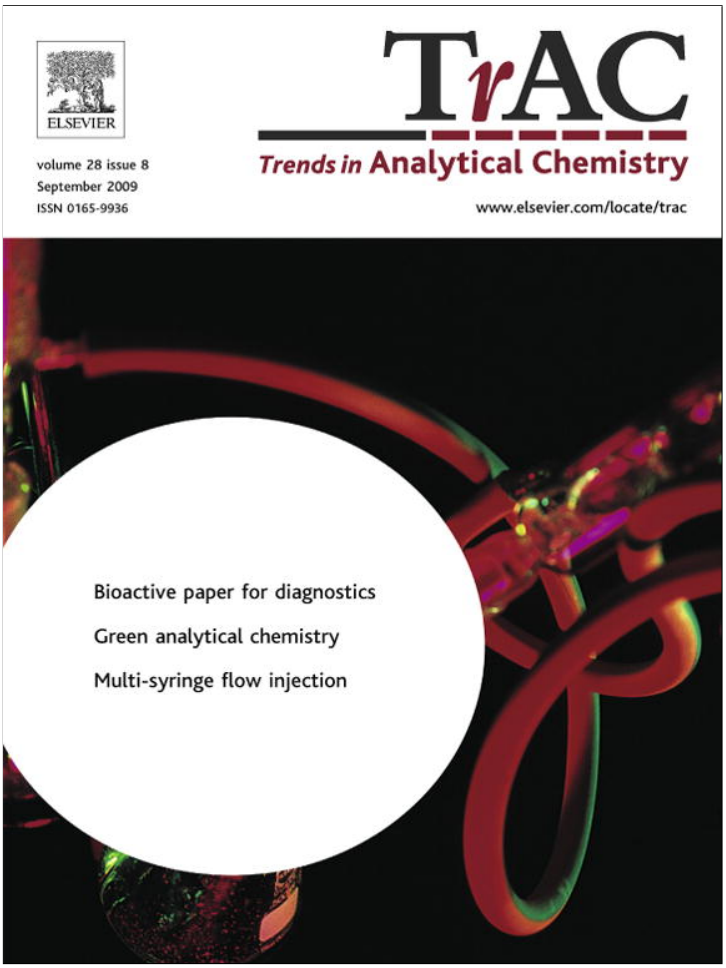

Laboratory intercomparison study on the analysis of short-chain chlorinated paraffins in an extract of industrial soil

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Short-chain chlorinated paraffins (SCCPs) comprise a class of organic pollutants used in many industrial applications and released into the environment. The analytical determination of SCCPs is very challenging. Although there is at present no fully validated measurement procedure that might be applied in routine monitoring, the European Union Water Framework Directive (WFD) has required regular monitoring of this class of compounds at river-basin scale since 2007.

To assess the *status quo* of the analysis of SCCPs in relation to the requirements of the WFD, we organized an interlaboratory comparison on the quantification of SCCPs in an extract of an industrial soil. Six laboratories participated in the exercise using three different techniques [i.e. gas chromatography (GC) coupled to mass spectrometry (MS) in electron-capture negative ionization mode, GC with atomic emission detection, and carbon-skeleton GC-MS]. The results reported were in the range 8.5–3200 mg/L. This confirms that reliable quantification of SCCPs is still very difficult to achieve and that the comparability of SCCP data reported to the European Commission is at least questionable.

Abbreviations: AED, Atomic emission detection; ASE, Accelerated solvent extraction; CSkGC, Carbon-skeleton gas chromatography; DCM, Dichloromethane; ECNI, Electron-capture negative ionization; EI, Electron impact; EQS, Environmental quality standard; GC, Gas chromatography; LCCP, Long-chain chlorinated paraffin; LRMS, Low-resolution mass spectrometry; MAB, Metastable atomic bombardment; MCCP, Medium-chain chlorinated paraffin; MS^2, Tandem mass spectrometry; PCB, Polychlorinated biphenyl; PVC, Polyvinyl chloride; RSD, Relative standard deviation; SCCP, Short-chain chlorinated paraffin; WFD, Water Framework Directive

Keywords: Carbon-skeleton method; Gas chromatography coupled to atomic emission detection (GC-AED); Gas chromatography coupled to mass spectrometry (GC-MS); Electron-capture negative ionization (ECNI); Laboratory intercomparison; Organic pollutants; Polychlorinated *n*-alkanes; Short-chain chlorinated paraffins (SCCPs); Soil analysis; Water Framework Directive

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1. Short-chain chlorinated paraffins and the Water Framework Directive

