IPCP Webinar Series: POPs in plastic and monitoring approaches
Part III: Extraction, clean-up, and analysis of POPs in plastics

Screening of SCCPs/MCCPs and other plasticizers in PVC without extraction/clean-up by pyrolysis GC/MS

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Introduction

- Flexible PVC relies on the use of plasticizers, some of which are globally banned due to health and environmental concerns
- The understanding of plasticizer usage patterns in flexible PVC products in Thailand remains limited
  - partly due to the complexity and the associated high costs of materials testing
    - In our literature search, we did not come across any published studies investigating the presence of S/MCCPs in Thai flexible PVC products.
    - There is also a dearth of studies examining the usage of (non-targeted) plasticizers.
- Pyrolysis/thermal desorption gas chromatography-mass spectrometry (Py/TD-GC-MS) is used as a standard test method for assessing phthalate esters (PAEs) in polymers.
  - Py/TD GC-MS test method can potentially be extended for simultaneous evaluation of other compounds, including chlorinated paraffins (CPs) and non-PAE alternatives

Flexible PVC relies on the use of plasticizers

Certain plasticizers have been global ban due to health and environmental concerns

Primary Plasticizers

Ortho-phthalate esters (**PAEs**)

- Low MW
  - Restricted under EU REACH
  - BBP, DBP, **DEHP**, DIBP
  - Most popular in the past
- High MW
  - **DINP**, DIDP, DPHP

- **Adipate esters** (DOA, DEHA, DINA)
- **Terephthalate esters** (DEHT (DOTP))
- **Cyclohexanoate esters** (DINCH)
- **Trimellitate esters** (TOTM)
- **Benzoate esters** (DEGDB, INB)
- **Citrate esters** (ATBC, TBC, TEC)
- **Phosphate esters** (TPP)

