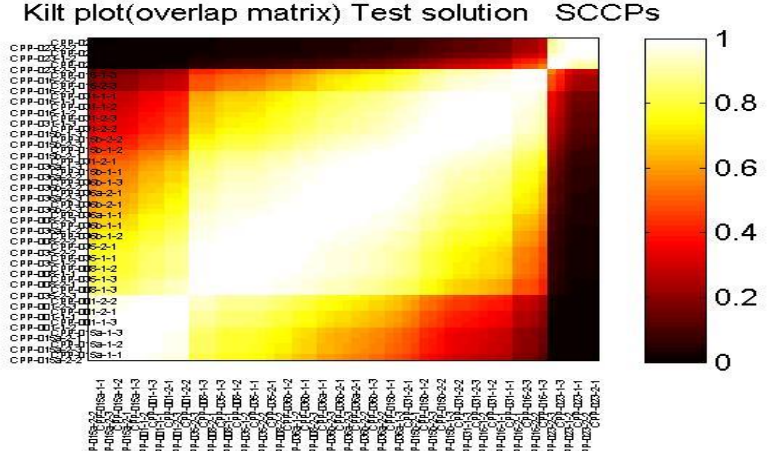
Appendix F Consistency of the data quantified with participants' own standard

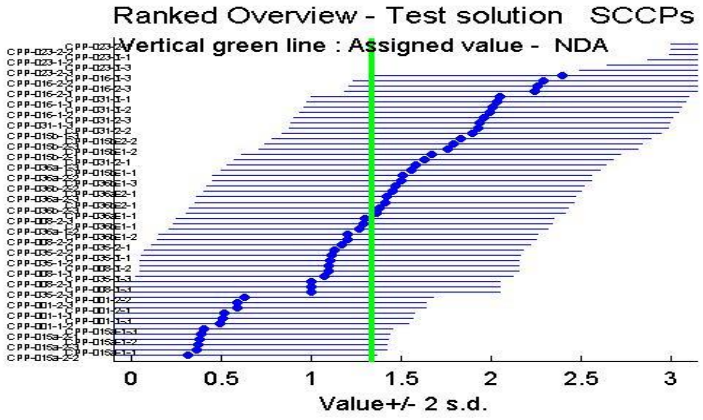
Matrix	CPP-001	CPP-008	CPP-015a	CPP-015b	CPP-016
Test solution	U-U-U-U-U-U	S-S-S-S-S-S	U-U-U-U-U-U	S-Q-U-S-Q-Q	U-U-U-U-U-U
Dust extract	U-U-U-U-U-U	S-S-S-S-S-S	U-U-U-U-U-U	S-S-S-S-S-S	U-U-U-U-U-U
Soil extract	S-S-S-S-B-S	Q-S-S-U-Q-Q	U-U-U-U-U-U	U-U-U-U-U-U	q-U-U-U-U-U
Fish extract	Q-U-U-U-U-Q	I-I-I-I-I-I	U-C-C-U-C-U	U-U-B-B-U-U	U-U-U-U-U-U

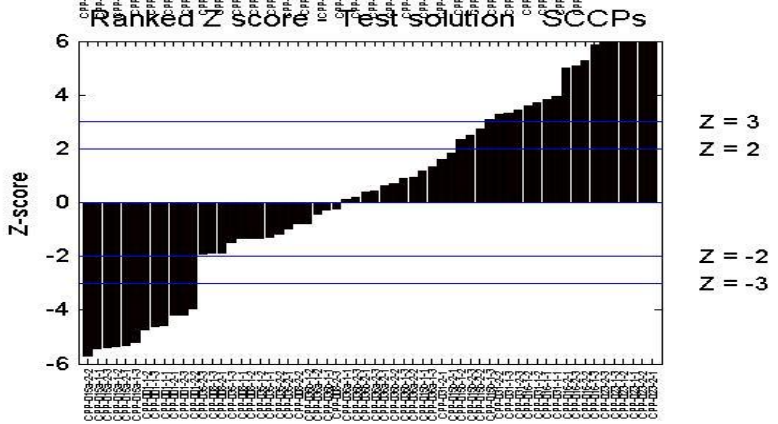
Matrix	CPP-023	CPP-031	CPP-035	CPP-036a	CPP-036b
Test solution	U-U-U-U-U-U	U-U-U-S-U-U	S-S-S-S-S-S	S-S-S-S-S-S	S-S-S-S-S-S
Dust extract	U-U-U-U-U-U	U-S-Q-U-Q-Q	U-U-U-U-U-U	S-S-S-S-S-S	S-S-S-S-S-S
Soil extract	B-B-B-B-B-B	S-S-S-S-S-S	Q-Q-U-Q-Q-U	S-S-S-S-S-S	Q-Q-S-S-S-S
Fish extract	B-B-B-B-B-B	U-S-S-Q-S-S	S-S-S-S-S-S	S-S-S-S-S-S	S-S-S-S-S-S

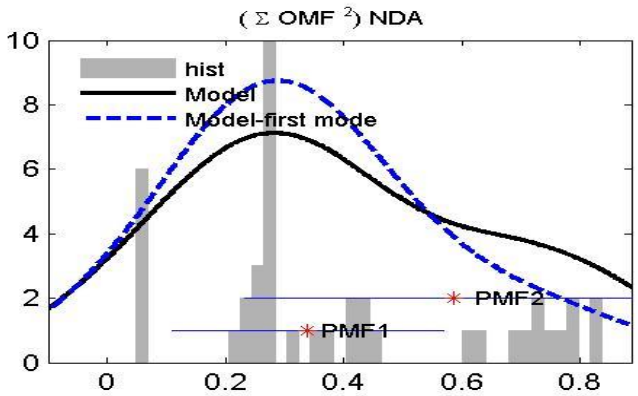
Appendix G Graphical output Cofino Statistics of results quantified with provided ILS standard

