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Pretreatment techniques and analytical methods for phenolic endocrine disrupting chemicals in food and environmental samples

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ABSTRACT

Phenolic endocrine disrupting chemicals (EDCs) have gained people's attention worldwide because of their hazards to human health as well as their wide distributions in environmental matrices (such as air, water, and soil), food samples, and food packaging materials. Many pretreatment techniques (mainly solid-phase extraction (SPE)) and detection methods (mainly chromatographic techniques) have been used to concentrate and detect the phenolic EDCs in various samples.

Bisphenol A (BPA), nonylphenol (NP), and octylphenol (OP) are representative phenolic EDCs that are the most widely distributed compounds and have received much attention. Therefore, we present a review of the physicochemical properties; applications; toxicities; pretreatment techniques; detection methods; and occurrence of these phenolic EDCs in food, food packaging, and environmental samples. Furthermore, we have made predictions about the future research directions of these phenolic EDCs, mainly including toxicity mechanism, applied eco-friendly materials, pretreatment techniques, and so on.

1. Introduction

Endocrine disrupting chemicals (EDCs) are exogenous substances that interfere with hormone synthesis, release, transmission, binding, excretion, action, or clearance in living organisms, wherein the functions of hormones include maintaining balance, promoting reproduction process and development, and adjusting various behaviors of the body [1].

EDCs are mainly divided into two major categories, namely, natural and synthetic, both of which have serious effects on the human and animal endocrine system. Estrogens such as estrone, 17β-estradiol, and estriol are produced naturally, and they can penetrate into the environment through human and animal wastes [2]. Synthetic EDCs were originally designed and manufactured for specific industrial and domestic purposes including pesticides (e.g., dichloro-diphenyl-trichloroethane and vinclozolin), plasticizer (phthalate esters), food antioxidant (butylhydroxyanisole), synthetic hormonal drugs (e.g., diethylstilbestrol and ethinylestriol), and industrial chemicals (e.g., bisphenol A [BPA] and alkylphenol) [3]. Phenolic EDCs are mainly attributed to synthetic EDCs and mainly include nonylphenol (NP) and octylphenol (OP), bisphenols (BPs), resorcinol, and pentachlorophenol [4]. Phenolic EDCs are widely used as a surfactant and a plasticizer in the production and synthesis of food packaging materials [5]. These EDCs can cause serious damage to the reproductive, nervous, and immune systems. Contamination with EDCs is closely related to many malignant tumors [6,7].

Among these phenolic EDCs, BPA, NP, and OP are the most widely distributed ones and have received much attention worldwide. BPA, NP, and OP are highly detectable in food packaging materials [8]; thus, they easily cause serious pollution in food [9], food additives [10], and water for aquaculture and food processing industries [11]. These phenolic EDCs from industries and urban sewage treatment plants enter the environmental water body and pollute it; they enter the food chain and have a negative impact on animals and humans. In China, these three kinds of phenolic EDCs have been detected in Dianchi Lake [12] as well as 22 rivers around it [13], such as Pearl Rivers (Liuxi, Zhujiang, and Shijing Rivers), especially the Shijing River [14]. In view of the health risks that these phenolic EDCs cause to people and other organisms, rapid,

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Abbreviations

APs Alkylphenols
Bond Elut Plexa the packaging material is a cation exchange resin
BPA bisphenol A
BPs bisphenols
Chromabonds HR-X the packaging material is polystyrene-divinylbenzene
Chromabonds HR-XAW the packaging material is a weakly basic secondary and tertiary ammonium polymeric anion exchanger
CNTs Carbon nanotubes
COFs covalent organic frameworks
DAD diode-array detection
DLLME dispersive liquid–liquid micro-extraction
DS-(POAP-DS) poly ortho-aminophenol doped with DS-(POAP-DS)
DS-(PPy-DS) polypyrrole doped with DS (PPy-DS)
dw dry weight
EC50 concentration for 50% of the maximal effect
ESI electrospray ionization
FLD fluorescence detector
GC gas chromatography
GC-MS gas chromatography–tandem mass spectrometry
G-IL graphene-ionic liquid
IL ionic liquid
LC liquid chromatography
LC50 semi-lethal concentration
LC-MS/MS liquid chromatography–tandem mass spectrometry
LLE liquid–liquid extraction
MAE microwave-assisted extraction
MIPs molecularly imprinted polymers
MISPE molecularly imprinted solid-phase extraction
MOFs metal organic frameworks
MSPDE matrix solid-phase dispersion extraction
MSPE magnetic solid-phase extraction
MWCNTs multiwall carbon nanotubes
NP nonylphenol
OP octylphenol
PA polyacrylate
PDA photodiode array detector
PDMS polydimethylsiloxane
PDMS/DVB polydimethylsiloxane/divinylbenzene
phenolic EDCs phenolic endocrine disrupting chemicals
PPy Nw polypyrrole nanowire
PS-DVB mono-disperse PS-DVB microspheres
QuEChERS quick, easy, cheap, effective, rugged, and safe
SERS surface-enhanced Raman spectroscopy
SPE solid-phase extraction
SPME solid-phase micro-extraction
TBBPA tetrabromobisphenol A
UHPLC ultra-high-pressure liquid chromatography
UHPSFC-MS/MS ultra-high-performance supercritical fluid chromatography–tandem mass spectrometry
UV ultraviolet–visible detector
ww wet weight

convenient, and sensitive extraction techniques and detection methods are required to provide insight into the pollution level of phenolic EDCs in food and environmental water samples [15,16].

We provide a review of the most relevant pretreatment techniques and analytical methods in determining three phenolic EDCs, namely, BPA, NP, and OP, which are the most widely distributed ones and have received much attention. The occurrence and distribution of these phenolic EDCs in food and environmental waters are also summarized in this review.

2. Phenolic EDCs

We introduce BPA, NP, and OP in terms of the following aspects: physical and chemical properties, sources and applications, hazards, and distribution in the organisms.

2.1. Physical and chemical properties

The three phenolic EDCs all contain phenyl groups in their structural formulas, and they are chemically stable and resistant to degradation. Table 1 shows the structural formulas and physicochemical parameters of phenolic EDCs [17,18]. As shown in Table 1, the three phenolic EDCs are all weakly acidic and lipophilic compounds.

The migration and transformation behavior of BPA, NP, and OP in the environment or food can be predicted from these data. The properties of low degradability, hydrophobicity, and high enrichment of these phenolic EDCs make them difficult to migrate and easy to be enriched in the soil, sediment, and organisms over a long duration [19].

2.2. Sources and applications

NP and OP are the main degradation products from NP and OP ethoxylates, respectively, and as they are not easily degraded again, they can be strongly adsorbed onto the soil [20].

NP is one of the most important intermediates in the petrochemical industry and organic synthesis industry. NP has a wide range of applications in plastic, resin, and stabilizer industries.

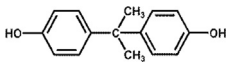
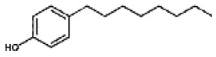
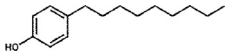
As an important raw material and intermediate for fine chemicals, OP is widely used in the production of nonionic surfactants. OP can also be used to produce solubilized phenolic resins, rubber auxiliaries, printing inks, and adhesives.

BPA is an important industrial compound used as an intermediate primarily in the production of polycarbonate plastics and epoxy resins. BPA is widely used in different products in daily life, including digital media (such as CD), electronic devices, automobiles, architectural glass, medical devices (such as dental sealants), and reusable bottles (such as baby bottles and food storage containers). To avoid direct contact between food and beverages with metals, researchers used epoxy as interior coatings for food packaging bags and beverage cans. Children's toys also contain BPA as plastic additives [21].

2.3. Distribution of phenolic EDCs in organisms and their hazards

The phenolic EDCs in the environment can be biologically accumulated in organisms through the food chain and consequently alter the functions of the endocrine system of living organisms and the human body. The distribution of phenolic EDCs in the organisms is closely associated with their hazards to the organisms [22].

Table 1
Chemical structure and physical–chemical properties of the different analytes.

Analytes	Abbr.	Chemical structure	Molecular weight	Boiling point (°C)	Log Kow [17]	Water solubility (mg L^{-1}at 20 °C) [18]	pKa [17]
Bisphenol A	BPA		228.29	220	3.6	120	10.3
Octyl phenol	OP		206.32	278.9	5.3	12.6	10.4
Nonyl phenol	NP		220.35	293–297	6.0	1.57	10.3

The distribution of phenolic EDCs in the organisms is listed in Table 2. As shown in Table 2, these compounds tend to be distributed in the muscle and liver [23–25], and their distribution in fish tissues is related to the fat content owing to the lipophilic property of phenolic EDCs [23].

NP and BPA are also detected in human blood, breast milk, and urine after long-term exposure to environments containing phenolic EDCs. The relevant data are shown in Table 2.

The three kinds of phenolic EDCs exert chronic toxicity and acute toxicity, and much emphasis was placed on the estrogenic effect [26–42]. All relevant contents are illustrated in Fig. 1.

3. Pretreatment techniques and analytical methods

Phenolic EDCs are found in food, food packaging, and environmental samples at fairly low concentration levels, thereby indicating that there is an urgent need for methods that are sensitive, have low limits of detection (LOD), and can achieve rapid detection. Many food matrices are extremely complicated. These food matrices interfere with detection results' accuracy. Convenient and flexible pretreatment methods are required for obtaining the most convincing experimental data. These extraction techniques play an important role in purifying the sample and preconcentrating the analytes [43].

Presently, the most frequently used technique for extracting phenolic EDCs from environmental samples and food, as well as some food packaging, is solid-phase extraction (SPE) [12,14,44–48].

Studies have reported the following:

- Liquid-liquid extraction (LLE) [49,50];
- Solid-phase microextraction (SPME) [51–53];
- Dispersive liquid-liquid microextraction (DLLME) [54–58];
- Magnetic SPE (MSPE) [17,59–62];
- Molecularly imprinted SPE (MISPE) [63–69];
- Microwave-assisted extraction (MAE) [70];
- QuEChERS (quick, easy, cheap, effective, rugged, and safe) [71–74];
- Matrix solid-phase dispersion extraction (MSPDE) [75–77].

An increasing number of modern detection methods have been used to detect phenolic EDCs. More detection techniques such as gas chromatography-tandem mass spectrometry (GC-MS) [12,14,49,50], liquid chromatography (LC) [54–56,59] and liquid chromatography–mass spectrometry (LC-MS/MS) [44–48], electrochemical analysis [78–80], spectroscopy [81–83], surface-enhanced Raman spectroscopy (SERS) [84,85], and enzyme-linked immunosorbent assay are available for the detection of BPA. However, for NP and OP, only GC-MS [12,14,50], LC [51,55,59,66], and LC-MS/MS [57,58,77] are the main detection methods. Modern chromatographic technology has been most widely used to date owing to its high sensitivity, low detection limit, flexible operation, and convenience.

