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Evolution of chlorinated paraffin and olefin fingerprints in sewage sludge from 1993 to 2020 of a Swiss municipal wastewater treatment plant

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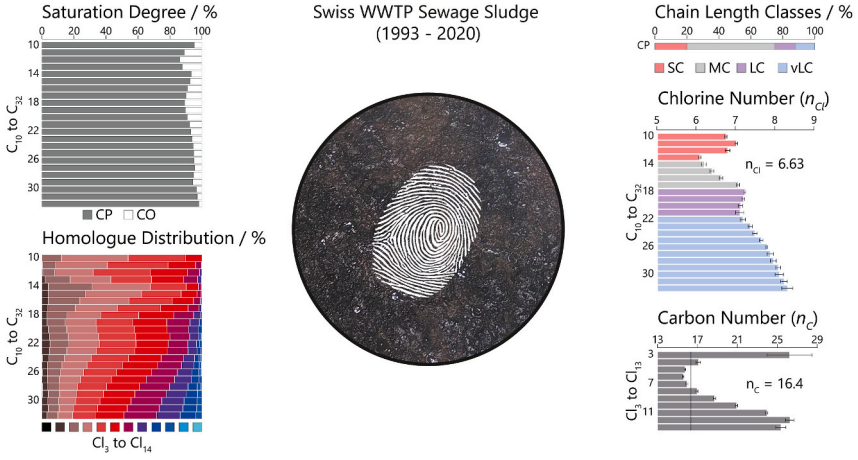
HIGHLIGHTS

- Up to 23000 CP and CO ions were searched for in sludge mass spectra with RASER.
- Sewage sludge from a municipal WWTP contained up to 240 CP homologues.
- About 200 CO homologues were also found in these sewage sludge samples.
- Levels of short-chain CPs and COs decreased by ~84% from 1993 to 2020.
- Medium- and long-chain CPs and COs also decreased by 60–70% in three decades.

GRAPHICAL ABSTRACT



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ABSTRACT

Exposure of humans to chlorinated paraffins (CPs) and chlorinated olefins (COs) can occur via contact with CP-containing plastic materials. Such plastic materials can contain short-chain CPs (SCCPs), which are regulated as persistent organic pollutants (POPs) under the Stockholm Convention since 2017. Municipal wastewater treatment plants (WWTP) collect effluents of thousands of households and their sludge is a marker for CP exposure. We investigated digested sewage sludge collected in the years 1993, 2002, 2007, 2012, and 2020 from a Swiss

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Fingerprinting
Orbitrap mass spectrometry
RASER (R-based automated spectra evaluation routine)

WWTP serving between 20000 and 23000 inhabitants. A liquid chromatography mass spectrometry (R > 100000) method, in combination with an atmospheric pressure chemical ionization source (LC-APCI-MS), was used to detect mass spectra of CPs and olefinic side products. A R-based automated spectra evaluation routine (RASER) was applied to search for ~23000 ions whereof ~6000 ions could be assigned to CPs, chlorinated mono- (COs), di- (CdiOs) and tri-olefins (CtriOs). Up to 230 CP-, 120 CO-, 50 CdiO- and 20 CtriO-homologues could be identified in sludge. Characteristic fingerprints were deduced describing C- and Cl-homologue distributions, chlorine- (n_{Cl}) and carbon- (n_C) numbers of CPs and COs. In addition, proportions of saturated and unsaturated material were determined together with proportions of different chain length classes including short- (SC), medium- (MC), long- (LC) and very long-chain (vLC) material. A substantial reduction of SCCPs of 84% was observed from 1993 to 2020. Respective levels of MCCPs, LCCPs and vLCCPs decreased by 61, 69 and 58%. These trends confirm that banned SCCPs and non-regulated CPs are present in WWTP sludge and higher-chlorinated SCCPs were replaced by lower chlorinated MCCPs. Combining high-resolution mass spectrometry with a selective and fast data evaluation method can produce characteristic fingerprints of sewage sludge describing the long-term trends in a WWTP catchment area.

1. Introduction

The industrial production of technical chloroparaffins increased to over 1 Mt/y (Glüge et al., 2016). Meanwhile, the production and use of short-chain CPs (SCCPs, C_{10}–C_{13}) have been regulated under the Stockholm Convention (UNEP, 2017). Despite the regulation in 2017, it is estimated that still around 0.4 Mt/y of SCCPs were produced and applied in 2020 (Chen et al., 2022). Legal actions on SCCPs have been implemented already before 2017. For example, the EU and Switzerland limited SCCP concentrations in consumer products to 1% (w/w) in 2002 (Bogdal et al., 2017). The limit was further reduced to 0.15% (w/w) in the year 2015. These regulations induced a shift to utilize CPs with longer chains instead of SCCPs (McGrath et al., 2021).

Another consequence of this shift is that analytical challenges further increased. The following topics have to be tackled analytically, (i) complex CP mixtures with chain lengths varying from C_9- up to C_{34}-homologues, named hereafter as C-homologues, (ii) mixtures with different chlorination degrees with chlorine numbers (n_{Cl}) ranging from Cl_3- to Cl_{20}-homologues, herein named as Cl-homologues, and (iii) mixtures containing a variety of unsaturated compounds, which can be distinguished from CPs based on their saturation degree (Schinkel et al., 2017; Yuan et al., 2019; Knobloch et al., 2022b). Unsaturated materials such as chlorinated olefins (COs), diolefins (CdiOs) and triolefins (CtriOs) have been detected in thermally exposed CP materials (Schinkel et al., 2017). If CPs were exposed to hot metal surfaces, e.g. in metal work, COs and CdiOs do form (Schinkel et al., 2018b). Even an enzyme-catalysed formation of COs from precursor CPs has been observed (Heeb et al., 2019). Recently, it was shown that CP-containing plastic also contains olefinic side products (Knobloch et al., 2022a; Mendo Diaz et al., 2023).

A consequence of this chemical diversity is that mass spectra of CPs can contain ten thousands of ions of hundreds of C- and Cl-homologues of CPs and unsaturated transformation products. CPs and olefinic material appear in a mass-to-charge (m/z) range of 300–1000. Based on the number of homologues expected, we estimated that about 23000 ions may exist in this mass range, on average, about 50 ions per mass unit (u, Da). In other words, mass spectrometers with a resolving power of ~100000 are highly recommended to be able to read out non- or minimal interfered m/z data from such complex mass spectra. Data processing of this large collection of ions can only be achieved in a time-efficient manner using automatic evaluation routines. We applied an elsewhere presented R-based automated spectra evaluation routine (RASER), which is suitable to read out CP and CO data from such mass spectra (Knobloch et al., 2022a).

RASER has been used to process mass spectra of CP-containing household plastic, electronic cables and consumer products (Mendo Diaz et al., 2023). Such data can be further processed to obtain characteristic fingerprints of CPs and as recently shown for polyfluoroalkyl substances (Joseph et al., 2023). We hypothesize that CPs and COs can be released from such common plastic items during direct contact with humans. CPs may also be discharged from households in other processes, e.g. via effluents reaching wastewater treatment plants (WWTPs), where CPs can partially accumulate in sewage sludge (Zeng et al., 2012; Brandsma et al., 2017; Wang et al., 2019).