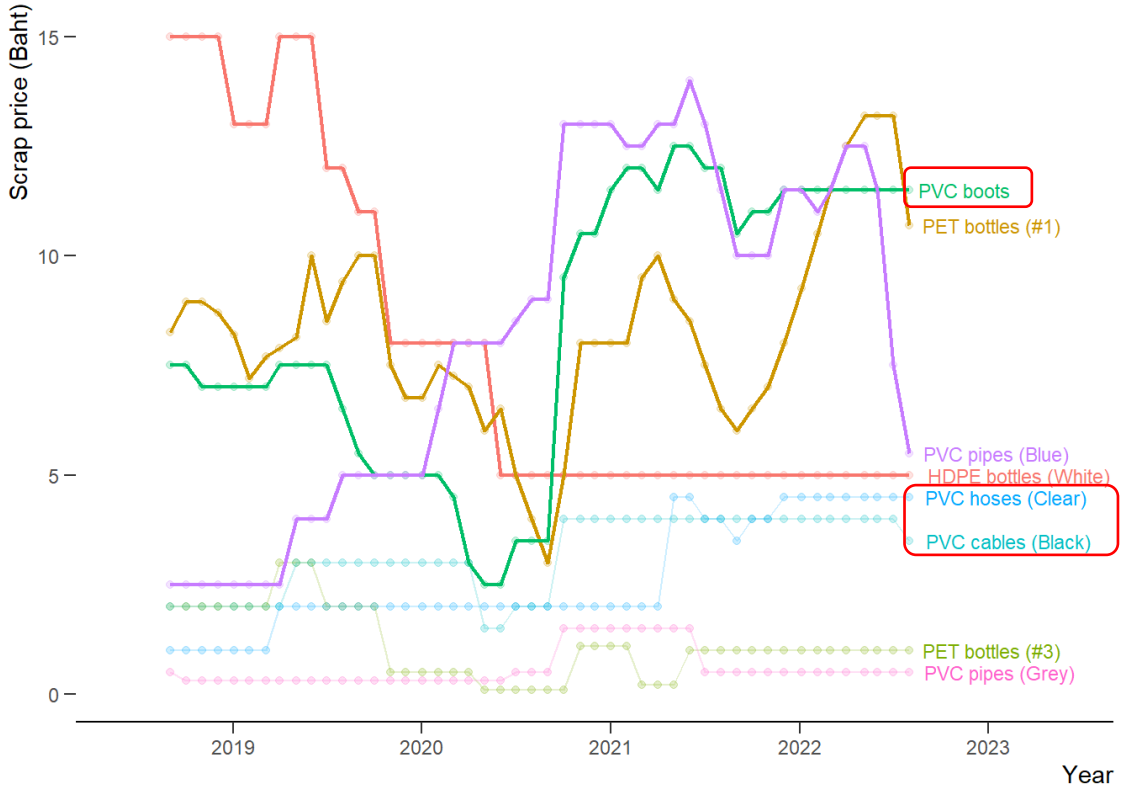
Secondary Plasticizers

- **SCCPs** — Listed in Annex A of SC
- **MCCPs** — Under review by POP reviewing committee
- **LCCPs**

Abbreviation
DEHA: di(2-ethylhexyl) adipate
DINA: diisononyl adipate
DEGDB: diethylene glycol dibenzoate
INB: isononyl benzoate
TPP: tris(2-ethylhexyl) phosphate
ATBC: Acetyl tributyl citrate
TBC: tributyl citrate
TEC: triethyl citrate (TEC))
For other more common PAEs please see page

Flexible PVC can be recycled

EOL PVC scraps can receive high 'buy-back' prices



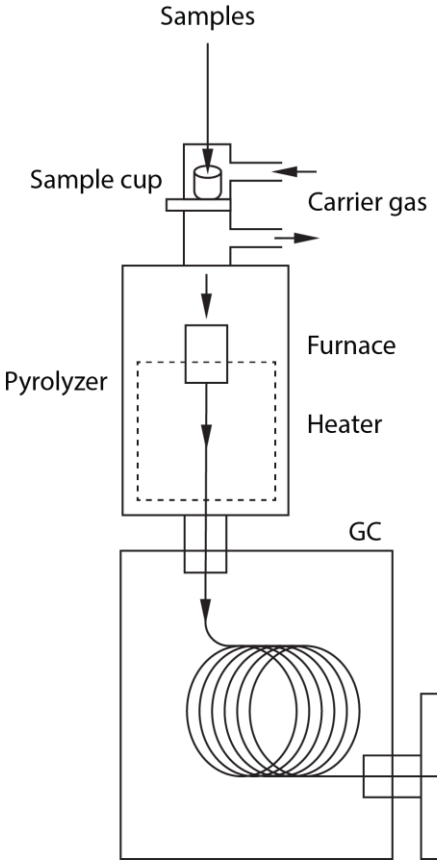
Buying prices of selected plastic scraps over the past 5 years, showing relatively high prices for flexible PVC scraps

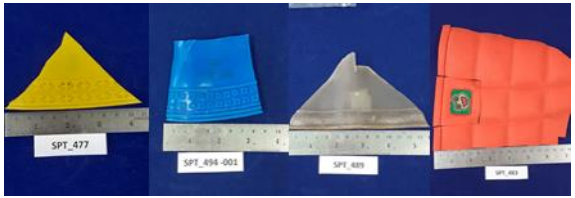
The targeted material for recycling of soft-PVC products may not be the PVC itself.

Data source: Wongpanit International, 2022, "Scrap Retail Price." http://www.wongpanit.com/list_history_price/

Py/TD-GCMS for screening of SCCPs/MCCPs and PAEs

- Adapted from IEC 62321-8: 2017 (Test method for PAEs in polymers)
- Analyze samples directly without the need for extraction or purification steps
  - save time & costs
  - reduce the risk of sample contamination or loss
  - can be useful for simultaneously screening of multiple constituents within the sample





PVC boots (n=35 boots, 43 samples)

PVC sheaths from wires and cables (n=56)

