



## Short Communication

## Characterization of synthetic single-chain CP standard materials – Removal of interfering side products

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## HIGHLIGHTS

- Photolytic chlorination on *n*-alkanes is a versatile route to medium chain CPs.
- Synthesis of five chlorinated tetra-decanes with variable chlorination degrees.
- Removal of unknown side products resulted in pure MCCP materials.
- Side products were removed with normal phase liquid chromatography.
- Cyclic sulfite- and sulfate di-esters are in accordance with observed mass spectra.

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## ABSTRACT

The photolytic chlorination of *n*-alkanes in presence of sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub>) was explored to produce new standard materials. Five mixtures of chlorinated tetradecanes were synthesized with chlorination degrees (*m*<sub>Cl,EA</sub>) varying from 43.7% to 59.4% (*m/m*) based on elemental analysis. Chlorine-enhanced negative chemical ionization mass spectrometry (CE–NCI–MS) forcing the formation of chloride-adduct ions [M+Cl]<sup>−</sup> was applied to characterize these materials which all contained tetra- to deca-chlorinated paraffins. Deconvolution of respective mass spectra revealed the presence of chlorinated olefins (COs). CO levels were highest in materials, which were exposed longest. All synthesized materials also contained two classes of polar impurities, tentatively assigned as sulfite- and sulfate-di-esters with molecular formulas of C<sub>14</sub>H<sub>28-x</sub>O<sub>3</sub>SCl<sub>x</sub> (*x* = 1–4) and C<sub>14</sub>H<sub>28-x</sub>O<sub>4</sub>SCl<sub>x</sub> (*x* = 3–6), respectively. MS data were in accordance with the proposed structures but further work is needed to deduce their constitutions. These compounds are thermolabile and were not detected with GC–MS methods. We could remove these sulfur-containing impurities from the CPs with normal-phase liquid chromatography. In conclusion, single-chain CP materials were synthesized via chlorination of *n*-alkanes with sulfuryl chloride, but these materials contained reactive side products which should be removed to gain non-reactive and stable CP materials suitable as standards and for fate and toxicity studies.

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## 1. Introduction

Chlorinated paraffins (CPs) are high production volume chemicals produced at >1 million t/y (Glüge et al., 2016; Van Mourik et al., 2015, 2016). They are widely used as cutting and cooling fluids and as flame retardants and plasticizers in plastic (Glüge et al., 2018). CPs are synthesized from alkane mixtures via radical chlorination.

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Short chain CPs (SCCPs, C<sub>10</sub>–C<sub>13</sub>) gained attention in the last years and their persistency, bioaccumulation potential and toxicity have been assessed. In 2017, SCCPs have been classified as persistent organic pollutants (POPs) and are now listed in the Stockholm Convention (UNEP, 2017). Due to the SCCP ban, MCCPs are now frequently found in environmental samples (Houde et al., 2008; Tomy et al., 1999, 2000, 2010; Glüge et al., 2016, 2018).

However, quantification of MCCPs is challenging and reliable standard materials are needed. We suggested using single-chain standard materials (type B standards) for quantification of CP mixtures (Schinkel et al., 2018a; Sprengel and Vetter, 2019). Such standards are superior to complex technical mixtures (type A standards). Single-chain standard materials can be used to reconstruct homologue pattern of all kinds of samples allowing the quantification of individual CP homologues. Single-chain materials are also ideal precursors for environmental fate and toxicological studies.

Attempts were made to synthesize single-chain MCCP standards from pure *n*-alkanes with sulfonyl chloride (SO<sub>2</sub>Cl<sub>2</sub>) as a chlorine source. This method has been applied before for SCCP synthesis (Tomy et al., 2000; Sprengel and Vetter, 2019). Single *n*-alkanes are exposed to UV-light in presence of sulfonyl chloride to yield CPs with differing chlorination degrees. The characterization of such CP materials has been achieved by gas chromatography mass spectrometry (Tomy et al., 2000; Krätschmer et al., 2018), by nuclear magnetic resonance methods (Sprengel et al., 2019) and by elemental analysis (Sprengel and Vetter, 2019). However, the applied GC-MS methods, either with electron impact (EI) or negative chemical ionization (NCI), induce fragmentation of CPs during ionization resulting in C–Cl and C–H bond breakages. We applied a soft ionization method based on atmospheric pressure chemical ionization (APCI) to minimize thermal stress and fragmentation of analytes. Introduced by Zencak and Oehme (2004), this method was applied with other instruments to detect thermolabile compounds like hexabromocyclododecanes (Heeb et al., 2012), CPs (Reth et al., 2005; Bogdal et al., 2015; Yuan et al., 2016; Schinkel et al., 2017) and hexachlorocyclohexanes (Heeb et al., 2017). In presence of dichloromethane, a formation of chloride-adduct ions [M+Cl]<sup>−</sup> is favored. We applied this method to characterize synthesized single-chain materials. Proportions of chloroparaffins (*p*<sub>CP</sub>) and chloroolefins (*p*<sub>CO</sub>) were deduced by mathematical deconvolution of full-scan mass spectra. The method was introduced by Schinkel et al. (2017). As a surprise, two classes of thermolabile side products were found in the synthesized materials. A normal-phase LC method was used to separate these side products from CPs and COs. Based on the obtained MS data, sulfite- and sulfate-diester were postulated as side products. Even though their constitutions are not clear, we recommend to remove them with the given procedure. Only purified materials should be used as standards and precursors in environmental fate and toxicity studies.