It was the aim of this work to investigate patterns of CPs and olefinic materials and describe changes of CP use. We applied RASER for a fast and selective analysis of high-resolution mass spectra of different sewage sludge samples and searched for up to 23000 ions corresponding to about 6000 homologues of CPs and olefinic side products. Furthermore, we deduced characteristic fingerprints for different sewage sludge samples of a Swiss municipal WWTP, covering a time period of about three decades (1993–2020).

2. Experimental

2.1. Chemicals

Dichloromethane (DCM), *n*-hexane, methanol (MeOH) and acetone from Biosolve (Valkenswaard, Netherlands) and deionised water (Milli-Q Reference A+, 18.2 MΩcm) were used as solvents for sample preparation and clean-up. Silica gel 60 (70–230 mesh, 63–200 μm, Merck, Darmstadt, Germany), copper (>230 mesh, <63 μm, Merck) and sodium sulphate (Merck) were used for sample treatment and chromatography. Isotopically labelled 1,5,5,6,6,10-hexachlorodecane ($^{13}C_{10}H_{16}Cl_6$, HCD, Cambridge Isotope Laboratories, Tewksbury, MA, USA) was used as internal Standard (IS).

2.2. Sampling of sewage sludge and extraction

In 1993, 2002, 2007, 2012 and 2020 samples of stabilized, digested sewage sludge (anaerobic, 35 °C) were collected from a Swiss WWTP in the greater Zurich area (Zennegg et al., 2013). The catchment area comprised ~20000 inhabitants in 1993 and ~23000 in 2020. Dewatered sewage sludge samples were collected in brown-glass flasks. Around 2 L of sludge were centrifuged for 30 min at 18 °C at 6000 rounds-per-minutes (HiCen XL, Herolab GmbH, Wiesloch, Germany). The residues were transferred into pre-cleaned aluminium recipients and further dried at room temperature for 2 weeks (covered by an aluminium foil). Dried sludge samples were ground in a vibrating cup mill (PULVERISETTE 9, Fritsch, Idar-Oberstein, Germany) for about 1 min. The ground samples were stored at room temperature in the dark. Aliquots (25 g) of ground samples were extracted with a mixture of hexane/acetone (1:1, *v:v*) in a Soxhlet apparatus for 8 h. Extracts were concentrated to 250 mL and further processed.

2.3. Sample preparation

Aliquots (10 mL) were concentrated to dryness together with ^{13}C-labelled hexachlorodecane ($^{13}C_{10}Cl_6H_{16}$, 60 ng) as internal standard. The residues were transferred with hexane (100 μL) onto multilayer

silica gel columns (SiO_2). Respective LC columns were prepared in advance with cleaned cotton wool, activated silica (1.7 g), acidic silica (2.8 g, 40% sulphuric acid) and sodium sulphate on top (Carro et al., 2018; Heeb et al., 2020). Prior to usage, silica was heated to 450 °C over night. Columns were rinsed with DCM and preconditioned with hexane. Samples were transferred to silica columns and fractions were prepared by eluting with hexane (Fr1, 10 mL) and DCM/hexane (Fr2, 1:1, *v:v*, 15 mL). It has been shown that a fractionation of CPs on silica does not induce a formation of COs under the applied chromatographic conditions (Knobloch et al., 2022b). However, we could show that olefinic material is eluting slightly slower from silica than CPs and can be enriched in late-eluting fractions. CP-containing fractions (Fr2) were further concentrated by a nitrogen stream at 30 °C. Interfering sulphur compounds were removed by adding activated copper particles in hexane until a black colour appeared (Iozza et al., 2008). After desulphurization, copper residues were removed by filtering through cleaned cotton wool and rinsed with DCM. The filtrates were concentrated (nitrogen stream) and transferred into vials with MeOH (200 µL).

2.4. Liquid chromatography - mass spectrometric analysis

A liquid chromatographic system (Dionex, Ultimate 3000, Thermo Fisher, Waltham, MA, USA) with a C_{18}-reversed-phase column (Zorbax SB C_{18}-RRHD, 1.8 µm, 3 mm × 50 mm, Agilent, Santa Clara, CA, USA) was used as injector and separation compartment. The injection volume was 6 µL and the eluents used were water (A) and a mixture of MeOH and DCM (B, 9:1, *v:v*) with a flow rate of 0.4 mL min^{-1}. A solvent gradient was applied starting at 40% of B for 1 min with a linear increase to 98% of B during 15 min, holding it for 7 min. An atmospheric pressure chemical ionization (APCI) source (Ion MAX API, Thermo Fisher) was used. Mass spectrometric analysis was performed with an Orbitrap mass analyser (Q Exactive, Thermo Fisher) operating in full scan mode in a *m/z* range of 80–1000 at 12 Hz scanning rate and a resolving power of 140000 at m/z 200. Samples were measured twice (n = 2).

2.5. Data processing

CPs and their transformation products have eluted in a time range of 7 to 21 min. Two subtractions with background from 5 to 6 and 22 to 23 min were achieved electronically (FreeStyle™ 1.5, Thermo Fisher, v1.5.93.34). The mass spectra evaluation was done by RASER (Knobloch et al., 2022a). This method allows pattern recognition of selected isotopologues. C-homologues from C_9 to C_{34} and Cl-homologues from Cl_2 up to Cl_{19} were searched for. The expected ion clusters were calculated with the enviPat isotope pattern calculator (v2.6) with an uncertainty in intensity of 10% and a mass accuracy of 0.2% (Loos et al., 2015). The detected peaks were corrected with their respective simulated relative abundance. The heights of the three most abundant isotopologue peaks were averaged and presented as $I_{100\%}$-signal of the respective homologue in counts (cts.). Normalised $I_{100\%}$-signals of CPs and COs given in Supplementary data (SD, Tables S1–S5) were used to deduce fingerprints of each sample.

2.6. Quality assurance

All glassware used were pre-cleaned with DCM. Procedure blanks were prepared with hexane/acetone (1:1, *v:v*, 10 mL) and treated as samples during clean-up. Detected total signal sums of the procedure blanks were around 1.2% and 0.2% for CPs and COs, respectively compared to sludge samples. Mean values (n = 2) of the procedure blanks are reported as SD (Table S2). Labelled ^{13}C-1,5,5,6,6,10-hexachlorodecane was used as internal standard. Samples containing only IS were measured within the sample sequence. Respective signals were used to calculate IS-recovery rates. The $I_{100\%}$-signals of the IS over all samples are given as SD (Table S1). The mean recovery was 89.7 ± 43.6%. All $I_{100\%}$-signals (Tables S1–S5) were corrected for IS signals and used for further data analysis.

