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Typical organic contaminants in hair of adult residents between inland and coastal capital cities in China: Differences in levels and composition profiles, and potential impact factors

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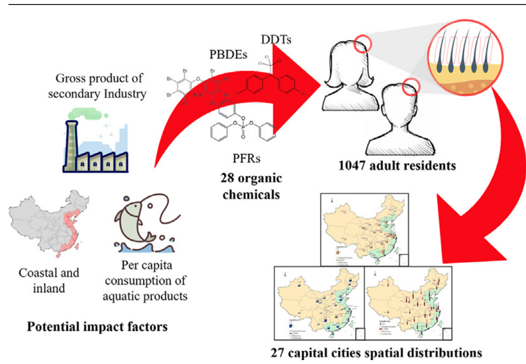
HIGHLIGHTS

- Studied potential impact factor on rising organic contaminant levels in China.
- Conducted large-scale biomonitoring of OCs based on hair sample analysis.
- Coastal residents showed significantly higher OC levels than inland residents.
- Dominant DDTs and PFRs significantly correlated with statistical indicators.
- Significant gender differences were observed in OC levels and compositions.

GRAPHICAL ABSTRACT



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ABSTRACT

The growing of urbanization, industrialization, and agricultural production have resulted in the increasing contamination of typical organic contaminants (OCs) in China. However, data on differences in exposure characteristics of typical OCs between the coastal and inland cities among residents in China are limited. In this study, hair samples were collected from adult residents in 10 and 17 provincial capital cities in coastal and inland China, respectively, to investigate the differences in the levels and composition profiles of typical OCs. The potential factors impacting the human exposure to OCs were also examined based on the relationship among the hair OC levels and the population characteristics and statistical indicators. The median concentrations of dichlorodiphenyltrichloroethane's (DDTs), polybrominated diphenyl ethers (PBDEs), and organophosphorus flame retardants (PFRs) in hair of coastal urban residents were 3.64, 5.58, and 268 ng/g, respectively, while their concentrations in samples from inland urban residents were 1.84, 3.85, and 202 ng/g, respectively. Coastal residents showed significantly higher hair OC concentrations than inland residents ($p < 0.05$). BDE209 and *p,p′*-DDE were the predominant chemicals for PBDEs and DDTs, respectively, in both coastal and inland cities. Tris(2-chloroisopropyl) phosphate (TCIPP) was the dominant PFR in coastal residents' hair, while triphenyl phosphate (TPHP) was the major PFR in inland residents' hair, possibly owing to the different usages of the PFRs. Significant gender differences were observed in the levels and composition profiles of OCs ($p < 0.05$). The levels of *p,p′*-DDE and TCIPP were significantly related to the gross domestic product (GDP), gross

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secondary industry product, and the per capita consumption of aquatic products ($p < 0.05$). This study provides scientific data for evaluating human exposure to OCs in urban residents at a large scale and its associations with statistical indicators including urbanization, industrialization, agricultural production, and diet in China.

1. Introduction

Pollution by organic contaminants (OCs) is a serious and growing global concern (Lin et al., 2020; Morin-Crini et al., 2022). Several typical OCs including organophosphorus flame retardants (PFRs), polybrominated diphenyl ethers (PBDEs), and dichlorodiphenyltrichloroethanes (DDTs) are ubiquitous in household and natural environments owing to their use in varied commercial products, as well as their persistence, bioaccumulation, and long-range transport properties (Morin-Crini et al., 2022). The production and consumption of chemicals are exponentially increasing in *recent decades in China* owing to the rapidly growing urbanization, industrialization, and agricultural production. This has led to the widespread occurrence of various OCs in environment, and pose great health risks.

Although DDTs and PBDEs have been regulated and restricted under the Stockholm Convention on Persistent Organic Pollutants, long-term exposure to these chemicals and their associated health risks are still of concerns owing to their massive historical use, persistence and bioaccumulation potential, and adverse effects on ecological and human health (Liu et al., 2016; Yuan et al., 2017; Zhang et al., 2017). The global restriction and phasing-out of PBDEs led to the increased production and use of PFRs as their primary substitute in recent years (Wei et al., 2015). PFRs are used as non-reactive additive chemicals in various consumer and industrial products around the world. Consequently, they are susceptible to leaching into the environment during manufacturing, transportation, use, and abandonment (Yao et al., 2021). PFRs ubiquitously exist in environmental matrices (Wei et al., 2015) and biological samples, including aquatic biota (Yao et al., 2021), human milk (Wei et al., 2015), and the placenta (Ding et al., 2016). Several PFRs, including tri-*n*-butyl phosphate (TNBP), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), and triphenyl phosphate (TPHP), are potentially mutagenic, carcinogenic, neurotoxic, or embryotoxic (Wang et al., 2015; Wei et al., 2015). Besides, chronic exposure to 2-ethylhexyl diphenyl phosphate is a potential risk factor for developmental toxicity (UK Environment Agency, 2009). Therefore, owing to their adverse effects on human health, PFRs have attracted growing attention in recent years.

China is the third largest country worldwide in term of geographical areas. The imbalance development of industrial and economic activities in different regions and diversified consumer behaviors and diet lifestyle of population between coastal and inland regions can lead to different OC exposure levels for urban residents (Landrigan et al., 2018; Zhang et al., 2008; Zhao, 2022). Human biomonitoring is a promising strategy for directly evaluating human exposure to OCs based on the measurement of the levels of parent chemicals or their metabolites in human samples (Huang et al., 2022). A negative association was observed between economic regional development level and ΣOH-Phe, a monohydroxylated metabolite of polycyclic aromatic hydrocarbon (PAH) levels in urine samples corresponding to the general population from 26 provincial capital cities in China (Huang et al., 2022). Human hair is alternately widely used as a non-invasive biomonitoring matrix for assessing human exposure to various OCs. Compared to urine, human hair is a much suitable biomonitoring material for evaluating human exposure to OCs on a large scale, given its associated advantages, including easy sampling, low cost, and convenient transportation and storage. For example, Peng et al. (2021) assessed the human exposure to OCs for the general population in Luxembourg via hair sample analysis from 497 adults. However, studies in China in this regard have been limited to certain geographical areas (e.g., specific single city, Eastern China, and e-waste recycling area) (Ding et al., 2016; Qiao et al., 2016; Tang et al., 2014; Zhang et al., 2017) or specific populations (e.g., children, pregnant women, and occupational population) (Kucharska et al., 2015a; Liu et al., 2016; Qiao et al., 2019; Zhang et al., 2007). To our knowledge, data on the differences in DDTs, PBDEs, and PFRs exposure in the general population between coastal and inland regions in China and their potential impact factors like population characteristics and statistical indicators of urbanization, industrialization, agricultural production, and diet are unavailable in the literature (Chen et al., 2014).

