IVM Institute for Environmental Studies

Interlaboratory Study on the Analysis of Chlorinated Paraffins in Environmental Matrices

Phase III

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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
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
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
w	weight
µg/g	microgram per gram
µL	microliter

Summary

The third round of the QUASIMEME interlaboratory study (ILS) on SCCP analysis was carried out by 13 laboratories, which determined the ΣSCCPs in sediment. The ILS involved a clean-up of a sediment extract and the quantification of this extract, together with a provided cleaned extract. The quantification was done with a standard solution provided, and in some cases also with quantification standards of the participants. A larger number of laboratories was able to hand in a dataset (e.g. 13 out of 16), compared to the second phase (11 out of 22).

Numerous different instrumental techniques, such as gas chromatography coupled to a mass spectrometry in low and high resolution (GC-LRMS and GC-HRMS), comprehensive two dimensional gas chromatography coupled to an electron capture detector (GC×GC-ECD), GC coupled to a tandem MS (GC-MS/MS) and GC coupled to a time of flight MS (GC-TOF-MS), were used for the total SCCPs (ΣSCCPs) determination. Between laboratory coefficients (CVs) of 80% and 86% were found for the quantification of SCCPs in the provided cleaned sediment extract and uncleaned sediment extract, respectively, indicating that different clean-up methods do not have a significant effect on the quantification. When using quantification standards of their own choice, larger between laboratory CVs were found, with 86% and 117% for the provided cleaned sediment and sediment extract cleaned by the participants, respectively, highlighting the importance of suitable quantification standards.

Remarkably, three out of the four participants that operated their GC-MS(/MS) in the electron impact (EI) mode with high ion source temperatures (220-230 °C), reported concentrations 10-30 fold higher than participants with other ionisation modes and instruments. Further research in investigating the difference in ΣSCCPs concentrations measured by GC/EI-MS and GC-MS operated in the electron capture negative ion (ECNI) mode is suggested.

Overall, the results of the third phase of the present ILS indicate that the determination of SCCPs is still very complex and further improvements are necessary. However, between laboratory CVs of this ILS phase are lower than those obtained in the second phase of this ILS. Ongoing ILSs are recommended.

1 Introduction

Chlorinated paraffins (CPs), also known as polychlorinated *n*-alkanes, are emerging persistent pollutants, existing as complex mixtures of various carbon chain lengths and chlorine atoms. Based on these carbon chain lengths, CPs are divided into three groups: short (C_{10}-C_{13}), medium (C_{14}-C_{17}) and long (C_{18}-C_{28}) chained. Concerns about the risks to the environment and humans associated with exposure of CPs are rising due to their high production volumes (e.g. up to 1 million tons year^{-1} in China alone in 2009 (Chen *et al.*, 2011) and persistency (Thompson and Noble, 2007). Especially short-chained CPs (SCCPs) are under particular scrutiny. As these compounds have a high bioaccumulation potential and are toxic, in particular to aquatic organisms (UNEP, 2015), SCCPs are listed as key compounds for monitoring in several legislations such as in the European Water Framework Directive. While SCCPs are also considered for classification as persistent organic pollutants (POPs) under the Stockholm Convention, relevant information on their presence, concentration and fate in the environment is still insufficient to facilitate such international classification. This is mostly due to significant limitations in identifying and quantifying these compounds. Apart from one ISO method for SCCPs in water (Geiß *et al.*, 2014), to date no validated analytical procedure exists for routine monitoring of SCCPs in environmental samples and only semi-quantative analysis is possible, while there is doubt on the reliability of the existing methods used. Nonetheless, an increasing number of studies have been published over the last five years on CP analysis, levels and fate in the environment. An understanding of the current state of CP analysis is therefore urgently needed in order to develop reliable risk and exposure assessments of CPs that supports future decision making on any future regulatory actions of these compounds.

In March 2010, the Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME) organized a workshop on the analysis of CPs in Ostend, Belgium. It was generally agreed that there was a clear need for an interlaboratory study (ILS), preferably designed in a step-wise way. Therefore, the Institute for Environmental Studies (IVM), in cooperation with the proficiency testing scheme of QUASIMEME, organized an ILS on SCCPs involving a comparison between the current different analytical techniques used, existing out of four phases, of which the first two phases are completed.

In the first phase of the study participants were requested to quantify the total concentration of SCCPs (ΣSCCPs) and the concentration of three individual SCCPs in an *iso*-octane solution of SCCPs using an analytical method of their choice. Results of this study show that the majority of the laboratories obtained satisfactory z-scores for the analysis of the three individual SCCPs. The coefficients of variation varied between the compounds from 22 to 46% for the congeners and 56% for ΣSCCPs.

In the second phase of the study participants were requested to quantify ΣSCCPs in a cleaned fish extract with a provided SCCP mixture solution in known concentrations, again with an analytical method of their choice. A larger number of laboratories subscribed for the second phase, showing an increasing interest in SCCP determination. For the ΣSCCPs analysis a between laboratory CV of 137% was found. The reported concentrations were observed to fall into two distinct groups with a difference of approximately 10-fold. Possible explanations for the variation are the different ionisation methods used and/or the separation difficulties between CPs and other interfering compounds that might have been present in the extract.

Therefore, the third phase of the ILS on the analysis of SCCPs, described in this report, focused on quantifying ΣSCCPs in two sediments extracts (one raw, one cleaned), using a common standard solution, which was provided. This involved clean-up of one of the sediment extract plus a blank using an in-house method, and quantification of the ΣSCCPs in both extracts with the provided standard solution. In total 16 laboratories subscribed for this round, of which 13 submitted data.

This study was carried out by IVM in collaboration with QUASIMEME (www.quasimeme.org).

2 Materials and methods

2.1 Study design

In the third round participants were asked to quantify, in triplicate, the total level of SCCPs in sediment extracts using standard solution (ampoule A) and two extracts (a cleaned and raw extract, ampoule B and C, respectively) provided. This involved clean-up of one of the sediment extracts plus a blank using an in-house method, and quantification of the ΣSCCPs in both extracts with the provided standard solution. Participants were also invited to send the results quantified with their in-house quantification standards. Finally, participants were asked to provide a short description of determination techniques used, to allow a more in-depth analysis of the submitted data and performance characteristics.

The identification of the participating laboratory was encoded. The concentrations of ΣSCCPs determined in the sediment extracts were reported in µg/g extract (e.g. weight/weight of solvent and not weight/volume of solvent) due to possible difference in temperature conditions between the laboratories.

The first invitation for participation in the study was sent in August 2014 and the samples were distributed in November 2014. In total, 16 laboratories participated, of which 13 were able to return data.

2.2 Material preparation

Three ampoules were send to the participating laboratories.

Ampoule A: a technical mixture solution of SCCPs (C_{10}-C_{13}, 63% Cl), for quantification

Ampoule B: a cleaned sediment extract

Ampoule C: a sediment extract, to be cleaned by the participants

Ampoule A contained a mixture of SCCPs (C_{10}-C_{13}, 63% Cl), 66.5960 µg/g in *iso*-octane: cyclohexane ± 1:1 (w/w). Ampoule B and C contained both a mix of sediment from Dublin (Ireland), Westerschelde (Belgium) and Liverpool (England), extracted by pressurised liquid extraction. This extract was screened on SCCP presence and a GC×GC-ECD chromatogram was obtained to check for interferences by toxaphene and other compounds (Figure 2.1). After confirmation on SCCP presence, the extract was split in two (~40:60) for ampoule B and C. The extract for ampoule B was treated with copper powder for sulphur removal and cleaned up by an alumina (8% deactivated with H_2O) column and neutral silica gel column (1,6% deactivated with H_2O). No syringe or surrogate standards were added to the extracts.

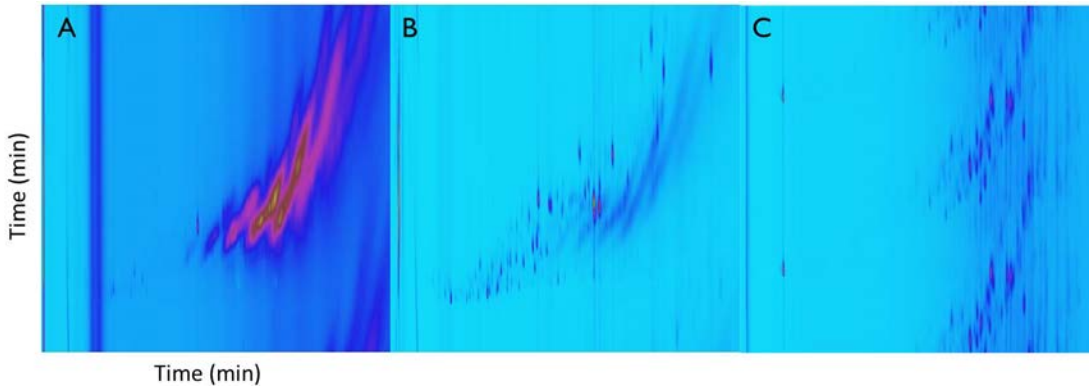


Figure 2.1 GC×GC-ECD chromatogram of A) quantification standard (ampoule A), B) sediment extract and C) technical toxpahene mixture, clearly showing that while SCCPs are present in the ILS sample, toxaphenes are not.

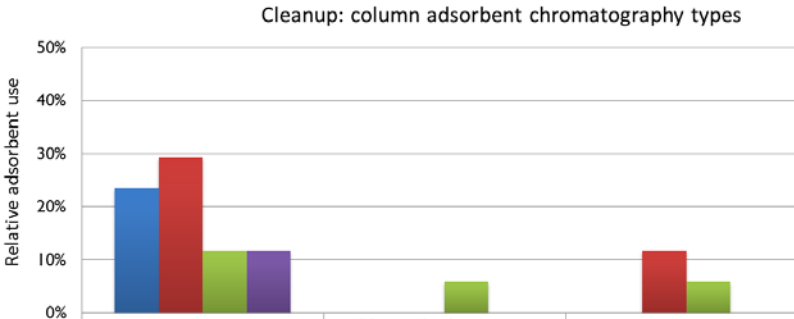
2.3 Methods used by participants

A detailed description of the methods reported by each individual participant is provided in Annex G.

Globally only a small number of laboratories are able to analyse CPs and consequently numbers of ILS participants for SCCPs is limited. Therefore, caution should be taken when making statements of the obtained data. Nonetheless, some comparisons can be made.

2.3.1 Clean-up

Clean-up methods that were used varied widely (Figure 2.2). Remarkably, only one of the participants reported the use of a multilayer column, which is in contrast to the increasing use of multilayer columns in recent CP studies published since 2010 (van Mourik *et al.*, 2015). Instead, one or two columns were used. One of the participants reported on using gel permeation chromatography. Florisil was most commonly applied with column chromatography, followed by aluminium oxide and normal silica gel.



	Adsorbent 1st column	Additional adsorbent 1st column	Adsorbent 2nd column	Total
Al2O3	24%			24%
Florisil	29%		12%	41%
SiO2	12%	6%	6%	24%
Acidic SiO2	12%			12%

Figure 2.2 Reported clean-up techniques for ΣSCCPs determination in sediment extract.

The majority of the participants (77%) used recovery standards such as $^{13}C_{10}$ 1,5,5,6,6,10-Hexachlorodecane (31%), 1,1,1,3,11,13,13,13-Octachlorotridecane, cis-chlordane, trans-chlordane, $^{13}C_6$-HCB and ^{13}C-PCB 153. One participants used two recovery standards (1,3,5-tribromobenzene and PCB 209).

2.3.2 Instrumental techniques

Numerous instrumental techniques were used (Figure 2.3) of which gas chromatography coupled to a mass spectrometry (GC-MS) was the most common instrumental approach. Other instrumental techniques that were applied include comprehensive two dimensional gas chromatography coupled to an electron capture detector (GC×GC-ECD) and GC coupled to a tandem mass spectrometry (GC-MS/MS). For the first time in the ILS rounds, a GC coupled to a time of flight mass spectrometry (GC-TOF-MS) was also used.

GC-MS, both high resolution (HR) and low resolution (LR), usually operated in the electron capture negative ion (ECNI) mode, with one exception of a participant that used electron ionization (EI) mode. EI mode was applied when using GC-MS/MS. Source block temperature varied between 120-300 ºC and the majority of the participants injected a volume of 1 µL (54%).

