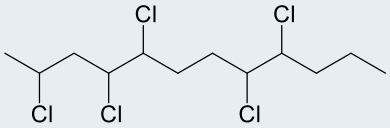
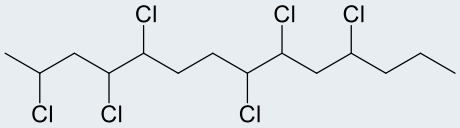
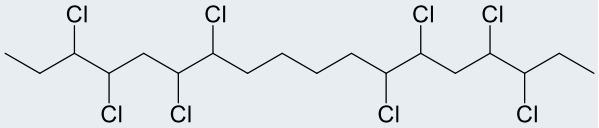
Analysis of SCCPs and MCCPs with LC-MS/MS

Hidenori Matsukami, Yago Guida, Natsuko Kajiwara
National Institute for Environmental Studies, Japan

Chlorinated paraffins (CPs)

Short-chain CPs (SCCPs)	Medium-chain CPs (MCCPs)	Long-chain CPs (LCCPs)
Alkanes, C_{10}-C_{13}, chloro-	Alkanes, C_{14}-C_{17}, chloro-	Alkanes, C_{18}-C_{30}, chloro-
		
$C_{12}H_{21}Cl_5$	$C_{14}H_{24}Cl_6$	$C_{18}H_{30}Cl_8$

- Since the 1930s, commercial mixtures of CPs have been produced mainly for use as metal-working lubricants and polyvinyl chloride (PVC) plasticizers.
- SCCPs are chemicals of concern because of their environmental persistence, bioaccumulation, and inherent toxicity.
- In 2017, SCCPs was listed in Annex A of the Stockholm Convention on POPs.

SCCP wastes under the Basel Convention

- SCCP wastes at concentrations above the low POP content value (100 or 10,000 mg/kg) must be destroyed or irreversibly transformed in an environmentally sound manner under the Basel Convention's technical guidelines on the management of POP wastes.

- The Estimated volumes of PVC and rubber waste containing SCCPs used in between 1935 to 2015 might reach about 2 million metric tons in total, be yet to peak around 2021, and continue until 2100 (Glüge et al., 2016).

- Little information exists on wastes and consumer products containing CPs for the appropriate management of SCCP wastes.

- Identification of wastes SCCPs content above the LPC value (100 or 10000 mg/kg) is needed for their effective environmentally sound management.

Analytical method for the determination of CPs

MS	Separation	Ionization	Sample	Reference
Magnetic sector-HRMS	GC	NCI	Biota, sediment	Tomy et al., 1997
TOF-HRMS	GC	NCI	Food	Takasuga et al., 2011
TOF-HRMS	-	APCI	Sludge, air	Bogdal et al., 2015
Orbitrap-HRMS	GC	NCI	Food	Krätschmer et al., 2018
QQQMSMS	GC	EI	Biota	Zencak et al., 2004
QMS	GC	NCI	Biota	Coelhan, 1999
QMS	GC	NCI	Leather	ISO 18219, 2015
QMS	GC	NCI	Water	ISO/DIS 12010, 2018

- HRMS can resolve homologues yielding ions, can reduce background interference, and can improve detection accuracy.
- Not all laboratories and institutions can afford, or have access to, an HRMS system.

Analytical method for the determination of CPs

MS	Separation	Ionization	Sample	Reference
Magnetic sector-HRMS	GC	NCI	Biota, sediment	Tomy et al., 1997
TOF-HRMS	GC	NCI	Food	Takasuga et al., 2011
TOF-HRMS	-	APCI	Sludge, air	Bogdal et al., 2015
Orbitrap-HRMS	GC	NCI	Food	Krätschmer et al., 2018
QQQMSMS	GC	EI	Biota	Zencak et al., 2004
QMS	GC	NCI	Biota	Coelhan, 1999
QMS	GC	NCI	Leather	ISO 18219, 2015
QMS	GC	NCI	Water	ISO/DIS 12010, 2018

- GC-NCI-QMS is a common means of determining CP content in industrial and environmental samples.
- This approach requires time-consuming clean-up and fractionation of samples to minimize interference from other halogenated compounds in the sample.
- Cheaper, more accessible, and practical methods for examining CP contamination in wastes are needed.

Our LC-MS/MS method

Chemosphere 244 (2020) 125531

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes

Hidenori Matsukami [a, *], Hiroaki Takemori [b], Takumi Takasuga [b], Hidetoshi Kuramochi [a], Natsuko Kajiwara [a]

[a] Center for Material Cycles and Waste Management Research, National Institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba, 305-8506, Japan
[b] Shimadzu Techno-Research, Inc. 1 Nishinokyo-Shimoai-cho, Nakagyo-Ku, Kyoto, 604-8436, Japan

HIGHLIGHTS

- Novel mass spectrometric method to quantify SCCPs in plastic wastes was developed.
- Major SCCP homologues were identified with good separation and peak width.
- Present data were in good agreement with high-resolution mass spectrometry data.
- Plastic wastes containing SCCPs above Basel Convention limits can be identified.

LC-MS/MS system is useful to measure not only SCCPs, but also MCCPs, LCCPs, PFAS, pesticides, pharmaceuticals, and many environmental contaminants.