Short-chain chlorinated paraffins (SCCPs) are highly complex technical mixtures of polychlorinated *n*-alkanes with a chlorine content of 49–70% by mass, and linear carbon-chain lengths in the range C_{10}–C_{13} that comprise thousands of isomers. They are clear or yellowish, mobile to highly viscous, oily liquids produced by chlorination of *n*-alkane feedstocks with elemental chlorine under high temperature and pressure and/or UV irradiation, and do not occur naturally. Due to their physical properties, they have been used in many different applications (e.g., extreme pressure additives in lubricants and cutting fluids, plasticizers in PVC, and flame retardants in paints, adhesives and sealants) [1].

The release of SCCPs into the environment can occur through metal-working fluids being disposed of improperly, leaching from polymers, or losses from paints and coatings containing SCCPs. SCCPs are dangerous to the environment because of their toxicity towards aquatic organisms, potential for bioaccumulation and persistency [2]. These dangers have increased concern about the further use of SCCPs in certain applications, so the European Commission (EC) has adopted a recommendation to take measures to restrict the use of SCCPs, in particular in metal-working fluids and leather-finishing products in order to protect the aquatic environment [3].

In 2001, the European Union (EU) included SCCPs in the list of priority substances in the field of water policy [4], amending the Water Framework Directive (WFD) 2000/60/EC [5]. To ensure a high level of protection against risks originating from priority substances, environmental quality standards (EQSs) have been set at European level for inland surface waters (rivers and lakes) and other surface waters (transitional, coastal and territorial waters). The next step is to extend setting of EQSs to sediments and biota. These are the matrices where SCCPs tend to accumulate, and where the presence of SCCPs should also be controlled.

Implementation of the WFD requires the design of water-monitoring programs to be carried out by laboratories of the Member States, which should be able to measure SCCPs reliably at the level lower than the EQS (0.4 ng/L). This requires the availability of validated methods capable of delivering comparable and traceable results with a fit-for-purpose measurement uncertainty as well as internal (e.g., reference materials) and external (e.g., proficiency-testing schemes) quality control tools.

2. Quality control in SCCP analysis

Numerous analytical approaches that are currently available for analysis of SCCPs have been reviewed in detail [6,7]. Among those approaches, gas chromatography with enhanced electron-capture negative ionization (GC-ECNI) is performed most often, although it greatly depends on the content of chlorine of the standard used for calibration and it requires clean-up of the sample to be thorough. Some advances for this method have been suggested by Reth et al. [8], who used the linear relationship between response factor and chlorine content.

Recent developments {metastable atomic bombardment with mass spectrometry (MAB-MS) [9], dichloromethane enhanced (DCM)-ECNI-MS [10] and electron impact with tandem mass spectrometry (EI-MS^2) [11]} have been proposed as alternative methodologies with a less pronounced dependency on the chlorine content, but they are not suitable for routine analysis. A completely different approach of analysis is the catalytic hydrodechlorination of SCCPs to *n*-alkanes by carbon-skeleton GC (CSkGC) [12].

The major difficulties in SCCP analysis arise from the more than 6000 isomers that constitute their mixtures, the lack of pure standards for calibrations and the lack of matrix-matched reference materials. So far, no methodology applicable to routine monitoring has been fully validated, and the comparability of data in the scientific community has been at least questionable [13,14].

To our knowledge, up to now, only one intercomparison for SCCP determination has been conducted [15], 10 years ago. This is possibly because of the difficulties in SCCP analysis and the limited number of laboratories committed to it worldwide.

With the aim of exploring the *status quo* in the analysis of SCCPs in Europe, an interlaboratory exercise was organized among several expert laboratories for the determination of SCCPs in an extract of an industrial soil. The present intercomparison study focused on evaluation of the quantification step. Due to the complexity of SCCP analysis, we decided to avoid introducing too many variables, the effects of which on the results would have been difficult to discriminate. Instead of providing the laboratories with the original material, an extract of it was used, allowing for the elimination of any uncertainty related to extraction and clean-up procedures.

Quantification is anyway a very challenging step. It depends on the calibration standards used, the detection method and the quantification function applied. Zencak et al. [16] reported that different instrumental techniques can lead to different patterns for the same sample because they do not measure the same group of compounds consistently and do not have the same analytical response. This is the main reason why comparing data of SCCP measurements is so difficult. As a consequence, the parameter chosen for this intercomparison was the sum of SCCPs C_{10}–C_{13}. This is also the way SCCPs are regulated at present in the WFD without further specificity. It would not have been easy to select some indi-

cator isomers from the 6000 [17]. The only data available so far on the toxicity of SCCPs were obtained using technical mixtures and were not related to specific isomers.