3.1. Pretreatment techniques

For the improvement of the accuracy and sensitivity of the instrumental determination, many pretreatment techniques are urgently needed. Table 3 lists the pretreatment techniques used in published studies to determine phenolic EDCs in environmental and food samples.

3.1.1. SPE

Various pretreatment techniques have been used before chromatographic detection. However, SPE is the most widely used extraction method because it is suitable in handling and

Table 2
Distribution of phenolic EDCs in the organisms.

Distribution organ	Species	Pollutant	Concentration	Country	Reference
Muscles and liver	Carp	NP, OP, and BPA	1.92 μg g^{-1} dw, 3.24 μg g^{-1} dw and 1.58 μg g^{-1} dw for NP, OP and BPA in muscle; 3.21 μg g^{-1} dw on average in the liver	Iran	[23]
Muscles	Wild salmon	NP, OP, and BPA	NP: 1290–3111 ng g^{-1} (ww) (July); 1132–1556 ng g^{-1} (ww), (November); OP: 6–46 ng g-1 (ww) (July); ND-22 ng g^{-1} (ww), (November); BPA: 4–41 ng g^{-1} (ww) (July); 6–59 ng g^{-1} (ww), (November);	China	[24]
Muscles	Purple mussel	NP, OP, and BPA	9.04–372 ng g^{-1} dw, 9.3–116.3 ng g^{-1} dw and ND-11.2 ng g^{-1} dw for NP, OP and BPA	Spain	[25]
Urine	Human	NP and BPA	NP: 0.1 μg L^{-1} or more (detection rate 51%); BPA: 0.101 μg L^{-1} or more (detection rate: 95%).	The United States	[137]
Human breast milk, blood, and urine	Human	NP, OP, and BPA	Urine: below 3 ng L^{-1} for NP and OP, but BPA was in the range of 0.36–8.9 ng L^{-1}; Blood: The highest concentrations for NP, OP, and BPA were 12 ng L^{-1}, 9.1 ng L^{-1}, and 7.1 ng L^{-1} Breast milk: the highest concentrations for NP, OP, and BPA were 5.6 ng L^{-1}, 2.8 ng L^{-1}, and 2.9 ng L^{-1} (detection rates < 50%)	Spain	[138]

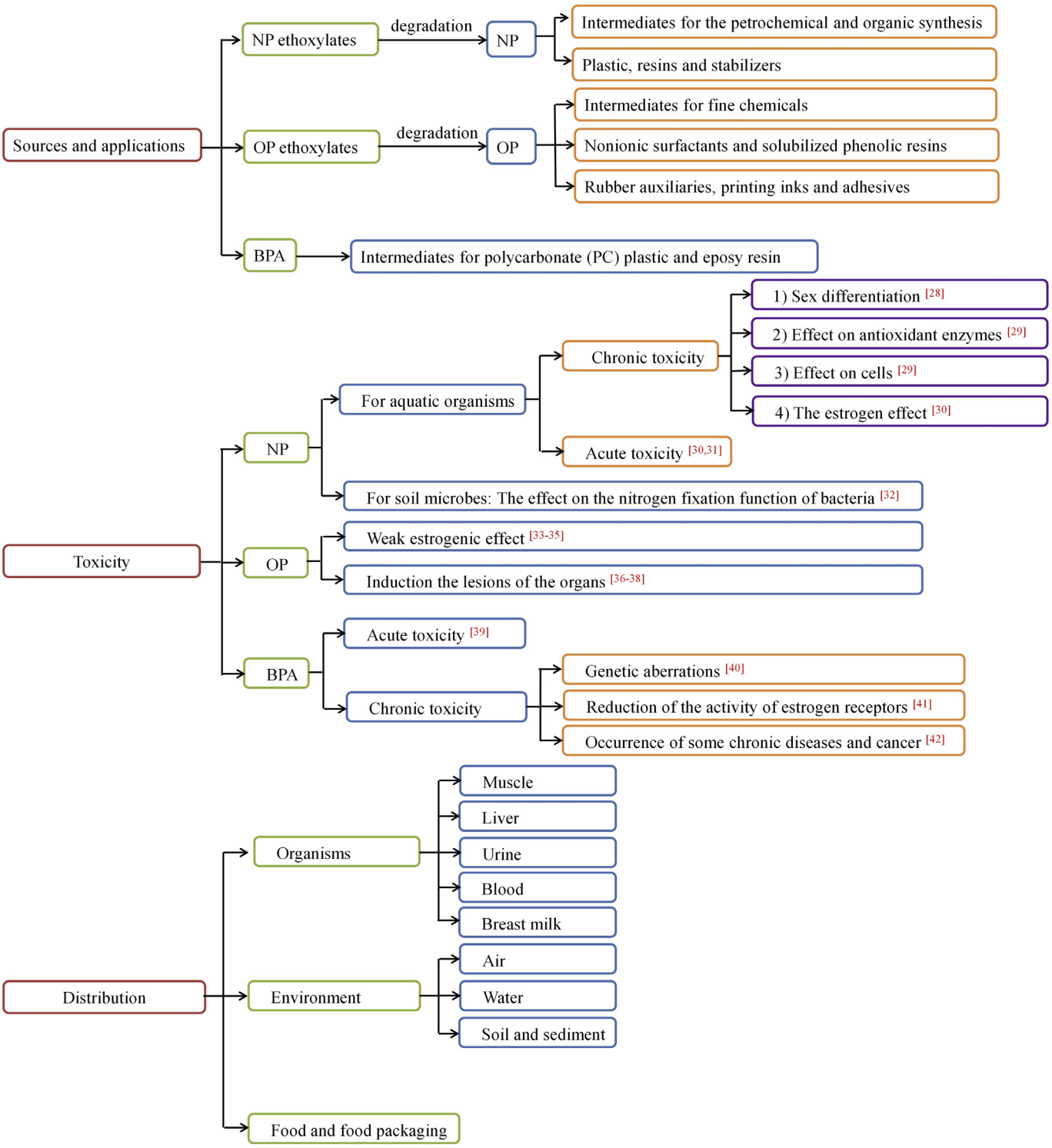


Fig. 1. Toxicities of the three kinds of phenolic EDCs.

preconcentrating a wide variety of analytes with different physicochemical properties.

The key component of the entire device of the SPE is the packing material of the SPE column. Traditional SPE packaging materials are generally chromatographic adsorbents and can be divided into three major categories: the first type is based on high polymer, such as HLB (divinylbenzene and vinyl pyrrolidinone), which was generally used in the extraction of phenolic EDCs [12,14,45]; the second type is based on silica gel (e.g., C_{18} [46,47], C_8 [64], and C_{30} [48]); the third type includes mainly inorganic materials, such as Florida silica, alumina, and graphitized carbon. An increasing number of novel materials such as carbon nanotubes (CNTs), metal organic frameworks (MOFs), covalent organic frameworks (COFs), and bamboo charcoal are also used as SPE sorbents to extract adaptable analytes.

Researchers compared the extraction and purification efficiencies of different SPE materials. In Tran's research [44], five types

Table 3
Analytical methods for determining phenolic EDCs in food and environmental water samples.

Samples	Analytes	Extraction technique	Detection technique	LODs (ng L^{-1})	Recoveries (%)	Reference
Surface water of Dianchi Lake	4-n-NP, 4-t-OP, BPA	SPE (Oasis HLB);	GC-MS	4-t-OP: 0.3, 4-n-NP: 0.2 BPA: 0.7	56.3–89.7	[12]
Water samples in the Pearl River	4-tert-octylphenol (4-t-OP), 4-nonylphenol (4-NP), bisphenol-A (BPA)	SPE (Oasis HLB);	GC-MS (negative chemical ionization (NCI))	4-t-OP: 0.3 4-n-NP: 2.0 BPA: 0.7	70–120	[14]
Water samples collected from Hangzhou Bay	BPA	SPE (Oasis HLB and MAX);	LC–MS/MS	BPA: 0.21–0.82	75.8–114.3	[45]
Raw wastewater, surface water, and groundwater samples	BPA	SPE (Chromabonds HR-X)	LC–MS/MS	BPA:1.0 (Milli-Q water) 1.5 (ground water) 1.5 (surface water) 5.0 (raw wastewater)	97.4–99.6	[44]
Samples from natural waters and drinking water treatment plants	BPA	SPE (LiChrolut RP-18 cartridges)	LC–MS/MS	6.30	81	[46]
Commercial canned milk	BPA	SPE (C_{18})	LC-ESI-MS	1.7 (The unit is ng kg^{-1})	97–104	[47]
bovine milk	BPA	SPE (C_{30})	LC–MS/MS	200	92.4–97.1	[48]
Urban wastewater	BPA	LLE (using trichloromethane)	GC-MS	6000	–	[49]
Mutton	4-NP BPA	LLE (using the mixture of acetonitrile-ethyl acetate (3:2,V/V))	GC-MS	4-NP: 25 (The unit is ng kg^{-1}) BPA: 24 (The unit is ng kg^{-1})	86.7–111.0	[50]
Water samples (tap water and river water)	BPA	DLLME (dispersing agent: acetone; extraction solvent: chloroform)	HPLC-UV detector	70	93.4–98.2	[56]
Seawater samples	BPA 4-t-OP 4-OP 4-n-NP NP	DLLME (dispersing agent and extraction solvent 1-octanol)	LC–ESI (electrospray ionization) -MS/MS	BPA: 6 4-t-OP: 3 4-OP: 3 4-n-NP: 1 NP: 10	84–104	[57]
Food packaging	BPA	IL-DLLME (Extraction solution: 1-Octyl-3-methylimidazoliumhexafluorophosphate ($[C_8MIM][PF_6]$))	HPLC-DAD detector	BPA: 500	97.8–103.1	[54]
Water samples (tap water, river water, and waste water)	4-NP BPA	IL-DLLME (Extraction solution: 1-butyl-3-methylimi-dazolium hexafluorophosphate ($[Bmim][PF_6]$)	HPLC-VWD detector	4-NP: 1250 BPA: 850	4-NP: 104.1–108.2 BPA: 95.2–101.5	[55]
Water samples (from sewage treatment plants (STP), river, and drain)	BPA 4-t-OP 4-n-OP 4-n-NP 4-NP	IL-DLLME (extraction solution: 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide)	LC-MS/MS	BPA: 24 4-t-OP: 6 4-n-OP: 8 4-n-NP: 8 4-NP: 14	BPA: 87.1–98.7 4-t-OP: 90.3–95.8 4-n-OP: 89.7–96.9 4-n-NP: 81.4–90.3 4-NP: 78.8–89.9	[58]
Plastic packaging drink samples	BPA 4-n-OP 4-n-NP	MSPE (Fe_3O_4@COF)	LC-FLD (RF-20A)	BPA: 80 4-n-OP: 120 4-n-NP: 170	BPA: 81.3–114.4 4-n-OP: 83.4–113.4 4-n-NP: 81.3–111.4	[59]
Environmental water samples (tap water, spring water, snow water, and waste water)	BPA	MSPE ($C–NH_2$@Fe_3O_4)	LC-MS/MS	BPA: 2.09	BPA: 90.9–110.0	[17]
Environmental water samples (water samples from Dongping Lake and Beijing-Hangzhou Canal)	BPA	MMSPD-DLLME (micro-particles of magnetic activated carbon (MAC))	HPLC-FLD (fluorescence detector)	BPA: 2	BPA: 86.6–106.3	[60]
Milk (human breast milk, full-fat milk (3.5% fat) and semi-skimmed milk (1.5% fat) samples)	BPA	MSPE (magnetic activated carbon prepared (Bmi))	HPLC-UV	BPA: 750	BPA: 80-95	[61]
Milk (whole, semi-skimmed, and skimmed milk)	BPA	MSPE (magnetic nanoparticle-nylon 6 composite)	HPLC-UV	BPA: 3050	BPA: 86-99	[62]
27 samples of commercially available milk	BPA	MISPE	HPLC-fluorescence (FLD) detector	BPA: 1.32 μg kg^{-1}	–	[69]
Milk	BPA	MISPE (dummy MIPs)	HPLC-DAD detector	BPA: 0.9 μg g^{-1}	BPA: 96	[67]
Vegetable (tomato and cabbage) and fruit juice samples (orange, apple, and mixed juice and tomato paste)	BPA	m-MISPE (nanofibrous molecularly imprinted membranes (nano-MIMs))	HPLC-2487 dual λ absorbance detector	BPA: 0.2 nmol L^{-1}	BPA: 72.25–89.97	[68]

