Quantification of SCCPs and MCCPs via GC/ECNI-LRMS

Dr. Jannik Sprengel
CVUA Stuttgart

PhD thesis on CPs: Universität Hohenheim (2017-2021)
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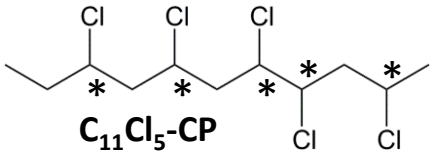
Chlorinated paraffins – what's that?

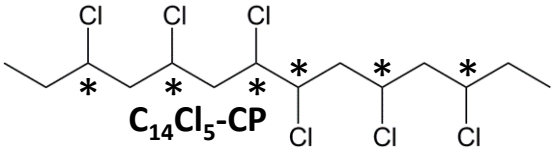
- chlorinated paraffins (CPs) = **polychlorinated *n*-alkanes** of anthropogenic origin
- synthesis via **free-radical chlorination of paraffin-*feedstocks***

➢ highly complex mixtures of **several thousand compounds**

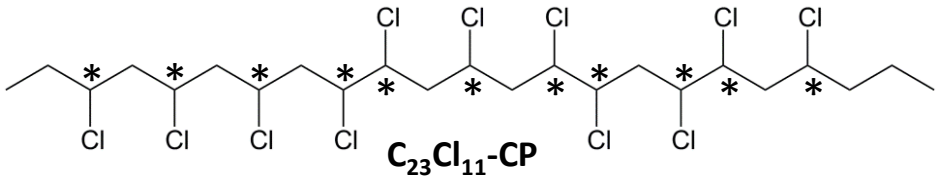
- usually subdivision into:
  - short chain CPs (**SCCPs**, **C_{10}-C_{13}-CPs**)
  - medium chain CPs (**MCCPs**, **C_{14}-C_{17}-CPs**)
  - long chain CPs (**LCCPs**, **>C_{17}CPs**)



$C_{11}Cl_5$-CP



$C_{14}Cl_5$-CP



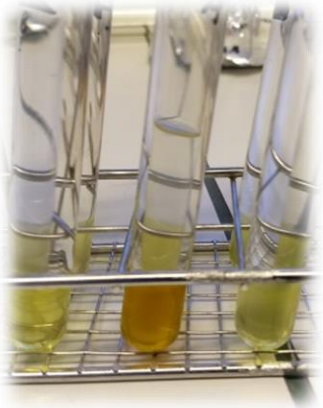
$C_{23}Cl_{11}$-CP

How to analyze CPs

- CPs are the „most challenging group of substances with respect to analysis and quantification”[1]
- no single „best“ setup (between 2017 and 2020: **18 different** setups)
  - ➢ each has its own advantages and disadvantages
- most often: **GC/ECNI-LRMS** (≈ 1/3 of published papers)
  - ➢ affordable and robust
- LC methods on the rise: analysis of LCCPs

Sample preparation

extraction of CPs (e.g. ASE) → 7.5 mL H_2SO_4 → 2.5 mL H_2SO_4 → column chromatography with deactivated silica gel → GC/ECNI -MS



[1] Steinwandter H, Schlüter H (1977), *Z. Anal. Chem*. 286

GC and MS parameters for CP analysis

GC:

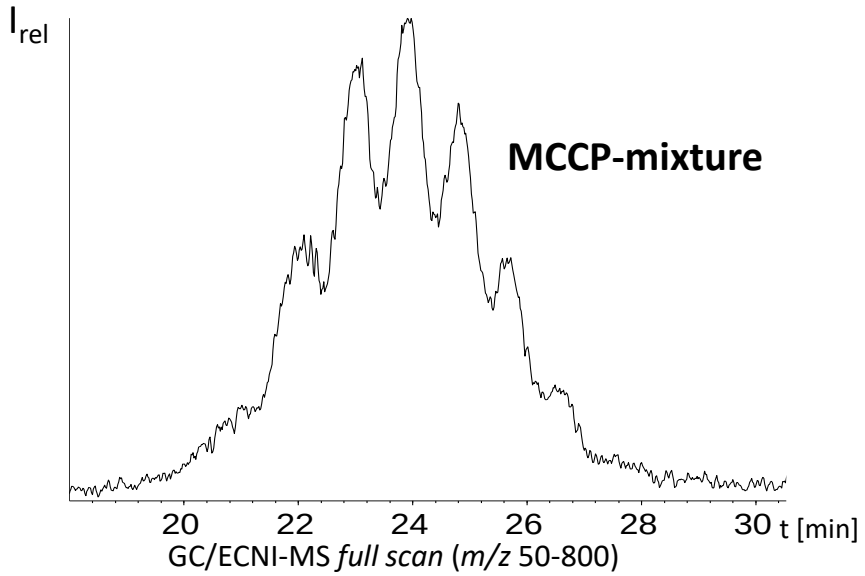
- Injector: **PTV** (Liner should be clean and deactivated)
  (otherwise **split/splitless**)
- Carrier gas: **Helium** 5.0 at 1.2 mL
- Oven temperature: 50°C (1 min) – 10°C/min – 300°C (19 min) = 40 min
- Column: (5%-Phenyl)-methylpolysiloxane (DB-5 etc.)
  100% Dimethylpolysiloxane (DB-1) also possible
  → separation through **boiling point**
  30 m preferred

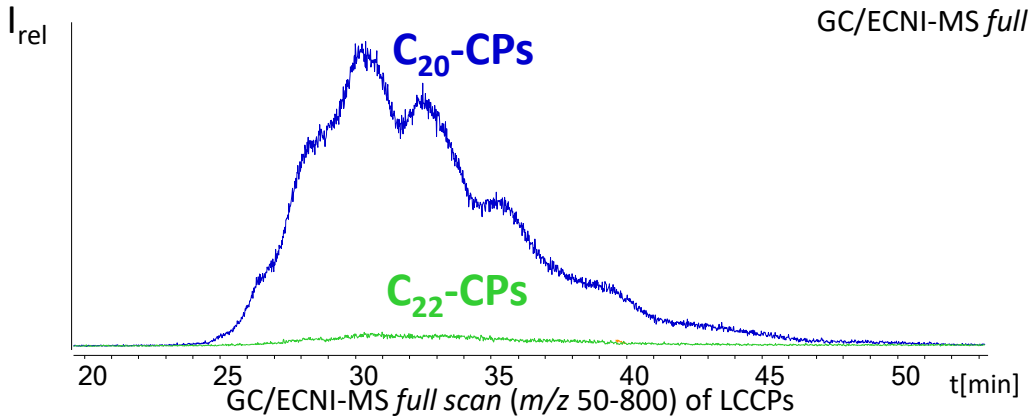
MS:

- ECNI negative mode
- moderating gas Methane 5.5 at $1.6*10^{-4}$ Torr
- **SIM mode**! (full scan too insensitive)

Quantification of chlorinated paraffins

- CPs **not seperable** through **chromatography**[1]
- characteristic **hump peaks**
- instrumental **response** highly influenced **by chlorination degree**
- basis of our research: Reth *et al.*[2]:
  - SCCPs, MCCPs as **sum parameters**
  - **LCCPs** not **quantifiable** via GC

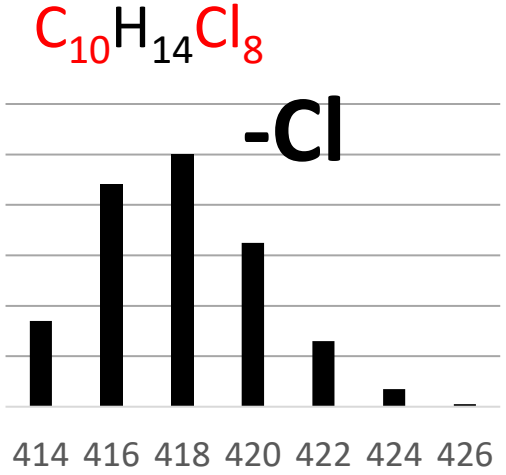




[1] Yuan B *et al.* (2019), Anal. Chim. Acta 1074, 16–32
[2] Reth M *et al.* (2005), J. Chromatogr. A 1081, 225–231

CP quantification by Reth *et al.*

- **Distinction** between **SCCPs** and **MCCPs**
- Monitoring of **[M-Cl]$^-$ ion** of each chain length from 4 to 1x Cl



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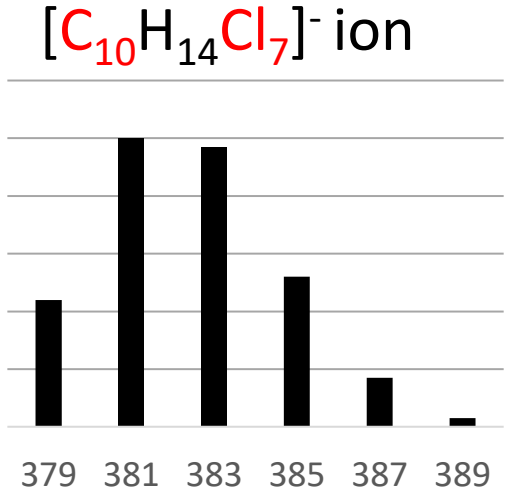

CP quantification by Reth *et al.*

- **Distinction** between **SCCPs** and **MCCPs**
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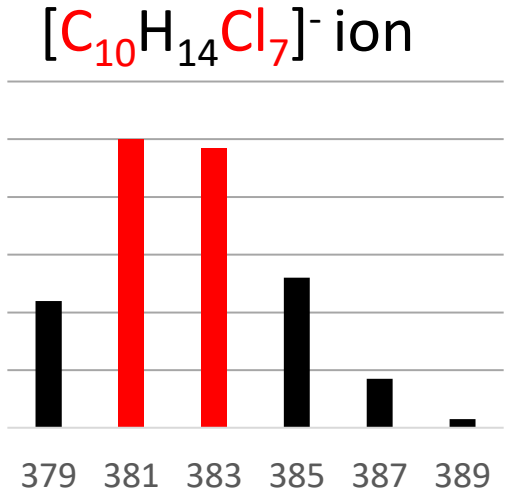
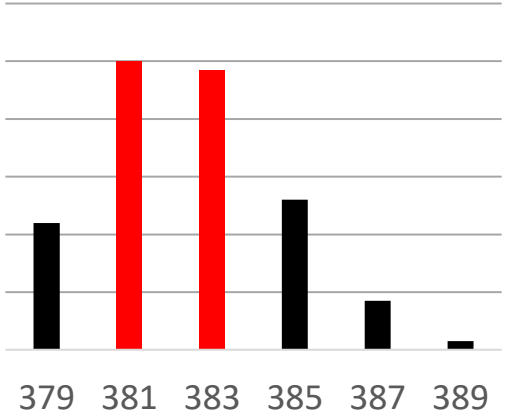
- **Most and 2nd most abundant** isotopes
  - ➢ **≈100 ions** for SCCPs and MCCPs combined



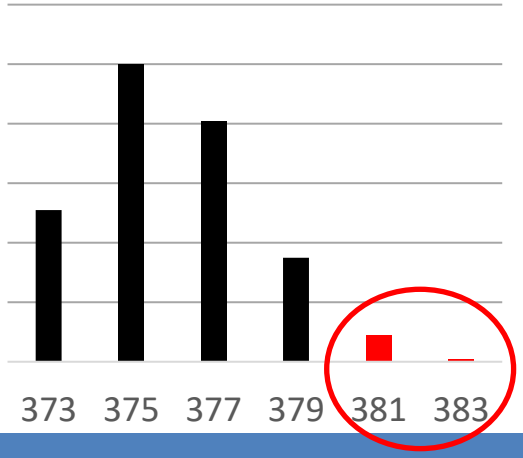
CP quantification – Overlap No. 1

- **Distinction** between **SCCPs** and **MCCPs**
- Monitoring of **[M-Cl]$^-$ ion** of each chain length from 4 to 1x Cl
- **Most and 2nd most abundant** isotopes
  - **≈100 ions** for SCCPs and MCCPs combined
- Problem: **Overlaps** possible
  - **±C_2**