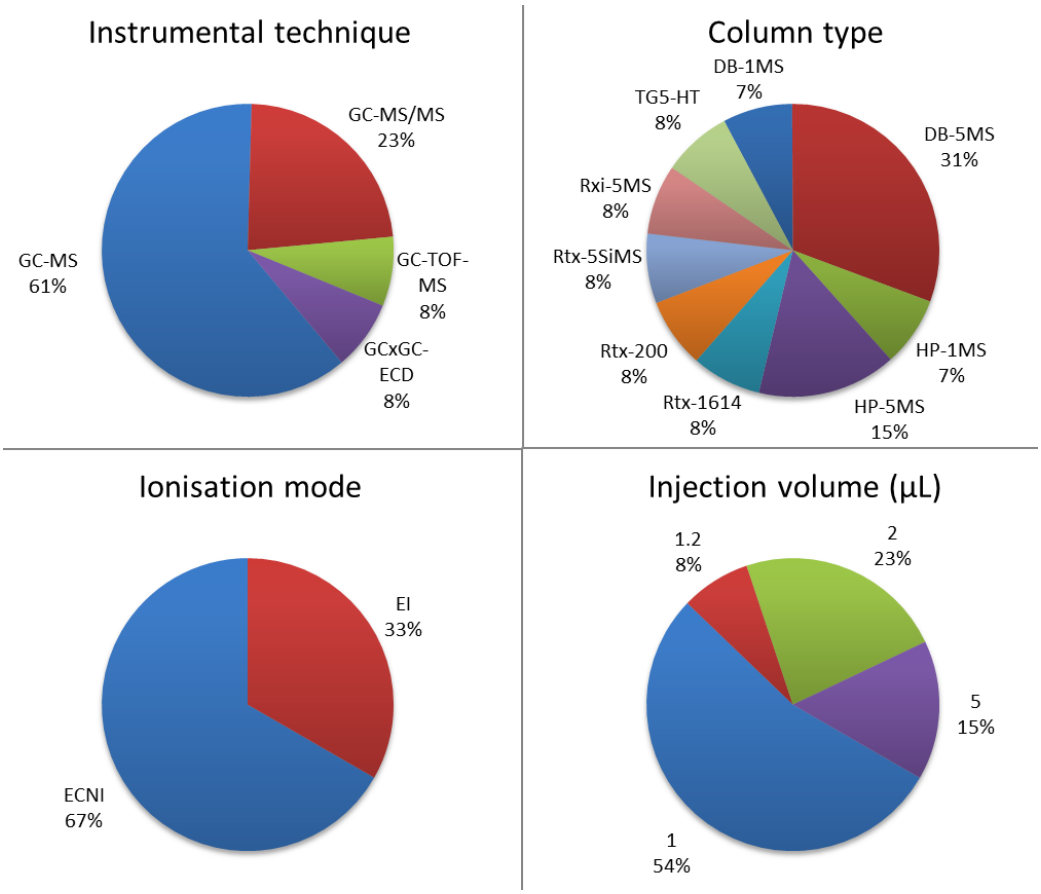


Figure 2.3 Reported detection techniques for ΣSCCPs determination in sediment extract.

2.3.3 Quantification

In total 13 participants submitted a dataset obtained by quantification of total SCCPs with the provided standard solution (ampoule A), in this report marked with M1. Eight participants submitted an additional dataset, obtained with quantification with in-house mixtures, marked with M2.

The majority of the participants (62%) used a syringe standard, like 1,2,3,4,5,6-hexachlorocyclohexane (15%), $^{13}C_6$-hexachlorobenzene (15%), ^{13}C-polychlorinated biphenyl 180, 4,4'-dibromo-octafluorobiphenyl, cyclododecane and trans-chlordane for the quantification of SCCPs.

The majority of the participants used a DB-5MS (31%) or HP-5MS (15%) as column (Figure 2.3), and most common dimensions were 30 m 0.25 mm 0.25 µm (38%) and 15 m 0.25 mm 0.25 µm (38%), followed by 15 m 0.25 mm 0.1 µm (15%) and 60 m 0.25 mm 0.1 µm (8%). Only two participants reported that they were able to quantify the separate alkane groups (C_{10}, C_{11}, C_{12}, C_{13}) and chlorine groups (Cl_7, Cl_8, Cl_9, Cl_{10}).

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 of the data 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 also 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 were provided elsewhere (Wells *et al.*, 2004, Wells and Scurfield, 2004), but in summary the approach is as follows:

- All data included in the assessment
- No data trimmed or down weighted
- AV based on Cofino NDA model
- All left censored values (LCV)[1] are also included, provided certain criteria are met (Chapter 2.4.2).

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

2.4.1 Plots

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 2.4). 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).

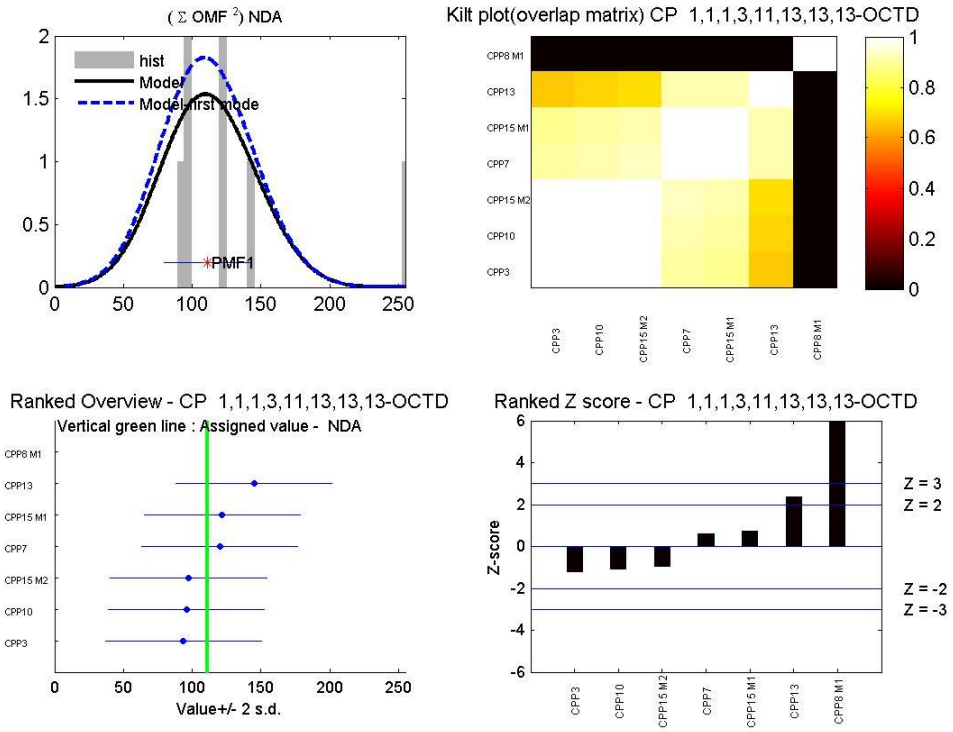


Figure 2.4 Examples of the graphical output of the Cofino Model statistics.

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.

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 0.

2.4.2 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 2.4), 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 ≥ 33% of values have a z-score of $|Z| < 2$. Where < 33% of the data has $|Z| < 2$ the value is indicative. *i.e.* at least 33% 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.

2.4.3 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 2.5 illustrates the interpretation of the z-scores:

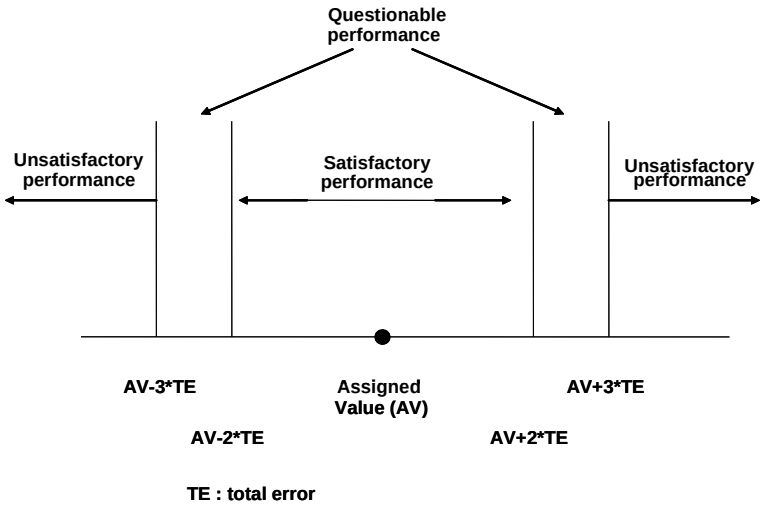


Figure 2.5 Interpretation of z-scores.

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 whenever the data met the criteria, as 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. Whenever less than values (LCV) were submitted, the percentage of consistent and inconsistent LCVs with the AV is given. The submitted data is presented in Annex G. Tables with individual z-scores are presented in Annex C, consistencies of the individual results are presented in Annex D and z-score plots in Annex E and F.

Table 3.1 Results of reported ΣSCCPs concentrations in sediment extract

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, based on all reported concentrations								
Cleaned sediment extract[c]	0.863	0.863	1.109	0.142	31.672	93	65	59
Sediment extract cleaned by in-house techniques [d]	1.497	1.497	1.935	0.534	30.943	84	64	59
Blank	0.029	0.029	0.03	0	0.432	105	68	31
ΣSCCPs, based on average reported concentrations								
Clean sediment extract	N.A.	0.879	1.148	0.149	30.774	101	68	21
Sediment extract cleaned by in-house techniques	1.496	1.496	1.935	0.587	30.500	87	66	21
Blank	0.031	0.031	0.047	0.000	0.432	121	65	14
ΣSCCPs, determined by provided standard								
Clean sediment extract	0.908	0.908	1.124	0.142	28.138	80	63	36
Sediment extract cleaned by in-house techniques	N.A.	1.473	1.932	0.539	29.156	86	62	36
Blank	0.024	0.024	0.026	0.000	0.398	83	61	20
ΣSCCPs, determined by in-house standard								
Clean sediment extract	N.A.	0.788	1.109	0.218	31.672	117	67	23
Sediment extract cleaned by in-house techniques	N.A.	1.544	1.995	0.534	30.943	86	67	23
Blank	0.034	0.034	0.048	0.000	0.432	78	65	11

[a] Min: lowest value submitted > LOQ
[b] Max: highest value submitted > LOQ
[c] Also known as ampoule B
[d] Also known as ampoule C
N.A. Not available

Table 3.2 Results of laboratory performance for ΣSCCPs concentrations in sediment extract

Determinand	AV[a] (µg/g)	% of data received	% of z-scores |Z|<2 Satisfactory	% of z-scores 3>|Z|>2 Questionable	% of z-scores 6>|Z|>3 Unsatisfactory	% of z-scores |Z|>6 Extreme
ΣSCCPs, based on all reported concentrations						
Cleaned sediment extract[b]	0.863	82	27	17	19	37
Sediment extract cleaned by in-house techniques[c]	1.497	82	25	19	17	39
Blank	0.029	64	46	4	2	15
ΣSCCPs, based on average reported concentrations						
Clean sediment extract	N.A.	88	N.A.			
Sediment extract cleaned by in-house techniques	1.496	88	29	14	19	38
Blank	0.031	88	43	5	0	19
ΣSCCPs, determined by provided standard						
Clean sediment extract	0.908	75	33	11	14	42
Sediment extract cleaned by in-house techniques	N.A.	75				
Blank	0.024	60	41	7	3	17
ΣSCCPs, determined by in-house standard						
Clean sediment extract	N.A.	96				
Sediment extract cleaned by in-house techniques	N.A.	96				
Blank	0.034	71	53	0	0	12

[a] AV Assigned Value
[b] Also known as ampoule B
[c] Also known as ampoule C
N.A. Not available

4 Discussion

Thirteen laboratories were able to submit data, of which eight submitted an additional dataset that was obtained by using their own quantification standards. While only one participant had less than one year experience in CP analysis, six participants had experience between 1-3 years and six over three years. No significant difference was observed between the reported ΣSCCPs concentrations and years of experience.

In general, laboratories that reported high SCCP concentrations in the ILS samples reported high levels of SCCPs in blanks too (Figure 3.1). Results were not corrected by blank value, except for one participant (CPP-18).