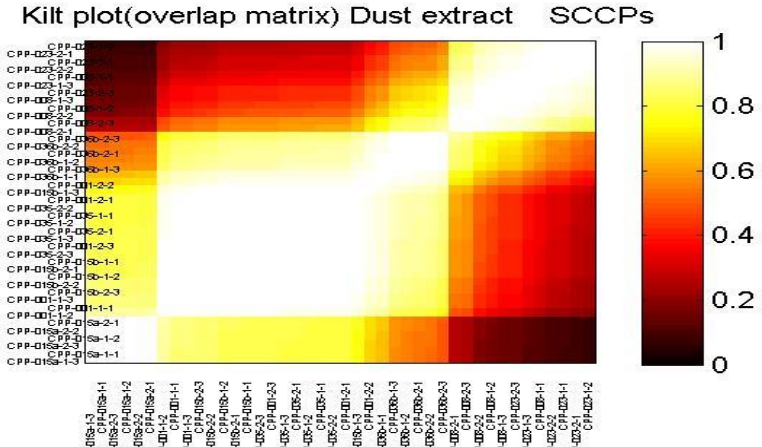


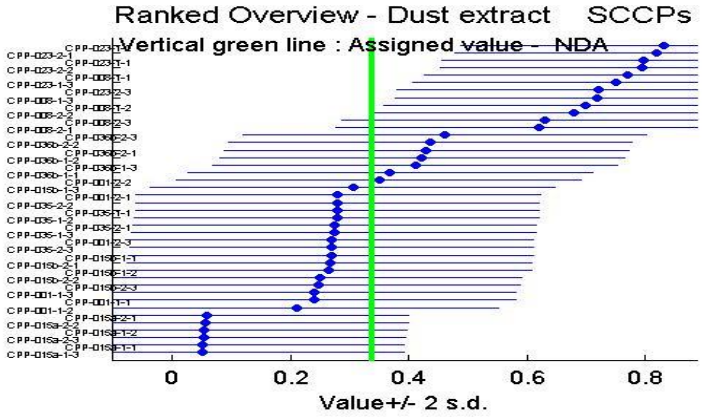


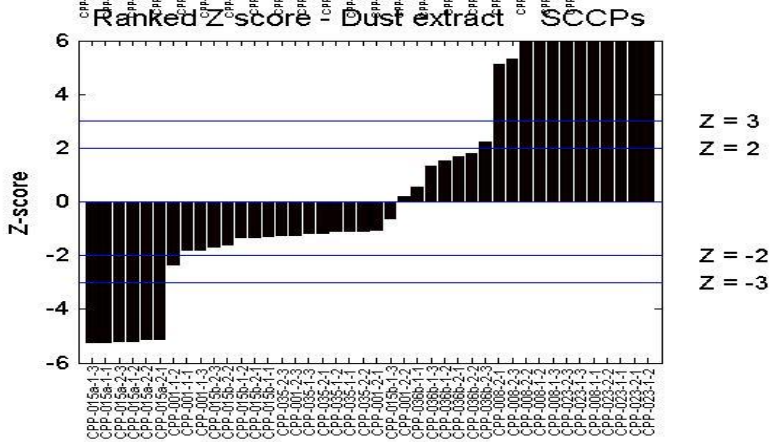


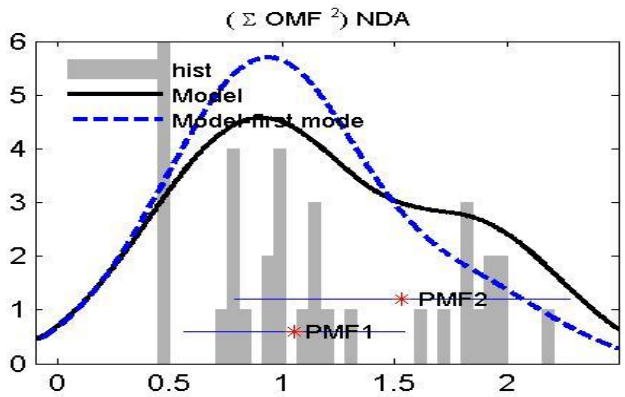


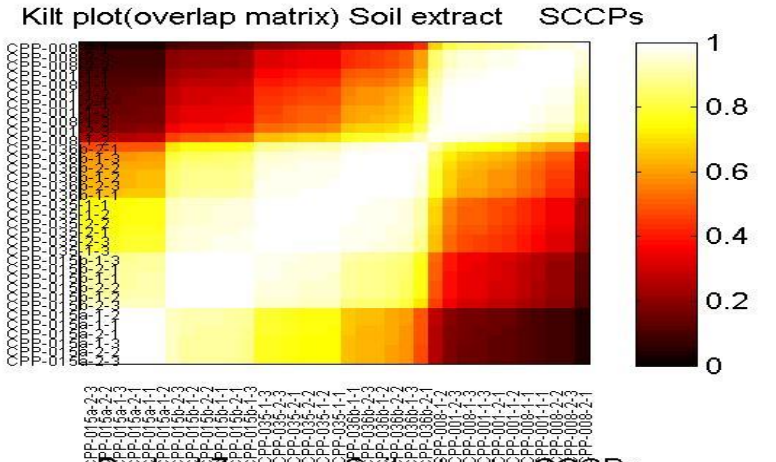

(Σ OMF 2) NDA
hist
Model
Model-first mode
PMF2
PMF1
0
2
4
6
8
10
0
0.2
0.4
0.6
0.8