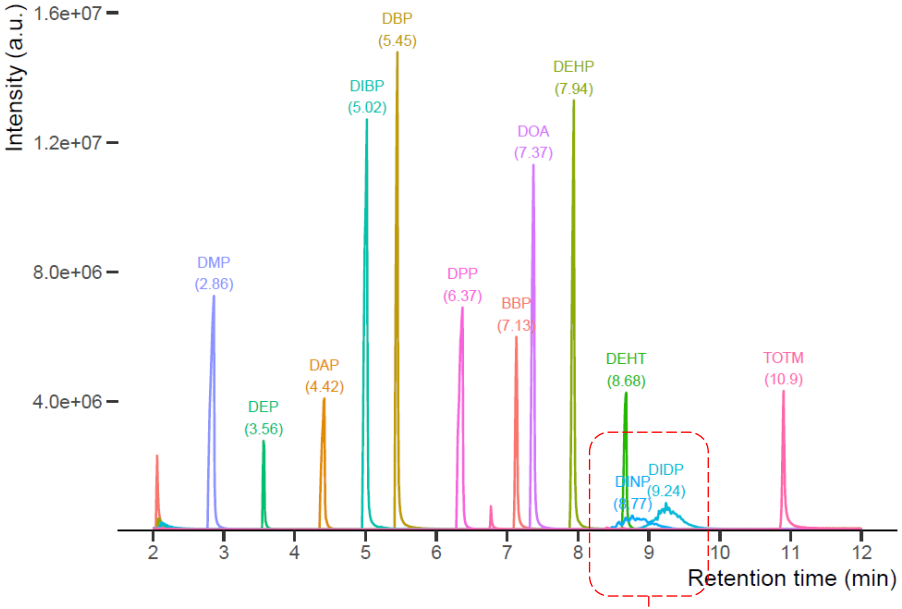
PVC (Vinyl) flooring sheets (n=24)

PVC Garden hoses (n=38)

Measurement conditions (adapted from IEC 62321-8: 2017)

Pyrolyzer	Frontier Lab; PY-2020ID; Single shot mode
Sample Mass	0.5 ± 0.3 mg
Furnace temperature	340°C, hold 1 minute
Py/GC interface temperature	300°C
GC	Shimadzu QP2010
Column	DB-5HT, 5% diphenyl/95% dimethyl polysiloxane 15 m × 0.25 mm × 0.05 µm
Injection mode	Split (split ratio: 1/300)
Inlet port temperature	300°C
Carrier gas	He (99.999%), 52.1 cm/s constant linear flow
Oven temperature program	80°C no hold, to 300°C at 20°C /min and hold for 5 min
MS	Shimadzu QP2010
Solvent Delay	2 min
Ion source temperature	230°C
Interface temperature	320°C
Detector voltage	Abs 0.85 kV
Ionization method	EI, 70 eV
SCAN range	50 – 1000 amu

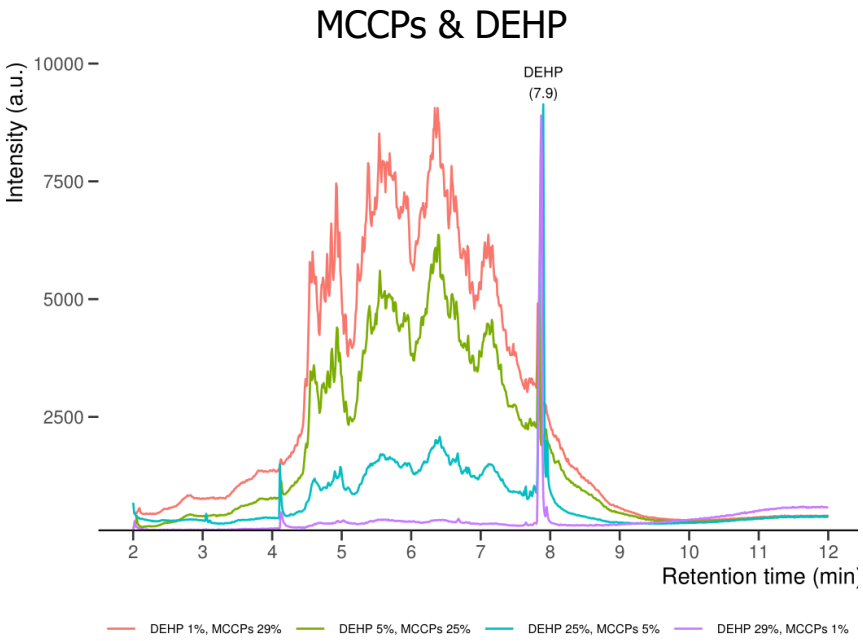
Py/TD GC-MS chromatograms from reference samples
(PAEs in PVC)

