

Selective and Fast Analysis of Chlorinated Paraffins in the Presence of Chlorinated Mono-, Di-, and Tri-Olefins with the R-Based Automated Spectra Evaluation Routine (RASER)

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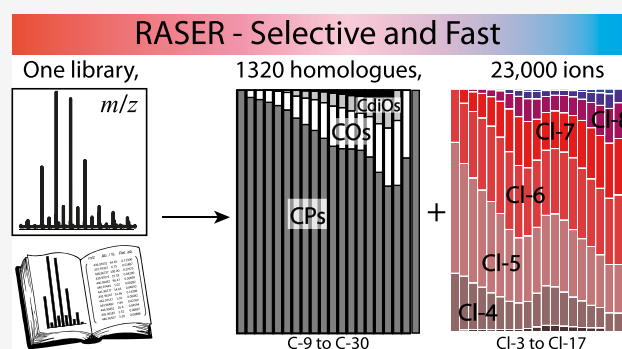
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ABSTRACT: Chlorinated paraffins (CPs) are complex mixtures consisting of various C homologues ($n_C \approx 10\text{--}30$) and Cl homologues ($n_{Cl} \approx 2\text{--}20$). Technical CP mixtures are produced on a large scale ($>10^6$ t/y) and are widely used such as plasticizers in plastic and coolants in metalwork. Since 2017, short-chain CPs ($C_{10}\text{--}C_{13}$) are classified as persistent organic pollutants (POPs) by the Stockholm Convention but longer-chain CPs are not regulated. Analysis of technical CP mixtures is challenging because they consist of hundreds of homologues and millions of constitutional isomers and stereoisomers. Furthermore, such mixtures can also contain byproducts and transformation products such as chlorinated olefins (COs). We applied a liquid-chromatography method coupled to an atmospheric pressure chemical ionization technique with a high-resolution mass detector (LC-APCI-Orbitrap-MS) to study CP and CO homologues in two plastic materials. Respective mass spectra can contain up to 23,000 signals from 1320 different C–Cl homologue classes. The R-based automated spectra evaluation routine (RASER) was developed to efficiently search for characteristic ions in these complex mass spectra. With it, the time needed to evaluate such spectra was reduced from weeks to hours, compared to manual data evaluation. Unique sets of homologue distributions could be obtained from the two plastic materials. CPs were found together with their transformation products, the chlorinated mono-olefins (COs), di-olefins (CdiOs), and tri-olefins (CtriOs) in both plastic materials. Based on these examples, it can be shown that RASER is an efficient and selective tool for evaluating high-resolution mass spectra of CP mixtures containing hundreds of homologues.



INTRODUCTION

Technical chlorinated paraffins (tCPs) are complex mixtures of hundreds of carbon homologues ($n_C \approx 10\text{--}30$) and chlorine homologues ($n_{Cl} \approx 2\text{--}20$). This corresponds to chlorination degrees of 30–70 m/m%.^{1,2} tCPs are produced on a large scale (>1 million t/y). They are widely used as flame retardants and plasticizers in plastic materials and as coolants and cutting fluids in metalwork.^{1,3} CPs are classified based on the carbon chain length into short-chain (SCCPs, $C_{10}\text{--}C_{13}$), medium-chain (MCCPs, $C_{14}\text{--}C_{17}$), long-chain (LCCPs, $C_{18}\text{--}C_{21}$), and very long-chain (vLCCPs, $C > 21$) CPs. Recently, also very short-chain CPs (vSCCPs, $C < 10$) gained some attention.^{4,5} Since 2017, SCCPs have been classified as persistent, bioaccumulating, and toxic (PBT) compounds and are regulated under the Stockholm Convention as persistent organic pollutants (POPs).⁶ MCCPs and LCCPs have been produced and used as substitutes of SCCPs. Currently, MCCPs are under evaluation for restrictions as they may also fulfill PBT criteria.^{7–9} Little is known about the environmental hazards and toxicities of LCCPs and vLCCPs.

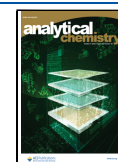
However, LCCPs can be present in environmental samples and may even exceed SCCP and MCCP levels.^{4,5,7,10–12}

The analysis of tCPs is a challenging conundrum due to the structural complexity of such mixtures with up to 10^8 isomers.^{13–16} Herein, isomers with either the same carbon chain length or chlorine number are described as homologues.¹⁷ Thus, C homologues have the same carbon chain length and Cl homologues the same chlorine number. Suitable reference CP materials are scarce, especially for longer-chain CPs.^{14,18–21} Current liquid (LC) and gas (GC) chromatographic methods cannot separate the many CP isomers.^{22–24} Furthermore, GC methods are limited to SCCPs and MCCPs,