3. Results and discussion

3.1. Fast and selective evaluation of complex mass spectra by RASER

With RASER up to 5851 ions of a sewage sludge mass spectrum could be assigned to 439 homologues of CPs and olefinic transformation products (Fig. 1A). The sludge was taken in 2012 from a municipal WWTP in Switzerland serving about 20000 inhabitants. The high-resolution spectrum (R > 100000) is obtained with an LC-APCI-Orbitrap-MS method, which favours the formation of chloride adduct ions $[M+Cl]^-$ for CPs and their unsaturated transformation products (Zencak et al., 2003; Schinkel et al., 2018a). In an *m/z* range of 300–1000 about 23000 ions were searched for with RASER, corresponding to about 1500 C- and Cl-homologues. The assigned ions correspond to 237 CP-, 124 CO-, 50 CdiO- and 28 CtriO-homologues (Fig. 1).

Fig. 1 also displays reconstructed mass spectra (RMS) for the detected CPs (B), COs (C), CdiOs (D) and CtriOs (E). We specifically searched for C_9- to C_{34}- (n = 26) and for Cl_3- to Cl_{19}- (x = 17) homologues (n · x = 442) for four classes of compounds. Fig. S1 displays zooms (x5000) of measured and reconstructed mass spectra of the sewage sludge from 1993 indicating the presence of mono-, di-, and tri-olefinic material next to paraffins, which dominate the spectrum. Differences between measured and simulated signal intensities were <5% and <20% for CPs and COs, respectively.

The evaluation of such a spectrum can be achieved with RASER in about 3 h. The zoom factors indicate that signal intensities of COs, CdiOs and CtriOs are 9-, 43- and 184-times smaller than the most intense CP-signal (Fig. 1). Concentrations of COs in sewage sludge are about one order of magnitude lower than those of CPs, whereas CdiOs and CtriOs contributed to <2.4% and <0.6%, respectively. RMS of CPs (Fig. 1B) and COs (Fig. 1C) are similar suggesting that respective homologue distributions are similar too. However, RMS of CdiOs (Fig. 1D) and CtriOs (Fig. 1E) do show some differences.

In total, RASER was able to assign 433 CP-, CO-, CdiO-, and CtriO-homologues in the 2012 sludge sample. CPs and olefinic transformation products were also found in all other sewage sludge samples.

3.2. Evolution of CP- and CO-homologue distributions in sewage sludge from 1993 to 2020

CPs and COs are abundant in the sludge samples of all years, whereas proportions of CdiOs and CtriOs were only <3% and <1%, respectively (Fig. 1). CP- and CO-homologue distributions of sewage sludge collected in 1993, 2007 and 2020 are displayed in Fig. 2. Homologue distributions of the years of 2002 and 2012 are given in SD (Fig. S2). Respective data for all sludge samples are listed in SD (Tables S3–S7). In total 199 to 237 CP-homologues and 89 to 126 CO-homologues were detected. Mainly C_9- to C_{34}- (n = 26) and Cl_3- to Cl_{14}-homologues (x = 12) were found for CPs and C_{10}- to C_{32}- (n = 23) and Cl_3- to Cl_{10}-homologues (x = 8) were detected for COs.

In the sludge collected in 1993, the CP-homologue distribution is trimodal with respect to C- and unimodal with respect to Cl-homologues. Maxima were observed for C_{12}-, C_{15}- and C_{24}- CPs with the $C_{15}Cl_6$-CPs as most abundant homologues (MAH). From the trimodal distribution of the C-homologues one could assume that at least three different CP-mixtures have been used in the past. The C-homologue distributions over the years seem to get more uniform. This could indicate that fewer sources contributed to the overall CP-burden in more recent years. In 2020, the CP-distribution was unimodal with $C_{14}Cl_6$-CPs as MAH.

It has been reported that COs are transformation products of CPs, which can form when CPs are exposed to heat and hot surfaces for example during metal work (Schinkel et al., 2018b; Heeb et al., 2019). CO-proportions varied from 7.4% to 9.5% with respect to CPs. This

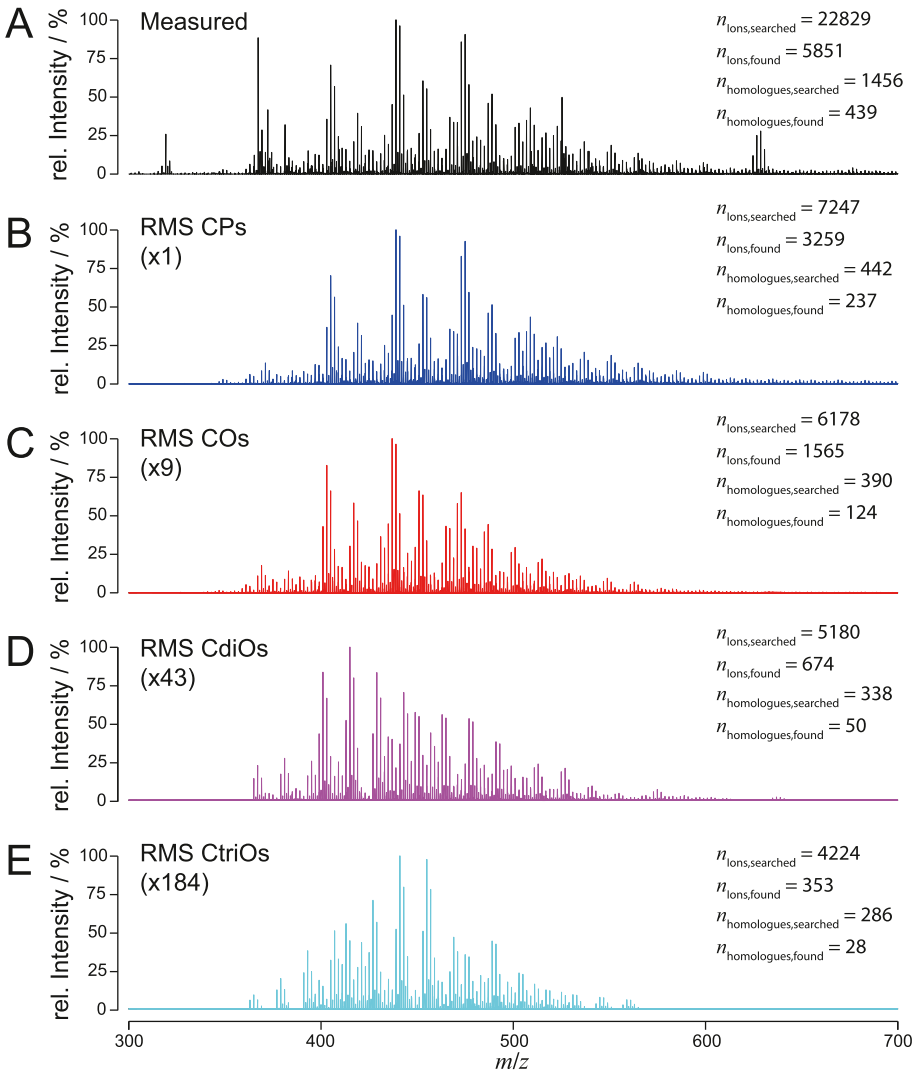

Fig. 1. Measured and reconstructed mass spectra (RMS) of a 2012 sewage sludge from a Swiss municipal WWTP. Compared are measured (A) and reconstructed spectra of CPs (B), COs (C), CdiOs (D) and CtriOs (E). Chloride adduct ions $[M+Cl]^-$ are formed under the given LC-APCI-Orbitrap-MS conditions. Respective data were evaluated by RASER. Zoom factors (x) in relation to the most abundant CP homologue are indicated together with numbers of searched and found ions and homologues.

corresponds to zoom factors (x) of 11 to 14 (Fig. 2). In all cases, the MAHs of CPs and COs were identical, $C_{15}Cl_6$-homologues were dominating in 1993, whereas $C_{14}Cl_6$-homologues were most abundant afterwards.