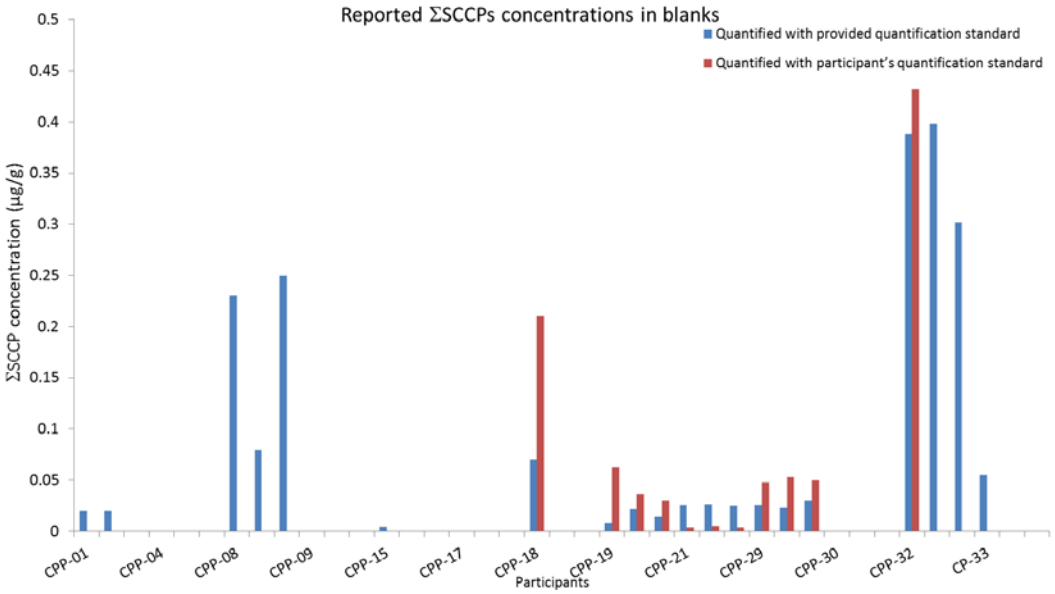


Figure 4.1 Plot of reported ΣSCCPs concentrations in blanks, determined with provided quantification standard (blue column, Ampoule A) and with participants own quantification standards (red column).

4.1 Laboratory performance

Numerous instrumental techniques were applied for ΣSCCPs determination in sediment (Figures 3.2 and 3.3). When the cleaned sediment extract was quantified with the provided quantification standard, a between laboratory CV of 80% was found for the ΣSCCPs analysis, suggesting that CP analysis is still complex. When the sediment extract that was cleaned by the participants, was quantified with the provided quantification standard, a between laboratory CV 86% was found. These findings indicate that clean-up methods have minor effects on a variation in ΣSCCPs analysis.

A larger variation of between laboratory CVs were found when the extracts were quantified with quantification standards of the participants (86-117%), suggesting that the choice of standards is critical. Responses of CPs may vary significantly, depending for example on the chlorination degree, chain length, and the ion source temperature when using ECNI-MS (Coelhan, 2010). As can be seen in figure 2.1, SCCPs were clearly present and the quantification standard was similar to that of the sample. Furthermore, no real interferences were observed.

Reported concentrations that were determined with GC×GC-ECD and GC-TOF-MS were in similar concentration ranges as those determined by GC-MS in ECNI mode (Figures 3.4 and 3.5). On their turn, concentrations determined by LRMS and HRMS were in similar ranges too, with one exception of higher reported concentrations with HRMS. In contrast, ΣSCCPs concentrations determined with GC-MS/MS in EI mode were generally 10-30-fold higher than those determined by other instruments (Figures 3.4 and 3.5).

Three of the four participants that used an ion source temperature of 220-230º C reported relatively high concentrations (Figures 3.6 and 3.7). Indeed, (Coelhan, 2010) suggested that responses of CPs may significantly vary depending on, next to other things, the ion source temperature. On the other hand, all three participants operated either their MS/MS or LRMS in the EI mode while the fourth participant, which did report concentrations in agreement of the AVs, used GC/ECNI-MS, suggesting that the use of the EI mode could be a factor. Another participant, that operated a GC/EI-MS/MS at an ion source temperature of 280 ºC, had only slightly higher concentrations compared to the AVs. Clearly, further research is needed to investigate the difference in reported ΣSCCPs concentrations between GC/EI-MS/MS and GC/ECNI-MS and ion source temperatures.

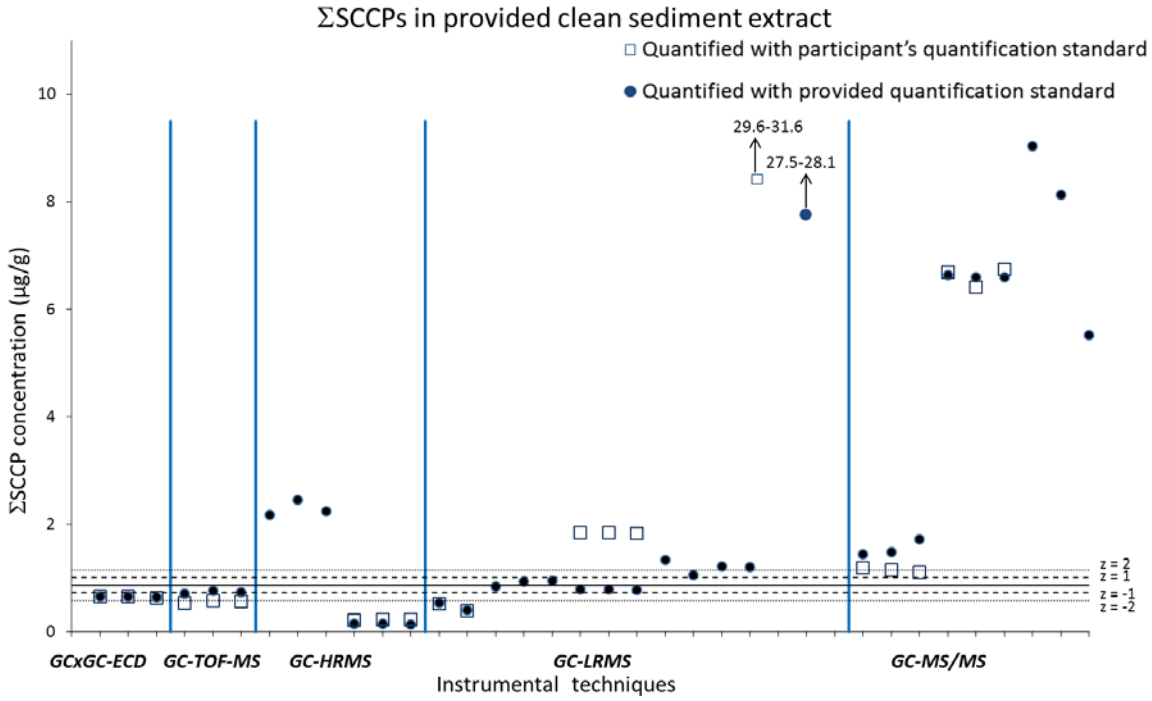


Figure 4.2 Plot of applied instrumental techniques and reported ΣSCCPs concentrations (in triplicate) in the provided clean sediment extract (Ampoule B), determined with provided quantification standard (blue circle; Ampoule A) and with participants own quantification standards (square).

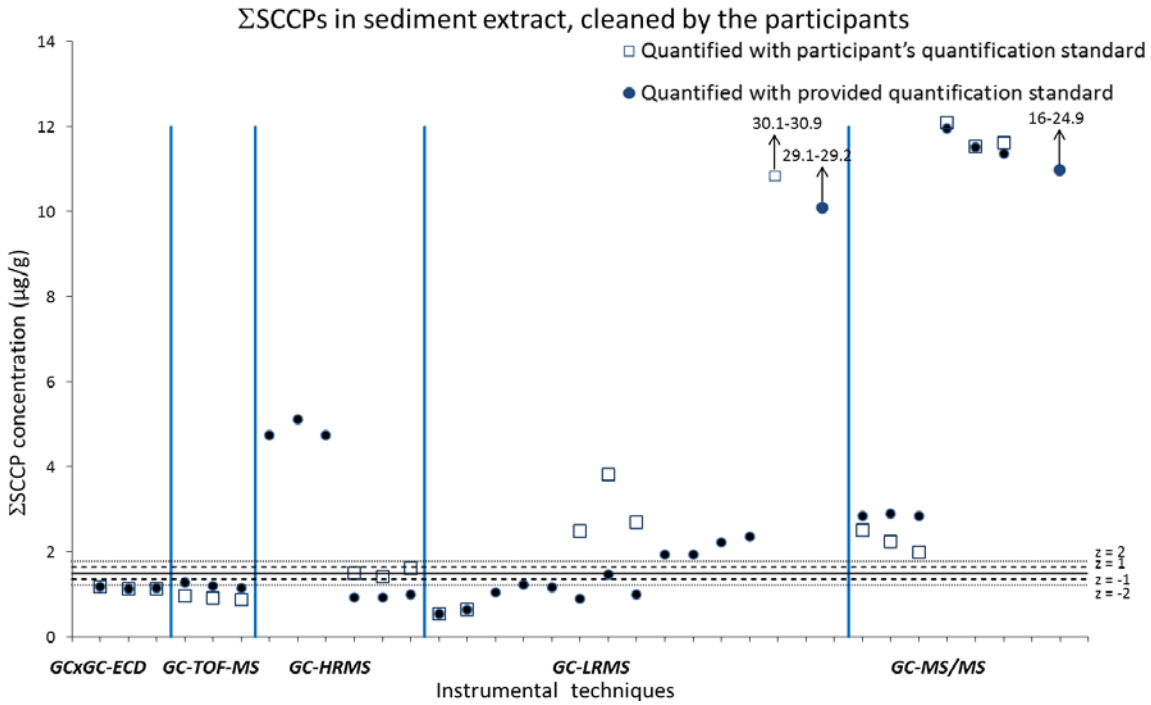


Figure 4.3 Plot of applied instrumental techniques and reported ΣSCCPs concentrations (in triplicate) in the sediment extract cleaned up by participants (Ampoule C) and determined with provided quantification standard (blue circle; Ampoule A) and with participants own quantification standards (square).

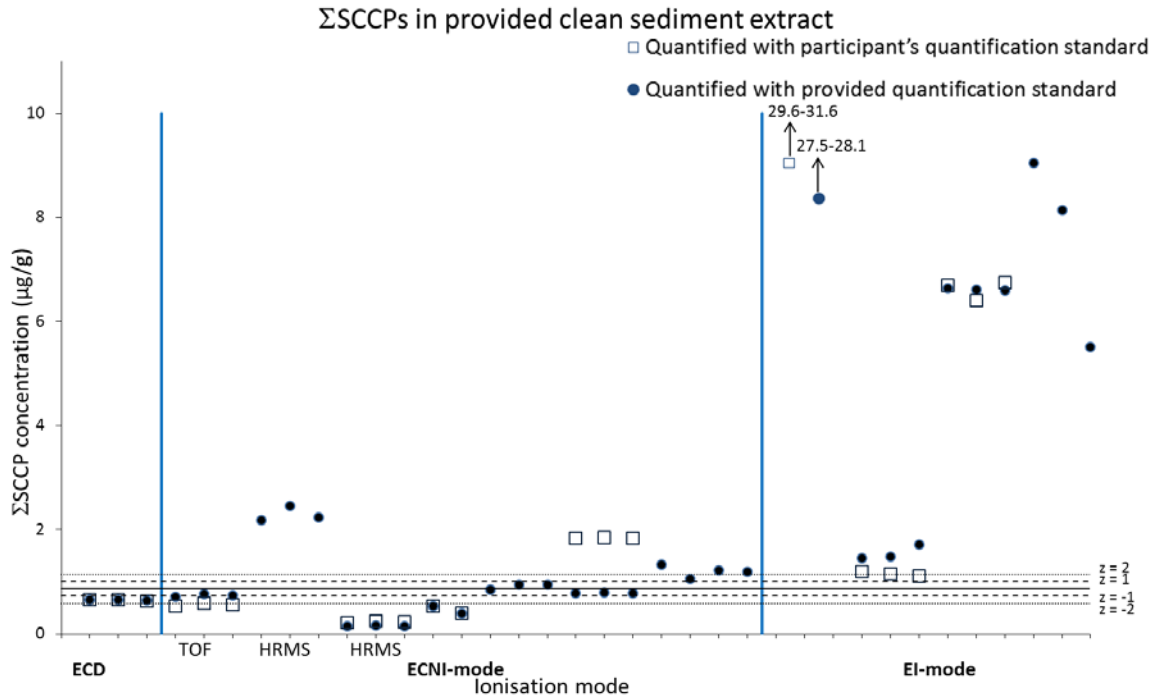


Figure 4.4 Plot of applied ionisation modes and reported ΣSCCPs concentrations (in triplicate) in the provided clean sediment extract (Ampoule B), determined with provided quantification standard (blue circle; Ampoule A) and with participants own quantification standards (square).

