

MEEF2021002 Phase 1 Completion Report (01 Jul 2021 – 31 Dec 2022)

Executive Summary

The proposed Phase 1 Project aims to determine the occurrences and distributions of a novel group of emerging organic contaminants related to electronic waste (e-waste), namely liquid crystal monomers (LCMs), in the Chinese White Dolphins (CWDs) within the western Hong Kong and Pearl River Estuary (PRE) waters. LCMs are key components in the manufacture of liquid crystal display panel. It is predicted that these e-waste related chemicals can be released into the marine environment during manufacture, usage, recycling, and disposal of electronic devices. They are also predicted to be persistent, bioaccumulative, and toxic in ecosystems. The CWDs living in the PRE region have been threatened by the pollution of a variety of hazardous substances discharged by human activity. However, the adverse impact caused by emerging LCMs pollution was not well understood.

To evaluate the current levels of LCMs contamination in the CWDs and predict their potential sources, this study has successfully established a robust analytical method to determine 39 target LCMs in environmental sample (i.e., estuarine sediment collected in the PRE region) and biota sample (i.e., CWD blubber samples collected from Hong Kong water). In total 10 LCMs were detected in at least one of the 45 samples, including 3VbcH, MeO3bcH, Pe3bcH, 5MeB, MePVbcH, MeP3bcH, 3cH2B, 2CB, 3OCB, and tFMeO-3bcHP. Among them, MePVbcH was detected in all sediment samples, followed by Pe3bcH (96%), 3VbcH (93%), tFMeO-3bcHP (80%), and MeP3bcH (73%), indicating their ubiquity in the PRE region. The LCM with the highest median concentration determined was 3VbcH (8.53 ng/g), followed by Pe3bcH (3.63 ng/g) and MePVbcH (3.08 ng/g). In total 30 LCMs were detected in dolphin tissues. The dominant LCMs accumulated in dolphin body were Pe3bcH, 5MeB, tFMeO-3bcHP, MePVbcH, MeP3bcH, and 3cH5cHB, with a similar distribution pattern compared to those in the PRE sediment samples. In addition, male dolphins accumulated more LCMs compared to female dolphins.

The results of this study, combining with the results to be obtained in the Phase 2 Project, can provide critical information for preliminary assessment on the potential threat of LCMs towards the CWDs, as well as for the recycling, disposal, and management of e-wastes in Hong Kong, contributing to the conservation and enhancement of marine lives particularly the CWDs living in the PRE and Hong Kong waters.

The way forward for this project

The Phase 1 Project has been proceeded following the proposed work schedule. We have developed a robust analytical method for determination of target LCMs in environmental and biota samples. We completed the sample pre-treatment, cleanup, instrumental analysis and data treatment process for all the collected Chinese White Dolphin samples.

In the Phase 2 Project, the established analytical method for determining target LCMs will be applied in determining the same list of compounds in the collected waste LCD screens. The obtained profile of LCMs in dolphins in the Phase 1 Project will be compared to the profiles of LCMs in the waste LCD screens obtained in the Phase 2

Project. The composition profiles of LCMs will be aligned between Chinese White Dolphins and waste LCD screens to predict the environmental release and migration of particular LCMs.

i) Project Title & Brief Description

Tracing a Novel Group of E-Waste Contaminants - Liquid Crystal Monomers - in the Chinese White Dolphins

The proposed project aims to determine the occurrences and distributions of a novel group of emerging organic contaminants related to electronic waste (e-waste), liquid crystal monomers (LCMs), in the Chinese White Dolphins (CWDs) within the western Hong Kong and Pearl River Estuary (PRE) waters. To evaluate the current levels of LCMs contamination in the CWDs and predict their potential sources, in the Phase 1 Project, this study successfully established a robust analytical method and assessed the composition profiles of 39 LCMs in the CWDs, in comparison with the real LCMs mixtures extracted from the PRE sediment, providing a concrete base for a preliminary assessment on the potential threat of LCMs towards the CWDs living in the PRE and Hong Kong waters.

ii) Progress against the Proposed Work Schedule

Table 1. The 1st funding cycle (2021.07-2022.06)

Activity (including Planning, Recruitment)	Date	Content	Anticipated no. of participants	Progress
Project planning & preparation	1 Jul 2021 – 31 Aug 2021	<ol style="list-style-type: none"> 1. Recruit a Senior Research Assistant and a PhD student. 2. Finalize the documentation and sampling plan for the CWDs (blubber) and LCD panels from the local market. 3. Purchase of standard chemicals for LCMs (high purity chemicals, TCI), analytical components (column, cartridge, etc.), and other laboratory consumables (glassware, chemicals, solvents, etc.). 	All key members (3); Senior research assistant (1); PhD student (1)	<ol style="list-style-type: none"> 1. Research staff (Dr. JIN Qianqian) and a PhD student were recruited. 2. Information on CWDs samples and LCD panels samples was documented. 3. Chemicals and consumables were purchased. <p>*We confirm that all tasks in this session have been completed following the original schedule.</p>
CWD sample collection, pre-treatment & cleaning	1 Aug 2021 – 31 Dec 2021	<ol style="list-style-type: none"> 1. Collection of the CWDs blubber samples from corpses/stranded animals. 2. Optimization of the pre-treatment and cleaning procedure for CWD samples. 3. Finish the progress report 	All key members (3); Senior research assistant (1); PhD student (1)	<ol style="list-style-type: none"> 1. The CWDs blubber samples were collected and archived 2. The pre-treatment and cleaning procedure for CWD samples was optimized. 3. Finish the progress report <p>*We confirm that all tasks in this session have been completed following the original schedule.</p>
Method development for LCMs in biota samples	1 Oct 2021 – 31 Jan 2022	<ol style="list-style-type: none"> 1. Establishment of the analytical method for LCMs in biota and marine sediment samples. 2. Optimization of the qualitative and quantitative methods for LCMs in biota and marine sediment sample. 	All key members (3); Senior research assistant (1); PhD student (1)	<ol style="list-style-type: none"> 1. Analytical method development has been completed. <p>*We confirm that all tasks in this session have been completed following</p>

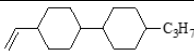

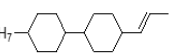
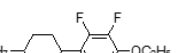
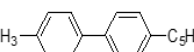
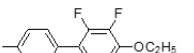
				the original schedule.
Quantification of LCMs in CWD blubbers samples	1 Jan 2022 - 30 Jun 2022	<ol style="list-style-type: none"> Determination of the target LCMs in collected sediment and blubber samples and generate the composition profiles of various LCMs in the PRE marine sediment and CWDs. QA/QC. Prepare the completion report. 	All key members (3); Senior research assistant (1); PhD student (1)	<ol style="list-style-type: none"> Target compounds in PRE marine sediment and CWD samples have been determined. QA/QC measures have been completed. Prepare completion report. <p>*The progress was delayed by several infection cases of COVID-19 in our lab</p>
Data reconfirm of LCMs in CWD blubbers samples	1 Jul 2022 - 31 Dec 2022	<ol style="list-style-type: none"> Determination of the target LCMs in collected sediment and blubber samples and generate the composition profiles of various LCMs in the PRE marine sediment and CWDs. QA/QC. Prepare the completion report. 	All key members (3); Senior research assistant (1); PhD student (1)	<ol style="list-style-type: none"> Target compounds in PRE marine sediment and CWD samples have been determined. QA/QC measures have been completed. Prepare completion report. <p>* We confirm that all tasks in this session have been completed</p>

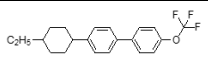
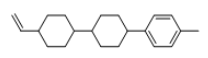
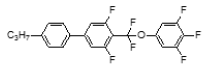
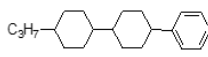
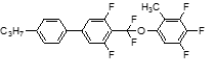
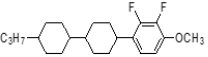
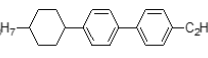
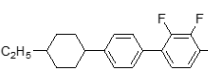
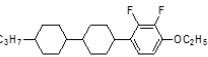
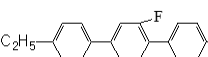
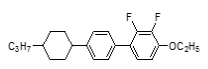
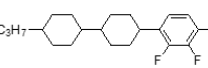
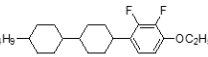
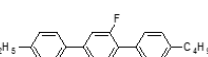
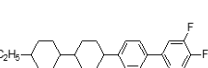
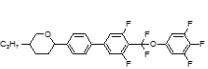
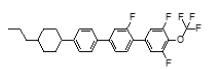
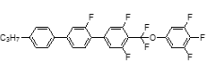
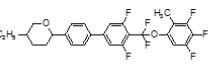
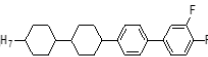
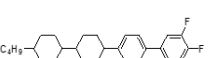
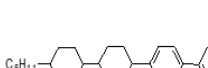
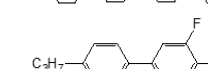
iii) Results

LCMs Standard

Standard chemicals of the 39 target LCMs were purchased from Tokyo Chemical Industry (TCI) Co., Ltd. (Hong Kong, China), J&K Chemical Ltd. (Shanghai, China), and LCM manufacturers, respectively (Table 2). Because stable isotope of LCM was currently not commercially available, isotope-labelled PCB-118 (¹³C₁₂-2,3',4,4',5-pentachlorobiphenyl) (Wellington Lab, Guelph, Canada) was selected as the surrogate standard of LCMs. High-performance liquid chromatography (HPLC) dichloromethane (DCM) was obtained from Duksan Pure Chemical (Seoul, Korea) and Merck KGaA (Darmstadt, Germany), respectively.

Table 2. The detail information on the LCM standards.

Abbr.	CASRN	Mol. Structure	MW (g/mol)	Purity	Suppliers
3VbcH	116020-44-1		234.4	98%	TCI
MeO3bcH	97398-80-6		238.4	98%	TCI
Pe3bcH	279246-65-0		248.5	98%	TCI
2O3cHdFP	174350-05-1		282.4	98%	TCI
5MeB	64835-63-8		238.4	98%	TCI
2OdF3B	157248-24-3		276.3	>99.8%	LCM factories

Abbr.	CASRN	Mol. Structure	MW (g/mol)	Purity	Suppliers
tFMeO-2cHB	650634-92-7		348.4	>99.8%	LCM factories
MePVbcH	155041-85-3		282.5	98%	TCI
tFPO-CF2-dF3B	303186-20-1		428.4	98%	TCI
MeP3bcH	84656-75-7		298.5	98%	TCI
tFMePO-CF2-dF3B	NA		442.4	>99.8%	LCM factories
MeOdFP3bcH	431947-34-1		350.5	>99.8%	LCM factories
3cH2B	84540-37-4		306.5	98%	J&K
2O2cHdFB	323178-01-4		344.5	>99.8%	LCM factories
2OdFP3bcH	123560-48-5		364.5	>99.8%	LCM factories
2F3T	95759-44-7		318.4	>99.9%	LCM factories
2O3cHdFB	189750-98-9		358.5	>99.8%	LCM factories
3OdFP3bcH	473257-14-6		378.6	>99.8%	LCM factories
2OdFP4bcH	473257-15-7		378.6	>99.8%	LCM factories
2F4T	825633-75-8		332.5	>99.8%	LCM factories
2bcHdFB	139195-63-4		382.5	>99.8%	LCM factories
tFPO-CF2-dF3PyB	NA		512.5	>99.8%	LCM factories
tFMeO-3cHtFT	NA		492.5	>99.8%	LCM factories
tFPO-CF2-tF3T	303186-36-9		522.4	>99.8%	LCM factories
tFMePO-CF2-dF3PyB	NA		512.5	>99.8%	LCM factories
3bcHdFB	119990-81-7		396.6	>99.8%	LCM factories
4bcHdFB	NA		410.6	>99.8%	LCM factories
5bcHdFB	136609-96-6		424.6	>99.8%	LCM factories
3dFB	118164-49-1		232.3	>99.8%	LCM factories

Abbr.	CASRN	Mol. Structure	MW (g/mol)	Purity	Suppliers
2CB	58743-75-2		207.3	99.92%	LCM factories
3OCB	52709-86-1		237.3	99.67%	LCM factories
tFMeO-3bcHP	133937-72-1		368.5	98%	TCI
2teFT	326894-55-7		330.3	>99.9%	LCM factories
5OCB	52364-71-3		265.4	99.89%	LCM factories
6OCB	41424-11-7		279.4	99.94%	LCM factories
8OCB	52364-73-5		307.4	99.95%	LCM factories
5CT	54211-46-0		325.5	99.86%	LCM factories
b3cHB	85600-56-2		402.7	99.97%	LCM factories
3cH5cHB	80955-71-1		430.7	99.81%	LCM factories

PRE Sediment Sample

In total 90 marine sediment samples (duplicate), covering 45 sampling points, have been retrieved from a scientific cruise sample in August 2018, covering the PRE and surrounding coastal region. The 45 sampling points are shown in [Figure 1](#). The colors indicate the concentration gradient of total LCMs. Briefly, duplicate sediment samples (top 10 cm) were collected using a stainless-steel sediment grabber (pre-cleaned with Milli-Q® water and MeOH) and stored in polypropylene tubes. Detailed information about sampling locations and basic water quality parameters (bottom water) (i.e., longitude, latitude, depth, temperature, salinity and dissolved oxygen) can be found in our recent publication Tao et al., 2022:

Tao D, Jin Q, Ruan Y, Zhang K, Jin L, Zhan Y, Su G, Wu J, Leung KMY, Lam PKS, He Y. Widespread occurrence of emerging E-waste contaminants - Liquid crystal monomers in sediments of the Pearl River Estuary, China. *J Hazard Mater.* 2022,437, 129377. doi: 10.1016/j.jhazmat.2022.129377.

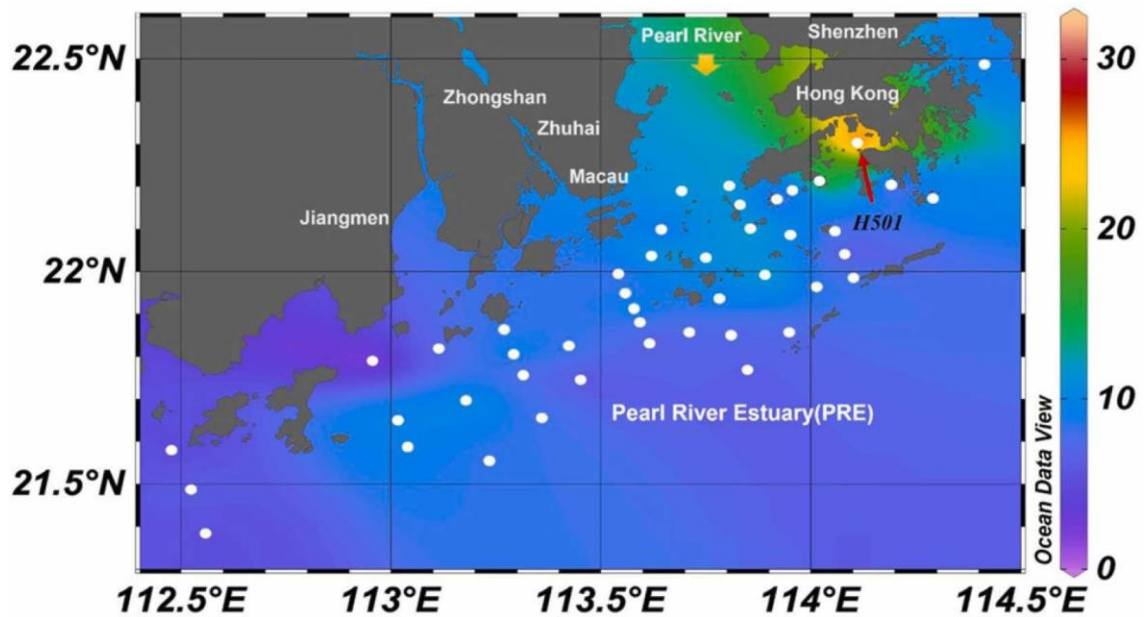


Figure 1. Distribution of Σ LCMs (ng/g dw) in sediments in the PRE and surrounding coastal region. White dots indicate the sampling points in this study. The red arrow indicates the area showing red color. The results for the part of the map not covered by sampling points are predictive only.

CWD Samples

The blubber samples of Indo-Pacific humpback dolphins ($n = X$) and finless porpoises ($n = Y$) and were obtained from stranded cetaceans collected by the Agriculture, Fisheries and Conservation Department in Hong Kong, China from 2018 (Table 3). All the samples have been retrieved from -80°C archive freezers.

Table 3. Information on Indo-Pacific humpback dolphins (SC) retrieved from archive freezers. Unclear information was marked as “?”.

Year	Code	Sex	Body Length	Condition ^a
2005	SC05-1906	M	106	4
2005	SC05-2701	F	234	3
2007	SC07-0101	?	267.5	3
2009	SC09-0406	?	107	?
2009	SC09-1802	M	103	?
2010	SC10-0809	F	109	?
2010	SC10-1506	M	264	?
2010	SC10-1908	M	250	?
2010	SC10-2706	F	265	?
2011	SC11-0312	M	112	?
2011	SC11-1506	M	114	?
2012	SC12-0507	F	224	?
2012	SC12-0807	?	261	?
2012	SC12-1207	M	115	?
2012	SC12-1208	?	110.5	?
2012	SC12-2310	?	258	?
2013	SC13-0210	F	107	?
2013	SC13-1207	F	115.3	?

2013	SC13-1805	F	103	?
2013	SC13-2405	F	246	?
2013	SC13-2503	F	78	?
2013	SC13-2706	F	108	?
2014	SC14-0407	?	250	4
2014	SC14-0606	F?	13.4	4
2014	SC14-1008	F	253	4
2014	SC14-1502	F	270	?
2014	SC14-2106	?	106.5	4
2014	SC14-2408	F	256.5	4
2014	SC14-2409	F	259	4
2014	SC14-2507	?	115	4
2014	SC14-2705	M	29.5	4
2015	SC15-0606	F	116	?
2015	SC15-1307	?	250	?
2015	SC15-1505	F	122	?
2015	SC15-1506	M	127	?
2015	SC15-2006	M	95	?
2015	SC15-2106	?	96	?
2015	SC15-2403	F	237	?
2015	SC15-3105	F	120	?
2016	SC16-2306a	M	272.5	4
2016	SC16-2306b	M	115	4
2017	SC17-0506	?	110	4
2017	SC17-0601	?	269	4
2017	SC17-1408	F	107	4
2018	SC18-0902	F	78	4
2018	SC18-1702	F	249	4
2018	SC18-2209	F	200	4
2018	SC18-2605	M	99	4
2018	SC18-2805	?	220	4
2018	SC18-2809	F	91	4
2019	SC19-1408	?	250	4
2020	SC20-0506M4	M	101	4
2020	SC20-0806F4	F	92	4
2020	SC20-0906U4	?	104	4
2020	SC20-1206F4	F	194	?
2020	SC20-1307F2	F	243	3
2020	SC20-1705U4	?	~100	4
2020	SC20-2508M4	M	~100	4

a condition was defined by veterinarians and officials of the Agriculture, Fisheries and Conservation Department, Hong Kong, as follows: 1= live animals; 2 = freshly dead animals; 3 = moderate decomposition; 4 = advanced decomposition; 5 = mummified remains.