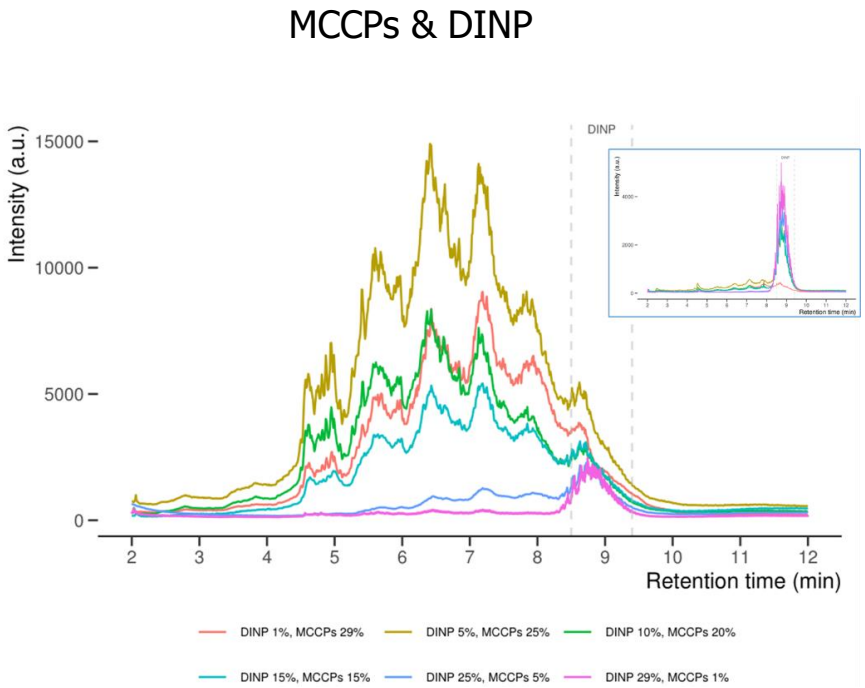


Py/TD-GC-MS total ion current chromatograms (SIM mode, overlaid, without normalization) from reference plasticized PVC samples, each with 30% of designated plasticizer and 70% virgin PVC resin.

DINP and DIDP are mixtures of branched isomers, which results in their chromatograms appearing as clusters of multiple low-intensity peaks but their GC-MS characteristics (retention times and at least 2 identifying ion masses, m/z) are distinguishable from the other plasticizers in this study

Py/TD GC-MS chromatograms from reference samples with binary mixture of MCCPs & DEHP (DINP)





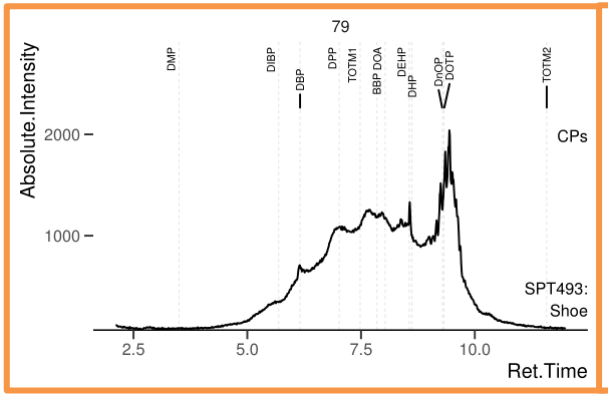
Due to the unavailability of commercial SCCPs, we were unable to produce flexible PVC samples with SCCPs & PAE mixtures (for pyrolysis study).

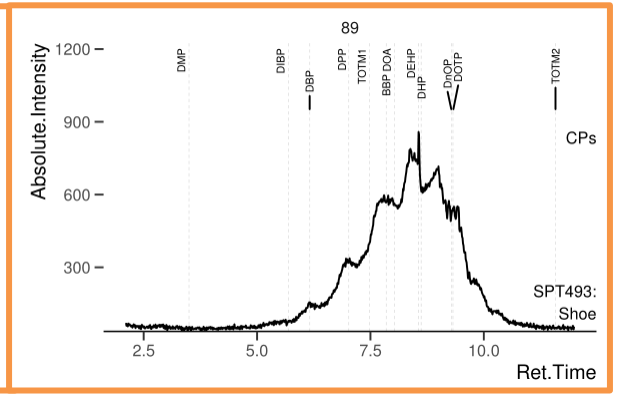
Targeted compounds & their MS characteristics