## 2. Experimental

### 2.1. Materials, chemicals, synthesis, fractionation

Five batches of chlorinated tetradecanes were synthesized via photolytic chlorination of *n*-tetradecane (Alfa Aesar, Karlsruhe, Germany) in sulfonyl chloride (SO<sub>2</sub>Cl<sub>2</sub>, Sigma Aldrich, Steinheim, Germany) and dichloromethane (Merck, Darmstadt, Germany) as described before (Gallistl and Vetter, 2015; Sprengel and Vetter, 2019). Chlorine contents (*m*<sub>Cl,EA</sub>) of these materials were determined by elemental analysis (Sprengel et al., 2019). Aliquots of the crude materials (100 µg, Hohenheim, Stuttgart, Germany) with specified chlorine contents *m*<sub>Cl,EA</sub> of 43.7%, 51.4%, 54.6%, 58.7% and

59.4% were characterized by MS and further purified by NP-LC as described in Supplementary material (SM). Racemic β-HBCD (Empa, Dübendorf, Switzerland) has been used as internal standard (IS). LC-grade methanol (Biosolve, Valkenswaard, Netherlands), deionized water (Milli-Q, Merck), dichloromethane (Merck), *n*-hexane (Biosolve), and silica (60, 63–200 µm, Merck) were used for LC.

### 2.2. Mass spectrometric analysis, deconvolution of interfered spectra

Crude and purified CP materials, different LC fractions and side products were analyzed by direct-injection MS. A liquid chromatography system (Agilent 1100, Santa Clara, CA, USA) operated without column, under isocratic flow (methanol/dichloromethane 9/1, 0.35 ml/min) delivered sample (5 µl) to the MS. An APCI module (Agilent, Jet stream) and a quadrupole time-of-flight mass spectrometer (Q-ToF-MS, Agilent 6520 Accurate Mass) was applied. More information on MS conditions is given in SM. A mathematical deconvolution method was applied to obtain non-interfered spectra of CPs, COs and CdiOs (Schinkel et al., 2017; Schinkel et al., 2018b/2018c). A scheme of the method and a description is given in SM.