Sample Extraction and Cleanup

The samples were freeze-dried prior to extraction. First, ~ 0.5 g (dw) of each sediment sample was spiked with $^{13}\text{C}_{12}$ -PCB-118 and $^{13}\text{C}_{12}$ -PCB-3 and transferred to a 15 mL PP tube (Corning). After equilibration for 30 min, 5 mL of dichloromethane (DCM) was added to each blubber sample. The sample was centrifuged under 10,000 rpm for 10 min. The sample were extracted with 5 mL of DCM, followed by 5 mL of DCM using ultrasonic extraction (30 min for each extraction step). The same extraction operation was repeated three times and the extracts were combined. The supernatants (~10 mL)

were combined and then concentrated under a gentle stream of high-purity nitrogen near to dryness. The solvent was exchanged to 1 mL DCM. A further cleanup for the extract was carried out on a Florisil column packed with 3 g of Florisil (deactivated with 5% of water) and 1 g silica, 1 g copper powder and 1 g of anhydrous sodium sulfate from bottom to top. The column was conditioned with 10 mL of DCM. Upon loading of the extract, the target LCMs was eluted with 20 mL of DCM. The eluate was concentrated to near dryness and then reconstituted in 200 μ L of DCM for GC-orbitrap analysis.

Instrumental Analysis

A Thermo Fisher Scientific 220 Trace 1300 GC coupled with a Q Exactive Orbitrap hybrid quadrupole (MS/MS) (Thermo Fisher Scientific) was used to quantify the target LCMs. The MS was operated in electron impact (EI) mode, and the analysis was performed in the full-mass scan mode. The GC column used for separation was DB-5HT (30 m \times 0.25 mm \times 0.1 μ m; Agilent). One μ L of the sample was injected in the splitless mode with an injector temperature of 285 $^{\circ}$ C. The flow rate of the carrier gas (helium) was 1.2 mL/min. The temperature program for oven was set as follows: started at 40 $^{\circ}$ C for 1 min, increased to 180 $^{\circ}$ C by 40 $^{\circ}$ C/min, further increased to 250 $^{\circ}$ C by 30 $^{\circ}$ C/min, held 2 min, ramped to 300 $^{\circ}$ C at 10 $^{\circ}$ C/min, and then held for 5 min. The ion source temperature and transfer line temperature were 290 and 260 $^{\circ}$ C, respectively, and the ion source filament voltage was 70 eV. The quantification and confirmation ions and retention times of the LCMs are listed in [Table 4](#).

Table 4. Results of the retention time, quantification ion, specific fragment ions, and standard working curve for the LCMs.

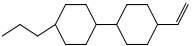
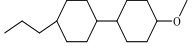
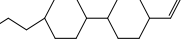
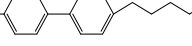
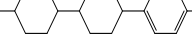
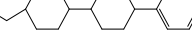
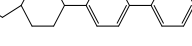
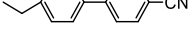
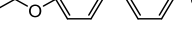
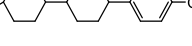
No.	Abbr.	Retention time (min)	Quantification Ion [M+H] ⁺	Specific Fragment Ion 1	Specific Fragment Ion 2	Standard Working Curve	
						R ²	Linearity (ng/mL)
1	3VbcH	6.21	205.195	234.2343	109.1012	0.9995	0.5-100
2	MeO3bcH	6.45	206.2029	163.1481	81.0699	0.9996	0.1-100
3	Pe3bcH	6.76	248.2499	123.1168	81.0699	0.9995	0.5-100
4	2O3cHdFP	7.06	282.1791	156.0382	169.046	0.9993	0.05-100
5	5MeB	7.35	238.1716	181.101	165.0698	0.9993	0.05-100
6	2OdF3B	7.37	276.132	219.0614	247.0928	0.999	0.05-100
7	tFMeO-2cHB	8.3	348.1693	277.0834	264.0757	0.9992	0.05-100
8	MePVbcH	8.48	282.2342	171.1169	118.0777	1.0000	0.5-100
9	tFPO-CF ₂ -dF3B	8.72	281.0948	252.0557	232.0495	0.9991	0.05-100
10	MeP3bcH	8.99	298.2654	118.0777	131.0856	0.9994	0.1-100
11	tFMePO-CF ₂ -dF3B	9.35	281.0948	252.0557	232.0495	0.9992	0.05-100
12	MeOdFP3bcH	9.95	350.2414	170.0538	127.0354	0.9993	0.1-100
13	3cH2B	10.07	306.2341	221.1324	193.1012	0.9994	0.05-100
14	2O2cHdFB	10.08	344.1945	316.1631	232.0693	0.9998	0.1-100
15	2OdFP3bcH	10.35	364.2571	156.0381	184.0694	0.9995	0.5-100
16	2F3T	10.48	318.1777	289.1385	274.1151	0.9993	0.05-100
17	2O3cHdFB	10.76	358.2101	330.1789	245.0772	0.9992	0.1-100
18	3OdFP3bcH	11.03	336.2258	378.2728	156.0382	0.9993	0.5-100
19	2OdFP4bcH	11.09	378.2727	184.0694	156.0381	0.9991	0.1-100
20	2F4T	11.22	332.1934	289.1386	274.1152	0.9991	0.1-100
21	2bcHdFB	12.9	382.2464	229.0824	216.0745	0.9992	0.1-100
22	tFPO-CF ₂ -dF3PyB	13.28	365.1522	219.0416	239.0479	0.9992	0.1-100
23	tFMeO-3cHtFT	13.3	394.0784	407.0865	365.1521	0.9992	0.5-100
24	tFPO-CF ₂ -tF3T	13.47	375.1164	346.0772	275.0668	0.9993	0.1-100
25	tFMePO-CF ₂ -dF3PyB	13.52	351.1366	170.0527	239.0479	0.9991	0.1-100
26	3bcHdFB	13.63	396.2622	203.0667	216.0745	0.9993	0.5-100
27	4bcHdFB	14.39	410.2779	203.0667	216.0745	0.9998	0.5-100
28	5bcHdFB	15.14	424.2938	216.0745	229.0824	0.9993	0.5-100
29	3dFB	5.9	203.0666	232.1058	183.0604	0.9996	0.05-100
30	2CB	7.05	192.0807	165.0701	207.1043	0.999	0.01-100
31	3OCB	7.97	195.0678	166.0652	237.1149	0.9992	0.5-100
32	tFMeO-3bcHP	8.46	368.2318	188.0443	175.0365	0.9993	0.05-100
33	2teFT	8.43	330.1025	315.079	275.0668	0.9993	0.05-100
34	5OCB	8.84	195.0678	166.0652	265.1462	0.9993	0.5-100

35	6OCB	9.36	195.0678	166.0652	279.1618	0.9991	0.5-100
36	8OCB	10.69	307.1931	195.0679	166.0652	0.9992	1-100
37	5CT	13.22	268.1122	325.1825	253.0168	0.9993	0.5-100
38	b3cHB	15.98	402.328	304.2186	317.2264	0.9995	0.5-100
39	3cH5cHB	18.13	430.3593	304.2186	332.25	0.9994	0.5-100

LCMs in PRE sediment samples

In total 10 LCMs were detected in at least one of the 45 samples, including 3VbcH, MeO3bcH, Pe3bcH, 5MeB, MePVbcH, MeP3bcH, 3cH2B, 2CB, 3OCB, and tFMeO-3bcHP (Figure 1, Table 5). The detected LCMs were estimated to have high half-life values in water (15.0 - 180.0 days) and high *n*-octanol–water partition coefficients (log K_{ow}) (logarithm values of 4.34–9.94), indicating their high persistence and bioaccumulation potential in the environment. Among them, MePVbcH was detected in all sediment samples, followed by Pe3bcH (96%), 3VbcH (93%), tFMeO-3bcHP (80%), and MeP3bcH (73%), indicating their ubiquity in the PRE region. Other details are provided in our recently published paper Tao et al., 2022.

Table 5. Chemical information, concentrations (Median, Mean \pm Sem and Range, ng/g dw) and detection frequency (DF, %) of the 10 detected LCMs in sediment samples from the PRE. N.D. means not detected. Sem means standard error of mean.

LCM	CAS No.	Molecular structures	Median conc.	Mean conc.	Range	DF
3VbcH	116020-44-1		8.53	4.76 \pm 3.18	N.D. - 18.4	93
MeO3bcH	97398-80-6		-	0.0001 \pm 0.0004	N.D. - 0.003	2
Pe3bcH	279246-65-0		3.08	1.72 \pm 1.11	N.D. - 4.20	96
5MeB	64835-63-8		0.17	0.33 \pm 0.33	N.D. - 0.474	71
MePVbcH	155041-85-3		3.63	2.05 \pm 0.91	0.662 - 5.65	100
MeP3bcH	84656-75-7		0.70	0.52 \pm 1.00	N.D. - 5.97	73
3cH2B	84540-37-4		-	0.055 \pm 0.15	N.D. - 0.673	11
2CB	58743-75-2		-	0.11 \pm 0.22	N.D. - 0.033	27
3OCB	52709-86-1		-	0.07 \pm 0.16	N.D. - 0.034	20
tFMeO-3bcHP	133937-72-1		0.20	0.31 \pm 0.28	N.D. - 0.314	80

LCMs in CWDs

In total 30 LCMs were detected in dolphin tissues (Table 6). The results indicated that the dominant LCMs accumulated in dolphin body were Pe3bcH, 5MeB, tFMeO-3bcHP, MePVbcH, MeP3bcH, and 3cH5cHB. The distribution of LCMs in dolphin were similar to the profile detected in PRE sediment samples. Overall, male dolphins accumulated

more LCMs compared to female dolphins (Table 7). This is probably because male dolphins were more active and tended to hunt larger prey which might contain higher level of organic contaminants.

Table 6. The distribution of 30 detected LCMs in different tissues in dolphin (ng/g)

No.	Abbr.	DF(%)	Kidney	Liver	Brain	Blubber	Muscle
1	Pe3bcH	54.84%	N.D.	N.D.-5.50	N.D.-0.02	N.D.-92.50	N.D.-99.10
2	5MeB	29.03%	N.D.	N.D.-0.01	N.D.-0.90	N.D.-4.80	N.D.-2.30
3	tFMeO-2cHB	1.61%	N.D.	N.D.	N.D.	N.D.	N.D.-0.20
5	MePVbcH	33.87%	N.D.	N.D.-1.50	N.D.-2.00	N.D.-23.90	N.D.-14.90
6	tFPO-CF2-dF3B	1.61%	N.D.	N.D.	N.D.	N.D.-0.40	N.D.
8	MeP3bcH	56.45%	N.D.-0.30	N.D.-0.80	N.D.-8.40	N.D.-10.80	N.D.-30.40
10	tFMePO-CF2-dF3B	1.61%	N.D.	N.D.	N.D.	N.D.	N.D.-0.30
11	MeOdFP3bcH	9.68%	N.D.-0.10	N.D.	N.D.-0.10	N.D.-1.70	N.D.-0.30
12	3cH2B	25.81%	N.D.	N.D.	N.D.	N.D.-0.40	N.D.-2.10
13	2O2cHdFB	3.23%	N.D.	N.D.	N.D.	N.D.-0.80	N.D.
14	2OdFP3bcH	4.84%	N.D.-0.20	N.D.	N.D.	N.D.-0.60	N.D.
15	2F3T	8.06%	N.D.	N.D.-0.20	N.D.-0.20	N.D.-0.80	N.D.-0.30
17	2O3cHdFB	6.45%	N.D.-0.10	N.D.	N.D.-0.10	N.D.-2.10	N.D.-0.10
18	3OdFP3bcH	8.06%	N.D.	N.D.	N.D.-0.40	N.D.-0.40	N.D.-0.60
19	2OdFP4bcH	1.61%	N.D.	N.D.	N.D.	N.D.-0.40	N.D.
20	2F4T	0.00%	N.D.	N.D.	N.D.-0.10	N.D.	N.D.
21	2bcHdFB	1.61%	N.D.	N.D.	N.D.-0.50	N.D.	N.D.-0.50
23	tFPO-CF2-dF3PyB	8.06%	N.D.	N.D.	N.D.	N.D.-1.50	N.D.-0.10
24	tFPO-CF2-tF3T	1.61%	N.D.	N.D.	N.D.	N.D.	N.D.-0.60
25	3bcHdFB	9.68%	N.D.	N.D.	N.D.	N.D.-1.30	N.D.-0.80
26	tFMePO-CF2-dF3PyB	6.45%	N.D.	N.D.	N.D.	N.D.-0.30	N.D.-0.10
27	4bcHdFB	4.84%	N.D.	N.D.	N.D.	N.D.-0.90	N.D.-0.80
28	5bcHdFB	6.45%	N.D.-2.90	N.D.	N.D.	N.D.-3.60	N.D.-2.90
4	tFMeO-3bcHP	19.35%	N.D.	N.D.	N.D.-3.10	N.D.-3.10	N.D.-4.50
7	5OCB	8.06%	N.D.	N.D.	N.D.-0.10	N.D.-0.70	N.D.-0.10
9	6OCB	3.23%	N.D.	N.D.	N.D.-0.10	N.D.-0.90	N.D.
16	8OCB	14.52%	N.D.-0.30	N.D.	N.D.	N.D.-3.70	N.D.-16.50
22	5CT	4.84%	N.D.	N.D.	N.D.-0.10	N.D.-2.20	N.D.-0.30
29	b3cHB	1.61%	N.D.	N.D.	N.D.	N.D.-0.60	N.D.
30	3cH5cHB	20.97%	N.D.	N.D.-2.30	N.D.	N.D.-8.00	N.D.-4.00

Table 7. The concentration distribution of LCMs in different sex in dolphin sample (ng/g).

	*total (n=71)		male (n=30)		female (n=13)	
	mean	range	mean	range	mean	range
total LCMs concentrations	11.69	0-263.53	69.89	0-263.53	8.66	1.13-202.84
Blubber	66.21	0-245.45	73.97	0-243.45	8.66	2-202.84
muscle	28.39	0.07-263.53	72.57	0.07-263.53	25.8	2.04-202.84
liver	5.49	0-14.71	/	/	6.7	1.78-14.71
brain	61.42	0.64-105.96	/	/	/	/
kidney	0.61	0.25-1.7	/	/	/	/

melon	0	0-1.13	/	/	/	/
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*n means the number of the sample

Some dolphin is difficult to determine their sex

Waste LCD Samples

According to the information of LCD-associated e-devices collected from the sampling site, the same band of e-devices, including but not limited to smartwatches, cell phones, tablets, laptops, desktop computers/monitors, and flat-screen televisions, with the high frequency of daily using time will be collected in May and June 2022. Briefly, small (< 6.5 inches), medium (6.5-13 inches), and large sizes (> 13 inches) of LCD-associated e-devices (each ~10) will be collected from local markets, second-hand shops, disposal/recycling sites. Particularly, the University Go-Green program will be the primary source of end-of-life e-devices to ensure the proposed project is as environmentally friendly as possible. The current available samples are summarized in Table 8.

Table 8. The current documentation for the collection of waste LCD panel samples.

Brand	Type	Size (inch)	Broken (Yes/No)	Time (h/day)	Service life (year)	Quantity (piece)
Apple	iPhone 7	4.7	Yes	8.5	3	2
Lenovo	ThinkPad	14	No	7.6	5	1
Apple	iPhone 8 Plus	5.5	Yes	9.1	3	5
BOLUNSHUAI	Monitor	27	No	5.8	4	1
LG	V50	6.4	Yes	8.9	3	2

Photo/Video/Social Media Platform

The 1st paper derived from this project titled “Widespread Occurrence of Emerging E-waste Contaminants - Liquid Crystal Monomers in Sediments of the Pearl River Estuary, China” has been published in Journal of Hazardous Materials.

(Impact factor 10.538; Doi: <https://doi.org/10.1016/j.jhazmat.2022.129377>).

The article covering this story titled “液晶单体 LCMs 于珠江口的分布及风险评估初探” has been released on our WeChat public account “Aqua Environment” for public access.

(https://mp.weixin.qq.com/s?__biz=MzcxNjI2NDA1Ng==&mid=2247483715&idx=1&sn=ffdef818ed6db963a0bff241cb9f7219&chksm=c153c454f6244d42ab5dbf0a82deb7db e9d7b8874a69c5d4c582cdfb7d65d456c947664e9bfc#rd)

iv) List of activities

Completed work

- Secure Dr. JIN’s appointment to this project
- Admit Ms. ZHAN as a PhD student
- Purchase chemicals and consumables
- Document all the archived CWD samples
- Develop the pre-treatment and cleanup method for CWD samples

- f) Develop the preliminary method for instrumental analysis of target LCMs
- g) Optimize the analytical method for organic-rich samples (i.e., biota and sediment samples)
- h) Determine the composition profile of LCMs in marine sediment collected from the PRE region where the CWDs are living
- i) Publish the updated results (i.e., widespread occurrence of LCMs in the PRE sediment) in a highly reputable journal
- j) Complete the instrumental analysis and data treatment of LCMs in dolphin blubber samples
- k) Generate a preliminary plan for collecting waste LCD panel and manage to collect 11 samples

The proposed tasks of the Project (Phase 1) have been completed. Currently there are 2 more manuscript under review or in preparation.

v) Evaluation of the project effectiveness

The project has been proceeded following the proposed work schedule. We have developed the preliminary method for the pre-treatment and cleanup of blubber and sediment samples and develop a robust analytical method for determination of target LCMs. We have also documented and retrieved all the archived CWD and sediment samples, and completed the sample pre-treatment, cleanup, instrumental analysis and data treatment process. One high quality paper has been published in a highly reputable journal. The article covering the story has also been generated and release on our public social media platform. Also, we have further established the sampling protocol for waste LCD panel and managed to collect 11 waste LCD samples for the next phase of the project.

Phase 1

1. Establish the analytical method for the determination of 39 LCMs in biota samples **(achieved, 100% completed)**
2. Determine the composition profile of LCMs in the sediment collected from the PRE region where the CWDs are currently living **(achieved, 100% completed)**
3. Determine the composition profile of LCMs in the CWDs living in the PRE/western Hong Kong waters **(achieved, 100% completed)**

vi) List of project asset

List of project asset are not disclosed due to confidentiality reasons.

vii) Financial statement

Financial statement are not disclosed due to confidentiality reasons.

viii) Supporting Receipts

CityU is Specified Recipient Organisation and we have opted for alternative financial reporting arrangement.

ix) Staff Recruitment and Attendance Record

Staff recruitment and attendance record are not disclosed due to confidentiality reasons.

Disclamation

I hereby irrevocably declare to the MEEF Management Committee and the Steering Committee of the relevant Funds including the Top-up Fund, that all the dataset and information included in the completion report has been properly referenced, and necessary authorisation has been obtained in respect of information owned by third parties.

Any opinions, findings, conclusions or recommendations expressed in this report do not necessarily reflect the views of the Marine Ecology Enhancement Fund or the Trustee.

Project Leader

A handwritten signature in black ink, appearing to read 'Yuhe He'.

Dr. Yuhe (Henry) He
Assistant Professor
School of Energy and Environment
City University of Hong Kong

2023.01.27

Appendix

Paper published (derived
from this Project)



Research Paper

Widespread occurrence of emerging E-waste contaminants – Liquid crystal monomers in sediments of the Pearl River Estuary, China

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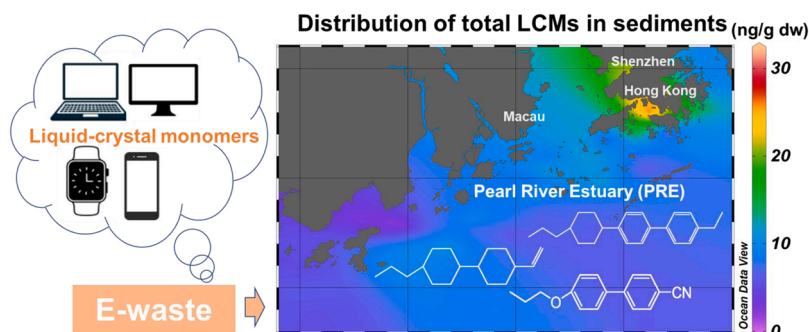
^g Office of the President, Hong Kong Metropolitan University, Hong Kong, China



HIGHLIGHTS

- A robust analytical method was developed to determine LCMs in marine sediment.
- Ten LCMs were detected and widely distributed in the Pearl River Estuary (PRE).
- A gradient of LCMs from inshore to offshore indicated their land-based origins.
- The Σ LCMs were relatively higher compared to PBDEs, PFASs, HCHs and DDTs in the PRE.
- 3VbcH, Pe3bcH and tFMeO-3bcHP are predicted to be the top 3 risk contributors in the PRE.