In summary, large numbers of different CP- and CO-homologues were detected in all sewage sludge samples. MCCPs and MCCOs were always the most abundant homologue classes. As mentioned, olefinic material was present in all sludge samples, showing that these compounds possibly are released together with CPs.

3.3. Variation of saturation degrees and Cl-homologue distributions

The proportions of CPs and COs of different C-homologues (C_{10}–C_{32}) are shown for sewage sludges from 1993, 2007 and 2020 (Fig. 3A). Plots of the years 2002 and 2012 and data corresponding to all the years are given in SD (Fig. S3 and Tables S8). In general, CO-proportions were low in sewage sludge, varying from 0 to 16%. CO-proportions increased from 5% for C_{10}- to 10% for C_{20}-homologues and decrease again to 6% for C_{26}-homologues. A local maximum of 16% was observed for C_{12}–COs in sludge collected in 1993, which decreased in more recent years to 8%.

Fig. 3 also depicts colour-coded Cl-homologue distributions of CPs (B) and COs (C) in sewage sludge from 1993, 2007 and 2020. In all sludge samples, Cl_4- (grey) to Cl_8- (red) homologues are abundant both for CPs and COs. COs were in general lower chlorinated than CPs and do not contain higher-chlorinated homologues ($Cl_{>10}$). Long- and very long-chain CPs ($C_{>17}$) contain relevant proportions of Cl_9- to Cl_{12}-homologues (up to 45%). The lower chlorination degree of COs compared to CPs is an indication that abiotic and biotic dehydrochlorination reactions (HCl loss) may be involved. Such transformation reactions which convert CPs to COs have been observed previously (Heeb et al., 2019; Schinkel et al., 2018b).

Overall, a broad range of different Cl-homologues both for CPs and COs can be found in sewage sludge from 1993 to 2020. The Cl-homologue distributions changed slightly during the three decades. Most remarkable changes were observed for short- and medium-chain homologues. This indicates that a replacement of SCCPs by MCCPs has already started in the '90s. COs are about one order of magnitude less abundant in sewage sludge than CPs. This contrasts with findings from various consumer plastic samples (Knobloch et al., 2022a; Mendo Diaz et al., 2023), where CO proportions were higher (up to 41%) and typically highest for long-chain homologues ($C_{>17}$). This could indicate that COs are converted faster than CPs under the conditions in a WWTP,

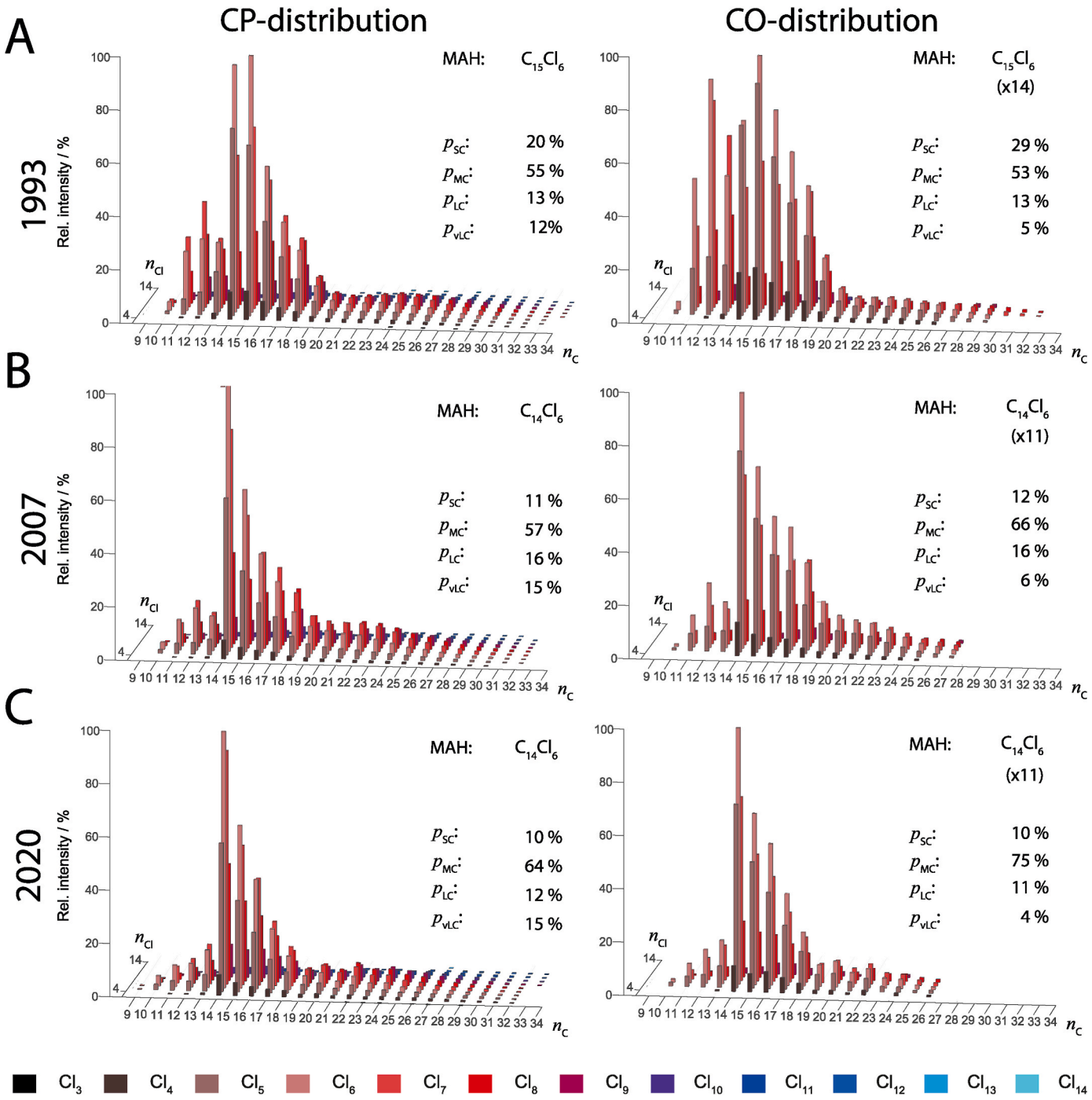

Fig. 2. CP- (left) and CO-homologue (right) distributions of sewage sludge of a municipal WWTP from 1993 (A), 2007 (B) and 2020 (C). Different Cl-homologues are distinguished according to the given colour code. Most abundant homologues (MAH, 100%) and zoom factors (x) for COs in relation to respective MAH of the CPs are indicated. In addition, proportions (*p*) of short- (C_{10}–C_{13}), medium- (C_{14}–C_{17}), long- (C_{18}–C_{21}) and very long-chain ($C_{\geq 22}$) CPs and COs are given.

which include stages with anaerobic and aerobic digestion.