$[C_{10}H_{14}Cl_7]^-$ ion



$[C_{12}H_{19}Cl_6]^-$ ion



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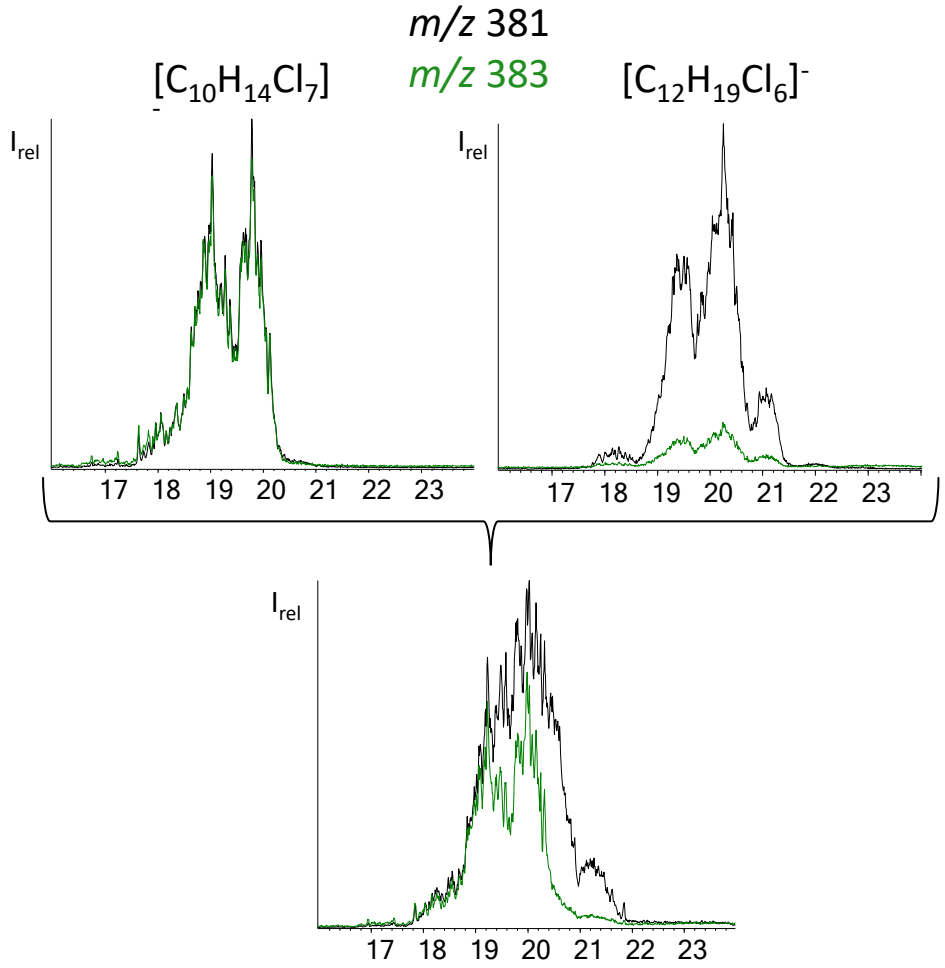

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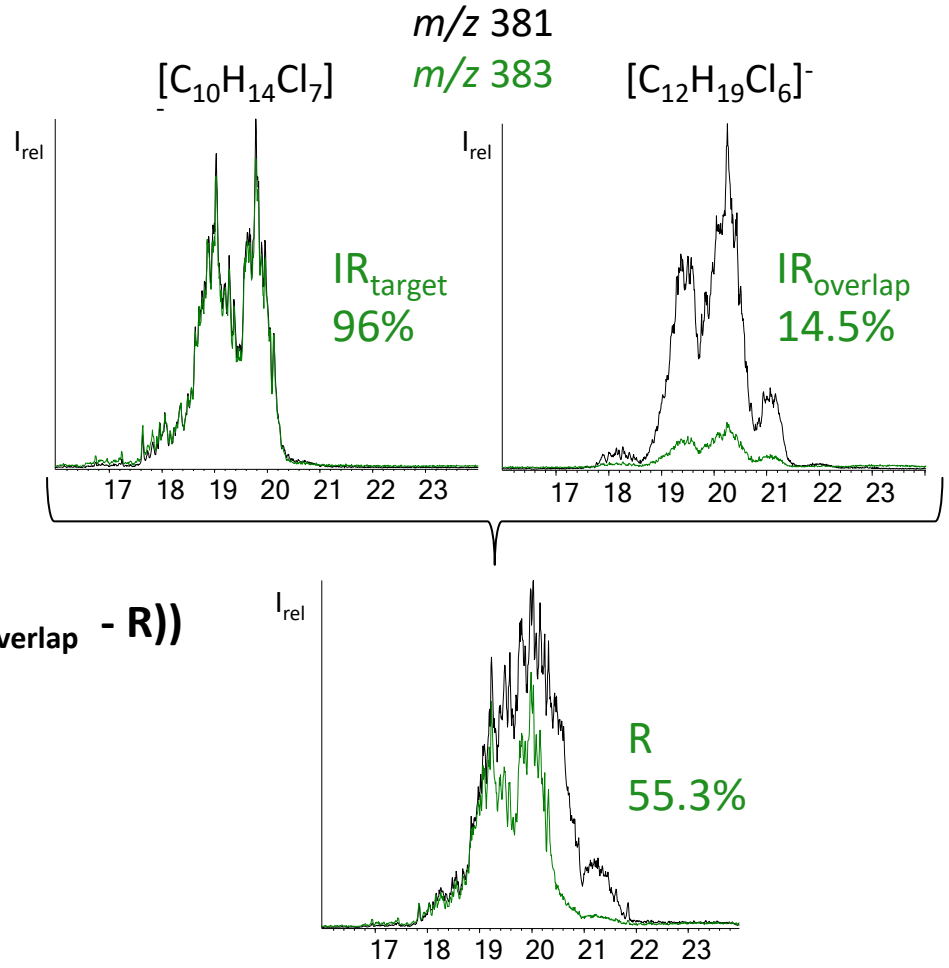
- Problem: **Overlaps** possible

$$c = (IR_{overlap} - R)*A/((R - IR_{target}) + (IR_{overlap} - R))$$

c =peak area from target CP
R = measured IR
A = measured peak Area



CP quantification – Common overlaps

- Isotope ratios of common overlaps:
- When $\mathbf{C_{x+2}}$ is more abundant:

Target homolog	Target IR	Overlap IR
Cl_8	96%	14.5%
Cl_9	89%	511%
Cl_{10}	78%	386%
Cl_{11}	87%	21.5%
Cl_{12}	97%	27.5%

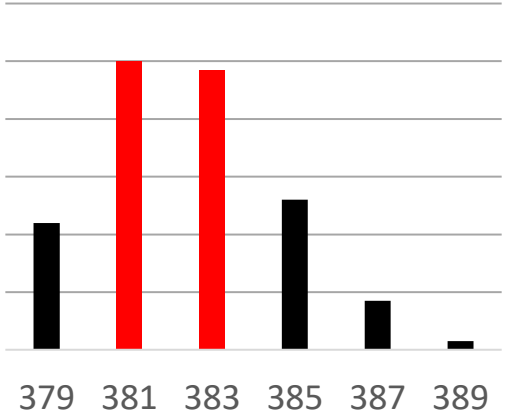
- When $\mathbf{C_{x-2}}$ is more abundant:

Target homolog	Target IR	Overlap IR
Cl_6	64%	603%
Cl_7	80%	748%
Cl_8	96%	193%

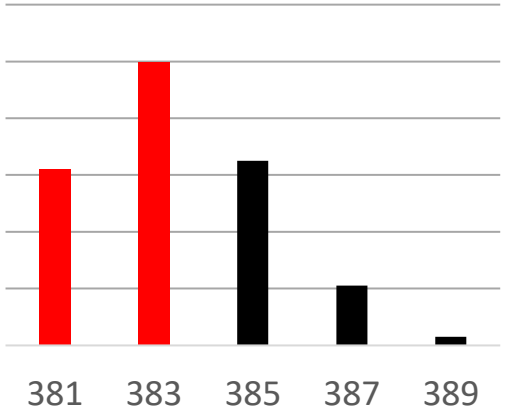
CP quantification – Overlap No. 2

- Problem: **Overlaps** possible
  - **±C_2**: Arithmetic correction via **isotope ratio**
  - **±C_5**

$[C_{10}H_{14}Cl_7]^-$ ion

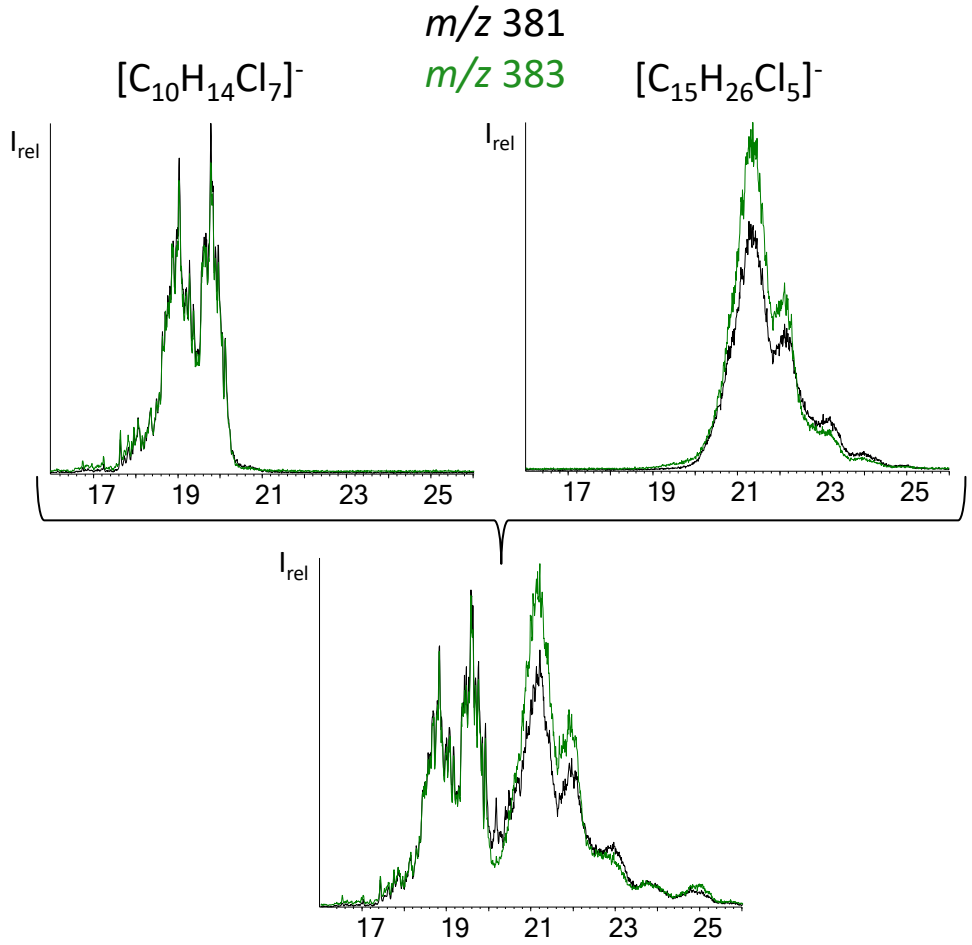


$[C_{15}H_{26}Cl_5]^-$ ion



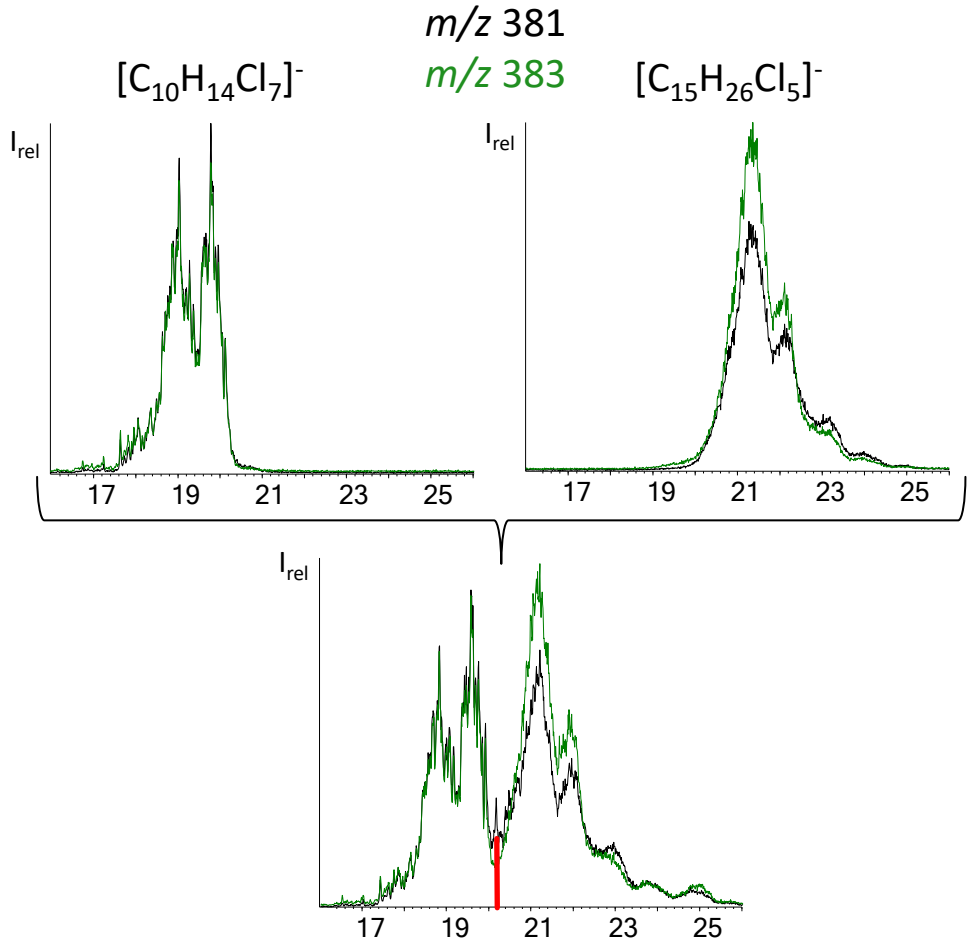
CP quantification – Overlap No. 2

- Problem: **Overlaps** possible
  - **$\pm C_2$**: Arithmetic correction via **isotope ratio**
  - **$\pm C_5$**



CP quantification – Overlap No. 2

- Problem: **Overlaps** possible
  - **±C_2**: Arithmetic correction via **isotope ratio**
  - **±C_5:** separation through **retention time**
  - **Always double check retention times with standards!**



CP quantification – advantageous use lof overlaps?

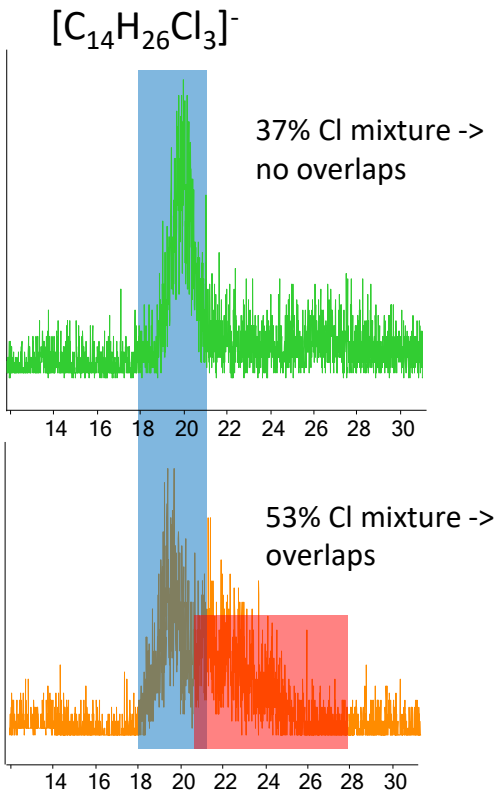