## 3. Results and discussion

### 3.1. Mass spectrometric characterization of synthetic MCCP mixtures

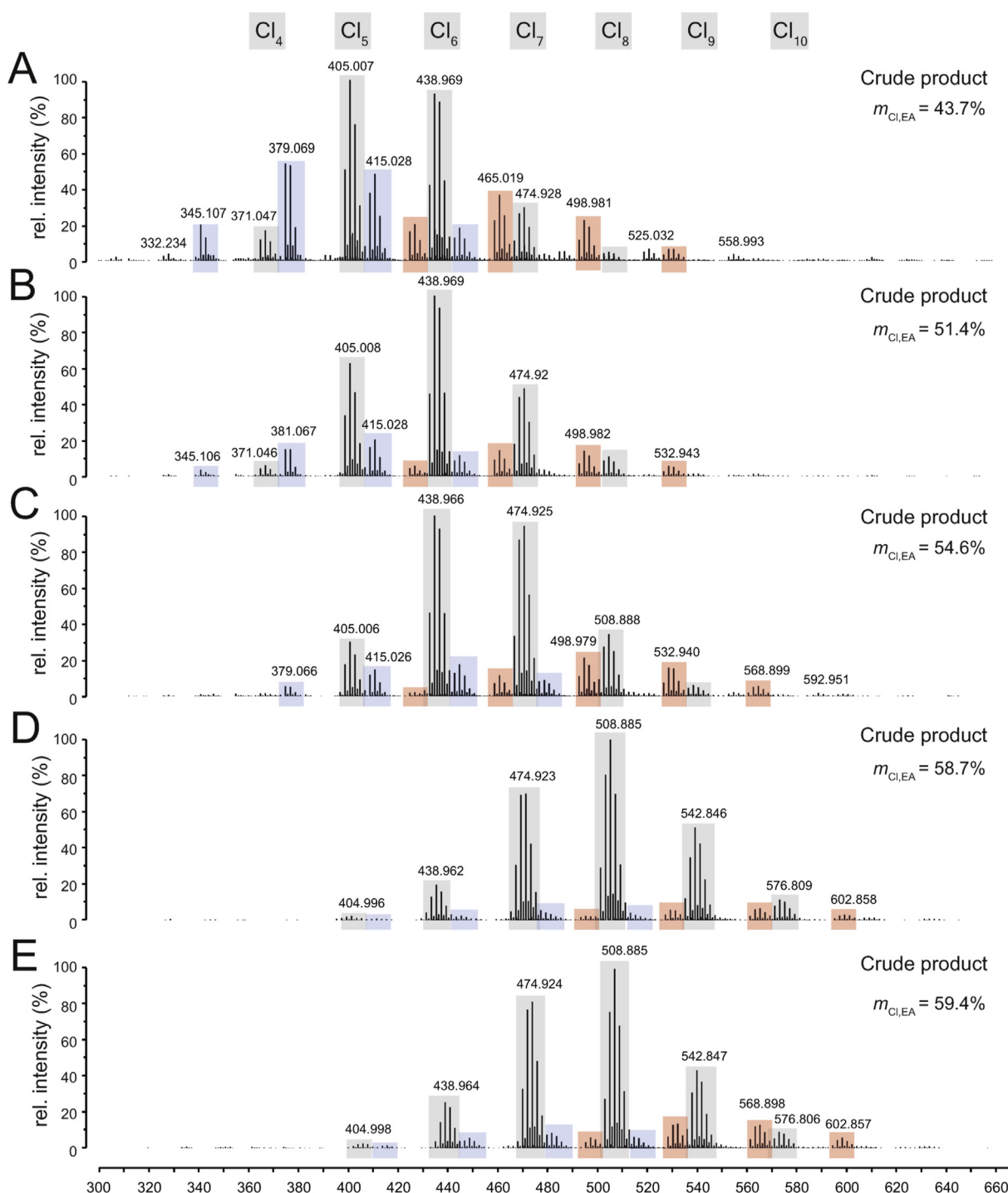
Fig. 1 displays Q-ToF mass spectra of five chlorotetradecane mixtures as obtained by synthesis from photolytic chlorination of *n*-tetradecane (C<sub>14</sub>) in presence of sulfonyl chloride (SO<sub>2</sub>Cl<sub>2</sub>). To obtain mixtures with different chlorination degrees (*m*<sub>Cl</sub>), UV-light exposure was varied from 90 to 260 min as described by Sprengel and Vetter (2019).

MS under soft ionization conditions in presence of dichloromethane supported the formation of chloride-adduct ions [M+Cl]<sup>−</sup>. Highlighted isotope clusters (Fig. 1, gray) represent tetra- (Cl<sub>4</sub>) to deca- (Cl<sub>10</sub>) chloro-tetradecanes. Additional signals of unknown polychlorinated compounds (Fig. 1, blue, red) appeared in these spectra. These impurities accounted for 20–50% of the MS signals and were more prominent in materials with lower chlorination degrees as discussed later.

Elongated reaction times led to increased proportions of higher chlorinated homologues and increased chlorination degrees. For instance, Cl<sub>5</sub>- and Cl<sub>6</sub>-homologues dominated in materials with chlorination degrees *m*<sub>Cl,EA</sub> = 43.7% and 51.4%, while Cl<sub>7</sub>- and Cl<sub>8</sub>-homologues were most abundant in materials with higher chlorination degrees of *m*<sub>Cl,EA</sub> = 58.7% and 59.4%.

Fig. 2 compares the mass spectrum of crude material with *m*<sub>Cl,EA</sub> = 43.7% (A), with spectra of purified material (B, fraction 4, gray) and side products (C, fraction 28, blue, red). Fractionation of these materials was achieved with NP-LC (silica, *n*-hexane/dichloromethane gradient). CPs eluted at non-polar conditions, whereas side products eluted at polar conditions. Two series of ions were observed for these side products, one consisted of Cl<sub>1</sub>-, Cl<sub>2</sub>-, Cl<sub>3</sub>- and Cl<sub>4</sub>-homologues (Fig. 2C, blue), the other of Cl<sub>3</sub>-, Cl<sub>4</sub>-, Cl<sub>5</sub>- and Cl<sub>6</sub>-homologues (Fig. 2C, red).

Accordingly, the other synthesized materials were purified by NP-LC. CP-containing fractions were pooled. MS analyses verified that purified materials contained only CPs but no side products (SM, Fig. S2).