In this study, human hair samples were collected from ordinary urban residents in 27 provincial capital cities in coastal and inland areas in China to identify and map the differences in human exposure levels to OCs and to investigate their potential impact factors. Such an initial contrastive study on human exposure to OCs in the coastal and inland regions with different levels of social and economic development would provide scientific information and enhance understanding for policy proposal-making, like the diet structure in different regions with respect to human exposure to OCs, especially in developing countries.

2. Materials and methods

2.1. Chemicals and materials

Seven PBDE congeners, 15 PFRs, and 6 DDTs were analyzed in this study. Detailed information regarding the target chemicals is presented in Table S1 in the Supplementary Information (SI) file.

2.2. Sample collection

A campaign to collect human hair samples was conducted from June 2020 to October 2020. A total of 1047 samples were collected from 17 and 10 capital cities in inland and coastal regions, respectively, comprising 20 provincial capital cities, five autonomous region capital cities, and two municipalities in China (Fig. S1). The participants were required to have inhabited the city for >2 years and have not undergone any hair treatment during that time. The demographic characteristics of the 1047 participants are provided in Table 1. All participants were recruited from urban cities. In China, 67 % of the total population inhabits urban cities, indicating that the results of this OC contamination study may be true for more than half of the Chinese population.

All the volunteers were fully informed of the scope and nature of the study and signed a written informed consent form before participation. Further, each participant completed a short questionnaire to provide information regarding age and sex. Approval was received from the Ethics Committee of South China Institute of Environmental Sciences. The hair samples of participants close to the scalp (0–3 cm) were cut using stainless steel scissors pre-cleaned with isopropyl alcohol. After collection, the hair samples were wrapped in aluminum foil and sealed in a polythene zipper bag. All the sample were transported to the laboratory and kept at −20 °C before pretreatment.

2.3. Sample preparation and instrumental analysis

The procedures for sample preparation and instrumental analysis of target chemicals in hair samples were performed as those in our previous study (Tang et al., 2021), and were described in details in the SI file.

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

Procedural blanks were included during individual sample batch experiments to track potential background contamination. Further, matrix spiking recovery experiments were conducted to confirm the efficacy of the extraction of the target chemicals. The trace levels of the target chemicals

Table 1
Demographic characteristics of 1047 participants recruited from 27 provincial capital cities across China.

Regions	Provinces/autonomous regions/municipalities	Cities	Sex		Age
			Female	Male	
Coastal (n = 356, 34.0 %)	Fujian	Fuzhou	19	17	18–46
	Zhejiang	Hangzhou	12	19	20–55
	Shandong	Jinan	22	20	18–52
	Jiangsu	Nanjing	16	10	20–44
	Shanghai	Shanghai	10	18	20–55
	Liaoning	Shenyang	14	19	18–53
	Tianjin	Tianjin	17	15	18–54
	Guangdong	Guangzhou	27	21	18–42
	Guangxi	Nanning	23	17	18–53
	Hainan	Haikou	20	20	20–40
Central (n = 691, 66.0 %)	Heilongjiang	Harbin	20	16	18–49
	Jilin	Changchun	19	28	23–33
	Anhui	Hefei	3	19	21–43
	Jiangxi	Nanchang	16	43	18–47
	Hunan	Changsha	26	16	18–42
	Inner Mongolia	Hohhot	19	29	20–42
	Shanxi	Taiyuan	23	35	18–35
	Henan	Zhengzhou	31	18	20–45
	Gansu	Lanzhou	9	41	20–46
	Xinjiang	Urumqi	14	29	18–50
	Shannxi	Xi'an	20	24	18–40
	Qinghai	Xining	20	14	18–50
	Ningxia	Yinchuan	20	9	19–43
	Sichuan	Chengdu	19	20	18–35
	Guizhou	Guiyang	14	22	18–43
	Yunnan	Kunming	12	21	21–43
	Xizang	Lhasa	7	15	19–46
Sum			472	575	18–55

were detected in the procedural blanks, and thereafter, subtracted from the values corresponding to the hair samples. The recoveries of the target analytes in the spiked matrix (n = 5) ranged from 86–112 %, 80–115 %, to 81–122 % for PBDEs, DDTs, and PFRs, respectively. The limit of quantitation (LOQ) was estimated as three times the standard deviation value of the target analytes detected in procedural blanks. For the undetected analytes in the procedural blanks, the LOQs were calculated based on a signal-to-noise ratio of 10 (S/N = 10) generated taking into consideration the lowest calibration point. The determined LOQ ranges for PBDEs, PFRs, and DDTs were 0.17–4.43, 0.01–52.3, and 0.06–0.48 ng/g, respectively.

2.5. Statistical analysis

Analytes with a detection frequency (DF) higher than 50 % were statistically analyzed using SPSS 21.0 (SPSS Inc., Chicago, IL, USA). During analysis, concentrations below the LOQs were considered to be half of the LOQ value for each OC. Additionally, the possible correlations between the concentrations of the chemicals in hair samples and population characteristics were evaluated via Spearman rank correlation analysis. The chemical profiles of the hair samples from coastal and inland urban residents were compared via principal component analysis (PCA). Data normality was evaluated via a Shapiro–Wilk test, and differences in hair OC concentrations between two groups (sex, age, and region) were examined using a Mann–Whitney *U* test. Further, the relationships between OC levels and statistical indicators of urbanization, industrialization, and agricultural production, including gross domestic product (GDP), gross secondary industry product, per capita consumption of aquatic products and so on, were assessed by multivariable linear analysis, multivariate ridge regression analysis and Spearman correlation analysis. Each OC was analyzed separately, and subsequently they were adjusted for all the potential confounding factors. Statistical significance in this regard was set at $p < 0.05$. Data were obtained from the City Statistical Yearbook 2020 and the China Statistical Yearbook 2020 published by the State Statistics Bureau (Table S2). Additionally, the spatial distribution of the contaminants in residents' hair in China was mapped using the ArcGIS software v.10.3 (ESRI Co., Redlands, CA, USA).

3. Results and discussion

3.1. OC levels between coastal and inland urban residents' hair

Varying levels of DDTs, PBDEs, and PFRs were detected in all the 1047 hair samples collected from coastal and inland urban residents in China (Tables S2, S3, and S4), and the concentrations varied between the two regions. Table 2 summarizes the levels of major PFRs, PBDEs, and DDTs in hair reported in the literature. The median levels of eight target chemicals, with the DFs > 50 % in the collected hair samples varied in an order as: TCIPP > TPHP > TEHP > iDPHP > *p,p′*-DDE > BDE209 > BDE28 > *p,p′*-DDT. The spatial distribution of the OCs in hair samples collected in this study was shown in Fig. 1.