(*continued on next page*)

Table 3 (*continued*)

Samples	Analytes	Extraction technique	Detection technique	LODs (ng L^{-1})	Recoveries (%)	Reference
Water samples (collected from a well, a lake, a pond, and the Pearl River (Guangzhou, China))	BPA 4-Tert-OP 4-NP	SPE-DLLME (VTTS-MGO@mSiO_2@MIP)	HPLC with a photodiode array detector (PDA)	BPA: 13 4-Tert-OP: 10 4-NP: 10	BPA: 81.54–106.7 4-tert-OP: 93.95–104.29 4-NP: 85.16–100.93	[66]
Tap water samples	BPA	MISPE (imprinted amino-functionalized silica gel material)	HPLC with a UV detector	–	BPA: 99.43–103.25	[64]
Water samples (tap water, wastewater, Yangtze River water)	BPA	MISPE (BPA-imprinted MIPs)	CE-UV (capillary electrophoresis with a UV detector)	3000, 5400, and 6900 in tap water, wastewater, and Yangtze River water	BPA: 98.69–105.40 in three samples	[65]
River water and red wine samples	BPA	MISPE (MIP/cryogel composite monoliths)	HPLC-UV–Vis detector	10 in river water	river water (94–102); red wine (90–98)	[63]
Seawater sample	BPA	EE-SPME (electro-enhanced solid-phase micro-extraction) (electro-enhanced PDMS fiber)	GC-MS	960	Seawater: 73.9	[52]
Drinking water, river water, effluents, and plastic packaging bag	BPA	SPME (multiwall carbon nanotubes)	HPLC-DAD	100	98.2–102.5 in four samples	[53]
Tap water, lake water, river water, milk 1, and milk 2	BPA, NP, and OP	SPME (polymeric ionic liquid-based multiple monolithic fiber)	HPLC-DAD	45, 110, and 75 for BPA, NP, and OP, respectively, in water; 93, 230, and 180 for BPA, NP, and OP, respectively, in milk	74.8–118 for BPA, 78.5–117 for OP,75.6–116 for NP	[51]
Influent and effluent wastewater samples collected from a pilot-scale wetland plant in Langenreichenbach	BPA, t-NP	SPME (polyacrylate as SPME fiber coatings)	GC-MS	200 for t-NP, 300 for BPA in pure water and 800 for t-NP, 1000 for BPA in effluent	–	[105]
Food samples (peas, corns, and beans)	BPA	SPME (PPy NW)	IMS (ion mobility spectrometer)	1 ng g^{-1}	93–96	[106]
Canned seafood (47)	BPA	QuEChERS-DLLME	GC-MS	0.2 μg kg^{-1}	68-104 (in canned tuna samples) 84-104 (in canned sardine samples)	[72]
Canned sea foods (Sardine, mussel, canned tuna, canned sardine, and canned mackerel samples) (25)	BPA	QuEChERS	LC-MS/MS	BPA: 0.02, 0.4, 0.8 μg kg^{-1} in fish, mussel, and seaweed samples	71-82 in fish; 70–76 in mussel, and 67–71 in seaweed	[73]
Beehive samples (5 honey, 10 pollen, and 12 wax samples)	$NP(EO)_{3\text{-}13}$, $OP(EO)_{3\text{-}13}$	QuEChERS	LC-MS	$NP(EO)_n$: 560 $OP(EO)_n$: 440 (in blank honey and pollen samples)	74-110 (for $NP(EO)_{3\text{-}13}$); 75–111 (for $OP(EO)_{3\text{-}13}$)	[71]
Three leafy vegetables, namely, cabbage, lettuce, and spinach (eight samples for each kind of vegetable)	NP_xEOs and OP_xEOs ($x = 2–20$)	QuEChERS	Ultra-high performance supercritical fluid chromatography –tandem mass spectrometry (UHPSFC-MS/MS)	NP_xEOs: 0.02–0.27 μg kg^{-1}; OPxEOs: 0.02–0.27 μg kg^{-1}	NP_xEOs: 74.1–119.9 OP_xEOs: 72.8–122.6	[74]
Egg samples (10) and milk samples (10)	BPA, OP, and NP	MSPDE (C18 as a dispersant)	Liquid chromatography –electrospray ionization–tandem mass spectrometry (LC–ESI–MS/MS)	BPA: 0.10 in eggs and 0.10 in milk; NP: 0.10 in eggs and 0.05 in milk; OP: 0.25 in eggs and 0.10 in milk; (The unit is μg kg^{-1})	BPA: 79.15–86.84 in eggs and 85.73–93.9 in milk; NP: 81.45–98.05 in eggs and 89.99–98.58 in milk; OP: 84.59–96.37 in eggs and 82.31–102.45 in milk	[77]
Carrot samples (5), onion samples (6), tomato samples (6) and lettuce samples (5)	BPA, NP	MSPDE (florisil as dispersant)	GC–MS/MS	BPA: 0.2 in lettuce and carrot; 0.1 in onion and tomato; NP: 0.1 in lettuce and tomato; 0.2 in onion and carrot (The unit is ng g^{-1})	BPA: 98–111 (in tomatoes), 74–82 (in carrots), 72–121 (in onions) and 84–120 (in lettuces) NP: 78–91 (in tomatoes), 56–99 (in carrots), 99–102 (in onions) and 102–118 (in lettuces)	[75]

Three water samples and six fish samples	4-t-OP, 4-NP, BPA	MSPDE (C8 as adsorbent)	UHPLC-MS/MS	BPA: 0.81 ng L^{-1} in water samples, 0.37 ng g^{-1} in fish; NP: 89.9 ng L^{-1} in water samples, 0.27 ng g^{-1} in fish; OP: 0.19 ng g^{-1} in fish	BPA: 104–109 in fish, 103 in particle-free water; NP: 103–107 in fish, 104 in particle-free water; OP: 75.2–83.5 in fish	[76]
Tap water and grape juice samples	BPA	–	An electrochemical sensing method (based on nontarget-induced bridge assembly and aptamer (Apt) extension reaction)	BPA: 15 pmol L^{-1}	88.6–97.3 in the tap water samples and 89.5–95.8 in the grape juice samples.	[78]
Tap and mineral water samples	BPA	US-MagMIP (Ultrasound-assisted magnetic molecularly imprinted polymer)	An electrochemical sensor (modified with a nanocomposite of carbon black nanoparticles (CBNPs), and gold nanoparticles (AuNPs))	8.8 nmol L^{-1}	103.5–104.3 in tap water and 96.4–98.4 in mineral water	[79]
Disposable paper cup (PE), disposable plastic bottle (PET), instant noodles cup (PE), and instant noodles cup (PS)	BPA	–	An electrochemical sensor (attaching AuNPs, which had a clean surface on the glassy carbon electrode modified with graphene-ionic liquid (G-IL GCE))	4.8 nM	93.3–103.3 in disposable paper cup (PE); 92.5–102.3 in disposable plastic bottle (PET); 98.3–110.0 in the instant noodles cup (PE); 96.0–100.0 in the instant noodles cup (PS)	[80]
Tap water, bottled water, and lake water	BPA	–	An optical biosensor (utilizing laser-induced fluorescence-based detection by the binding of biomolecules to the surface of an integrated TriPleX™ waveguide chip on a glass substrate (fused silica, FS))	60	85-116 in the tap water, 104–110 in the bottled water, and 101–108 in the lake water	[82]
Thermal paper: A and B	BPA	–	An sensor based on aptamer/AuNP	9	–	[81]
Polycarbonate plastic	BPA	–	A MIPs@AgNPs surface-enhanced Raman scattering (SERS) sensor	50 nmol L^{-1}	92–103.5	[85]

of SPE cartridges, namely, Chromabonds HR-X (500 mg, 6 mL), Chromabonds HR-XAW (500 mg, 6 mL), Bond Elut Plexa (200 mg, 6 mL), Oasis HLB Plus (225 mg, 6 mL), and SampliQ C18 (500 mg, 6 mL) were tested to obtain the optimal detection results. The results showed that HR-X cartridge is the most effective tool for BPA. In Maragou's research [47], C_{18}, PS-DVB, and hydroxylated PS-DVB were tested to extract BPA from water, and C_{18} SPE cartridge with the highest BPA extraction rate was selected as the SPE cartridge.

3.1.2. LLE

LLE is a traditional sample preparation method that uses the difference in the solubility of various components in different extract solvents in liquid samples to separate the target from the matrix. The extraction efficiency depends on differences in the chemical potential of the target between the two phases. LLE coupled with GC-MS was used to determine phenolic EDCs from urban wastewater [49] and mutton [50] and obtain LODs as low as $\mu g\ L^{-1}$ and $\mu g\ kg^{-1}$.

The LLE technology does not require special equipment and is easy to operate, thereby making it adaptable for sample pretreatment. However, the excessive use of organic solvent, loss of analytes, and low extract efficiencies of LLE decrease the use of this technology.