GRAPHICAL ABSTRACT



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Keywords:

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Sediment
Emerging contaminants
E-waste

ABSTRACT

Liquid crystal monomers (LCMs), commonly used in screens of electronic devices, have recently been identified as a group of emerging chemicals of concern associated with e-waste. They are potentially persistent, bio-accumulative, and toxic substances, and may pose a threat to the marine ecosystem. The Pearl River Estuary (PRE) receives organic contaminants discharged from the Pearl River Delta region, where primitive handling of e-waste is widespread. However, information on the pollution status of LCMs in the PRE is absent. Herein, a rapid and robust analytical method was established using ultrasonic extraction, solid phase extraction cleanup, and GC-Orbitrap-MS analysis. The spatial distribution of 39 target LCMs was investigated in 45 surface sediment samples from the PRE. Ten LCMs were detected, with Σ LCMs ranged from 0.9 to 31.1 ng/g dry weight. Our results demonstrated a widespread occurrence of LCMs in the sediments of the PRE, and a gradient of their contamination from inshore to offshore regions, indicating land-based origins. Our reported Σ LCMs concentrations were relatively higher compared to many other legacy and emerging pollutants found in the same

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investigated area. Preliminary risk assessment showed 3VbCh, Pe3bcH and tFMeO-3bcHP might be the top 3 risk contributors in the PRE. Further investigation on the ecological impact of LCMs on marine benthic ecosystems, as well as identification of their sources and control measures are warranted.

1. Introduction

Liquid crystal display (LCD), taking a prominent position in the market of flat-panel displays, has become a vital part of many electronic devices (e-devices), such as cellphones, tablets, laptops, and smart televisions over the recent decades (Cucchiella et al., 2015; Savvilitidou et al., 2014). In 2018, it was estimated that the global annual production of LCD panels was 198 million m², and over 48.5 million pieces of LCD instruments were discarded as electronic waste (e-waste) (Orbis Research, 2019). Liquid crystal monomers (LCMs) are critical materials used in the manufacture of LCD panels. Thousands of LCMs with various chemical structures have been synthesized and commercialized since 1888 (Reinitzer, 1989). A mixture of 10–20 different LCMs is usually used in producing one kind of LCD panel (Kim and Song, 2009). A typical LCM consists of a rigid hydrocarbon backbone and cyclohexyl/aromatic rings with side chains and/or terminal functional groups such as diphenylacetylene, biphenylnitrile group, and fluorophenyl, and these structures can potentially lead to persistent, bioaccumulative, and toxic (PBT) properties of these compounds (Tsydenova and Bengtsson, 2011; Izhar et al., 2019; Chen et al., 2017).

Given that these substances are not fixed in LCD panels, LCMs can be easily released into the environment during the production, use, and disposal processes of LCD products as e-waste (Zhu et al., 2021). However, the environmental behavior and ecological impacts of LCMs have been rarely reported. Based on the computational estimation of physicochemical properties of 330 LCMs, it was predicted that 297 LCMs could persist in the environment and bioaccumulate in specific tissues of organisms (e.g., liver) (Li et al., 2018). Among them, 89 LCMs could be highly persistent chemicals with an estimated half-life as long as 1621 days in sediment (Li et al., 2018). In a pioneering study, 33 individual LCMs were qualified by gas chromatography–mass spectrometry (GC-MS) and screened in 53 dust samples collected from the indoor environments in China (Su et al., 2019; Dubocq et al., 2021). Due to the lack of chemical standards, only 10 LCMs were quantified in the pioneering study, while concentrations of the other 23 LCMs were semi-quantified by referring to a standard compound with a similar molecular structure (Su et al., 2019). LCMs were also found to be present in indoor dust in Sweden and Canada (Dubocq et al., 2021), which were likely associated with their release from LCD of e-devices (Liu and Abbatt, 2021). Recently, a sample pre-treatment method for the determination of LCMs in freshwater sediments has been established (Su et al., 2021). It combined accelerated solvent extraction and cleanup using in-house adsorption chromatography and gel permeation chromatography, which, however, was very time-consuming. Su et al. (2021) reported that LCMs in the sediment samples from rivers around LCM/LCD manufacturers exhibited the highest mean concentration of 26.1 ng/g dry weight (dw), followed by those from e-waste recycling site areas (1.15 ng/g dw) and Taihu Lake (0.076 ng/g dw) in China. LCMs can be released into the environment from e-waste dismantling (e.g., LCD Panels) (Reinitzer, 1989). For example, it has been reported that total concentrations of 34 determined LCMs (i.e., fluorinated biphenyl analogs, FBAs) were in the range of 225–976,000 ng/g in dust of LCD e-waste (Zhu et al., 2021; Liang et al., 2021). More recently, a novel sample pre-treatment method, combining ultrasonic enhancement extraction, saponification, and silica/Florisil packed column purification, has been proposed by our research group for the determination of 39 target LCMs in municipal landfill leachate (max ΣLCMs = 1120 ng/L) (Jin et al., 2022). Although the LCMs presence has been reported in indoor dust (Häggbloom et al., 2020), landfill leachate (Jin et al., 2022), and freshwater sediment (Su et al., 2021), there is a lack of analytical

method and quantitative data of LCMs regarding their environmental occurrence, transport, and fate in sediments from estuarine and coastal environments.

The Pearl River Delta (PRD) region, located in Southeastern China, is one of the most urbanized estuarine regions, which is heavily affected by the rapid economic (GDP > 400 billion USD) and population growth (> 80 million inhabitants) (Wang and Rainbow, 2020). The PRD region is also one of the primary LCD manufacturing and e-waste recycling centers in the world, with a few large-scale dumping sites with associated dismantling and recycling activities (Wang and Rainbow, 2020). During the dismantling and recycling process, e-waste contaminants can be directly discharged into the surrounding aquatic environment, thereby impacting estuarine and coastal ecosystems in this region (Wang and Rainbow, 2020). Concentrations of various anthropogenic organic contaminants in the PRD region have been extensively monitored over the past decades via a series of sampling campaigns, most of which aimed at the screening of persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) (Zou et al., 2007; Zhang et al., 2009). For example, the annual release of PBDEs in wastewater effluents discharged into the Pearl River Estuary (PRE) was estimated to be 2280 kg per year (Luo et al., 2009). However, LCMs have yet to be measured in this region. It is hypothesized that LCMs originated from land-based sources are entering the marine environment of the PRE and accumulating in sediments. If this hypothesis is true, then LCMs can pose potential threats to marine benthos. Therefore, a comprehensive investigation of their occurrence and environmental risks is urgently needed, especially considering the rapid growth of e-device manufacturing, consumption, and recycling activities in the PRD region.

In this study, we aimed to: (1) develop and optimize the analytical method for LCMs in marine sediment; (2) investigate the spatial distributions of 39 target LCMs in sediments in the PRE, China, and (3) explore the contamination status and perform a preliminary risk assessment of LCMs in the PRE. The results of this study not only establish a rapid and robust analytical method for the determination of LCMs in marine sediment, but also provide evidence-based insights on the extent of contamination of LCMs in the PRE and their potential sources for further investigation.

2. Materials and methods

2.1. Materials and standards

Standard chemicals of the 39 target LCMs were purchased from Tokyo Chemical Industry Co., Ltd. (Hong Kong, China), J&K Chemical Ltd. (Shanghai, China), and LCM manufacturers, respectively (Table S1). Because stable isotope of LCM was currently not commercially available, isotope-labeled PCB-118 (¹³C₁₂-2,3',4,4',5-pentachlorobiphenyl) (Wellington Lab, Guelph, Canada) was selected as the surrogate standard of LCMs. High-performance liquid chromatography (HPLC) grade methanol (MeOH) and dichloromethane (DCM) were obtained from Duksan Pure Chemical (Seoul, Korea) and Merck KGaA (Darmstadt, Germany), respectively. Other details about the chemicals and solvents are provided in the Supporting Information (SI).

2.2. Sample collection

A scientific cruise covering the PRE and surrounding coastal region was launched in August 2018. The 45 sampling points are shown in Fig. S1. The detailed sampling procedures were described in previous

studies (Feng et al., 2021; Wang et al., 2019). Briefly, duplicate sediment samples (top 10 cm) were collected using a stainless-steel sediment grabber (pre-cleaned with Milli-Q® water and MeOH) and stored in polypropylene tubes. Detailed information about sampling locations and basic water quality parameters (bottom water) (i.e., longitude, latitude, depth, temperature, salinity, and dissolved oxygen) at the sediment sampling points is shown in Table S2. All sediment samples were stored at $-20\text{ }^{\circ}\text{C}$ until further treatment.

2.3. Sample extraction and cleanup

A robust analytical method was developed to determine 39 target LCMs in marine sediments modified from our previous study (Jin et al., 2022). The sediment samples were freeze-dried prior to extraction. The surrogate standard ($^{13}\text{C}_{12}$ -PCB-118, 10 ng/g) was incubated with the sediments for 24 h prior to extraction to allow for equilibrium. First, 2 g (dw) of each sediment sample were extracted with 5 mL of DCM, followed by 5 mL of DCM/MeOH (4:1, v/v) and 5 mL of DCM/MeOH (1:1, v/v) using ultrasonic extraction (30 min for each extraction step). The sample was centrifuged under 10,000 rpm for 10 min for each extraction step. The supernatants (~10 mL) were combined and then concentrated under a gentle stream of high-purity nitrogen near dryness. The extract was then reconstituted in 2.5 mL of MeOH and diluted to 50 mL of ~5 % MeOH in Milli-Q water. Solid phase extraction (SPE) was used for sample cleanup. The C18 cartridge (Agilent Bond Elut, 500 mg, 6 mL) was pre-conditioned with 6 mL of DCM, followed by 6 mL of MeOH and 6 mL of Milli-Q water. The obtained extract sample (50 mL) was loaded onto the cartridge at a flow rate of 4 mL/min. After sample loading, the cartridge was washed with 6 mL of MeOH/Milli-Q water (1:1, v/v) and dried under 10 mmHg vacuum for 1 h. The analytes were subsequently eluted with 6 mL of MeOH and 6 mL of DCM. The eluent was concentrated under a gentle stream of high-purity nitrogen near to dryness, and the final extract was top up to 0.5 mL with trimethylpentane (TMP) and subject to instrumental analysis.

2.4. Instrumental analysis

A Thermo Fisher Scientific 220 Trace 1300 GC coupled with a Q Exactive Orbitrap hybrid quadrupole (MS/MS) (Thermo Fisher Scientific) was used to quantify the target LCMs. The MS was operated in electron impact (EI) mode, and the analysis was performed in the full-mass scan mode. The GC column used for separation was DB-5HT (30 m \times 0.25 mm \times 0.1 μm ; Agilent). One μL of the sample was injected in the splitless mode with an injector temperature of 285 $^{\circ}\text{C}$. The flow rate of the carrier gas (helium) was 1.2 mL/min. The temperature program for the oven was set as follows: started at 40 $^{\circ}\text{C}$ for 1 min, increased to 180 $^{\circ}\text{C}$ by 40 $^{\circ}\text{C}/\text{min}$, further increased to 250 $^{\circ}\text{C}$ by 30 $^{\circ}\text{C}/\text{min}$, held 2 min, ramped to 300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$, and then held for 5 min. The ion source temperature and transfer line temperature were 290 and 260 $^{\circ}\text{C}$, respectively, and the ion source filament voltage was 70 eV. The quantification and confirmation ions and retention times of the LCMs are listed in Table S3.

2.5. Quality assurance and quality control (QA/QC)

In total, 45 sediment samples with duplicate samples were analyzed in our study. For every 5 sediment samples, one procedure blank was included to correct the matrix interference, and 1 surrogate standard, 1 internal standard mixture and 1 solvent blank were included for every 10 samples during the instrumental analysis. The calibration curves of 39 target LCMs consisted of a series of concentrations of LCMs (8–10 points), with the correlation coefficients of 0.9990–1 (Table S3). The feasibility of the procedure for the analyses of LCMs was evaluated by the recoveries of the LCMs. The recovery efficiencies, method precision (intraday variability), and instrumental detection limits of the target LCMs throughout the analytical method were evaluated by spiking

experiments (2, 10, and 50 ng of LCMs in sediment samples, $n = 3$ for each level) (Table S4). The three levels of spiking showed similar performance on LCMs recoveries, demonstrating the feasibility of the procedure, which was further assured by the mean recoveries of the surrogate standard ($82.3 \pm 2.5\%$, Mean \pm Standard Deviation, $n = 3$; $^{13}\text{C}_{12}$ -PCB-118) (Fig. S2). The method limit of quantification (MQL) was defined as $X/Y * 3$, where X is Instrument Detection Limit (IDL), Y is Enrichment ratio (Enrichment ratio = 4). All the obtained concentrations were normalized to dry weight (dw) of sediments.

2.6. Data treatment and statistical analysis

Statistical analyses were performed using IBM SPSS Statistics® version 23.0 (SPSS Inc., Chicago, IL, USA), GraphPad Prism® version 8.0 (San Diego, CA), and Origin Pro 2021 (OriginLab, USA). Prior to the use of parametric statistical procedures, the Shapiro-Wilk test was conducted to test for normality of data, and then the assumption of homogeneity of variance was evaluated by use of Levene's test. Pearson correlation analysis was conducted when the data met the assumptions of normality and homogeneity of variances. Kruskal-Wallis Test was performed to compare Σ LCMs concentrations among 45 sampling points. Cluster Analysis based on the method of group average and distance type of correlation and Principal Component Analysis (PCA) based on regression factor score were performed to categorize the distributions of Σ LCMs as well as individual LCMs among various sampling points. All analyzed sediment samples in which the detected concentrations were less than the MQL were reported as not detected. According to the oceanic topography, Ocean Data View (ODV) software was used to predict the concentrations of LCMs for the area not covered by the sampling points following our previous studies (Wang et al., 2019; Higgins et al., 2005). In the software, the gridded field function was chosen to simulate the predictive levels of target LCMs in the absence of sediment data.

3. Results and discussion

3.1. The establishment of the LCMs analysis method

LCMs have been proposed as a class of emerging pollutants related to e-devices/e-waste (Su et al., 2019; Jin et al., 2022). However, it is challenging to extract LCMs from sediment samples containing complex interferences. As stated in Section 1, Su et al. (2021) reported a sample pre-treatment method for freshwater sediment, but it was time-consuming and labor-intensive, which could hinder the analysis for a large quantity of environmental samples (Su et al., 2021). In the current study, a rapid and robust analytical method for 39 target LCMs was developed. Ultrasonic extraction with DCM and MeOH was used as the first extraction step for the analysis of environmental matrices due to its quick, efficient, and highly selective characteristics (Jin et al., 2022). Then cleanup was performed using SPE. All target LCMs dissolved well in DCM in the current study. The SPE cleanup method achieved a low background noise level (Fig. S3a). For the selection of SPE cartridges, C18 cartridge, which was universal for the extraction of low- to mid-polarity compounds, achieved better performance for LCMs extraction compared to HLB cartridge, and thus was applied for the optimization of LCMs recoveries (Fig. S3b) (Higgins et al., 2005; Wagil et al., 2015). As indicated in Table S4, the average relative recovery ranges of the LCMs at three spiking levels (2, 10, and 50 ng of LCMs in 2 g of the sediment, Table S4) were 74.5–121.9 %, 65.9–114.3, and 76.1–121.1 %, respectively, which are comparable to our previous study targeting landfill leachate (Jin et al., 2022). These results also suggested that interfering substances from the sediment samples did not significantly influence the recoveries of LCMs.

3.2. Levels and composition of LCMs in the PRE sediment samples

Concentrations and detection frequencies (DFs) of the target LCMs in the sediment samples collected from the PRE are summarized in Table 1 and Table S5. Totally 10 LCMs were detected in at least one of the 45 samples, including 3VbcH, MeO3bcH, Pe3bcH, 5MeB, MePVbcH, MeP3bcH, 3cH2B, 2CB, 3OCB, and tFMeO-3bcHP (Table 1). The detected LCMs were estimated to have high half-life values in water (15.0–180.0 days) and high *n*-octanol–water partition coefficients (log K_{ow}) (logarithm values of 4.34–9.94), indicating their high persistence and bioaccumulation potential in the environment (Table S1) (Li et al., 2018). Among them, MePVbcH was detected in all sediment samples, followed by Pe3bcH (96 %), 3VbcH (93 %), tFMeO-3bcHP (80 %), and MeP3bcH (73 %), indicating their ubiquity in the PRE region. These five LCMs were also the predominant components with high concentrations in computer and television LCD panels (up to 1670,000 ng/g) (Zhu et al., 2021; Liang et al., 2021).

The spatial distribution of ΣLCMs in marine sediments is shown in Fig. 1. There were significant differences in the ΣLCMs levels among all 45 sampling points ($p < 0.01$, Table S5). Several specific sampling points (e.g., H501, H101, etc.) showed significantly higher ΣLCMs concentrations than other points (Fig. S4, Table S5). The highest concentration of ΣLCMs in the sediment samples was observed at sampling points in the estuary area and in the western waters of Victoria Harbour of Hong Kong (i.e., inshore waters), with an average concentration of 5.0 ng/g dw, while the levels in samples collected from the surrounding offshore areas were below the MQL (Fig. 1). The Pearl River runs through several industrialized and urbanized cities in the PRD region, including Guangzhou, Shenzhen, and Zhuhai, and finally discharges into the PRE. The town of Guiyu, located in the northeast of Guangdong Province, is known as the largest e-waste dismantling center in the world. It is expected that a significant amount of e-waste contaminants, likely including LCMs, are being discharged into the watershed of the PRD region and eventually end up in the PRE (Zeng et al., 2016). In addition, several large-scale sewage treatment plants and municipal landfills in Hong Kong, Shenzhen, and Jiangmen also discharge large amounts of partially treated wastewater effluents into the PRE and surrounding seawater (Wang et al., 2019; Feng et al., 2021). For instance, the Stonecutters Island Sewage Treatment Works discharges over 1 million tonnes of partially treated wastewater effluent per day into the western waters of Victoria Harbor of Hong Kong (Yin and Harrison, 2007). The West New Territories Landfill of Hong Kong, with a

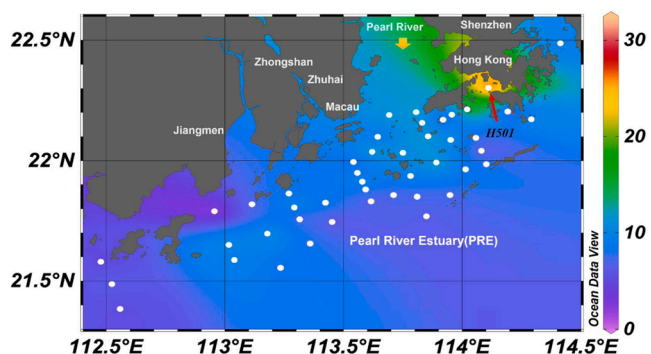


Fig. 1. Distribution of ΣLCMs (ng/g dw) in sediments in the PRE and surrounding coastal region. White dots indicate the sampling points in this study. The red arrow indicates the area showing red color. The results for the part of the map not covered by sampling points are predictive only.

daily load of 6400 tonnes of municipal and special waste per day, can discharge up to 1200 m³ of partially treated leachate into the PRE (Chen et al., 2016). Such a massive discharge is likely introducing a variety of organic contaminants, including LCMs, into the marine environment. It is not surprising that higher levels of LCMs were observed along the coastal areas of Hong Kong, Shenzhen, Zhuhai, and Jiangmen, and their levels decreased with distance offshore, which showed a positive correlation with the total carbon content (TOC) as the indicator of organic pollutants (Pearson $r = 0.22$, $n = 47$, $p < 0.01$) (Fig. S6). The overall gradient of LCMs concentrations in the sediment also decreased from west to east, possibly due to the dilution effect by the ocean current at the PRE and the surrounding coastal region during the summer monsoon (Feng et al., 2021; Li et al., 2011).

