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## Bringing to light vinyl chloride oligomers, a class of polychlorinated alkanes differing from chlorinated paraffins

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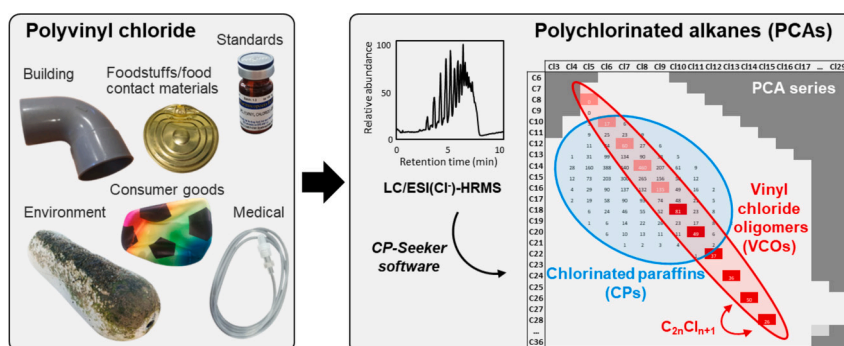
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### HIGHLIGHTS

- Ubiquity of vinyl chloride oligomer (VCO) series in PVC items
- Predominance of monounsaturated “<sup>1</sup>VCOs”
- Signal overlap untangled between VCOs and chlorinated paraffin components
- Human exposure shown from occurrence in indoor dust and canned foodstuffs
- Complete environmental and human exposure assessments needed.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Polyvinyl chloride (PVC) is one of the most widely used polymers, which contrasts with the low amount of literature on the leaching of associated additives and in particular unintended oligomers, a class of non-intentionally added substances (NIAS). This study sheds light on the occurrence of vinyl chloride oligomers (VCOs) in a variety of PVC analytical standards ( $n = 4$ ), PVC items employed for construction, medical or food contact applications ( $n = 14$ ), as well as in foodstuffs and environmental matrices ( $n = 10$ ). Samples were analysed by liquid chromatography coupled to high-resolution mass spectrometry hyphenated with chloride-enhanced electrospray ionisation. Series of saturated (<sup>0</sup>VCO), monounsaturated (<sup>1</sup>VCO), diunsaturated (<sup>2</sup>VCO) and triunsaturated (<sup>3</sup>VCO) VCOs were revealed. The dominant series remained <sup>1</sup>VCOs of the general formula  $C_{2n}H_{3n}Cl_n$ , accounting for ~80 % of VCOs in PVC standards. A risk of signal overlap was found between <sup>0</sup>VCOs of the general formula  $C_{2n}H_{3n+1}Cl_{n+1}$  (accounting for ~8 % in PVC standards) and polychlorinated alkanes making up chlorinated paraffins, given that they share the same chemical formulas. A methodology for discriminating between signals arising from VCOs and chlorinated paraffins has been proposed. VCOs were detected in 88 % of the samples analysed (other than standards), and in particular in some foodstuffs and environmental matrices,

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suggesting that VCOs have the capacity to leach out of PVC materials, and thus contaminate food and the environment.

Overall, these results call for greater attention to be paid to vinyl chloride oligomers and raise the question of whether they pose a risk to living organisms.

## 1. Introduction

Since the 1950s, the widespread use of synthetic polymers has brought important benefits for society notably in terms of health, safety and energy (Andrady and Neal, 2009). Despite this, substantial quantities of plastics have leaked into all the environmental compartments due to the vast increase in production volumes, as illustrated by annual growth rates of 8.4 % (Geyer et al., 2017), coupled with improper management of associated waste. It is estimated that 82 to 358 trillion plastic particles were floating on surfaces of the oceans in 2019 (Eriksen et al., 2023). Of these particles, microplastics, which range in size from  $10^{-4}$  to 5 mm, attract the most attention (Windsor et al., 2019). Recently, the scientific community has become increasingly interested in smaller nanoplastics ( $10^{-6}$ – $10^{-3}$  mm) (ter Halle et al., 2016) as well as other components of plastics, including plastic additives (da Costa et al., 2023). Typical examples are phthalates, a class of intentionally added substances (IAS) used for plasticising purposes, the omnipresence and associated ecological risk of which have recently been emphasised (Luo et al., 2022; Vasseghian et al., 2023). These additives are not covalently bonded to the polymer and can be easily leached. This is also the case for non-intentionally added substances (NIAS), which are much less studied. These include oligomers, which arise mainly from incomplete polymerisation processes (Shi et al., 2023) or from degradation of products during their life cycle. The amount of literature on these NIAS is uneven, however, as illustrated by a query on a scientific search engine (ScienceDirect, 2024/01/24) yielding 13,000–30,000 results for the widely-used polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyester but only 4700 results for polyvinyl chloride (PVC). In addition, the few works on vinyl chloride oligomers (VCOs) were carried out in the 1980s–1990s and for the most part concerned only the base resins (Forrest, 1988; Dawkins et al., 1995; Castle et al., 1996). This scarcity of knowledge contrasts with the widespread use of this polymer, which accounts for 19 % of global plastic production and 6 million tonnes produced in the European Union in 2019 alone (Fernández-González et al., 2022). A diversity of applications is reported, including construction, leisure and sports, healthcare, the electrical sector (Mijangos et al., 2023) or even food contact materials (FCMs) (ResAP(2004)1, 2009 for metal coatings; EU Reg 10/2011 for plastics), thanks to PVC's good processability, durability, high compatibility with additives or mechanical properties (Hruska et al., 2007). The pollution of soil and the aquatic environment by PVC particles, as well as the toxicities reported in relation to the leaching of associated additives (but not VCOs), were recently reviewed by Kudzin et al. (2024). In another recent study, PVC-based micro- and nanoplastics were found in 64 human blood samples, this polymer being the most predominant after polyethylene (Brits et al., 2024). This raises questions about the health risk of VCOs but, to our knowledge there are no toxicological data available for these oligomers.

VCOs are part of the polychlorinated alkanes (PCAs), which also include the much more studied main components of chlorinated paraffins (CPs). These industrial chemicals manufactured in large volumes are mostly composed of polychlorinated alkanes (PCAs) (Fernandes et al., 2023). There are several hundred homologue groups (depending on the C-chain length and the Cl number), each composed of innumerable isomers. As CPs have become ubiquitous (United Nations Stockholm Convention POP Review Committee, 2017, 2022), procedural contamination issues and the lack of reference standards add to the analytical challenge (Schinkel et al., 2018a) that still hampers their risk assessment. During previous early analytical developments based on high-

resolution mass spectrometry (HRMS; Mézière et al., 2020a) and open-source software to characterise homologue patterns (McGrath et al., 2024), unconventional and occasional procedural contamination consistent with a  $-(CH_2-CHCl)-$  series was observed and eventually linked to PVC clamps used to hold the purification columns. More recently, although this bias has been precluded, similar unconventional patterns have also been observed in indoor dust as well as in canned foods and in wild boar shoulder wrapped in stretch film (unpublished work). These  $-(CH_2-CHCl)-$  series suggest the occurrence of VCOs alongside CP components, and therefore there is a need to shed light on the widespread distribution of VCOs and to clear up any confusion with CPs and PCAs.

In this context, the present work aimed to emphasise the ubiquitous presence of VCOs in diverse compartments. To that end, a variety of samples including PVC analytical standards, PVC items used in various sectors (construction, medical, food contact), as well as foodstuffs and environmental matrices were collected. Next, the objective of this work implied examining the occurrence and composition of VCOs by applying the methodology developed for CPs. In parallel, a structural characterisation was also carried out by NMR analysis and derivatisation by hydrogenation.

## 2. Material and methods

In this article, we refer to the nomenclature harmonised by Fernandes et al. (2023) for terms and abbreviations relating to CPs and PCAs in order to avoid any ambiguity.

### 2.1. Chemicals

Solvents of Picograde quality (acetone, *n*-hexane, dichloromethane and toluene) were provided by Biosolve (Dieuze, France). LC-MS grade acetonitrile and water were obtained from Merck (Darmstadt, Germany). For the preparation of a low molecular weight fraction (LMWF-PVC), tetrahydrofuran (THF) was purchased from Thermo Scientific (99.5 % or 99.8 %, Illkirch, France). For hydrogenation, THF and diethyl ether were of reagent grade (Merck). In this case, THF was obtained in the dry state after fresh distillation over sodium and benzophenone. Hydrogen gas was obtained from a compressed gas cylinder and provided by the Messer group.

Stock solutions of two  $^{13}C$ -labelled CP congeners ( $100 \text{ ng } \mu\text{L}^{-1}$  in isooctane) were obtained from Chiron (Trondheim, Norway). 19,20,21- $^{13}C_3$ -3,4,6,7,9,10,18,19-Octachlorohenicane was used as internal standard (IS). Working solutions were prepared by dilution in acetonitrile at  $5 \text{ ng } \mu\text{L}^{-1}$  or in toluene at  $0.04 \text{ ng } \mu\text{L}^{-1}$ . 14,15,16- $^{13}C_3$ -1,2,8,9,13,14-Hexachlorohexadecane was used as recovery standard (RS). The working solution was prepared by dilution in acetonitrile at  $0.12 \text{ ng } \mu\text{L}^{-1}$ .

Silica gel 60, palladium over carbon (10 % wt., Pd/C) and Celite 545 mesh were purchased from Merck (Darmstadt, Germany), sulphuric acid (98 %) from Panreac (Barcelona, Spain), and Florisil from LGC Promochem (Wesel, Germany).

### 2.2. Samples

VCOs were analysed in various samples described in Table 1. Refer to Table S1 for pictures and Table S2 for further details.

The PVC raw materials were purchased as PVC analytical standards from Sigma-Aldrich.