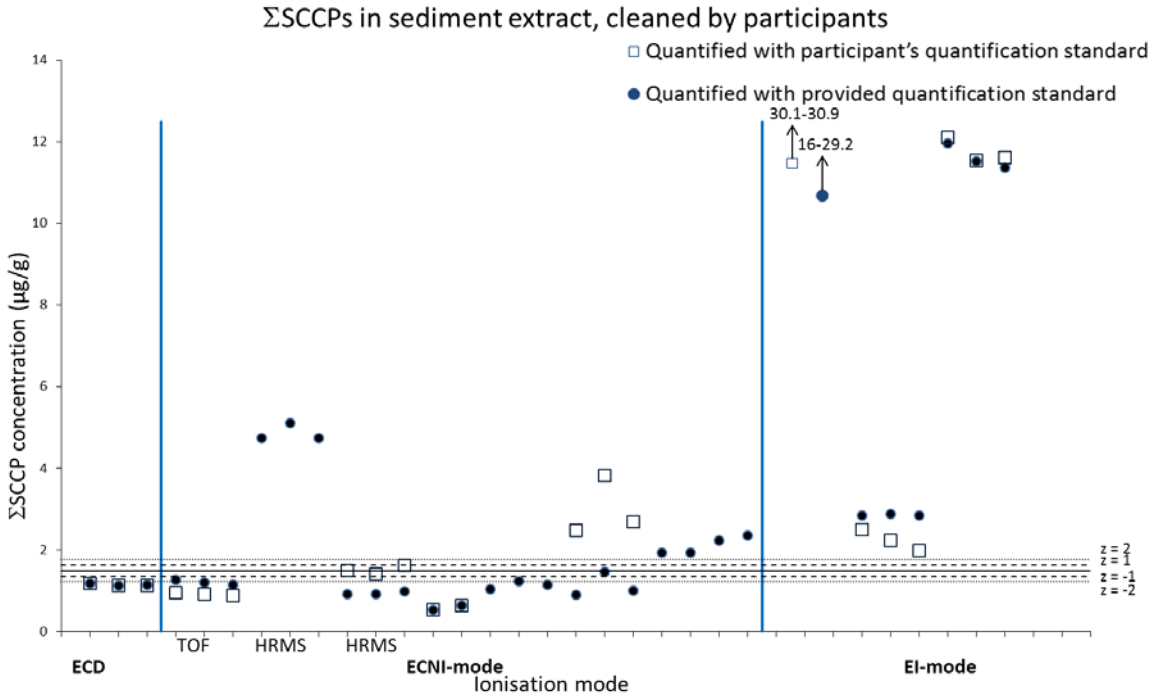


Figure 4.5 Plot of applied ionisation modes and reported ΣSCCPs concentrations (in triplicate) in the sediment extract cleaned up by participants (Ampoule C) and determined with provided quantification standard (blue circle; Ampoule A) and with participants own quantification standards (square).

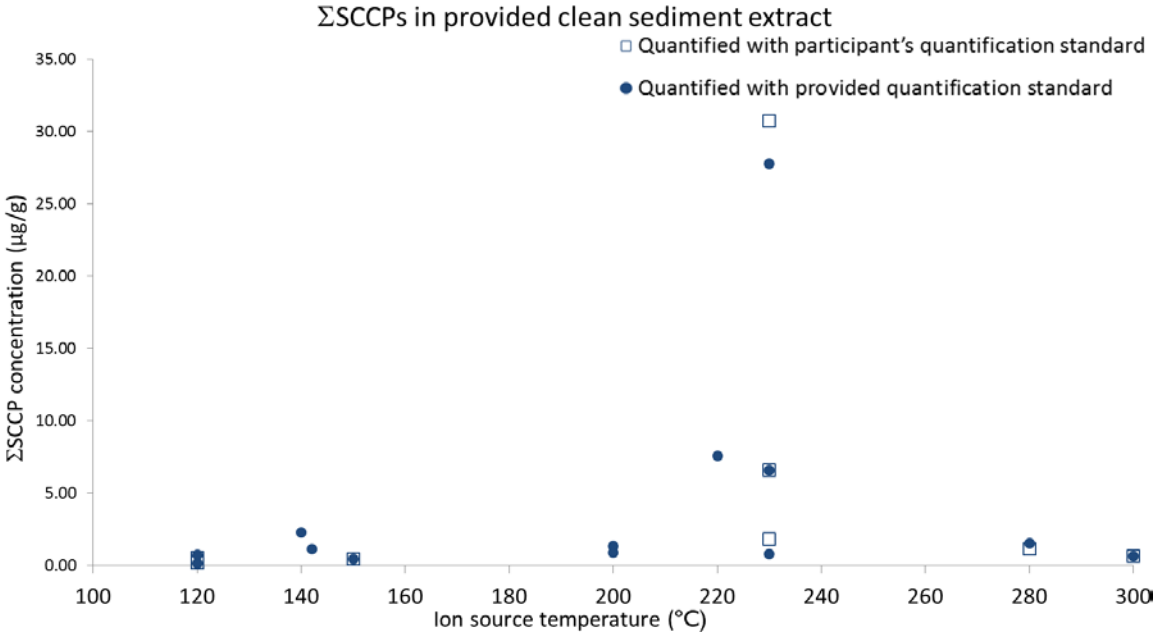


Figure 4.6 Plot of reported ion source temperatures and average reported ΣSCCPs concentrations in the provided clean sediment extract (Ampoule B), determined with provided quantification standard (blue circle; Ampoule A) and with participants own quantification standards (square).

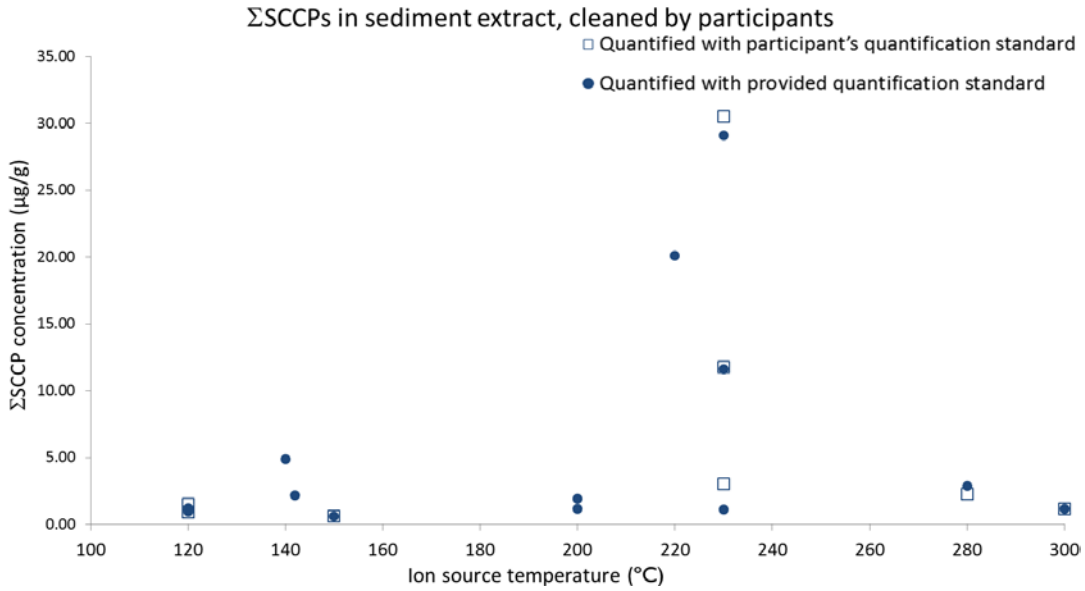


Figure 4.7 Plot of reported ion source temperatures and reported average ΣSCCPs concentrations in the sediment extract cleaned up by participants (Ampoule C) and determined with provided quantification standard (blue circle; Ampoule A) and with participants own quantification standards (square).

4.2 Comparison with other ILSs

This ILS compares reported CP concentrations in sediment extracts obtained by different analytical techniques. The overall performance of the participants in the analysis of ΣSCCPs in the present study improved compared to the performance of the previous round of this ILS (137%; van der Veen *et al.*, 2014) and compared to that of the ILS of Pellizzato *et al.* (2009), in which SCCP concentrations based solely on LRMS varied up to 2 orders of magnitude in a soil extract.

Lower CVs were found in the ILS on CP analysis in fish extract of Tomy *et al.* (27 and 47%; 1998) and in a water sample (22-34%; Geiß *et al.*, 2011; Geiß *et al.*, 2012). In these two ILSs, however, participants followed a prescribed GC/ECNI-LRMS method (Geiß *et al.*, 2011; Geiß *et al.*, 2012) or same instrumental technique (GC/ECNI-MS; Tomy *et al.*, 1998). Also, concentrations in the fish extracts of Tomy *et al.* (1999) were up to 2-fold higher compared to the sediments extracts of this ILS.

LRMS measurements can exceed those of HRMS by more than 300% (Sverko *et al.*, 2012). In this ILS, results obtained by ECNI/LRMS and ECNI/HRMS were in a more similar concentration range, suggesting an increasing consensus in concentrations between LRMS and HRMS measurements when operated in the ECNI mode. However, when MS is operated in the EI mode with different ion source temperatures, measurements can be extremely variable.

5 Conclusion

Thirteen laboratories provided data for the third round of the QUASIMEME interlaboratory study on SCCP analysis, which included a determination of the ΣSCCPs concentration in a cleaned and uncleaned sediment extract. More laboratories were able to hand in a dataset compared to the second phase (n=11).

A number of different instrumental techniques were used for the ΣSCCPs determination. Between laboratory CVs of 80% and 86% was found for the quantification with the provided standard solution in the cleaned sediment extract and uncleaned sediment extract, respectively, indicating that the different clean-up methods do not have an effect the reported concentration. When using quantification standards of the participant's own choice, larger between laboratories CVs was found, with (86-117%, clean-uncleaned), which underlines the importance of suitable quantification standards. In general, concentrations that were obtained with GC/EI-MS were higher than that of GC/ECNI-MS and further research on these observations is advised.

Overall, differences in reported ΣSCCPs concentrations in sediment extracts between the laboratories of this ILS are still too large. Nonetheless, the results are better than those of previous interlaboratory studies. The differences are most likely due to differences in quantification methods. More interlaboratory comparison exercises are recommended to improve the analysis of CPs.

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References

Chen, M.Y., Luo, X.J., Zhang, X.L., He, M.J., Chen, S.J. & Mai, B.X. (2011). Chlorinated paraffins in sediments from the Pearl River Delta, South China: Spatial and temporal distributions and implication for processes. *Environmental Science & Technology, 45*, 9936–9943.

Coelhan, M. (2010). Levels of chlorinated paraffins in water. *Clean - Soil, Air, Water, 38*, 452–456.

Cofino, W.P., van Stokkum, I.H.M., van Steenwijk, J. & Wells, D.E. (2005). A new model for the inference of population characteristics from experimental data using uncertainties. Part II. Application to censored datasets. *Analytica Chimica Acta, 533,* 31–39.

Cofino, W.P., Wells, D.E., Arise, F., van Stokkum, I., Wegener, J.W. & Peerboom, R. (2000). A new model for the inference of population characteristics from experimental data using uncertainties. Application to interlaboratory studies. *Chemometrics and Intelligent Laboratory Systems, 53*, 37–55.

Geiß, S., Lettmann, N., Rey, A., Lepper, H., Körner, B., Mais, S., Prey, T., Hilger, B., Engelke, M., Lebertz, S., Chatellier, C., Sawal, G., Löffler, D. & Schillings, T. (2011). Preliminary Interlaboratory Trial for ISO/DIS 12010: Determination of Short Chain Polychlorinated Alkanes (SCCP) in Water. *Clean - Soil, Air, Water, 39*, 537–542.

Geiß, S., Löffler, D., Körner, B., Engelke, M., Sawal, G. & Bachhausen, P. (2014). Determination of the Sum of Short Chain Chlorinated n-Alkanes with a chlorine content between 50% and 67% in sediment samples by GC-ECNI-MS and Quantification by Multiple Linear Regression. *Microchem. J.*

Geiß, S., Schneider, M., Donnevert, G., Einax, J.W., Lettmann, N., Rey, A., Lepper, H., Körner, B., Prey, T., Hilger, B., Engelke, M., Strub, M.P., Adrien, H., Sawal, G., Löffler, D., Schillings, T., Hussy, I., Steinbichl, P., Scharf, S., Ruderisch, A., Olmos, J.E., Santos, F.J., Bartolome, A. & Caixach, J. (2012). Validation interlaboratory trial for ISO 12010: Water quality-Determination of short-chain polychlorinated alkanes (SCCP) in water. *Accreditation and Quality Assurance 17*, 15–25.ISO 13528. Statistical methods for use in proficiency testing by interlaboratory comparisons (2005).

van Mourik, L.M., Leonards, P.E.G., Gaus, C. & de Boer, J. (2015). Recent developments in capabilities for analysing chlorinated paraffins in environmental matrices: A review. *Chemosphere, 136*, 259–272.