Interestingly, different LCMs showed different distribution patterns in the PRE region, and two main groups of distribution patterns in the map were proposed based on the obtained results (Fig. 2). MeO3bcH is not included here because it was only detected at one site. Among the 9 widely detected LCMs, the distribution of each LCM among different sampling points was examined by Cluster Analysis and PCA (Fig. S5). Generally, emission source could be the most important reason resulting in the observed distribution of ΣLCMs. More than half of the detected LCMs followed Group I distribution patterns, mainly distributed in sediment near Hong Kong and Shenzhen as well as the southwest coast of the PRE, indicating active local discharges of LCMs. Among the 6

Table 1

Chemical information (i.e., abbreviation, CAS No., and molecular structure), concentrations (Median, Mean \pm Sem and Range, ng/g dw) and detection frequency (DF, %) of the 10 detected LCMs in sediment samples from the PRE. N.D. means not detected. Sem means standard error of mean.

LCM	CAS No.	Molecular structures	Median conc.	Mean conc.	Range	DF
3VbcH	116020-44-1		8.53	4.76 \pm 3.18	N.D. - 18.4	93
MeO3bcH	97398-80-6		–	0.0001 \pm 0.0004	N.D. - 0.003	2
Pe3bcH	279246-65-0		3.08	1.72 \pm 1.11	N.D. - 4.20	96
5MeB	64835-63-8		0.17	0.33 \pm 0.33	N.D. - 0.474	71
MePVbcH	155041-85-3		3.63	2.05 \pm 0.91	0.662–5.65	100
MeP3bcH	84656-75-7		0.70	0.52 \pm 1.00	N.D. - 5.97	73
3cH2B	84540-37-4		–	0.055 \pm 0.15	N.D. - 0.673	11
2CB	58743-75-2		–	0.11 \pm 0.22	N.D. - 0.033	27
3OCB	52709-86-1		–	0.07 \pm 0.16	N.D. - 0.034	20
tFMeO-3bcHP	133937-72-1		0.20	0.31 \pm 0.28	N.D. - 0.314	80

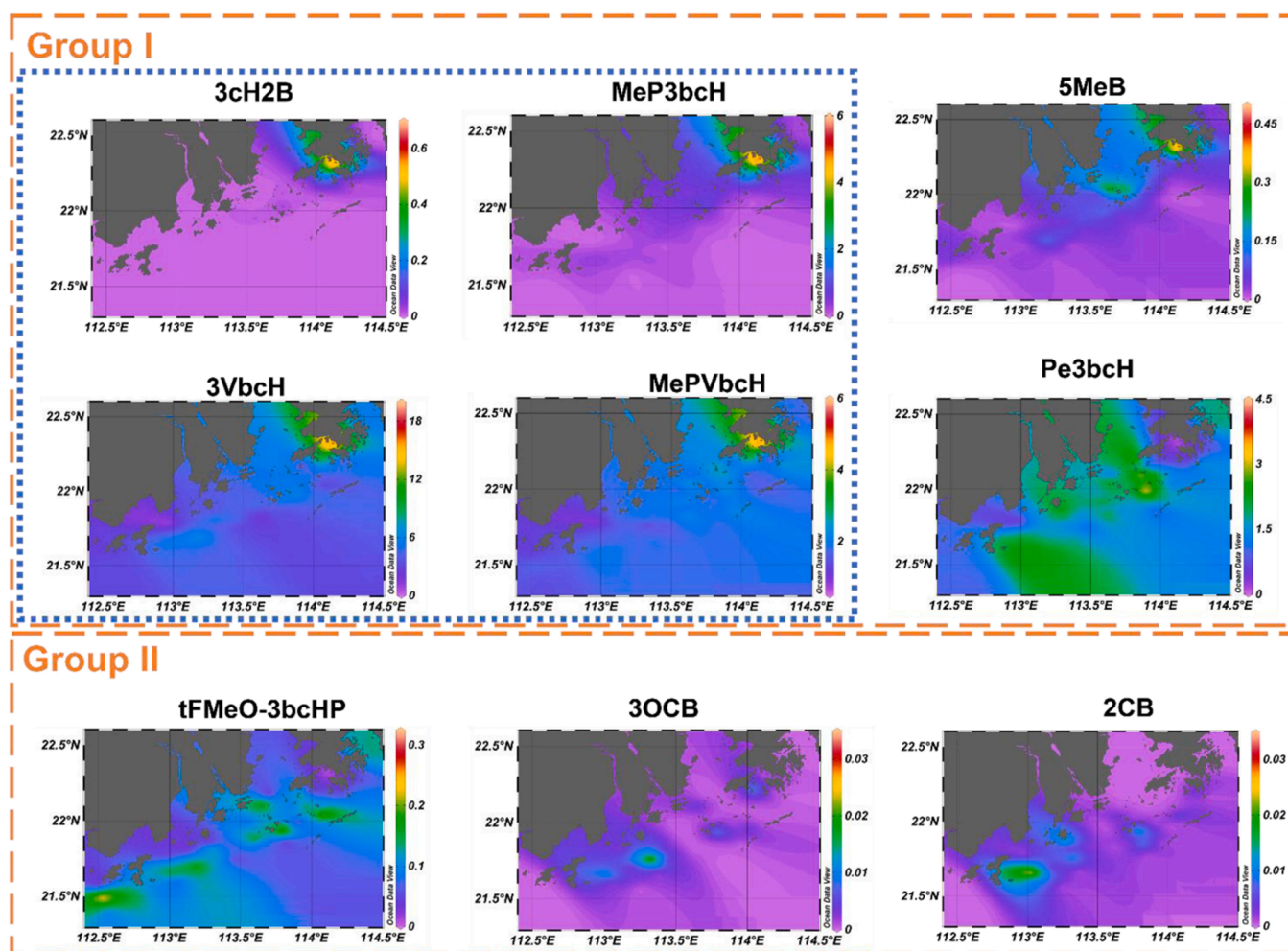


Fig. 2. Distribution of the 9 detected LCMs (ng/g dw) in sediments in the PRE (MeO3bcH excluded). Their distribution patterns are classified into two main groups. Group I: distributed at the west coast of Hong Kong and Shenzhen and/or southwest of the study area in the PRE. Group II: concentrated in several specific offshore points.

LCMs in Group I, 4 of them (i.e., 3CH2B, MeP3bcH, 3VbcH, and MePVbcH) showed a very similar distribution at the west coast of Hong Kong and Shenzhen. Hong Kong, a cosmopolitan city with 7.5 million population, is a consumption and distribution center of smart devices with an estimated market value of 134 million dollar in 2021 (Lasquet-Reyes, 2021). Shenzhen is one of the metropolises in Guangdong Province, where several world's largest manufacturers of liquid crystals and LCDs are located (Yang, 2016). In particular, most imported and domestic e-wastes have been disposed in this region in China since the 1990s (Fu et al., 2018). 5MeB and Pe3bcH showed a similar distribution pattern but with a broader area of diffusion from the Pearl River to the southwest of the PRE, and further, to the surrounding coastal region, especially at sampling points near Zhuhai and Jiangmen, indicating a wider source of input. The spatial distributions of 5MeB and Pe3bcH in sediments were also likely impacted by river outflows and ocean currents, and its concentrations decreased from the estuary to the offshore region due to the dilution effect (Zhu et al., 2022). These results suggested that the discharge from the inland area (e.g., LCD manufacturers and e-waste dismantling facilities in Guangdong Province) might be the main source for Group I LCMs (Yu et al., 2010). For Group II (i.e., 3OCB, and 2CB, and tFMeO-3bcHP), these LCMs tended to deposit in some specific locations. 3OCB and 2CB only occurred in a few restricted locations, indicating the possibility of unique source(s), while tFMeO-3bcHP, the only fluorinated LCM detected in the current study, followed a similar pattern with more ubiquitous distribution in the study

region in several distanced hot spots. Meanwhile, the hot spots of Group II LCMs (i.e., 3OCB, and 2CB, and tFMeO-3bcHP) showed relatively high TOC content, particularly near Jiangmen where 3OCB and 2CB were accumulated (Fig. S6), though the results were not statistically significant. The reason for such a distribution of Group II LCMs is unknown. A possible explanation is that Jiangmen could be one of the main sources of 3OCB, 2CB, and tFMeO-3bcHP, where many LCMs consuming industries are located nearby, including household appliance companies, chemical industries, and consumer e-device manufactories (Yu et al., 2010). Group II LCMs might be released from these manufacturers through partially treated wastewater effluent, and then reached the hot spots via submarine outfalls. As a consequence, these LCMs contaminants, together with other organic pollutants, could contribute to the high level of TOC in several hot spots, suggesting a more prevalent contamination issue. Our results suggested that at least a large proportion of LCMs detected in the PRE sediment could be associated with coastal urban areas (i.e., the west coast of Hong Kong and Shenzhen), indicating urban discharge might be a significant source of LCMs contamination in addition to the industrial discharge from upstream.

3.3. Comparison of levels of LCMs with other matrices

As a class of new chemicals of concern, sources and concentrations of LCMs in different matrices were also recently investigated in several pioneer studies. LCMs were detected in the indoor dust samples

collected from residential buildings and e-waste dismantling lines (Zhu et al., 2021; Su et al., 2019; Häggblom et al., 2020). As shown in Fig. 3, up to 10^6 ng/g dw was detected in LCD panels, especially for BAs (biphenyls/bicyclohexyls and analogues) (Liang et al., 2021). High concentrations of LCMs were also found in dust samples collected from e-waste recycling facilities, especially for FBAs (Zhu et al., 2021). LCD panels can end up in landfills as municipal solid waste, and LCMs may leachate out and eventually enter the marine environment through surface runoff, wastewater effluent discharge and groundwater migration (Jin et al., 2022). Our previous study reported similar or even higher contamination levels of LCMs in landfill leachate, compared to other e-waste related contaminants such as PBDEs and PFASs, suggesting landfill leachate might be an important source of environmental LCMs (Jin et al., 2022). According to the data obtained from the current study, the concentration of Σ LCMs in the PRE sediment was higher than those collected in Taihu Lake, and slightly higher than those collected near recycling sites, but lower than those collected around LCD manufacturing sites (Su et al., 2021). Overall, our results suggest a concerning contamination status of LCMs in the PRE and the surrounding coastal region.

Compositions of the main LCMs in the sediment samples collected from four representative regions and leachate samples collected from Hong Kong and Shenzhen were compared (Fig. 4). T5MeB was detected in all samples, especially in the sediment from the e-waste recycling site (45 %) and Taihu Lake (28 %). In total, five LCMs (3VbCh, 5MeB, MePVbCh, 3cH2B, and 2CB) detected in the current study were also detected in the sediments samples around LCD manufacturers and Taihu Lake in the YRD region (Su et al., 2021). Pe3bCh, tFMeO-3bcHP, 3OCB, and MePVbCh were newly found in marine sediment samples in the present study. The current results showed that the dominant LCMs species detected in marine sediments collected from the PRE (3VbCh, followed by MePVbCh and Pe3bCh) demonstrated a similar composition profile compared to those in municipal landfill leachate samples collected from Hong Kong and Shenzhen. However, it shows a different composition profile compared to those in freshwater sediment samples collected from LCMs manufacturers/e-waste recycling sites (3cH2B, followed by MeP3bCh and 2OdFP3bCh) and dust samples at an E-waste dismantling sites (2O3cHdFB, followed by 2OdFP3bCh and tFPO-CF2-dF3B) in the YRD (Zhu et al., 2021). The compositions of LCMs in the landfill leachate from Hong Kong showed a significantly positive correlation with those in the PRE sediments (Pearson $r = 0.743$, $n = 39$, $p < 0.01$). The compositions of LCMs in the sediment from Taihu

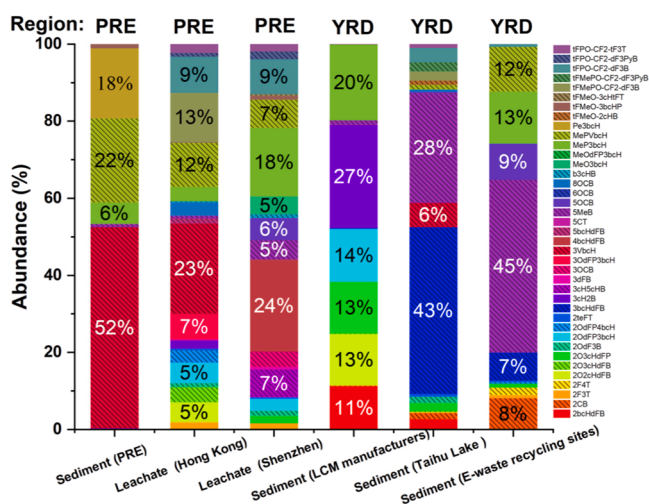


Fig. 4. Composition profiles of LCMs in marine sediment samples from the PRE (i.e., the current study), in landfill leachate samples from Hong Kong and Shenzhen, and in freshwater sediments from the YRD (Jin et al., 2022; Liang et al., 2021; Su et al., 2021; Wang et al., 2019; Zhu et al., 2021).

Lake also showed a significant correlation with those in the sediment around the e-waste recycling sites in the same region (Pearson $r = 0.572$, $n = 39$, $p < 0.01$). Hong Kong is located within the PRE region, whereas Taihu Lake and E-waste recycling site (Taizhou, China) are located in the YRD region. Interestingly, MeO3bcH, which was the most abundant LCM detected in indoor dust samples in the Sweden study (up to 1590 ng/g dw), was only detected in one sample site (up to 0.003 ng/g dw) in the current study. Composition profiles of LCMs in different samples demonstrated regional and matrix differences probably due to different industrial and/or domestic source(s) (e.g., LCD manufacturers using different technologies and LCMs materials, and/or direct emission from various e-devices during daily usage). In the current study, the compositions of LCMs in the PRE sediment showed a positive correlation with those in the landfill leachate from Hong Kong and Shenzhen, suggesting a significant local input from municipal discharge(s). Further study is needed to characterize the sources and environmental behaviors of different LCMs in different environmental matrices on a regional scale.

Meanwhile, the concentrations of LCMs were compared with other groups of organic contaminants in sediments collected from the PRE. As shown in Fig. S7, the highest concentrations of total detected LCMs were higher than the reported concentrations of other legacy and emerging organic contaminants including per- and polyfluoroalkyl substances (PFASs), hexachlorocyclohexanes (HCHs), polybrominated diphenyl ethers (PBDEs), and dichlorodiphenyltrichloroethanes (DDTs). The sampling period focused on 2017–2018 except for PCBs (2011), SCCPs (2012) and MCCPs (2012), for which there was no recent data available. DDTs and HCHs were mass-produced pesticides for agricultural purposes and vector control from 1950 to 1980 (Fan et al., 2021; Zhang et al., 2010). PCBs and PBDEs are often associated with e-waste (Hosoda et al., 2014; Chen et al., 2019; Cai et al., 2020). In addition, LCMs, together with PFASs, PBDEs, DDTs, and PCBs detected in the PRE sediment samples followed the same pattern that higher concentrations were found in the central part of the study area and the coastal areas of Shenzhen, indicating similar anthropogenic source(s) of these pollutants in the PRE (Wang et al., 2019; Feng et al., 2021; Tang et al., 2020). SCCPs and MCCPs were widely used as metal-working lubricants, plasticizers, flame retardants, adhesives, paints, rubber, and sealants, and softeners in various materials (Bayen et al., 2006). SCCPs and MCCPs have been widely detected in the study area, with relatively high total concentrations compared to other contaminants including LCMs (Zeng et al., 2017).

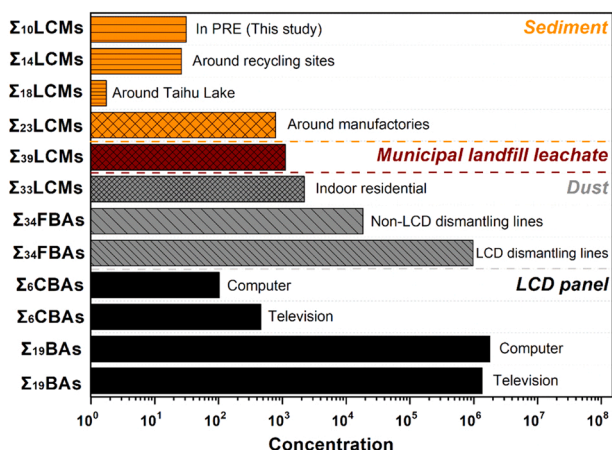


Fig. 3. Comparison of Σ LCMs in the marine sediment samples from the PRE with other documented data (Jin et al., 2022; Liang et al., 2021; Su et al., 2021; Wang et al., 2019; Zhu et al., 2021). Σ LCMs were determined based on the same 39 target LCMs. FBAs, BAs (biphenyls/bicyclohexyls and analogues), and CBAs (cyanobiphenyls and analogues) are different classes of LCMs. The concentration units are ng/g dw (sediment, dust, LCD panel) or ng/mL (leachate).

3.4. Preliminary risk assessment, environmental implications and future study

We have detected 10 LCMs in marine sediments of the PRE and surrounding coastal region, but the potential adverse impacts of these LCMs on marine benthos and ecosystems are still largely unknown. Toxicity data are virtually unavailable for these 10 LCMs. Quantitative structure–activity relationships (QSARs) was, therefore, used to predict the fate and toxicity of 10 LCMs detected in this study using the USEPA EPI Suite™ 4.11 and the OECD QSAR Toolbox 4.4.1 (Table S6). Toxic potencies estimated by ECOSAR indicated that these LCMs might exhibit acute and chronic toxic effects on aquatic organisms. Risk assessment of aquatic organisms exposed to LCMs can be performed based on the measured concentrations in sediment using the risk quotient approach (Lam et al., 2016; Lam and Lam, 2015; U.S. EPA, 2003). Due to the lack of toxicological data, the estimated exposure concentrations, predicted organic carbon-water partitioning coefficient (K_{oc}) values, and predicted chronic toxicity levels in seawater (from Mysid shrimps) were used to calculate the risk quotient. Details are provided in SI (Text S1, Tables S6, S7).

The preliminary risk assessment was conducted on 9 widely detected LCMs among all 45 sampling points. The detailed results are showed in Table S7 and Table S8. Among all 45 sampling points, there are 11 points showing the risk quotient of total LCMs ($RQ_{\Sigma LCMs} > 1$). The $RQ_{\Sigma LCMs}$ of Point H501, located in the west end of Victoria Harbour of Hong Kong, was estimated to be 2.78, which is more than 2-fold of the level of concern ($LOC = 1$), indicating a very high risk. There are another 10 points showing high risk quotient values ($2 > RQ_{\Sigma LCMs} > 1$). In total, 87 % of the sampling points (39 out of 45) showed the $RQ_{\Sigma LCMs}$ values > 0.5 , suggesting medium to high risks in the study area. For individual LCM, 3VbcH contributed the highest average proportion of $RQ_{\Sigma LCMs}$ (33.6 %), followed by Pe3bcH (24.0 %) and tFMeO-3bcHP (18.6 %) (Table S8). These computational estimation results suggested that the current contamination status of LCMs in the PRE might already be alarming, of which 3VbcH, Pe3bcH and tFMeO-3bcHP might be the top 3 risk contributors. Further in vivo studies are needed to obtain more toxicological data for the comprehensive risk assessment of LCMs in the PRE.