Zeng et al. (2011), Environ. Sci. Technol. 45

- combination of two chain lengths into one run

However, we found that the simultaneous detection of SCCPs and MCCPs combined with chemical calculation can effectively identify and exclude interferences. Considering instrument sensitivity decreases with the increase of number of monitored ions in a given retention time window, it was necessary to divide all monitored ions of SCCPs and MCCPs into four groups: C_{10} and C_{15}, C_{11} and C_{16}, C_{12} and C_{17}, C_{13} and C_{14}.

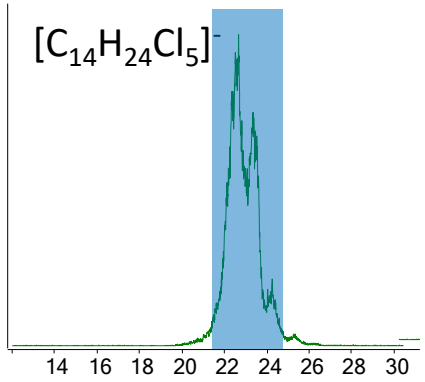
CP quantification - Cl_4 and Cl_5 homolog groups

- Additional **overlaps** from (probably) higher chlorinated homologs of the **same chain length:**



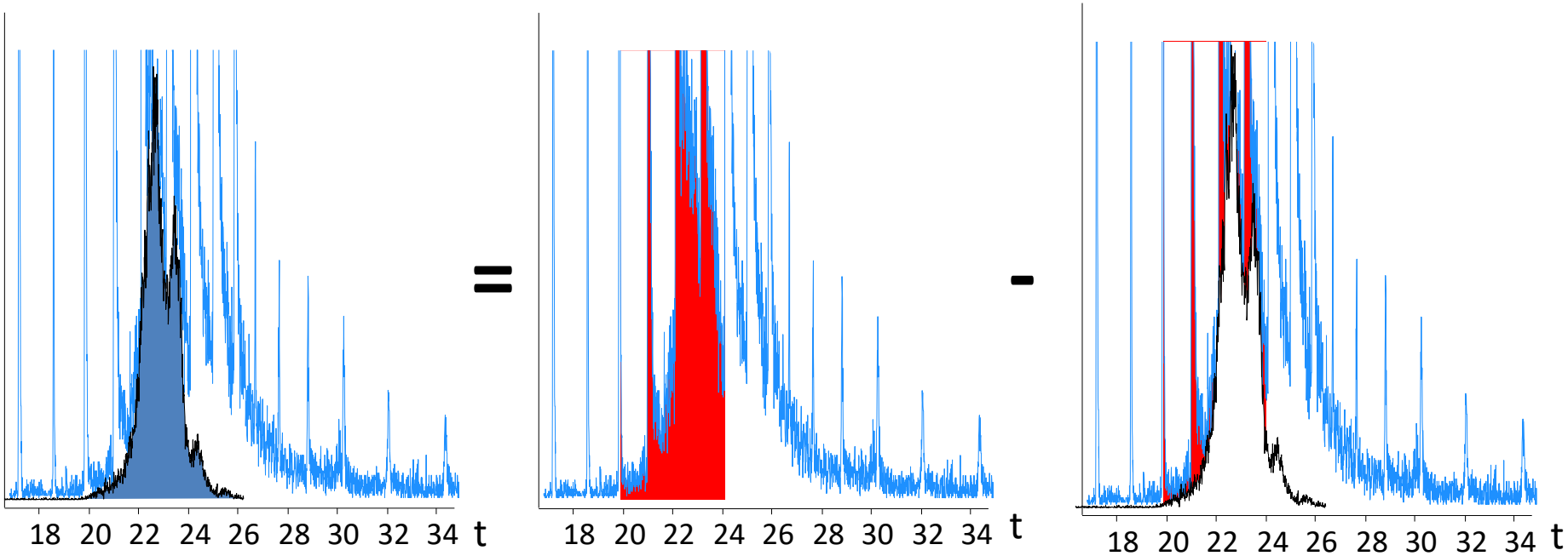
- Solution: Experience!
- +1 chlorine atom ≈ +x minutes
- Peak width very similar for each homolog group (gets broader with more chlorine atoms)