3.4. Chlorine- and carbon-number trends

Weighted chlorine numbers (n_{Cl}) of different C-homologues for CPs (A) and COs (B) of sewage sludge collected in 1993, 2007 and 2020 are reported (Fig. 4). Respective data and the ones for 2002 and 2012 are given in SD (Fig. S4 and Tables S9–S12).

CP chlorine numbers of 6.63, 6.64, 6.77, 6.82, and 6.80 were found in sludge from 1993, 2002, 2007, 2012 and 2020, respectively. The ones for COs were 6.22, 6.23, 6.17, 6.26 and 6.21. Thus, CPs in general are higher chlorinated than COs. Chlorine numbers of CPs increased slightly during the last three decades, while those of COs remained rather constant.

In general, chlorine numbers of different CP-homologues increase with carbon-chain length from ~6 (C_{10}) to ~8 (C_{32}). Overall, these trends are stable for all samples but some variations of n_{Cl} are observed mainly for SCCPs (red) and MCCPs (grey). Mean SCCP chlorine numbers decreased from 6.84 (1993) to 6.58 (2007) to 6.53 (2020), indicating that SCCP-material with higher chlorination degree was used in the '90s and replaced later with lower chlorinated material. A second n_{Cl}-maximum is observed for LCCPs (violet) in 1993 and 2007 sludge, most

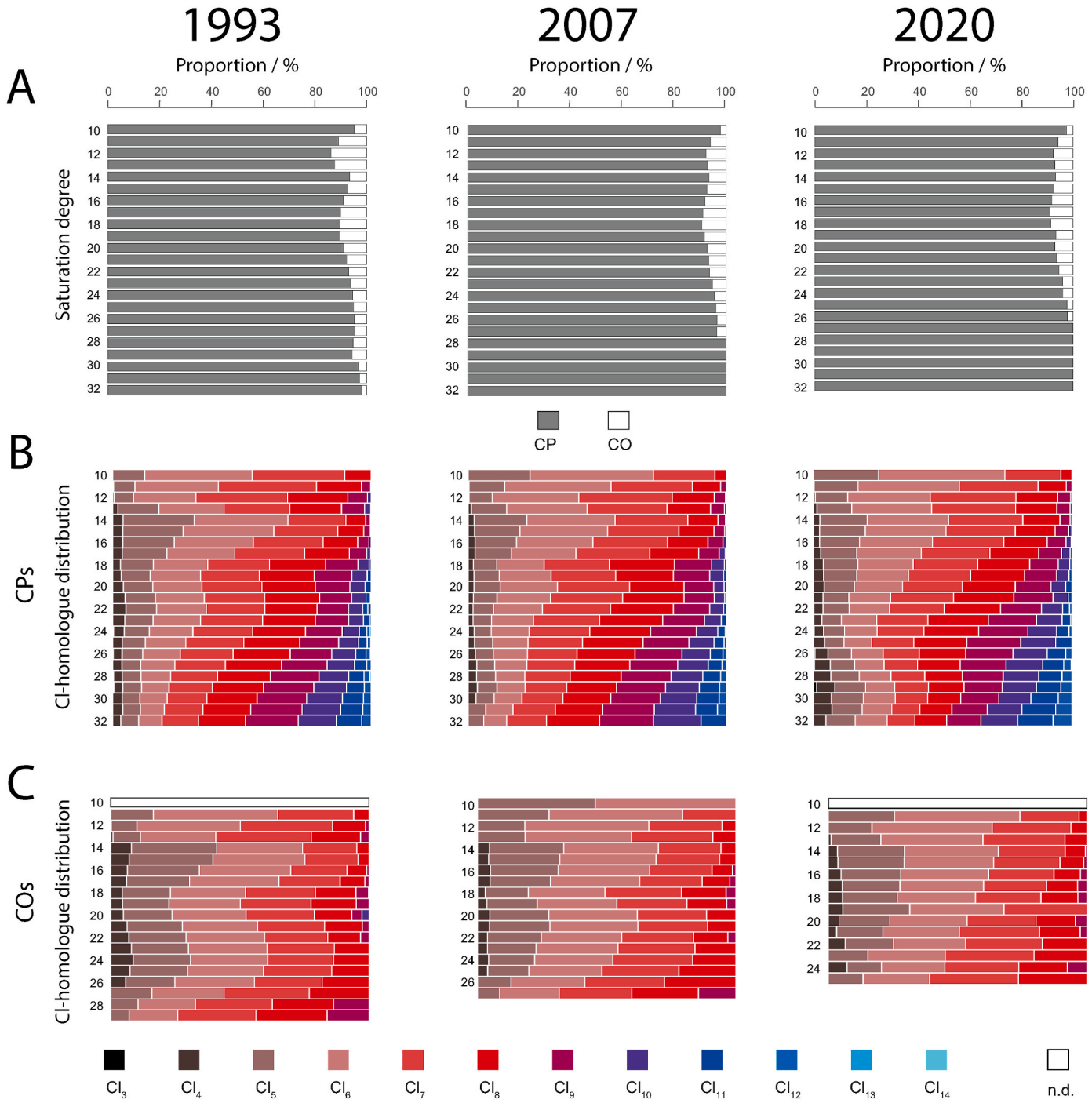

Fig. 3. CP- and CO-proportions and Cl-homologue distributions in sewage sludge of a municipal WWTP collected in 1993, 2007 and 2020. Proportions of CPs (grey) and COs (white) are distinguished for different C-homologues (A). Different Cl-homologues for CPs (B) and COs (C) are distinguished according to the given colour code.

pronounced for C_{18}-homologues both for CPs and COs (Fig. 4A and B).

Weighted carbon numbers (n_C) for different Cl-homologues show U-shaped plots both for CPs and COs (Fig. 4C and D). High carbon numbers are found for Cl_3- and for Cl_{10}-, Cl_{11}- and Cl_{12}-homologues. Lowest carbon numbers were observed for Cl_6-homologues in all cases. Weighted mean carbon numbers varied from 16.0 to 17.0 for CPs and from 15.6 to 16.4 for COs over the observed time period. No systematic trends could be observed over time, neither for CPs nor for COs.

In summary, chlorine numbers of CPs slightly increased from 1993 to 2020. Those of COs were always lower without systematic trends. Carbon numbers of CPs remained constant. Respective CO carbon numbers were always lower, indicating that longer-chain COs are less abundant in sewage sludge than longer-chain CPs.