In addition, aldehydes, benzyl alcohols, phenols, anilines, and hydroquinone substances could be generated as metabolites of LCMs, which might further exert genotoxicity in exposed organisms (Table S6). More relevant toxicity tests are required to further elucidate the potential hazardous effects and toxic mechanism(s) of LCMs in marine organisms, especially those associated with the benthic ecosystem. LCMs may accumulate in benthos via their food and sediment, which may be governed by biota–sediment accumulation factors (Su et al., 2019). The quality of demersal seafood (e.g., crustaceans, clams, and scallops) would be influenced by LCMs if sediment concentrations of these chemicals were high (Liu et al., 2018).

Due to the potential PBT properties of LCMs, it would be anticipated that LCMs may behave like PBDEs and PFASs to have similar detrimental health effects to marine mammals (Zhu et al., 2014; Ruan et al., 2018a, 2018b). The bioaccumulation and biomagnification potential of LCMs in marine food webs need to be evaluated (Loi et al., 2011). The PRE is also one of the precious habitats for many marine organisms, including the Indo-Pacific humpback dolphins (i.e., Chinese white dolphins) and finless porpoises. As the apex predators of the marine food web, dolphins are susceptible to the exposure of high levels of e-waste related pollutants (e.g., PBDEs) in the PRE (Ruan et al., 2018a; Lam et al., 2009). LCMs associated with e-waste may also be present in elevated concentrations in dolphins. Further investigations on exposure levels and possible health effects of LCMs in local dolphins are warranted.

In this study, a novel analytical method, which is rapid and robust, has been successfully established for determining 39 target LCMs in marine sediments. Ten of the target LCMs were detected in marine sediment samples collected from the PRE. The results showed that these

10 LCMs were widely distributed in this region, and largely concentrated in the urbanized coastal regions of Shenzhen and Hong Kong. LCMs concentrations in PRE sediments were comparable and even higher than other legacy and emerging organic pollutants, such as DDTs, HCHs, PCBs, PAHs, PBDEs, and PFASs. Our findings also suggest that emissions of LCMs from coastal cities would be a potential source of LCMs contamination in sediments of the coastal marine environment.

CRedit authorship contribution statement

Danyang Tao: Investigation, Data curation, Formal analysis, Visualization, Writing – original draft. **Qianqian Jin:** Investigation, Formal analysis, Writing – review & editing. **Yuefei Ruan:** Investigation, Writing – review & editing. **Kai Zhang:** Resources, Writing – review & editing. **Linjie Jin:** Resources, Writing – review & editing. **Yuting Zhan:** Visualization, Writing – review & editing. **Guanyong Su:** Methodology, Writing – review & editing. **Jiaxue Wu:** Resources, Project administration, Funding acquisition, Writing – review & editing. **Kenneth M.Y. Leung:** Supervision, Funding acquisition, Writing – review & editing. **Paul K.S. Lam:** Supervision, Funding acquisition, Writing – review & editing. **Yuhe He:** Conceptualization, Methodology, Supervision, Funding acquisition, Writing – original draft, Writing – review & editing.

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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Supporting Information

The supporting information include: Method of preliminary risk assessment (Text S1); Detail information on the LCM standards (Table S1); Location of sampling points and water quality parameters (Table S2, Fig. S1); Results of the retention time, quantification ion, specific fragment ions, and standard working curve for the LCMs (Table S3); Results of the recoveries of 39 LCMs (Table S4, Fig. S2); Concentrations of the target LCMs in the sediment samples collected from the PRE and surrounding coastal region (Table S5); Results of QSAR prediction of fate, toxicity and metabolites of LCMs (Table S6); Risk quotient values of 10 detected LCMs at specific sampling point (Table S7); Proportion of risk quotient of individual LCM contributing to $\Sigma LCMs$ (Table S8); Optimization of SPE method (Fig. S3); Analysis of $\Sigma LCMs$ distribution in the studying area (Fig. S4); Analysis of individual LCM distribution in the studying area (Fig. S5); Distribution of TOC in sediments in the studying area (Fig. S6); Comparison of $\Sigma LCMs$ with other groups of organic contaminants in the studying area (Fig. S7); Reference for SI.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.129377.

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Widespread Occurrence of Emerging E-waste Contaminants - Liquid Crystal Monomers in Sediments of the Pearl River Estuary, China

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Text S1. Method of preliminary risk assessment

The risk quotient (RQ) of an individual LCM at a specific sampling point was calculated following previous studies [1, 2], using the following equation:

$$RQ_{LCMx} = \frac{MEC_{LCMx, \text{sediment}} / K_{OC, LCMx}}{ChV_{LCMx, \text{Mysid, SW}} \times 1,000}$$

Where $MEC_{LCMx, \text{sediment}}$ is the measured environmental concentration of the individual LCM (LCM_x) in the sediment sample (ng/g); $K_{OC, LCMx}$ is the predicted organic carbon-water partitioning coefficient value of LCM_x (mL/g); $ChV_{LCMx, \text{Mysid, SW}}$ is the predicted chronic toxicity level of LCM_x on seawater (SW) Mysid Shrimp (Mysid) (mg/L). For a particular organic compound, the conversion of the sediment concentration (ng/g) to water concentration (mg/L) is achieved by division with predicted K_{OC} following an USEPA guideline on Equilibrium Partitioning Sediment Benchmarks (ESBs) for protecting benthic organisms [3]. The level of concern (LOC) is defined as 1. If RQ_{LCMx} is > 2 ($2 \times LOC$), LCM_x will be defined at very high risk; If $2 > RQ_{LCMx}$ is > 1 , LCM_x will be defined at high risk; If $1 > RQ_{LCMx} > 0.5$, LCM_x will be defined at medium risk; If $RQ_{LCMx} < 0.5$, LCM_x will be defined at low risk.

For a particular sampling point, the overall RQ of the 9 widely detected LCMs will be calculated using the following equation:

$$RQ_{\Sigma LCMs} = \sum_{x=1}^9 RQ_x$$

Where $RQ_{\Sigma LCMs}$ is the overall RQ combining the 9 widely detected LCMs; x is the individual LCM.

The proportion of the RQ contributed by an individual LCM (P_{LCMx}) is calculated using the following equation:

$$P_{LCMx} = \frac{RQ_{LCMx}}{RQ_{\Sigma LCMs}} \times 100\%$$

Table S1. The detail information on the LCM standards.

Abbr.	CASRN	Name	Molecular Structure	MW (g/mol)	Purity	Half-life in water (day)	Suppliers	Log(K_{ow})
3VbcH	116020-44-1	1-(4-propylcyclohexyl)-4-vinylcyclohexane		234.4	98%	37.5	TCI ^a	8.03
MeO3bcH	97398-80-6	1-methoxy-4-(4-propylcyclohexyl)cyclohexane		238.4	98%	37.5	TCI	6.42
Pe3bcH	279246-65-0	1-(prop-1-enyl)-4-(4-propylcyclohexyl)cyclohexane		248.5	98%	37.5	TCI	8.45
2O3cHdFP	174350-05-1	1-ethoxy-2,3-difluoro-4-(4-propylcyclohexyl)benzene		282.4	98%	180.0	TCI	7.18
5MeB	64835-63-8	4-methyl-4'-pentylbiphenyl		238.4	98%	15.0	TCI	6.82
2OdF3B	157248-24-3	1-ethoxy-2,3-difluoro-4-(4-propylphenyl)benzene		276.3	>99.8%	180.0	LCM factories	6.26
tFMeO-2cHB	650634-92-7	4-(4-ethylcyclohexyl)-4'-(trifluoromethoxy)biphenyl		348.4	>99.8%	60.0	LCM factories	8.53
MePVbcH	155041-85-3	4-(4-methylphenyl)-4'-vinyl-1,1'-bi(cyclohexyl)		282.5	98%	37.5	TCI	8.82
tFPO-CF ₂ -dF3B	303186-20-1	4-[difluoro(3,4,5-trifluorophenoxy)methyl]-3,5-difluoro-4'-propylbiphenyl		428.4	98%	180.0	TCI	9.1
MeP3bcH	84656-75-7	1-methyl-4-(4-(4-propylcyclohexyl)cyclohexyl)benzene		298.5	98%	37.5	TCI	9.44
tFMePO-CF ₂ -dF3B	1690317-23-7	4-[difluoro(2-methyl-3,4,5-trifluorophenoxy)methyl]-3,5-difluoro-4'-propylbiphenyl		442.4	>99.8%	180.0	LCM factories	9.65

Table S1. The detail information on the LCM standards.

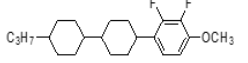
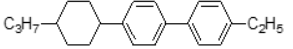
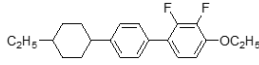
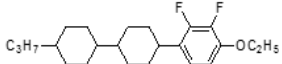
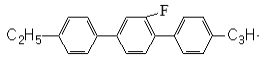
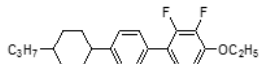
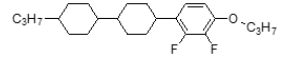
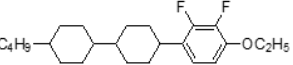
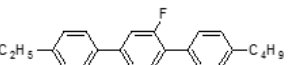
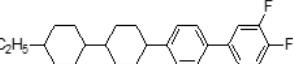
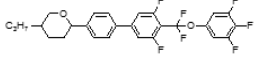
Abbr.	CASRN	Name	Molecular Structure	MW (g/mol)	Purity	Half-life in water (day)	Suppliers	Log(K_{ow})
MeOdFP3bcH	431947-34-1	2,3-difluoro-1-methoxy-4-(4-(4-propylcyclohexyl)cyclohexyl)benzene		350.5	>99.8%	180.0	LCM factories	9.38
3cH2B	84540-37-4	1-ethyl-4-(4-(4-propylcyclohexyl)phenyl)benzene		306.5	98%	37.5	J&K	9.01
2O2cHdFB	323178-01-4	2,3-difluoro-1-ethoxy-4-(4-(4-ethylcyclohexyl)phenyl)benzene		344.5	>99.8%	180.0	LCM factories	8.46
2OdFP3bcH	123560-48-5	1-ethoxy-2,3-difluoro-4-(4-(4-propylcyclohexyl)cyclohexyl)benzene		364.5	>99.8%	180.0	LCM factories	9.87
2F3T	95759-44-7	4''-ethyl-2'-fluoro-4-propyl-1,1':4',1''-terphenyl		318.4	>99.9%	60.0	LCM factories	8.29
2O3cHdFB	189750-98-9	4-ethoxy-2,3-difluoro-4'-(4-propylcyclohexyl)biphenyl		358.5	>99.8%	180.0	LCM factories	8.95
3OdFP3bcH	473257-14-6	2,3-difluoro-1-propoxy-4-(4-(4-propylcyclohexyl)cyclohexyl)benzene		378.6	>99.8%	180.0	LCM factories	10.36
2OdFP4bcH	473257-15-7	1-(4-(4-butylcyclohexyl)cyclohexyl)-4-ethoxy-2,3-difluorobenzene		378.6	>99.8%	180.0	LCM factories	10.36
2F4T	825633-75-8	4-butyl-4''-ethyl-2'-fluoro-1,1':4',1''-terphenyl		332.5	>99.8%	60.0	LCM factories	8.78
2bcHdFB	139195-63-4	3,4-difluoro-4'-[4'-ethyl-1,1'-bi(cyclohexyl)-4-yl]biphenyl		382.5	>99.8%	180.0	LCM factories	10.57
tFPO-CF ₂ - dF3PyB	NA	4-[difluoro(3,4,5-trifluorophenoxy)methyl]-3,5-difluoro-4'-[(5-propyl-tetrahydro-2H-pyran)-yl]-biphenyl		512.5	>99.8%	180.0	LCM factories	10.04

Table S1. The detail information on the LCM standards.

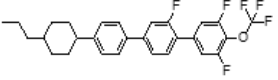
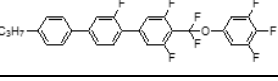
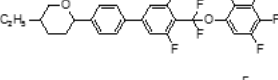
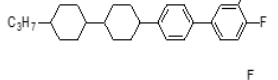
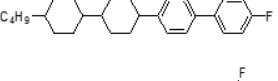
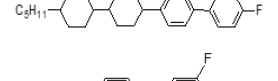
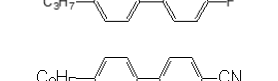
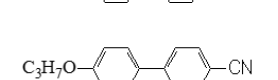
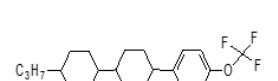
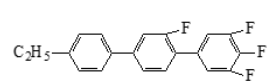

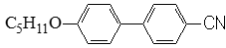
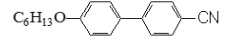
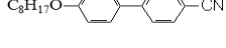
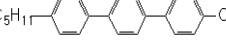
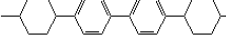
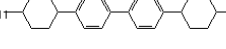
Abbr.	CASRN	Name	Molecular Structure	MW (g/mol)	Purity	Half-life in water (day)	Suppliers	Log(K_{ow})
tFMeO-3cHtFT	524709-77-1	4-trifluoromethoxy-3,5-difluoro-2'-fluoro-4''-(4-propylcyclohexyl)-1,1':4',1''-terphenyl		492.5	>99.8%	180.0	LCM factories	11.39
tFPO-CF ₂ -tF3T	303186-36-9	4''-Propyl-4-[difluoro(3,4,5-trifluorophenoxy)methyl]-2',3,5-trifluoro-1,1':4',1''-terphenyl		522.4	>99.8%	180.0	LCM factories	11.07
tFMePO-CF ₂ -dF3PyB	1700444-88-7	4-[difluoro(2-methyl-3,4,5-trifluorophenoxy)methyl]-3,5-difluoro-4'-[(5-ethyl-tetrahydro-2H-pyran)-yl]-biphenyl		512.5	>99.8%	180.0	LCM factories	10.1
3bcHdFB	119990-81-7	3,4-difluoro-4'-[4'-propyl-1,1'-bi(cyclohexyl)-4-yl]biphenyl		396.6	>99.8%	180.0	LCM factories	11.06
4bcHdFB	119990-82-8	3,4-difluoro-4'-[4'-butyl-1,1'-bi(cyclohexyl)-4-yl]biphenyl		410.6	>99.8%	180.0	LCM factories	11.55
5bcHdFB	136609-96-6	3,4-difluoro-4'-[4'-pentyl-1,1'-bi(cyclohexyl)-4-yl]biphenyl		424.6	>99.8%	180.0	LCM factories	12.04
3dFB	118164-49-1	3,4-difluoro-4'-propyl-1,1'-Biphenyl		232.3	>99.8%	60.0	LCM factories	5.69
2CB	58743-75-2	4'-ethylbiphenyl-4-carbonitril		207.3	99.92%	37.5	LCM factories	4.34
3OCB	52709-86-1	4'-propoxy-4-biphenylcarbonitrile		237.3	99.67%	37.5	LCM factories	4.37
tFMeO-3bcHP	133937-72-1	4-propyl-4'-[4-(trifluoromethoxy)phenyl]-1,1'-bicyclohexyl		368.5	98%	180.0	TCI	9.94
2teFT	326894-55-7	4''-ethyl-2',3,4,5-tetrafluoro-1,1':4',1''-terphenyl		330.3	>99.9%	180.0	LCM factories	7.36

Table S1. The detail information on the LCM standards.

Abbr.	CASRN	Name	Molecular Structure	MW (g/mol)	Purity	Half-life in water (day)	Suppliers	Log(K_{ow})
5OCB	52364-71-3	4-cyano-4'-pentyloxybiphenyl		265.4	99.89%	15.0	LCM factories	5.35
6OCB	41424-11-7	4'-hexyloxy-4-biphenylcarbonitrile		279.4	99.94%	37.5	LCM factories	5.84
8OCB	52364-73-5	4'-(octyloxy)-4-biphenylcarbonitrile		307.4	99.95%	37.5	LCM factories	6.82
5CT	54211-46-0	4-cyano-4''-pentyl-p-terphenyl		325.5	99.86%	37.5	LCM factories	7.58
b3cHB	85600-56-2	4,4'-bis(4-propylcyclohexyl)biphenyl		402.7	99.97%	60.0	LCM factories	12.19
3cH5cHB	80955-71-1	4-(4-pentylcyclohexyl)-4'-(4-propylcyclohexyl)biphenyl		430.7	99.81%	37.5	LCM factories	13.17

^a TCI, Tokyo Chemical Industry Co., Ltd.

^b J&K, Acceleration Scientific and Industrial Development Thereby Serving Humanity.

^c “?” represents the unknown purities of the standards.

Table S2. GPS locations and basic water quality parameters in bottom waters of the sediment sampling points. “-” indicates data missing due to limited sample amounts. “DO” is dissolved oxygen. “TOC” is total organic content.