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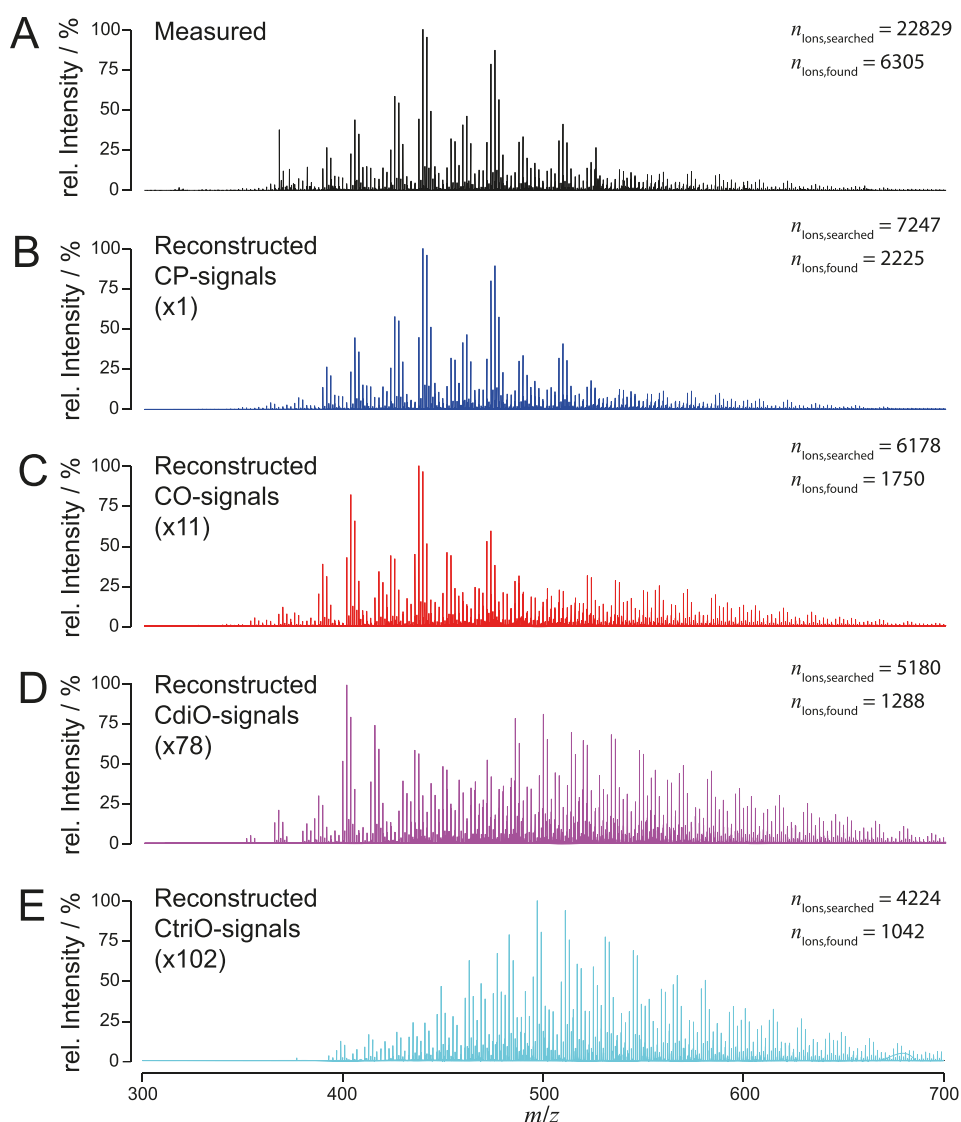


Figure 1. Measured (A) and reconstructed mass spectra (RMS) from LC-APCI-Orbitrap-MS of CPs (B), COs (C), CdiOs (D), and CtriOs (E) as found in the extract of plastic material M2. RASER was applied to extract and validate ions of specific $[M+Cl]^-$ isotope clusters of CP, CO, CdiO, and CtriO homologues. The total number (n) of searched and found ions and respective scaling factors (x) in relation to the most abundant CP ion are indicated.

due to the low volatility of longer-chain CPs.¹⁰ However, chromatographic separation can reduce matrix effects and interferences.^{20,25,26}

LC methods coupled to soft-ionization techniques such as atmospheric pressure chemical ionization (APCI) and to mass selective detectors are suitable to detect CPs of all chain lengths.^{7,10,27} CP mass spectra can be interfered from signals of byproducts or transformation products.^{18,20,25} In particular, insufficient mass resolution can lead to severe mass interferences between different CP homologues and CP transformation products such as chlorinated mono-olefins (COs) and di-olefins (CdiOs).^{20,26,28,29} Even mass spectra of CP standard and reference materials can contain such interferences.^{14,15,18,20,26}

Mass spectra of CPs, COs, and CdiOs interfere at mass resolutions of $R < 30,000$.^{26,28,30} A mathematical deconvolution procedure has been developed, which can resolve CP, CO, and CdiO interferences.^{26,28,31} With this approach, the HCl elimination of CPs during exposure to heat or certain enzymes to produce COs and CdiOs could be demonstrated.^{26,30,32}

However, the mathematical deconvolution of complex mass spectra of tCP mixtures is not feasible because of severe interferences between homologues.²⁸ Therefore, high-resolution mass detectors, capable of resolving paraffinic and olefinic ions, are required.

We hypothesized that CPs and their olefinic transformation products are present in plastic materials from consumer products. We applied an LC-APCI-Orbitrap-MS method to study the C and Cl homologue distributions of two plastic materials. Figure 1A shows the herein measured full-scan mass spectrum of a plastic material. The identification of different isotope clusters and the extraction of respective data from such complex spectra are time-consuming processes. The mass spectrum in Figure 2 shows that ions of CPs, COs, CdiOs, and even CtriOs can be present in plastic materials. Respective signals, which differ by about 18 m_u , can be resolved by the Orbitrap mass detector. However, manual evaluation of technical CP mass spectra is not reasonable because of workloads of weeks.