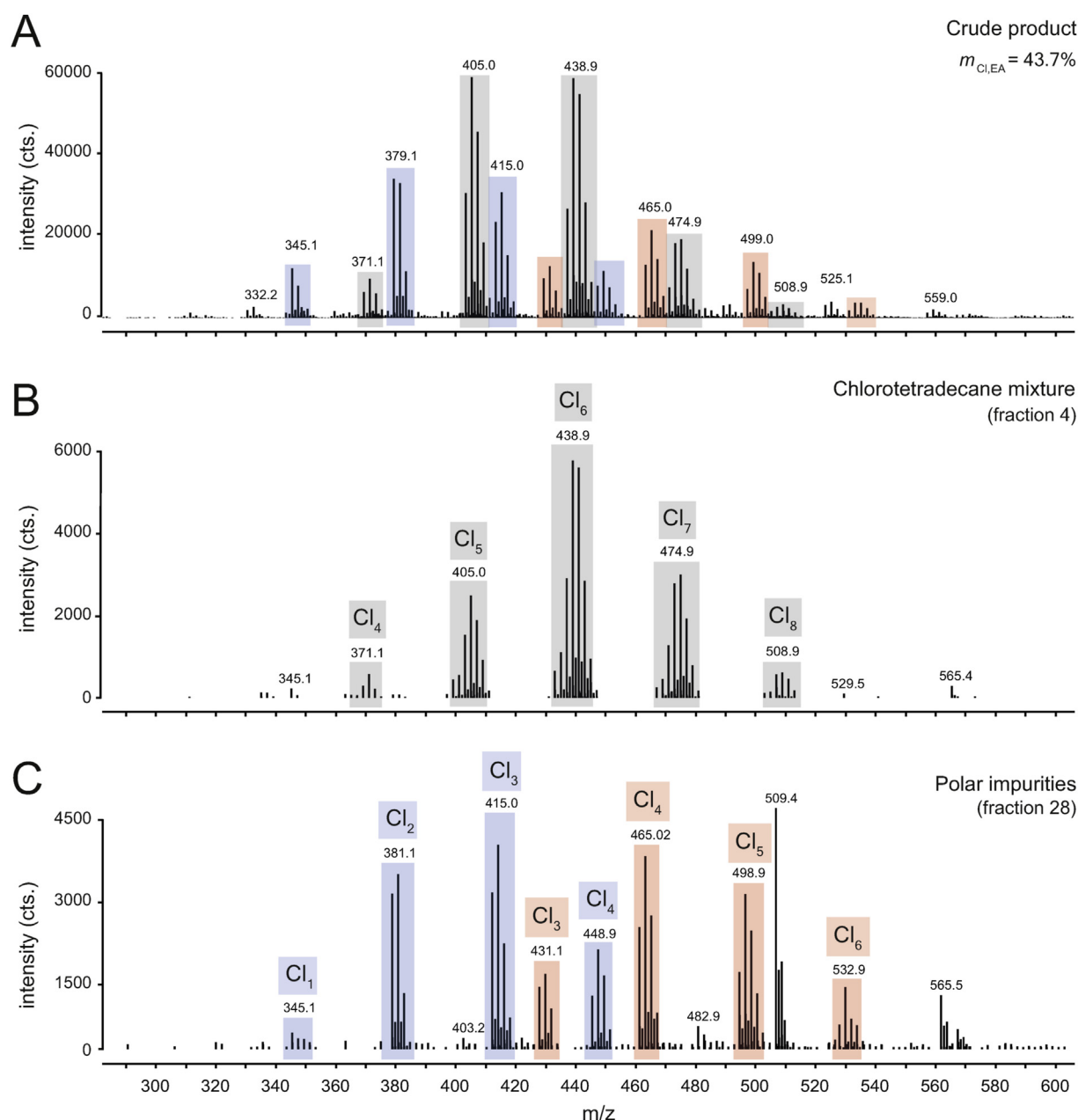
**Fig. 1.** Q-ToF mass spectra ( $m/z$  300–660,  $R \sim 8'000$ ) of five synthetic chlorotetradecane mixtures. These mixtures were synthesized from photolytic chlorination of *n*-tetradecane in presence of sulfuryl chloride. Chlorination degrees ( $m_{\text{Cl,EA}}$ ) varied from 43.7, 51.4, 54.6, 58.7 to 59.4%. Chloride-enhanced atmospheric pressure chemical ionization (CE-APCI) supports the formation of chloride-adduct ions  $[\text{M}+\text{Cl}]^+$ . Tetra- to deca-chloro-tetradecanes ( $\text{Cl}_4$ – $\text{Cl}_{10}$ , gray) were detected in these materials together with various side products (red, blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

### 3.2. Deconvolution of paraffinic and olefinic material, chlorine contents

Chlorinated paraffins can be transformed to chlorinated olefins (COs). Increased temperatures or exposure to reactive metal surfaces can induce the release of hydrochloric acid and the formation of olefinic material (Schinkel et al., 2017, Schinkel et al., 2018b/

2018c). However, mass spectra of CPs and COs strongly interfere. For example, a mass resolution of 31'000 is needed to resolve  $\text{Cl}_{10}$ -CPs and -COs. Herein we used a deconvolution procedure to distinguish chlorinated paraffins, olefins and diolefins as described in Fig. S1 (SM).