Pellizzato, F., Ricci, M., Held, A., Emons, H., Böhmer, W., Geiss, S., Iozza, S., Mais, S., Petersen, M. & Lepom, P. (2009). Laboratory intercomparison study on the analysis of short-chain chlorinated paraffins in an extract of industrial soil. TrAC Trends in *Analytical Chemistry, 28*, 1029–1035.

Sverko, E., Tomy, G.T., Marvin, C.H. & Muir, D.C. (2012). Improving the quality of environmental measurements on short chain chlorinated paraffins to support global regulatory efforts *Environmental Science & Technology, 46*, 4697–4698.

Thompson, M. & Wood, R. (1993). International harmonised protocol for proficiency testing of (chemical) analytical laboratories. *Journal of AOAC INTERNATIONAL*, *76*, 926–940.

Thompson, M., Ellison, S.L.R. & Wood, R. (2006). The international harmonised protocol for proficiency testing of analytical chemistry laboratories. IUPAC Technical report. Interdivisional working party for harmonization of quality assurance schemes. *Pure and Applied Chemistry, 78,* 145–196.

Thompson, R.S. & Noble, H. (2007). *Short-chain chlorinated paraffins (C10-13, 65% chlorinated): Aerobic and anaerobic transformation in marine and freshwater sediment systems*. Draft Report No. BL8405/B Brixham Environmental Laboratory,

AstraZeneca UK Limited. (as cited in Substance of very high concern support document from European chemicals agency 2008).

Tomy, G.T., Westmore, J.B., Stern, G.A., Muir, D.C.G. & Fisk, A.T. (1998). Interlaboratory study on quantitative methods of analysis of C10–C13 polychloro-n-alkanes. *Analytical Chemistry, 71*, 446–451.

UNEP, 2015. Short-chained chlorinated paraffins: Revised draft risk profile UNEP/POP/PORC.X/X. United Nations Environmental Programme Stockholm Convention on Persistent Organic Pollutants, Geneva.

van der Veen, I., Cofino, W., Crum, S. & de Boer, J. (2012). *Interlaboratory study on the analysis of chlorinated paraffins in environmental matrices, phase 1*. QUASIMEME report (W-12/11). IVM Institute for Environmental Studies, VU University Amsterdam.

van der Veen, I., Crum, S. & de Boer, J. (2014). *Interlaboratory study on the analysis of chlorinated paraffins in environmental matrices, phase 2*. QUASIMEME Report (R-14/18). IVM Institute for Environmental Studies, VU University Amsterdam..

Wells, D.E. & Scurfield, J.A. (2004). *Assessment rules for the evaluation of the QUASIMEME laboratory performance studies data*. FRS Marine Laboratory, 375 Victoria Road, Aberdeen AB11 9DB, UK, version 2, pp.390 -391.

Wells, D.E., Cofino, W.P. & Scurfield, J.A. (2004). *The application of the Cofino model to evaluate laboratory performance study data using bandwidth estimator*. FRS Marine Laboratory, 375 Victoria Road, Aberdeen 388 AB11 9DB, UK. Report No. 04/04.

Annexes

A. List of participants.

B. Results and graphical representation

C. Numerical z-score values per matrix

D. Consistency of data

E. Graphical output of the Cofino Model statistics for ΣSCCPs determination in provided cleaned sediment extract

F. Graphical output of the Cofino Model statistics for ΣSCCPs determination in a sediment extract, cleaned by the participants

G. Additional method information

Annex A List of participants

Laboratory	Contact person	Delivery address	City and postal code	Country	E-mail
AsureQuality Ltd - Wellington	Ushma Dahya	1C Quadrant Drive, Waiwhetu	Lower Hutt 5010 Wellington	New Zealand	wgtn-quality@asurequality.com
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IRRM - European Commission - JRC - Institute for Reference Materials and Measurements	Marina Ricci	Retieseweg 111	B-2440 Geel	Belgium	Marina.ricci@ec.europa.eu
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Laboratory	Contact person	Delivery address	City and postal code	Country	E-mail
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WESSLING GmbH	Andrea Kaiser	Am Umweltpark 1	44793 Bochum	Germany	andrea.kaiser@wessling.de

Annex B Results and graphical representation

ΣSCCPs (µg/g)	Assigned value	Model Mean	Median	Min	Max	Model Between-lab CV%	Model percentage in PMF1	n>LOQ
Cleaned sediment extract	0.863	0.863	1.109	0.142	31.672	93	65	59
Raw sediment extract	1.497	1.497	1.935	0.534	30.943	84	64	59

Participant code:	**CPP1**	**CPP1**	**CPP1**	**CPP4**	**CPP4**	**CPP4**	**CPP4 M2**	**CPP4 M2**	**CPP4 M2**	**CPP8**	**CPP8**	**CPP8**	**CPP9**	**CPP9**	**CPP9**
Date Samples Received:	NA			30/11/2014			30/11/2014			2/12/2014			13/11/2014		
Date Analysed:	22/02/2015			14/01/2015			14/01/2015			30/01/2015			16/01/2015		
	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C
Weight Received (g):	7.7102		7.6807	7.6891		7.7095	7.6891		7.7095	7.72838		7.7047	7.642		7.69030
Weight Analysed (g):	7.711		7.6807	0.05		0.05	0.05		0.05	1.96		1.99	7.64241		7.6905
ΣSCCPs (µg/g)	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Cleaned sediment extract (Ampoule B)	2.18	2.45	2.24	0.531	0.397	NA	0.527	0.393	NA	0.847	0.938	0.943	0.783	0.785	0.779
Raw sediment extract (Ampoule C)	4.74	5.11	4.74	0.539	0.645	NA	0.534	0.639	NA	1.039	1.234	1.156	0.902	1.47	1.002
Blank	0.02	0.02	NA	NA	NA	NA	NA	NA	NA	0.23	0.08	0.25	0	0	0

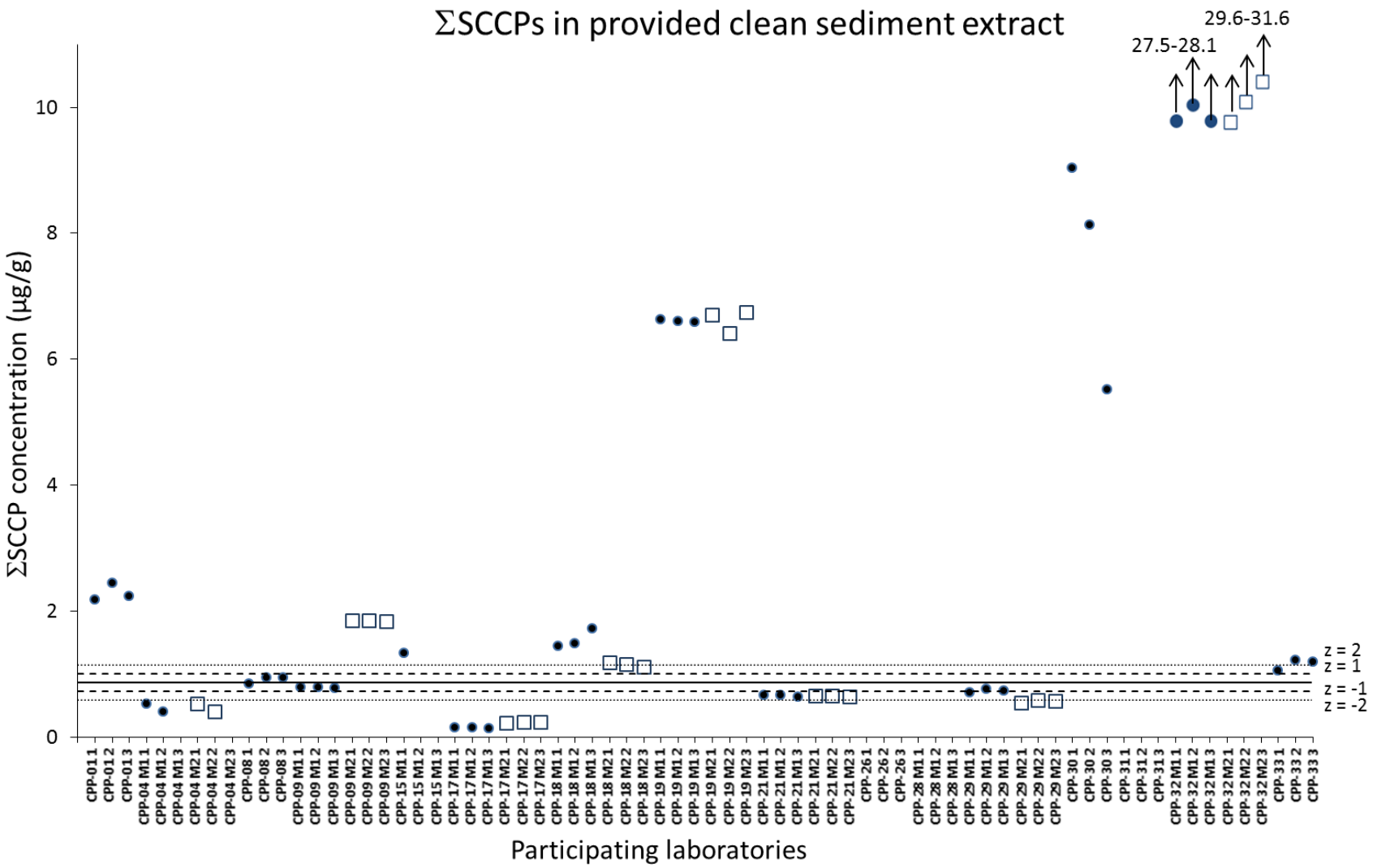
ND: not detected
NA: not analysed
M2: quantified with participants own

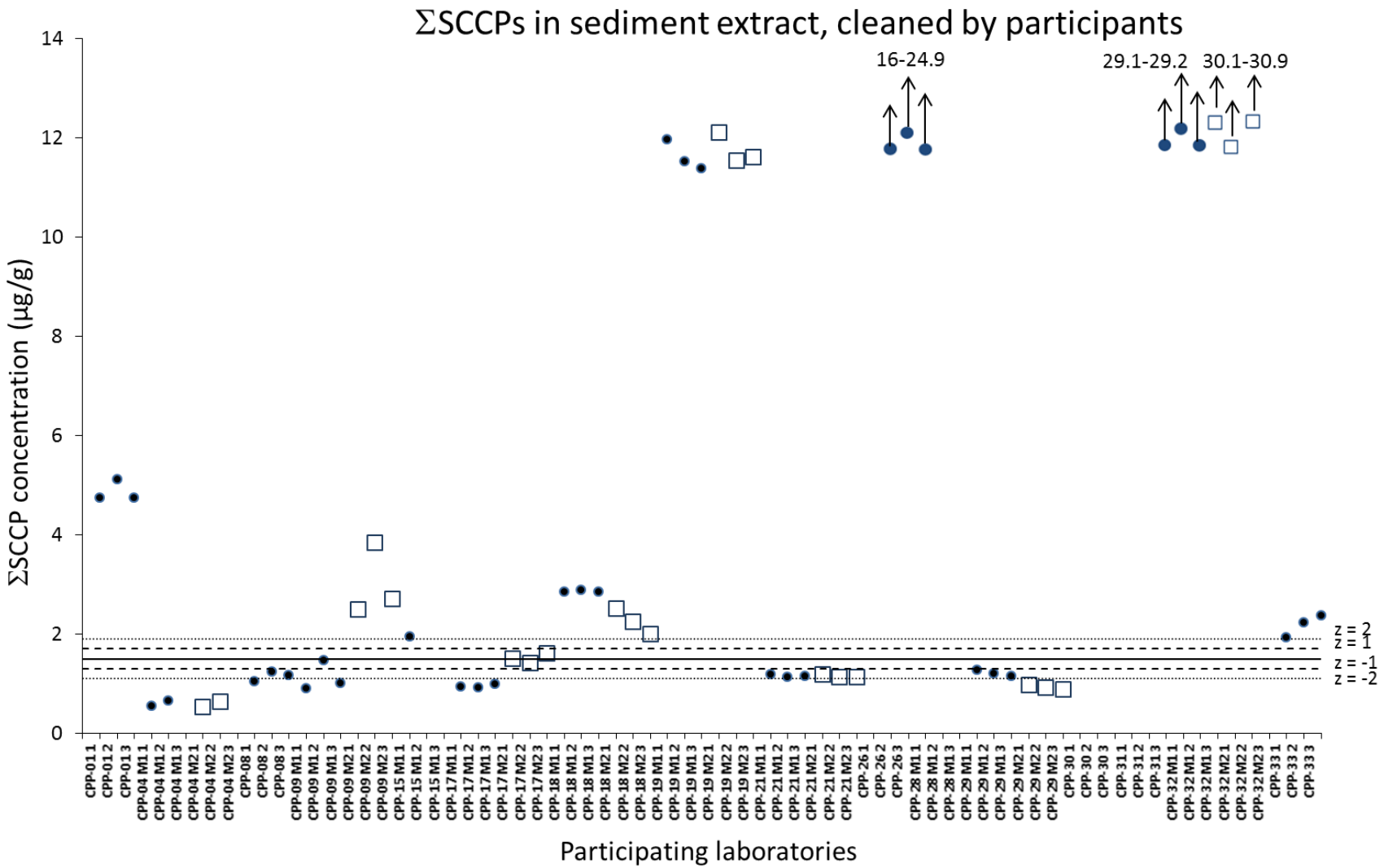
Participant code:	CPP9 M2	CPP9 M2	CPP9 M2	CPP15	CPP15	CPP15	CPP17	CPP17	CPP17	CPP17 M2	CPP17 M22	CPP17 M23	CPP18	CPP18	CPP18
Date Samples Received:	13/11/2014			12/11/2015			25/11/2014			25/11/2014			19/11/2014		
Date Analysed:	16/01/2015			13/02/2015			02/02/2015			02/02/2015			10/12/2014		
	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C
Weight Received (g):	7.642		7.69030	7.7297		7.6194	7.587		7.7354	7.587		7.7354	7.7749		7.6203
Weight Analysed (g):	7.64241		7.6905	1.9982		1.9999	6.3633		7.7096	6.3633		7.7096	7.7749		7.6197
ΣSCCPs (µg/g)	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Cleaned sediment extract (Ampoule B)	1.841	1.846	1.831	1.3308 15782	NA	NA	0.15	0.1543	0.1421	0.847	0.938	0.943	1.446	1.478	1.718
Raw sediment extract (Ampoule C)	2.486	3.828	2.696	1.9350	NA	NA	0.9247	0.9233	0.9891	1.039	1.234	1.156	2.852	2.887	2.843
Blank	0	0	0	0.0041	NA	NA	ND	ND	ND	ND	ND	ND	0.07	NA	NA
ND: not detected NA: not analysed M2: quantified with participants own															