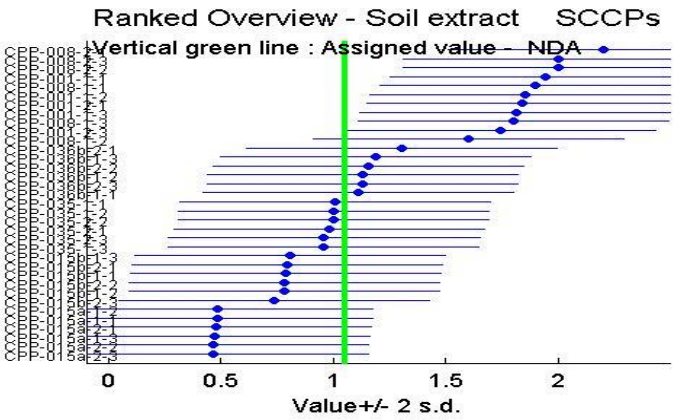

Kilt plot(overlap matrix) Dust extract SCCPs
1
0.8
0.6
0.4
0.2
0

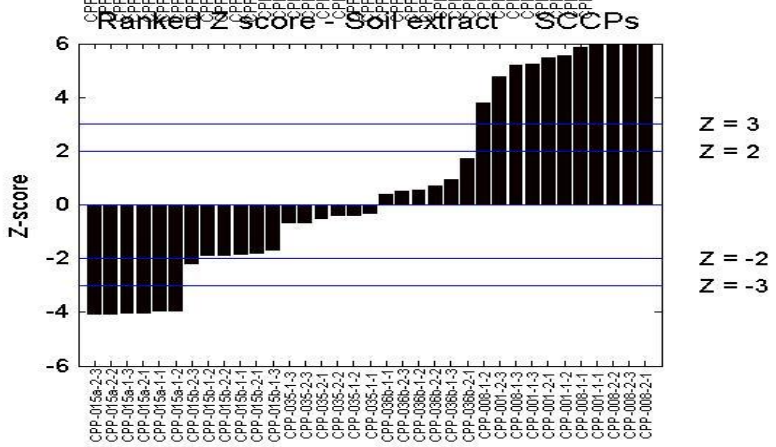

Ranked Overview - Dust extract SCCPs
Vertical green line : Assigned value - NDA
0
0.2
0.4
0.6
0.8
Value+/- 2 s.d.

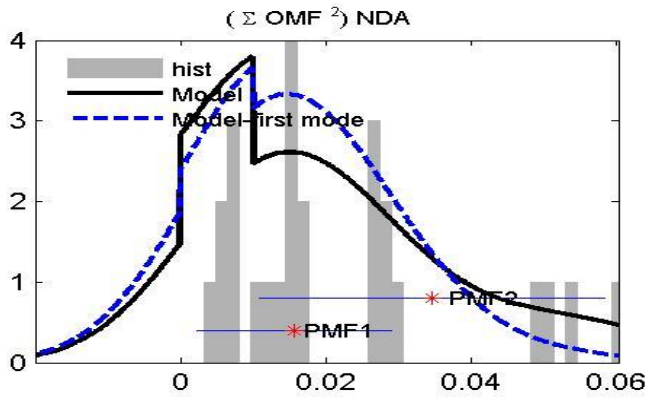

Ranked Z-score - Dust extract SCCPs
Z-score
6
4
2
0
-2
-4
-6
Z = 3
Z = 2
Z = -2
Z = -3