Although the agricultural use of technical DDT mixture has been banned for decades, DDTs were widely detected in hair samples in this study. The DFs of *p,p′*-DDE were the highest in both coastal (94.9 %) and inland hair samples (92.9 %), followed by *p,p′*-DDT (68.3 % and 52.1 % for coastal and inland hair, respectively), while those for the other DDTs varied in the range of 19.1–36.0 %. Hair samples from coastal urban residents showed higher DFs for all six DDT chemicals than the samples collected from inland urban residents (Table S3). The Σ_6DDT levels were nd–382 ng/g (median 3.64) and nd–183 ng/g (median 1.84 ng/g) for coastal and inland hair samples, respectively. These values were 1–3 orders of magnitude lower than the Σ_6DDT levels reported for hair samples collected from northern Poland residents (Wielgomas et al., 2012) and Romanian residents in 2009, 1989, and 1968 (Covaci et al., 2008). Herein, the levels of *p,p′*-DDE, *p,p′*-DDT, and Σ_6DDT in coastal residents' hair were significantly higher compared to inland residents' hair ($p < 0.001$). Similarly, the concentration of DDTs in maternal plasma, human milk, placenta, and hair of residents in coastal areas were higher compared to inland areas (Man et al., 2014; Rollin et al., 2009). The levels of hexachlorobenzene (HCB), β-hexachlorocyclohexane (β-HCH), polychlorinated biphenyls-118 (PCB-118), PCB-138, PCB-153, PCB-180, mirex, and *p,p′*-DDE in serum of lactating women from coastal areas were found to be significantly higher than those from inland areas ($p < 0.01$) (Bravo et al., 2019). The levels of Σ_6DDT and the dominant chemical, *p,p′*-DDE were significantly correlated with the per capita consumption of aquatic products (Fig. S4b, $p < 0.05$), which was consistent with the result found in a previous study (Sarcinelli et al., 2003). Furthermore, the per capita consumptions of aquatic products of coastal cities were significantly higher than those of inland cities ($p < 0.01$). The transportation and deposition of DDTs into the estuarine regions by rivers could be the indirect causes for their relative high exposure levels for coastal urban residents (Li et al., 2016b). On the other hand, the use of DDT-containing antifouling paint in the boats is also an important source of DDTs in the coastal areas (Li et al., 2016b).

Seven PBDE congeners were detected (DFs: 8.7–90.0 %) in hair samples, and DFs > 50 % were found for BDE209 (90.0 %) and BDE28 (52.8 %) (Table S4). Σ_7PBDE, the sum of the concentrations of the seven congeners, for the hair samples from coastal and inland urban residents varied in the ranges nd–168 ng/g (medians 5.58 ng/g) and nd–789 ng/g (medians 3.85 ng/g), respectively. These values were comparable to those reported in previous studies for hair samples from Yunnan, Guangzhou, and Wenling residents, but much lower than those reported for samples from residents of Canada, Poland, Shanghai, and Langfang (Table 2). Overall, the levels of BDE28, BDE209, and Σ_7PBDE in hair of coastal urban residents were significantly higher than those of inland urban residents ($p < 0.001$). Similarly, higher concentrations of hydroxylated PBDEs (OH-PBDEs) were observed in sewage sludge in coastal areas than inland regions in China (Sun et al., 2013). The overall levels of POPs including PBDEs, DDTs, PCBs, HCHs, HCB, and hexabromocyclododecanes (HBCDs) were also found higher in seagulls (coastal resident bird) compared to pigeons (inland resident bird) (Hong et al., 2014). In this study, the hair Σ_7PBDE level observed for Harbin was the highest among all the

Table 2
Concentrations (ng/g dw) of OCs in hair samples from the general population in different countries and regions.

Area	Sampling time	Sample size	OCs	Range	Median	Average	Primary chemicals	References
America	2014	Urban (50)	PFRs	210–10,800	1530	1600	TDCIPP, TPHP	(Liu et al., 2016)
Norway	/	Urban (102)	PFRs	<1– 3744	/	/	TBOEP, TNBP, TPHP	(Kucharska et al., 2015b)
Belgium	2013	Urban (20)	PFRs	2–5032			TNBP	(Kucharska et al., 2014)
China	2020	Coastal (356)	PFRs	nd-2490	268	373	TCIPP, TPHP, TDCIPP, TEHP	This study
		Inland (691)		nd-2870	202	287	TPHP, TCIPP, TDCIPP, TCEP	
Spain	/	Urban (16)	PBDEs	1.4–19.9	/	/	BDE209	(Tadeo et al., 2009)
Langfang, China	2011	Urban (45)	PBDEs	1.5–861	/	112	BDE209	(Tang et al., 2014)
Wenling, China	2015	Urban (20)	PBDEs	nd-60.6	/	12.9	BDE209	(Liang et al., 2016)
Shanghai, China	2010	College student (25)	PBDEs	4.04–99	Male 12 Female 27.7	Male 12 Female 40.6	BDE209	(Tang et al., 2013)
Shanghai, China	2011	Urban (11)	PBDEs	12.6–127	/	40.3	BDE209, BDE47	(Ma et al., 2011)
Polan	2012	Urban (12)	PBDEs	nd-33	14	17	BDE209	(Krol et al., 2014)
Canada	/	Urban (50)	PBDEs	30.9–2484	109	/	BDE47, BDE99, BDE209	(Poon et al., 2014)
Yunnan, China	2014	(10)	PBDEs	2.1–14	4.3	5.2	BDE209	(Yuan et al., 2016)
Guangzhou, China	2014	College student (43)	PBDEs	0.28–34.1	5.27	/	BDE209	(Qiao et al., 2018)
China	2020	Coastal (356) Inland (691)	PBDEs	nd-168 nd-789	5.58 3.85	10.3 8.85	BDE209 BDE209	This study
Yunnan, China	2014	(13)	DDTs	Σ_6DDTs: 2.07–3.93	/	Σ_6DDTs: 2.85	*p,p′*-DDT, *p,p′*-DDE	(Yuan et al., 2017)
Pakistan	/	Infertile males (45)	DDTs	*p,p′*-DDE:0.024–14.94; *p,p′*-DDT: nd–2.86	/	*p,p′*-DDE:0.858; *p,p′*-DDT:0.125	*o,p′-DDE*	(Amir et al., 2021)
Iran	2007–2008	Urban (37) Rural (19)	DDTs	Σ_6DDTs: 0.8–54 Σ_6DDTs:8–305	Σ_6DDTs:8 Σ_6DDTs:27	Σ_6DDTs: 10.2 Σ_6DDTs: 49	*p,p′*-DDE *p,p′*-DDT	(Dahmardeh Behrooz et al., 2012)
Romania	2002–2003	(42)	DDTs	Σ_6DDTs: 20.1–6550	Σ_6DDTs: 394	/	*p,p′*-DDT	(Covaci et al., 2008)
China	2020	Coastal (356)	DDTs	Σ_6DDTs: nd-382	Σ_6DDTs: 3.64	Σ_6DDTs: 9.36	*p,p′*-DDE, *p,p′*-DDT	This study
		Inland (691)		Σ_6DDTs: nd-183	Σ_6DDTs: 1.84	Σ_6DDTs: 4.54	*p,p′*-DDE, *p,p′*-DDT	