Today's topics

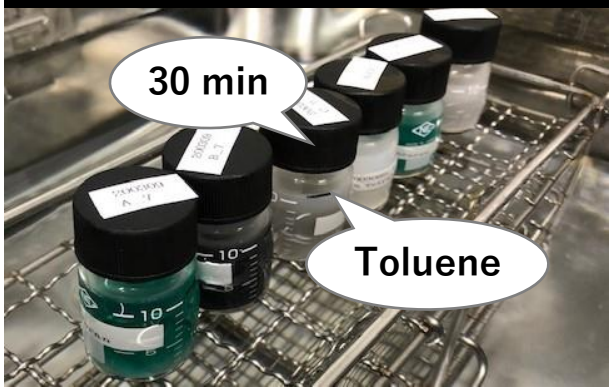
1. **Our LC-MS/MS method to screen wastes and consumer products containing CPs.**
2. Results of the inter-laboratory study for the screening of wastes and consumer products containing CPs.

Screening for wastes and consumer products containing CPs

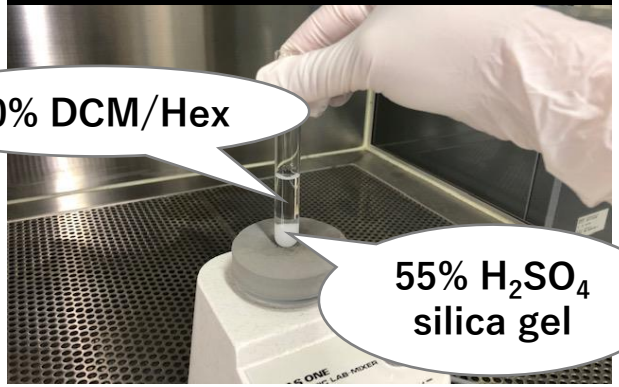
National Institute for Environmental Studies, Japan

1. Powdering

2. Ultrasonic extraction

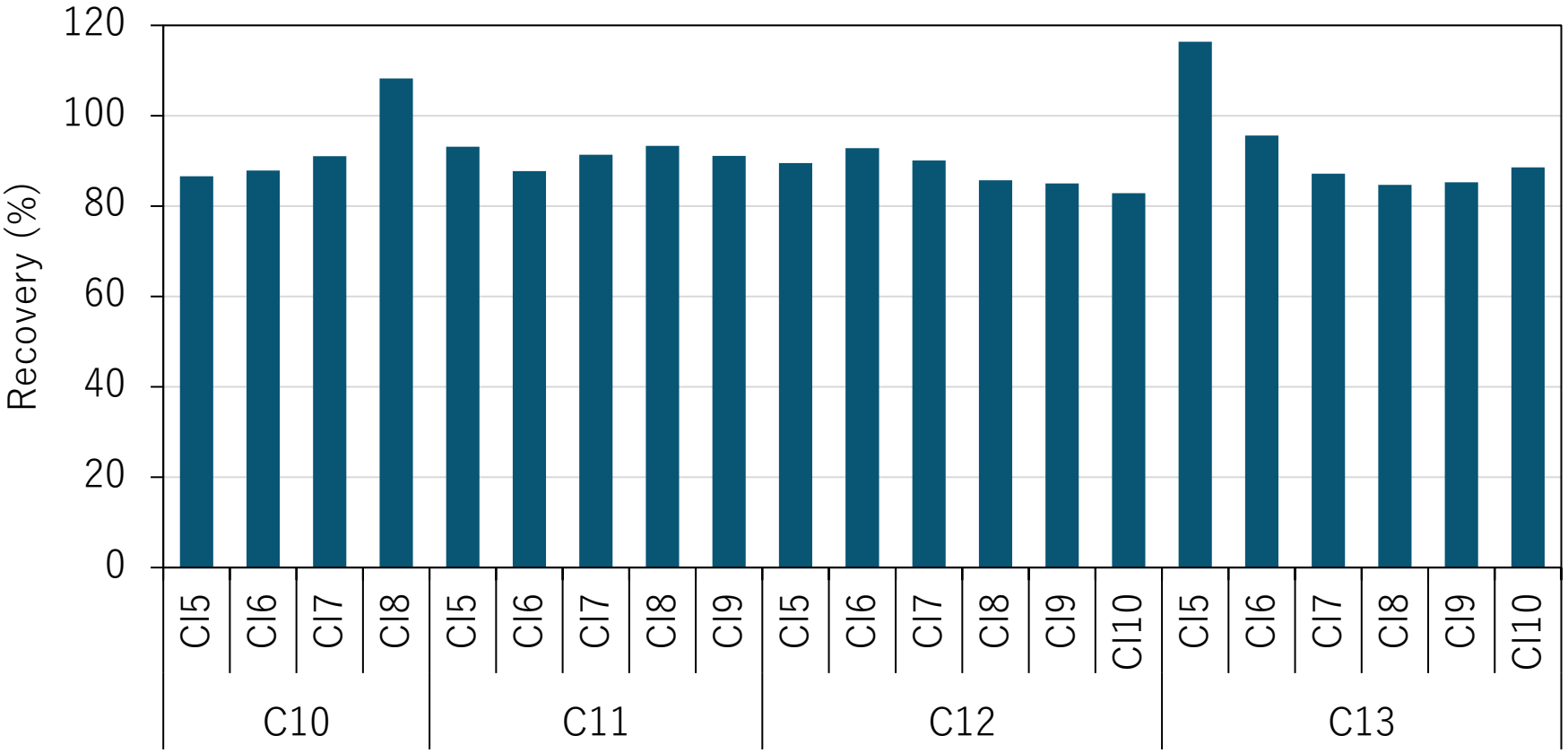


3. Cleanup



4. LC-MS/MS measurement

QAQC of waste sample preparation



Average recoveries of SCCP homologues from the spiked wastes were 85–104%.