**Table 1**  
Description of the sample collection.

Name	Code	Collection year	Geographical sampling origin	Condition
Standards (n = 4)				
PVC, low molecular weight	Std-1	2023	–	–
PVC, high molecular weight	Std-2	2023	–	–
PVC, average Mw ~233,000	Std-3	2023	–	–
PVC, pharmacopeia reference standard	Std-4	2023	–	–
PVC items <sup>a</sup> (n = 14)				
Construction and consumer goods (n = 6)				
Sewage pipe	PVC-S	2023	Nantes, France	Worn
Electrical cable sheath	PVC-E	2023	Nantes, France	Worn
Floor covering	PVC-F	2023	Nantes, France	Worn
Boots	PVC-B	2023	Nantes, France	Worn
Toy (ball)	PVC-T	2023	Nantes, France	New
Laboratory clamps	PVC-L	2023	Nantes, France	Worn
Medical devices (n = 2)				
Perfusion tube	MED-P	2023	Nantes, France	New
Blood bag	MED-B	2023	Nantes, France	New
Food contact materials (n = 6)				
Gloves	FCM-G	2023	Nantes, France	New
Can coating (tuna, in salt brine) <sup>b</sup>	FCM-C1a/b <sup>c</sup>	2023	Nantes, France	–
Can coating (mackerel, in salt brine) <sup>b</sup>	FCM-C2a/b <sup>c</sup>	2023	Nantes, France	–
Stretch film	FCM-F	2023	Nantes, France	New
Foodstuffs (n = 3)				
Canned tuna, in salt brine <sup>b</sup>	FS-C1	2023	Nantes, France	–
Canned mackerel, in salt brine <sup>b</sup>	FS-C2	2023	Nantes, France	–
Sausage, raw	FS-S	2023	Nantes, France	–
Environment (n = 7)				
Indoor dust	EM-D	2017	Fukuoka, Japan	–
Sewage sludge (n = 3)	EM-S1 to S3	2023	Achères, France	–
Marine sediment	EM-MS	2017	Fos-sur-Mer, France	–
Macroplastic (fender, inner/outer parts)	EM-MA1	2023	Le Croisic, France	Worn
Macroplastic (panel)	EM-MA2	2023	Toulon, France	Worn

<sup>a</sup> Or suspected.

<sup>b</sup> The can coatings and foodstuffs (tuna, mackerel) belong to the same purchased can.

<sup>c</sup> a: the top-end part of the can; b: body/bottom-end of the can.

To investigate direct sources of VCOs, PVC items representative of the main PVC application sectors were collected. They included the construction sector (sewage pipe, electrical cable sheath, floor covering), consumer goods (boots, children's toy), the medical sector (perfusion tube, blood bag) and FCMs (gloves, coatings from 2-piece cans of fish products, stretch film also known as cling film). In addition, analyses were carried out on PVC laboratory clamps since VCOs had been detected in these as mentioned in the introduction. All the PVC samples were collected from supermarkets, online retailers or sampled at home. Samples were kept in polypropylene containers at ambient temperature until extraction and analysis. The likelihood of a geographical bias arising from the fact that PVC items and foodstuffs

were predominantly collected from one region was overlooked, given that their manufacture is global.

The foodstuffs included the two canned fish products in the cans sampled. They were selected on the basis of previous work revealing —(CH<sub>2</sub>—CHCl)— series that suggested the occurrence of VCOs, which could originate from PVC coatings used in fish-based canned products (Lestido-Cardama et al., 2022). In addition, raw sausage was used for a cooking experiment with the stretch film. Indeed, poaching or simmering food in plastic film has become a popular cooking habit. Although direct contact with food was contraindicated by the manufacturer, other manufacturers of PVC cling film recommend simmering food for a period <15 min at maximum temperature of 100 °C. Cooks may not adhere strictly to these recommendations. In detail, about 150 g of a sausage were placed in the film and cooked in water (80–85 °C) for 15 min.

The environmental occurrence of VCOs was finally investigated by analysing several matrices from various environmental compartments. A sample of indoor dust from Japan (Fukuoka prefecture) was collected in 2017 from a household vacuum cleaner and sieved to keep the fraction below 500 µm, as detailed by McGrath et al. (2023). Three end-of-treatment samples of sewage sludge from the urban catchment of the Seine Aval wastewater treatment plant near Paris were taken in 2023 as part of a program aimed at monitoring the long-term dynamics of known and/or potential pollutants (DOI: <https://doi.org/10.5281/zenodo.6724910>). A marine sediment collected in the Gulf of Fos in 2017 was obtained during the French research project FOS-SEA (ANR-16-CE34-0009) aimed at assessing the risk of biological fouling control along the Mediterranean coast (Manasfi et al., 2019). Two macroplastic samples were obtained and included a PVC panel immersed for one year at a depth of one-meter in the Bay of Toulon (France) during a French national research project (Philippe et al., 2023). Finally, a boat fender was found abandoned on a beach at Le Croisic, France. It should be noted that the inner and outer parts of the latter sample were analysed separately for evidence of any differences in the pattern of VCOs suggesting environmental degradation.

### 2.3. Sample treatment

For PVC standards, 20–50 mg were weighted into 15 mL amber glass tubes. For the PVC items and macroplastic samples, 4 cm<sup>2</sup> were cut using a stainless steel blade (see Table S2 for detailed dimensions and masses). One hundred nanograms of IS (in 20 µL acetonitrile) were then deposited on the surface of each PVC item and left to dry. After addition of 2 mL of acetonitrile, the tubes were maintained at 40 °C for 24 h, then agitated for 2 min using a vortex-mixer and centrifuged for 10 min (2000 rpm, 20 °C). An aliquot of 40 µL was then transferred to a 200 µL amber glass vial, together with 20 µL of RS working solution.

The wet samples (food, sewage sludge) were lyophilised in glass dishes for 48 to 72 h, homogenised using a stainless steel laboratory blender, and stored in amber glass containers until extraction and analysis. Extraction and purification were carried out according to a protocol previously developed for PCAs constitutive of chlorinated paraffins by Mézière et al. (2021a, 2021b), with slight modifications. Briefly, 2 g of dried sample were weighed into glass tubes, then 25 µL of IS working solution in toluene and 18 mL of a mixture of toluene and acetone (70:30, v/v) were added. Two successive extraction cycles, with solvent renewal, were carried out using the Microwave Extraction Reactor Monowave Extra (Anton Paar, France) with the following parameters: cycle duration of 15 min, stirring set at 600 rpm, and temperature of 120 °C. After centrifugation (10 min, 2000 rpm, 20 °C), the supernatants from the two successive extractions were poured into a glass flask and concentrated to dryness using a rotary evaporator. The dry residue was determined gravimetrically for sausage and canned foods (Table S3). After reconstitution in *n*-hexane, the extract was purified on a column filled from bottom to top with sodium sulphate, 10 g neutral silica gel, 20 g acidified silica gel (44 % H<sub>2</sub>SO<sub>4</sub>), and sodium

sulphate. Note that for the marine sediment, an activated copper spatula was placed under the neutral silica gel for sulphur removal. After conditioning with 60 mL of dichloromethane and 60 mL *n*-hexane, the columns were rinsed with 50 mL of *n*-hexane, eluted with 60 mL of dichloromethane/*n*-hexane (1:1, v/v) and the eluates were rotary-evaporated. A further purification was carried out using a column packed with sodium sulphate, 6 g of Florisil deactivated with 3 % of ultrapure water and sodium sulphate. After column conditioning with 20 mL dichloromethane followed by 20 mL *n*-hexane, the extract was loaded onto the top of the column. *n*-Hexane (20 mL) was used to rinse the column and dichloromethane (20 mL) for the elution of the analytes. The purified extracts were reconstituted in 30  $\mu$ L of RS working solution.

The dust sample was extracted and purified according to the method described by McGrath et al. (2023). Briefly, this involved ultrasonication of 50 mg using a mixture of *n*-hexane and dichloromethane (3:1, v/v), followed by clean-up using acidified silica (44 % H<sub>2</sub>SO<sub>4</sub>, w/w) and solid phase extraction on Bond Elut silica cartridges (500 mg). Final extracts were reconstituted in 100  $\mu$ L of acetonitrile containing 20  $\mu$ L of RS working solution.

All the extracts were stored in the dark at  $-20$  °C until analysis.

#### 2.4. LC/HRMS

Extract analyses were performed by high-performance liquid chromatography (Ultimate 3000 system, Thermo Fischer Scientific) coupled to high-resolution mass spectrometry (Q Exactive Orbitrap HRMS, Thermo Fischer Scientific) as optimised by Mézière et al. (2020a). Extracts (5  $\mu$ L) were injected onto a Hypersil Gold analytical column (100 mm  $\times$  2.1 mm, 1.9  $\mu$ m) (Thermo Fischer Scientific) maintained at 30 °C. Partial separation of the analytes was achieved using a water/acetonitrile mobile phase at a flow rate of 0.4 mL min<sup>-1</sup>, increasing from 70 % acetonitrile to 100 % at 6 min, maintained for 6 min. A mixture of acetonitrile and dichloromethane (1:1, v/v) was introduced into the ionisation source at a flow rate of 0.08 mL min<sup>-1</sup>, using a post-column T-connection, to enhance the formation of chloride adduct ions. Negative mode electrospray ionisation (ESI) was used with probe operated at a voltage of 2.5 kV. The capillary temperature, sheath gas and auxiliary gas flow rate were set at 275 °C, 50 and 5 arbitrary units (AU), respectively. Data acquisition was carried out in full scan mode (*m/z* range of 300–1500), with a resolving power of 140,000 full width half maximum at *m/z* 200 and automatic gain control target set at  $5 \times 10^5$ .

#### 2.5. LC/HRMS data processing

The data obtained from LC/HRMS analysis were processed using CP-Seeker (v2.1.2), an open-source software application designed for ergonomic and automated signal processing and peak integration of chemical classes related to chlorinated and brominated *n*-alkanes. A detailed description has been provided by McGrath et al. (2024). Briefly, this involved signal deconvolution using the enviPat package (Loos et al., 2015) with the mass analyser setting to obtain a list of the homologue group isotopic patterns in the ranges of C<sub>6–36</sub> and Cl<sub>3–30</sub>. Non-Gaussian chromatographic signals of spectrometric peaks above 1 % of the base peak were then automatically integrated. The output comprised the sum area of homologue groups and, for identification confidence, a pattern score and an average mass deviation.