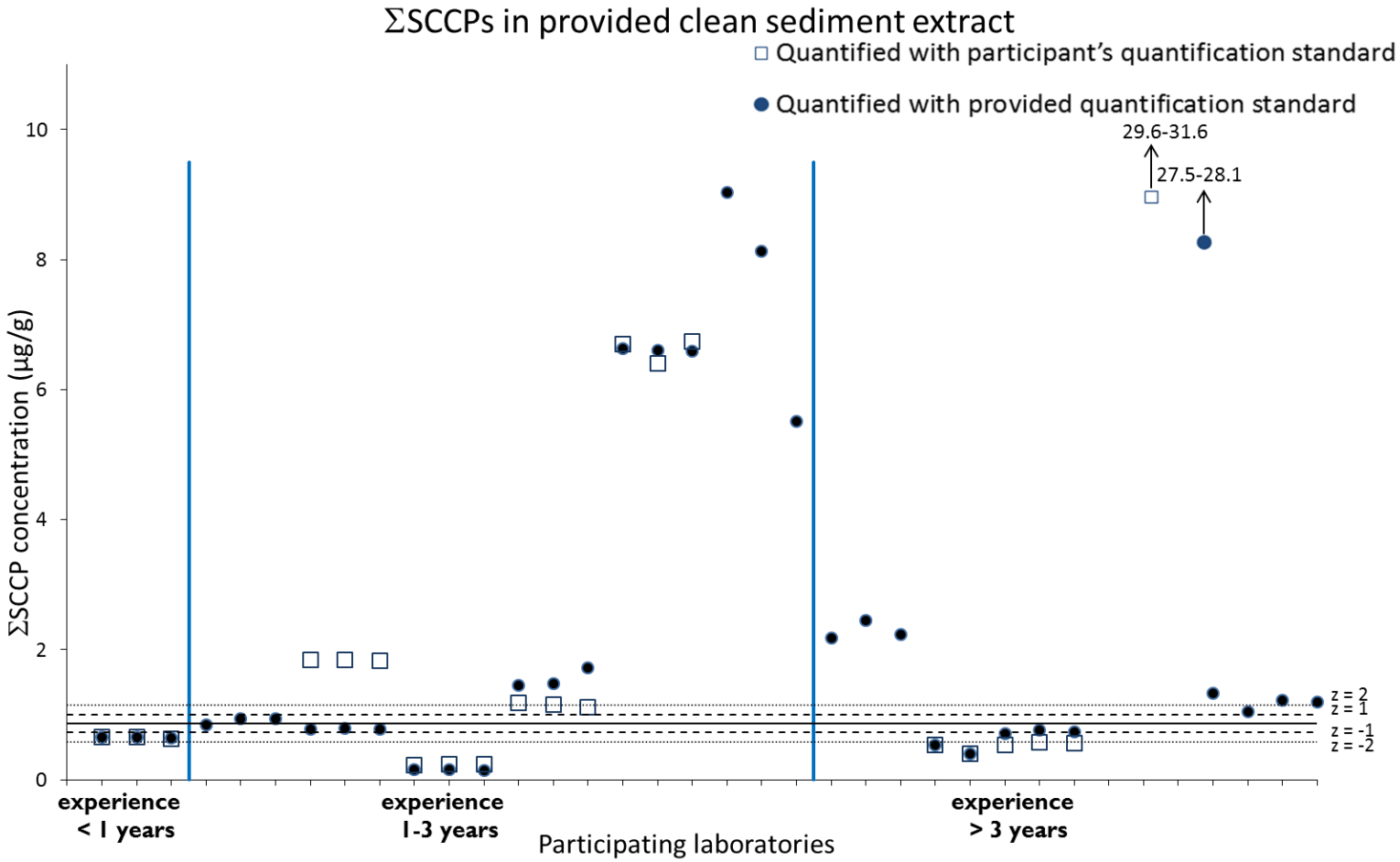
Participant code:	CPP18 M2	CPP18 M2	CPP18 M2	CPP19	CPP19	CPP19	CPP19 M2	CPP19 M2	CPP19 M2	CPP21	CPP21	CPP21	CPP21 M2	CPP21 M2	CPP21 M2
Date Samples Received:	19/11/2014			28/11/2014			28/11/2014			1/12/2014			1/12/2014		
Date Analysed:	10/12/2014			28/01/2015			28/01/2015			29/01/2015			29/01/2015		
	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C
Weight Received (g):	7.7749		7.6203	7.6375		7.7106	7.6375		7.7106	7.797		7.762	7.797		7.762
Weight Analysed (g):	7.7749		7.6197	7.6384		7.7088	7.6384		7.7088	7.797		7.761	7.797		7.761
ΣSCCPs (µg/g)	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Cleaned sediment extract (Ampoule B)	1.184	1.15	1.109	6.634	6.604	6.593	6.698	6.408	6.743	0.66	0.661	0.641	0.651	0.652	0.631
Raw sediment extract (Ampoule C)	2.504	2.238	1.995	11.954	11.522	11.368	12.096	11.539	11.614	1.189	1.136	1.139	1.184	1.13	1.133
Blank	0.21	NA	NA	0.008	0.022	0.015	0.063	0.036	0.03	0.0256	0.0264	0.0252	0.0038	0.0047	0.0034
ND: not detected NA: not analysed M2: quantified with participants own															

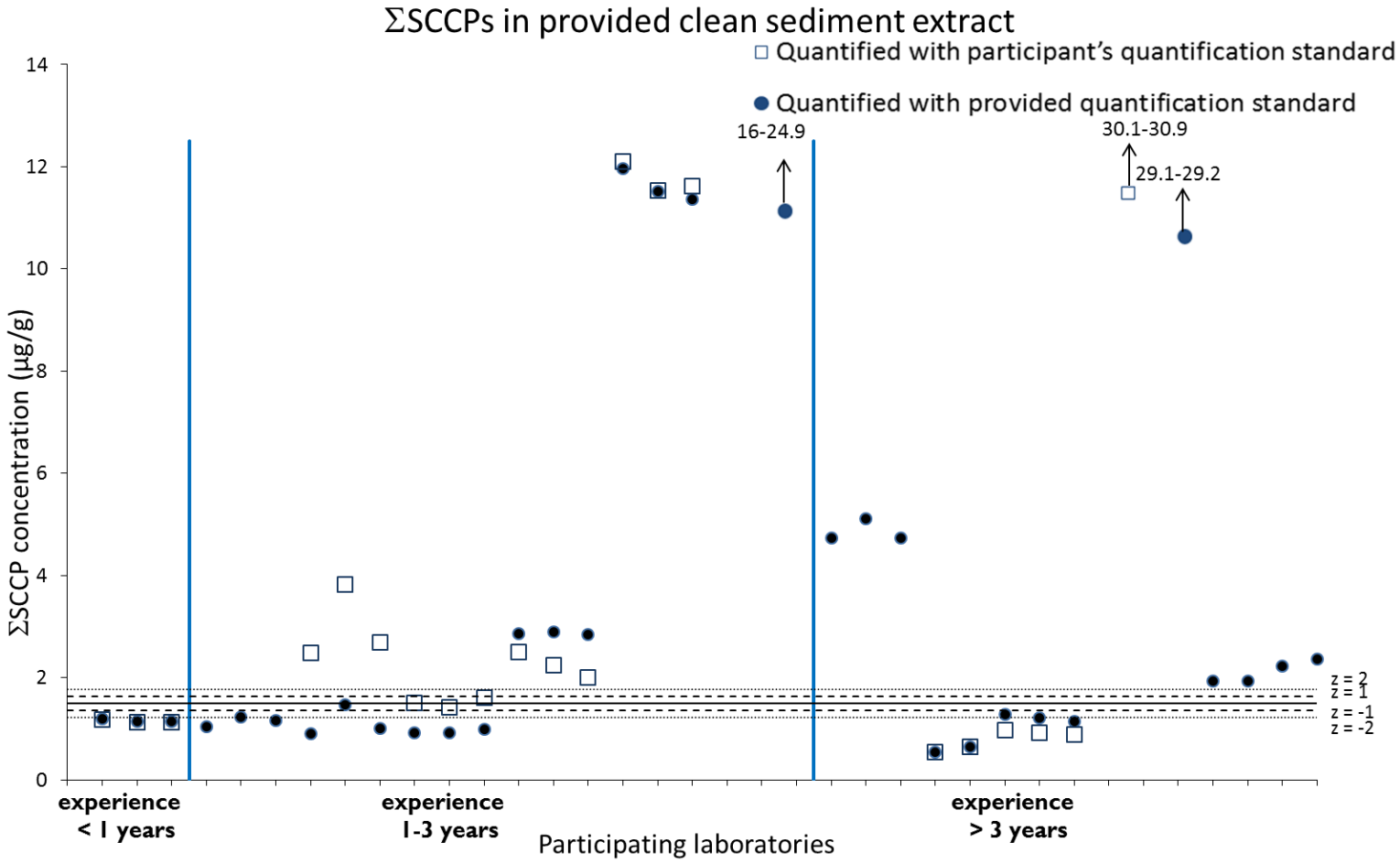
Participant code:	CPP26	CPP26	CPP26	CPP28	CPP28	CPP28	CPP29	CPP29	CPP29	CPP29 M2	CPP29 M2	CPP29 M2	CPP30	CPP30	CPP30
Date Samples Received:	NA			NA			NA			NA			17/11/2014		
Date Analysed:	NA			NA			08/01/2015			08/01/2015			12/12/2014		
	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C
Weight Received (g):	NA		NA	NA		NA	NA		NA	NA		NA	NA		NA
Weight Analysed (g):	NA		NA	NA		NA	7.717		7.759	7.717		7.759	NA		NA
ΣSCCPs (µg/g)	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Cleaned sediment extract (Ampoule B)	NA	NA	NA	NA	NA	NA	0.704	0.761	0.736	0.534	0.579	0.562	9.041	8.135	5.513
Raw sediment extract (Ampoule C)	NA	NA	NA	NA	NA	NA	1.277	1.206	1.141	0.963	0.914	0.879	24.887	19.439	15.98
Blank	NA	NA	NA	NA	NA	NA	0.026	0.023	0.03	0.048	0.053	0.05	<0.5	<0.5	<0.5
ND: not detected NA: not analysed M2: quantified with participants own															