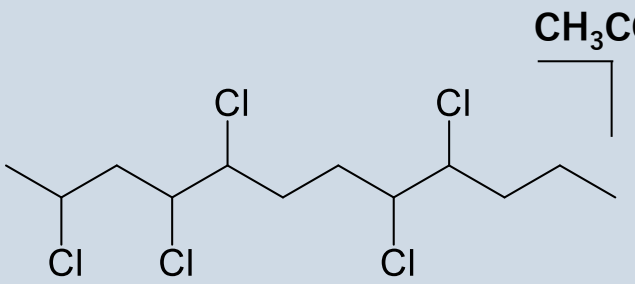
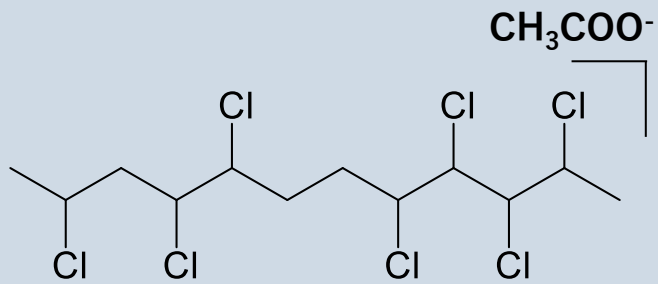
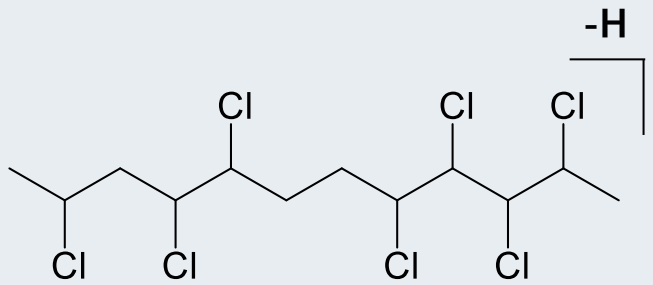
SCCP homologues in procedural blanks were below the method detection limits.

LC-MS/MS parameters

Liquid chromatograph	Waters ACQUITY UPLC H-Class
Column	ZORBAX SB-CN (2.1x100 mm, 1.8 μm) (Agilent)
Column temperature	40℃
Mobile phase A	H_2O with 5 mM ammonium acetate
Mobile phase B	Methanol with 5 mM ammonium acetate
Gradient (%B)	0 min (60%) – 5 min (73%) – 20 min (99%) – 22 min (99%) – 22.1 min (60%)
Flow rate	0.4 mL/min
Injection volume	5 μL

Mass spectrometer	Waters Xevo TQ-S micro
Ionization method	ESI negative
Capillary voltage	0.75 kV
Ion source temperature	110℃
Desolvation temperature	500℃
Desolvation gas flow	1000 L/hr
Cone gas flow	20 L/hr
Cone voltage	20 V

MRM transition

	Lower chlorinated congener $C_{12}H_{21}Cl_5$	Higher chlorinated congener $C_{12}H_{19}Cl_7$
Precursor ion	 Acetate-adduct molecule	 Acetate-adduct molecule
Product ion	CH_3COO^- Acetate ion	 Deprotonated molecule

MRM transitions (SCCPs)

MRM (C10 Cl4-8)	
C10Cl4	m/z 339>59
C10Cl5	m/z 373>59
C10Cl6	m/z 407>347
C10Cl7	m/z 441>381
C10Cl8	m/z 477>417
C10Cl9	NA
C10Cl10	NA

MRM (C11 Cl4-9)	
C11Cl4	m/z 353>59
C11Cl5	m/z 387>59
C11Cl6	m/z 421>361
C11Cl7	m/z 455>395
C11Cl8	m/z 491>431
C11Cl9	m/z 525>465
C11Cl10	NA

MRM (C12 Cl4-10)	
C12Cl4	m/z 367>59
C12Cl5	m/z 401>59
C12Cl6	m/z 435>375
C12Cl7	m/z 469>409
C12Cl8	m/z 505>445
C12Cl9	m/z 539>479
C12Cl10	m/z 573>513

MRM (C13 Cl4-10)	
C13Cl4	m/z 381>59
C13Cl5	m/z 415>59
C13Cl6	m/z 449>389
C13Cl7	m/z 483>423
C13Cl8	m/z 519>459
C13Cl9	m/z 553>493
C13Cl10	m/z 587>527

MRM transitions (MCCPs)

MRM (C14 Cl4-10)	
C14Cl4	m/z 395>59
C14Cl5	m/z 429>59
C14Cl6	m/z 463>59
C14Cl7	m/z 497>437
C14Cl8	m/z 533>473
C14Cl9	m/z 567>507
C14Cl10	m/z 601>541

MRM (C15 Cl4-10)	
C15Cl4	m/z 409>59
C15Cl5	m/z 443>59
C15Cl6	m/z 477>59
C15Cl7	m/z 511>451
C15Cl8	m/z 547>487
C15Cl9	m/z 581>521
C15Cl10	m/z 615>555

MRM (C16 Cl4-10)	
C16Cl4	m/z 423>59
C16Cl5	m/z 457>59
C16Cl6	m/z 491>59
C16Cl7	m/z 525>465
C16Cl8	m/z 561>501
C16Cl9	m/z 595>535
C16Cl10	m/z 629>569

MRM (C17 Cl4-10)	
C17Cl4	m/z 437>59
C17Cl5	m/z 471>59
C17Cl6	m/z 505>59
C17Cl7	m/z 539>479
C17Cl8	m/z 575>515
C17Cl9	m/z 609>549
C17Cl10	m/z 643>583