In the present work, the following compound families were targeted: polychlorinated alkanes (PCAs, C<sub>n</sub>H<sub>2n+2-x</sub>Cl<sub>x</sub>) and polychlorinated monoolefins (PCmonoOs; C<sub>n</sub>H<sub>2n-x</sub>Cl<sub>x</sub>), diolefins (PCdiOs; C<sub>n</sub>H<sub>2n-2-x</sub>Cl<sub>x</sub>), triolefins (PCtriOs; C<sub>n</sub>H<sub>2n-4-x</sub>Cl<sub>x</sub>), as well as the <sup>13</sup>C-labelled standards. Chloride adduct ions were targeted at an *m/z* tolerance of 5 ppm. Only homologue groups exhibiting a pattern score higher than 70 % were considered. Mass deviations were <1 ppm. The absence (or negligible levels) of [M – H]<sup>-</sup> ions was checked to avoid possible confusions between chemical classes.

#### 2.6. QA/QC

All temperature-resistant glassware was heated at 400 °C for 4 h before use. Other materials were rinsed three times with dichloromethane. Procedural blanks (*i.e.* empty glass tubes) were prepared in each extraction series ( $n = 3$  for PVC items and macroplastics,  $n = 4$  for samples extracted using microwaves) plus  $n = 1$  from lyophilisation. No procedural contamination was observed for the blanks associated with PVC items and macroplastics. On the contrary, traces of PCmonoOs and in particular PCAs were observed in the blanks associated with food-stuffs and environmental matrices. This residual contamination is typically due to the ubiquitous presence of medium-chain CPs, despite the drastic precaution taken (McGrath et al., 2023). Blank subtraction was applied to samples if the averaged homologue area in the blanks was higher than 10 % of that of the sample.

For the instrumental analysis, solvent blanks were injected every 3–6 samples, as well as IS with RS every 10 samples for checking the instrument response ( $n = 5$ ). The associated variability was satisfactory, as illustrated by relative standard deviations (RSD) of 24 % and 22 %, respectively associated to the IS and RS. A higher value of 42 % was observed for the RS spiked in the final extracts of the samples ( $n = 33$ ), which illustrates of matrix effects. These ranged from  $-29$  and  $+42$  % (average of  $+1$  %) except for the electrical cable sheath, the laboratory clamps and the macroplastic fender (Fig. S2). These stronger negative matrix effects observed are likely due to ion suppression caused by the high levels of additives co-extracted from these samples made of soft PVC (Stuart, 2005). For the IS, higher variability was observed compared with the RS (*i.e.* RSD of 66 %). The recoveries presented in Fig. S3 were generally satisfactory (average of 86 %, 25th and 75th centiles comprised between 44 and 90 %), except for the sediment and some PVC items; the matrix effect mentioned above is probably expected for the latter samples. Overall, these results were considered acceptable with regard to the objectives of the study aimed at qualitatively assessing the presence of VCOs.

#### 2.7. Preparation and hydrogenation of a low molecular weight fraction of PVC standard (LMWF-PCV)

For further chemical and structural investigations of VCOs, a low molecular weight fraction (LMWF-PVC) was prepared from Std-1, according to Castle et al. (1996) with slight modifications. Sixty grams dissolved in 0.4 L of THF were precipitated by dropwise addition of 3.6 L of *n*-hexane for  $\sim 4$  h, under magnetic stirring. After filtration (12.5–25  $\mu$ m, Whatman), the solvent was evaporated using a rotary evaporator and a dry residue (120 mg) was obtained after removal of solvent traces in a fume hood.

For hydrogenation, Pd/C (10 mg) was added to a solution of the dry residue (75 mg) in THF (2 mL). After flushing the flask three times with hydrogen gas, the reaction mixture was stirred for 18 h at room temperature under hydrogen atmosphere. The reaction mixture was filtered over Celite for removal of the palladium. After washing three times with diethyl ether, the resulting filtrate was dried under reduced pressure to obtain a hydrogenated sample of LMWF-PVC (59 mg).

Aliquots of LMWF-PVC were characterised without or with hydrogenation by LC/HRMS as described above (200 ng on column) as well as by <sup>1</sup>H NMR. <sup>1</sup>H NMR spectra were recorded on a Bruker Avance 400 spectrometer fitted with a 5 mm i.d. BBFO+ probe carefully tuned to the recording frequency of 400.13 MHz (for <sup>1</sup>H). The spectra are referenced to the solvent in which they were run (7.26 ppm for <sup>1</sup>H CDCl<sub>3</sub>).

### 3. Results and discussion

#### 3.1. Characterisation of PVC standards

##### 3.1.1. Series of VCOs revealed by LC/HRMS

Data treatment using CP-Seeker software suggested the presence of

series saturated ( $^0\text{VCOs}$ ), monounsaturated ( $^1\text{VCOs}$ ), diunsaturated ( $^2\text{VCOs}$ ) and triunsaturated ( $^3\text{VCOs}$ ) VCOs in all the ACN extracts of the four PVC standards studied. The  $^0\text{VCOs}$  belong to the PCAs, and the  $^1\text{VCOs}$ ,  $^2\text{VCOs}$  and  $^3\text{VCOs}$  to the PCOs. Several homologue groups were detected, as illustrated in Fig. 1 for the Std-1 standard. Homologue group patterns for the other standards are shown in Fig. S4. Each of the four chemical subclasses investigated ( $^0\text{VCOs}$ ,  $^1\text{VCOs}$ ,  $^2\text{VCOs}$ ,  $^3\text{VCOs}$ ) exhibited a homologue series based on the repeating unit of the PVC polymer,  $\text{C}_2\text{H}_3\text{Cl}$ . More specifically, 14  $^0\text{VCO}$  homologue groups were detected, from the tetramer ( $\text{C}_8\text{H}_{13}\text{Cl}_5$ ) to the heptadecamer ( $\text{C}_{34}\text{H}_{52}\text{Cl}_{18}$ ), i.e. as PCAs- $\text{C}_{2n}\text{Cl}_{n+1}$  ( $4 \leq n \leq 17$ ). For  $^1\text{VCOs}$ , a series of  $\text{C}_{2n}\text{Cl}_n$  homologue groups ranging from  $\text{C}_{10}\text{H}_{15}\text{Cl}_5$  (pentamer) to  $\text{C}_{36}\text{H}_{54}\text{Cl}_{18}$  (octadecamer) was observed ( $5 \leq n \leq 18$ ). For  $^2\text{VCOs}$  and  $^3\text{VCOs}$ , the number of homologue groups detected was much lower, equal to 6 ( $\text{C}_{2n+1}\text{Cl}_{n+2}$ ,  $12 \leq n \leq 17$ ) and 5 ( $\text{C}_{2n+1}\text{Cl}_{n+1}$ ,  $13 \leq n \leq 17$ ), respectively. As detailed in Fig. S4, Std-3 (average Mw  $\sim 233,000$ ) showed other  $^1\text{VCO}$  series, however at much lower intensities, with the following formulas:  $\text{C}_{2n}\text{Cl}_{n+1}$  ( $5 \leq n \leq 9$ ),  $\text{C}_{2n+1}\text{Cl}_{n-1}$  ( $7 \leq n \leq 15$ ),  $\text{C}_{2n+1}\text{Cl}_{n-2}$  ( $7 \leq n \leq 17$ ) and  $\text{C}_{2n+1}\text{Cl}_{n-5}$  ( $10 \leq n \leq 17$ ). The occurrence of these parallel series could be related to the synthesis process specific to this standard exhibiting the highest molecular weight among the four standards analysed in the present work. Series with uneven C-chain lengths may stem from structural defects resulting from various mechanisms (Starnes Jr., 2012).

Strong similarities between the homologue patterns of the different PVC standards were observed for  $^0\text{VCOs}$  and  $^1\text{VCOs}$ , as detailed in Table S4 (Spearman correlation coefficients between 0.75 and 0.98). Lower coefficients were observed for  $^2\text{VCOs}$  and  $^3\text{VCOs}$ , as a varying number of homologue groups was detected depending on the PVC standard. We therefore considered that the VCO homologue patterns were very similar and hardly influenced by the type of standard. The nonamer ( $\text{C}_{18}\text{Cl}_{10}$ ) and decamer ( $\text{C}_{20}\text{Cl}_{10}$ ) were the dominant homologue groups within the PCAs and PCOs, respectively. However, discussion on the homologue pattern is hampered by the fact that the LC/ESI( $\text{Cl}^-$ )-HRMS responses obtained in the present work do not reflect concentrations due to the instrument-dependent sensitivity with regard to the chlorine content (Mézière et al., 2020b). In particular, the lack of sensitivity of LC/ESI( $\text{Cl}^-$ )-HRMS for VCOs- $\text{Cl}_{<4}$  could partly explain the non-detection of these homologue groups in the present work, and oligomers above a given molecular weight may not elute from the column (see the ion chromatogram in the graphical abstract). In addition, simultaneous removal of the most volatile oligomers along with the carcinogenic vinyl chloride monomer after PVC polymerisation and during steam stripping processes (Gilbert and Patrick, 2017) could also be expected.

Based on the  $\Sigma\text{PCAs}+\text{PCOs}$  observed for the four PVC standards, the relative contributions decreased as follows:  $^1\text{VCOs}$  ( $81 \pm 2\%$ ),  $^3\text{VCOs}$  ( $10 \pm 1\%$ ),  $^0\text{VCOs}$  ( $8 \pm 2\%$ ) and  $^2\text{VCOs}$  ( $1 \pm 1\%$ ). To explain the predominance of the monounsaturated olefins, Dawkins et al. (1995) proposed a formation mechanism for the monounsaturated tetramer during polymerisation. More specifically, it involved chlorine transfer to the vinyl chloride monomer, followed by head-to-tail and head-to-head additions, 1,2 chlorine migration and chlorine radical loss leading to monounsaturated oligomer. Forrest hypothesised another formation mechanism involving initiation with a chlorine radical and, like Dawkins, observed  $^1\text{VCOs}$  in a PVC base resin (trimer to heptamer) (Forrest, 1988). Another explanation for the presence of  $^1\text{VCOs}$  could rely on the structural defects inherent in PVC leading to a typical structure including unsaturations (Stuart, 2005). A further source of oligomers could be linked to the thermal degradation of PVC, which could occur during PVC moulding and imply the formation of conjugated polyene sequences. Indeed, although the mechanisms of thermomechanical degradation of PVC are still being debated, the main mechanism of dehydrochlorination of PVC is generally recognised to be under the effect of thermomechanical stress. Due to the many structural defects produced during polymerisation, a number of labile chlorines may leave