3. Organization of the laboratory intercomparison

There are no reference materials dedicated to the analysis of SCCPs, so the presence of SCCPs in materials certified for other constituents was investigated. For this purpose, a range of different types of soil and sediment reference materials obtained from the EC's Joint Research Centre, Institute for Reference Materials and Measurements (IRMM, Geel, Belgium) was screened for the presence of SCCPs:

- BCR-142R (light sandy soil certified for elements);
- BCR-320R (channel sediment certified for elements);
- BCR-462 (coastal sediment certified for elements);
- BCR-481 (industrial soil certified for PCBs);
- BCR-524 (industrial soil certified for organic pollutants);
- BCR-536 (freshwater-harbor sediment certified for organic pollutants);
- BCR-701 (lake sediment certified for elements).

Due to its high content of SCCPs, BCR-481 was selected as the starting material to be extracted for the intercomparison study.

Two independent extracts of BCR-481 were prepared at IRMM using the following procedure. 1 g of BCR-481 was extracted by accelerated solvent extraction (ASE) (ASE-200 Dionex, Sunnyvale, CA, USA) using DCM at a temperature of 100°C and at a pressure of 13.8 MPa for 10 min (two static cycles of 5 min each). Removal of sulfur compounds was achieved during extraction by adding copper powder to the soil sample directly in the ASE cell.

After concentration of the extract to smaller volume by rotary evaporation (Laborota 4001, Heidolph, Kelheim, Germany), the extract was cleaned up on a glass column (1.5 cm i.d., 20 cm length, equipped with a glass frit and a Teflon stopcock), manually packed with 5 g activated Florisil, by eluting first with 20 mL of *n*-hexane, and subsequently with 40 mL of a mixture of *n*-hexane/DCM (1:1) and 10 mL of DCM. The combined eluates were concentrated to 1.5 mL by rotary evaporation. This extract constituted the sample for the exercise. Immediately after preparation, extracts were ampouled in 1-mL glass vials. Each vial was filled with 200 ± 3 μL of the extract and flame sealed by an ampouling machine.

Each laboratory received two ampoules, labeled as vial 1 and vial 2, dispatched with cooling elements in order to avoid possible degradation of the samples. The laboratories were asked to store the vials at −20°C until analysis.

A letter to the participants contained the instructions to be followed. Participants were asked to provide two independent analytical results of the total sum of SCCPs for each vial. The reporting of results for the individual groups of congeners of SCCPs was also encouraged, where the method used allowed it. The choice of the standards for calibration and the calibration method were left to each participant. Laboratories were asked to carry out the analysis under repeatability conditions to simplify the comparison of results. Furthermore, details on the extraction procedure used for sample preparation were communicated to the participants. They could therefore decide whether it was necessary to clean up further according to the requirements of the methodology they applied.

4. Analytical methods used by participants

Table 1 provides a short description of the methods used by the participants and any additional clean-up (if performed) of the sample extracts, together with details of the chromatographic and detection conditions applied. To maintain confidentiality, a code (1–6) was assigned to each laboratory.

Three different techniques were applied by the six laboratories for the quantification of SCCPs in the extract. GC-ECNI-MS was the method of preference (four out of six laboratories); GC-AED and CSkGC were the other methods used.

Laboratory 1 provided the results of vial 1 after dilution 1:500 and of vial 2 after dilution 1:100. The high dilution applied by Laboratory 1 was considered necessary to minimize the possible effects of interfering substances present in the soil extract. The quantification procedure used by this laboratory was optimized for the analysis of water samples and for the first time, on the occasion of this intercomparison exercise, applied to a matrix richer in interferences. Laboratory 2 was the only other laboratory to dilute the extract (1:10).

Despite the difficulties related to the complexity of the matrix chosen, caused by many interfering compounds, all but one of the laboratories decided not to clean up the extracts further. Laboratory 3 was the only one performed an additional clean-up [using aluminum oxide (2% water)].