Sampling Points	Longitude	Latitude	Temperature (°C)	Salinity (‰)	DO (mg/L)	TOC (%)	Depth (m)
A08	113.812558	22.20003791	25.62	32.6	1.52	0.91	28.2
A09	113.84075	22.15375694	25.81	32.37	1.75	0.84	21.3
A10	113.857778	22.09920423	25.53	33.04	2	0.90	21.9
A12	113.898436	21.99094644	23.88	34.08	1.54	0.76	25.7
A14	113.955081	21.85489859	23.51	34.22	3.4	0.37	30.8
B01	113.71841	21.85421283	23.49	34.29	2.5	0.46	30.1
F101	113.124607	21.81922125	23.87	34.17	1.31	0.76	14.8
F103	113.189522	21.69510101	23.86	34.28	4.67	1.01	29.3
F104	113.24692	21.56059906	23.57	34.3	4.84	-	31.1
F203	113.429263	21.82537342	23.58	34.26	1.44	0.87	26.4
F204	113.463595	21.74893107	24	34.27	4.38	0.46	32.4
F301	113.547093	21.99294908	28.96	29.9	3.35	1.08	11.1
F301C	113.633155	22.03359583	28.98	24.84	5.63	0.87	10.2
F301D	113.652892	22.09882174	28.37	23.9	3.99	1.01	8.9
F302	113.568729	21.94729451	24.88	33.97	1.16	1.01	18.1
F303	113.58749	21.91076572	24.08	34.21	0.11	1.12	23.1
F304	113.599279	21.88135553	23.59	34.27	0.71	0.97	26.9
F305	113.6262	21.83164634	23.56	34.29	2.49	0.52	29.6
F401	113.699943	22.18583729	28.7	19.54	4.48	0.90	7.3
F404	113.76236	22.03021079	25.5	33.16	0.91	0.81	15.6
F405	113.791195	21.9358329	23.53	34.26	2.06	0.73	26.6
F406	113.814216	21.85162114	23.46	34.29	3.38	1.05	33
F407	113.856176	21.76784135	23.46	34.3	3.69	-	37
F601	114.2926	22.1682	27.34	28.33	4.5	-	-
F602	114.062957	22.09391117	23.8	34.16	1.2	0.82	25.4
F603	114.08556	22.0389568	23.72	34.22	1.62	0.82	29.6

F604	114.103978	21.98539853	23.58	34.21	2.23	0.85	28.6
F901A	113.9656	22.1886	29.07	29.28	6.46	-	-
H002	113.9259	22.1721	28.73	28.48	6.95	-	-
H101	114.023	22.2109	28.97	28.34	7.37	-	-
H201	114.198	22.1992	28.54	29.11	7.26	-	-
H501	114.1169	22.3	28.24	29	5.51	-	-
MS05	114.4222	22.4843	29.12	30.99	5.4	-	-
P101	112.487407	21.58321371	24.31	34.19	1.41	1.00	15
P102	112.531166	21.48876657	23.58	34.31	3.62	1.01	21
P103	112.566846	21.38718175	23.42	34.32	4.4	0.61	31
P201	112.968405	21.78944999	23.97	34.14	3.31	0.61	11
P203	113.02239	21.65333993	23.65	34.29	4.67	1.12	26.8
P204	113.051454	21.59268617	23.52	34.31	4.75	0.92	30
P301	113.281698	21.86218003	28.43	28.19	2.59	0.95	12.9
P302	113.303082	21.81162208	23.69	34.25	2.65	1.12	21.3
P303	113.325013	21.7621398	23.91	34.24	3.7	1.13	28.8
P304	113.371497	21.65866207	23.93	34.23	4.68	-	31.6
P502	113.960995	22.08695464	24.58	33.86	1.5	0.97	22.9
P503	114.021388	21.96173774	23.62	34.23	2.49	1.02	32.6

Table S3. Results of the retention time, quantification ion, specific fragment ions, and standard working curve for the LCMs

No.	Abbr.	Retention time	Quantification Ion	Qualitative Ion 1	Qualitative Ion 2	Standard Working Curve	
		(min)	(m/z)	(m/z)	(m/z)	R ²	Linearity (ng/mL)
1	3VbcH	6.21	205.195	234.2343	109.1012	0.9995	0.5-100
2	MeO3bcH	6.45	206.2029	163.1481	81.0699	0.9996	0.1-100
3	Pe3bcH	6.76	248.2499	123.1168	81.0699	0.9995	0.5-100
4	2O3cHdFP	7.06	282.1791	156.0382	169.046	0.9993	0.05-100
5	5MeB	7.35	238.1716	181.101	165.0698	0.9993	0.05-100
6	2OdF3B	7.37	276.132	219.0614	247.0928	0.999	0.05-100
7	tFMeO-2cHB	8.3	348.1693	277.0834	264.0757	0.9992	0.05-100
8	MePVbcH	8.48	282.2342	171.1169	118.0777	1.0000	0.5-100
9	tFPO-CF ₂ -dF3B	8.72	281.0948	252.0557	232.0495	0.9991	0.05-100
10	MeP3bcH	8.99	298.2654	118.0777	131.0856	0.9994	0.1-100
11	tFMePO-CF ₂ -dF3B	9.35	281.0948	252.0557	232.0495	0.9992	0.05-100
12	MeOdFP3bcH	9.95	350.2414	170.0538	127.0354	0.9993	0.1-100
13	3cH2B	10.07	306.2341	221.1324	193.1012	0.9994	0.05-100
14	2O2cHdFB	10.08	344.1945	316.1631	232.0693	0.9998	0.1-100
15	2OdFP3bcH	10.35	364.2571	156.0381	184.0694	0.9995	0.5-100
16	2F3T	10.48	318.1777	289.1385	274.1151	0.9993	0.05-100
17	2O3cHdFB	10.76	358.2101	330.1789	245.0772	0.9992	0.1-100
18	3OdFP3bcH	11.03	336.2258	378.2728	156.0382	0.9993	0.5-100
19	2OdFP4bcH	11.09	378.2727	184.0694	156.0381	0.9991	0.1-100
20	2F4T	11.22	332.1934	289.1386	274.1152	0.9991	0.1-100
21	2bcHdFB	12.9	382.2464	229.0824	216.0745	0.9992	0.1-100
22	tFPO-CF ₂ -dF3PyB	13.28	365.1522	219.0416	239.0479	0.9992	0.1-100
23	tFMeO-3cHtFT	13.3	394.0784	407.0865	365.1521	0.9992	0.5-100
24	tFPO-CF ₂ -tF3T	13.47	375.1164	346.0772	275.0668	0.9993	0.1-100
25	tFMePO-CF ₂ -dF3PyB	13.52	351.1366	170.0527	239.0479	0.9991	0.1-100
26	3bcHdFB	13.63	396.2622	203.0667	216.0745	0.9993	0.5-100

27	4bcHdFB	14.39	410.2779	203.0667	216.0745	0.9998	0.5-100
28	5bcHdFB	15.14	424.2938	216.0745	229.0824	0.9993	0.5-100
29	3dFB	5.9	203.0666	232.1058	183.0604	0.9996	0.05-100
30	2CB	7.05	192.0807	165.0701	207.1043	0.999	0.01-100
31	3OCB	7.97	195.0678	166.0652	237.1149	0.9992	0.5-100
32	tFMeO-3bcHP	8.46	368.2318	188.0443	175.0365	0.9993	0.05-100
33	2teFT	8.43	330.1025	315.079	275.0668	0.9993	0.05-100
34	5OCB	8.84	195.0678	166.0652	265.1462	0.9993	0.5-100
35	6OCB	9.36	195.0678	166.0652	279.1618	0.9991	0.5-100
36	8OCB	10.69	307.1931	195.0679	166.0652	0.9992	1-100
37	5CT	13.22	268.1122	325.1825	253.0168	0.9993	0.5-100
38	b3cHB	15.98	402.328	304.2186	317.2264	0.9995	0.5-100
39	3cH5cHB	18.13	430.3593	304.2186	332.25	0.9994	0.5-100

Table S4. Results of recoveries of 39 LCMs.

Abbr.	Intraday Variability						*IDL (ng/ml)	*MQL (ng/g, sediment)
	Low Conc.	RSD (%)	Medium Conc.	RSD (%)	High Conc.	RSD (%)		
	Spike Recovery (%)		Spike Recovery (%)		Spike Recovery (%)			
3VbcH	108.8±6.3	5.8	114.3±3	2.6	84.7±8.6	10.2	0.1	0.1
MeO3bcH	98.4±12.5	12.7	83.2±12.9	15.6	76.1±5.4	7	0.001	0.001
Pe3bcH	97±5.6	5.7	97.4±3.1	3.2	67.1±2.4	3.5	0.1	0.1
2O3cHdFP	87.1±3.9	4.5	78.7±4.8	6.1	113.4±7.5	6.6	0.50	0.50
5MeB	79.6±6	7.5	78.2±5.7	7.3	114.0±14.4	12.7	0.01	0.01
2OdF3B	90.5±7.4	8.2	77.8±4.7	6	94.7±7.6	8	0.05	0.05
tFMeO-2cHB	98.4±3.7	3.8	84.7±7.8	9.2	121.1±7.8	6.4	0.05	0.05
MePVbcH	121.9±2.4	2	77.5±2.6	3.4	99.0±9.5	9.6	0.1	0.1
tFPO-CF ₂ -dF3B	80.1±9.4	11.7	77.3±4.7	6.1	110.6±3.4	3	0.05	0.05
MeP3bcH	111.5±3.9	3.5	92.6±21.3	23	88.9±10.1	11.4	0.1	0.1
tFMePO-CF ₂ -dF3B	90.4±4.8	5.3	82.1±2.2	2.7	100.8±8.3	8.2	0.05	0.05
MeOdFP3bcH	91.7±2.8	3.1	78.8±0.9	1.1	96.1±8.8	9.2	0.1	0.1
3cH2B	84.6±1.9	2.2	79.8±6.6	8.2	103.3±8.3	8	0.01	0.01
2O2cHdFB	112±10	8.9	89.8±6.6	7.4	111.3±8.3	7.5	0.1	0.1
2OdFP3bcH	110.3±10.9	9.9	75.6±6	7.9	92.7±6.8	7.3	0.5	0.5
2F3T	88.7±6.8	7.7	82.8±3.1	3.7	110.2±7.6	6.9	0.05	0.05
2O3cHdFB	86.2±3.8	4.5	86.5±7.7	8.9	107.7±3.5	3.3	0.1	0.1
3OdFP3bcH	95.9±2.2	2.3	91.3±6.2	6.8	96.3±6.0	6.3	0.5	0.5
2OdFP4bcH	83.9±8	9.5	79.5±5.3	6.7	98.0±2.2	2.2	0.1	0.1
2F4T	89.5±2.3	2.6	90.9±5.3	5.9	104.7±1.6	1.5	0.1	0.1
2bcHdFB	103.7±6.5	6.3	93.7±4.1	4.3	87.4±2.8	3.3	0.1	0.1
tFPO-CF ₂ -dF3PyB	86.7±6.4	7.4	95.8±3.6	3.8	105.7±2.5	2.4	0.1	0.1
tFMeO-3cHtFT	88.3±7	8	88.3±4.3	4.8	97.3±10.8	11.1	0.1	0.1
tFPO-CF ₂ -tF3T	97.4±8.5	8.7	90.9±6.6	7.2	101.7±7.2	7	0.1	0.1

tFMePO-CF ₂ -dF3PyB	90.7±3.6	3.9	94.2±4.5	4.8	103.7±3.8	3.6	0.1	0.1
3bcHdFB	102.3±5.8	5.7	93.3±5.3	5.7	93.3±0.6	0.7	0.1	0.1
4bcHdFB	93.7±10.1	10.8	107.8±8.7	8	84.7±3.2	3.7	0.1	0.1
5bcHdFB	103.6±9.6	9.2	95.5±7	7.4	88.0±3.3	3.7	0.1	0.1
3dFB	92.5±11.2	12	65.9±3.3	5	89.9±5.3	5.9	0.01	0.01
2CB	108.4±2.9	2.7	79.6±3.6	4.5	101.0±4.1	4.1	0.01	0.01
3OCB	102.6±5.7	5.5	82.5±5.1	6.2	107.4±1.4	1.3	0.01	0.01
tFMeO-3bcHP	82±5.5	6.7	80.1±1.1	1.4	95.8±9.9	10.4	0.01	0.01
2teFT	81.4±4.5	5.6	81.6±1	1.3	113.2±6.6	5.8	0.01	0.01
5OCB	99.6±1.4	1.4	73.4±4.2	5.8	83.1±5.0	6	0.1	0.1
6OCB	87±4.8	5.5	81±1.8	2.2	89.9±6.0	6.7	0.1	0.1
8OCB	88.2±3.8	4.4	97.3±0.6	0.6	100.1±4.8	4.8	0.1	0.1
5CT	74.5±4.7	6.3	95.8±3.4	3.6	106.1±6.8	6.4	0.1	0.1
b3cHB	105.9±2.5	2.3	103±7.3	7.1	96.7±8.0	8.3	0.1	0.1
3cH5cHB	114.5±7.1	6.2	107.1±3.2	3	101.8±2.0	2	0.1	0.1

* Method Limit of Quantification $MQL = X/(Y*3)$, where X is Instrument Detection Limit (IDL), Y is Enrichment ratio (Enrichment ratio = 4)

Table S5. Concentrations (ng/g, dw) of the target LCMs in the sediment samples collected from the Pearl River Estuary (PRE) and surrounding coastal region. “-” indicates not detected. The summary of Kruskal-Wallis Test is attached at the end.

No.	Points	Sig.	Total LCMs	3VbcH	MeO3bcH	Pe3bcH	5MeB	MePVbcH	MeP3bcH	3cH2B	2CB	3OCB	tFMeO-3bcHP
1	A08	**	54.02±9.95	5.88	-	4.74	0.20	2.79	1.15	0.28	-	-	0.87
2	A09	*	47.13±18.63	6.57	-	1.35	1.00	3.25	0.41	-	-	-	0.95
3	A10	***	55.16±4.99	5.53	-	4.71	0.19	3.92	0.85	-	-	-	0.63
4	A12	***	54.83±5.87	6.85	-	4.24	0.39	2.62	-	-	-	-	-
5	A14		28.02±4.64	3.75	-	0.79	0.34	2.37	-	-	-	-	0.63
6	B01		27.97±16.50	3.95	-	1.24	0.21	1.73	-	-	-	-	0.47
7	F101		29.15±8.22	3.82	-	1.49	0.24	1.95	-	-	0.55	-	-
8	F103	*	46.49±0.29	7.56	-	1.65	0.15	1.81	0.24	-	-	-	0.24
9	F104		32.72±18.74	3.96	-	2.36	1.00	1.72	-	-	-	-	0.14
10	F203		35.60±10.46	5.78	-	1.25	0.16	1.93	0.49	-	-	-	0.49
11	F204		19.08±6.33	2.44	-	0.84	0.25	1.45	-	-	0.25	-	0.23
12	F301		26.45±5.79	3.34	-	1.48	-	1.50	0.34	-	-	-	0.44
13	F301C	***	53.65±3.65	6.57	-	2.65	0.37	2.84	0.85	-	0.59	-	0.12
14	F301D		29.55±10.58	4.46	-	0.82	0.16	1.39	0.35	-	-	0.64	0.23
15	F302	**	32.69±0.44	3.65	-	1.54	0.76	2.13	0.75	0.45	-	-	0.14
16	F303	**	49.11±8.59	5.92	-	2.92	0.84	2.82	0.42	-	-	-	0.14
17	F304		26.27±6.85	3.70	-	1.75	0.16	1.16	0.47	-	0.29	-	0.23
18	F305		21.79±0.67	-	-	2.46	0.40	2.67	0.24	-	-	-	0.44
19	F401	*	43.74±9.09	6.20	-	1.98	0.88	2.30	0.76	-	-	-	-
20	F404		39.99±2.71	5.67	-	1.62	0.30	1.73	1.27	0.54	-	-	0.90
21	F405		38.56±0.11	5.96	-	1.46	0.89	1.48	0.35	-	0.18	0.14	0.29
22	F406		26.43±11.98	2.91	-	1.59	0.50	1.88	0.18	-	0.12	-	-
23	F407		25.33±6.27	3.33	-	1.59	0.19	1.79	-	-	-	-	0.63
24	F601HK	*	43.72±1.99	5.69	-	1.86	0.66	2.76	0.44	-	-	-	0.16
25	F602		24.50±1.01	3.56	-	1.18	-	1.21	0.13	-	-	-	0.72
26	F603		15.11±16.99	1.14	-	0.84	-	1.48	-	-	0.99	-	0.31
27	F604		35.42±0.93	5.35	-	1.61	-	1.65	0.22	-	-	-	0.69

28	F901A	25.61±8.04	3.54	-	0.68	0.87	1.50	0.64	-	-	-	-
29	H002	8.10±6.05		-	0.22	0.17	1.53	0.33	-	-	-	0.26
30	H101	**** 90.78±12.14	14.54	-	-	-	4.38	3.45	0.32	-	0.18	-
31	H201	12.02±9.21	1.98	-	0.25	-	0.66	0.79	-	0.56	-	0.25
32	H501	**** 124.48±16.01	18.36	-	-	0.47	5.65	5.97	0.67	-	-	-
33	MS5	37.81±1.34	5.47	-	1.89	0.37	1.74	0.19	-	-	-	0.13
34	P101	19.94±10.72	2.62	-	0.99	0.56	1.15	0.18	-	-	-	-
35	P102	26.39±2.45	3.44	-	1.83	-	1.80	-	-	-	-	0.29
36	P103	21.40±5.39	2.98	-	0.94	-	1.37	-	-	-	-	0.67
37	P201	3.50±1.93	-	0.003	0.16	-	0.67	-	-	-	0.47	0.34
38	P203	41.90±21.17	5.98	-	2.26	-	1.58	0.47	-	0.33	0.14	0.17
39	P204	37.09±0.54	4.14	-	2.77	0.33	2.15	0.17	-	0.55	-	0.46
40	P301	32.24±26.13	2.88	-	2.79	1.00	1.93	0.35	-	0.18	0.39	-
41	P302	47.37±7.83	7.00	-	2.25	-	2.18	0.25	-	-	0.11	0.17
42	P303	23.59±14.06	3.30	-	1.20	0.12	1.74	0.22	-	0.16	0.35	0.14
43	P304	32.44±20.24	3.91	-	1.97	-	1.93	0.27	-	-	-	0.11
44	P502	** 46.05±9.82	5.93	-	3.60	0.67	2.17	0.15	-	-	-	0.19
45	P503	32.56±0.70	4.39	-	1.72	-	1.95	-	-	-	0.59	0.76

Kruskal-Wallis Test Summary

The distribution of *Total LCMs* in the same across categories of *Smapping Points*

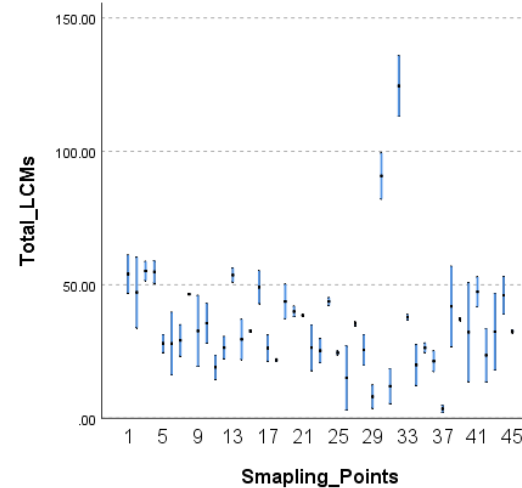
Total N	90
Test Statistic	68.785 ^a
Degree of Freedom	44
Asymptotic Sig. (2-sided test)	0.010

a. The test statistic is adjusted for ties

Multiple Comparisons Summary

- **** indicates significantly higher than 40% of the total sampling points
- *** indicates significantly higher than 20% of the total sampling points
- ** indicates significantly higher than 10% of the total sampling points
- * indicates significantly higher than 5% of the total sampling points

Independent-Samples Kruskal-Wallis Test



Continuous Field Information Total_LCMs

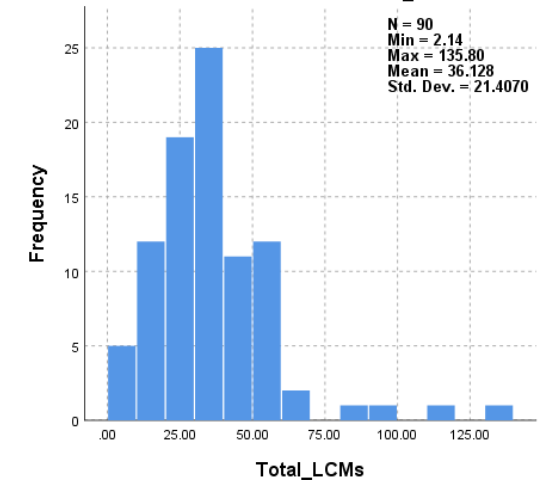


Table S6. The predicted fate, toxicity and metabolism of 9 widely detected LCMs using quantitative structure–activity relationships (QSARs).