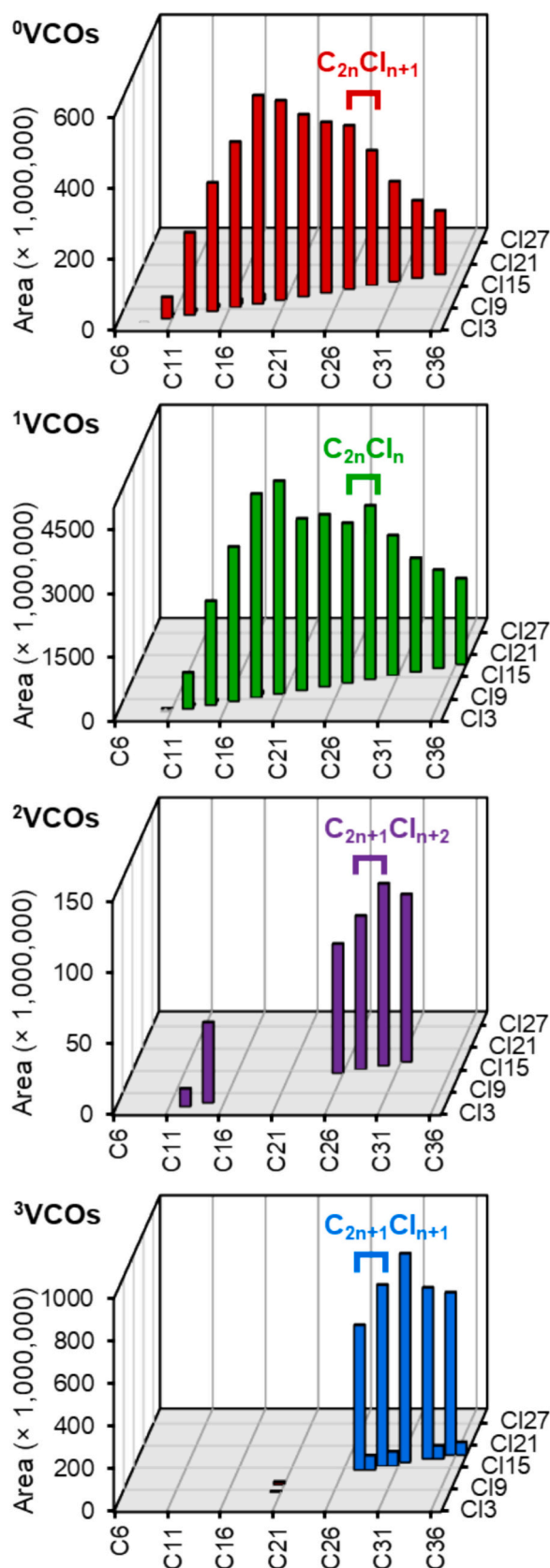


Fig. 1. Distribution of saturated ( $^0\text{VCOs}$ , red), monounsaturated ( $^1\text{VCOs}$ , green), diunsaturated ( $^2\text{VCOs}$ , purple) and triunsaturated ( $^3\text{VCOs}$ , blue) homologue groups of vinyl chloride oligomers in the Std-1 standard sample.

the chain in the form of hydrochloric acid gas, resulting in the formation of a double bond in the PVC chain. To the best of our knowledge, the presence of saturated  $^0\text{VCOs}$  has not been reported in the literature, and a formation mechanism has yet to be proposed.

### 3.1.2. Hydrogenation assay and possible structure of VCOs

For the sake of similarity with CPs in the initial interpretation of the results and in accordance with the literature (Dawkins et al., 1995; d'Antuono et al., 2005; Stuart, 2005), we considered that all the compounds detected had linear structures. However, while the spectrometric method implemented provided high degree of confidence in the chemical formula, we could not entirely presume the presence of monoolefinic  $^1\text{VCOs}$  rather than cyclic  $^1\text{VCOs}$ . Indeed, a double-bond equivalent of 1 could correspond to either unsaturation or to a cycle. It has been described that cyclic species arise during the elongation step of several polymers, for example polyesters plastics (Castle et al., 1989) and can coatings (Cariou et al., 2022) or polyamides (Heimrich et al., 2015). To address this question, a low molecular weight fraction was prepared from Std-1 (LMWF-PCV) and subjected to hydrogenation (reduction). LC/HRMS and  $^1\text{H}$  NMR analyses were carried out to observe whether the so-called  $^1\text{VCOs}$  signals would be turned into PCA signals. The results are described below and illustrated in Figs. S5 and S6, respectively.

Firstly, according to the LC/HRMS results, the  $^0\text{VCOs-C}_{2n}\text{Cl}_{n+1}$  series remained stable after hydrogenation, confirming that this series was fully saturated. Secondly, the most intense series ( $^1\text{VCOs-C}_{2n}\text{Cl}_n$ ) disappeared while a  $^0\text{VCO-C}_{2n}\text{Cl}_{n-1}$  series appeared at a similar intensity after hydrogenation. Hydrogenation was confirmed by the disappearance of the  $^1\text{H}$  NMR signal at 5.88 ppm likely originating from vinylic protons, as well as by the complexification of the signal at 1.18 ppm likely originating from newly formed methyl groups. The additional loss of a Cl atom can be explained by an over-reduction reaction due to the insertion of palladium into the carbon-halogen bond, which is actually well established in the case of primary chlorinated hydrocarbons (Boros et al., 2004). Thirdly, a  $^1\text{VCOs-C}_{2n}\text{Cl}_{n-1}$  series, less intense than the  $^0\text{VCOs-C}_{2n}\text{Cl}_{n+1}$  series, appeared after reduction (also supported by the  $^1\text{H}$  NMR signal at 5.72 ppm). Its origin remains unclear as it is indicative of incomplete hydrogenation. It could result from the loss of a Cl atom while maintaining the double bond.

### 3.1.3. Semi-quantification attempt

Based on the  $\Sigma\text{PCAs}+\text{PCOs}$  mass spectrometric responses and using both internal and external PCA standards, rough semi-quantification led to levels of extracted VCOs corresponding to 0.01–0.09 % of PVC standard masses. Assuming that extraction was complete after dissolution and precipitation using THF and *n*-hexane, this content increased to ~0.2 % for Std-1, indicating that acetonitrile alone did not entirely deplete the matrix. Nevertheless, such levels of oligomer should be considered with caution given the large uncertainty in quantification arising from the use of only two PCA standards and, as mentioned above, the strong dependence of the response factors on the chlorination degree. To our knowledge, no study has provided VCO content. However, similar ranges to the PVC oligomer content found in the present work have been reported for PET (0.5–1.3 %) and polyester (0.8–1.2 %) oligomers (Receu et al., 2002; Hoppe et al., 2017).

## 3.2. Differentiating vinyl chloride oligomers from chlorinated paraffin components

As observed before, although the VCOs detected in the PVC standards are mostly  $^1\text{VCOs}$ , about 10 % are represented by  $^0\text{VCOs}$ . The  $^0\text{VCOs}$  belong to the PCAs, the chemical family of which also includes the main components of CPs, a much more studied group of substances, implying a possible overlap of signals from these two groups (*i.e.* CPs and VCOs). This issue is of particular concern since, as highlighted in a recent review on the recommended terms for PCAs (Fernandes et al., 2023), in many

publications CPs are reported as the sum of measured PCA homologue groups. In this context, a misidentification of VCOs has probably occurred in published literature.

A typical example of this signal overlap between CPs and VCOs is given in Fig. 2A, which shows the distribution of  $\text{C}_n\text{Cl}_x$  groups obtained with the CP-Seeker software for an indoor dust extract. Although the VCO and CP homologue groups share the same formula, some elements emphasised in Fig. 2A to D appear helpful in distinguishing the signals arising from these two substance groups. These are based on the fact that CPs and VCOs have overlapping homologue groups but with distinct isomerisms. In particular, CPs are intentionally added substances produced for a wide range of applications. Depending on these uses, different technical mixtures of varying carbon and chlorine content are used. Such diversity is reflected by a much higher number of  $\text{C}_n\text{Cl}_x$  groups compared with VCOs (Fig. 2A), which by definition are repetitions of the same monomer unit. It also implies that a given carbon chain is substituted by a fixed number of chlorine atoms, unlike CPs, as illustrated in Fig. 2B.

Moreover, the chlorination of the *n*-alkane feedstock during the synthesis of CPs is non-selective. Thus, a very high number of isomers is expected for a given  $\text{C}_n\text{Cl}_x$  group, in contrast to VCOs. Only partial separation of these isomers is then achieved using conventional chromatography techniques, leading to typically broad and unresolved chromatographic peaks, as illustrated in Fig. 2C for the  $\text{C}_{14}\text{Cl}_7$  group. In contrast, oligomer formation involves a more limited number of isomers with Gaussian-like chromatographic peak shapes (see Fig. 2C PCAs- $\text{C}_{18}\text{Cl}_{10}$  and  $\text{C}_{28}\text{Cl}_{15}$  groups). These peak shapes are illustrated in Figs. S7 and S8 for a PVC standard and the indoor dust sample, respectively. In addition, the plot between their monoisotopic masses and chromatographic retention times, revealing a polynomial relationship, is a further consistent indication of the presence of such series of compounds.

Finally, based on the findings presented in §3.1,  $^1\text{VCOs}$  are thought to be the major subclass of VCOs. Even though such chlorinated olefins can be found as impurities in CPs mixtures (Schinkel et al., 2018b), those characteristic of VCOs form a series differing by  $\text{C}_2\text{H}_3\text{Cl}$  repeating unit. Moreover, as for  $^0\text{VCOs}$ , Gaussian shapes were observed for the chromatographic peaks of  $^1\text{VCOs}$  as well as a correlation between their retention times and monoisotopic masses (Figs. S9 and S10).