27 cities. The levels of low-brominated BDEs in urban air decreased between 2008 and 2013, whereas the levels of BDE209 increased within this period owing to the late prohibition of the Deca-BDE technical mixture; BDE209 contamination in urban air in northeastern China remains serious (Li et al., 2016a). Most noteworthily, the heating period in winter is longer for Harbin (October to April) than for other cities in North China (November to March), and the indoor temperature (18–24 °C) in Harbin is even higher than for South China in the winter season. As a result, PBDEs are more readily released from interior decoration materials, electronic appliances, and furniture in Harbin (Yang et al., 2012). Moreover, indoor ventilation conditions are poor in Harbin during winter, resulting in higher PBDE levels in an indoor environment and a higher degree of exposure risk for residents.

A total of 15 PFRs (DFs: 5.37–98.1 %) were detected in hair from the general population in China in this study (Table S5). PFRs showed predominance in the three chemical groups observed in hair samples. TPHP, TEHP, TCIPP, and iDPHP were the most frequently detected PFRs in both coastal and inland hair samples. The DFs of TCEP and BDP in coastal residents' hair were >50 %, but <50 % for inland residents' hair. The Σ_{15}PFR value corresponding to hair samples from coastal and inland urban residents were 6.95–2490 ng/g (median 268 ng/g) and nd–2870 ng/g (median 202 ng/g), respectively. These values were lower than those reported for residents of Belgium (Kucharska et al., 2014), Norway (Kucharska et al., 2015a), and the US (Liu et al., 2016). Overall, the levels of Σ_{15}PFR and individual PFR chemicals with DFs > 50 %, apart from TPHP, in coastal residents' hair were significantly higher than those in inland residents' hair ($p < 0.05$). TPHP is widely used in polyurethane foam in furniture, displays, and cables, and is ubiquitous in the environment in both coastal and inland areas (Kim et al., 2014; van der Veen and de Boer, 2012). Absorption via indoor dust was the major pathway for human exposure to PFRs, while other pathways of PFR intake such as dietary or dermal absorption via soil may still be significant (Yadav et al., 2017). The nationwide spatial distribution of PFRs in soils in residential areas in China also indicated that higher PFR levels in soil in Eastern China than those in other regions in China (He et al., 2019). Furthermore, PFRs in drinking water presented a gradually increasing trend from cities in inland cities to coastal cities of China (Zhang et al., 2021), and the levels of PFRs in fish in Pearl River were almost twice higher as those in inland rivers including Xijiang River, Beijiang River, and Dongjiang revier (Liu et al., 2019). These could be related to overpopulation, high urbanization, and industrialization in Guangzhou and surrounding coastal areas (Liu et al., 2019). However, no information regarding the consumption and production of PFRs congeners and the PFRs pollution of indoor dust between coastal and inland areas in China is available (He et al., 2019).

3.2. The composition profiles of OCs between coastal and inland residents' hair

Among the six DDTs detected in hair samples in this study, *p,p'*-DDE was predominant in both coastal and inland areas, followed by *p,p′*-DDT (Table S6, Fig. 2a). *p,p'*-DDE in human hair primarily originates from internal exposure (Yuan et al., 2017). This chemical has also been detected in the human placenta and fetal adipose tissue (Man et al., 2014). *p,p'*-DDE is the primary and stable metabolite of *p,p′*-DDT (Mrema et al., 2013), and its persistence (half-life) is longer than those of other DDT chemicals. The levels of *p,p'*-DDE were significantly positive associated with those of *p,p′*-DDT ($r = 0.57$), consistent with the results of previous studies

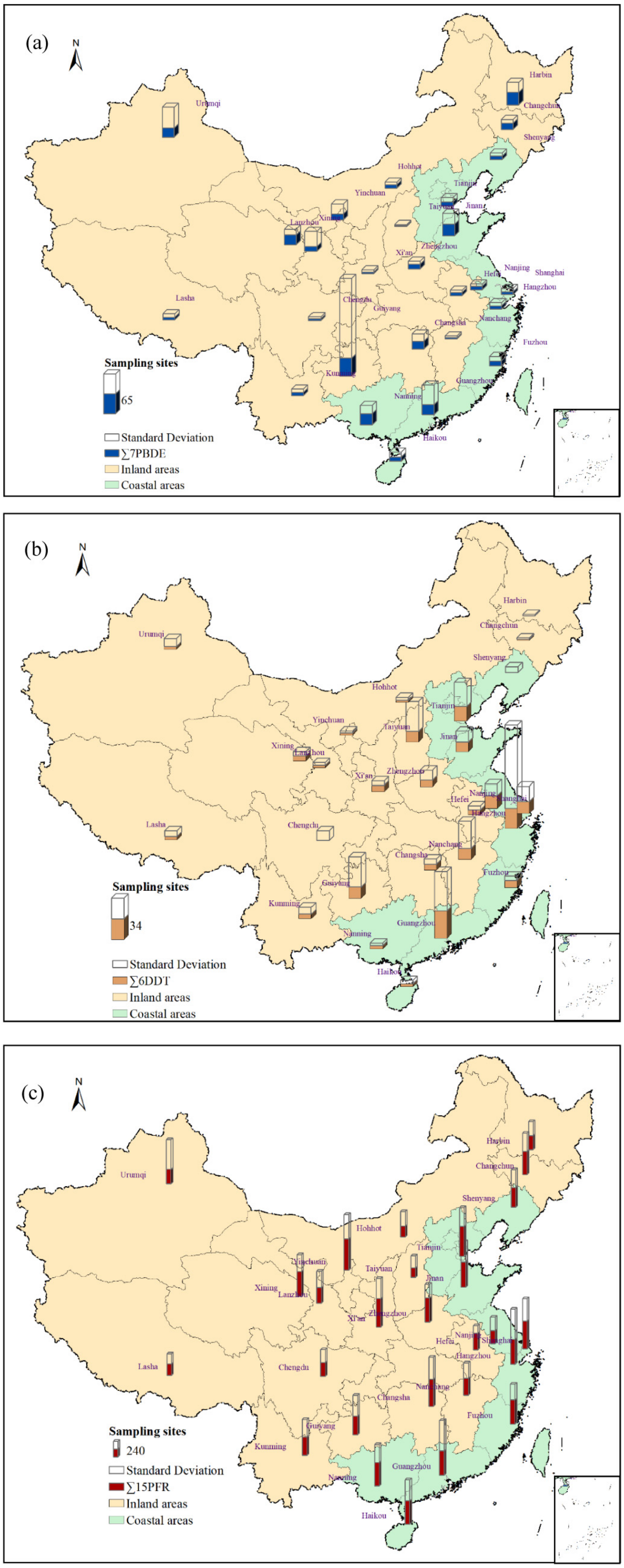

Fig. 1. Average concentrations and standard deviations of Σ_7PBDE, Σ_6DDT, and Σ_{15}PFR in human hair samples from the residents of 27 provincial cities in coastal and inland areas in China.