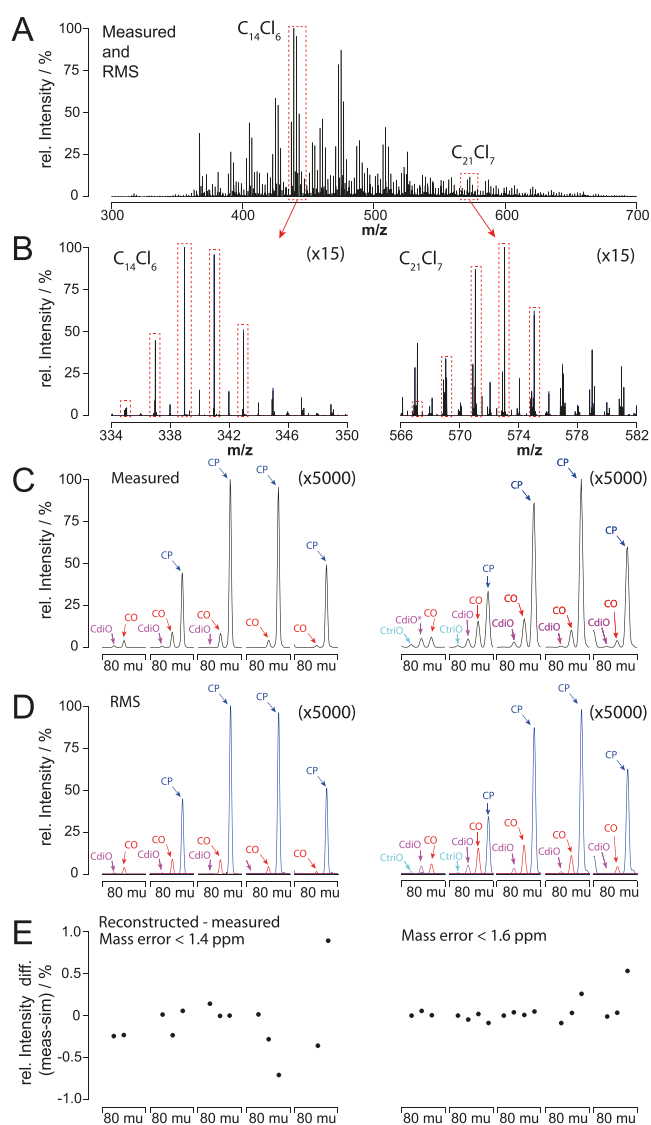


Figure 2. Measured and RMS (A) of plastic material M2. Zoom-ins of the x -axis of $\times 15$ (B) and $\times 5000$ (C) of isotope clusters from $C_{14}Cl_6$ and $C_{21}Cl_7$ homologues are given. Well-resolved signals of CPs (blue), COs (red), CdiOs (magenta), and CtriOs (cyan) are observed in both the measured (C) and reconstructed spectra (D). The differences between the signal heights of reconstructed and measured isotopomer groups are below 1% for all evaluated ions (E).

Herein, we present a new, fast, and selective R-based automated spectra evaluation routine (RASER). We applied RASER to evaluate such complex spectra and extracted quasi-molecular ions of CPs and their olefinic transformation products. RASER allowed an efficient data processing of these complex spectra in 3 h. Data extraction resulted in complete C and Cl homologue distributions of CPs and chlorinated mono-olefins and di-olefins and, for the first time, chlorinated tri-olefins (CtriOs). The procedure also revealed that both plastic materials contain relevant amounts of chlorinated mono-olefins and di-olefins and in one case even tri-olefins. The focus of this study is to demonstrate the time-efficient homologue-specific RASER procedure to evaluate complex mass spectra from two different plastic materials.

MATERIALS AND METHODS

Chemicals. Dichloromethane (DCM), methanol, and n -hexane (all from Biosolve, Valkenswaard, Netherlands) were used as solvents. Water (Milli-Q Reference A+, 18.2 M Ω cm) was generated and fetched daily. Isotopically labeled 1,5,5,6,6,10-hexachlorodecane ($^{13}C_{10}H_{16}Cl_6$, Cambridge Isotope Laboratories, USA) was used as the internal standard (IS).

Sample Preparation. Two plastic samples (M1, blue sports mat, and M2, black wire insulation) were cut, and aliquots (0.5 g) were extracted with DCM in a Soxhlet apparatus for 4 h. Aliquots of these extracts were mixed with IS (20 ng) and loaded to a normal-phase chromatographic column (1.2 g SiO_2 , diameter 5 mm). The column was precleaned with DCM (3 mL) and conditioned with n -hexane (3 mL). Fractions (5 mL each) of n -hexane (F1) and a mixture of n -hexane and DCM (8/2, F2) were collected. Solvent of F2 was removed using a gentle nitrogen stream at 30 $^{\circ}C$. The residue was dissolved in methanol (100 μ L) and analyzed by LC-APCI-Orbitrap MS.

Chemical Analysis. LC conditions and solvents were applied as described before^{28,33} with the following adjustments. A liquid chromatographic system (Dionex Ultimate 3000, Thermo Fisher Scientific, USA) with a C_{18} -reversed phase column (Zorbax, SBC18 RRHD 1.8 μ m, 3 mm \times 50 mm) was used. Injection volumes of samples were 6 μ L. Water (eluent A) and a mixture of methanol and DCM (9/1, eluent B) were used as eluents with a flow of 0.4 mL/min. A solvent gradient was applied, starting from 60% A and held for 1 min, followed by a linear increase to 98% A in 15 min and held for 7 min. After a linear decrease in 1 min and conditioning for 1 min, initial conditions were reached. The applied APCI conditions supported the formation of chloride adduct ions $[M+Cl]^-$ of paraffinic and olefinic homologues.^{15,34–36} The Orbitrap mass analyzer (Q Exactive, Thermo Scientific, USA) was operated at a resolution mode of 140,000 (at $m/z = 200$), at a 1.5 Hz scanning frequency and scanning range from 100 to 1100 m/z .