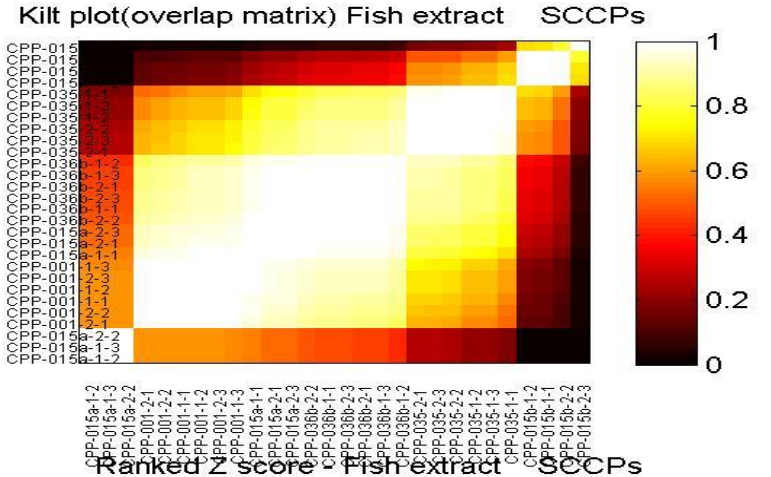

(Σ OMF 2) NDA
hist
Model
Model first mode
PMF2
PMF1
0
0.5
1
1.5
2
0
1
2
3
4
5
6

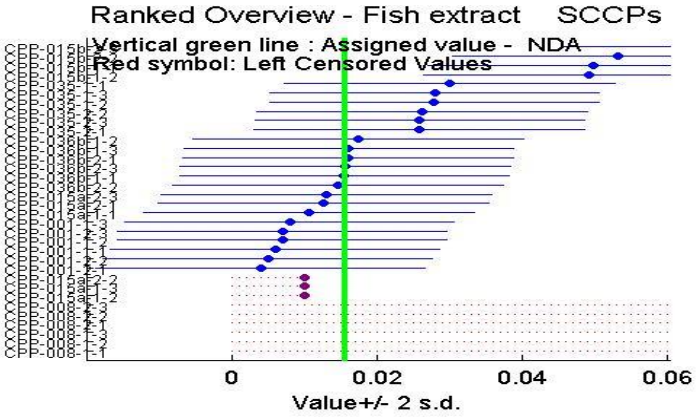

Kilt plot(overlap matrix) Soil extract SCCPs
1
0.8
0.6
0.4
0.2
0

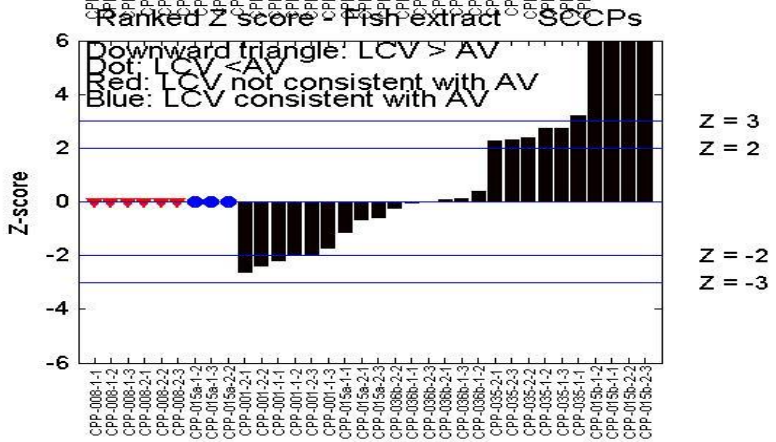

Ranked Overview - Soil extract SCCPs
Vertical green line : Assigned value - NDA
0
0.5
1
1.5
2
Value+/- 2 s.d.


Ranked Z score - Soil extract SCCPs
Z-score
Z = 3
Z = 2
Z = -2
Z = -3
6
4
2
0
-2
-4
-6