Fig. 3 displays measured and reconstructed  $[\text{M}+\text{Cl}]^+$  isotope patterns of  $\text{Cl}_6^-$ ,  $\text{Cl}_7^-$ ,  $\text{Cl}_8^-$ ,  $\text{Cl}_9^-$ ,  $\text{Cl}_{10}^-$  and  $\text{Cl}_{11}^-$ -tetradecanes of



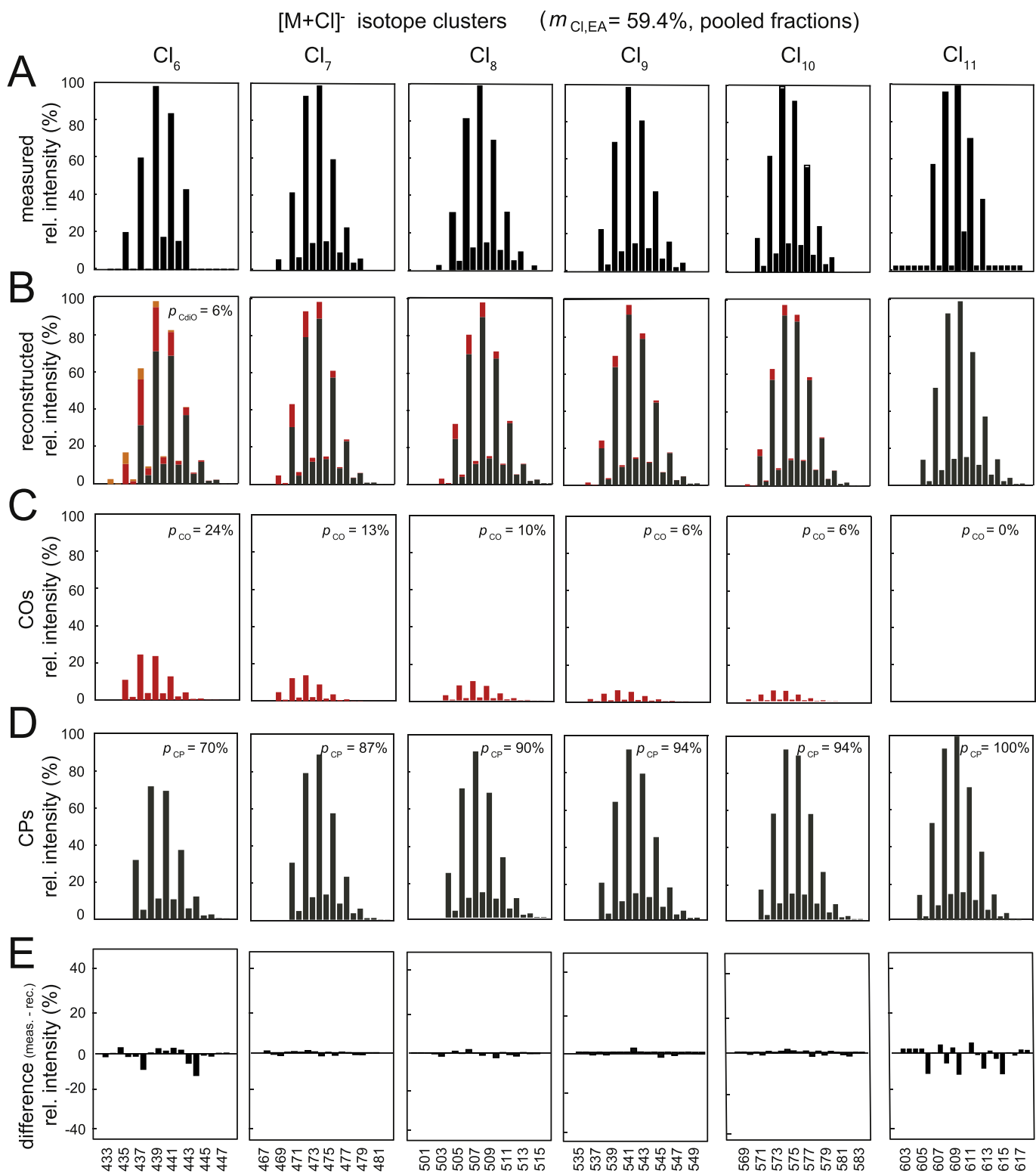
**Fig. 2.** Q-ToF mass spectra ( $m/z$  290–600,  $R \sim 8'000$ ) of crude (A) and purified (B) chlorotetradecane materials and separated side products (C). Chlorotetradecane homologues (gray) were found in the crude material (A) and in fraction 4 (B). Two classes of side products (blue, red) were found in fraction 28 (C). Chloride-enhanced atmospheric pressure chemical ionization (CE-APCI) conditions support the formation of chloride-adduct ions  $[\text{M}+\text{Cl}]^-$ . (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