➢ Comparison of elution ranges and peak width helps identify „true“ Cl_4 (and Cl_5) homologs



CP quantification – matrix effects

- Overlap with matrix/other substances possible
- Solution: integrate shared area and subtract onset peaks



CP quantification – final touches

- Final homolog patterns should be close to **Gaussian curve** for each chain length

Yuan B *et al.* (2017), Environ. Sci. Technol. 51

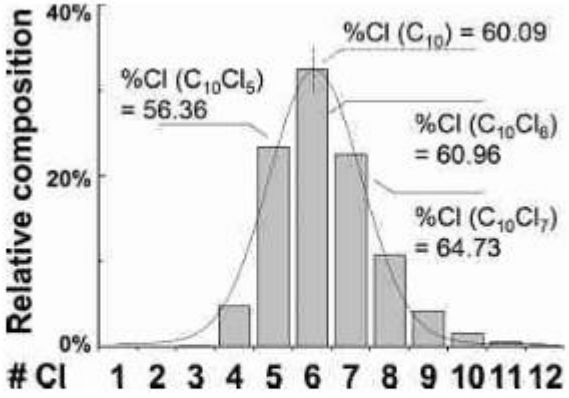
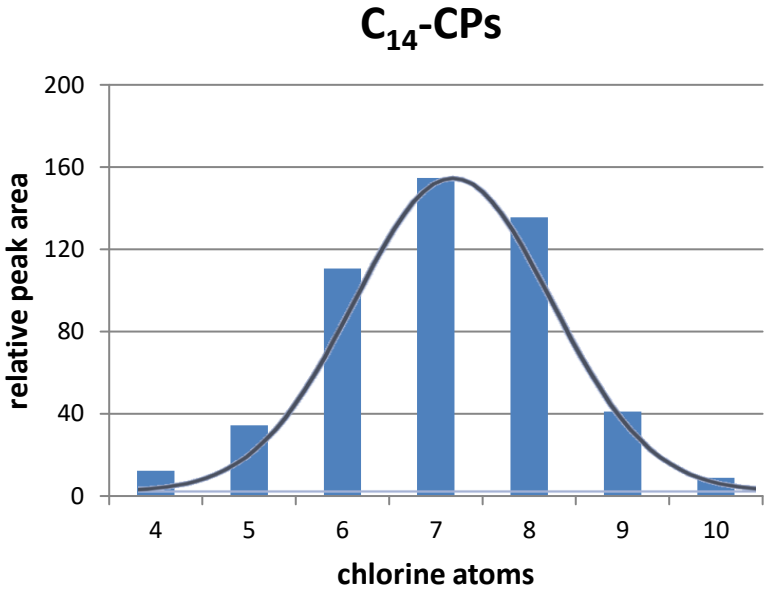


Figure 1. Schematic Gaussian distribution of $C_{10}Cl_m$ in the C_{10} 60.09% Cl reference standard. The curve is the Gaussian peak, the center of which is 60.09%Cl. The columns represent one possible relative composition of each $C_{10}Cl_m$ calculated from the eq 4 setting σ_i of 0.05.

Gao Y *et al.* (2016), Environ. Sci. Technol. 50

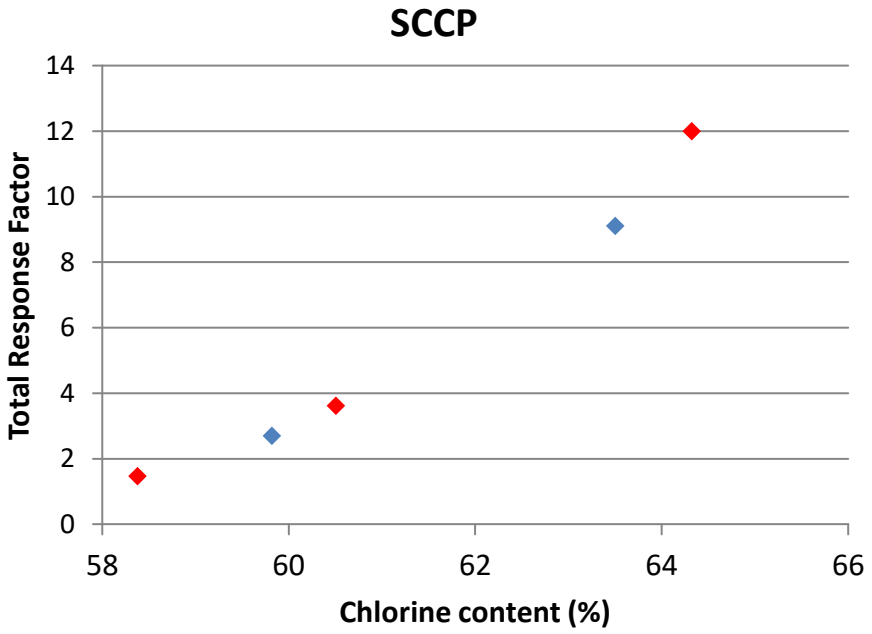
mixture standards (51% Cl and 63% Cl) were 50.0% and 60.9%, respectively. The chlorine distribution on the fixed carbon chain is nearly conformed to a Gaussian curve (Figure S6).