(Dahmardeh Behrooz et al., 2012; Wielgomas et al., 2012; Zhang et al., 2007).

Although the use of technical DDT for agricultural production has been banned for over 3 decades, DDT is still used as a raw material to produce acaricide dicofol and antifouling paint for fishing boats (Liu et al., 2012). The *p,p′*-DDE and *p,p′*-DDT ratio could provide information regarding the accumulation of *p,p′*-DDT; i.e., a ratio <5 for hair samples indicates fresh exposure to parent DDT (Peng et al., 2020; Yuan et al., 2017). In this study, the *p,p′*-DDE/*p,p′*-DDT ratios were <5 for 88.5 % and 88.0 % of the coastal and inland hair samples, respectively, suggesting that the observed hair DDT input in most of the participants was relatively fresh. The *o,p′*-DDT/*p,p′*-DDT ratio ranges between 0.2 and 0.33 (average: 0.25) for antifouling paint samples was reported in a previous study (Yu et al., 2011). In this study, the average *o,p′*-DDT/*p,p′*-DDT value for coastal residents' hair was 0.31; while was 0.14 for inland residents' hair (with detectable *p,p′*-DDT). Therefore, we could infer that antifouling paint was the primary exposure source for coastal urban residents (Xin et al., 2011), whereas dicofol was probably the main source of fresh parent DDT for inland urban residents. Even though DDTs in hair from urban residents in China were in relatively low levels, the fresh DDT input as well as the historical residue remain a serious concern as they could cause endocrine disorder and increase the risk of offspring urogenital system malformation (Fernandez et al., 2007; Michalakis et al., 2014; Shen et al., 2008; vom Saal et al., 2001).

BDE209 was the predominant PBDE congener in urban residents' hair in both coastal and inland areas, with relative contributions of 65.9 % and 65.8 %, respectively (Fig. 2a), consistent with those found in previous studies (Liu et al., 2016; Qiao et al., 2018). BDE209 is also the dominant PBDE congener in various environmental media in China, such as urban soils (Han et al., 2021), house/indoor dust (Guo et al., 2020; Niu et al., 2018), and atmospheric fine particles (Zhang et al., 2019). The contributions of the other congeners were <15 % in hair, similar to the results for soils in China (Yin et al., 2021). This could be attributed to two reasons. On the one hand, the three commercially produced PBDE technical mixtures, i.e., Penta-, Octa-, and Deca-BDEs, have been widely used in various types of industrial and commercial products (Wu et al., 2021). Particularly, Penta- and Octa-BDE mixtures are extensively used in Europe and North America, while Deca-BDE is used in the largest quantity in China (Liu et al., 2016). On the other hand, BDE209 was recently included in the list of POPs of the Stockholm Convention in 2017 (UNEP, 2017), while commercial Penta- and Octa-BDE mixtures were earlier incorporated in 2009 (UNEP, 2009).

TCIPP and TPHP were the dominant PFR chemicals in coastal and inland hair samples, respectively, accounting correspondingly for 29.8 % and 27.7 % (Fig. 2b). TCIPP is a chemical recalcitrant to degradation in the environment, which accounted for over 55 % of the total PFR output worldwide (van der Veen and de Boer, 2012). A previous study showed that the main PFR chemicals in Belgium residents' hair are TDCIPP and TCEP (Kucharska et al., 2014), while TBOEP, TNBP, and TPHP have been identified as the major PFRs in residents' hair from Norway (Kucharska et al., 2015a). Liu et al. (2016) indicated that TCEP, TDCIPP, and TPHP are the predominant PFRs in hair of American residents. Differences in PFR compositions among countries and regions may be related to the varied use of household products and the various types of PFRs added to them. For example, TCIPP is mainly used in plastic components of household products (Reemtsma et al., 2008), while TPHP is commonly added to nitrocellulose, polyvinyl chloride (PVC), and other materials, like flame-retardant plasticizers. Thus, they can be easily released into the atmosphere owing to their low vapor pressures (Kim et al., 2014; van der Veen and de Boer, 2012; Yin et al., 2019). Preferences in household products between regions can also result in differences in the compositions of PFRs in the indoor environment. In recent years, TCIPP has been used as a replacement for TCEP (He et al., 2019). In this study, the TCIPP/TCEP concentration ratios in hair of coastal urban residents were significantly higher than those of inland urban residents, suggesting that the shift to the use of TCIPP as a replacement for TCEP was faster in coastal areas (He et al., 2019). Particularly, a TCIPP/TCEP ratio < 1 was observed for 88 % and 68 % of residents'

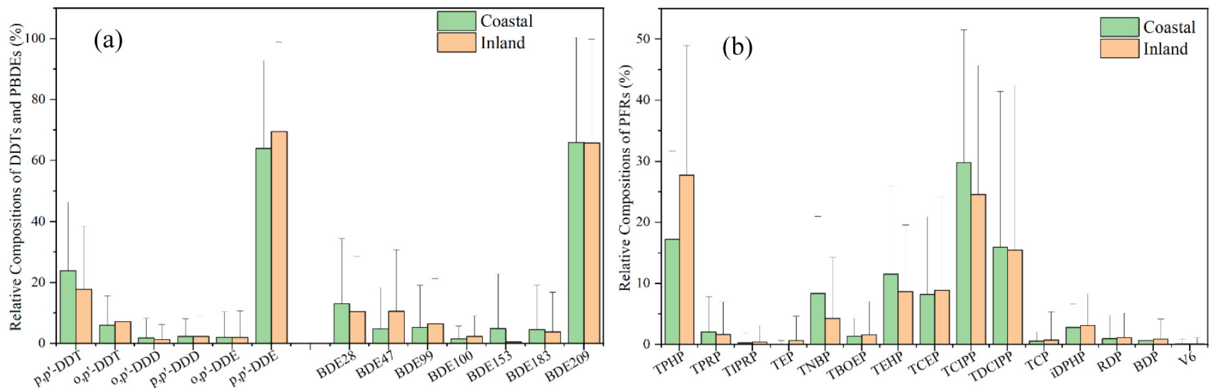

Fig. 2. Congener profiles of DDTs and PBDEs (a), and PFRs (b) in hair samples from residents in coastal and inland China.

hair in Zhengzhou and Xining, respectively, where TCEP was identified as the most abundant PFR. Similar ratio of TCIPP/TCEP was also observed in the PM2.5 samples collected in Xinxiang, a city located adjacent to Zhengzhou (Yang et al., 2019).