Compound	Abbr	CAS No	Retention time (min)	Identifying ion (m/z)*
Dimethyl phthalate	DMP	131-11-3	2.86	163, 77, 135, 94
Diethyl phthalate	DEP	84-66-2	3.56	147, 177, 65
Medium-chain chlorinated paraffins (C14-17)	MCCPs	Various (e.g., 85535-85-9, 198840-65-2, 1372804-76-6)	4.0 - 9.0	79, 89, 91, 105, 115, 125, 151
Short-chain chlorinated paraffins (C10-13)	SCCPs	Various (e.g., 85535-84-8, 68920-70-7, 85536-22-7)	not identified in this study due to lack of reference materials	79, 89, 91, 105, 115, 125, 151
Diallyl phthalate	DAP	131-17-9	4.42	149, 104, 189, 63
Diisobutyl phthalate	DIBP	84-69-5	5.02	149, 57, 104, 223
Dibutyl phthalate	DBP	84-74-2	5.45	149, 205, 223
Dipentyl phthalate	DPP	131-18-0	6.37	149, 55, 104, 237
Benzyl butyl phthalate	BBP	85-68-7	7.13	149, 91, 104, 206
Di(2-ethylhexyl) Adipate	DOA	103-23-1	7.37	129, 57, 147
Dicyclohexyl phthalate	DCHP	84-61-7	7.82	149, 55, 83, 249
Diheptyl phthalate	DHP	3648-21-3	7.91	147, 57, 265
Diethylhexyl phthalate	DEHP	117-81-7	7.94	149, 57, 113, 279
Diisononyl cyclohexane-1,2-dicarboxylate	DINCH	166412-78-8	8.10 - 9.00	155, 127, 281
Diisononyl phthalate	DINP	28553-12-0# and 68515-48-0	8.25 - 9.75	149, 71, 85, 293
Di-n-Octyl phthalate	DnOP	117-84-0	8.63	149, 57, 279
Di(2-ethylhexyl) terephthalate	DEHT	6422-86-2	8.68	70, 112, 261
Diisodecyl phthalate	DIDP	26761-40-0	8.75 - 10.00	149, 57, 85, 307
Tris(2-ethylhexyl) trimellitate	TOTM	3319-31-1	6.77 10.9	70, 83, 175 305, 57, 193, 113

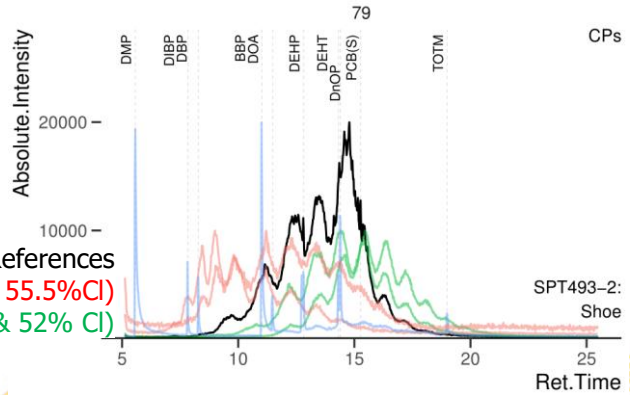
Results

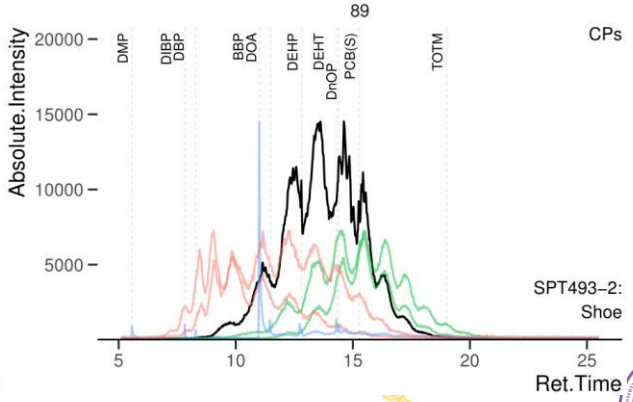
Py/TD
GC-MS





Solvent
Extraction
GC-MS





References
Red=SCCPs (63% & 55.5%Cl)
Green=MCCPs (57% & 52% Cl)

Random confirmation
@ 20% frequency

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Results summary

Performance of the Py/TD-GC-MS screening method,
as validated by ultrasonic solvent extraction GC-MS method

No false positive.