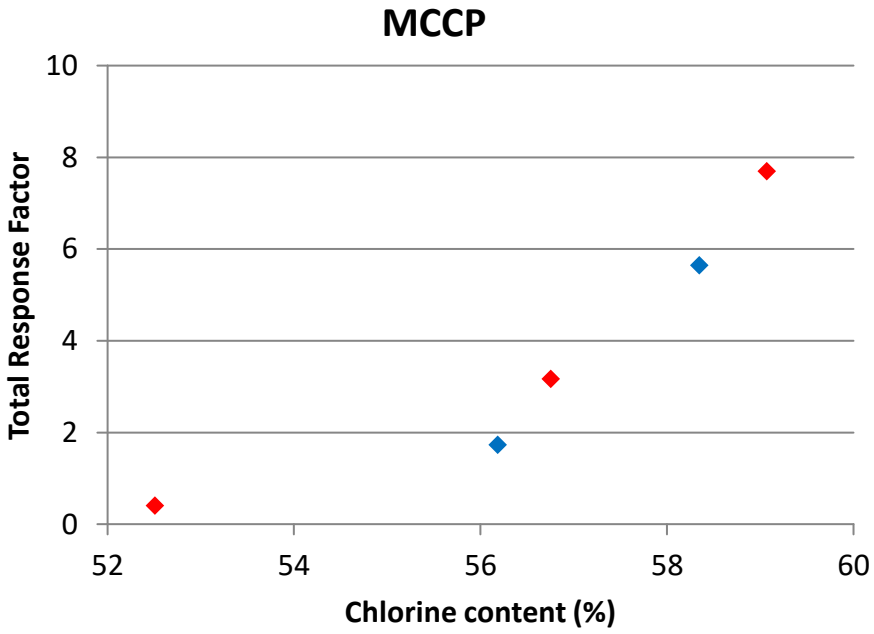


Quantification via linear regression - Principle

- Total Response Factor (TRF) = ∑SCCP/MCCP homolog group areas/concentration
- **Linear regression:** TRF over **chlorine content**[1]
- Commercial mix standards, 1+1 mixtures:

SCCP	51.5%	53.5%	55.5%	59.3%	63% Cl
MCCP	42%	47%	52%	54.5%	57% Cl





[1] Reth M *et al.* (2005), J. Chromatogr. A 1081

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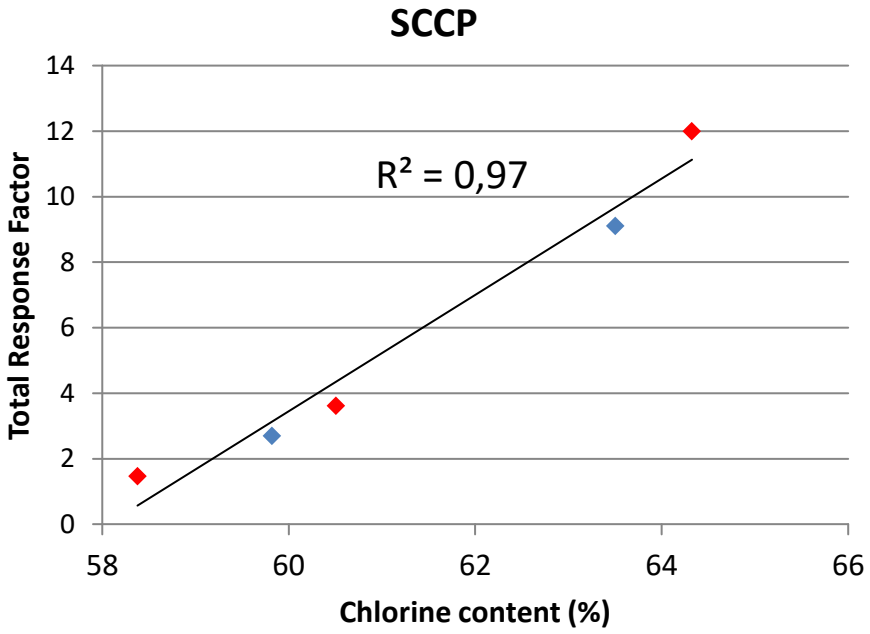
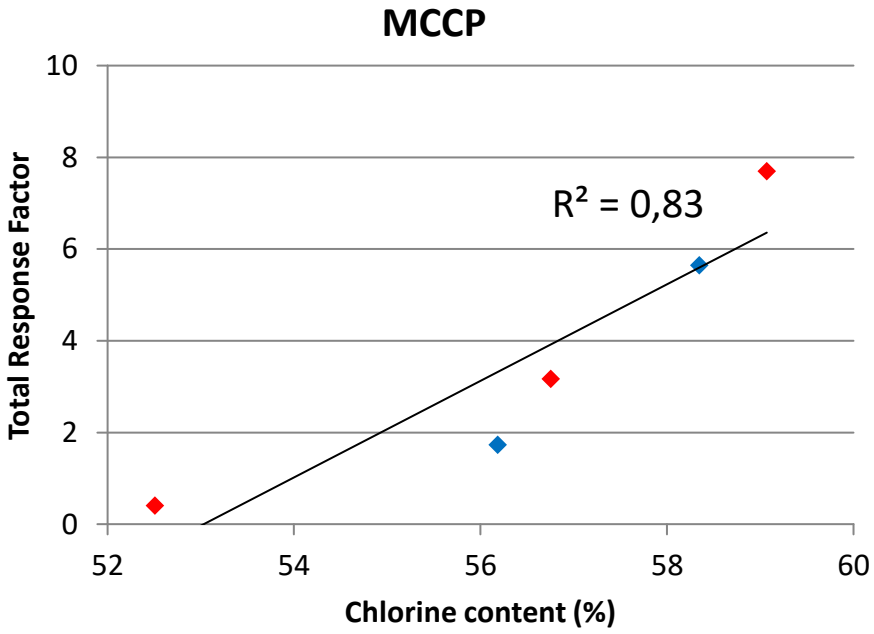




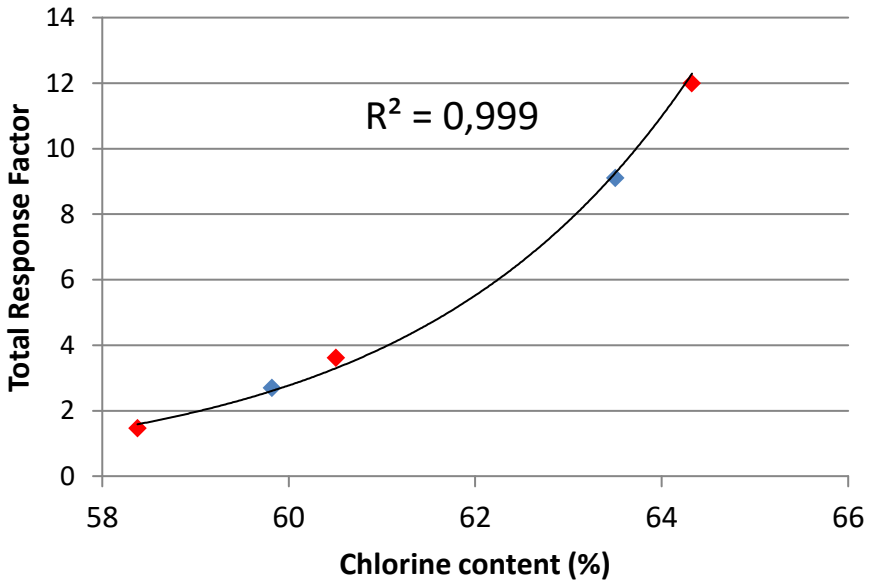
[1] Reth M *et al.* (2005), J. Chromatogr. A 1081