purified material with a chlorine content  $m_{\text{Cl,EA}} = 59.4\%$ . In general, proportions of diolefinic material ( $p_{\text{Cdio}}$ ) were low except for  $\text{Cl}_6$ -homologues, which contained up to 6% diolefins (Fig. 3, orange). Chlorinated olefins were more abundant (Fig. 3, red). On the premise of equal MS responses, proportions of chlorinated olefins ( $p_{\text{COs}}$ ) decreased with increasing chlorine content from 24% over 13%, 10%, 6%, 6% to 0%, for  $\text{Cl}_6$ - to  $\text{Cl}_{11}$ -homologues, respectively.

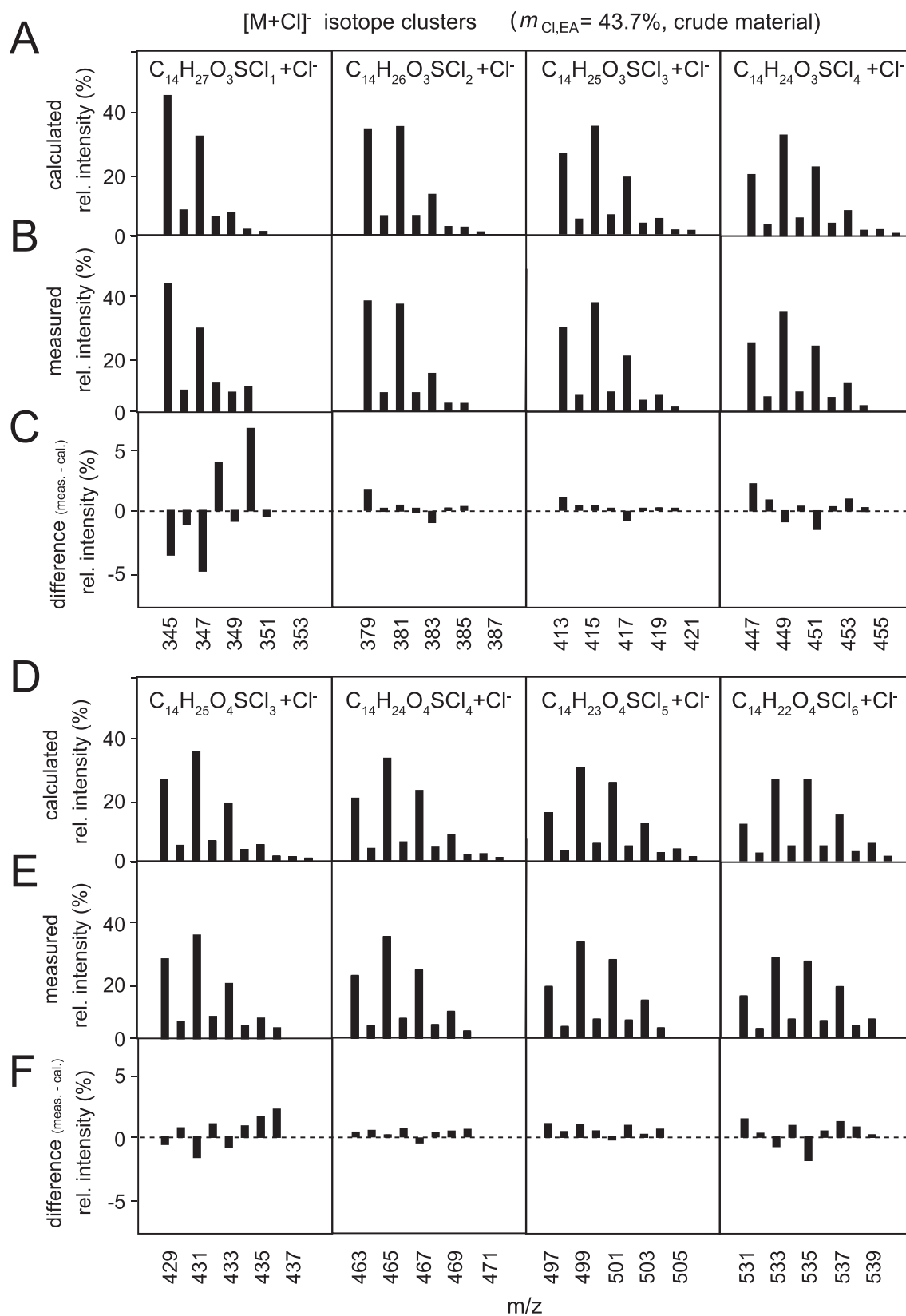
Similarly, Fig. S3 (SM) displays measured and reconstructed  $\text{Cl}_4$ - to  $\text{Cl}_9$ -isotope patterns of purified material with a lower chlorine content  $m_{\text{Cl,EA}} = 51.4\%$ . Table S4 lists paraffin-, olefin- and diolefin-proportions of purified materials. Two trends can be observed when comparing Fig. 3 and S3: (i) chlorinated olefins are more abundant in materials that were exposed longer and (ii) within one