As PFRs are increasingly being used as replacements for PBDEs in all types of furniture, electronics, and electrical products, the potential risks of human exposure to PFRs are on the rise (Tang et al., 2022). TPHP and TCIPP are two predominant PFRs as "emerging" flame-retardants. In this study, the ratios of TPHP/BDE209 and TCIPP/ BDE209 were calculated to investigate the differences in human exposures to the "emerging" flame-retardants between the coastal and inland residents. It showed significantly higher TPHP/BDE209 ratios for hair samples from inland urban residents than those from coastal urban residents ($p < 0.001$). Whereas, opposite results were observed for the TCIPP/BDE209 ratios, though the difference was not statistically significant. These results suggested a higher shift of "legacy" (PBDEs) to "emerging" contaminant (TPHP) exposures in inland residents than in coastal residents, while the shift of "legacy" (PBDEs) to "emerging" contaminant (TCIPP) was higher in coastal residents (Tang et al., 2022).

The correlation matrices of the nine pollutants with DF > 50 % are presented in Table S7 and Fig. 3. Significant correlations were observed between chemicals, such as TPHP, TEHP, TCIPP, and iDPHP for PFRs (r = 0.23–0.38). As mentioned above, *p,p′*-DDE and TCIPP in the general population primarily originate from dietary exposure and secondary industry pollution, respectively. Thus, the concentration ratios of *p,p′*-DDE and TCIPP for the different regions could represent the ratio of internal and external exposure sources. The average *p,p′*-DDE/TCIPP ratio for hair samples from coastal urban residents was higher compared to inland urban residents. This finding emphasized that more attention should be paid to the consumption of aquatic products given the level of DDT contaminates in hair of coastal urban residents. As for the specific city, the geomean *p,p′*-DDE/TCIPP ratio was observed highest in the coastal city,

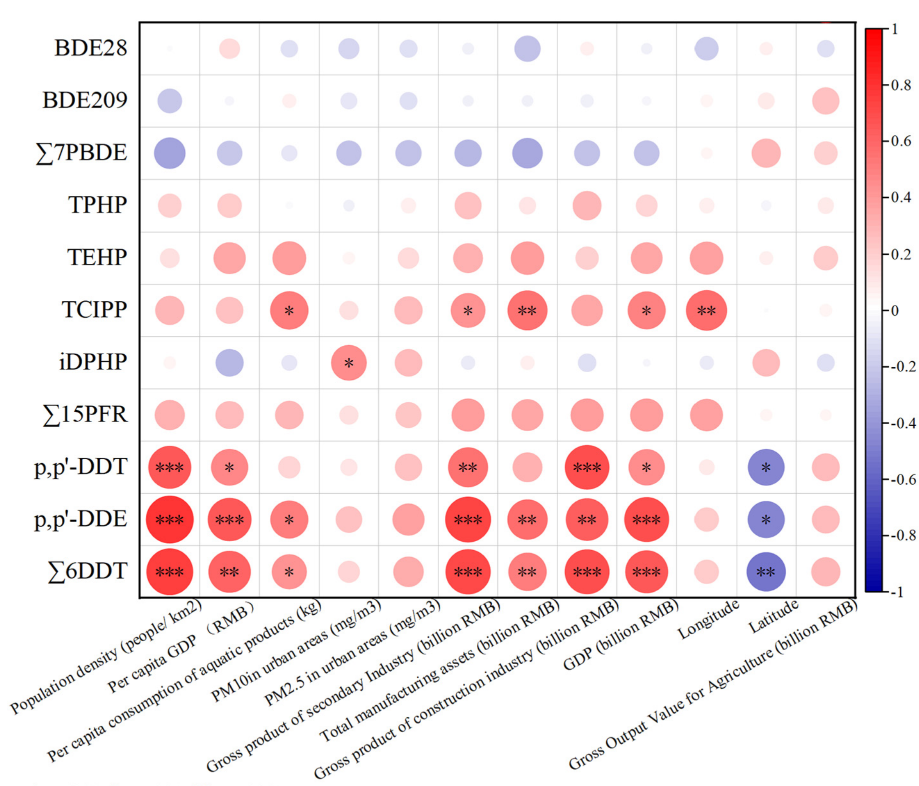

Fig. 3. Correlation matrices between pollutants with DFs > 50 % in hair samples collected from 27 provincial capital cities and statistical indicators.

Nanjing, whereas the lowest was found in Changchun, in line with the analysis above. The highest and lowest geomean levels of *p,p′*-DDE and TCIPP were observed in Nanjing. Among 27 cities, the geomean concentration of *p,p′*-DDE was the lowest in Changchun. Interestingly, the *p,p′*-DDE/TCIPP ratios in female hair samples were significantly higher compared to males ($p < 0.01$). Similarly, Zhang et al. (2017) reported that females showed higher exposure levels of DDTs than males through dietary exposure in Nanjing.

3.3. Potential impact of population characteristics

A weakly significant correlation was observed between the ages of all participants and the levels of BDE28, TCIPP, TEHP, and *p,p′*-DDE in hair (Table S8). Both PBDEs and DDTs are listed as POPs with high bioaccumulation and persistence properties, and thus, life-long accumulation of these chemicals in the human body is expected. Although BDE28 and BDE209 were detected over 50 % hair samples among the seven target PBDEs, the concentrations of BDE209 were not significantly related to age. This is corresponding to the *facts that* BDE209 was readily debrominated to low brominated congeners in the human body (Zheng et al., 2014). *p,p′*-DDE is the primary and stable metabolite of *p,p′*-DDT (Mrema et al., 2013), and its persistence (half-life) is longer than those of other DDT chemicals (Dahmardeh Behrooz et al., 2012; Wielgomas et al., 2012; Zhang et al., 2007). Hou et al. (2021) also found a significant increase of TCIPP in blood with age due to decreased metabolic and/or excretory capacities of the elderly. As for the two groups of population in coastal and inland regions, significant positive correlations were observed between ages and *p,p′*-DDE in coastal residents' hair as well as BDE28 in inland residents' hair ($r = 0.169, p < 0.001$; $r = 0.087, p < 0.05$, respectively). These results suggested that lifestyle of residents in different regions probably is an important factor underlying the age differences in OCs levels, and more studies are required to elucidate the influence of age on OC exposure (Huang et al., 2022).