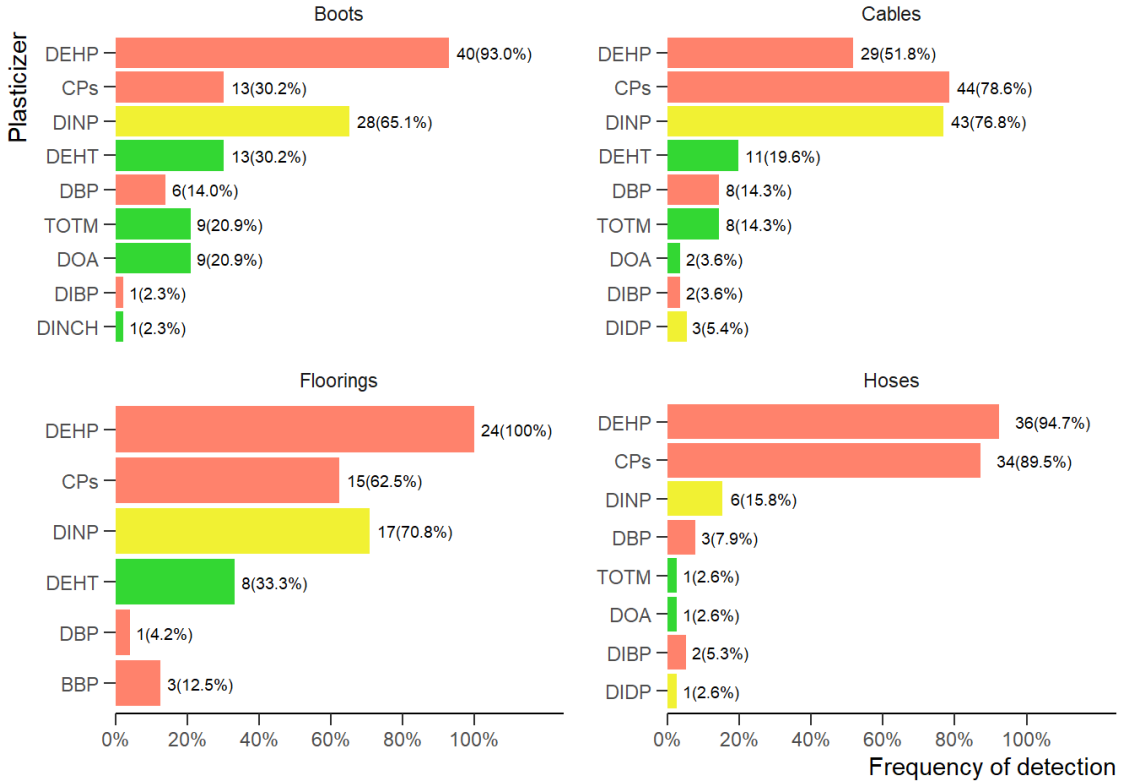
The false negatives can be attributed to our method's limitations in detecting specific substances at low concentrations, which is a trade-off we accepted to enable simultaneous screening of all targeted plasticizers.

Indicator	BBP	CPs	DBP	DEHP	DEHT	DIBP	DIDP	DINCH	DINP	DOA	TOTM	Overall
True positive (TP)	1	23	7	27	11	2	0	0	19	6	6	102
True negative (TN)	32	10	22	4	19	31	33	32	9	20	13	225
False negative (FN)	0	0	4	2	3	0	0	1	5	7	14	36
False positive (FP)	0	0	0	0	0	0	0	0	0	0	0	0
Accuracy (%)	100	100	87.8	93.9	90.9	100	100	96.9	84.8	78.7	57.5	**90.0**
Precision (%)	100	100	100	100	100	100	NA	NA	100	100	100	100
Sensitivity (%)	100	100	63.6	93.1	78.5	100	NA	0	79.1	46.1	30	73.9
Specificity (%)	100	100	100	100	100	100	100	100	100	100	100	100
F1-Score (%)	100	100	77.7	96.4	87.9	100	NA	NA	88.3	63.1	46.1	84.9