Quantification via exponential regression

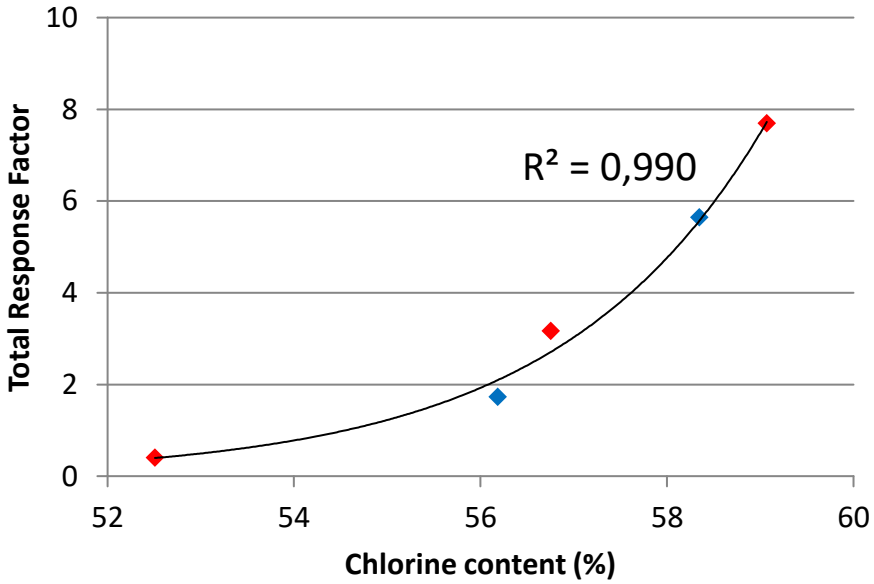
- **exponential calibration curve** → much better fitting[1]
- ILC deviations:

	exponential
SCCPs	25%
MCCPs	4%
SCCP/MCCP mixture	15%/28%

SCCP



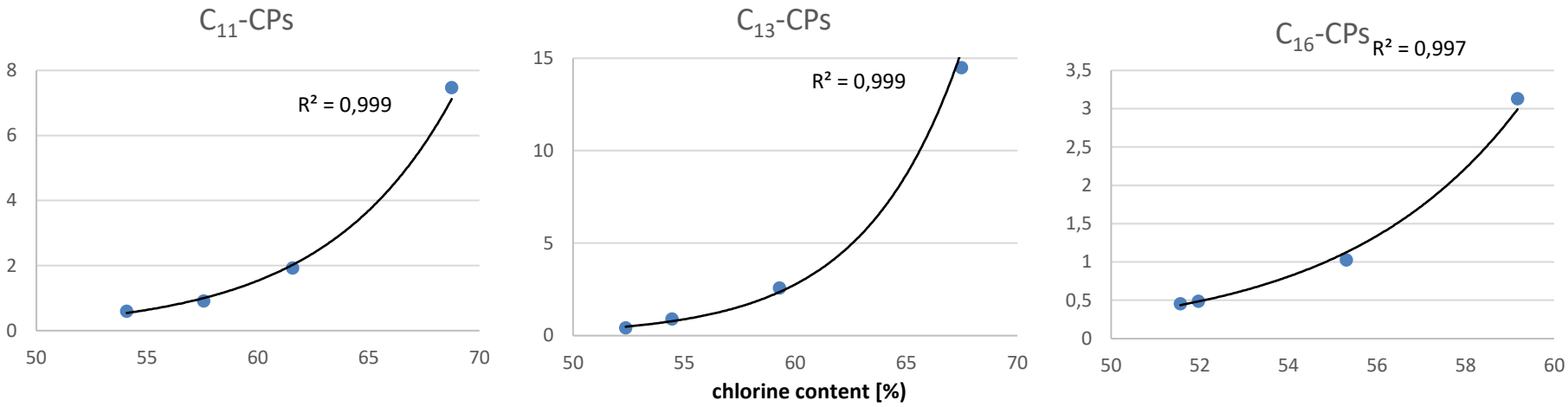
MCCP



[1] Sprengel J, Vetter W. (2019), Rapid Commun. Mass Spectrom. 33

Quantification of single chain CPs

- use of **single chain CP standards** instead of SCCP/MCCP mixtures[1]



- **precise quantification** of single chain CPs (ILC deviations)**:**

	exponential	**single chain exponential**
SCCPs	25%	**2%**
MCCPs	4%	**3%**
SCCP/MCCP mixture	15%/28%	**9%/16%**

Quantification of single chain CPs

- each homolog group has its own response[1]
- matrix of homolog group specific **response factors (iterative)**
  - ➢ apply before TRF calculation[2]
- determination of **chlorine content** (max. 2 % off)
- different for each setup:

Meziere M *et al.* (2020), J. Am. Soc. Mass Spectrom, 31

Table S5. Correction factors for CP homologues analyzed using GC/ECNI-MS.

C_xCl...	Correction factors for polychlorinated terphenyls [1]	Proposed correction factors for SCCPs/MCCPs
4	10	-
5	6/5	15
6	6/6	7/3
7	6/7	4/7
8	6/8	3/8
9		3/9
10		3/10
11		3/11
12		3/12

[1] N. Rosenfelder, W. Vetter. Polychlorinated terphenyl patterns and levels in selected marine mammals and a river fish from different continents. *Environ. Int.* 2014, 62, 119-124.

[1] Yuan B *et al.*(2017), Environ. Sci. Technol. 51
[2] Sprengel J, Vetter W. (2021), Environ. Monit. Assess. 193

CP quantification via GC/ECNI-LRMS - Conclusion

- GC/ECNI-LRMS allows for precise and robust quantification of SCCPs and MCCPs
- **single chain specific quantification** and determination of chlorine content possible
- Need for:
  - **experienced** analyst
  - adequate **standards** (certified mixtures, single chains)
  - rigorous **quality assurance**
- **Know your setup, stay creative**

Thank you for your attention.