3.1.3. DLLME

The general mode of operation of the DLLME is as follows: analyte extraction, extract separation by centrifugation, or other methods and extract phase injection (containing the target compounds) into the instrument (GC, LC, and MS).

The main reagents of the DLLME are the extraction solvent (a metal ion complexing agent or chelating agent is also required when enriching the trace metal ions) and the dispersing agent.

In DLLME, the dispersing agent mainly plays the role of a bridge. The primary task of the dispersing agent is to disperse the extraction solvent into uniform organic droplets to ensure sufficient interaction between the extraction solvent and target molecules. The commonly used dispersing agent is mainly organic solvents such as acetonitrile.

The main function of the extraction solvent is extracting and concentrating the analytes. Choosing the right extraction solvent is the key to improve the extraction efficiency. According to the principle of similar compatibility, the properties of the extraction solvent must match those of the analytes. Low water solubility and volatility, large density, and good chromatographic properties are also essential properties for the extraction solvent. Traditional organic solvents are often used as the extraction solvent. Rezaee et al. [56] used acetone as the dispersing agent and chloroform as the extraction solvent to establish a DLLME method for BPA extraction from water samples, and it took only 3 min to achieve this process. Gonzalez [57] simplified the dispersive extraction factors further and established a two-element extraction system by using 1-octanol as an extraction agent.

With the development of DLLME, ionic liquid (IL), as a new type of green extraction solvent, has been widely used in DLLME [86]. The following IL-DLLME modes are widely used: 1) conventional IL-DLLME; 2) temperature-controlled IL-DLLME; 3) ultrasound-assisted, microwave-assisted, or vortex-assisted IL-DLLME; and 4) in-situ IL-DLLME [86]. In the conventional IL-DLLME, IL was used as the extraction solvent and the dispersive solvent at the same time of extracting the analytes from the aqueous solution, and the entire process was simple and quick. This technology coupled with HPLC was used to detect phenolic EDCs widely from food packaging [54] and water samples [55], and the LODs were as low as several ng mL^{-1}. In-situ DLLME, which is accompanied by the metathesis reaction simultaneously during the extraction process, was also used to determine phenolic EDCs [58].

3.1.4. MSPE

MSPE was introduced in the 1990s to overcome certain restrictions occurring in the process of using the SPE pretreatment technique, and it has become a revolutionary technology in the field of separation and enrichment in the 21st century [87,88]. According to the theory of liquid-solid-phase chromatography, MSPE is a dispersive SPE technique that uses magnetic or magnetizable materials as adsorbents.

MSPE adsorbents play an important role in the entire MSPE process, and they determine the efficiency of the MSPE process. Novel materials such as Fe_3O_4@COF microspheres [59], aminosilanized magnetic carbon microspheres (Fe_3O_4@C—NH_2) [17], micro/mesoporous activated carbon with magnetite (Fe_3O_4, Bmi) [61], magnetic nylon 6 composite [62], Fe_3O_4/graphene quantum dots (Fe_3O_4/GQDs) magnetic nanocomposite [89], Fe—Fe_2O_3/graphene oxide composite (Fe@Fe_2O_3/GO) [90], polydopamine-coated magnetic Fe_3O_4 composites (Fe_3O_4@PDA) [91], IL-coated magnetic Fe_3O_4 nanoparticles (NPs) [92], and some types of magnetic molecularly imprinted polymers (MIPs) have been used as MSPE adsorbents to extract a low level of phenolic EDCs from the environment and food samples. The MSPE pretreatment method on the basis of these new materials coupled with LC, LC-MS, and GC-MS can detect low LODs (several $ng{\cdot}mL^{-1}$ or $ng{\cdot}L^{-1}$) and a wide linear range (2—3 orders of magnitude).

MSPE can also be combined with other pretreatment techniques to detect phenolic EDCs. In Diao's research [60], the microparticles of magnetic-activated carbon (MAC) were synthesized and used as MSPE adsorbents. Magnetic matrix solid-phase dispersion (MMSPD)-assisted DLLME was used as the pretreatment technique, and the entire process is shown in Fig. 2. HPLC with a fluorescence detector (HPLC-FLD) was used to detect BPA from actual water samples. Low LODs (2 ng L^{-1}) and a wide linear range (6—5000 ng L^{-1}) were obtained, and the relative recovery ranges from 86.6% to 106.3%.

3.1.5. MISPE

MIPs are structured based on the antigen—antibody formation theory. The synthesized MIPs, which have a high specific recognition function to the template molecules, are obtained through a simple and low-cost polymerization reaction and can be used

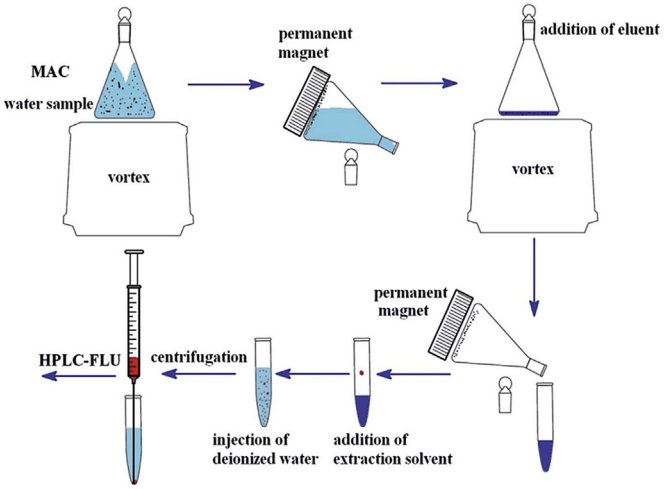


Fig. 2. Schematic procedure of MMSPD-DLLME [60].

under high temperature, acid, alkali, organic solvents, and other extreme conditions. Therefore, MIPs have wide applications in various areas such as in biomimetic electrode, chromatographic separation, SPE, and so on.

An increasing number of MIPs were designed and used in the SPE to capture and enrich phenolic EDCs from milk [67,69], wine [63], juice and vegetables [68], and other foods, as well as environmental samples [63–65,67]. The proposed MISPE method showed higher extraction efficiency and selectivity for phenolic EDCs than the traditional SPE method by using a C_8 [64] and a C_{18} SPE column [65].

Magnetic MIPs are the most preferred approach. Xie [66] used the synthesized VTTS-MGO@mSiO_2 (mesoporous silica-coated magnetic GO modified with vinyl groups) as the supporter, and MIP was prepared on the VTTS-MGO@mSiO_2 surface by a surface molecular imprinting technique. The MISPE pretreatment method using this novel material was employed to extract several phenolic compounds (BPA, 4-t-OP, and 4-NP) from four water samples, and HPLC with a photodiode array detector (PDA) was used for detection. Improved maximum adsorption capacities (16.81, 35.97, and 61.73 mg g^{-1}) and decreased LODs (0.010–0.013 μg L^{-1}) were obtained.

3.1.6. SPME

SPME technology is a sample pretreatment method that can combine the processes of collection, extraction, concentration, and matrix removal as a whole. SPME was first developed in the 1990s by Pawliszyn et al. [93,94]. This pretreatment method can extract and preconcentrate the organic molecules in the sample solution by coating the high polymer material uniformly on the surface of the quartz fiber. Selecting the most suitable adsorption coating material according to the nature of the analyte is the key step in establishing a new SPME technology. Many commonly used coatings are generally composed of high-molecular-weight polymers such as polydimethylsiloxane (PDMS), PDMS/divinylbenzene (PDMS/DVB), PDMS/carbon molecular sieve, polyacrylonitrile (PA), and so on [95]. New materials such as multiwall CNTs (MWCNTs) [53], oriented ZnO nanorods [96], ordered mesoporous carbon [97,98], Scholl-coupling microporous polymers [99], polymeric IL-based adsorbent [100], multiple monolithic fiber [101,102], IL-functionalized silica aerogel [103], melamine-formaldehyde aerogel functionalized with polydopamine [104], and so on are also used as SPME coatings.

Many studies on the application of the SPME pretreatment method for the analysis of phenolic EDCs have been conducted. SPME in combination with GC or GC-MS can be used to detect phenolic EDCs from human blood; seawater [52]; wastewater [105]; and canned peas, corn, and soybeans [106] and determine the LODs as low as several ng L^{-1} [52] and μg kg^{-1} [106]. HPLC in combination with SPME can be used to detect phenolic EDCs in environmental water samples [51,53], plastic packaging bag [53], and milk [51]. An ion mobility spectrometer can be used after the SPME process to detect BPA in canned foods [106].

The efficiencies of different SPME fiber coatings in phenolic EDCs were compared. Braun [105] compared the extraction efficiencies of three coatings, namely, polyacrylate, PDMS, and PDMS/DVB, to those of NP and BPA, and the results showed that polyacrylate is the most suitable fiber coating. Similarly, Kamalabadi et al. [106] used three types of fibers, namely, polypyrrole nanowire (PPy NW), polypyrrole doped with DS-(PPy-DS), and poly ortho-aminophenol doped with DS-(POAP-DS) films prepared by electropolymerization, as the adsorption layer to conduct the headspace SPME process for BPA detection in canned foods. Finally, PPy NW was chosen as the SPME fiber coating because of its high sensitivity to BPA.

3.1.7. MAE

MAE utilizes the difference in microwave-absorbing ability of different components. The separation of the components and matrix is achieved by microwave heating or microwave treatment. This time- and reagent-saving, simple, and convenient method can meet the requirements of simultaneous processing of various samples; thus, it is widely used in many areas. Zhang et al. [70] compared MAE with LLE and ultrasonic extraction to extract BPA diglycidyl ether and its derivatives from canned food; MAE could reduce the pretreatment time and the consumption of the organic solvent in processing many samples simultaneously. Thus, MAE was chosen as the extraction technique for the analytes. MAE was coupled with the SPE process by using a PS-DVB SPE column to purify the samples. Then, the target compounds were detected using HPLC with fluorescence detection and LODs changed from 0.79 ng g^{-1} to 3.77 ng g^{-1} for different analytes based on S/N = 3. The analytical relative recoveries were between 70.46% and 103.44%, and the RSD for repeatability was <8.64%.

3.1.8. QuEChERS

QuEChERS is a sample preparation technology that was developed newly for agricultural product detection worldwide. QuEChERS was developed by Professor Anastassiades of the US Department of Agriculture in 2003. The principle of this pretreatment technology is similar to that of HPLC and SPE; it uses the interaction between the adsorbents and the impurities in the matrix to adsorb impurities and for purification. The QuEChERS method is widely accepted because of its convenience, rapidity, and simplicity, and it is also commonly used to extract and detect phenolic EDCs in samples.