Efficient Spectra Evaluation with RASER. Figure 3 shows the workflow (steps A–H) of the R-based automated spectra evaluation routine (RASER). Average full-scan mass spectra were acquired at high resolution ($R = 140,000@200$ m/z) in the retention time window from 7 to 21 min with subtraction of background spectra from 5 to 6 and from 22 to 23 min (A). The acquired MS data in the .raw format were opened, extracted, and background corrected with the FreeStyle software (V1.8.51.0, Thermo Fisher Scientific, USA). Measured m/z and intensity values (I_{meas}) were exported as profiles in the .csv format (Figure 3A). As shown in Figure 3B, isotope clusters of predefined $[M+Cl]^-$ adduct ions of different CP, CO, CdiO, and CtriO homologues with C homologues varying from C_9 to C_{30} and Cl homologues from Cl_3 to Cl_{17} were simulated with the *enviPat* package (V2.4).³⁷ A threshold was set to 1%, corresponding to the signal height of the most abundant isotopomer groups of each isotope cluster. This resulted in a library of 1320 isotope clusters.

The calculated m/z values, the abundances in relation to the most abundant isotopomer group (100%), and the relative abundance (sum = 1) of a given homologue are stored in a matrix I_{sim} . Measured data are imported to the R-program (V4.0.5, Figure 3C). The routine detects measured m/z values in a range of ± 2 μ (≈ 2 ppm). Matching m/z values are

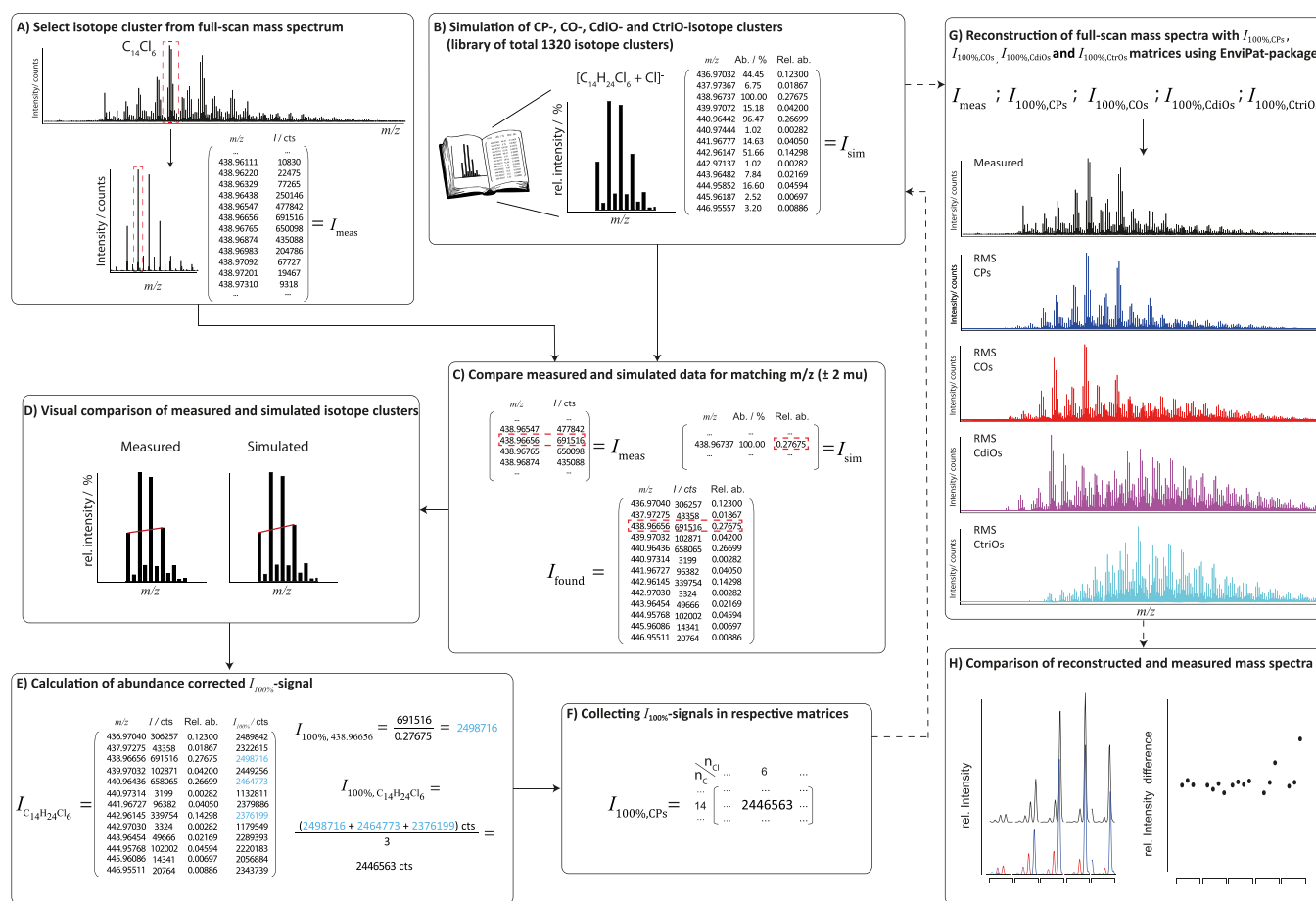


Figure 3. Workflow of the R-based automatic spectra evaluation routine (RASER). In total, up to 23,000 ions of CP, CO, CdiO, and CtriO homologues were extracted, evaluated, and abundance corrected from high-resolution Orbitrap mass spectra with RASER. Reconstructed mass spectra (RMS) were obtained from mean $I_{100\%}$ signals and the isotope cluster library (*enviPat*³⁷) for CPs (blue), COs (red), CdiOs (magenta), and CtriOs (cyan) in step G.