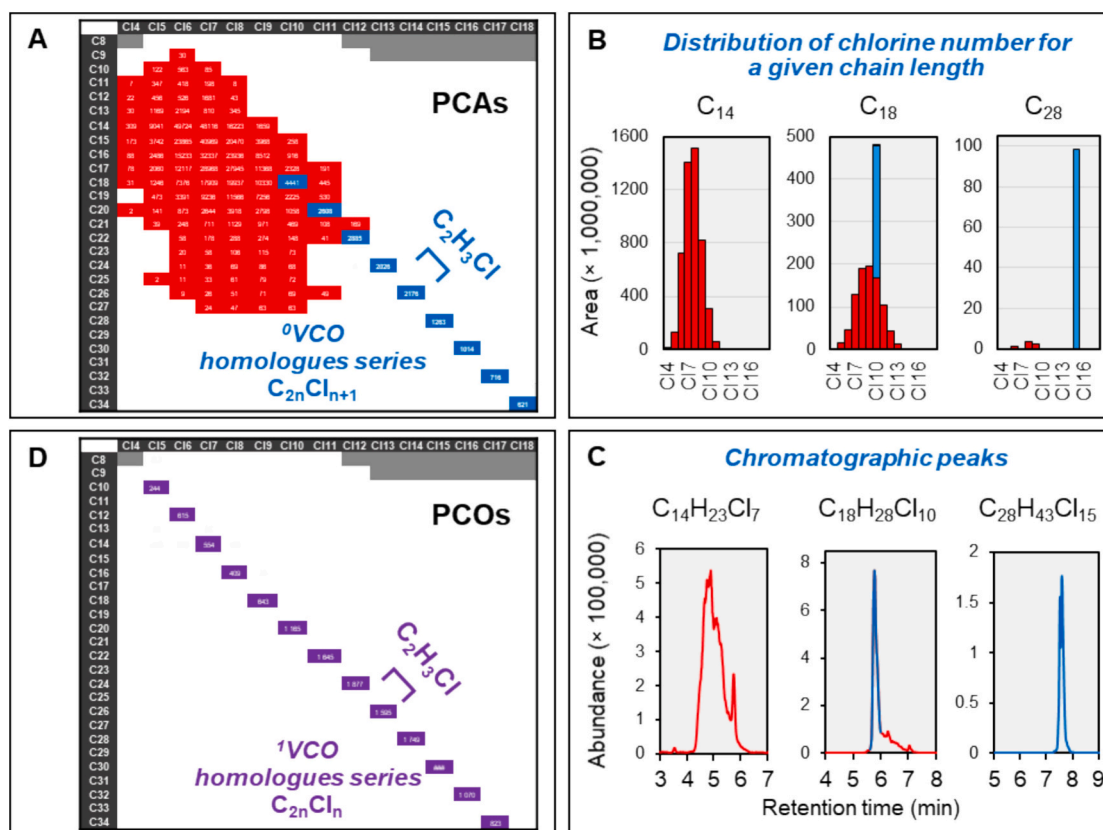
Overall, these results highlight the need for researchers to be vigilant when reporting results for CPs and to avoid confusion between CPs and PCAs, as already stressed by Fernandes et al. (2023), since the latter can include other groups of contaminants such as VCOs.

## 3.3. Characterisation of other samples

### 3.3.1. Occurrence of VCOs in PVC items

Using the methodology presented to discriminate PCA signals arising from CPs and VCOs, the ubiquity of the latter in PVC items could be demonstrated. In fact, saturated, mono-, di- and tri-unsaturated VCO series were found in 12 out of 14 PVC items. The relative contributions of PCA and PCO series to their sum areas are given in Fig. 3 (detailed in Table S5), with a further dichotomy according to whether they correspond to VCO or non-VCO compounds.

Firstly, in PVC items compared to PVC standards, the average contribution of PCAs to  $\Sigma\text{PCAs}+\text{PCOs}$  increased sharply from 8 % to 51 %, which could be partly related to the increased contribution of the non-VCOs (*i.e.* 34 % vs. 0.8 % in PVC standards), as illustrated in Fig. 3. As previously mentioned, the non-VCO PCAs belong to the CPs, which presence in PVC items could be linked to their use as flame retardants or secondary plasticisers for soft PVCs (Stuart, 2005). The latter use could further explain the higher contribution of CPs to  $\Sigma\text{PCAs}+\text{PCOs}$  in soft PVC items such as the electrical cable sheathing (85 %) and laboratory clamps (94 %). For the latter, sorption of CPs from the laboratory atmosphere cannot be ruled out, particularly as this PVC item was worn. This sorption of CPs present from the surrounding environment is also a possible explanation for their presence in the boots, also worn and which



**Fig. 2.** Discrimination of polychlorinated alkane (PCA) signals arising from chlorinated paraffins (CPs, red) and saturated vinyl chloride oligomers ( $^0$ VCOs, blue) in an indoor dust sample, including the examination of the PCA homologue pattern (A), the distribution of chlorine number for a given chain length (B), the chromatographic peak shapes (C), and the presence of monounsaturated vinyl chloride oligomers ( $^1$ VCOs, purple) (D).

were not PVC-based, and in the weathered macroplastic fender. For PCOs, as for PCAs, a slight increase in the contribution of non-VCO compounds in the PVC items compared with the standards was observed, as illustrated in Fig. 3. However, VCOs remain the predominant group.

Considering all PCA and PCO homologue groups, the average contribution of VCOs reached 76 % in the PVC items, a value lower than the 98 % contribution found for the PVC standards. Very high contributions (>90 %) were specifically observed in 9 out of the 14 PVC items analysed, including sewage pipe, floor covering, toys, the two medical devices and in 3 out of the 4 food can coatings. Hence, these results are indicative of the predominance of VCOs in a variety of items made of PVC employed for a wide range of applications including construction, clothing, leisure, healthcare and food contact. These observations also apply to the PVC macroplastics found in the marine environment.

### 3.3.2. Occurrence of VCOs in foodstuffs and environmental matrices

The potential ability of VCOs for migration was further evidenced by their presence in foodstuffs and environmental matrices.

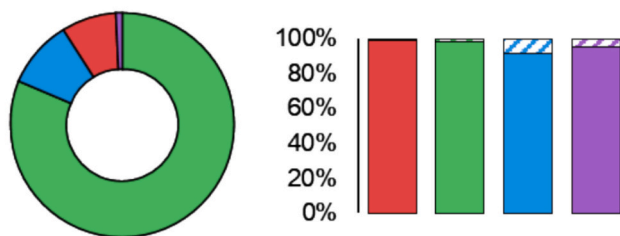
Regarding foodstuffs, an experiment was carried out to determine whether VCOs present as non-intentionally added substances in the stretch film could migrate to the sausage stuffing during simmering. Unfortunately,  $^0$ VCOs and  $^1$ VCOs were detected in both the raw and cooked sausage, so that no conclusions could be drawn. The origin of this contamination remains unknown and this sample was excluded from the following discussions. For the other foodstuffs (*i.e.* canned), the maximum contributions of VCOs to the  $\Sigma$ PCAs+PCOs were observed in canned mackerel (85 %). This probably reveals their migration as non-intentionally added substances from the corresponding coatings in which they were observed to be predominant as discussed above. For canned tuna, however, the contribution of VCOs decreased to 20 %,

which could be linked on the one hand to the detection of VCOs mostly in the body/bottom coating, contrary to the mackerel can (VCOs found in both body/bottom and top of the can). The traces found in the top-end of the mackerel can may be due to sorption. On the other hand, the higher lipid content of the canned mackerel (11 % vs. 2 % for tuna, see Table S3) probably enhanced the migration of these substances thought to be lipophilic due to the similarity of their structure with the lipophilic CPs (van Mourik et al., 2016). Another work focusing on CPs in foodstuffs purchased from Belgian retailers highlighted high levels of long-chain CPs (including  $C_{>30}$  chains) in some samples, notably canned mackerels (McGrath et al., 2021). The authors hypothesised food processing and/or CP market shift towards long-chain CPs of use to longer chain PCAs. The methodology proposed in §3.2 to discriminate CP components from VCOs was applied retrospectively to the archived HRMS data. Our results clearly revealed the presence of VCOs in mackerel fillets canned in olive oil (Fig. S11), confirming the occurrence of such substances in canned foodstuffs and therefore human dietary exposure. In addition, of the few publications available on PVC oligomers, other authors have also demonstrated the presence of such substances (*i.e.* tetramer) in beverage PVC bottles, and no migration in four food simulants at their limit of detection (5–10  $\mu\text{g kg}^{-1}$ ) (Castle et al., 1996).

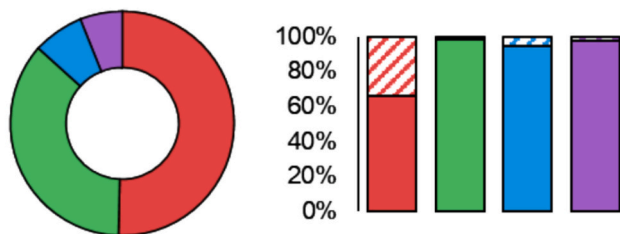
In indoor dust from Japan, VCOs accounted for 19 % of the  $\Sigma$ PCAs+PCOs. A plausible mechanism implies the volatilisation of VCOs from the omnipresent PVC items of daily life (window frames, floor coverings, electronic equipment, upholstery ...) in which they are ubiquitous, followed by their sorption to dust.

Considering all the foodstuffs and environmental matrices characterised, even though PCAs were detected in all samples, as in the case of PVC standards and PVC items, detection frequencies gradually decreased from 100 to 40 % for mono- to tri-unsaturated olefins. In

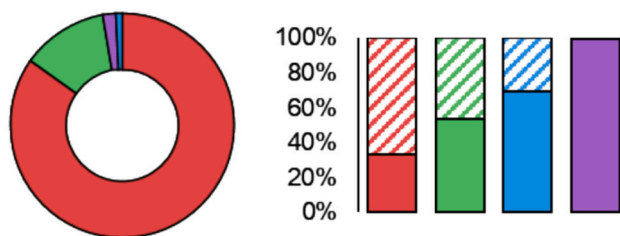
## PVC standards



## PVC items



## Foodstuffs, environmental matrices



**Fig. 3.** Averaged relative contributions of polychlorinated alkanes (PCAs), mono-, di- and tri-unsaturated olefins (PCmono-, di-, and tri-Os) in PVC standards, PVC items, foodstuffs and environmental matrices (left), and average relative contributions of vinyl chloride oligomers (VCOs) and non-VCOs for each subclass group (right).

addition, VCOs accounted for only 18 % of  $\Sigma$ PCAs+PCOs in the non-polymeric environmental matrices, which is specifically in line with the predominance of CPs, as illustrated in Fig. 3. Furthermore, CPs contributed to >97 % of total PCAs+PCOs in sediments and the three sewage sludge samples. In fact, CPs can be expected to have been produced and consequently released into the environment (see Glüge et al., 2016, 2018 for short-chain and medium-chain CPs, respectively) in much larger quantities than VCOs. To illustrate this, an estimate of total VCO tonnages was conducted in the present work. For doing so, the 0.2 % oligomer content calculated in §3.1.1 for Std-1 (extracted using THF) was combined with the total plastic production between 1950 and 2015 (i.e. 8.3 billion tons), of which about 10 % consisted of PVC (Geyer et al., 2017). Using these values, cumulative production volumes of around 1.7 million tons of VCOs could be estimated, which appears substantially lower than the 33 million tons of CPs produced and used between 1930 and 2020 (Chen et al., 2022). However, substantial uncertainties in VCO

tonnages can be anticipated, in line with the quantification errors discussed in §3.1.1, but also with batch-to-batch variability in oligomer content and other factors (e.g. PVC processing including removal of the carcinogenic vinyl chloride monomer, or moulding).