Traditional QuEChERS-based extraction methods can be used to analyze BPA and tetrabromobisphenol A (TBBPA) in seafood such as fish, bivalves, and seaweeds [73]. Traditional QuEChERS-based extraction methods can also be used to detect NP and OP precursors. Chen et al. [71] extracted NP polyethoxylates ($NP(EO)_{3\text{-}13}$) and OP polyoxyethylene ($OP(EO)_{3\text{-}13}$) by using the QuEChERS approach from beehive samples. Jiang [74] also detected the precursor NP ethoxylates (NP_xEOs) and OP ethoxylates (OP_xEOs), (x = 2–20) of OP and NP in the three types of leafy vegetables, namely, cabbage, lettuce, and spinach. HPLC-MS/MS [71,73] or ultra-high-performance supercritical fluid chromatography–tandem mass spectrometry (UHPSFC-MS/MS) [74] was used to detect the target molecules, and the obtained LODs of these studies are as low as approximately 1 ppb.

QuEChERS can be combined with other pretreatment methods to extract the phenolic EDCs. Cunha [72] used QuEChERS followed by DLLME to extract BPA and BPB from canned seafood, and GC-MS was used to detect the target compounds. The scheme of the entire QuEChERS-DLLME process is shown in Fig. 3. In the QuEChERS process, the combination of the C_{18} and ENVI-Carb was compared with the mixture of C_{18} and graphitized carbon black (GCB), and the two adsorbent combinations achieved the same purifying effect. However, as the latter can significantly reduce the cost, it was ultimately selected. The procedure of DLLME and the conditions of extraction and derivatization were also optimized. Then, under optimal conditions, low LODs (0.2 μg kg^{-1} for BPA and 0.4 μg kg^{-1} for BPB) were obtained, and the relative recoveries for BPA and BPB in canned sea food samples were in the range of 68%–104%, which illustrated the accuracy and precision of this new method.

3.1.9. MSPDE

MSPDE is a pretreatment method that combines sample crushing and homogenization with extraction. MSPDE was introduced by Barker et al. in the 1980s, and it is mainly used to treat solid and semisolid samples. The principle of MSPDE includes

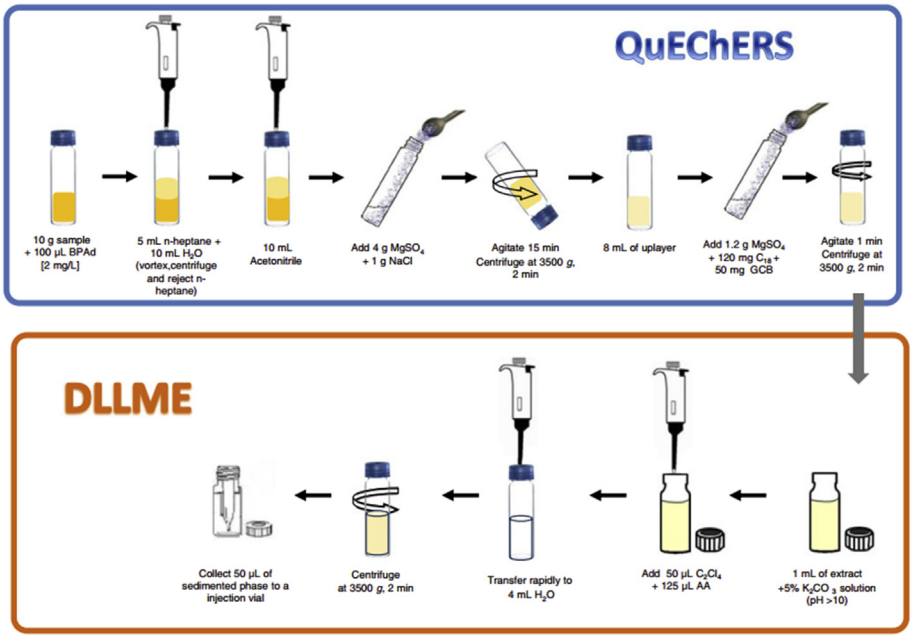


Fig. 3. Schematic diagram of QuEChERS-DLLME [72].

grinding the mixture of the SPE materials, packing it in the column, and the eluting the analytes. This method simplifies the process of sample homogenization, extraction, and purification. Moreover, it requires low reagent usage and less time and has high recovery rates.

Different materials were used in the MSPDE to enrich NP, OP, and BPA from various matrices. The materials that are commonly used are as follows: silica gel-based materials such as C_{18} [80], C_8 [76], and inorganic materials such as florisil and alumina [75]. The phenolic EDCs in eggs and milk [77], vegetables [75], river water, and tissue [76] were enriched through the MSPDE pretreatment method. LC-MS/MS [76,77] and GC-MS [75] were used for detection, and the obtained LODs were <0.5 ng g^{-1} for food samples and <100 ng L^{-1} for water samples.

As mentioned previously, reducing the usage of the organic solvent to prevent environmental pollution, thereby saving analysis time; simplifying the pretreatment procedure; and enhancing the extract efficiencies are the major trends in the area of analytical chemistry. This approach is also reflected in the enrichment and analysis of phenolic EDCs in various food and environmental samples. In the future, other novel sample pretreatment methods and new materials should be applied in the sample pretreatment to increase the extract efficiencies and reduce the environmental impacts.

3.2. Analytical methods

3.2.1. Chromatographic techniques

As shown in Table 3, GC or LC coupled with MS or MS/MS was the most commonly used detection method for the qualitative and quantitative analyses of phenolic EDCs in water, food, and food packaging.

3.2.1.1. GC-MS. GC refers to chromatography by using gas as the mobile phase. According to the difference in boiling point, polarity, and adsorption properties of each component, GC is an effective detection method with high-speed analysis and good separation efficiency [107,108].

SPME-GC (GC-MS) methods, which are used to detect the phenolic EDCs, have gained wide attention. The thermal desorption of the target compounds in the SPME process allows them to be directly vaporized at the inlet of the GC, followed by injection. Considering the small injection volume and the high response of the instrument, the reactions of derivatization are generally not required when phenolic EDCs are detected using the SPME-GC (GC-MS) method [52,105].

However, GC has high volatility requirements for the components to be analyzed. Thus, the application range is narrow. NP, OP, and BPA can be directly determined by GC-MS. However, to improve the sensitivity, protect the chromatographic columns, and avoid the false-positive results, when GC or GC-MS coupled with other pretreatment methods (such as DLLME and QuEChERS) instead of SPME is used to determine the three phenolic EDCs, it is necessary to derive them before the analysis [12,14,72,75]. For phenols, the derivatization method is used to determine an ideal reagent to derivatize the hydroxyl group, and the products after derivatization should be easy to analyze. The separation of the components after derivatization is improved, the sensitivity is high, and the lifetime of the column after derivatization is significantly improved.

The derivatization methods used for phenolic compounds before GC analysis mainly include three approaches, namely, acetylation, silylation, and alkylation derivatization [109]. Acylation derivatization mostly uses heptafluorobutyric anhydride or acetic anhydride as the derivatizing agent. Silylating agents are the most widely used derivatizing reagents. The commonly used trimethylsilylating agents are bis(trimethylsilyl)trifluoroacetamide (BSTFA) and N-methyltrimethylsilyl trifluoroacetamide (MSTFA). If a small amount of trimethylchlorosilane (TMCS) is added proportionally to BSTFA (TMCS:BSTFA = 1:99), then new derivatizing reagents, namely, TMS, which can be used to improve derivative effect, can be obtained. The alkylation-derived reagents are mainly diazomethane and pentafluorobenzyl bromide. The use of diazomethane decreases because of its high toxicity and explosiveness [109].

These three derivatization methods are extremely commonly used to detect phenolic EDCs before GC or GC-MS. Moreover, different operation processes of derivatization, such as manual [110] and in situ derivatization technology [75], were compared in some studies. The in situ derivatization technology referred to the derivatization reaction that occurs in the GC inlet with the multilayer injection. In the analysis process of BPA, in situ derivatization was chosen usually and the underlying reason was that it had superiorities over the manual derivatization, such as better chromatographic peaks; stronger chromatographic response; less regent usage for sample pretreatment; and less time consumption, less manipulation, and low laboratory costs. However, one potential disadvantage of the in situ derivatization is that the direct injection of the reagent with high concentration into the GC inlet negatively will affect the chromatographic column and reduce the lifetime of the column [75].

Different derivatization methods and reagents were also compared in some studies. Cunha [72] used QuEChERS-DLLME pretreatment coupled with GC-MS to detect the BPA and BPB from canned seafood. The derivatization reaction using silylating and acetylating reagents has been reported previously and can be verified to obtain improved results. The acetylating reagents show a slight advantage of permitting the derivatization reaction to occur at the same time as the DLLME procedure. Acetyl derivatives show improved analytical signal and decreased interfering compounds (Fig. 4). In summary, the derivatization reaction by using the acetylating reagents was chosen as the derivatization method. Similarly, Yu [12] extracted four types of phenolic EDCs, namely, 4-n-NP, 4-t-OP, BPA, and 4-CP, from Dianchi Lake, China, by using the SPE pretreatment method and detecting with GC-MS. Two kinds of derivatization methods (i.e., methylation with PTA-OH and silylation with BSTFA + 1% TMCS) were compared based on the derivatization reagent, namely, the time and temperature of the derivatization process and other aspects. As a result, methylation derivatization with PTA-OH was used as the optimal derivatization method in the entire research.

Different derivatization methods by using different derivatization agents have been used to study phenolic EDCs. The relevant derivatization data are summarized in Table 4 to provide references for the future derivatization of phenolic EDCs.

3.2.1.2. LC and LC-MS/MS. The derivatization process requires additional time and consumes chemical reagent, thereby making the extraction process complicated. Thus, as shown in Table 3, LC and LC-MS are more commonly used than GC or GC-MS for the detection of phenolic EDCs, and it is easy to achieve the combination with various pretreatment methods.

HPLC is a new type of chromatographic technique after GC that was developed in the early 1970s and uses liquid as the mobile phase.

The entire HPLC system generally consists of the sample injection, transfusion, separation, detection, and data processing systems [111].