mixture, olefin proportions were higher in lower chlorinated homologues. This trend was observed before and we postulated that CO and CP levels are related assuming that COs do form from CPs via HCl-loss (Schinkel et al., 2018c).

Table S5 compares chlorine contents from MS data ( $m_{\text{Cl,MS}}$ ) and from elemental analysis ( $m_{\text{Cl,EA}}$ ) of crude materials. Chlorine contents of 51.6, 52.5, 54.8, 58.7 and 59.1% were deduced from respective mass spectra, whereas 43.7, 51.4, 54.6, 58.7 and 59.4% were found from elemental analysis. Thus, MS and EA data differed by 7.9, 1.1, 0.2, 0.0 and  $-0.3\%$  (Table S5). Deviations were larger for materials with lower chlorination degrees. As mentioned, all synthesized CP materials also contained two classes of side products (Fig. 2A, red, blue) of unknown chemical nature but lower chlorine



**Fig. 3.** Mathematical deconvolution of interfered CP, CO and CdiO isotope clusters. Q-ToF mass spectra of synthesized chlorotetradecane material with a chlorine content  $m_{\text{Cl,EA}}$  of 59.4% were evaluated. Paraffin- ( $p_{\text{CP}}$ , gray), olefin- ( $p_{\text{CO}}$ , red) and diolefin- ( $p_{\text{CdiO}}$ , orange) proportions were deduced for each homologue with a mathematical deconvolution procedure. Olefin- (C) and paraffin- (D) proportions and differences (E) of modeled (B) and measured isotope clusters (A) are indicated. Deviations are largest for hexa- and undeca-chlorinated CPs due to low signal intensities in measured clusters (A). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 4.** Calculated and measured isotope clusters of the proposed chlorinated sulfite- (A, B) and sulfate-diester (D, E). Respective deviations are also shown (C, F). The polar fraction of the synthesized material with a chlorination degree  $m_{Cl,EA} = 43.7\%$  was studied. Chloride-enhanced atmospheric pressure chemical ionization supports the formation of chloride-adduct ions  $[M+Cl]^-$ .

contents.

### 3.3. Chromatographic and spectrometric characterization of side products

Both classes of side products were separated from the less polar CPs and COs by NP-LC (Fig. 2C). Despite their elution into one fraction (fraction 28), members of both compound classes could be distinguished by MS. Two series of isotope clusters of polychlorinated compounds differing by 34 mass units were recorded at  $m/z$  345, 379, 413 and 447 (Fig. 2C, blue) and  $m/z$  429, 463, 497 and 531, respectively (Fig. 2C, red). Considering that sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) was used as chlorine source, we hypothesize that sulfite- and sulfate-esters could be formed under such conditions.

Measured and calculated isotope clusters of different homologues with molecular formulas of  $\text{C}_{14}\text{H}_{28-x}\text{O}_3\text{SCl}_x$ :  $x = 1$  to 4 and  $\text{C}_{14}\text{H}_{28-x}\text{O}_4\text{SCl}_x$ :  $x = 3$  to 6 were in good agreement (Fig. 4). We assume that these compounds also form chloride-adduct ions under the CE-APCI conditions. Hence,  $\text{Cl}_1$ -,  $\text{Cl}_2$ -,  $\text{Cl}_3$ - and  $\text{Cl}_4$ -homologues with the formula  $\text{C}_{14}\text{H}_{28-x}\text{O}_3\text{SCl}_x$  were assigned as sulfite diesters. The  $\text{Cl}_3$ -,  $\text{Cl}_4$ -,  $\text{Cl}_5$ - and  $\text{Cl}_6$ -homologues with the general formula  $\text{C}_{14}\text{H}_{28-x}\text{O}_4\text{SCl}_x$  were described as sulfate diesters.