As regards the chromatographic conditions, all GC columns used by the participants were non-polar. Four laboratories employed 5% phenyl 95% dimethylarylene siloxane, and two (Laboratories 3 and 4) 5% phenyl 95% dimethylpolysiloxane. All laboratories utilized splitless injection (Laboratories 1, 2 and 3 in the pulsed mode) with injection temperatures in the range 250–300°C. All laboratories used MS for detection, except Laboratory 4, which employed AED. In addition to ECNI-MS, Laboratory 5 also performed EI-MS^2 measurements. MS detec-

Table 1. Additional clean-up, analytical techniques, GC and detection parameters used by participating laboratories

Laboratory number	Additional clean-up	Analytical technique	Column phase and dimension (length, film, i.d.)	Inj. type/Inj. port temperature	Temperature program	Detector	Type of source/ Temperature of quadrupole	GC-MS interface	Ion source	Ion source temperature
1	Dilution of the extract 1:500 and 1:100	GC-ECNI-LRMS	DB-5MS 15 m 0.25 μm 0.25 mm	Pulsed splitless 275°C	100°C hold 2 min 70°C/min to 280°C hold 2.50 min70°C/min to 320°C hold 7 min	MS		280°C	ECNI	
2	Dilution of the extract 1:10	GC-ECNI-LRMS	DB-5MS 15 m 0.10 μm 0.25 mm	Pulsed splitless 275°C	120°C hold 2 min 50°C/min to 325°C hold 3 min	MS	Quadrupole 150°C	280°C	ECNI	150°C
3	Additional clean up on aluminum oxide (2% water)	GC-ECNI-LRMS	DB-5 10 m 0.25 μm 0.25 mm	Pulsed splitless 250°C	90°C hold 3 min 120°C/min to 120°C 10°C/min to 320°C hold 5 min	MS	Quadrupole 106°C	320°C	ECNI	150°C
4	None	GC-AED	HP5-MS 30 m 0.25 μm 0.32 mm	Splitless 280°C	100°C hold 2 min 20°C/min to 300°C hold 8 min	AED		280°C		
5	None	GC-ECNI-LRMS	DB-5MS 15 m	Splitless 275°C	100°C hold 2 min 15°C/min to 280°C hold 4 min, 50°C/min to 300°C hold 1.6 min	MS	Triple quadrupole	280°C	ECNI	200°C
		GC-EI-MS^2	0.25 μm 0.25 mm		100°C hold 3 min 50°C/min to 300°C hold 3 min	MS^2	Triple quadrupole	280°C	EI	200°C
6	None	CSkGC-LRMS	DB5-MS 60 m 0.25 μm 0.25 mm	Splitless 300°C	50°C hold 3 min 10°C/min to 280°C hold 10 min	MS	Quadrupole		EI	

Table 2. Types of standard solution and calibration/quantification procedure used by the participating laboratories

Laboratory number	Standards used	Calibration/Quantification procedure
1	SCCPs 51.5%; 55.5%; 63% from Dr. Ehrenstorfer	Multiple linear regression
2	SCCPs 51.5%; 55.5%; 63% from Dr. Ehrenstorfer SCCPs 60% blending from 55% and 63%	Matching of sample with most similar SCCP standard
3	SCCPs 51.5%; 55.5%; 63% from Dr. Ehrenstorfer SCCPs 60% from Promochem	Matching of sample with most similar SCCP standard
4	SCCPs 51.5%; 55.5%; 63% from Dr. Ehrenstorfer	One regression curve for each chlorine content with four calibration levels
5	SCCPs 51.5%; 55.5%; 63%; MCCPs 52%; 57% from Dr. Ehrenstorfer	Correlation between total response factor of CP mixtures and chlorine content [13]
6	Pure standards of *n*-alkanes from Merck	Response factor from approximate matching of six calibration points

tors were four single-quadrupole systems and one triple-quadrupole system.

Table 2 gives further details regarding the calibration and quantification methods and the type of standard solutions employed by participant laboratories. Five of the six laboratories conducted calibration using synthetic SCCP mixtures of three different chlorine contents (51.5%, 55.5% and 63% Cl) purchased from Dr. Ehrenstorfer (Augsburg, Germany).

Laboratory 6 was an exception, using pure standards of *n*-alkanes as calibrants because of the specific method employed (CSkGC) [12].

All laboratories applied different quantification procedures. Laboratory 1 quantified the SCCPs in the extracts using a multiple linear regression of the responses of a certain number of specific mass fragments of SCCPs. Nine calibration levels were utilized in the concentration range 0.5–9 μg/L.

Laboratories 2 and 3 followed the approach of Tomy et al. [18]. They quantified via the standard that best matched the sample among the four standard solutions available for chlorine contents in the range 51.5–63%. Laboratory 2 looked at *m/z* 70, 374 and 409 as target ions, while Laboratory 3 monitored the $[M\text{-}Cl]^-$ ions of each congener group.