Participant code:	CPP30 M2	CPP30 M2	CPP30 M2	CPP31	CPP31	CPP31	CPP32	CPP32	CPP32	CPP32 M2	CPP32 M2	CPP32 M2	CPP33	CPP33	CPP33
Date Samples Received:	17/11/2014			NA			29/10/2014			29/10/2014			01/12/2012		
Date Analysed:	12/12/2014			NA			19/02/215			19/02/215			29/01/2015		
	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C	Ampoule B		Ampoule C
Weight Received (g):	NA		NA	NA		NA	7.78484		7.70555	7.78484		7.70555	7.797		7.762
Weight Analysed (g):	NA		NA	NA		NA	7.78556		7.70612	7.78556		7.70612	7.797		7.761
ΣSCCPs (µg/g)	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Cleaned sediment extract (Ampoule B)	8.581	7.939	6.078	NA	NA	NA	27.501	28.138	27.680	29.642	31.009	31.672	1.052	1.217	1.196
Raw sediment extract (Ampoule C)	19.823	15.958	13.504	NA	NA	NA	29.156	29.054	29.075	30.943	30.106	30.452	1.929	2.23	2.364
Blank	<0.5	<0.5	<0.5	NA	NA	NA	0.388	0.398	0.302	0.432	NA	NA	0.055	NA	NA
ND: not detected NA: not analysed M2: quantified with participants own															


ΣSCCPs in provided clean sediment extract
29.6-31.6
27.5-28.1
ΣSCCP concentration (µg/g)
10
8
6
4
2
0
z = 2
z = 1
z = -1
z = -2
CPP-01 1
CPP-01 2
CPP-01 3
CPP-04 M11
CPP-04 M12
CPP-04 M13
CPP-04 M21
CPP-04 M22
CPP-04 M23
CPP-08 1
CPP-08 2
CPP-08 3
CPP-09 M11
CPP-09 M12
CPP-09 M13
CPP-09 M21
CPP-09 M22
CPP-09 M23
CPP-15 M11
CPP-15 M12
CPP-15 M13
CPP-17 M11
CPP-17 M12
CPP-17 M13
CPP-17 M21
CPP-17 M22
CPP-17 M23
CPP-18 M11
CPP-18 M12
CPP-18 M13
CPP-18 M21
CPP-18 M22
CPP-18 M23
CPP-19 M11
CPP-19 M12
CPP-19 M13
CPP-19 M21
CPP-19 M22
CPP-19 M23
CPP-21 M11
CPP-21 M12
CPP-21 M13
CPP-21 M21
CPP-21 M22
CPP-21 M23
CPP-26 1
CPP-26 2
CPP-26 3
CPP-28 M11
CPP-28 M12
CPP-28 M13
CPP-29 M11
CPP-29 M12
CPP-29 M13
CPP-29 M21
CPP-29 M22
CPP-29 M23
CPP-30 1
CPP-30 2
CPP-30 3
CPP-31 1
CPP-31 2
CPP-31 3
CPP-32 M11
CPP-32 M12
CPP-32 M13
CPP-32 M21
CPP-32 M22
CPP-32 M23
CPP-33 1
CPP-33 2
CPP-33 3
Participating laboratories


ΣSCCPs in sediment extract, cleaned by participants
16-24.9
29.1-29.2
30.1-30.9
ΣSCCP concentration (µg/g)
14
12
10
8
6
4
2
0
z = 2
z = 1
z = -1
z = -2
CPP-01 1
CPP-01 2
CPP-01 3
CPP-04 M11
CPP-04 M12
CPP-04 M13
CPP-04 M21
CPP-04 M22
CPP-04 M23
CPP-08 1
CPP-08 2
CPP-08 3
CPP-09 M11
CPP-09 M12
CPP-09 M13
CPP-09 M21
CPP-09 M22
CPP-09 M23
CPP-15 M11
CPP-15 M12
CPP-15 M13
CPP-17 M11
CPP-17 M12
CPP-17 M13
CPP-17 M21
CPP-17 M22
CPP-17 M23
CPP-18 M11
CPP-18 M12
CPP-18 M13
CPP-18 M21
CPP-18 M22
CPP-18 M23
CPP-19 M11
CPP-19 M12
CPP-19 M13
CPP-19 M21
CPP-19 M22
CPP-19 M23
CPP-21 M11
CPP-21 M12
CPP-21 M13
CPP-21 M21
CPP-21 M22
CPP-21 M23
CPP-26 1
CPP-26 2
CPP-26 3
CPP-28 M11
CPP-28 M12
CPP-28 M13
CPP-29 M11
CPP-29 M12
CPP-29 M13
CPP-29 M21
CPP-29 M22
CPP-29 M23
CPP-30 1
CPP-30 2
CPP-30 3
CPP-31 1
CPP-31 2
CPP-31 3
CPP-32 M11
CPP-32 M12
CPP-32 M13
CPP-32 M21
CPP-32 M22
CPP-32 M23
CPP-33 1
CPP-33 2
CPP-33 3
Participating laboratories


ΣSCCPs in provided clean sediment extract
Quantified with participant's quantification standard
Quantified with provided quantification standard
29.6-31.6
27.5-28.1
ΣSCCP concentration (µg/g)
10
8
6
4
2
0
z = 2
z = 1
z = -1
z = -2
experience < 1 years
experience 1-3 years
experience > 3 years
Participating laboratories


ΣSCCPs in provided clean sediment extract
Quantified with participant's quantification standard
Quantified with provided quantification standard
16-24.9
30.1-30.9
29.1-29.2
ΣSCCP concentration (µg/g)
14
12
10
8
6
4
2
0
z = 2
z = 1
z = -1
z = -2
experience < 1 years
experience 1-3 years
experience > 3 years
Participating laboratories

Annex C Numerical z-score values per matrix

Cleaned sediment extract

Determinand	CPP1	CPP4 m1	CPP4 m2	CPP8	CPP9 m1	CPP9 m2	CPP15	CPP17 m1	CPP17 m2	CPP18 m1	CPP18 m2	CPP19 m1
Total CP	11.84	-3.32	-3.35	0.38	-0.67	8.1	3.88	-5.93	-5.27	5.68	2.36	47.72

Determinand	CPP19 m2	CPP21 m1	CPP21 m2	CPP26	CPP28	CPP29 m1	CPP29 m2	CPP30	CPP31	CPP32 m1	CPP32 m2	CPP33
Total CP	47.77	-1.74	-1.82	NR	NR	-1.08	-2.53	55.63	NR	223.45	248.38	2.42

NR = Not Reported

Raw sediment extract, cleaned by participants

Determinand	CPP1	CPP4 m1	CPP4 m2	CPP8	CPP9 m1	CPP9 m2	CPP15	CPP17 m1	CPP17 m2	CPP18 m1	CPP18 m2	CPP19 m1
Total CP	11.85	-3.32	-3.35	0.38	-.067	8.1	3.88	-5.93	-5.27	5.68	2.36	47.72

Determinand	CPP19 m2	CPP21 m1	CPP21 m2	CPP26	CPP28	CPP29 m1	CPP29 m2	CPP30	CPP31	CPP32 m1	CPP32 m2	CPP33
Total CP	47.77	-1.74	-1.82	NR	NR	-1.08	-2.53	93.21	NR	138.27	145.31	3.39

NR = Not Reported

Annex D Consistency of data

Cleaned sediment extract

Determinand	CPP1	CPP4 m1	CPP4 m2	CPP8	CPP9 m1	CPP9 m2	CPP15	CPP17 m1	CPP17 m2	CPP18 m1	CPP18 m2	CPP19 m1
Total CP	U-U-U	Q-U-B	Q-U-B	S-S-S	S-S-S	S-U-U	U-B-B	U-U-U	U-U-U	U-U-U	Q-Q-Q	U-U-U

Determinand	CPP19 m2	CPP21 m1	CPP21 m2	CPP26	CPP28	CPP29 m1	CPP29 m2	CPP30	CPP31	CPP32 m1	CPP32 m2	CPP33
Total CP	U-U-U	S-S-S	S-S-S	NR	NR	S-S-S	Q-Q-Q	U-U-U	NR	U-U-U	U-U-U	S-Q-Q

NR = Not Reported

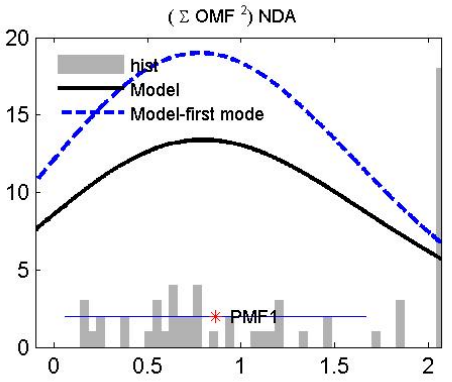
Raw sediment extract, cleaned by participants

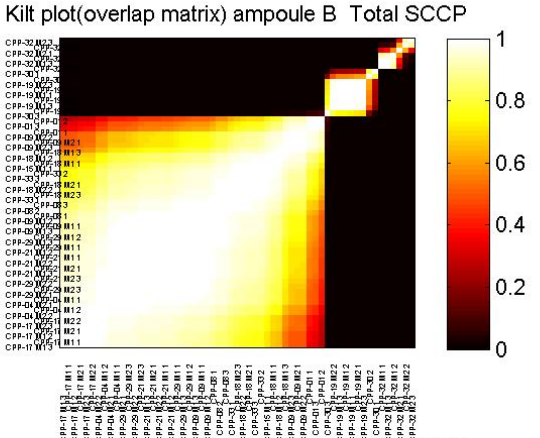
Determinand	CPP1	CPP4 m1	CPP4 m2	CPP8	CPP9 m1	CPP9 m2	CPP15	CPP17 m1	CPP17 m2	CPP18 m1	CPP18 m2	CPP19 m1
Total CP	U-U-U	U-U-B	U-U-B	Q-S-S	Q-S-Q	U-U-U	Q-B-B	Q-Q-Q	S-S-S	U-U-U	U-U-Q	U-U-U

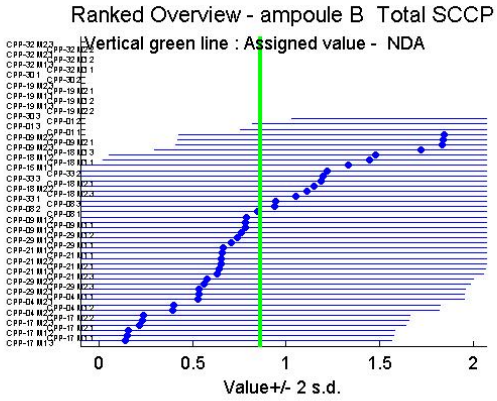
Determinand	CPP19 m2	CPP21 m1	CPP21 m2	CPP26	CPP28	CPP29 m1	CPP29 m2	CPP30	CPP31	CPP32 m1	CPP32 m2	CPP33
Total CP	U-U-U	S-S-S	S-S-S	NR	NR	S-S-S	Q-Q-U	U-U-U	NR	U-U-U	U-U-U	Q-U-U

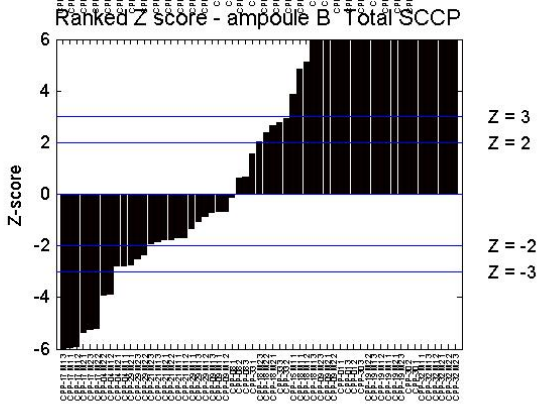
NR = Not Reported

Annex E Graphical output of the Cofino Model statistics for ΣSCCPs determination in provided cleaned sediment extract