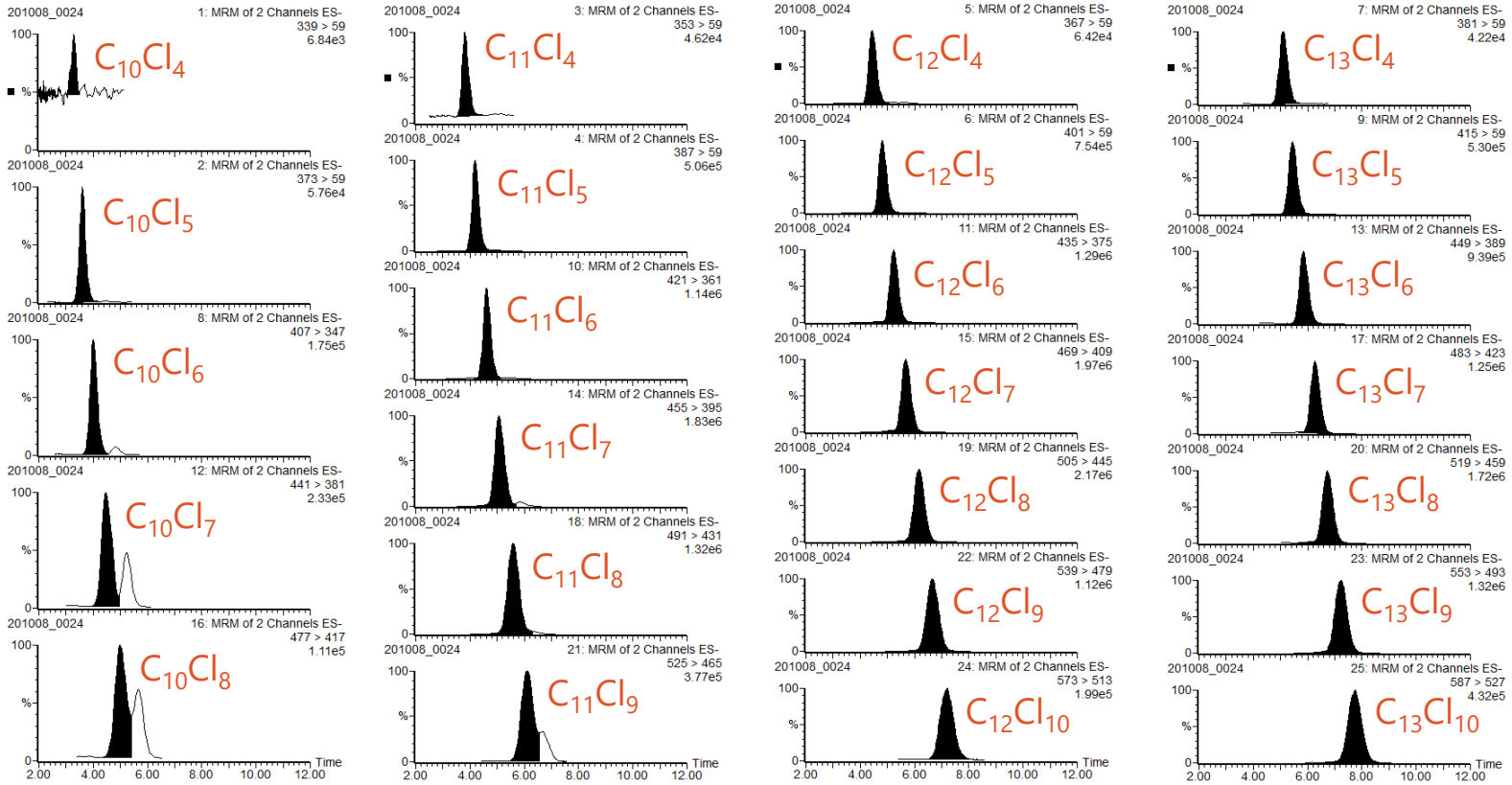
MRM transitions (LCCPs)

MRM (C18 Cl4-10)	
C18Cl4	m/z 451>59
C18Cl5	m/z 485>59
C18Cl6	m/z 519>59
C18Cl7	m/z 553>493
C18Cl8	m/z 589>529
C18Cl9	m/z 623>563
C18Cl10	m/z 657>597

MRM (C19 Cl4-10)	
C19Cl4	m/z 465>59
C19Cl5	m/z 499>59
C19Cl6	m/z 533>59
C19Cl7	m/z 567>507
C19Cl8	m/z 603>543
C19Cl9	m/z 637>577
C19Cl10	m/z 671>611