3.5. *Time trends of different chain length classes*

Proportions (A) and time trends (B) of different chain length classes are presented in Fig. 5. Distinguished are short- (C_{10}–C_{13}, SC), medium- (C_{14}–C_{17}, MC), long- (C_{18}–C_{21}, LC) and very long-chain ($C_{\geq 22}$, vLC) CPs and COs. Respective data is summarized in SD (Table S13). Medium-chain homologues are most abundant in all sewage sludge samples (Fig. 5A). Proportions of MCCPs varied from 55.0 to 68.6%, those of SC-,

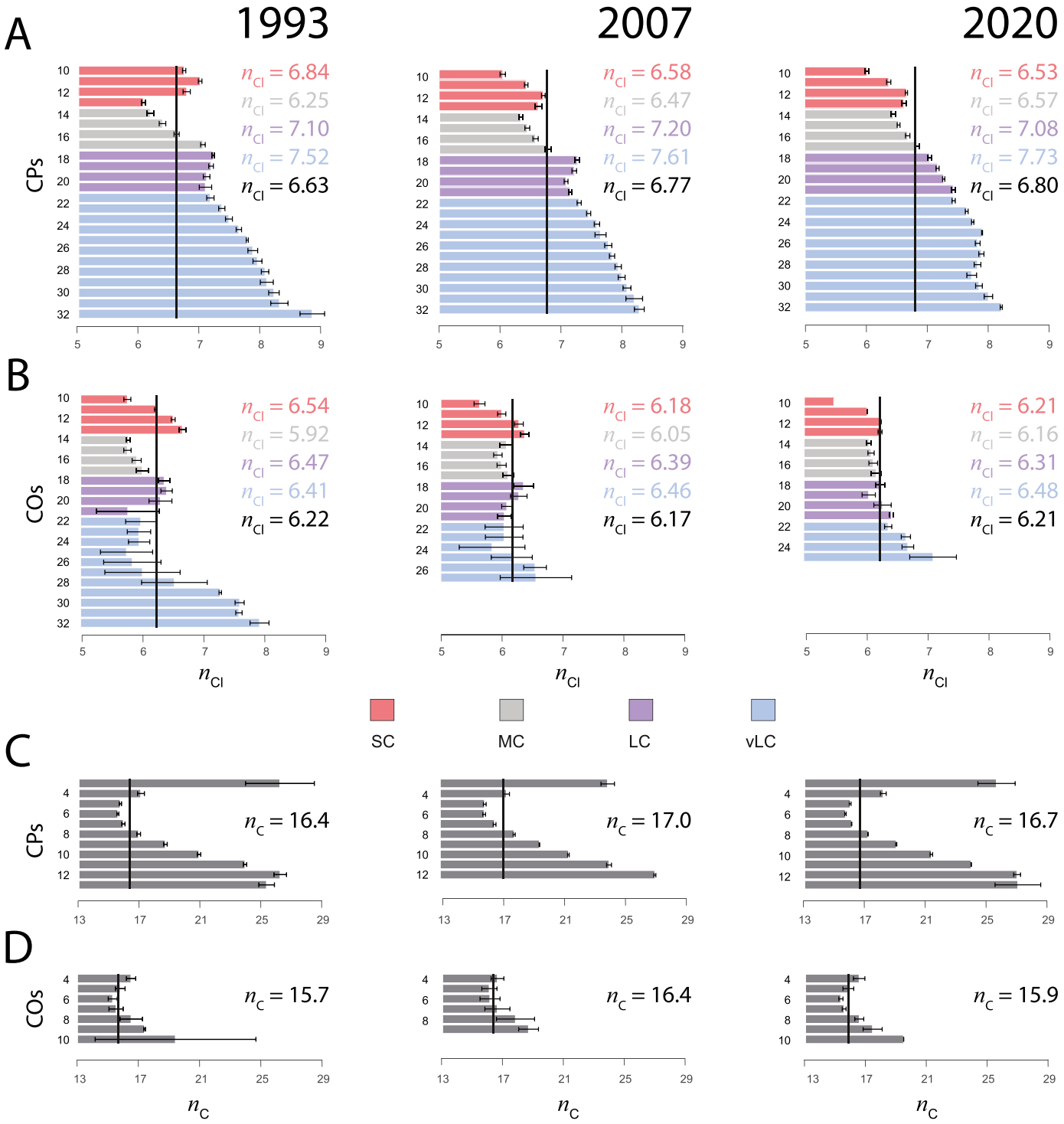

Fig. 4. Weighted chlorine- (n_{Cl}, A and B) and carbon- (n_C, C and D) numbers of CPs and COs in municipal WWTP sewage sludge from 1993, 2007 and 2020. Different C-homologue classes are distinguished according to the given colour code. Weighted mean chlorine- and carbon-numbers of all homologues are indicated (black lines). In addition, chlorine numbers of SC- (red), MC- (grey), LC- (violet) and vLC- (blue) homologue classes are given. Standard deviations (n = 2) are indicated.

LC- and vLCCPs were 9.5–19.9%, 8.6–16.2% and 9.0–15.4%, respectively. SCCP proportions decreased from 19.9% in 1993 to 9.5% in 2020, while proportions of LCCPs and vLCCPs varied to some degree with no systematic trends.

Similar trends can be observed for COs (Fig. 5A). MCCOs are most abundant in all samples, while proportions of SCCO decreased from 29.1% in 1993 to 9.6% in 2020. Accordingly, MCCO-proportions increased from 52.8% in 1993 to 75.3% in 2020. Proportions of LCCOs varied from 7.9 to 16.1%, those of vLCCOs from 3.7 to 6.4%. Altogether, SCCP- and SCCO-proportions decreased over the years, while proportions of MCCPs and MCCOs increased.

Relative signal intensities ($I_{100\%}$) of different CP- and CO-classes are scaled to the maximum levels, which were reached in 1993 for all classes (Fig. 5B). In relation to 1993, levels of all CP- and CO-classes decreased. Levels of SC-, MC-, LC- and vLC-CPs decreased by 84%, 61%, 69% and 58%, respectively, those of COs decreased by 89%, 51%, 61% and 62%. Overall, the reduction of SCCP- and SCCO-levels were most substantial over the three decades and MCCPs and MCCOs remained most abundant