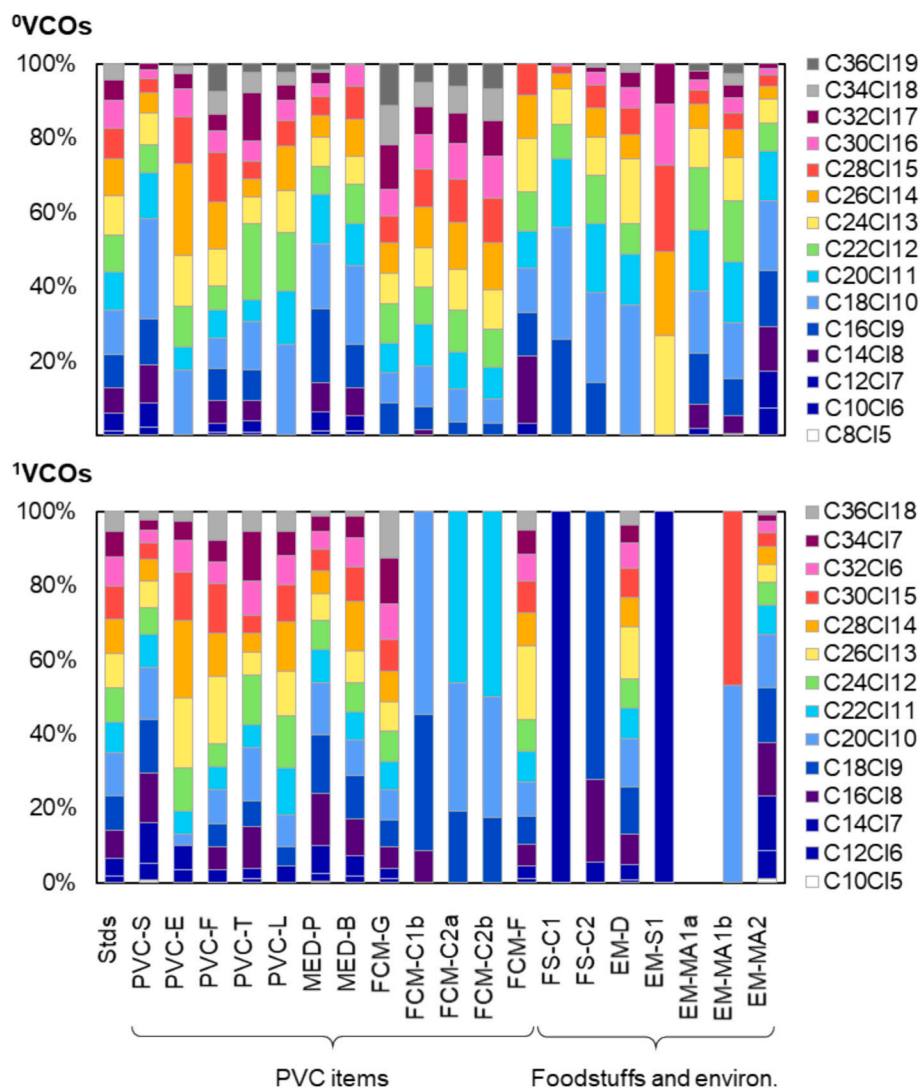
Another hypothesis for the low predominance of VCOs lies in the possible degradation of these substances once they are released in the environment. In particular, PVC is recognised as being more sensitive to UV rays compared with other polymers currently in use (Fernández-González et al., 2022). Such photodegradation involves the formation of polyene sequences by dechlorination (Gewert et al., 2015). Given the structural similarity between the PVC polymer and its oligomers, degradation processes involving UV rays and altering the former could also affect the latter. Other pathways likely to affect the environmental behaviour of VCOs include biotic degradation, volatilisation, leaching into the aqueous environment as well as potential selective uptake and metabolism occurring in living organisms. The observation of the outer and inner parts of the macroplastic fender is indicative of the possible depletion and/or degradation of VCOs in the present work. In the outer part, which appeared to have been weathered,  $^0$ VCOs,  $^1$ VCO and  $^2$ VCOs were 3 to 5 fold less intense compared to the inner part, and  $^3$ VCOs only detected in the outer part. This could indicate a greater susceptibility of the unsaturated oligomers to degradation and/or leaching. However, for the other macroplastic, the PVC panel, the relative contribution of PCOs was similar to those of the other PVC items, which prevents any conclusions from being drawn.

## 3.3.3. VCO homologue group patterns

For a better insight into the compositional patterns of VCOs, the homologue patterns for the two predominant subclasses detected,  $^0$ VCOs and  $^1$ VCOs, are presented in Fig. 4, as along with the average number of chlorine and carbon atoms.

In the canned foods, the number of  $^1$ VCO homologue groups detected was much lower than in the other samples (Fig. 4, FCM and FS samples). Interestingly, a substantially higher contribution of  $^2$ VCOs, equal to  $23 \pm 1$  % in 3 can coatings vs.  $1.7 \pm 1.6$  % on average in the other PVC items, was observed. This could be attributed to thermal degradation linked to hot filling or to the specificity of the PVC resin (i.e. vinylic organosol resin composed of high molecular weight PVC) (LaKind, 2013). As detailed in Table S6, strong positive correlations were found between the PCA patterns of the mackerel and tuna coatings (mean Spearman's R of 0.57–0.77), suggesting that these coatings are made from similar PVC resins. In addition, the patterns of the food matrices and their coatings correlated well (Spearman's R of 0.65–1.00), supporting the hypothesis of VCO migration from the coatings. These strong correlations do not, however, apply to PCOs (Spearman's R of  $-0.14$ – $0.39$ ), which also coincides with the decreasing relative contributions of the latter families to  $\Sigma$ PCAs+PCOs (PCmono-, di- and tri-Os contribution of 6 and 16 % in foodstuffs compared with an average of 38 % for the coatings). This suggests a preferential migration of VCOs from the coatings to the foodstuffs. Such selective migration is further illustrated by the increase of the relative contribution of  $C_{16}Cl_9$  to total PCAs, from 4 % in the coatings to 20 % in the foodstuffs (Fig. 4), and by a decrease from 6 % down to 0 % for the  $C_{36}Cl_9$  homologue group. These results are not surprising, as diffusion coefficients are expected to be lower for the VCOs of lower molecular weight (Schwarzenbach et al., 2002).

As with canned foods, migration could be expected from the medical blood bag (MED-B) and perfusion tube (MED-P), as short-chain VCOs contributed substantially to the  $^0$ VCO and  $^1$ VCO totals (Fig. 4). In contrast, the patterns of the PVC laboratory clamps (PVC-L) and the electrical cable sheath (PVC-E) presented relatively low contributions of short-chain VCOs. These items were the most worn, implying possible depletion of such lower VCOs from the PVC items. This hypothesis has already been put forward in §3.3.2 to explain the contamination of the indoor dust sample. It is supported by the similarities existing between the PCA and PCO patterns of the dust sample and those of the PVC



**Fig. 4.** Relative contributions of <sup>0</sup>VCOs-C<sub>2n</sub>Cl<sub>n+1</sub> and <sup>1</sup>VCOs-C<sub>2n</sub>Cl<sub>n</sub> homologue groups in PVC standards ( $n = 4$ ), PVC items ( $n = 12$ ), foodstuffs and environmental matrices ( $n = 7$ ) in which they were observed, with sample codes detailed in Table 1.

standards on the one hand (averaged Spearman's R of 0.74), and of other daily-life PVC items on the other hand (averaged Spearman's R of 0.50) (Table S7).

Finally, the examination of the PCA and PCO composition patterns between the PVC sewage pipe (PVC-S) and the PVC macroplastic panel (EM-MA2) could also give an indication of possible environmental degradation, as these were made from the same unplasticised PVC material. Very low correlations were observed between the patterns of <sup>2</sup>VCOs (Spearman's R of 0.09) and <sup>3</sup>VCOs (Spearman's R = 0.09), which could be partly related to the lower detection of these families. By contrast, the very high Spearman's R observed for <sup>0</sup>VCOs and <sup>1</sup>VCOs, equal to 0.94, is in favour of the absence of environmental degradation. Note that despite the immersion of the PVC panel for one year, its physical aspect did not show any alteration, except for important biofouling (Table S1). For the PVC fender found on a beach (EM-MA1), patterns of <sup>0</sup>VCOs corresponding to the inner part and to the weathered outer part were very similar, with Spearman's R of 0.95. However, an overall decrease in the signal intensities from the inner to the outer part suggested leaching rather than degradation (Fig. S12).

#### 4. Conclusion and perspectives

The primary objective of this study was to shed light on polyvinyl

chloride oligomers (VCOs), a class of compounds formed unintentionally in PVC. Their poor detectability by conventional non-targeted approaches involving GC/MS (low volatility of VCOs), LC/APCI-MS or LC/ESI-MS (Vaclavikova et al., 2016; Mézière et al., 2020b) explains why, so far, they have been disregarded, which contrasts with the large-scale use and production of PVC. Thanks to a LC method coupled with HRMS detection hyphenated with electrospray and chloride adduct enhancement, series of polychlorinated *n*-alkanes (PCAs) but also polychlorinated olefins (PCOs) of different saturation degrees, belonging to VCO series, could be described in the present work.