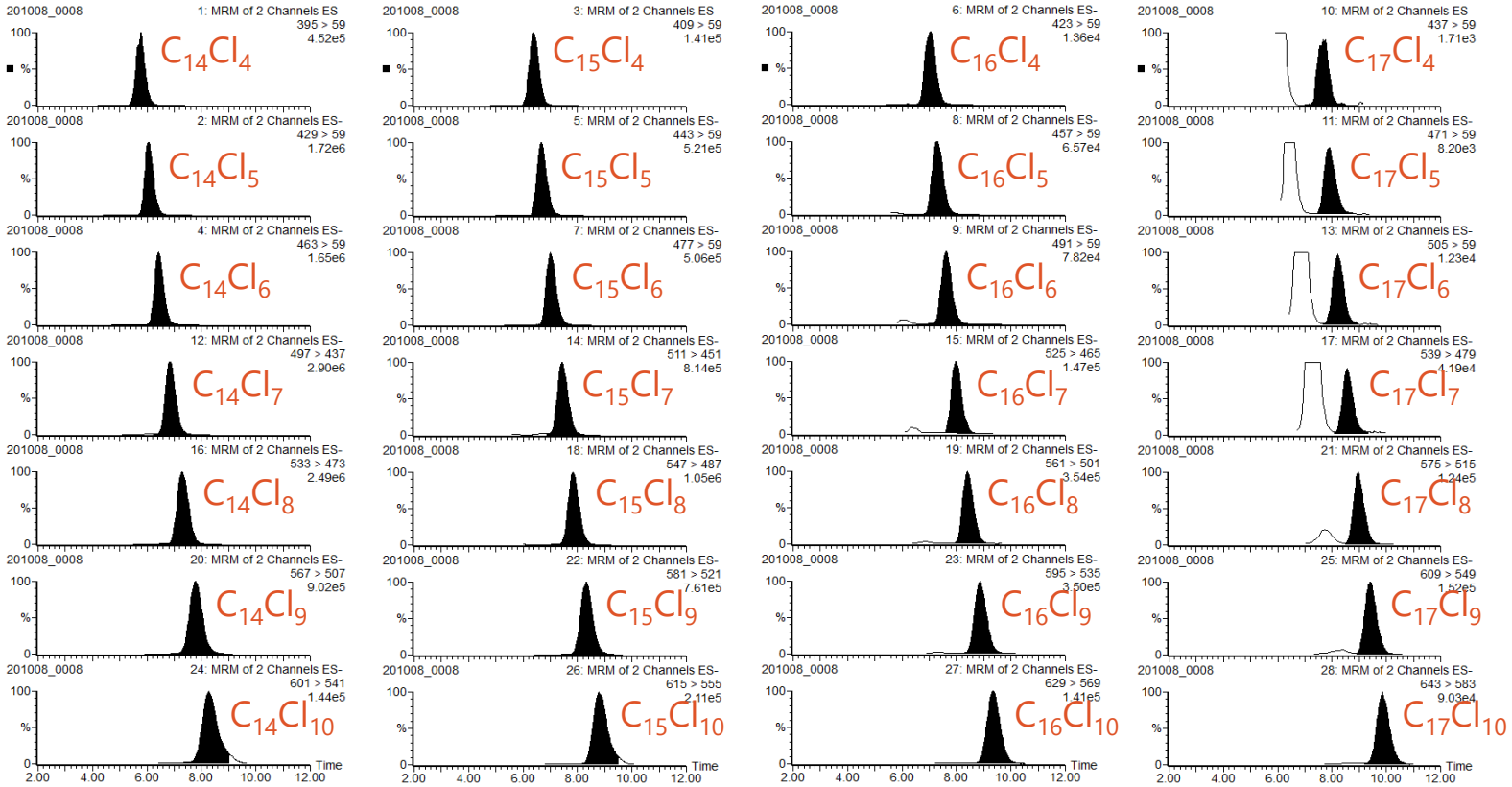
MRM (C20 Cl4-10)	
C20Cl4	m/z 479>59
C20Cl5	m/z 513>59
C20Cl6	m/z 547>59
C20Cl7	m/z 581>521
C20Cl8	m/z 617>557
C20Cl9	m/z 651>591
C20Cl10	m/z 685>625

Chromatograms of SCCPs



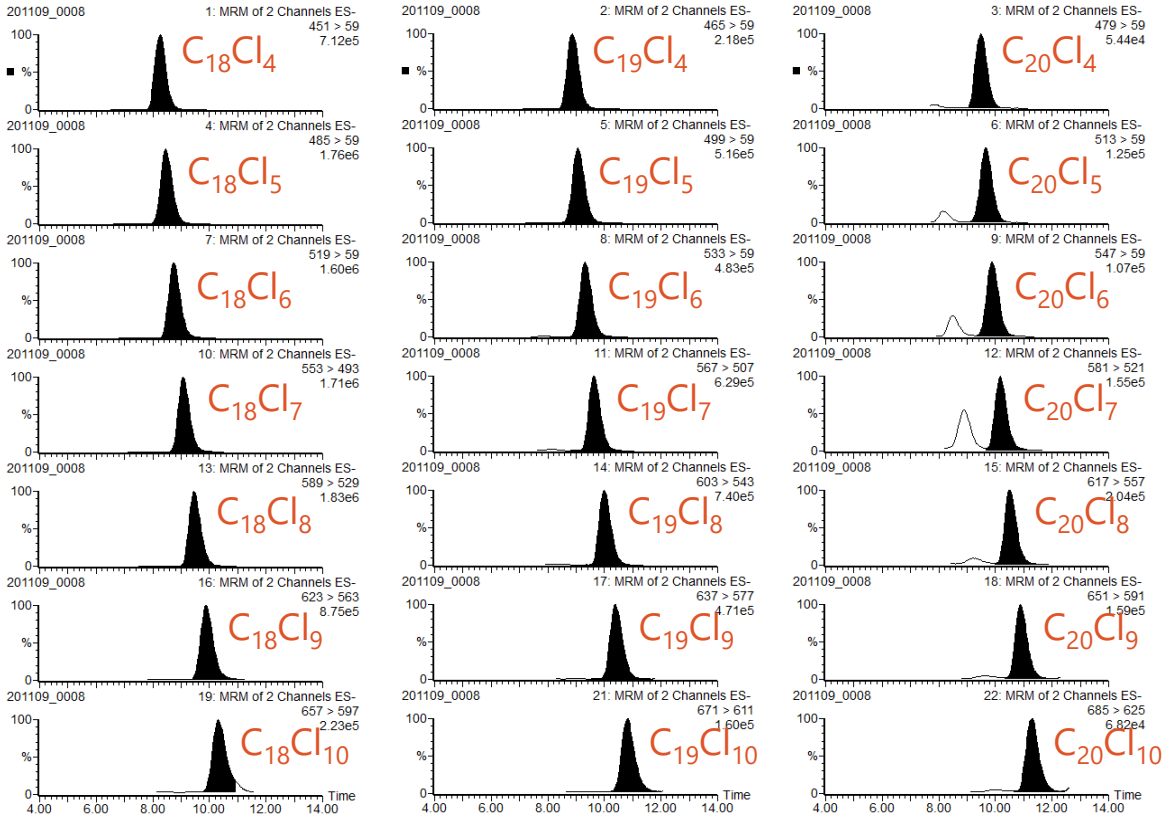
A marked improvement in peak separation of 25 congeners of SCCPs was achieved by our LC-MS/MS method.