Laboratory 4 performed a linear regression with four calibration levels for each of the chlorine contents (i.e. 51.5%, 55.5% and 63%).

Laboratory 5 used the approach proposed by Reth et al. [8] of correlation between the total response factors of SCCP mixtures and their chlorine content. The amount of SCCPs was calculated as the relative total area in the sample divided by the total response factor calculated for the sample from the regression curve.

Laboratory 6 quantified by means of the response factor of that calibration standard in which the ratio area of compound/area of internal standard was the closest to the ratio found in the sample (so-called ''approximate matching'' approach).

5. Intercomparison results

Table 3 shows the results of two replicate measurements of the sum of SCCPs C_{10}-C_{13} (expressed as mg/L) for vial 1 and vial 2, respectively, provided by the participants, together with the estimated chlorine content. Fig. 1 represents the results graphically.

Laboratory 6 provided only one result for each vial.

Table 3. Sum of SCCPs C_{10}-C_{13} (expressed as mg/L), mean of the means and standard deviation (SD) of the four replicates, relative SD (RSD) and reported chlorine content

Laboratory number	Extract vial 1		Extract vial 2		Mean of the means ± SD	RSD (%)	Chlorine content (%)
	Inj. 1	Inj. 2	Inj. 1	Inj. 2			
1	2900	3200	2880	3200	3045 ± 179	6	51
2	13.8	13.6	14.6	13.9	14.0 ± 0.4	3	60
3	8.5	9.1	11.2	11.0	10 ± 1	14	~60
4	54.3	58.5	60.9	54.1	57 ± 3	6	
5	13.0	13.3	15.8	16.1	15 ± 2	11	63.8
6	14.8		16.0		15.4 ± 0.9	6	

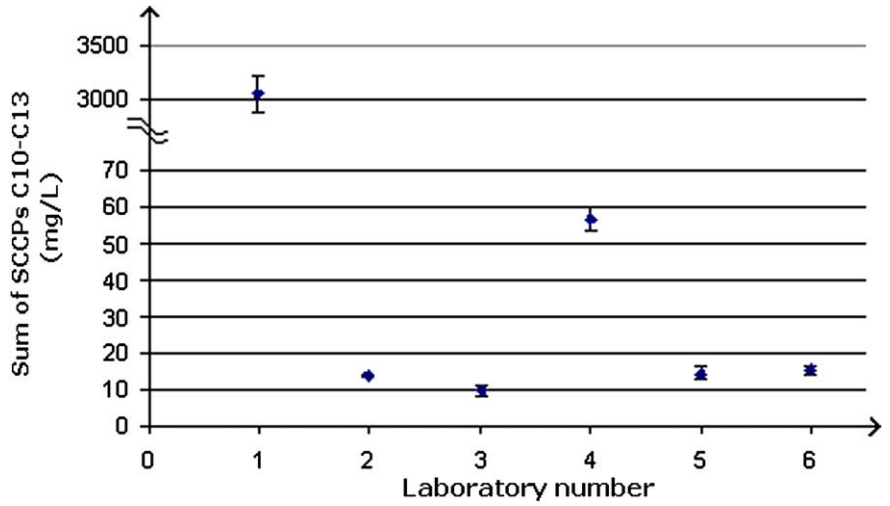

Figure 1. Graphical representation of the sum of SCCPs C_{10}-C_{13} expressed as mg/L reported by the participating laboratories (pooled results for extracts in vial 1 and 2). Error bars represent the standard deviation of the four replicates.

The reported concentrations were in the range 8.45–3200 mg/L for the first extract and 11.0–3200 mg/L for the second. Since vial 1 and vial 2 represented samples obtained from the same reference material by extraction under repeatability conditions, the two results of each laboratory were pooled together, giving acceptable relative standard deviations (RSDs) of the mean of the means in the range 3–14%.

Four laboratories provided results that agreed well (Laboratories 2, 3, 5 and 6). Laboratory 4 reported a higher value, but of the same order of magnitude. This could be explained on the basis that this laboratory did not apply any further clean-up, but stated that the presence of other chlorinated compounds in the extract led to an overestimation of the quantification of SCCPs when using the element-specific detection method, namely GC-AED.

Laboratory 1 gave a result more than one order of magnitude above the others. When including this laboratory, the coefficient of variation for all the data goes up to 209%. After discussion with the laboratory concerned, there was no technical reason to exclude this result. Anyway, if this figure was to be removed from the calculation, the coefficient of variation would decrease to 82%. Excluding both the results from Laboratories 1 and 4, the coefficient of variation would further decrease to 18%. Due to the high scatter of some data and the small number of datasets, no scoring of laboratory performance was carried out and no reference value was assigned.