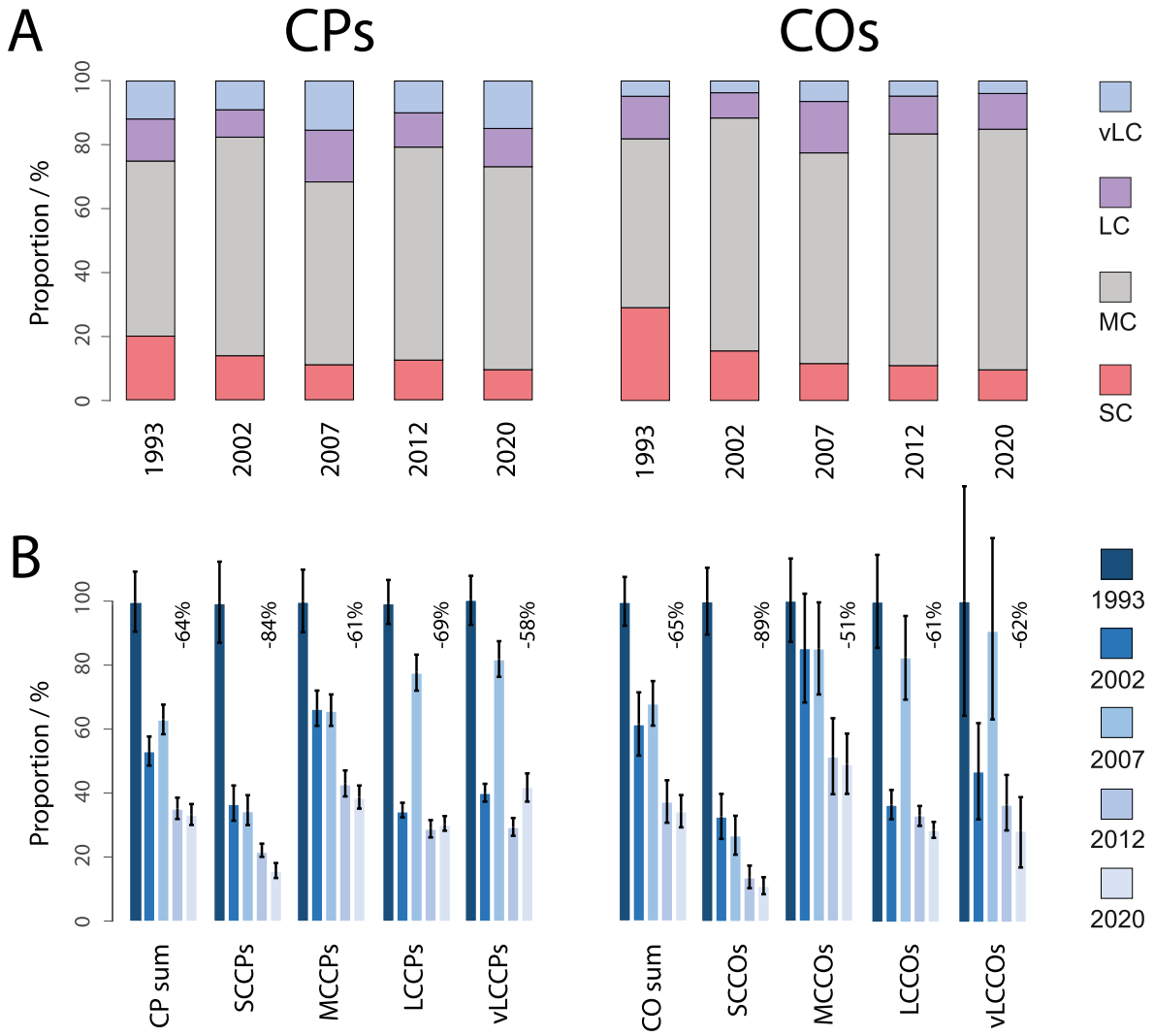

Fig. 5. Proportions (A) and time trends (B) of different CP- and CO- chain length classes in sewage sludge. Proportions of short- (SC, red, C_{10}–C_{13}), medium- (MC, grey, C_{14}–C_{17}), long- (LC, violet, C_{18}–C_{21}) and very long-chain (vLC, blue, $C_{\geq 22}$) CPs and COs are distinguished (A). Time trends of different CP- and CO-chain length classes from 1993 to 2002, 2007, 2012 and 2020 are displayed (B). Intensities of the 1993 sample were used to scale intensities of later years. Standard deviations (n = 2) are indicated together with overall reduction efficiencies.

in sewage sludge for almost 30 years. Therefore, we can report a shift from now regulated SCCPs to not yet regulated MCCPs. Since it is expected that MCCPs will be regulated in the future, we expect that LCCP and vLCCP levels will increase in sewage sludge in the future.

3.6. Comparison of CP/CO-mixing ratios

CPs with the general formula $C_nH_{2n+2-x}Cl_x$ can eliminate HCl under certain conditions to form lower-chlorinated COs with the formula $C_nH_{2n-(x-1)}Cl_{x-1}$ as shown in SD (Fig. S5). Intensity ratios of different CO transformation products and respective precursor CPs are presented in Fig. 6. In general, such ratios were well conserved for sludge samples of different years. CO/CP-ratios varied between 0.02 and 0.25. Ratios of lower-chlorinated homologues such as the Cl_5–CO/Cl_6-CP ratios remain below 0.1, those of higher-chlorinated homologues e.g. the Cl_8–CO/Cl_9-CP ratios reached values up to 0.25.

Highest Cl_5–CO/Cl_6-CP ratios of >0.1 are reached for C_{17}-homologues. Cl_6–CO/Cl_7-CP ratios are highest for C_{17}-homologues too but reach a second maximum for C_{12}-homologues of 0.15. Maxima further increase to 0.20 and 0.25 for C_{12}- and C_{13}-homologues of Cl_7–CO/Cl_8-CP- and Cl_8–CO/Cl_9-CP ratios. Overall CO/CP ratios in sewage sludge were stable over the three decades but depend on both the carbon-chain length and the chlorination degree. With this study, it is not possible to confirm that new CO material is formed from precursor CPs during sewage sludge production.

4. Conclusions

The periodic analysis of archived sewage sludge from WWTPs allows to monitor the exposure of households and inhabitants to POPs such as CPs and to document changes of burdens and the appearance of new products and formulations.

CPs and their olefinic transformation products indeed were found in five sewage sludge samples of a Swiss WWTP covering a time period of three decades. The automated data analysis routine RASER was used to investigate complex high-resolution mass spectra of these samples. About 23000 ions, corresponding to 6000 homologues, were searched for. About 55% of the identified ions were assigned to CPs, 27% to mono-, 11% to di- and 7% to tri-olefinic material, respectively. This corresponds to about 240 CP-, 120 CO-, 50 CdiO- and 30 CtriO-homologues.