The detection sensitivity of LC depends on the detector in a large scale. Two categories of detectors, namely, ultraviolet (UV)—visible detector and fluorescence detector (FLD), have been used in LC and

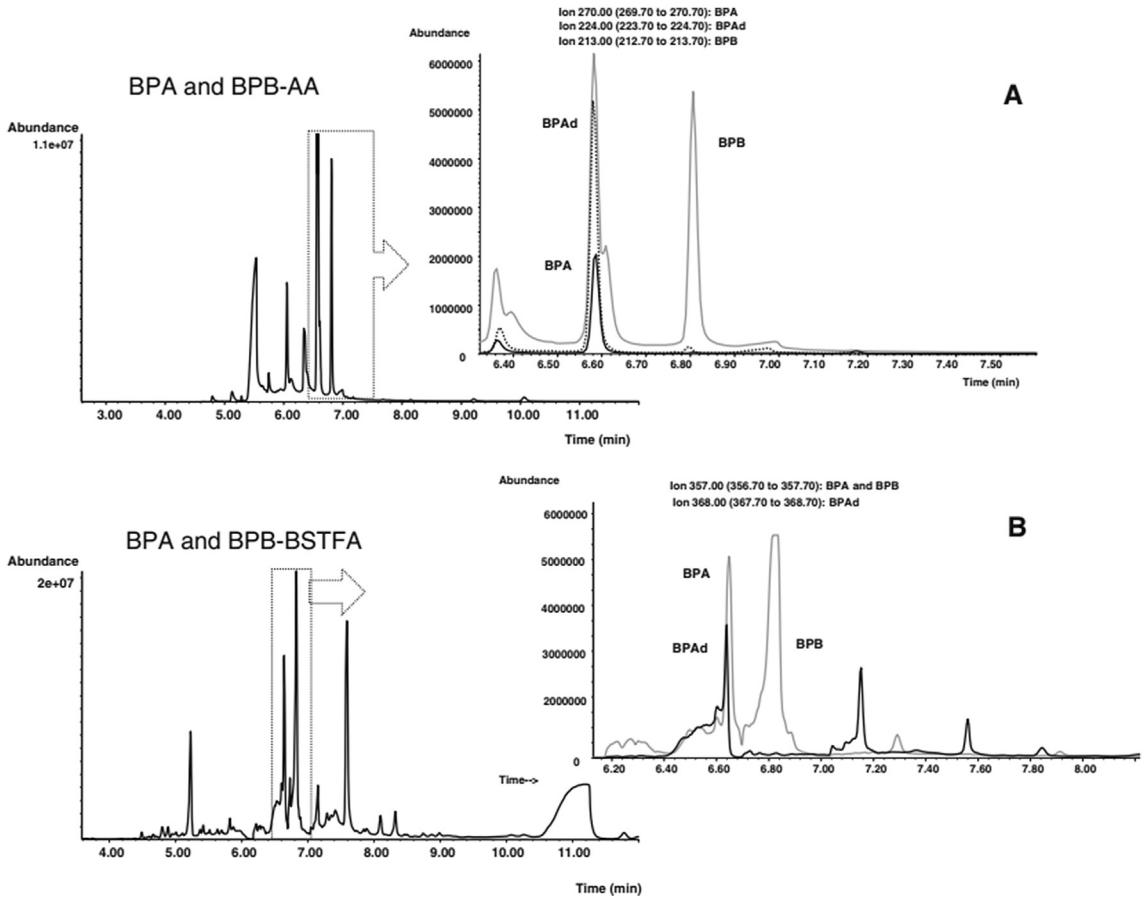


Fig. 4. Total ion chromatograms (TIC) of a tuna sample (spiked with 1.0 mg/L each of BPA, BPB, and BPAd) obtained by (A) QuEChERS and DLLME with acetyl derivatization (AA) or (B) QuEChERS and DLLME with silyl derivatization (BSTFA with 1% TMCS), together with the individual chromatograms in the SIM mode of each analyte [72].

Table 4
Different derivatization methods for the GC or GC-MS detection of phenolic EDCs.

Analytes	Derivatization methods	Derivatization agent	Derivatization solvent	Derivatives	Conditions	References
4-t-OP, 4-n-NP, and BPA	Methylation derivatization	PTA-OH (Hydroxy terephthalic acid)	Ethyl acetate	Methylated derivatives	PTA-OH (0.05 mL in 1 L water), and reacting at 20 °C for 5 min	[12]
4-t-OP, 4-NP, BPA, E1 (estrone), E2 (estradiol), and TCS (triclosan)	Pentafluorobenzoylation derivatization (a kind of acylation derivatization)	10% pyridine in toluene and 2% PFBOCl in toluene	n-hexane	Pentafluorobenzyl derivatization	50 μL of 10% pyridine in toluene and 50 μL of 2% PFBOCl in toluene (added in sequence in 1 L water) reacting at room temperature for 30 min	[14]
BPA and BPB	Acetylation derivatization	Acetic anhydride (AA)	performed directly in standard solution (MeOH)	Di-acetyl derivatives	125 μL of AA (added with 50 μL of T4CE) in 1 mL of standard solution of BPA and BPB (T4CE as the final acceptor)	[72]
Estrone (E1), 17β-estradiol (E2), estriol (E3), 17α-ethinylestradiol (EE2), nonylphenol (NP), and bisphenol A (BPA)	Silylation derivatization	BSTFA:TMCS (99:1, v/v) and pyridine (was added due to its catalytic properties)	Performed directly in standard solution (ACN)	Silylated derivatives	25 μL of BSTFA:TMCS (99:1, v/v) and 25 μL of pyridine were added to the standard solution (50 μL) at 60 °C for 10 min	[75]

UHPLC to determine phenolic EDCs in food, food packaging, and environmental samples. The detectors used in HPLC to detect phenolic EDCs are listed in Table 3.

The UV–visible detector is most commonly used in HPLC to detect phenolic EDCs [56,61–64] because of the strong ultraviolet absorption of phenolic substances. Different types of UV detectors such as diode-array detection (DAD) detectors [51,53,54,67], PDA [66], and variable wavelength scanning ultraviolet detector (VWD) [55] were also used to analyze phenolic EDCs in the milk, sediment, human urine [67], and various water samples [55,66]. The obtained LODs are in the range of 0.01–1.25 $\mu g\ L^{-1}$ or at the level of $\mu g\ kg^{-1}$.

FLD is one of the most widely used LC detectors [59,60,69]. In these studies, the excitation wavelength is in the range of 220–283 nm, and the emission wavelength is in the range of 300–323 nm.

These results indicated that the HPLC system with a traditional detector such as UV–visible, DAD, PDA, VWD, FLD, and so on detects LODs at the level of $\mu g\ kg^{-1}$ and $\mu g\ L^{-1}$, which cannot satisfy the requirement of the detection sensitivity for some time. As a result, LC-MS/MS is widely used to detect the trace phenolic EDCs from the complex food and environmental matrix.

LC coupled with MS/MS can reduce the detection limit of the target significantly. Negative-ion mode with multiple reaction monitoring (MRM) was mostly used in the detection of phenolic EDCs by MS to analyze several compounds simultaneously at the level of $ng\ L^{-1}$ [44,45].

Electrospray ionization (ESI) is frequently coupled with LC and used to detect phenolic EDCs because it is a soft ionization technique suitable for the detection of polar compounds. However, when the ESI is used for quantitative analysis, an adverse aspect of the occurrence of ion suppression or enhancement in complex samples will have a negative effect on the detection efficiency [112]. This adverse aspect may lead to responses of the analytes in an evidently different manner when the analytes are detected in the complex samples (compared with the pure standard solution). An established method to overcome this disadvantage in the detection process is the addition of the deuterated internal standard. For example, in Maragou's research [47], SPE pretreatment method by using C_{18} cartridges and BPA-d_{16} as the internal standard coupled with LC-ESI-MS was used to detect BPA from the commercial canned milk samples, and the mean relative recoveries spiking with three levels (5, 50, and 500 $ng\ g^{-1}$) were in the range of 97%–104%, thereby indicating that the addition of the deuterated internal standard can overcome the inaccuracy caused by ion suppression during ESI and the interferences from the sample preparation effectively. Similarly, Salgueiro-González [57] used DLLME coupled with LC-ESI-MS to determine alkylphenols (4-t-OP, 4-OP, 4-n-NP, and NP) and BPA from seawater samples. BPA-d_{16} and 4-NP-d_4 were used as the internal standard for BPA and APs, respectively, to remove the matrix interference and ion suppression during ESI, and the relative recoveries were in the range of 84%–104% for all analytes. LC-MS/MS has been used to detect phenolic EDCs frequently owing to its high sensitivity, low LODs, rapidity, and convenience.

3.2.2. Other techniques

In addition to chromatographic techniques, some new techniques have been developed and assessed to detect phenolic EDCs, especially for BPA [113].

Few papers have reported methods on the basis of capillary electrophoresis (CE) because of its high LODs. However, Mei's research [65] used the MISPE method coupled with CE-UV to detect BPA from tap water, wastewater, Yangtze River water, soil from the Yangtze River, shrimp, and human urine; the LODs obtained were 3.0 $\mu g\ L^{-1}$, 5.4 $\mu g\ L^{-1}$, 6.9 $\mu g\ L^{-1}$, 2.1 $\mu g\ L^{-1}$, 1.8 $\mu g\ L^{-1}$, and 84 $\mu g\ L^{-1}$, respectively, which are lower than those of other relevant studies.

The electrochemical analysis method is a type of instrumental analysis method on the basis of some electrochemical properties of substances in a solution. The determination of the analytes in the solution is based on the definite relationship between certain electrical parameters of the battery (such as resistance, conductance, potential, electric current, and so on) and the analyte concentrations to be measured [114]. Abnous et al. [78] developed a novel electrochemical sensing method to detect BPA from tap water and grape juice samples successfully, and low LODs (15 $pmol\ L^{-1}$) and a wide linear range (0.08–15 $nmol\ L^{-1}$) were obtained. The relative recoveries, which were in the range of 88.6%–97.3%, can also illustrate the feasibility and accuracy of this newly built method. Electrochemical sensors modified with different

nanocomposites such as carbon black NPs (CBNPs) and AuNPs [79] and graphene-ionic liquid (G-IL GCE) [80] were used to detect BPA from the tap and mineral water samples [79], disposable paper cups, plastic bottles, and noodles cups [80]. The obtained LODs were 8.8 [79] and 4.8 nmol L^{-1} [80], and the relative recoveries were in the range of 93.3%–110.0%.

Spectral analysis is the method of identifying substances and determining their chemical composition and relative content based on the spectrum of a substance. Spectral analysis is an analytical method on the basis of the spectroscopy of molecules and atoms. Spectral analysis consists of three main processes, as follows: 1) the energy source providing the energy, 2) the energy and the substance interacting with each other, and 3) the detection signal generated. One of the detection methods for BPA is UV–visible spectrophotometry, which is mainly based on the fluorescence resonance energy transfer theory [114]. New biosensors such as a biosensor integrated with TriPleX™ waveguide chip [82], a biosensor modified with aptamer/AuNP [81], and an integrated array fluorescent biosensor platform [83] coupled with spectral analysis have been used in the sensitive detection of phenolic EDCs from various water samples. LODs in the range of 9–60 ng L^{-1} were obtained, and the detection results had slight difference from the results obtained using HPLC [81]. SERS as a new type of spectral analysis technology, which was developed based on ordinary Raman spectroscopy combined with the surface enhancement technology, has been applied widely in BPA detection [114–116]. Lin et al. [84] proposed an application method in the BPA surface-enhanced Raman scattering lateral flow assay (SERS-LFA) kit by using an SERS-LFA binary system to obtain the visual and Raman signals. The detection limit of the SERS signal is 0.073 μg L^{-1}. Wang [85] used the MIPs@AgNPs SERS sensor to detect BPA and obtained low LODs (50 nmol L^{-1}). SERS has the characteristics of strong stability, convenience, and rapidity, and it is hardly interfered by water and fluorescence. Thus, the MIPs@AgNP SERS sensor is expected to become one of the rapid and equipment portable detection methods for the nondestructive detection of various contaminants.