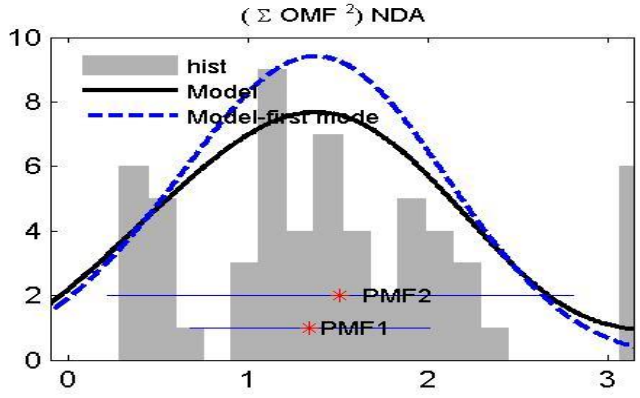

(Σ OMF 2) NDA
hist
Model
Model-first mode
PMF2
PMF1
0
1
2
3
4
0
0.02
0.04
0.06

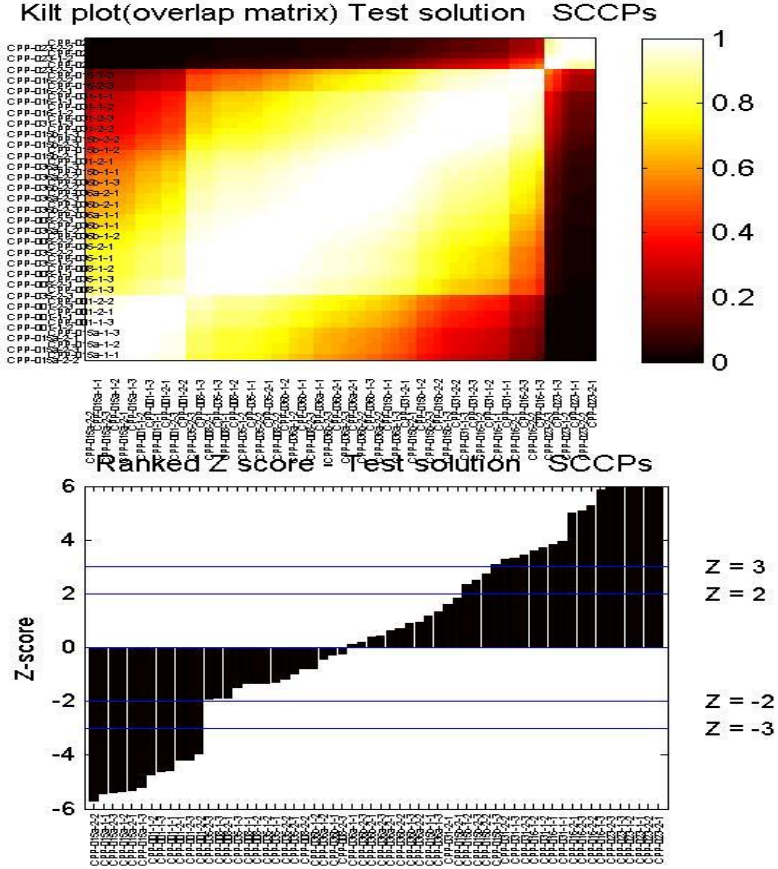

Kilt plot(overlap matrix) Fish extract SCCPs
1
0.8
0.6
0.4
0.2
0

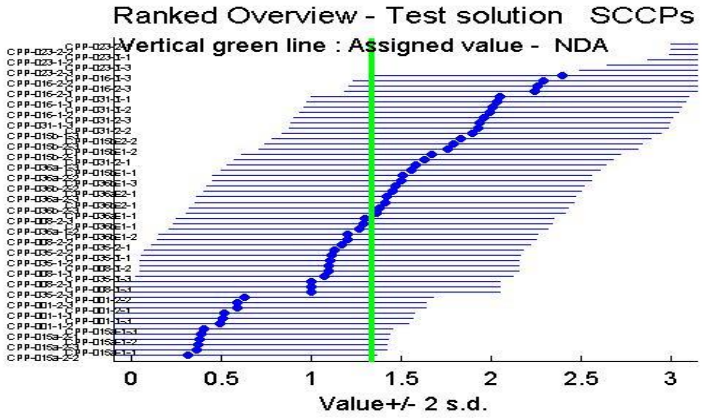

Ranked Overview - Fish extract SCCPs
Vertical green line : Assigned value - NDA
Red symbol: Left Censored Values
0
0.02
0.04
0.06
Value+/- 2 s.d.

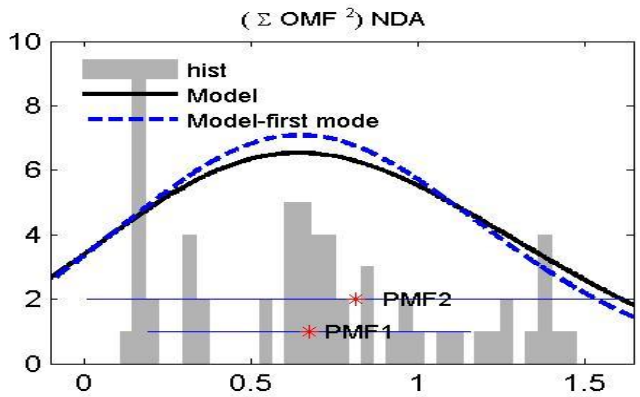

Ranked Z score - Fish extract SCCPs
Downward triangle: LCV > AV
Dot: LCV <AV
Red: LCV not consistent with AV
Blue: LCV consistent with AV
Z-score
Z = 3
Z = 2
Z = -2
Z = -3
6
4
2
0
-2
-4
-6

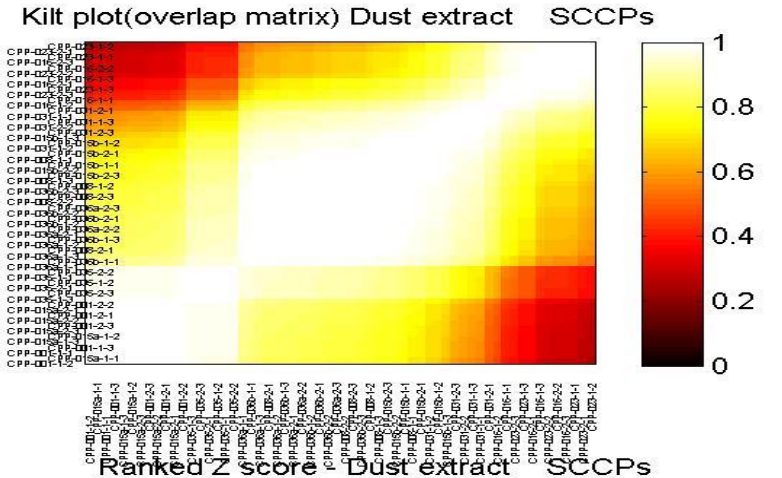
Appendix H Graphical output Cofino Statistics of results quantified by participants own standards