Characteristic fingerprints of these sewage sludge samples were deduced after a comprehensive data analysis. This allows to elaborate specific features of these fingerprints describing C- and Cl-homologue

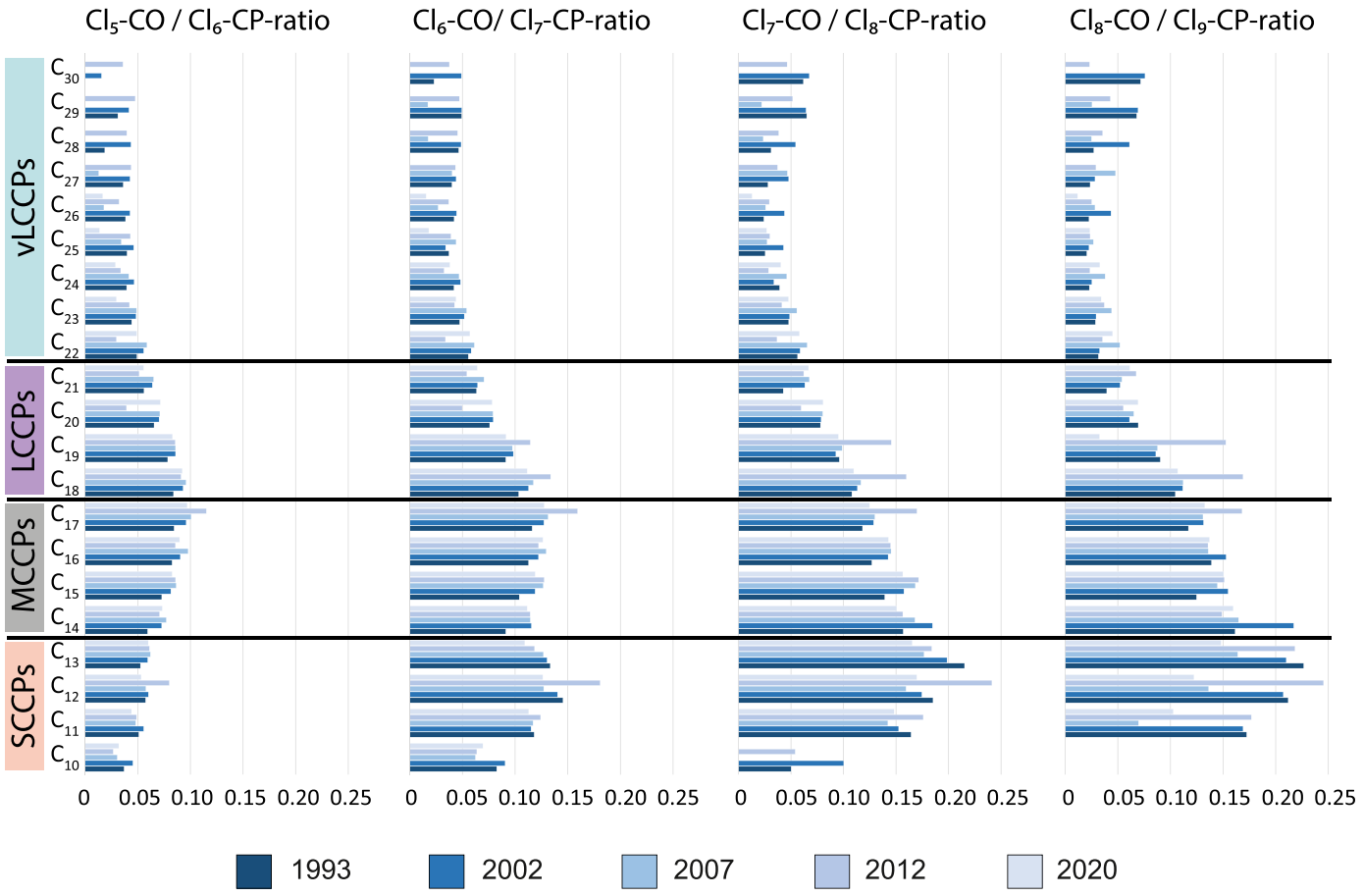

Fig. 6. CO/CP mixing ratios in sewage sludge from 1993 to 2020. Ratios of CO transformation products with the general formula $C_nH_{2n-(x-1)}Cl_{x-1}$ to potential precursor CPs with the formula $C_nH_{2n+2-x}Cl_x$ are calculated based on $I_{100\%}$ signals. Four different product/precursor ratios for different pairs of C-homologues and sampling years are distinguished according to the given colour code.

distributions, Cl-homologue patterns, chlorine- and carbon-numbers as well as saturation degrees. Furthermore, pattern changes and trends for short-, medium-, long- and very long-chain CPs and COs were recorded.

We showed that SCCP and SCCO levels and proportions were highest in 1993. Proportions of short-chain materials steadily decreased until 2020 together with the chlorine numbers. Accordingly, MCCP and MCCO proportions increased. These trends indicate that the exposure with SCCP-containing materials in households and with it the SCCP levels in WWTP sewage sludge could be reduced from 1993 to 2020 by about 80%. Pattern changes further indicate that some of the SCCP-containing materials used in the '90s, with high chlorination degrees (n_{Cl} = 6.84, m_{Cl} = 60.78%) were replaced by MCCPs with a lower chlorination degrees (n_{Cl} = 6.57, m_{Cl} = 52.25%).

However, the shift occurred already two decades before the worldwide ban of SCCPs in 2017. We interpret these trends as the result of national regulations on SCCPs, which were implemented already in 2002 in Switzerland (Bogdal et al., 2017). But the sewage sludge samples examined are from one WWTP only and may reflect the CP usage on a local scale.

Nevertheless, CPs and COs were present in all sludge samples from 1993 to 2020. If such sludge is used as fertilizer in agriculture, CPs and COs are inevitably released into the environment. In 2006, the use of sewage sludge as fertilizer has been stopped in Switzerland (Kacprzak et al., 2017). Since then, sludge is fermented and residues are combusted in incinerators. But the application of sludge as fertilizer is still common practice in various European countries such as Italy or Germany (Collivignarelli et al., 2019).

Therefore, a transfer of CPs, including SCCPs, to soils and surface waters via this path is still possible. Because agricultural land is used for feedstock and food production, one can expect that the uptake of CPs via this route is relevant too. Recently, the transfer of polychlorinated biphenyls (PCBs), including dioxin-like PCBs, from contaminated soil to grass-feeding cattle and from milk to calves has been documented (Driesen et al., 2022). Due to similar physicochemical properties of CPs and PCBs, an uptake of CPs from contaminated soils to cows and via dairy products and meat to humans must be expected too. This path remains important in those countries where the use of sewage sludge as fertilizer still is allowed.

CRediT authorship contribution statement

Marco C. Knobloch: Data curation, Formal analysis, Investigation, Software, Validation, Visualization, Writing - original draft, Writing - review & editing. **Jules Hutter:** Data curation, Visualization, Writing - original draft, Writing - review & editing. **Oscar Mendo Diaz:** Conceptualization, Visualization, Writing - review & editing. **Markus Zennegg:** Data curation, Investigation, Resources, Writing - review & editing. **Jean Claude Vogel:** Resources. **Edith Durisch:** Data curation, Resources, Writing - review & editing. **Urs Stalder:** Formal analysis, Resources. **Laurent Bigler:** Formal analysis, Resources, Writing - review & editing. **Susanne Kern:** Supervision, Writing - review & editing. **Davide Bleiner:** Project administration, Supervision, Writing - review & editing. **Norbert V. Heeb:** Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing.

Declaration of competing interest

All authors declare that there are no conflicts of interest.

Data availability

Data will be made available on request.

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Appendix B. Supplementary data

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