stored together with the corresponding measured intensity and the relative abundance in the matrix I_{found} . The measured and simulated isotope clusters are plotted and compared visually for their signal distributions (Figure 3D, red line). Some examples are given in Figure S2 (Supporting Information). If the signal distributions (Figure 3D) do not match, the homologue is considered as not detected ($I_{100\%} = 0$ cts). If the signal distribution does match, the abundance-corrected signal is computed, and the average of the three most prominent isotopomer groups are reported as mean $I_{100\%}$ signals (Figure 3E, blue). In other words, the isotopomeric distributions of the measured isotope clusters are validated based on a visual comparison with the simulated isotope clusters. Calculated $I_{100\%}$ signals of all detected homologues are collected in respective matrices (Figure 3F), which are further used to calculate homologue distributions and mean chlorine (n_{Cl}) and carbon (n_C) numbers. Furthermore, the $I_{100\%}$ matrices are used to calculate the RMS of CPs, COs, CdiOs, and CtriOs (Figure 3G). Obtained $I_{100\%}$ values are redistributed to respective isotope clusters by multiplying the $I_{100\%}$ signals with the respective relative abundances. The signals are modeled as Gaussian peaks by the *enviPat* R-package. The reconstructed and the measured mass spectra are compared, and differences are calculated (Figure 3H). In both studied plastic samples, differences of measured and reconstructed signals of isotopomer groups were below 1%,

and mass errors were below 1.6 ppm. The provided workflow in Figure 3 enables one to setup a RASER-like approach conceptually; the corresponding author may be contacted for further information on the script itself.

RESULTS AND DISCUSSION

Complex Mass Spectra of CPs and Their Olefinic Transformation Products. Figure 1 compares the measured mass spectrum of plastic material M2 (A) and the reconstructed mass spectra (RMS) of CPs (B), COs (C), CdiOs (D), and CtriOs (E). Figure S1 (Supporting Information) shows respective spectra of plastic material M1. These RMS visualize the different abundances of CPs, COs, CdiOs, and CtriOs in both plastic materials. RMS of the plastic material M2 are less complex than the measured spectrum, which contains 6305 ions. RMS of CPs, COs, CdiOs, and CtriOs include 2225, 1750, 1288, and 1042 ions, respectively (Figure 1). RMS of material M1 contain in total 3653 ions, whereas 1808, 903, 524, and 418 ions were assigned to CPs, COs, CdiOs, and CtriOs (Figure S1). We have searched for C_9 to C_{30} homologues and Cl_3 to Cl_{17} homologues, which can be expected as constituents in the plastic materials. This corresponds to $22 \times 15 = 330$ expected isotope clusters for each class of compounds. Thus, 1320 homologues, or in total 22,829 ions, are expected. With an estimated read-out time of 10 min per isotope cluster, we expect a workload of about 55 h