Among the 1047 adult resident participants, the male-to-female ratio was 575:472. The detection of OCs in hair slightly varied between different sexes. In female hair samples, 9 chemicals, i.e., BDE28, BDE209, TPHP, TEHP, TCIPP, TCP, iDPHP, *p,p′*-DDT, and *p,p′*-DDE, showed DFs > 50 %. In male hair samples, 7 compounds, i.e., BDE209, TPHP, TEHP, TCIPP, TCEP, iDPHP, and *p,p′*-DDE, showed DFs > 50 %. The results of the Mann-Whitney test revealed that the concentrations of BDE28, BDE209, TPHP, TEHP, TCIPP, TCP, iDPHP, *p,p′*-DDT, and *p,p′*-DDE in female hair samples were significantly higher than those in male hair samples (Fig. S2), while the opposite trend was observed for TCEP ($p < 0.05$). In previous studies, the results of sex differences in PBDEs and PFRs in residents' hair were contradictory. For instance, Σ_7PBDE levels in hair of female college students are significantly higher than those in male students in Shanghai (Tang et al., 2013), and those of BDE28 and BDE47 in female residents' hair were twice those in males (Krol et al., 2014). On the other hand, no sex difference was found for PBDEs in hair of residents in Canada (Poon et al., 2014). Conversely, higher concentrations of PBDEs in hair of males than in females were observed in Spain (Tadeo et al., 2009). Among PFRs, Liu et al. (2016) reported a similar result, whereby TPHP in hair of American female college students was significantly higher compared to males. Similarly, Qiao et al. (2018) found that the levels of Σ_{15}PFR in female hair were significantly higher compared to males but the difference was reversed when the analysis was conducted using the same position and length of hair (0–5 cm from the scalp) for both sexes. The inconsistency among previous results may be due to different hair sample collection and analysis methods across studies.

As for DDTs, significantly higher levels of *p,p′*-DDT and *p,p′*-DDE in female hair have also been found in Beijing, Romania, and America (Altshul et al., 2004; Covaci et al., 2008; Zhang et al., 2007). The sex differences in OC levels in hair may be attributed to the causes as follows: first, females show a preference for the intensive use of hair care and hairdressing products. Thus, they are more susceptible to using shampoo containing lindane or cosmetic products containing lanoline contaminated with DDT, and FRs (Polese et al., 2000). Second, ingestion was determined as the main route for human exposure to DDTs, and the ingestion exposure of DDTs for females was significantly higher than that of males (Zhang et al., 2017). Finally, the anatomical and physiological differences in the distribution volume of fat-soluble substances are also important issues related to the differences in gender exposure (Butter, 2017). While the larger average lean body mass and higher water content in men result in a higher dilution of contaminants, women have larger relative fat mass and bioaccumulation capacity for lipophilic contaminants.

The composition profiles for target compounds in hair of urban residents between sexes are shown in Fig. S3. The overall compositions of PBDEs, PFRs, and DDTs in hair of urban residents were similar between sexes in China. The results suggested similar exposure sources of OCs in hair of urban females and males. In particular, female hairs had significantly higher proportions of *p,p′*-DDT and lower *p,p′*-DDE among the total DDTs than those in males ($p < 0.01$). This result supported the hypothesis of greater exposure through diet for males and the presence of other contamination sources for females (Covaci et al., 2008). The average ratio of *p,p′*-DDT/ *p,p′*-DDE in female hair was 0.88, while in male hair, it was 0.40, indicating that the degradation rate of *p,p′*-DDT into *p,p′*-DDE in females was significantly lower compared to males (Qiu et al., 2005).

3.4. Potential impact of urbanization, industrial, agricultural, air pollution, and dietary parameters

Given the imbalance development in industrial activities and diversified behaviors on the consumer and diet habit between different cities, different OC exposure levels for urban residents might exist (Zhang et al., 2008; Zhao, 2022). As thus, the potential impacts of urbanization (population density, GDP, per capita GDP), industrialization (gross product of secondary industry, total manufacturing assets, and gross product of construction industry), agricultural production (gross output value agriculture), air pollution (average concentration of PM10 in urban and average concentration of PM2.5 in urban), and dietary habit (per capita consumption of aquatic) in 27 cities on residents' hair OC concentrations were analyzed in this study. The values of GDP, longitude, population density, and per capita consumption of aquatic products were significantly higher in coastal region than in inland region ($p < 0.05$). Multiple linear regression analysis was first conducted for statistical indicators and pollutant concentrations of all participants. Only the regression model of *p,p′*-DDE and per capita GDP showed significant statistical significance ($F = 4.294$, $p < 0.01$), under the premise that there was no substantial collinearity between independent variables (Fig. S4). Then, multivariate ridge regression analysis was performed, and the regression models were neither significant. This was probably because statistical indicators, like per capita consumption of aquatic products, are averages of all residents for the whole city, but not for the participants, which could show collinearity. Thus, the simple linear regression model was applied to analyze the associations between each statistical indicator and the exposure levels of target OCs in urban residents. The levels of Σ_6DDT and the dominant chemical, *p,p'*-DDE were significantly correlated not only with the per capita consumption of aquatic products, but also with per capita GDP, and GDP (Fig. S4, $p < 0.05$). This observation implied the contributions of consumption of polluted aquatic products and economic activities for DDTs in residents' hair (Johnson-Restrepo et al., 2005; Petersen et al., 2020), as DDT is currently used as a raw material to produce anti-rust paint for fishing boats (Liu et al., 2012). Additionally, dietary exposure accounts for >90 % of the total DDT burden for the general adult populations (Mrema et al., 2013). Therefore, adjusting diet structures to reduce aquatic product consumption would be an appropriate strategy for minimizing the exposure of DDT on residents in coastal cities in China.

We also observed significant correlations between hair TCIPP levels and the per capita consumption of aquatic products owing to relatively higher water solubility of TCIPP ($p < 0.05$) (Ren et al., 2019). Moreover, hair TCIPP, the dominant PFR, was significantly positively related to GDP, gross product of secondary industry, total manufacturing assets, and gross product of the construction industry (Fig. 3 and Fig. S5), suggesting that residents' exposure to PFRs was primarily affected by industrial activities. PFR concentrations in soils and dust from urban areas or economically developed counties were much higher than those observed for rural areas in Chinese cities (Li et al., 2020; Yin et al., 2019). Furthermore, the levels of PFRs in drinking water and fish were higher in coastal areas than inland areas in China (Liu et al., 2019; Zhang et al., 2021), implying that PFRs pollution was more serious in areas with more developed industries. No significant association was observed between BDE28, BDE209, and Σ_7PBDE in hair and the statistical indicators. This was probably because of the global restriction on PBDEs by the Stockholm Convention on Persistent Organic Pollutants in 2009 and 2017. The levels of PBDEs were declined in the environment and human body. Therefore, exposure sources for residents may be residual of old products and appliances (Kim et al., 2018; Tang et al., 2022).