Abbr.	Predicted K_{oc} (mL/g)	Predicted Acute (mg/L) Species, 96-h	Predicted Chronic (mg/L) Species, 30-d	ECOSAR Class	Cramer Class	Genotoxicity/Mutagenicity		
						Parent compound	Rat liver S9 metabolism simulator metabolites	Skin metabolism simulator metabolites
3VbcH <chem>C=CC(CC2)CCC2C1CC C(CCC)CC1</chem>	8.755E4	1.19E-05 Mysid	1.72E-07 Mysid, SW	Neutral Organics	Low (Class I)	no alert found	C=CC1CCC(CC1)C1CCC(CCC=O)CC 1(Aldehydes)	CCCC1CCC(O)(CC1)C1CCC(CC1)C =C (Cramer high class III)
MeO3bcH <chem>CCCC1CCC(C2CCC(O C)CC2)CC1</chem>	1.177E4	1E-03 Mysid	2.33E-05 Mysid, SW	Neutral Organics	High (Class III)	no alert found	C=O(Aldehydes); COC1CCC(CC1)C1CCC(CCC=O)CC1 (Aldehydes)	CCCC1CCC(C(O)C1)C1CCC(CC1)O C,CCCC1CCC(CC1)C1CCC(CC1)O C,COC1CCC(CC1)C1CCC(CC1)CC(C)O,COC1CCC(CC1)C1CCC(CCCO) CC1 (Cramer high class III)
Pe3bcH <chem>CC=CC(CC2)CCC2C1C CC(CCC)CC1</chem>	1.595E5	4.08E-06 Mysid	5.22E-08 Mysid, SW	Neutral Organics	Low (Class I)	no alert found	CCCC1CCC(CC1)C1CCC(CC1)C=CC O(Alpha-,Beta-unsaturated alcohols,Viny/Alcohols); CCCC1CCC(CC1)C1CCC(O)(CC1)C= CC(Viny/Alcohols)	CCCC1CCC(CC1)C1CCC(CC1)C=C CO (Alpha-,Beta-unsaturated alcohols,Viny/Alcohols)
5MeB <chem>Cc1ccc(c2ccc(CCCCC)c c2)cc1</chem>	1.524E5	3.41E-04 Mysid	7.08E-06 Mysid, SW	Neutral Organics	High (Class III)	no alert found	Cc1ccc(cc1)- c1ccc(CCCCC=O)cc1(mono aldehydes); CC(O)CCCc1ccc(cc1)- c1ccc(C)cc1O(Phenols and Anilines); CCCCC1ccc(cc1)- c1ccc(C)cc1O(Phenols and Anilines, Aldehydes)	CCCCC1ccc(cc1)-c1ccc(C)cc1O (Phenols and Anilines, Aldehydes) High(Class III)
MePVbcH <chem>Cc(cc3)ccc3C(CC2)CCC 2C1CCC(C=C)CC1</chem>	8.861E5	1.69E-06 Mysid	1.93E-08 Mysid, SW	Neutral Organics	Intermediate (Class II)	no alert found	Cc1ccc(C2CCC(CC2)C2CCC(CC2)C= C)c(O)c1(Phenols); Cc1ccc(cc1O)C1CCC(CC1)C1CCC(CC 1)C=C(Phenols); Cc1ccc(cc1)C1(O)CCC(CC1)C1CCC(C	OCc1ccc(cc1)C1CCC(CC1)C1CCC(C C1)C=C (Benzyl Alcohols)

							C1C=C(Benzyl Alcohols); OCc1ccc(cc1)C1CCC(CC1)C1CCC(CC1)C=C(Benzyl Alcohols);Cc1ccc(cc1)C1CCC(CC1)C1CCC(O)(CC1)C=C(Viny/Alyl Alcohols)	
MeP3bcH Cc(cc3)ccc3C(CC2)CCC2C1CCC(CCC)CC1	1.615E6	3.19E-07 Mysid	3.04E-09 Mysid, SW	Neutral Organics	Intermediate (Class II)	no alert found	CCCC1CCC(CC1)C1CCC(CC1)c1ccc(CO)cc1(Benzyl Alcohols); CCCC1CCC(CC1)C1CCC(O)(CC1)c1ccc(C)cc1(Benzyl Alcohols)	CCCC1CCC(CC1)C1CCC(O)(CC1)c1ccc(C)cc1(Benzyl Alcohols)
3cH2B CCCC1CCC(c2ccc(c3cc c(CC)cc3)cc2)CC1	3.08E6	1.07E-06 Mysid	1.16E-08 Mysid, SW	Neutral Organics	High (Class III)	no alert found	CCCC1CCC(CC1)c1ccc(cc1)-c1ccc(CC=O)cc1 (mono aldehydes); CCc1ccc(cc1)-c1ccc(cc1)C1CCC(CCC=O)CC1(mono aldehydes)	CCCC1CCC(O)(CC1)c1ccc(cc1)-c1ccc(CC)cc1 (Benzyl Alcohols)
2CB C(#N)c(ccc(c(ccc(c1)CC)c1)c2)c2	1.033E4	2.60E-01	1.10E-02 Mysid, SW	Neutral Organics	High (Class III)	no alert found	O=CCc1ccc(cc1)-c1ccc(cc1)C#N (mono aldehydes); OCC(=O)c1ccc(cc1)-c1ccc(cc1)C#N (Ketones)	O=CCc1ccc(cc1)-c1ccc(cc1)C#N (mono aldehydes)
3OCB C(#N)c(ccc(c(ccc(OCCC)c1)c1)c2)c2	7.18E3	2.70E-01 Mysid	1.20E-02 Mysid, SW	Neutral Organics	High (Class III)	no alert found	Oc1ccc(cc1O)-c1ccc(cc1)C#N(Hydroquinones); CCC=O(Aldehydes); O=CCCCOc1ccc(cc1)-c1ccc(cc1)C#N (Aldehydes)	CC(O)COc1ccc(cc1)-c1ccc(cc1)C#N,OCCCCOc1ccc(cc1)-c1ccc(cc1)C#N (High (Class III))
tFMeO-3bcHP c1(C2CCC(C3CCC(CC)CC3)CC2)ccc(OC(F)F)F)cc1	2.554E6	1.00E-07	8.24E-010 Mysid, SW	Neutral Organics	High (Class III)	no alert found	CCCC1CCC(CC1)C1CCC(CC1)c1ccc(OC(F)(F)F)c(O)c1 (Phenols); CCCC1CCC(CC1)C1CCC(O)(CC1)c1ccc(OC(F)(F)F)cc1 (Benzyl Alcohols); CCCC1CCC(CC1)C1CCC(CC1)c1ccc(OC(F)(F)F)c(O)c1 (-acceptor-path3-H-acceptor)	No metabolites

Table S7. Risk Quotient values of the 10 detected LCMs at specific sampling point. “-” indicates not detected. “0.000” indicates the RQ is < 0.001.

No.	Points	3VbcH	MeO3bcH	Pe3bcH	5MeB	MePVbcH	MeP3bcH	3cH2B	2CB	3OCB	tFMeO-3bcHP	RQ _{ΣLCMs}
1	A08	0.390	-	0.569	0.000	0.163	0.234	0.008	-	-	0.413	1.7786
2	A09	0.436	-	0.162	0.001	0.190	0.084	-	-	-	0.451	1.3243
3	A10	0.367	-	0.566	0.000	0.229	0.173	-	-	-	0.299	1.6348
4	A12	0.455	-	0.509	0.000	0.153	-	-	-	-	-	1.1177
5	A14	0.249	-	0.095	0.000	0.139	-	-	-	-	0.299	0.7822
6	B01	0.262	-	0.149	0.000	0.101	-	-	-	-	0.223	0.7359
7	F101	0.254	-	0.179	0.000	0.114	-	-	0.000	-	-	0.5469
8	F103	0.502	-	0.198	0.000	0.106	0.049	-	-	-	0.114	0.9691
9	F104	0.263	-	0.283	0.001	0.101	-	-	-	-	0.067	0.7145
10	F203	0.384	-	0.150	0.000	0.113	0.100	-	-	-	0.233	0.9796
11	F204	0.162	-	0.101	0.000	0.085	-	-	0.000	-	0.109	0.4572
12	F301	0.222	-	0.178	-	0.088	0.069	-	-	-	0.209	0.7656
13	F301C	0.436	-	0.318	0.000	0.166	0.173	-	0.000	-	0.057	1.1511
14	F301D	0.296	-	0.098	0.000	0.081	0.071	-	-	0.000	0.109	0.6567
15	F302	0.242	-	0.185	0.001	0.125	0.153	0.013	-	-	0.067	0.7845
16	F303	0.393	-	0.351	0.001	0.165	0.086	-	-	-	0.067	1.0616
17	F304	0.246	-	0.210	0.000	0.068	0.096	-	0.000	-	0.109	0.7289
18	F305	-	-	0.295	0.000	0.156	0.049	-	-	-	0.209	0.7099
19	F401	0.412	-	0.238	0.001	0.134	0.155	-	-	-	-	0.9396
20	F404	0.377	-	0.195	0.000	0.101	0.259	0.015	-	-	0.428	1.3740
21	F405	0.396	-	0.175	0.001	0.087	0.071	-	0.000	0.000	0.138	0.8676
22	F406	0.193	-	0.191	0.000	0.110	0.037	-	0.000	-	-	0.5313
23	F407	0.221	-	0.191	0.000	0.105	-	-	-	-	0.299	0.8163
24	F601HK	0.378	-	0.223	0.001	0.161	0.090	-	-	-	0.076	0.9289
25	F602	0.236	-	0.142	-	0.071	0.026	-	-	-	0.342	0.8175
26	F603	0.076	-	0.101	-	0.087	-	-	0.000	-	0.147	0.4104
27	F604	0.355	-	0.193	-	0.096	0.045	-	-	-	0.328	1.0178
28	F901A	0.235	-	0.082	0.001	0.088	0.130	-	-	-	-	0.5356

29	H002		-	0.026	0.000	0.089	0.067	-	-	-	0.124	0.3068
30	H101	0.966	-	-	-	0.256	0.703	0.009	-	0.000		1.9333
31	H201	0.131	-	-	-	0.039	0.161		0.000	-	0.119	0.4498
32	H501	1.219	-	-	0.000	0.330	1.216	0.019	-	-		2.7848
33	MS5	0.363	-	0.227	0.000	0.102	0.039	-	-	-	0.062	0.7928
34	P101	0.174	-	0.119	0.001	0.067	0.037	-	-	-		0.3973
35	P102	0.228	-	0.220	-	0.105	-	-	-	-	0.138	0.6913
36	P103	0.198	-	0.113	-	0.080	-	-	-	-	0.318	0.7093
37	P201	-	0.000	0.019	-	0.039	-	-	-	0.000	0.162	0.2200
38	P203	0.397	-	0.271	-	0.092	0.096	-	0.000	0.000	0.081	0.9375
39	P204	0.275	-	0.333	0.000	0.126	0.035	-	0.000	-	0.219	0.9869
40	P301	0.191	-	0.335	0.001	0.113	0.071	-	0.000	0.000		0.7114
41	P302	0.465	-	0.270		0.127	0.051	-	-	0.000	0.081	0.9943
42	P303	0.219	-	0.144	0.000	0.102	0.045	-	0.000	0.000	0.067	0.5765
43	P304	0.260	-	0.237	-	0.113	0.055	-	-	-	0.052	0.7164
44	P502	0.394	-	0.432	0.001	0.127	0.031	-	-	-	0.090	1.0745
45	P503	0.292	-	0.207	-	0.114	-	-	-	0.000	0.361	0.9733

Red colour: $RQ_{\Sigma LCMs} > 2$ ($n = 1$)

Orange colour: $2 > RQ_{\Sigma LCMs} > 1$ ($n = 10$)

Yellow colour: $1 > RQ_{\Sigma LCMs} > 0.5$ ($n = 28$)

Table S8. Proportion of RQ of an individual LCM contributing to the total LCMs (P_{LCM_x}) (%).

No.	Points	3VbcH	MeO3bcH	Pe3bcH	5MeB	MePVbcH	MeP3bcH	3cH2B	2CB	3OCB	tFMeO-3bcHP
1	A08	22.0	-	32.0	0.0	9.2	13.2	0.4	-	-	23.2
2	A09	32.9	-	12.2	0.1	14.3	6.3	-	-	-	34.1
3	A10	22.5	-	34.6	0.0	14.0	10.6	-	-	-	18.3
4	A12	40.7	-	45.6	0.0	13.7	-	-	-	-	-
5	A14	31.8	-	12.1	0.0	17.7	-	-	-	-	38.3
6	B01	35.6	-	20.2	0.0	13.7	-	-	-	-	30.3
7	F101	46.4	-	32.7	0.0	20.8	-	-	0.0	-	-
8	F103	51.8	-	20.4	0.0	10.9	5.0	-	-	-	11.8
9	F104	36.8	-	39.7	0.1	14.1	-	-	-	-	9.3
10	F203	39.2	-	15.3	0.0	11.5	10.2	-	-	-	23.8
11	F204	35.4	-	22.1	0.1	18.5	-	-	0.0	-	23.9
12	F301	29.0	-	23.2		11.5	9.0	-	-	-	27.3
13	F301C	37.9	-	27.6	0.0	14.4	15.0	-	0.0	-	5.0
14	F301D	45.1	-	15.0	0.0	12.4	10.9	-	-	0.0	16.6
15	F302	30.9	-	23.6	0.1	15.9	19.5	1.6	-	-	8.5
16	F303	37.0	-	33.0	0.1	15.5	8.1	-	-	-	6.3
17	F304	33.7	-	28.8	0.0	9.3	13.1	-	0.0	-	15.0
18	F305		-	41.6	0.1	22.0	6.9	-	-	-	29.5
19	F401	43.8	-	25.3	0.1	14.3	16.5	-	-	-	-
20	F404	27.4	-	14.2	0.0	7.4	18.8	1.1	-	-	31.1
21	F405	45.6	-	20.2	0.1	10.0	8.2	-	0.0	0.0	15.9
22	F406	36.4	-	35.9	0.1	20.7	6.9	-	0.0	-	-
23	F407	27.1	-	23.4	0.0	12.8	-	-	-	-	36.7
24	F601HK	40.7	-	24.0	0.1	17.4	9.6	-	-	-	8.2
25	F602	28.9	-	17.3	-	8.7	3.2	-	-	-	41.9
26	F603	18.4	-	24.6	-	21.1	0.0	-	0.0	-	35.9
27	F604	34.9	-	19.0	-	9.5	4.4	-	-	-	32.2
28	F901A	43.9	-	15.2	0.2	16.4	24.3	-	-	-	-

29	H002	-	-	8.6	0.1	29.2	21.9	-	-	-	40.3
30	H101	49.9	-	-	-	13.2	36.3	0.5	-	0.0	-
31	H201	29.2	-	-	-	8.6	35.8	-	0.0	-	26.4
32	H501	43.8	-	-	0.0	11.9	43.7	0.7	-	-	-
33	MS5	45.8	-	28.6	0.0	12.8	4.9	-	-	-	7.8
34	P101	43.8	-	29.9	0.1	16.9	9.2	-	-	-	-
35	P102	33.0	-	31.8	-	15.2	-	-	-	-	19.9
36	P103	27.9	-	15.9	-	11.3	-	-	-	-	44.9
37	P201	-	0.0	8.7	-	17.8	-	-	-	0.0	73.4
38	P203	42.4	-	29.0	-	9.9	10.2	-	0.0	0.0	8.6
39	P204	27.9	-	33.7	0.0	12.7	3.5	-	0.0	-	22.1
40	P301	26.9	-	47.1	0.1	15.9	10.0	-	0.0	0.0	-
41	P302	46.8	-	27.2	-	12.8	5.1	-	-	0.0	8.1
42	P303	38.0	-	25.0	0.0	17.6	7.8	-	0.0	0.0	11.5
43	P304	36.2	-	33.0	-	15.8	7.7	-	-	-	7.3
44	P502	36.6	-	40.2	0.1	11.8	2.8	-	-	-	8.4
45	P503	30.0	-	21.2	-	11.7	0.0	-	-	0.0	37.1
Average		36.1	0.0	25.7	0.1	14.3	12.0	0.9	0.0	0.0	23.3
Standard deviation		8.0	N/A	9.6	0.0	4.2	10.1	0.5	0.0	0.0	14.8

$P_{LCMx} = RQ_{LCMx} / RQ_{\Sigma LCMs} * 100\%$.

3VbcH, Pe3bcH, and tFMeO-3bcHP (in orange color) are the top 3 contributors.

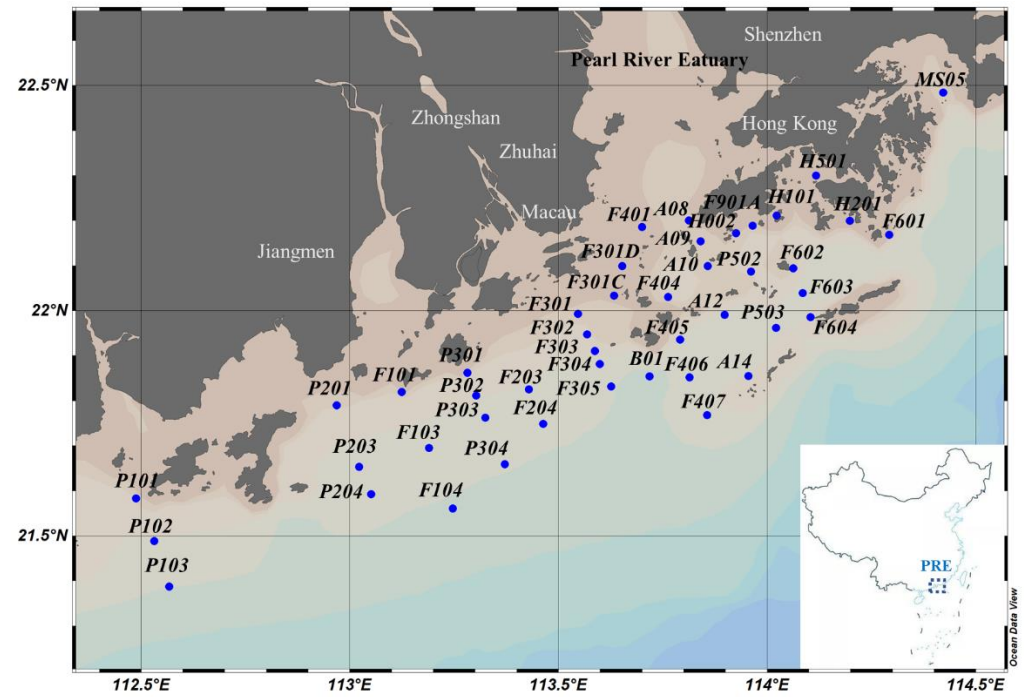


Figure S1. Locations of the 45 sediment sampling points in the PRE and the surrounding coastal region.

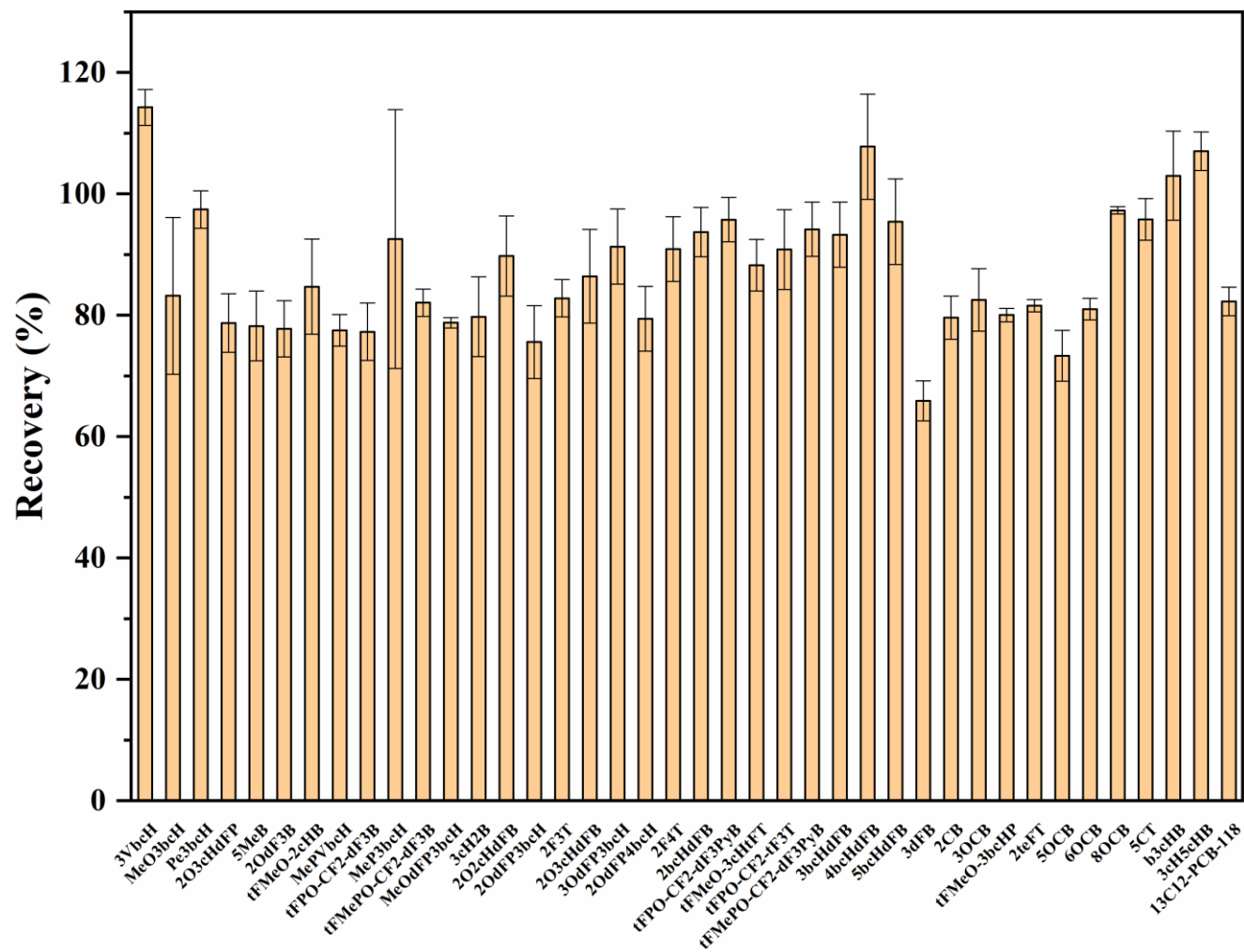


Figure S2. Column plot of 39 target analytes and 1 surrogate recoveries at the medium spiking level (10 ng/g LCMs) in sediments.