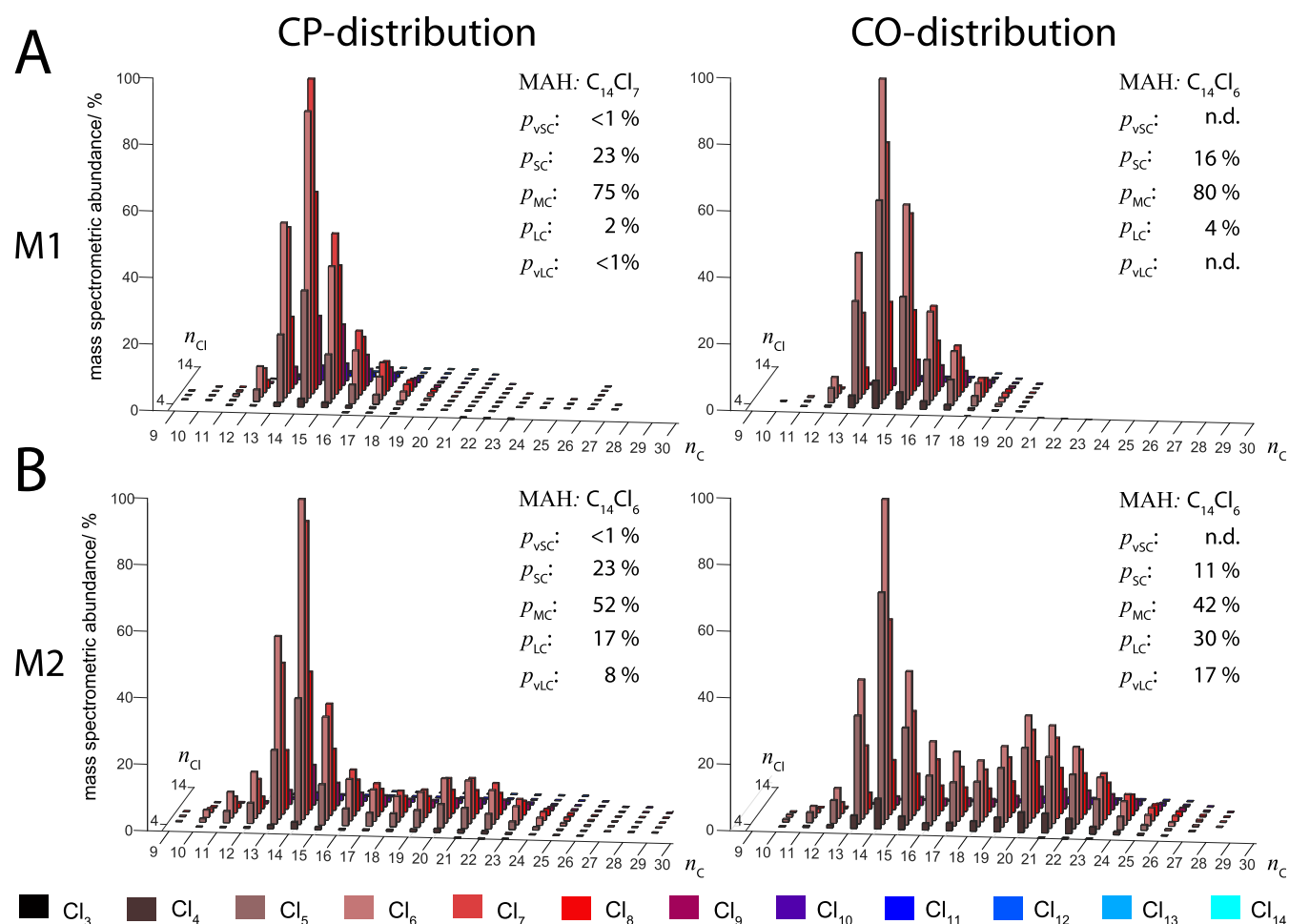


Figure 4. C and Cl homologue distributions of CPs and COs in plastic materials M1 and M2 obtained by applying high-resolution mass spectrometry and RASER. Mass spectrometric abundances (z-axis) in relation to the most abundant homologue (MAH) are given for Cl_3 – Cl_{14} homologues (y-axis, color coded) and C_9 – C_{30} (x -axis) homologues. Proportions of very short- (p_{vSC} , C_9), short- (p_{SC} , C_{10} – C_{13}), medium- (p_{MC} , C_{14} – C_{17}), long- (p_{LC} , C_{18} – C_{21}), and very long-chain (p_{vLC} , $C_{>21}$) CP and CO homologues are given. 2D-representations of Cl homologue distributions for individual carbon chains can be found in the [Supporting Information](#).

per class and about 6 weeks of work for the entire mass spectrum. The estimation is based on our own experience from manual signal evaluation. This shows the need for a computer-assisted procedure to evaluate such complex mass spectra, which can contain up to 23,000 ions. Therefore, we developed an R-based automated spectra evaluation routine (RASER) to process such large data sets. RASER simulates the isotope clusters of the predefined homologues using the *enviPat* package,³⁷ stores them in a spectra library for each run and searches for matching m/z values in full-scan mass spectra. Furthermore, RASER normalizes the read-out intensities and reports them as $I_{100\%}$ signals. Validation is done visually by comparing measured isotope clusters with simulated ones and by reconstructing the full-scan mass spectra of different classes of compounds (Figure 1). Figure S2 compares detected and calculated CP, CO, CdiO, and CtriO isotope clusters in material M2. Displayed are homologues which were detected in low, medium, and high abundances (10^2 to 10^6 cts). Visual comparison of the isotopic pattern show that measured and simulated isotope clusters correspond well above $I_{100\%} = 500$ cts for CPs, COs, and CtriOs with root-mean-square errors (RMSE) below 5%. Therefore, homologues corresponding to less than 0.01% relative to the most abundant CP homologue in both samples show matching measured and calculated

isotope clusters. Isotopic clusters below $I_{100\%} = 500$ cts may be considered as detected, but consistency of the isotopic pattern might not be ensured.

Some deviations of calculated and measured CdiO isotope clusters were noticed at lower m/z values of respective isotope clusters. However, measured CdiO signals at higher m/z values agree well with the simulated ones and were used for further calculations.

CPs and their olefinic transformation products cannot be separated chromatographically.^{15,18} Therefore, studying transformation reactions, which convert CPs to COs (HCl loss), requires a high mass resolution.^{30,33} Figure 2 compares the measured full-scan mass spectrum (A) of the plastic material M2 and the reconstructed mass spectra of CPs, COs, CdiOs, and CtriOs. Zoom-ins of the $C_{14}Cl_6$ and $C_{21}Cl_7$ isotope clusters are shown in (B) and (C) with zoom factors of 15 and 5000. A comparison of measured (C) and simulated (D) spectra shows the presence of paraffinic and olefinic isotopomer group signals. Simulated and measured signals did not differ more than 1%, and mass deviations were below 1.6 ppm. Furthermore, Figure 2 shows that high-resolution mass spectrometric methods ($R \approx 100,000$) are needed to resolve mass spectra of CPs, COs, CdiOs, and CtriOs.