PCAs are a class of compounds often misnamed as chlorinated paraffins (CPs), the latter being a family of industrial chemicals produced in high volumes for a wide variety of applications (Fernandes et al., 2023). However, considering that PCAs also include saturated polyvinyl chloride oligomers (<sup>0</sup>VCOs), we proposed a methodology aimed at discriminating the signals arising from CPs from those arising from <sup>0</sup>VCOs. The presence of VCOs was then reported in a variety of PVC standards, PVC items used in various sectors (construction, consumer goods, healthcare, food contact materials), foodstuffs and environmental matrices. For VCOs, <sup>1</sup>VCOs were found to be the predominant group, followed by <sup>0</sup>VCOs, with up to 14 homologue groups detected. The structure of the former group was confirmed by <sup>1</sup>H NMR elucidation.

Like CPs, the ubiquitous presence of VCOs in PVC polymers

evidenced in this study implies possible releases to the environment via these primary sources, but also from *de novo* sources arising from alteration and degradation of PVC. These sources should be studied especially in view of the large volumes of improperly managed PVC waste that have already entered or will enter the environment over the next few decades. Considerable quantities of macro- and microplastics are already present in the environment (Shi et al., 2023) and ~500 million tons of PVC waste are expected by 2050 for China alone (Liu et al., 2020). The methodology proposed here would be helpful in studies focusing on micro- and nanoplastics, on the one hand by helping to resolve the common misidentification of aged PVC plastics that occurs when classical infrared spectroscopy is applied (Fernández-González et al., 2022). On the other hand, as stated in a recent review (Shi et al., 2023), the contribution of the oligomers and that of micro- and nanoplastics, in terms of their occurrence or toxicological profile, could be differentiated.

With regard to human exposure, several routes may be examined, including dermal contact and inhalation of indoor air in view of the widespread use of PVC in buildings and homes, dietary exposure linked to the consumption of foodstuffs in contact with PVC, or exposure through leaching of VCOs contained in PVC-based medical devices. To achieve this, analytical standards of VCOs are required for properly characterise human exposure routes, environmental occurrence and transformation pathways. These standards are also needed for toxicological studies, even though most of the VCOs identified in this work had masses >1000 Da, a fraction with a low probability of being absorbed by the gastro-intestinal tract (EFSA Panel, 2008). This is of crucial importance since, in the present study, we could not rule out the fact that these compounds might share structural similarities with the carcinogenic vinyl chloride monomer (IARC, 2012).

Overall, this study sheds light on vinyl chloride oligomers and raises the question of whether they pose a risk to the environment and humans.

#### CRediT authorship contribution statement

**Mathilde Godéré:** Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Guy Louarn:** Writing – review & editing, Validation. **Thomas J. McGrath:** Writing – review & editing, Investigation, Funding acquisition. **Antonin Padioleau:** Writing – review & editing, Investigation. **Cherine Amoura:** Writing – review & editing, Investigation. **Bruno Le Bizec:** Resources, Funding acquisition. **Gaud Dervilly:** Writing – review & editing, Supervision. **Arnaud Tessier:** Writing – review & editing, Validation, Resources, Methodology, Investigation, Formal analysis. **Ronan Cariou:** Writing – original draft, Visualization, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2025.178890>.

#### Data availability

Data will be made available on request.

#### References

- Andrady, A.L., Neal, M.A., 2009. Applications and societal benefits of plastics. *Philos. Trans. R. Soc. B* 364, 1977–1984. <https://doi.org/10.1098/rstb.2008.0304>.
- Boros, E., Bertha, F., Fetter, J., Vida, L., Kajtár-Peredy, M., Czira, G., 2004. Reductive dehalogenation of 4-halogenomethyl azetidin-2-one derivatives. Synthesis of (4-oxo-azetidin-2-yl)acetone nitriles. *J. Chem. Res.* 2004, 558–563. <https://doi.org/10.3184/0308234042563848>.
- Brits, M., van Velzen, M.J.M., Sefiloglou, F.Ö., Scibetta, L., Groenewoud, Q., Garcia-Vallejo, J.J., Vethaak, A.D., Brandsma, S.H., Lamoree, M.H., 2024. Quantitation of micro and nanoplastics in human blood by pyrolysis-gas chromatography–mass spectrometry. *Microplastics Nanoplastics* 4, 12. <https://doi.org/10.1186/s43591-024-00090-w>.
- Cariou, R., Rivière, M., Hutinet, S., Tebbaa, A., Dubreuil, D., Mathé-Allainmat, M., Lebreton, J., Le Bizec, B., Tessier, A., Dervilly, G., 2022. Thorough investigation of non-volatile substances extractable from inner coatings of metallic cans and their occurrence in the canned vegetables. *J. Hazard. Mater.* 435, 129026. <https://doi.org/10.1016/j.jhazmat.2022.129026>.
- Castle, L., Mayo, A., Crews, C., Gilbert, J., 1989. Migration of poly(ethylene terephthalate) (PET) oligomers from PET plastics into foods during microwave and conventional cooking and into bottled beverages. *J. Food Prot.* 52, 337–342. <https://doi.org/10.4315/0362-028X-52.5.337>.
- Castle, L., Price, D., Dawkins, J.V., 1996. Oligomers in plastics packaging. Part 1: migration tests for vinyl chloride tetramer. *Food Addit. Contam.* 13, 307–314. <https://doi.org/10.1080/02652039609374412>.
- Chen, C., Chen, A., Zhan, F., Wania, F., Zhang, S., Li, L., Liu, J., 2022. Global historical production, use, in-use stocks, and emissions of short-, medium-, and long-chain chlorinated paraffins. *Environ. Sci. Technol.* 56, 7895–7904. <https://doi.org/10.1021/acs.est.2c00264>.
- da Costa, J.P., Avellan, A., Mouneyrac, C., Duarte, A., Rocha-Santos, T., 2023. Plastic additives and microplastics as emerging contaminants: mechanisms and analytical assessment. *TrAC Trends Anal. Chem.* 158, 116898. <https://doi.org/10.1016/j.trac.2022.116898>.
- d'Antuono, P., Botek, E., Champagne, B., Wieme, J., Reyniers, M.-F., Marin, G.B., Adriaensens, P.J., Gelan, J.M., 2005. Density functional theory investigation of the stereochemistry effects on <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts of poly(vinyl chloride) oligomers. *Chem. Phys. Lett.* 411, 207–213. <https://doi.org/10.1016/j.cplett.2005.06.011>.
- Dawkins, J.V., Moody, C.J., Price, D., Castle, L., Howarth, O.W., 1995. Isolation and structural characterization of tetrameric oligomers of vinyl chloride. *Macromolecules* 28, 2985–2987. <https://doi.org/10.1021/ma00112a053>.
- EFSA Panel, 2008. Note for guidance for the preparation of an application for the safety assessment of a substance to be used in plastic food contact materials. *EFSA J.* 6, 21r. <https://doi.org/10.2903/j.efsa.2008.21r>.
- Eriksen, M., Cowger, W., Erdle, L.M., Coffin, S., Villarrubia-Gómez, P., Moore, C.J., Carpenter, E.J., Day, R.H., Thiel, M., Wilcox, C., 2023. A growing plastic smog, now estimated to be over 170 trillion plastic particles afloat in the world's oceans—urgent solutions required. *PLoS One* 18, e0281596. <https://doi.org/10.1371/journal.pone.0281596>.
- EU Reg 10/2011 Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Off. J. Eur. Union*, 15.1.2011.
- Fernandes, A.R., Krätschmer, K., McGrath, T.J., Yuan, B., Brandsma, S., Brits, M., Cariou, R., Letcher, R.J., Mueller, J., Muir, D., Vetter, W., Wang, T., Yu, G., Bergman, Å., 2023. Recommended terms and abbreviations for polychlorinated alkanes (PCAs) as the predominant component of chlorinated paraffins (CPs). *TrAC Trends Anal. Chem.* 169, 117363. <https://doi.org/10.1016/j.trac.2023.117363>.
- Fernández-González, V., Andrade-Garda, J.M., López-Mahía, P., Muniategui-Lorenzo, S., 2022. Misidentification of PVC microplastics in marine environmental samples. *TrAC Trends Anal. Chem.* 153, 116649. <https://doi.org/10.1016/j.trac.2022.116649>.