Chromatograms of MCCPs



28 congeners of MCCPs were also separated and identified by our LC-MS/MS method.

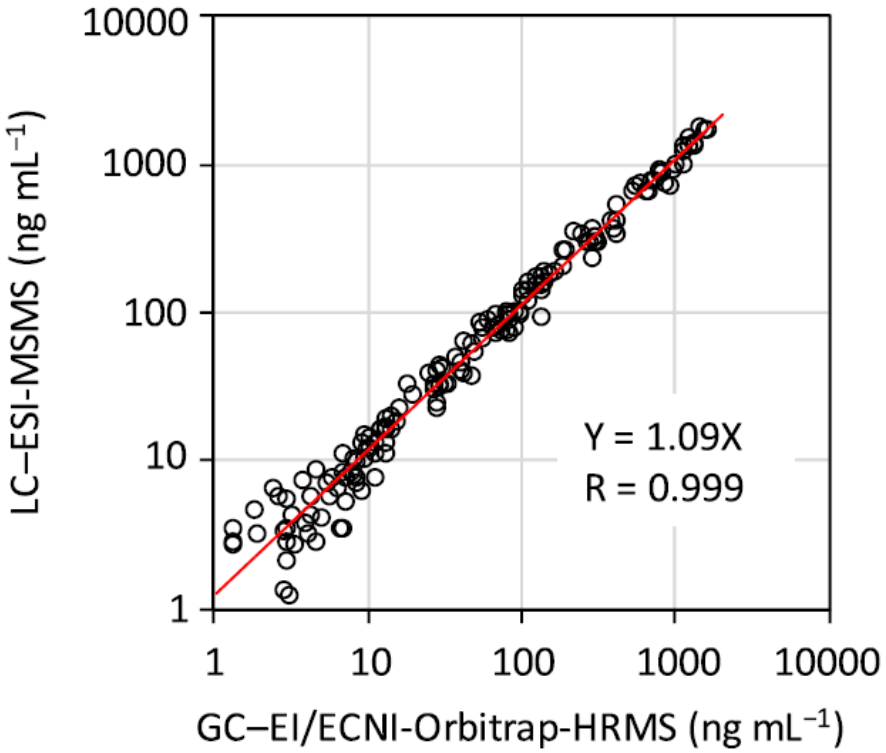
Chromatograms of LCCPs



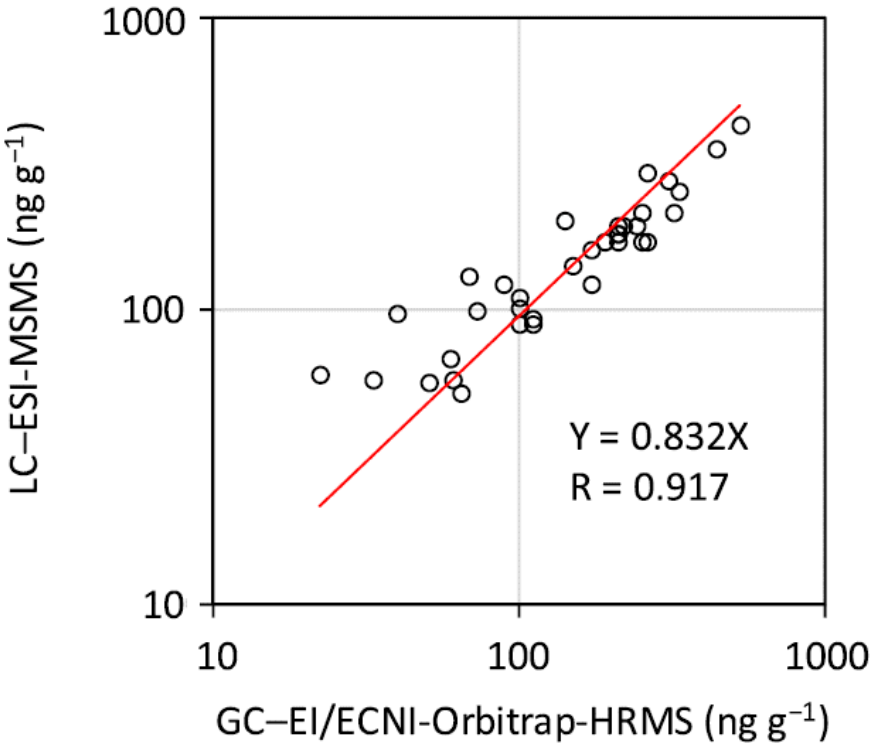
21 congeners of LCCPs were also measured by our LC-MS/MS method.