The detection of phenolic EDCs by using a large-scale instrument has the advantages of high sensitivity and good selectivity, but its operation is complicated. Raman spectroscopy has the advantage of not destroying the samples. The electrochemical method and colorimetry have the advantages of low cost, high sensitivity, and rapidity. If these methods are combined with signal amplification, then the limitations of weak detection signals and narrow detection ranges can be effectively improved.

4. Occurrence of phenolic EDCs in environment, food, and food packaging

Increasing attention has been paid to the phenolic EDCs, and additional studies about the occurrence and detection of phenolic EDCs in various matrices have been listed in Tables 5–8.

4.1. Occurrence of phenolic EDCs in environment

NP, OP, and BPA do not occur naturally and exist in the environment simply because of the human activities. NP, OP, and BPA are mainly discharged into the environment through industrial and municipal sewage treatment plants. Studies have shown that alkylphenols and BPA are widely distributed in air, water, soil, and sediment [117,118].

4.1.1. Occurrence of phenolic EDCs in air

Studies on phenolic EDCs in the atmosphere are limited owing to the adsorption tendency of the phenolic EDCs to the soil and sediment, and the main research countries include the United States, the European Union, and Japan [118]. Most of the pollutants in the air are associated with sewage from wastewater treatment plants [118] and their concentrations varied with seasons [119]. Indoor air can also be polluted by these compounds, and the concentration is tenfold higher than that of outdoor [120]. The relevant studies are listed in Table 5.

4.1.2. Occurrence of phenolic EDCs in surface water

The occurrence of phenolic environmental hormones in overlying water is manifested in the distribution of sewage, estuaries, rivers, lakes, and other places, and the relevant data are summarized in Table 6. Therefore, many seas, freshwater rivers, and lakes worldwide have been contaminated by phenolic EDCs [52,57,121–123], and this situation is remarkable in China [12,14,42,45,60,66,76,124,125], thereby negatively affecting fishes and other aquatic animals.

Chen [76] detected several types of EDCs (including 4-t-OP, 4-NP, BPA, and so on) in three water samples, three sediment samples, and six fish samples collected from the Tamsui River in Taipei, Taiwan. NP was detected in all of the water samples and all of the sediment samples, and BPA was detected in all types of samples. Then, NP and BPA were detected in all fish samples at concentrations of 238 ng g^{-1} ww and 30.8 ng g^{-1} ww. Phenolic EDC contamination in fish may be caused by the pollution of water and sediment. The degree of contamination in aquatic organisms such as fish is largely determined by the extent of pollution in the basin.

In addition to water in natural watersheds, wastewater and water from sewage treatment plants have also aroused people's interests internationally [44,46,49,56,58,105,126,127] and in China [46,55,128,129]. Rodriguez-Mozaz et al. [46] used the SPE-LC-MS/MS method to monitor BPA in the water samples from the river, aquifer, and after each treatment stage (sand filtration, ozonation, activated carbon filtration, and postchlorination) in Spain, and these water samples were collected monthly from February to August in 2002. After detection, the concentration of various pollutants can be maintained at a low level of <0.1 μg L^{-1}, thereby indicating that the BPA concentration decreased significantly in the process of waterworks treatment (significantly in the process of the sand filtration step).

Table 5
Occurrence of phenolic EDCs in the air.

Country	Pollutants	Concentration range	Inspection point	Reference
USA	NP	2.2–70 ng m^{-3}	New Jersey	[118]
USA	NP, OP	<56.3 ng m^{-3}(NP); <1.0 ng m^{-3}(OP)	Estuary detection point: Sandy Hook	[119]
USA	NP, OP	0.13–81 ng m^{-3}(NP); 0.01–2.5 ng m^{-3} (OP)	Urban inspection point: New Brunswick	[119]
Germany	NP	0.534 μg dm^{-3}	Suburbs	[139]
		0.062 μg dm^{-3}	Urban areas	
		0.099 μg dm^{-3}	Rural areas	
Japan	NP, OP, and BPA	3.3–183.9 ng m^{-3}, <0.1–48.5 ng m^{-3}, and <0.1–3.6 ng m^{-3}, respectively	Indoor air samples	[140]

Table 6
Occurrence of phenolic EDCs in the surface water.

Samples	Pollutants	Concentrations (ng L^{-1})	Country	References
Samples from the coastal estuary of the Baltic Sea	NP, OP, BPA	NP: 2.5−13.8 OP: 0.12−0.6 BPA: 0.22 −5.4	Sweden	[123]
Samples in Morro Bay	NP	0.42 ± 0.16 μg L^{-1}	The United States	[122]
Samples at the mouth of the Mondugu River	NP, OP, BPA	NP: 81−1003 OP: 30−27502 BPA: 8.5 −182	Portugal	[121]
Samples from three rivers	NP, OP, BPA	NP: 2200 OP: 16.3 BPA: 136	India	[121]
Samples in Jiaozhou Bay of the Shandong Peninsula	NP, OP, BPA	NP: 212.9 OP: 21.7 BPA:36.6	China	[42]
Samples from the Liuxi River, Pearl River, and Shijing River in the Pearl River system	NP, OP, BPA	NP: 28.1−8890 OP: 1.0−2470 BPA: 2.2−1030	China	[14]
Samples from six major rivers in China (i.e., Songhua River, Liaohe River, Haihe River, Yangtze River, Huaihe River, and Pearl River)	NP, OP, BPA	NP: 280.19 OP: 710.65, BPA: 89.52 (the highest)	China	[125]
The overlying water and sediment in Honghu Lake and Dongting Lake	NP, OP, BPA	NP: 19.53 OP: 59.47 BPA: 31.13 (in the overlying water of Dongting Lake); NP: 44.31 OP: 60.97 BPA: 44.78 (in Honghu Lake)	China	[124]
Wastewater	NP, OP	NP: 17-37000 OP: 370	The USA	[127]
Wastewater	NP	NP: 330000	The UK	[126]
Samples from the inlet of four sewage treatment plants in Beijing	NP	0.115−0.347 μmol L^{-1} (removal rate: 75.7−90.8%)	China	[129]
Samples from municipal wastewater treatment plants	NP	174 nmol L^{-1} (in the inflow water); 37.2 nmol L^{-1} (in the effluent); the total removal rate: 71%	China	[128]
Surface water of Dianchi Lake	4-n-NP 4-t-OP BPA	13.6−141.6, N.D.-56.5 N.D.-4713.6	China	[12]
Water samples collected from Hangzhou Bay in Zhejiang	BPA	6.59−74.58	China	[45]
Raw wastewater, surface water, and groundwater samples collected from a local catchment area	BPA	Ground water (n = 30): <MQL−239, Surface water (n = 42): <MQL−324 Raw wastewater (n = 20): <MQL−839	Singapore	[44]
Natural waters and samples from drinking water treatment plants	BPA	0.065−0.295	China	[46]
Urban wastewater	BPA	–	Spain	[49]
Water samples (tap water and river water)	BPA	N.D	Iran	[56]
Sea water samples	BPA 4-t-OP 4-OP 4-n-NP NP:	BPA: N.D.-0.035 4-t-OP: N.D.-0.11 4-OP: N.D.-0.065 4-n-NP: N.D.-0.059 NP: <MQL-0.14	Spain	[57]
Water samples (tap water, river water, and waste water)	4-NP BPA	4-NP: N.D. BPA: N.D.	China	[55]
Water samples (from sewage treatment plants (STP), river, and drain)	BPA 4-t-OP 4-n-OP 4-n-NP 4-NP	BPA: N.D-292 4-t-OP: 308-382 4-n-OP: N.D. 4-n-NP: N.D. 4-NP: 1162-1643	Poland	[58]
Environmental water samples (tap water, spring water, snow water, and waste water)	BPA	BPA: 7.79 (waste water)	China	[17]
Environmental water samples (water samples from Dongping Lake and Beijing-Hangzhou Canal)	BPA	BPA: 9 (water samples from Dongping Lake)	China	[60]
Water samples (collected from a well, a lake, a pond, and the Pearl River (Guangzhou, China))	BPA 4-Tert-OP 4-NP	BPA: well water (0.13 μg L^{-1}, lake water (0.15 μg L^{-1}); 4-tert-OP: 1.05, 1.15, 1.17, and 1.19 μg L^{-1} in well water, lake water, pond water, and river water, respectively 4-NP: 0.41, 0.60, 2.04, and 0.80 μg L^{-1} in well water, lake water, pond water, and river water, respectively	China	[66]
Tap water sample	BPA	BPA: N.D.	China	[64]
Water samples (tap water, wastewater, Yangtze River water)	BPA	–	China	[65]
River water	BPA	–	Italy	[63]
Seawater samples	BPA	BPA: N.D	Saudi Arabia	[52]
Drinking water, river water, effluents, and plastic packaging bag	BPA		China	[53]

Table 6 (*continued*)

Samples	Pollutants	Concentrations (ng L^{-1})	Country	References
		BPA: N.D. in the drinking water, river water, and effluents, 3260 ng L^{-1} in the plastic packaging bag		
Tap water, lake water, river water, milk 1 and milk 2	BPA, NP, OP	BPA: N.D.	China	[51]
Influent and effluent wastewater samples collected from a pilot-scale wetland plant in Langenreichenbach	BPA, t-NP	–	Germany	[105]
Three water samples	4-t-OP, 4-NP, BPA	OP: N.D. in the water and 36.3 ng g^{-1} wet weight (ww) in the fish; NP: 1026 ng L^{-1} in the water samples; BPA: 808 ng L^{-1} in the water samples;	Taiwan, China	[76]

Hao et al. [130] also detected different NP concentrations in various stages of the sewage treatment process in China and found that NP is also present in the sludge recycling process. The NP concentration in the primary and secondary sedimentation tanks significantly reduces due to the adsorption of the activated sludge. The biodegradation of the aeration tank is also a removal method of NP.