Laboratory 5 also reported a value for the sum of medium-chain chlorinated paraffins (MCCPs) obtained by GC-ECNI-MS. The results (expressed as mg/L) of the two replicate measurements on the two extracts were 1.2 and 1.2 for extract 1, and 1.2 and 1.4 for extract 2, respectively. The calculated chlorine content for the sum of MCCPs was 56.4% in both cases. By using GC-EI-MS^2, they could also provide a value for total CP concentration [i.e. sum of SCCPs, MCCPs, and long-chain chlorinated paraffins (LCCPs)] [11]. The results reported for the total CPs (expressed as mg/L) were 14.6 and 10.0 for the first extract, and 16.8 and 17.7 for the second, respectively.

For methods based on GC-ECNI-MS, estimation of the chlorine content was also possible. This was not the case for Laboratory 4 because AED does not allow this information to be obtained. In CSkGC, this information is lost during the catalytic conversion [12], so Laboratory 6 did not report any estimate of the chlorine content in the sample.

Looking at the data available in Table 3, it can be seen that the value given by Laboratory 1 (i.e. 51%) did not agree with those reported by the other laboratories (i.e. 60% and 63.8%). Indeed, in the GC-ECNI-MS methods applied by Laboratories 2 and 3 (calibration using a single standard) [18] and Laboratory 5 (calibration using a linear correlation between total response factor of a CP mixture and its chlorine content) [8], correct estimation of the chlorine content is important, because it strongly affects the quantification process [8,10,18]. In the first approach (by Laboratories 2 and 3), the pattern of the standard used for the quantification should resemble as much as possible the one of the sample, in terms of molecular weight and chlorine content to allow reliable quantification. In the second approach (by Laboratory 5), knowledge of the chlorine content is mandatory to extrapolate the total response of SCCPs in the sample from the regression line.

However, the calibration approach used by Laboratory 1 (multiple linear regression using standards of different chlorine contents) should be independent of the knowledge of the chlorine content. If this helds true, under-

estimation of the chlorine content in the sample should not be the reason for the overestimation of the SCCP content reported by Laboratory 1. At present, we cannot give any other explanation for the strongly deviating results of Laboratory 1.

The measurement unit mainly used for expressing the sum of SCCPs C_{10}-C_{13} is mass concentration (e.g., mg/L). This is not exactly correct from a metrological point of view. Since SCCPs are not specifically defined single compounds at the molecular level, but rather mixtures of molecules with different carbon chain lengths and numbers of chlorine atoms, the link to mass-related measurement units is not known exactly. However, this unit is widely used in data comparisons. A future international agreement on the measurand ''SCCPs'' could also solve this problem of a sound measurement unit.

In the only previous interlaboratory exercise on SCCPs [15], the variability observed was explained by the use of different commercial solutions as external standards. In the present exercise, the variability observed in the results cannot be attributed to this, but rather to differences in detection and calibration methods. Although the choice of the standard was left to the participants, all laboratories turned out to use the same commercial mixtures as calibration standards, except Laboratory 6, which used *n*-alkanes as calibrant solutions for CSkGC. In addition, another issue that should be addressed is the lack of standard solutions of SCCPs of stated purity. Whatever quantification method is applied, impurities present in the available commercial mixtures can contribute to the uncertainty of the calibration step.

6. Conclusions

Despite efforts in the past few years to develop a method for reliable determination of SCCPs, the scientific community does not at present agree on any analytical methodology. This leads to different measurands and to major problems regarding harmonized compliance with WFD requirements for routine monitoring of SCCPs.

The results of the laboratory intercomparison reported in this article, only the second ever conducted on SCCPs, clearly show that not all results submitted by participants were comparable. There was good agreement among four laboratories applying different analytical techniques as well as different calibration protocols. A discrepancy in the results for one of the laboratories could be explained by lack of sufficient clean-up of the extract using a non-selective type of detection (i.e. AED). No explanation could be found for the strongly deviating results of another laboratory.

This study confirms that the analysis of SCCPs is very challenging and is far from being satisfactory. Further efforts should be made to develop a standardized method for the routine and reliable determination of this class of pollutants.

Disclaimer

Certain commercial equipment, instruments, and materials are identified in this article to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the EC, nor does it imply that the material or equipment is necessarily the best available for the purpose.

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