Method verification

(A) Commercial CP mixtures



(B) Mixed plastic wastes



Good agreement was observed in commercial CP mixtures and mixed plastic wastes between the developed method and HRMS method

Today's topics

1. Our LC-MS/MS method to screen wastes and consumer products containing CPs.
2. **Results of the inter-laboratory study for the screening of wastes and consumer products containing CPs.**

Sample content

Sample ID	Sample content	
PVC-A	Fine powder of PVC toys	
PVC-B	Fine powder of PVC sheathing from electric cords	
PVC-C	Fine powder of PVC toys	
PVC-D	Fine powder of PVC sheathing from electric cords	

Participating laboratories

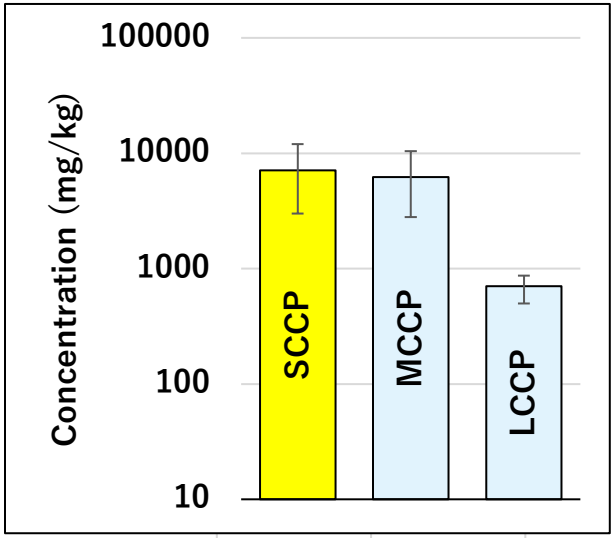
Instrument	Resolution	MS	Ionization	Column	Lab ID
LCMS	High	Orbitrap	APCI⁻	BEH C18	#11
		TOF	APCI⁻	-	#10
		TOF	APCI⁻	BEH C8	#03
	Low	Triple Q	ESI⁻	SB-CN	#07
		Single Q	APCI⁻	Cortecs C8	#04
		Single Q	APCI⁻	Inertsil C4	#05
GCMS	High	Orbitrap	EI/ECNI	DB-5MS DB-1HT	#01
		TOF	EI/ECNI	DB-5MS	
		TOF	EI/ECNI	DB-5MS	#02
	Low	Single Q	ECNI	DB-5MS	#09
		Single Q	ECNI	HP5-MSUI	#06

Results from all the participants

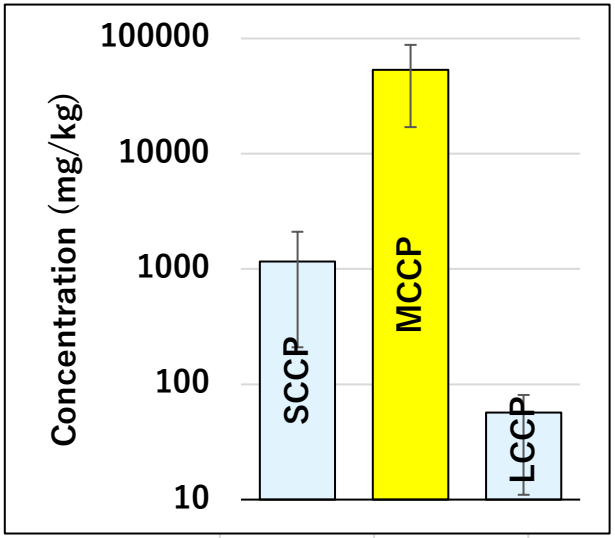
Sample ID	Compound	Concentration (mg/kg)	CV (%)
PVC-A	SCCP	220(110～410)	45
	MCCP	2100(1000～4300)	53
	LCCP	ND	-
PVC-B	SCCP	1200(210～2100)	62
	MCCP	53000(17000～88000)	35
	LCCP	57(11～81)	70
PVC-C	SCCP	7100(3000～12000)	37
	MCCP	6200(2800～10000)	44
	LCCP	700(500～870)	26
PVC-D	SCCP	8600(2800～20000)	59
	MCCP	56000(23000～89000)	34
	LCCP	2800(2300～3600)	20