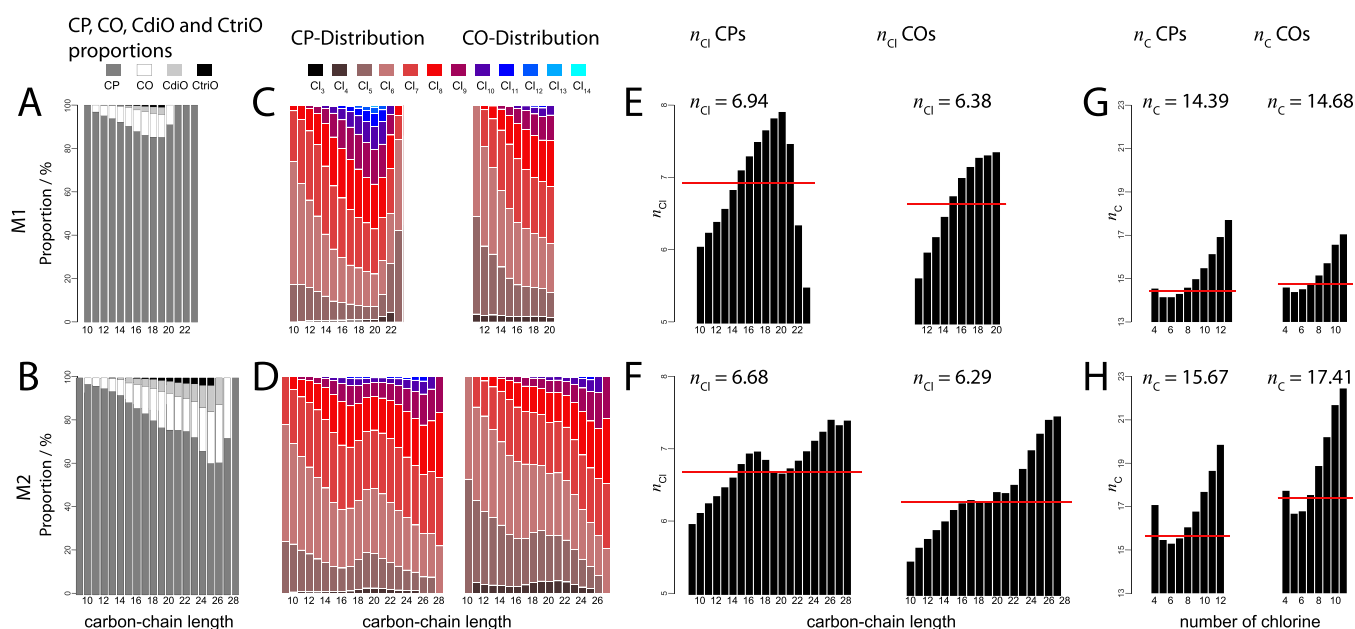


Figure 5. Homologue distributions, as well as chlorine (n_{Cl}) and carbon (n_C) number distributions of plastic materials M1 and M2, of CPs (gray), COs (white), CdiOs (light gray), and CtriOs (black) are displayed for different C homologues (A, B). Normalized Cl homologue patterns and the respective color code are displayed for CPs and COs (C, D). Mean chlorine (n_{Cl}) and carbon (n_C) numbers for different C homologues (E, F) and Cl homologues (G, H) are given for CPs and COs. Weighted mean chlorine and carbon numbers of homologues with $I_{100\%}$ signals > 500 cts are also indicated in E–H (red lines).

Selective and Fast Spectra Evaluation. Figure 3 shows the workflow of RASER, which was applied to high-resolution mass spectra of two plastic consumer products. The application of RASER allowed the extraction of CP, CO, CdiO, and CtriO signals to obtain comprehensive C and Cl homologue distributions. Overall, the evaluation of 1320 isotope clusters of paraffinic and olefinic ions needed in total about 3 h, mostly computation time. Compared to a manual spectra evaluation time of about 220 h, RASER reduces the workload by a factor of 73. In other words, data evaluation time is reduced from weeks to hours. In addition, the highest selectivity is provided which is needed to distinguish between CPs, COs, CdiOs, and CtriOs. To the best of our knowledge, this could not be achieved so far with other methods.

CP and CO Homologue Distributions in Plastic Materials of Consumer Products. Figure 4 shows 3D representations of CP and CO distributions of C homologues (x -axis, C_9 – C_{30}) and Cl homologues (y -axis, Cl_3 – Cl_{14}) in two plastic materials M1 and M2. Both samples were analyzed by high-resolution MS, and data were evaluated with RASER. Respective 2D representations of CPs, COs, CdiOs, and CtriOs are shown in Figures S3–S6 for M1 and S7–S10 for M2. Distributions and proportions were calculated based on $I_{100\%}$ signals, given in Tables S1–S8. The Cl homologue distributions (Figure 4, y -axis) of different C homologue classes show Gaussian-like distributions, with Cl_5 – Cl_8 homologues as the most abundant CP and CO homologues in both materials. The C homologue distributions (x -axis, Figure 4) of CPs and COs in material M1 are unimodal (Gauss like) with a maximum at C_{14} homologues. Material M2 shows bimodal C homologue distributions both for CPs and COs, with maxima at C_{14} and C_{20} homologues. MCCPs (C_{14} – C_{17}) are the most abundant homologues in M1 (Figure 4A) with relative abundances of 75%. SCCPs and LCCPs were detected in abundances of 23% and 2%. vLCCPs account for less than

1%. Short-, medium-, and long-chain CO homologues were found in relative abundances of 16%, 80%, and 4%. Very long-chain COs were not detected.