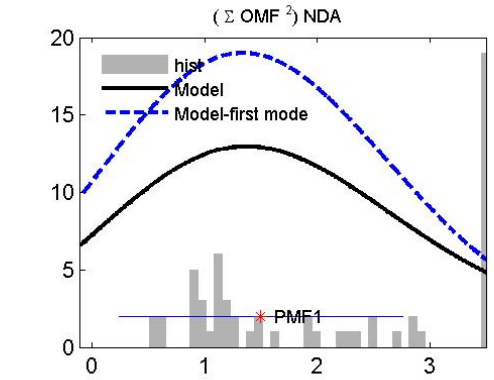


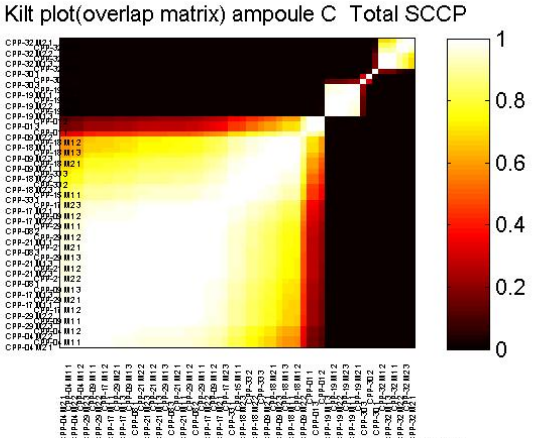


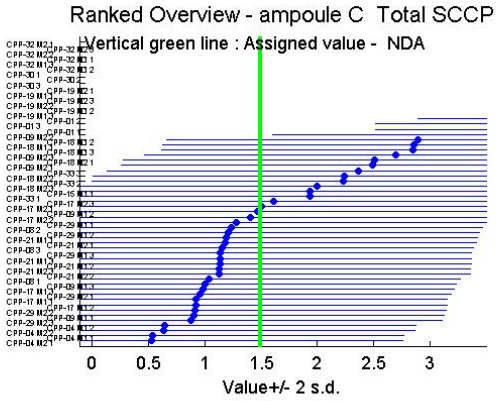


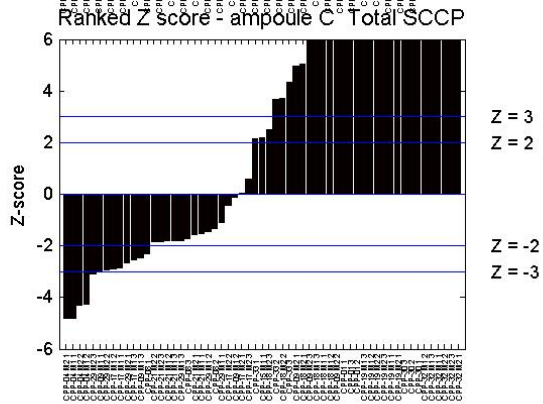


Annex F Graphical output of the Cofino Model statistics for ΣSCCPs determination in a sediment extract, cleaned by the participants









Annex G Additional method information

		CPP-01	CPP-04	CPP-08
Instrument	Type	GC	GC	Shimadzu GCMS-QP2010 Plus Series
	GC injector	Splitless	splitless	Pulsed splitless
	Detector type	HRMS	MS	MSD
	Other		-	
	Column	Agilent HP-1 ms, 15 m, 0.25 mm, 0.25 µm	Rtx-200 (30m * 0.25mm; 0.25 µm film)	Rtx-5SiMS 30m x 0.25 mm x 0.25 µm
	Second column		-	N.A.
	Pre-column		-	N.A.
	Flow rate/ gas speed	1 mL/min	1.5 ml/min	0.88mL/min on column
	Carrier gas	He	He	Helium
	Reagent gas	Methane		Methane
	Injection volume (µL)	1	2 µl	1µL
	Amount of injections	1		3
	Column temp. (°C)	90	90°C	290°C
	Injector temp. (°C)	260	250 °C	245°C
	Interface temp. (°C)	260	290 °C	250°C
			-	
	Gradient/ temperature program	90˚C (1.2 min) 20˚/min to 245˚C (0 min) 50˚/min 300˚C (0 min)	90°C (1 min) 120°C/min to 140°C (0 min) 15°C/min to 320°C (10 min)	105°C (1 min) 34°C /min to 190°C (1 min) 8°C/min to 250°C (0 min) 40°C/min to 290°C (8 min)
Detection	Type	HRMS		Low resolution MS
	Ionization mode (CI/ EI)	ECNI	CI	Negative
	Pos/Neg mode	Neg	Neg	CI
	Desolvation gas and setting		CH4	N.A.
	Temperatures (specify which)			200°C Source temperature
	Source block temp. (°C)	140	150°C	N.A.
	Desolvation temp. (°C)			N.A.
	Other			8.4×10^{-4} Pa
Additional questions:	*Is your quantification method based on a method developped by published work and if so, do you have a citation?*			Castells P, Santos FJ, Galceran MT. (2004); Rapid Commun. Mass Spectrom. 18: 529-536
	Did you use in-house standard solution as well? Briefly describe the type of calibration, if different than above:			As an additional comparison we tested our own in-house standard against the standard solution provided by the study and found them to be in good agreement.
	Are you able to quantify the separate alkane groups (C10, C11, C12, C13) and Clorine groups (Cl7, Cl8, Cl9, Cl10)?			Not currently with this technique

		CPP-09	CPP-15	CPP-17	CPP-18
Instrument	Type	GC-ECNI MS	GC	GC	GC
	GC injector	On-column	Pulsed splitless	splitless	PTV
	Detector type	ECNI MS	LMRS	Thermo Finnigan MAT 95	MS/MS
	Other				
	Column	RTX1614 15x25x0.1	DB-5 J&W 122-5012 15*25*0.25	Restek Rxi-5ms, 15m x 0.25mm ID, 0.25 µm film	HP5-MS Length 15m x Diam. 0.25 mm x Film 0.25µm Agilent
	Second column	n/a	x	n.a	DB5-MS Length 0.5m x Diam. 0.15 mm x Film 0.15µm Agilent
	Pre-column	n/a	x		-
	Flow rate/ gas speed	Constant pressure 15psi	1 mL/min	100 kPa	1.4 ml/min
	Carrier gas	Helium	helium	He	Helium
	Reagent gas	Methane	methane	Argon	-
	Injection volume (µL)	1	1	2	5
	Amount of injections	1	4		1
	Column temp. (°C)	100	x	110	60
	Injector temp. (°C)	120	275	260	70
	Interface temp. (°C)	280	300	280	280
	Gradient/ temperature program	100°C (10 min) 10°C/min to 260°C (30 min)	90°C (2 min) 15°C/min to 325°C (10 min)	110°C 10°C/min to 310°C	60°C (1 min) 50°C/min to 300°C (5 min)
Detection	Type	MS	LRMS	HRMS	MS/MS
	Ionization mode (CI/ EI)	CI	CI	CI	EI
	Pos/Neg mode	NI	neg	Neg	-
	Desolvation gas and setting				-
	Temperatures (specify which)		200		
	Source block temp. (°C)	230		120	280
	Desolvation temp. (°C)				-
	Other				
Additional questions:	*Is your quantification method based on a method developped by published work and if so, do you have a citation?*	I. Hussy et al Chemosphere vol 88, 2012	Reth&Oehme	Analytical method according to Tomy et al. 1997	
	Did you use in-house standard solution as well? Briefly describe the type of calibration, if different than above:	Yes, same as above	x	I checked the standard solution you sent us with our in-house standard.	
	Are you able to quantify the separate alkane groups (C10, C11, C12, C13) and Clorine groups (Cl7, Cl8, Cl9, Cl10)?	No	kind of	Yes	

		CPP-19	CPP-21	CPP-29
Instrument	Type	GC-MS/MS Agilent	GCxGC	GC MS TOF with ECNI
	GC injector	Splitless	splitless	PTV
	Detector type	MSD	ECD	MS TOF Agilent 7200
	Other			
	Column	HP-5ms, 30 m x 0.25 mm x 0.25 µm	DB1 30x250x0.25	J&W 122-1011: 325 °C: 15 m x 250 µm x 0.1 µm
	Second column	restrictor column fused silica, 4 m x 0.2 mm x 0 µm	Rtx-PCB 1.6x180x0.18	
	Pre-column		N.A.	
	Flow rate/ gas speed	column 1: 1,4 ml column 2: 1,8 ml	1.2 ml/min	2,6 ml/min 59 cm/s at the start
	Carrier gas	He	He	He
	Reagent gas		5% argon in methane	Methane
	Injection volume (µL)	2	1	5 µl
	Amount of injections			
	Column temp. (°C)	130	80	80
	Injector temp. (°C)	275	250	70
	Interface temp. (°C)	280		280
	Gradient/ temperature program	130°C (4 min) 40 °C/min to 300°C (4.25 min)	80°C (2 min) 10°C/min to 160°C (0 min) 4°C/min to 280°C (5 min)	80°C (1 min) 50 °C/min to 300°C (4 min)
Detection	Type	MS/MS	ECD	
	Ionization mode (CI/ EI)	EI		CI
	Pos/Neg mode			neg
	Desolvation gas and setting			no
	Temperatures (specify which)	150 (quadrupole)	300°C	
	Source block temp. (°C)	230		120
	Desolvation temp. (°C)			
	Other			emission 35 µA
Additional questions:	*Is your quantification method based on a method developped by published work and if so, do you have a citation?*	No	No, the method used is sonsidered for publishing	Microchemical Journal 119 (2015) 30–39 Determination of the sum of short chain chlorinated n-alkanes with a chlorine content between 50% and 67% in sediment samples by GC–ECNI-MS and quantification by multiple linear regression
	Did you use in-house standard solution as well? Briefly describe the type of calibration, if different than above:	Yes: see also form F, comments, 1-point calibration with a 51,5% chlorine content C10-C13 standard	Yes	Look to draft ISO 18635 The selected ion chromatogram is integrated over the full retention time range of the SCCPs. The
	Are you able to quantify the separate alkane groups (C10, C11, C12, C13) and Clorine groups (Cl7, Cl8, Cl9, Cl10)?	No	No	no

		CPP-30	CPP-32	CP-33
Instrument	Type	GC	GC	GC
	GC injector	Gerstel cold injection system, PTV splitless	splitless	splitless
	Detector type	MS/MS triple quad	MS single quadrupole	LR-MS, ECNI mode
	Other	-		
	Column	Thermo TG5-HT, 15 m x 0,25 mm x 0,25 µm	DB5-MS 30m 0.25mm 0.25 um	Agilent J&W DB-5 (60m, 0.25mm i.d., 0.1µm film thickness)
	Second column	-	no	N.A.
	Pre-column	-	no	Restek inert phase deactivated guard column (5m, 0.25mm i.d.)
	Flow rate/ gas speed	1,5 mL/min	2 mL/min	Constant pressure mode, therefore variable flow, ~ 2mL/min
	Carrier gas	He	Hydrogen	Helium
	Reagent gas	-	Hydrogen	Methane
	Injection volume (µL)	1,2 µL	1 uL	1
	Amount of injections	1 / run		
	Column temp. (°C)	up to 320 °C	gradient	60
	Injector temp. (°C)	up to 290 °C	300 °C	240
	Interface temp. (°C)	320 °C at transfer line	280 °C	180
	Gradient/ temperature program	25 °C/min to 320	50°C (3 min) 10 °C/min to 280°C (10 min)	60°C (1 min) 15°C/min to 320°C (13.7 min)
Detection	Type	MS/MS	MS single quadrupole	LR-MS
	Ionization mode (CI/ EI)	EI	EI	ECNI
	Pos/Neg mode	positive		negative
	Desolvation gas and setting			N.A.
	Temperatures (specify which)			
	Source block temp. (°C)	220 °C	230 °C source, 150 °C quadrupole	142
	Desolvation temp. (°C)	-		N.A.
	Other	collision gas used is argon	SIM mode, dwell time 100 ms	
Additional questions:	*Is your quantification method based on a method developped by published work and if so, do you have a citation?*	Z. Zencak, M. Reth, M. Oehme, Determination of Total Polychlorinated n-Alkane Concentration in Biota by Electron Ionization-MS/MS, Anal. Chem. 2004, 76, 1957.	Yes, F. Pellizzato, M. Ricci, A. Held and H. Emons, Accred Qual Assur 14 (2009) 529-540	Schmid, P.P. & Müller, M.D., 1985. Trace level detection of chlorinated paraffins in biological and environmental samples, using gas chromatography/mass spectrometry with negative-ion chemical ionization. Journal Association of Official Analytical Chemists, 68(3), pp.427-430, Tomy, G.T. et al., 1997. Quantifying C10–C13 Polychloroalkanes in Environmental Samples by High-Resolution Gas Chromatography/Electron Capture Negative Ion High-Resolution Mass Spectrometry. Anal. Chem., 69(14), pp.2762-2771
	Did you use in-house standard solution as well? Briefly describe the type of calibration, if different than above:	see above, The Reference standard calibration has a slope of 1,21 x10^-3 ng/ml per count. The in House calibration has a slope of 0,87 x10^-3 ng/ml per count.	Yes, Quantification with single n-alkanes (decane, undecane, dodecane, tridecane) standard solutions (from Merks company), Quantification based on response factor and on % efficiency of catalyst (Pd) conversion.	No
	Are you able to quantify the separate alkane groups (C10, C11, C12, C13) and Clorine groups (Cl7, Cl8, Cl9, Cl10)?	no	YES, the quantification is based on separation of the single alkane groups. Information about the chlorine content is lost, due to the inherent characteristics of the method (based on dechlorination of SCCPs).	No.