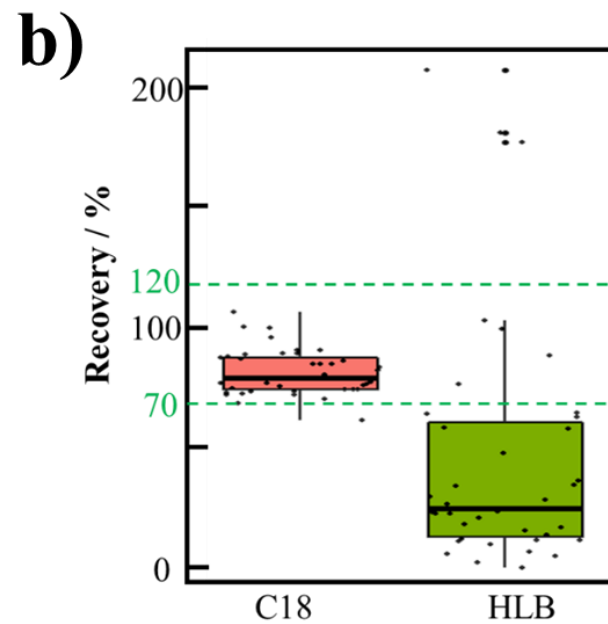
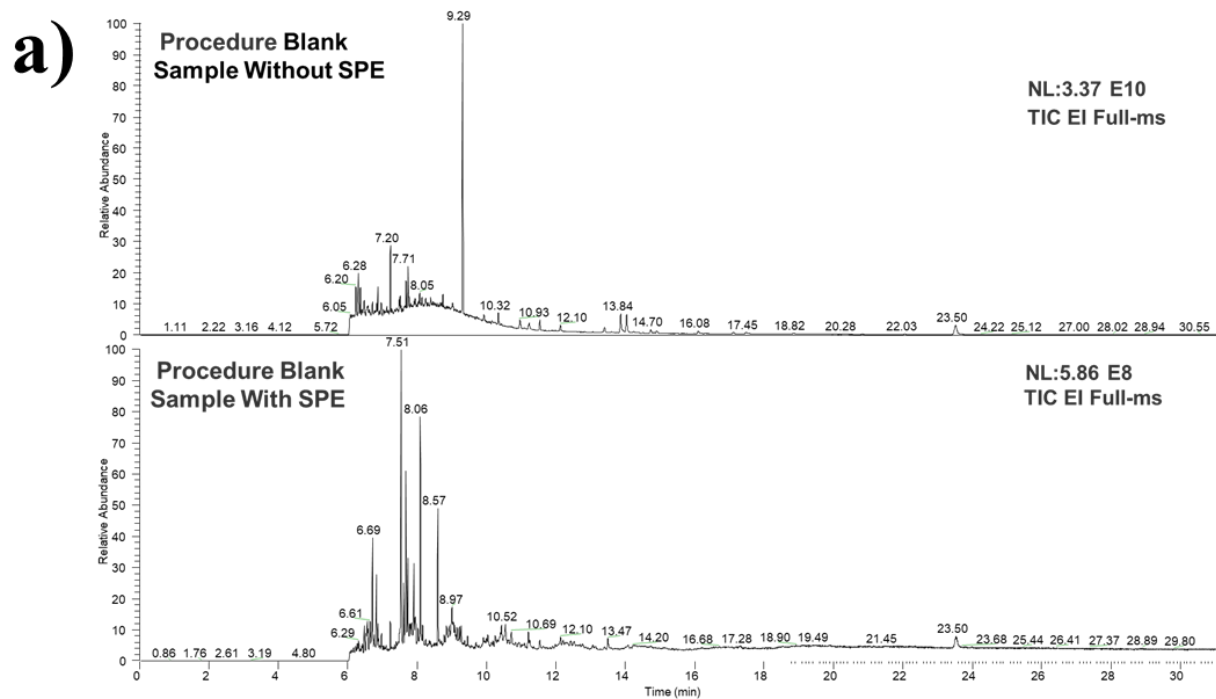


Figure S3. Optimization of SPE method. a) Background noise of SPE cleanup on GC-MS; b) Comparison of LCMs recoveries between C18 and HLB SPE cartridges.

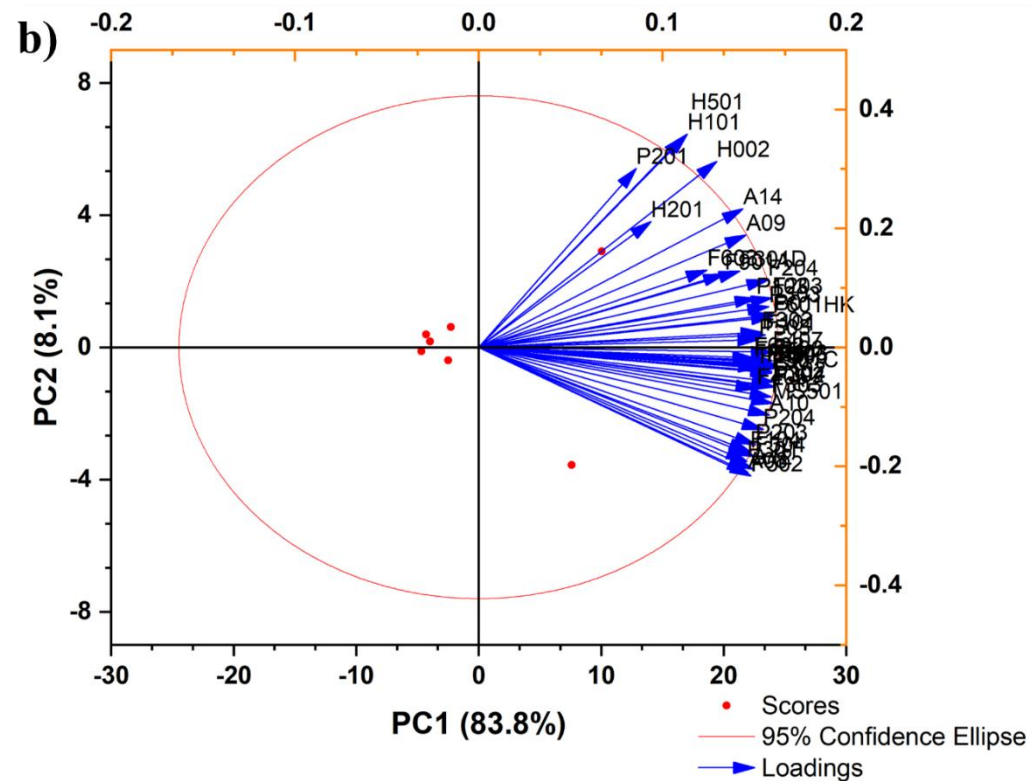
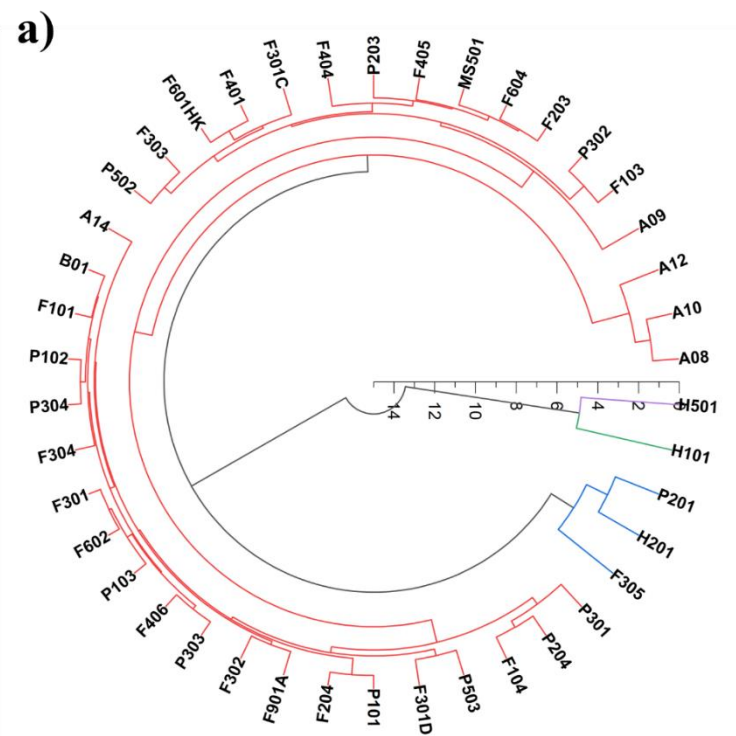


Figure S4. Analysis of Σ LCMs distribution in the studying area. a) Cluster Analysis on different sampling points; b) PCA on different sampling points.

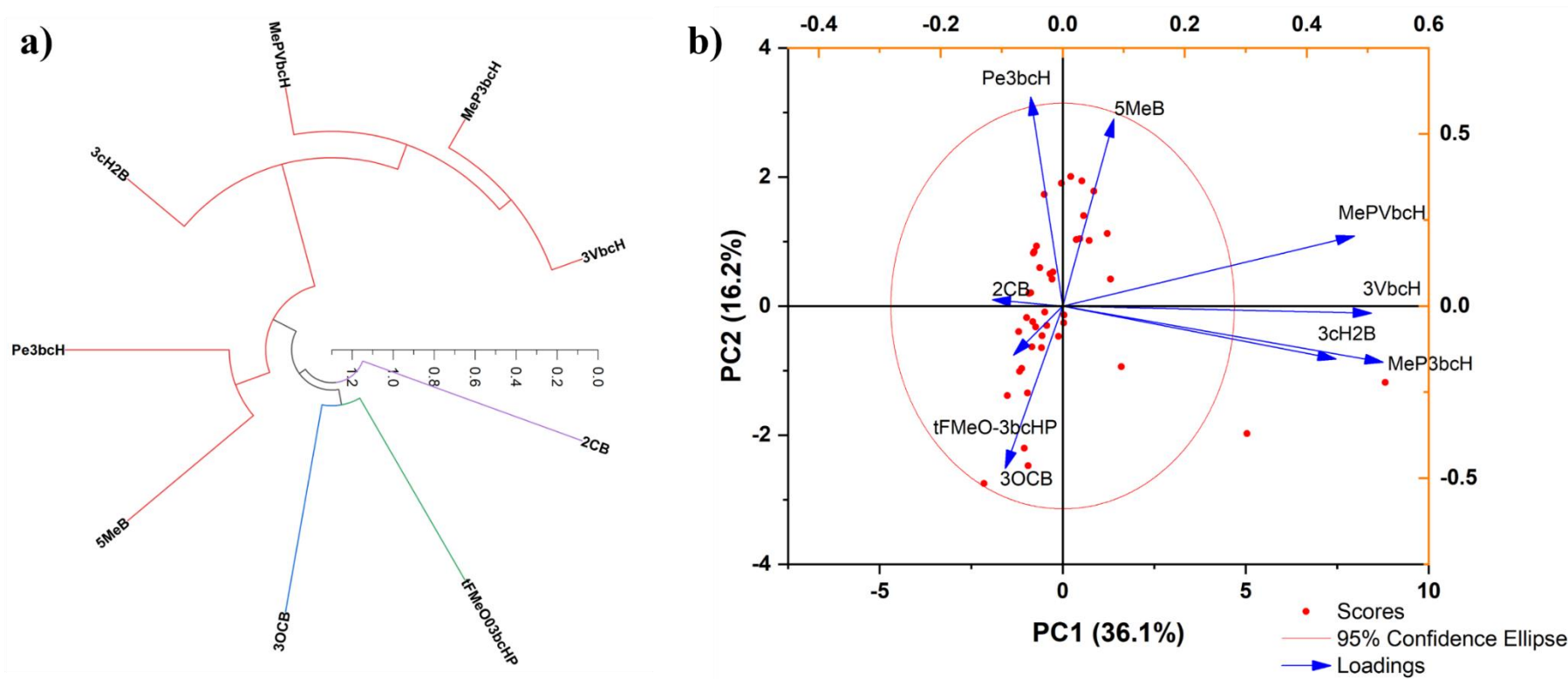


Figure S5. Analysis of individual LCM distribution in the studying area. a) Cluster analysis of individual LCM distribution; b) PCA of individual LCM distribution.

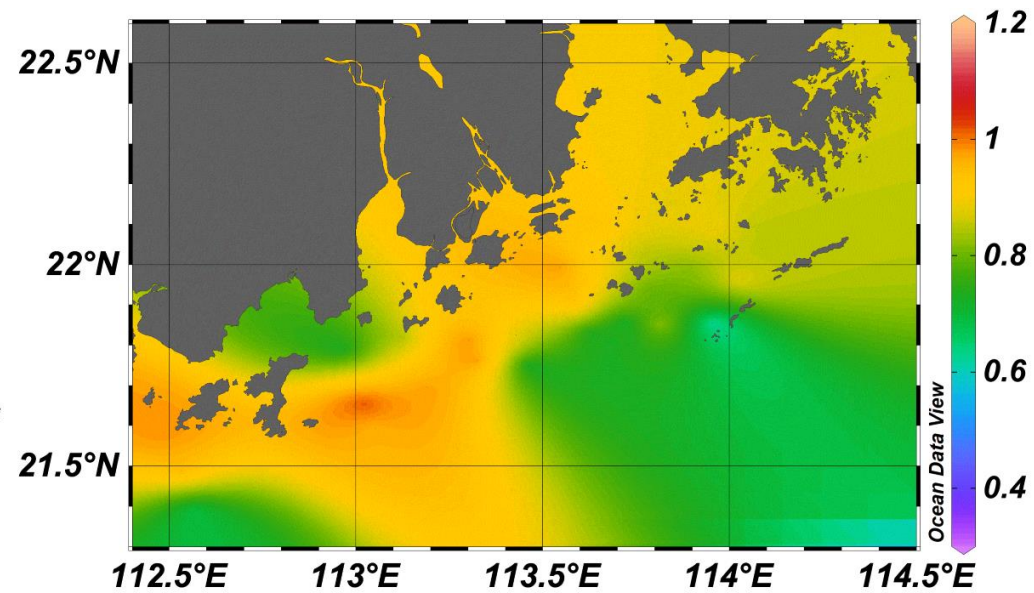


Figure S6. Distribution of Total Organic Carbon (%) in sediments in the PRE and surrounding coastal region.

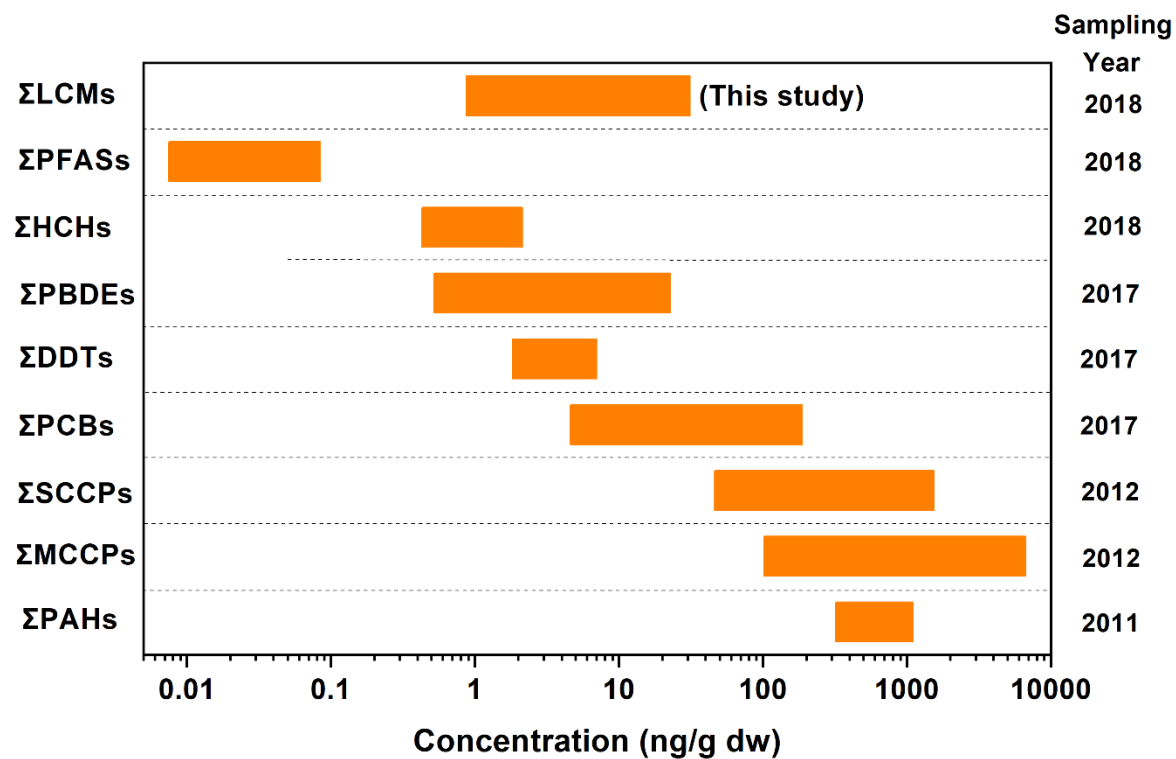


Figure S7. The concentration comparison of ΣLCMs with other groups of organic contaminants (PBDEs[28], PFASs[24], PAHs[45], DDTs[42], HCHs[42], SCCPs[44], MCCPs[44] and PCBs [42]) in the sediments from the PRE obtained from previous reports. See references in the main text.

Reference

- [1] Lam, J.C.; Lyu, J.; Kwok, K.Y.; Lam, P.K.S. 2016. Perfluoroalkyl substances (PFASs) in marine mammals from the South China Sea and their temporal changes 2002-2014: Concern for alternatives of PFOS? *Environmental Science and Technology*, 50 (13), 6728-6736.
- [2] Lam, J.C.; Lam, P.K.S. 2015. Occurrence and ecological risk of halogenated flame retardants (HFRs) in coastal zones. In *Comprehensive Analytical Chemistry*; Zeng, E.Y., Ed.; Elsevier: Amsterdam, Netherlands, 2015, pp 389-409.
- [3] U.S. EPA. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Dieldrin. EPA-600-R-02-010. Office of Research and Development. Washington, DC 20460.