Our method has not yet been capable of differentiating S/MCCPs

Key findings

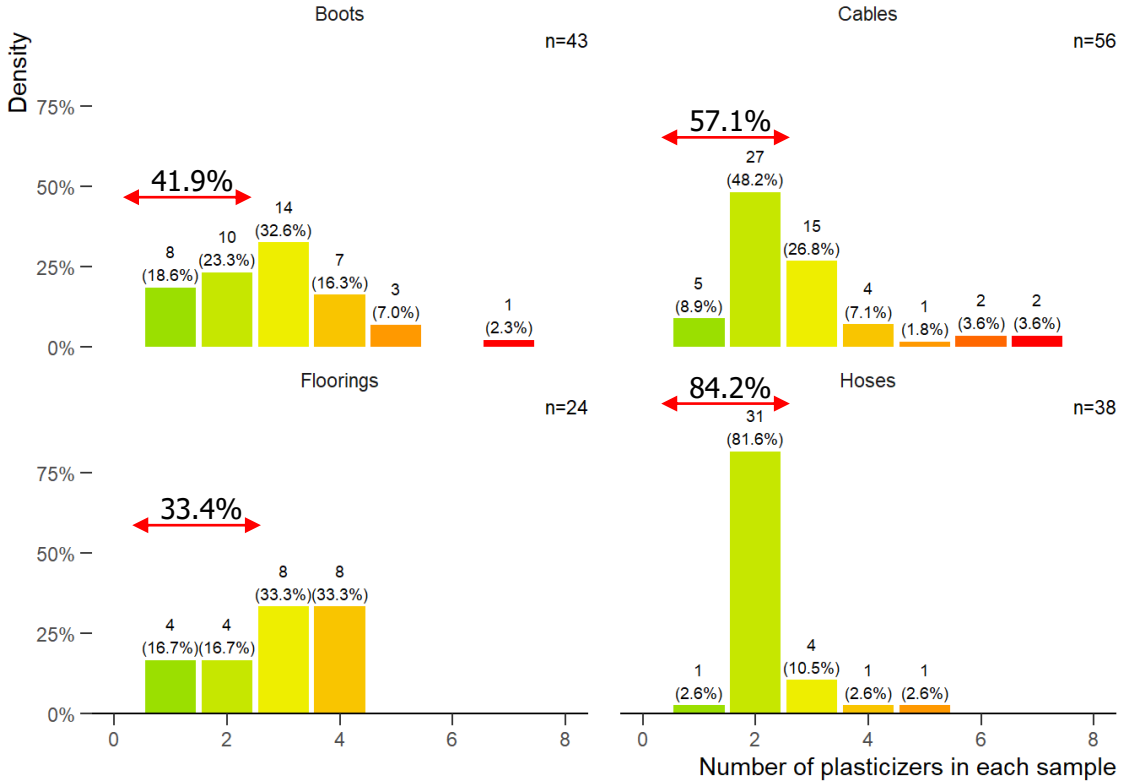
most 'popular' plasticizers



Mixture of DEHP and CPs is the most popular plasticizer combination, except for cable sheaths where DEHP has been replaced by DINP.

Key findings (2)

number of plasticizers within each sample



High number of plasticizers within each sample indicating high degree of mixing of feedstocks from diverse sources

The hoses exhibit a low degree of mixing, likely attributed to their clear appearance.

Conclusion

- We have demonstrated that Py/TD-GC-MS can be used to simultaneously screen PAEs, PAE alternatives, and CPs in soft PVC products
  - The method is fast and economical, hence allows us to cover sufficiently large number of samples to reveal plasticizer usage patterns.
- This study shows the widespread intermixing of several plasticizers, restricted and non-restricted, in the selected product groups that can come into close and prolonged contact with users
  - Since there is no obvious incentive for producers to intentionally apply many types of plasticizers into each individual product, this intermixing can be attributed to uncontrolled open-loop recycling.
- In order to transition towards a circular economy (CE) safely, the risks associated with this indirect recycling of plasticizers should be managed, preferably from the design stage or upstream of the product's first life.

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Circular economy without chemicals controls? Evidence of recirculated toxic plasticizers in flexible PVC products

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THANK YOU

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