When the relationships between urban residents' hair OC concentrations and statistical indicators in inland and coastal regions were analyzed separately, different results were obtained (Fig. S6). No significant correlation was found between the levels of TCIPP and *p,p′*-DDE with per capita consumption of aquatic products in both inland and coastal regions. This is likely because the values of per capita consumption of aquatic products of residents in the same region were similar ($p > 0.05$), and the data of the same region were limited (just 10 coastal cities and 17 inland cities). A significant positive relationship was observed between the levels of TCIPP and total manufacturing assets ($p < 0.01$) in inland areas, but not in coastal areas, suggesting that TCIPP exposure on residents was more significantly affected by manufacturing in inland cities than coastal cities. For example, the manufacturers of PFRs in the inland region of China are twice of coastal region (https://china.guidechem.com/) (Ren et al., 2019). Inversely, the levels of TEHP were significantly positively associated with PM10 and PM2.5 contaminations in coastal cities ($p < 0.05$) (Fig. S7), but not in inland cities. According to a previous study, the resuspension of dust and soil was a major contributor of PM in inland area, while the crustal dust & cement dust contributed relatively higher at coastal cities because of more construction in the fast-developing areas (Tian et al., 2018). Indoor dust was the primary exposure source of PFRs on residents (Yadav et al., 2017). Moreover, significant positive relationship was observed between the levels of TEHP in human blood and indoor dust which were prominently derived from the released of consumer products and building materials (Hou et al., 2021). As thus, the higher proportion of building dust in the sources of PM pollutions in coastal areas may be one of the proper reasons for the significant relationship of PM pollution and the exposure levels of TEHP in human hair. Similarly, significant positive relationships were found between *p,p′*-DDE and GDP, per capita GDP for coastal cities ($p < 0.05$) but not inland cities. More researches should be conducted on the OC contamination between different regions to determine the efficiency factors among statistical indicators.

Furthermore, PCA was conducted to further identify the relative contributions of aquatic product consumption and industries to the OCs detected in hair of coastal and inland residents. The contributions of these factors were determined based on an eigenvalue >1 for both coastal and inland areas. We observed that two factors (PC1 and PC2) accounted for 49.9 % and 57.5 % of the variation in the data, respectively. As shown in the component score coefficient matrix (Table 3), *p,p′*-DDT and *p,p′*-DDE appeared to be clustered in the same group for both coastal and inland hair samples (PC2 for group 2 and PC1 for group 1). This result indicated that dietary intake was the primary source of DDTs for residents in both coastal and inland areas. In coastal areas, BDE28, TEHP, and iDPHP from building materials were clustered into group 1 (PC1), whereas TPHP and TCIPP from household products were clustered into group 3 (PC3). By comparison, TPHP, TCIPP, and iDPHP formed group 2, while BDE28, BDE209, and TEHP formed group 3 for inland areas. BDE209 was clustered into both group 1 and group 2 for coastal areas, indicating that coastal residents were exposed to BDE209 not only via dietary intake (endogenous source), but also via industrial activities (exogenous source). BDE209 for inland residents' hair fell into group 3 (PC3), mainly derived from exogenous sources.

Table 3
Component score coefficient matrix of OCs in hair samples from coastal and inland urban residents.

	Factors (coastal areas)			Factors (inland areas)		
	1 (18.1 %)	2 (17.83 %)	3 (14.0 %)	1 (21.4 %)	2 (20.3 %)	3 (15.8 %)
BDE28	0.405	−0.041	0.010	0.030	−0.316	0.702
BDE209	0.087	0.241	0.209	−0.043	0.093	0.406
TPHP	−0.195	−0.036	0.815	0.003	0.430	0.025
TEHP	0.522	0.031	−0.122	−0.001	0.199	0.400
TCIPP	0.123	0.016	0.439	−0.021	0.420	−0.088
iDPHP	0.466	−0.018	−0.016	0.020	0.377	−0.104
p,p′-DDT	−0.063	0.566	0.025	0.540	0.009	0.009
p,p′-DDE	−0.023	0.565	−0.095	0.537	0.000	−0.032

4. Conclusions

The present study is the first report on the difference of levels and compositions of OC exposure in general adult urban population between inland and coastal regions via human biomonitoring based on the analysis of hair samples. In summary, our results indicated that adult urban residents in China were extensively exposed to DDTs, PBDEs, and PFRs, and the contaminations were significantly associated with population characteristics (i.e., age and sex). The levels of OCs with DF > 50 % in human hair samples from coastal urban residents were significantly higher relative to samples from inland urban residents ($p < 0.05$), possibly owing to the higher levels of consumption of contaminated seafood and more serious secondary industrial pollution in coastal areas. The compositions of OCs were generally similar between the two regions, but the diversified behaviors on the consumer, diet habits, and lifestyle may lead to some specific compositional differences.

5. Limitations of the study

Nevertheless, this study had several limitations and uncertainties which need consideration. The potential impact factor, statistical indicators, including per capita consumption of aquatic products, are averages of all residents for the whole city, but not for participants in each city, and this could lead to the uncertainties of the present results on the correlations between the hair OC levels and statistical indicators. Moreover, potential sources of OCs in hair samples, like food, air, and dust particles were failed to investigate in this study.

Ethics approval

The study was approved by the Medical Ethics Committee of the South China Institute of Environmental Science, Ministry of Ecology and Environment, PR China.

Consent to participate

All donors involved in this study signed an informed consent form before the sample collection.

CRediT authorship contribution statement

Min Li: Methodology, Writing - Original draft preparation. **Bin Tang:** Methodology, Writing - Review & editing. **Jing Zheng:** Conceptualization, Funding acquisition, Project administration, Supervision,Writing - review & editing. **Weikeng Luo:** Software, Visualization, Writing - Review & editing. **Shimao Xiong:** Validation, Writing - Review & editing. **Yan Ma:** Data curation, Validation, Writing - Review & editing. **Mingzhong Ren:** Supervision, Writing - Review & editing. **Yunjiang Yu:** Resources, Funding acquisition, Writing - Review & editing. **Xiaojun Luo:** Formal analysis, Writing - Review & editing. **Bixian Mai:** Supervision, Writing - Review & editing.

Data availability

The data that has been used is confidential.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.161559.

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