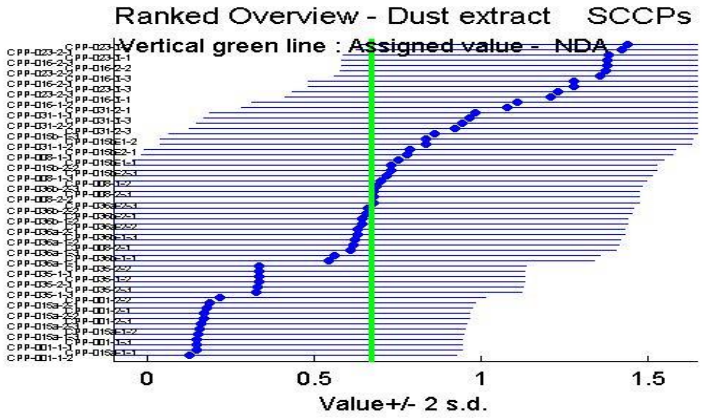


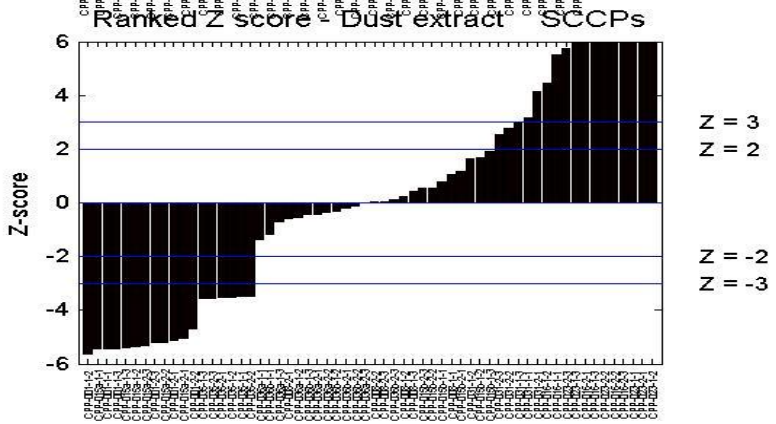


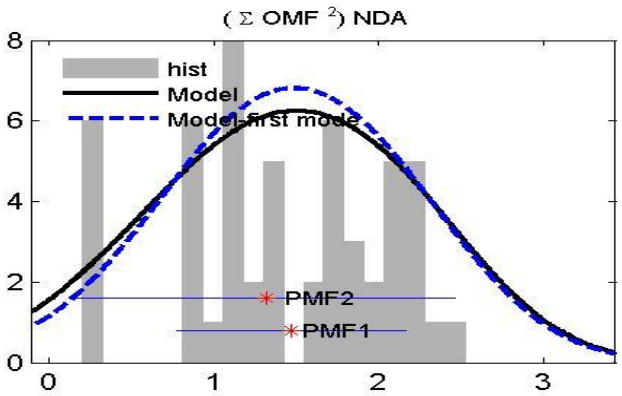


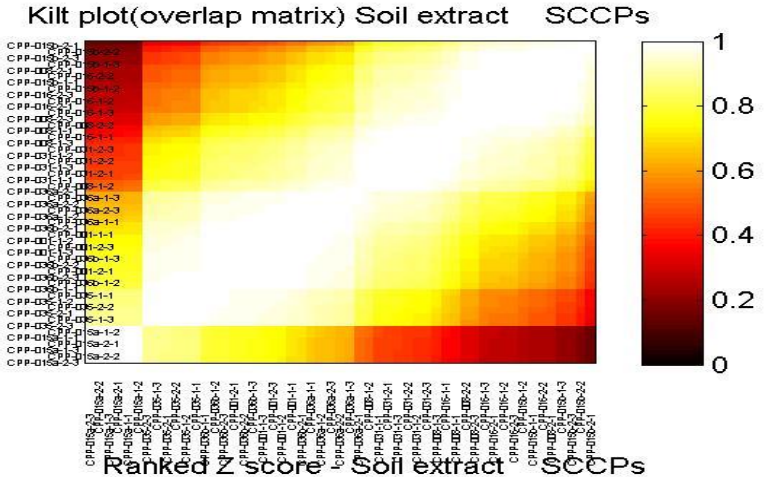

(Σ OMF 2) NDA
hist
Model
Model-first mode
PMF2
PMF1
10
8
6
4
2
0
0
0.5
1
1.5

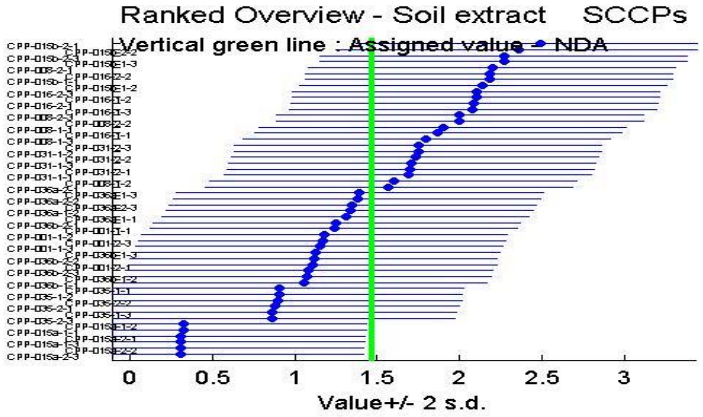

Kilt plot(overlap matrix) Dust extract SCCPs
1
0.8
0.6
0.4
0.2
0

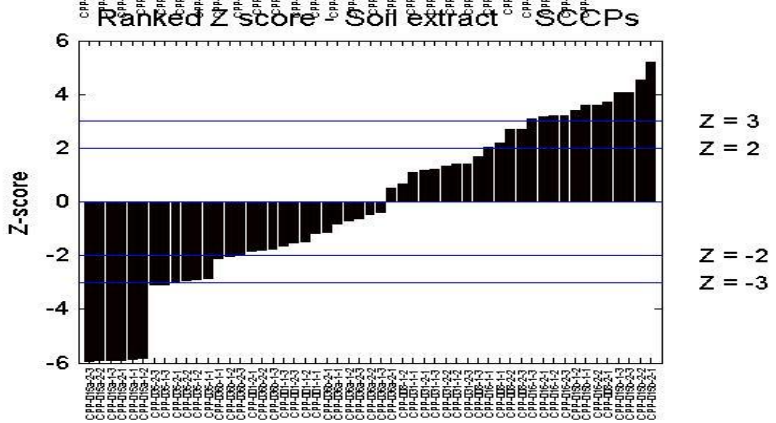

Ranked Overview - Dust extract SCCPs
Vertical green line : Assigned value - NDA
0
0.5
1
1.5
Value+/- 2 s.d.