CV values for SCCPs: PVC-C < PVC-A < PVC-D < PVC-B

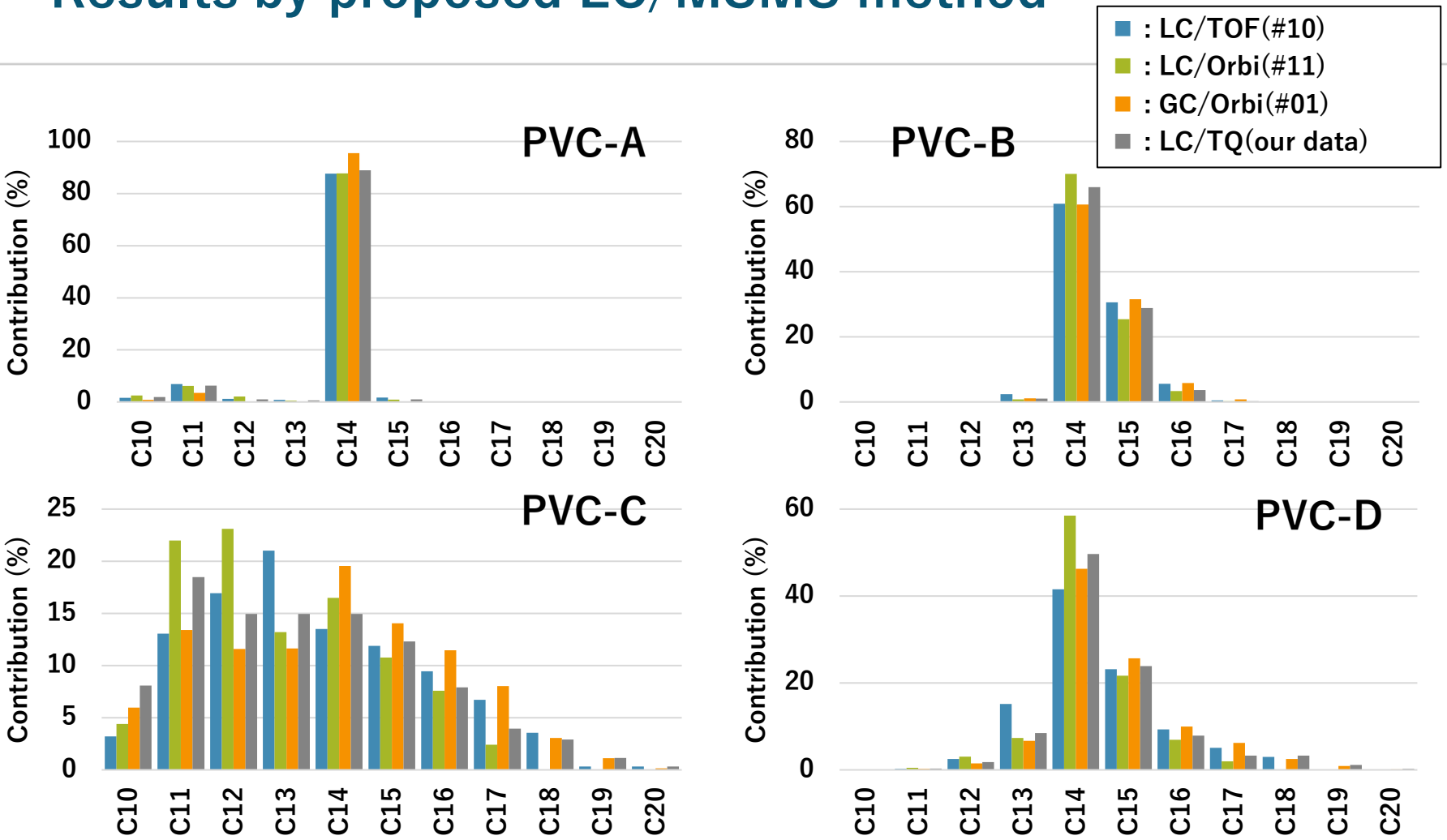
Results of SCCPs in PVC-C



Results of SCCPs in PVC-B



Results by proposed LC/MSMS method



Good agreement was observed in this study between the proposed LC/MSMS method and HRMS methods.

Conclusion

- Data by our LC-MS/MS method were both quantitatively and qualitatively comparable with those by HRMS methods.

- Our LC-MS/MS method is cheaper, more accessible, and practical to use than HRMS methods and it showed retention with good separation and peak shapes of CP congeners.

Acknowledgement

- **Technical support:**
  - **Ms. Mino Hasegawa (NIES)**
  - **Mr. Humiaki Kato (NIES)**

- **Research funds:**
  - **Environment Research and Technology Development Fund (no. 3-1901) of the Environmental Restoration and Conservation Agency, Japan.**

Relevant literature

Contents lists available at ScienceDirect

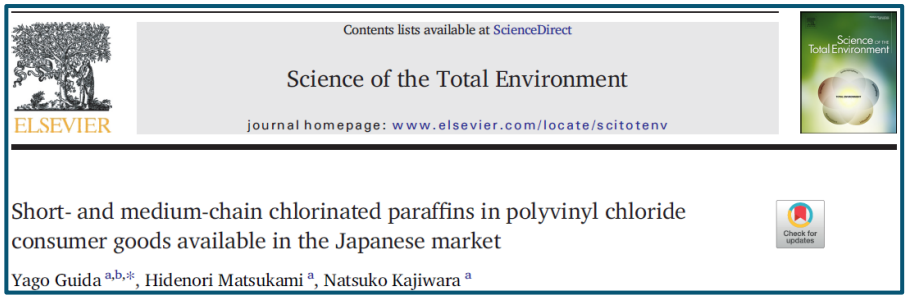
Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Liquid chromatography–electrospray ionization-tandem mass spectrometry for the determination of short-chain chlorinated paraffins in mixed plastic wastes

Hidenori Matsukami [a, *], Hiroaki Takemori [b], Takumi Takasuga [b], Hidetoshi Kuramochi [a], Natsuko Kajiwara [a]

Chemosphere 244, 125531, 2020.



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Short- and medium-chain chlorinated paraffins in polyvinyl chloride consumer goods available in the Japanese market

Yago Guida [a,b,*], Hidenori Matsukami [a], Natsuko Kajiwara [a]

Science of the Total Environment 849, 157762, 2022.

International Journal of Environmental Research and Public Health

Article

Short- and Medium-Chain Chlorinated Paraffins in Polyvinylchloride and Rubber Consumer Products and Toys Purchased on the Belgian Market

Thomas J. McGrath [1,*], Giulia Poma [1], Hidenori Matsukami [2], Govindan Malarvannan [1], Natsuko Kajiwara [2] and Adrian Covaci [1,*]

International Journal of Environmental Research and Public Health 18, 1069, 2021.

Thank you for your kind attention.