Cyclic sulfite- and sulfate-diester (Fig. 5) would be in accordance with the observed exact masses and isotope patterns. While five-, six- and seven-membered ring structures seemed to be most appropriate, other constitutional isomers may be possible. The photo-induced decomposition of sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) produces chlorine radicals and sulfuryl chloride radicals. Both may abstract hydrogen from  $n$ -alkanes forming alkyl radicals. Recombination reactions of chlorine and alkyl radicals lead to CPs, as anticipated. Yet, recombination of alkyl radicals with sulfuryl chloride radicals would result in sulfur- and oxygen-containing compounds. These compounds could be the precursors of the proposed sulfite- and sulfate-diester. Cyclization may occur if a second alkyl radical in the carbon chain is formed via hydrogen abstraction. Oxygen contents in these side products are higher than in sulfuryl chloride. This indicates an up-take of water or molecular oxygen, which may occur during UV-exposure and quenching.

However, full assignment of the chemical structures of all these side products requires additional work. If their constitutions are

known, further speculations about reaction mechanism may become appropriate.

## 4. Conclusions

Since 2017, SCCPs are regulated under the Stockholm convention and their use has been stopped in signatory states (UNEP, 2017). As a consequence, MCCPs and LCCPs are now widely used as substitutes. Thus, suitable standard materials for  $\text{C}_{14}$ - up to  $\text{C}_{30}$ -CPs are urgently needed to be able to quantify MCCPs and LCCPs in consumer products, food and feed (Schinkel et al., 2018a).

MCCPs and LCCPs are increasingly found in environmental samples and their persistency, bioaccumulation potential and toxicity must be assessed as well. The photolytic chlorination of  $n$ -alkanes with sulfuryl chloride is a versatile route to generate single-chain standard materials (Sprengel and Vetter, 2019). But as shown herein, such materials can be contaminated with polar, sulfur-containing chlorinated compounds of unknown structure, reactivity and toxicity.

These side products have lower chlorination degrees than the respective CPs, affecting the overall chlorine content of the crude material. By removing these impurities, one would expect that chlorine contents of purified materials increase. This could indeed be observed when comparing respective mass spectra. An NP-LC method was presented to remove side products. We recommend using this clean-up procedure to obtain pure materials that can be used as quantification standards or as starting materials for environmental fate studies and toxicological tests.

## Declaration of interest statements

The authors do not have any conflicts of interest with other entities or researchers regarding a publication of their data. Any opinions, findings, conclusions and recommendations expressed in this publication are those of the authors and do not necessarily reflect the view of the funding agency.

## Credit of authors statements

Research ideas were developed by N.V.H., P.L., D.B. and W.V. Synthesis of new standard materials in the laboratory was achieved by J.S. and M.K. Spectrometric and chromatographic characterization and data analyses of synthesized materials were performed by S.I., L.S., M.K., J.S. and N.V.H. The manuscript was written by W.V. and N.V.H. All authors have discussed the results and approved the manuscript.

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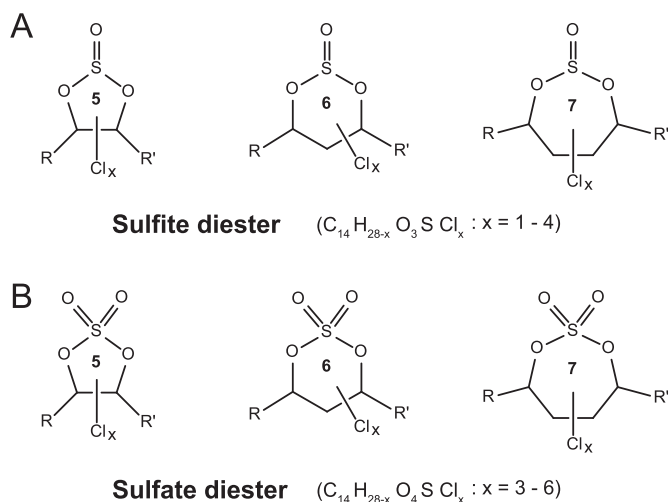
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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126959>.

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**Fig. 5.** Proposed structures of the cyclic sulfite- and sulfate-diester. Based on the observed isotope clusters, cyclic mono-, di-, tri- and tetra-chlorinated sulfite diesters (A) and tri-, tetra-, penta- and hexa-chlorinated sulfate diesters (B) are proposed as side products forming during the sulfuryl chloride-induced chlorination of  $n$ -tetradecane.

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