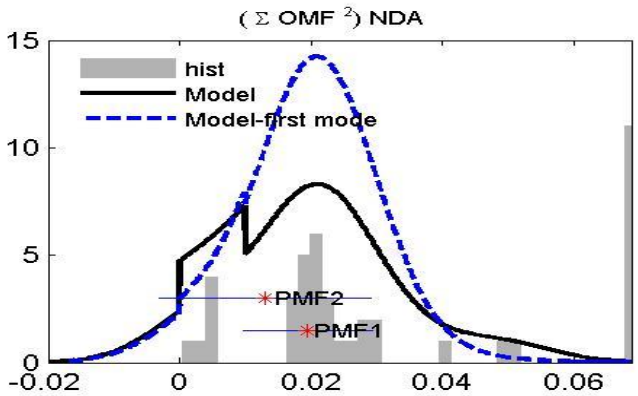

Ranked Z score - Dust extract SCCPs
Z-score
6
4
2
0
-2
-4
-6
Z = 3
Z = 2
Z = -2
Z = -3

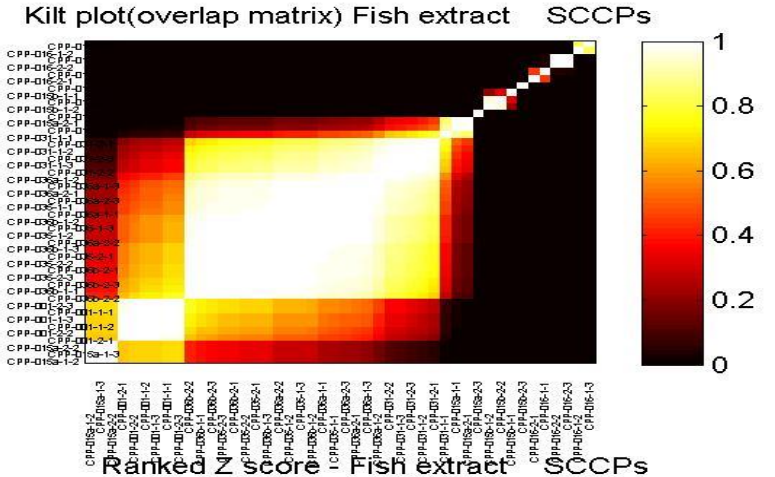

(Σ OMF 2) NDA
hist
Model
Model-first mode
PMF2
PMF1
0
2
4
6
8
0
1
2
3

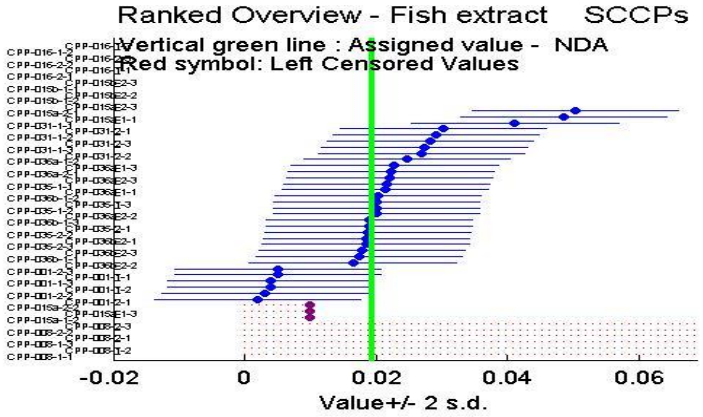

Kilt plot(overlap matrix) Soil extract SCCPs
1
0.8
0.6
0.4
0.2
0

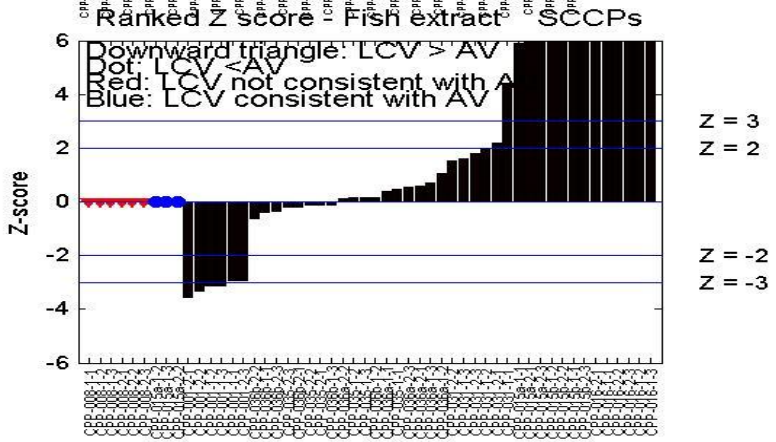

Ranked Overview - Soil extract SCCPs
Vertical green line : Assigned value
NDA
0
0.5
1
1.5
2
2.5
3
Value+/- 2 s.d.


Ranked Z score - Soil extract SCCPs
Z-score
6
4
2
0
-2
-4
-6
Z = 3
Z = 2
Z = -2
Z = -3


(Σ OMF 2) NDA
hist
Model
Model-first mode
PMF2
PMF1
15
10
5
0
-0.02
0
0.02
0.04
0.06


Kilt plot(overlap matrix) Fish extract SCCPs
1
0.8
0.6
0.4
0.2
0


Ranked Overview - Fish extract SCCPs
Vertical green line : Assigned value - NDA
Red symbol: Left Censored Values
-0.02
0
0.02
0.04
0.06
Value+/- 2 s.d.