Plastic material M2 shows relative abundances for short-, medium-, long-, and very long-chain CPs of 23%, 52%, 17%, and 8% and 11%, 42%, 30%, and 17% for respective COs. Thus, medium-chained CPs and COs are most abundant in both materials. However, material M2 shows broader CP and CO distributions with relevant contributions of short-, medium-, long-, and very long-chain homologues. Material M1 has narrow distributions with short- and medium-chain homologues, accounting for 98% and 96% of all homologues. Both materials show CO distributions which are slightly shifted toward longer-chained homologues compared to respective CP distributions.

Figures S11 and S12 show CO proportions in relation to CPs for different C homologues (C_{10} – C_{29}). Highest CO proportions were found for less chlorinated homologues (Cl_4 , Cl_5). CO proportions gradually decreased from ~40% for Cl_4 to less than 5% for Cl_{12} homologues in M1. CO proportions in M2 show similar behaviors for the shorter homologues ($C < 20$). However, longer homologues ($C > 20$) in general do show increased CO proportions at more highly chlorinated homologues (Cl_9 , Cl_{10}) too, which produces U-shaped distributions.

Homologue Pattern in Plastic Materials. Figure 5 shows the proportions of CPs, COs, CdiOs, and CtriOs based on the relative $I_{100\%}$ signals of homologues detected in materials M1 (A) and M2 (B). Plots are based on $I_{100\%}$ signals > 500 cts (Tables S1–S8). Both materials show decreasing CP proportions with increasing carbon chain length until minima of 85% and 59% are reached for C_{19} and C_{26} homologues, respectively. Accordingly, proportions of COs, CdiOs, and CtriOs reach maxima of 11%, 3%, and 1% for M1 and 26%, 13%, and 3% for M2.

Thus, olefinic materials can be a relevant part in such technical CP mixtures with unknown effects on persistency, bioaccumulation, and toxicity.

Figure 5 also shows chlorine numbers (n_{Cl}) and carbon numbers (n_{C}). Mean values for CPs and COs in both plastic materials are shown. Cl_3 to Cl_{14} homologues are found for CPs in M1, while Cl_4 to Cl_{12} homologues were observed for COs. In M2, Cl homologues ranged from Cl_4 to Cl_{12} CPs and from Cl_4 to Cl_{11} COs. Cl_5 to Cl_8 homologues are most abundant in both materials. Weighted mean chlorine numbers (n_{Cl}) of CPs and COs are 6.94 and 6.38 for M1 and 6.68 and 6.28 for M2. Thus, the chlorination degrees of COs are lower than the ones of CPs in both materials. This is reasonable when assuming that COs form from CPs after elimination of hydrochloric acid.^{30,32} Maxima of $n_{\text{Cl}} = 7.98$ and 7.07 were found for C_{20} CP and CO homologues in M1. Bimodal distributions were found for M2 with maxima at C_{17} and C_{26} CPs of $n_{\text{Cl}} = 6.98$ and 7.45 and at C_{17} and C_{27} COs of $n_{\text{Cl}} = 6.33$ and 7.54. Thus, COs up to C_{20} homologues are in both materials less chlorinated than respective CPs. However, material M2 shows an increase of the chlorine numbers (n_{Cl}) of COs for carbon chain lengths $C > 21$, even exceeding n_{Cl} values of respective CPs. Mean carbon numbers (n_{C}) in Figure 5 show U-shaped trends for CPs and COs in both materials. Weighted mean carbon numbers n_{C} of 14.39 and 14.68 were found for CP and CO homologues in material M1. Respective values for M2 were 15.67 and 17.41. Therefore, mean detected carbon numbers n_{C} of COs are slightly higher than for CPs in both materials. Hence, average formulas of CPs and COs are $\text{C}_{14.39}\text{H}_{23.84}\text{Cl}_{6.94}$ and $\text{C}_{14.68}\text{H}_{22.98}\text{Cl}_{6.38}$ for M1. Material M2 can be described as $\text{C}_{15.67}\text{H}_{26.65}\text{Cl}_{6.68}$ and $\text{C}_{17.41}\text{H}_{28.54}\text{Cl}_{6.29}$, respectively. Comparing the chlorination degrees of CPs and COs indicates that M1 is more highly chlorinated than M2.

CONCLUSION

High-resolution MS together with RASER is an efficient way to evaluate CP, CO, CdiO, and even CtriO distributions in tCP mixtures used in plastic materials. With this efficient data evaluation, it can be shown that both materials show characteristic C and Cl homologue distributions of both CPs and COs. Material M1 has unimodal CP and CO distributions of mainly MC and SC homologues. Material M2 has bimodal distributions for both CPs and COs, with relevant contributions of LC and vLC homologues. MCCPs were the major compounds (>50%) in both materials. Relevant amounts (23%) of now banned SCCPs were found. These are indications that quite different CP mixtures were used in plastic materials.

In addition, we could identify and extract thousands of ions of olefinic CP transformation products in the mass spectra. Relevant proportions (up to 41%) of olefinic compounds were found in both plastic materials. Thus, these plastic materials contain numerous CP and CO homologues with varying distributions. CP and CO materials may eventually leach out into the environment and can be taken up by living organisms. Considering the high production volume, the potential hazards need to be evaluated for all CP and CO homologues. However, to the best of our knowledge, LCCPs, vLCCPs, and COs in general are currently not under wide-range environmental and toxicological evaluations. Thus, tCPs used in plastic contain materials with unknown effects on the environment and human health. The combined LC-APCI-Orbitrap-MS and RASER approach can be used to generate data for evaluation

studies of CPs and COs from plastic consumer products and environmental samples.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.analchem.2c02240>.

Additional documentation about the analytical method, the obtained $I_{100\%}$ signals, and respective data needed to produce figures (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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