- Forrest, M.J., 1988. Characterisation of vinyl chloride oligomers (thesis). Loughborough University of Technology, p. 312. <https://hdl.handle.net/2134/27931>.
- Gewert, B., Plassmann, M.M., MacLeod, M., 2015. Pathways for degradation of plastic polymers floating in the marine environment. *Environ Sci Process Impacts* 17, 1513–1521. <https://doi.org/10.1039/C5EM00207A>.
- Geyer, R., Jambeck, J.R., Law, K.L., 2017. Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. <https://doi.org/10.1126/sciadv.1700782>.
- Gilbert, M., Patrick, S., 2017. Chapter 13 - poly(vinyl chloride). In: Gilbert, M. (Ed.), *Brydson's Plastics Materials*, Eighth edition. Butterworth-Heinemann, pp. 329–388. <https://doi.org/10.1016/B978-0-323-35824-8.00013-X>.
- Glüge, J., Wang, Z., Bogdal, C., Scheringer, M., Hungerbühler, K., 2016. Global production, use, and emission volumes of short-chain chlorinated paraffins – a minimum scenario. *Sci. Total Environ.* 573, 1132–1146. <https://doi.org/10.1016/j.scitotenv.2016.08.105>.
- Glüge, J., Schinkel, L., Hungerbühler, K., Cariou, R., Bogdal, C., 2018. Environmental risks of medium-chain chlorinated paraffins (MCCPs): a review. *Environ. Sci. Technol.* 52, 6743–6760. <https://doi.org/10.1021/acs.est.7b06459>.
- Heimrich, M., Nickl, H., Bönsch, M., Simat, T.J., 2015. Migration of cyclic monomer and oligomers from polyamide 6 and 66 food contact materials into food and food simulants: direct food contact. *Packag. Technol. Sci.* 28, 123–139. <https://doi.org/10.1002/pts.2094>.
- Hoppe, M., Fornari, R., de Voogt, P., Franz, R., 2017. Migration of oligomers from PET: determination of diffusion coefficients and comparison of experimental versus modelled migration. *Food Addit. Contam. Part A* 34, 1251–1260. <https://doi.org/10.1080/19440049.2017.1322222>.
- Hruska, Z., Guesnet, P., Salin, C., Couchoud, J.-J., 2007. Poly(chlorure de vinyle) ou PVC. *Techniques de l'Ingénieur* 23. <https://www.techniques-ingenieur.fr/base-documentaire/materiaux-th11/matieres-thermoplastiques-monographies-42147210/poly-chlorure-de-vinyle-ou-pvc-am3325/applications-am3325v2niv10004.html> (accessed 9.3.24).
- IARC, 2012. Chemical agents and related occupations. In: *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, volume 100F. World Health Organization.
- Kudzin, M.H., Piwowska, D., Festinger, N., Chrusciel, J.J., 2024. Risks associated with the presence of pPolyvinyl chloride in the environment and methods for its disposal and utilization. *Materials* 17, 173. <https://doi.org/10.3390/ma17010173>.
- LaKind, J.S., 2013. Can coatings for foods and beverages: issues and options. *Int. J. Technol. Policy Manag.* 13, 80–95. <https://doi.org/10.1504/IJTPM.2013.050999>.
- Lestido-Cardama, A., Sendón, R., Bustos, J., Nieto, M.T., Paseiro-Losada, P., Rodríguez-Bernaldo de Quirós, A., 2022. Food and beverage can coatings: a review on chemical analysis, migration, and risk assessment. *Compr. Rev. Food Sci. Food Saf.* 21, 3558–3611. <https://doi.org/10.1111/1541-4337.12976>.
- Liu, Y., Zhou, C., Li, F., Liu, H., Yang, J., 2020. Stocks and flows of polyvinyl chloride (PVC) in China: 1980–2050. *Resour. Conserv. Recycl.* 154, 104584. <https://doi.org/10.1016/j.resconrec.2019.104584>.
- Loos, M., Gerber, C., Corona, F., Hollender, J., Singer, H., 2015. Accelerated isotope fine structure calculation using pruned transition trees. *Anal. Chem.* 87, 5738–5744. <https://doi.org/10.1021/acs.analchem.5b00941>.
- Luo, H., Liu, C., He, D., Sun, J., Li, J., Pan, X., 2022. Effects of aging on environmental behavior of plastic additives: migration, leaching, and ecotoxicity. *Sci. Total Environ.* 849, 157951. <https://doi.org/10.1016/j.scitotenv.2022.157951>.
- Manasfi, T., Lebaron, K., Verlande, M., Dron, J., Demelas, C., Vassalo, L., Revenko, G., Quivet, E., Boudenne, J.-L., 2019. Occurrence and speciation of chlorination byproducts in marine waters and sediments of a semi-enclosed bay exposed to industrial chlorinated effluents. *Int. J. Hyg. Environ.* 222, 1–8. <https://doi.org/10.1016/j.ijheh.2018.06.008>.
- McGrath, T.J., Limonier, F., Poma, G., Bombeck, J., Winand, R., Vanneste, K., Andjelkovic, M., Van Hoeck, E., Joly, L., Covaci, A., 2021. Concentrations and distribution of chlorinated paraffins in Belgian foods. *Environ. Pollut.* 291, 118236. <https://doi.org/10.1016/j.envpol.2021.118236>.
- McGrath, T.J., Poma, G., Hutinet, S., Fujii, Y., Dodson, R.E., Johnson-Restrepo, B., Muenhor, D., Dervilly, G., Cariou, R., Covaci, A., 2023. An international investigation of chlorinated paraffin concentrations and homologue distributions in indoor dust. *Environ. Pollut.* 333, 121994. <https://doi.org/10.1016/j.envpol.2023.121994>.
- McGrath, T.J., Saint-Vanne, J., Hutinet, S., Vetter, W., Poma, G., Fujii, Y., Dodson, R., Johnson-Restrepo, B., Muenhor, D., Le Bizec, B., Dervilly, G., Covaci, A., Cariou, R., 2024. Detection of bromochloro alkanes in indoor dust using a novel CP-Seeker data integration tool. *Anal. Chem.* 96, 4942–4951. <https://doi.org/10.1021/acs.analchem.3c05800>.
- Mézière, M., Cariou, R., Larvor, F., Bichon, E., Guitton, Y., Marchand, P., Dervilly, G., Le Bizec, B., 2020a. Optimized characterization of short-, medium, and long-chain chlorinated paraffins in liquid chromatography-high resolution mass spectrometry. *J. Chromatogr. A* 1619, 460927. <https://doi.org/10.1016/j.chroma.2020.460927>.
- Mézière, M., Krätschmer, K., Perks, I., Zacs, D., Marchand, P., Dervilly, G., Le Bizec, B., Schächtele, A., Cariou, R., Vetter, W., 2020b. Addressing main challenges regarding short- and medium-chain chlorinated paraffin analysis using GC/ECNI-MS and LC/ESI-MS methods. *J. Am. Soc. Mass Spectrom.* 31, 1885–1895. <https://doi.org/10.1021/jasms.0c00155>.
- Mézière, M., Marchand, P., Hutinet, S., Larvor, F., Baéza, E., Le Bizec, B., Dervilly, G., Cariou, R., 2021a. Transfer of short-, medium-, and long-chain chlorinated paraffins to eggs of laying hens after dietary exposure. *Food Chem.* 343, 128491. <https://doi.org/10.1016/j.foodchem.2020.128491>.
- Mézière, M., Marchand, P., Larvor, F., Baéza, E., Le Bizec, B., Dervilly, G., Cariou, R., 2021b. Accumulation of short-, medium-, and long-chain chlorinated paraffins in tissues of laying hens after dietary exposure. *Food Chem.* 351, 129289. <https://doi.org/10.1016/j.foodchem.2021.129289>.
- Mijangos, C., Calafel, I., Santamaría, A., 2023. Poly(vinyl chloride), a historical polymer still evolving. *Polymer* 266, 125610. <https://doi.org/10.1016/j.polymer.2022.125610>.
- Philippe, A., Noël, C., Eyheraguibel, B., Briand, J.-F., Paul-Pont, I., Ghiglione, J.-F., Coton, E., Burgaud, G., 2023. Fungal diversity and dynamics during long-term immersion of conventional and biodegradable plastics in the marine environment. *Diversity* 15, 579. <https://doi.org/10.3390/d15040579>.
- Receu, P., Gorenšek, M., Žigon, M., 2002. The influence of treatment conditions on the quantity and composition of oligomers extracted from polyester fabric. *Text. Res. J.* 72, 447–453. <https://doi.org/10.1177/004051750207200512>.
- ResAP(2004)1, 2009. Policy statement concerning coatings intended to come into contact with foodstuffs. Version 3 – 12.02.2009. Partial Agreement in the social and public health field. Council of Europe. <https://rm.coe.int/16805156e5>.
- Schinkel, L., Lehner, S., Heeb, N.V., Marchand, P., Cariou, R., McNeill, K., Bogdal, C., 2018a. Dealing with strong mass interferences of chlorinated paraffins and their transformation products: an analytical guide. *TrAC Trends Anal. Chem.* 106, 116–124. <https://doi.org/10.1016/j.trac.2018.07.002>.
- Schinkel, L., Lehner, S., Knobloch, M., Lienemann, P., Bogdal, C., McNeill, K., Heeb, N.V., 2018b. Transformation of chlorinated paraffins to olefins during metal work and thermal exposure – deconvolution of mass spectra and kinetics. *Chemosphere* 194, 803–811. <https://doi.org/10.1016/j.chemosphere.2017.11.168>.
- Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2002. *Environmental Organic Chemistry*. John Wiley & Sons. <https://doi.org/10.1002/0471649643>.
- Shi, C., Wang, M., Wang, Z., Qu, G., Jiang, W., Pan, X., Fang, M., 2023. Oligomers from the synthetic polymers: another potential iceberg of new pollutants. *Environ. Health.* <https://doi.org/10.1021/envhealth.3c00086>.
- Starnes Jr., W.H., 2012. Overview and assessment of recent research on the structural defects in poly(vinyl chloride). *Polym. Degrad. Stab.* 97, 1815e1821. <https://doi.org/10.1016/j.polymdegradstab.2012.05.037>.
- Stuart, P., 2005. *Practical Guide to Polyvinyl Chloride*. iSmithers Rapra Publishing.
- ter Halle, A., Ladirat, L., Gendre, X., Goudouneche, D., Pusineri, C., Routaboul, C., Tenailleau, C., Duployer, B., Perez, E., 2016. Understanding the fragmentation pattern of marine plastic debris. *Environ. Sci. Technol.* 50, 5668–5675. <https://doi.org/10.1021/acs.est.6b00594>.
- United Nations Stockholm Convention POP Review Committee, 2017. Short-chain chlorinated paraffins, Decision POPRC-12/3. <https://www.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/Default.aspx>.
- United Nations Stockholm Convention POP Review Committee, 2022. Chlorinated paraffins with carbon chain lengths in the range C<sub>14-17</sub> and chlorination levels at or exceeding 45 per cent chlorine by weight, Decision POPRC-18/4. <https://www.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/Default.aspx>.
- Vaclavikova, M., Paseiro-Cerrato, R., Vaclavik, L., Noonan, G.O., DeVries, J., Begley, T. H., 2016. Target and non-target analysis of migrants from PVC-coated cans using UHPLC-Q-Orbitrap MS: evaluation of long-term migration testing. *Food Addit. Contam. Part A* 33, 352–363. <https://doi.org/10.1080/19440049.2015.1128564>.
- van Mourik, L.M., Gaus, C., Leonards, P.E.G., de Boer, J., 2016. Chlorinated paraffins in the environment: a review on their production, fate, levels and trends between 2010 and 2015. *Chemosphere* 155, 415–428. <https://doi.org/10.1016/j.chemosphere.2016.04.037>.
- Vasseghian, Y., Alimohamadi, M., Dragoi, E.-N., Sonne, C., 2023. A global meta-analysis of phthalate esters in drinking water sources and associated health risks. *Sci. Total Environ.* 903, 166846. <https://doi.org/10.1016/j.scitotenv.2023.166846>.
- Windsor, F.M., Durance, I., Horton, A.A., Thompson, R.C., Tyler, C.R., Ormerod, S.J., 2019. A catchment-scale perspective of plastic pollution. *Glob. Change Biol.* 25, 1207–1221. <https://doi.org/10.1111/gcb.14572>.