Ranked Z score - Fish extract SCCPs
Downward triangle: LCV > AV
Dot: LCV <AV
Red: LCV not consistent with A
Blue: LCV consistent with AV
Z-score
6
4
2
0
-2
-4
-6
Z = 3
Z = 2
Z = -2
Z = -3

Appendix I Additional method information

Participant code:	**CPP-01**	**CPP-008**	**CPP-015a**
Final volume in vial for analysis (µL):	20	~20µl	100
Instrument:			
Instrument type	GC	Shimadzu GCMS-QP2010 Plus Series	GC
Detection system	MS	MS	MS
Ionisation mode	ECNI	ECNI	ECNI
High Res/Low Res:	High Res	Low Res	Low Res
Type	Sector	MS	LRMS
Resolution (estimation):	8000	1	1000
GC column 1:			
Type	HP-Ultra 2	Rtx-5SiMS	DB-1
Specifications	20 m, 0.200 mm, 0.11 µm	30m x 0.25 mm x 0.25 µm	50x0.25x0.25
GC column 2 (optional):			
Type:		N.A.	N.A.
Specifications:		N.A.	N.A.
Oven temperature program:	90°, 1 mi, 20°/min, 245°, 0 min, 50°/min, 300°, 5 min	105°C 1.0min, 34°C/min 190°C 1.0min, 8°C/min 250°C 0 min, 40°C/min 290°C 8.0min	90 ºC for 2 min, at 30 ºC/min to 290 ºC, at 15 ºC/min to 325 ºC, and 7 min at 325 ºC
Ion source temperature:	140	200°C	300
Carrier gas:	He	Helium	Helium

Reagent gas:	Methane	Methane	Methane
Injection volume (µL):	1	2	1
Amount of injections:	1	3	4
Other information:		Pulsed splitless injection.	
Internal Standard:			
Yes/no	Yes	Yes	Yes
If yes, which compound?	13C10 1,5,5,6,6,10-Hexachlorodecane	d10-Anthracene	PCB-26
Standard Method used from literature			
Yes/no	Yes	Yes	Yes
If yes, which method	Tomy et al.	Castells P, Santos FJ, Galceran MT. (2004); Rapid Commun. Mass Spectrom. 18: 529-536	Reth et al. 2005

Participant code:	CPP-015b	CPP-016	cp-023
Final volume in vial for analysis (µL):	100	200	100
Instrument:			
Instrument type	GCxGC	GC	GC
Detection system	ECD	MS	MS
Ionisation mode	NA	ECNI	ECNI
High Res/Low Res:		LR	Low

Type		GC-NCI-MS Agilent Technology 5977N	
Resolution (estimation):			
GC column 1:			
Type	HP-5MS	DB5-MS	DB 1MS
Specifications	30x0.25x0.25	15m x 250µm x 0,1µm	15m x 0,25mm x 0,25 µm
GC column 2 (optional):			
Type:	zb-50		
Specifications:	5X0.25x0.25		
Oven temperature program:	90 ºC for 2 min, at 10 ºC/min to 180 ºC for 2 min, at 1.5 ºC/min to 280 ºC, at 30 °C/min to 320 °C, and at 320 °C for 10 min	Start with 2min. 80°C; 70°C/min to 280°C ->hold 2min, 70°C/min to 300°C -->hold 2 min	110°C (1min) 15°C/min to 330 °C
Ion source temperature:	300	150°C	150°C
Carrier gas:	He	He	He
Reagent gas:	makeup gas nitrogen		CH4
Injection volume (µL):	1	2	2
Amount of injections:	1	1	1
Other information:	FR 115 ml/min nitrogen, F1 1.3 and F2 22 mL/min		
Internal Standard:			
Yes/no	Yes	Yes	No

If yes, which compound?	PCB-26	1,2,5,5,6,9,10-Heptachlorodecan	
Standard Method used from literature			
Yes/no	No	Yes	No
If yes, which method	Based on Reth et al. 2005	Internal Method with reference to ISO 18635	

Participant code:	**CPP-031**	**CP-035**	**CPP-036**
Final volume in vial for analysis (µL):	40	50 µL for B-D samples ; approx. 50 µL for E extracts	100; 50 µ L for extracts
Instrument:			
Instrument type	LC (direct injection)	GC	LC
Detection system	MS	MS	MS
Ionisation mode	APCI	ECNI	APCI
High Res/Low Res:	High Res	High Resolution	High res
Type	QTOF	ToF	QToF
Resolution (estimation):	8200 FWHW	7500 (at m/z 400) for samples B-D; 12500 for samples E	10000
GC column 1:			
Type		HP-5MS	no column
Specifications		15 m x 0.25 mm id x 0.1 µm	
GC column 2 (optional):			
Type:			

Specifications:			
Oven temperature program:		90°C (hold time 1 min), 25°C/min to 290 °C (hold time 3 min); total run time: 12 min	NA
Ion source temperature:		150 °C	NA
Carrier gas:		He, 1.8 mL/min (constant flow)	NA
Reagent gas:		methane	Solvent: Acetonitrile
Injection volume (µL):		1 (2 for extracts E)	5
Amount of injections:		3 per sample	1
Other information:			
Internal Standard:			
Yes/no	yes	no	yes
If yes, which compound?	Dechlorane 603		13C-PCP
Standard Method used from literature			
Yes/no	No	Yes	Yes
If yes, which method		Adapted from Diefenbacher, P.S. et al. (2015). Environ .Sci. & Technol. 49, 9778	Bogdal et al. 2015 (a) & Reth et al. 2005 (b)