4.1.3. Occurrence of phenolic EDCs in the soil and sediment

Phenolic EDCs also exist in the soil and sediment, which mainly occur by human activities. The relevant data are listed in Table 7. The excess sludge in the sewage treatment plant is an important source of phenolic EDCs in soil. According to the Danish survey data in 2002, 66% of the sludge is recycled [131]. Another study showed that if the field is added with sludge with an NP concentration of 1.4–1.6 mg kg^{-1}, then the NP concentration in the surface run-off is between 14 and 34 μg kg^{-1}, which is much higher than the NP concentration in the run-off without adding sludge (0.01 μg kg^{-1} to 0.98 μg kg^{-1}). Phenolic EDCs in landfill leachate and overlying water also penetrate into the soil owing to their hydrophobic physicochemical properties [132,133]. The organic carbon content is highly correlated with the phenolic EDC contents [132], thereby revealing why phenolic endocrine disruptors tend to deposit in the sediment.

4.2. Occurrence of phenolic EDCs in food and food packaging

The two main sources of phenolic EDCs in foods are as follows: on the one hand, some pollution is caused by the surrounding environment; on the other hand, some pollution is caused by the process of treatment and the release and dissolution of phenolic EDCs in food packaging materials. The second aspect is more important than the first one [5]. Research data about the pollution status of phenolic EDCs in food and food packaging are summarized in Table 8.

On the one hand, fresh foods may be contaminated by the phenolic EDCs due to pollution in the environment. The phenolic EDC concentrations in mutton can reach the level of mg kg^{-1} [50], and their concentrations in eggs, milk [77], and vegetables [75] are at the level of μg kg^{-1}, which is much lower than that in the mutton. The possible reason for this result is that EDCs are often used in animal husbandry and aquaculture to increase feed conversion and animal growth rates illegally [11].

On the other hand, BPA, OP, and NP are important raw materials for epoxy resin, phenolic resin, and plastic production, respectively. Thus, the treatment process and the release and dissolution of these phenolic EDCs from food packaging materials are the other important pollution sources. Increasing studies concentrate on these three types of phenolic EDCs in food packaging and their migration behaviors.

These phenolic EDCs can be detected in plastic food packaging bags [54], disposable paper cup (PE), disposable plastic bottle polyethylene terephthalate [PET]), and many disposable products [80].

The migration behavior of phenolic EDCs also attracted people's attention. In the NP dissolution test of high-density polyethylene (HDPE), PET, and PVC mineral water bottles, the concentrations of the released NP in HDPE and PVC bottled water are 180 and 300 ng L^{-1}, respectively. Assuming that each person consumes 2 L of water per day, for adults, 4.8% (or 8%) of the NPs consumed per day is from HDPE (PVC) bottled drinking water. The same results were also obtained in the test of released content of NP in milk [134]. The change in external factors such as the prolongation of the storage time of food, usage time, and microwave heating time and the increase in temperature, acidity or ethanol concentration, and some internal factors, such as oil content can also increase the migration of EDCs from the packaging material to the food [135,136]. Hence, the appropriate use of plastic food packaging materials is important for food safety and personal health.

Foods such as canned juice [68], tomato paste [68], canned vegetable samples [106], and canned seafood [72,73] were also found to be contaminated by phenolic EDCs owing to their migration from the packaging materials.

Phenolic EDCs in food packaging materials, food, and environmental samples have potential toxicity hazards; therefore, it is of vital importance to establish an efficient, rapid, and

Table 7
Occurrence of phenolic EDCs in the soil and sediment.

Samples	Pollutants	Concentrations	Country	Reference
Sediment from 31 sampling points of Ulsan Bay	NP, OP, BPA	NP: 1040 ng g^{-1} dw, OP: 120 ng g^{-1}dw BPA: 54 ng g^{-1} dw	Korea	[132]
Sediment from 21 sampling points in the Enzeli wetland	NP, OP, BPA	NP: 29 μg g^{-1} dw, OP: 4.3 μg g^{-1} dw BPA: 7 μg g^{-1} dw (highest)	Iran	[141]
Sediment from 25 sampling points in the Songhua River	NP, OP, BPA	NP: 11.2–119.54 μg g^{-1}dw, OP: 0.14–1.7 μg g^{-1} dw, BPA: 1.56–17.3 μg g^{-1} dw,	China	[142]

Table 8
Occurrence of phenolic EDCs in food and food packaging.

Samples	Compounds	Concentrations (ng L^{-1})	Country	Reference
Commercial canned milk samples	BPA	<1.7–15.2 (The unit is ng g^{-1})	China	[47]
Bovine milk	BPA	–	China	[48]
Mutton	4-NP	N.D.-0.11	China	[50]
	BPA	0.18–0.36 (The unit is mg kg^{-1})		
Food packaging	BPA	BPA: 38710	China	[54]
Plastic packaging drink samples	BPA	BPA: N.D.	China	[59]
	4-n-OP	4-n-OP: N.D.		
	4-n-NP	4-n-NP: N.D.		
Milk (human breast milk, full fat milk (3.5% fat) and semi-skimmed milk (1.5% fat) samples)	BPA	BPA: N.D.	Greece	[61]
Milk (whole, semi-skimmed, and skimmed milk)	BPA	BPA: N.D.	Spain	[62]
27 samples of commercially available milk	BPA	BPA: 176 μg kg^{-1} (detected in one sample (canned evaporated milk))	Ireland	[69]
Milk	BPA	BPA: N.D.	China	[67]
Vegetable (tomato and cabbage) and juice samples (orange, apple, and mixed juice and tomato paste)	BPA	BPA: Orange juice: 33.220 Apple juice: 29.892 Mixed juice: 36.304 Tomato paste: 68.166 (The unit is nmol kg^{-1}) Tomato and cabbage: N.D.	China	[68]
Plastic packaging bag	BPA	BPA: 3260 ng L^{-1} in the plastic packaging bag	China	[53]
Milk 1 and milk 2	BPA, NP, OP	BPA: N.D.	China	[51]
Food samples (peas (2), corns (2), beans (2))	BPA	BPA: 152 ± 10 to 697 ± 40 ng g^{-1} (found in all of the samples)	Iran	[106]
Canned seafood (47)	BPA	BPA: 1.0–99.9 μg kg^{-1} (found in 83% of the samples)	Portugal	[72]
Canned sea foods (Sardine, mussel, canned tuna, canned sardine, and canned mackerel samples) (25)	BPA	BPA: 23.93 ng g^{-1} ww and 15.25 ng g^{-1} ww for BPA (in canned samples of tuna and mackerel)	Portugal	[73]
Beehive samples (5 honey, 10 pollen, and 12 wax samples)	$NP(EO)_{3\text{-}13}$, $OP(EO)_{3\text{-}13}$	$NP(EO)_n$: 26 to 10,239 (26–91 in honey, 171–604 in pollen, and 51–10239 in wax) $OP(EO)_n$: N.D.-398 (N.D. in honey, N.D.-69 in pollen, N.D.-398 in wax) (The unit is μg L^{-1})	USA	[71]
Three leafy vegetables, including cabbage, lettuce, and spinach (eight samples for each kind of vegetable)	NP_xEOs and OP_xEOs (x = 2–20)	OP_xEOs: 0–8.67 μg kg^{-1}, NP_xEOs: 15.75–95.75 μg kg^{-1}	China	[74]
Egg samples (10) and milk samples (10)	BPA, NP, and OP	BPA: N.D.-10.45 in eggs (detected in three egg samples); N.D.-0.49 in milk (detected in only one milk sample); NP: N.D.-2.94 in eggs (detected in eight egg samples); N.D.-15.93 in milk samples (detected in seven milk samples); OP: N.D.-0.41 in eggs (detected in one egg sample); N.D.-0.1 in milk samples (detected in three milk samples) (The unit is μg kg^{-1}).	China	[77]
Carrot samples (5), onion samples (6), tomato samples (6), and lettuce samples (5)	BPA, NP	NP: < LOQs in carrots (number of samples with the analytes: 5); <LOQs in tomatoes (2); BPA: 5.1–16.3 in carrots (5); 2.1–12.1 in onions (6); 3.4–8.0 in lettuce (5), 1.7–8.3 in tomatoes (6).(The unit is ng g^{-1})	Spain	[75]
Fish samples (6)	4-t-OP, 4-NP, BPA	OP: N.D. in the water and 36.3 ng g^{-1} wet weight (ww) in the fish; NP: 238 ng g^{-1} (ww) in the fish; BPA: 30.8 ng g^{-1} (ww) in the fish samples	Taiwan, China	[76]
Disposable paper cup (PE), disposable plastic bottle (PET), instant noodles cup (PE), and instant noodles cup (PS)	BPA	0.30 in the disposable paper cup (PE), 0.15 in the disposable plastic bottle (PET), 0.06 in the instant noodles cup (PE) and 0.20 in the instant noodles cup (PS). (The unit is μM).	China	[80]
Thermal paper: A and B	BPA	N.D. in paper A; 63.3 ± 7.9 μg mL^{-1} in paper B.	Korea	[81]
The polycarbonate plastic	BPA	0.184–2.07 mg L^{-1}	China	[85]
Food packaging of different materials such as plastic, paper, ceramics, and rubber (30)	NP	26.33–3374.32 μg kg^{-1} (detection rate: 80%)	China	[143]
Industrial polyvinyl chloride (PVC) membranes (12), and household PVC membranes (10)	NP	Industrial PVC membranes (detection rate: 83.3%); Household PVC membranes (detection rate: 20%).	Japan	[144]
Plastic wrap and composite bag samples (30)	NP, OP	Detection rate for NP and OP: 20%	China	[8]
Four kinds of food packaging materials: plastic bag, disposable paper cup, instant noodles box, and plastic bowl samples	BPA	0.98, 1.47, 2.03, and 1.68 μg g^{-1} in these four kinds of samples, respectively	China	[145]

MQL: Method quantification limits.

sensitive detection method for phenolic EDCs, thereby establishing relevant criteria and implementing corresponding protection measures to meet the needs of modern food and environment safety.

5. Conclusion

BPA, NP, and OP are phenolic environmental endocrine disruptors with estrogen-like effects, which are easily accumulated,

hard to degrade, and easily distributed in the environment, thereby making them detectable in air, water, sediment, and soil. These three kinds of phenolic EDCs can be detected in some food packaging materials. These compounds can also further contaminate the food through pollutant migration. As a result, phenolic EDCs can enter the animal and human bodies, thereby affecting the endocrine, nervous, immune, and reproductive systems and possibly causing cancer. The mechanism of interference action is to interact with related substances (directly) or with the estrogen-related receptors (indirectly).

In this review, the physicochemical properties; application; distribution; pretreatment techniques; detection methods; and occurrence in the food, food packaging, and environmental samples are summarized in this review. However, many studies are still urgently needed.

In view of the toxicity and pollution statuses of the three phenolic EDCs, future research can focus on the following directions:

(1) Using evolving biotechnology to study the toxicity mechanism of these compounds at the cellular level and illustrating the relevant interference mechanism further.
(2) Conducting research on the occurrence of phenolic EDCs in the human body. At present, most studies focus on the pollution status of these analytes on the environmental media, such as water bodies and the organisms, which are mostly aquatic animals (such as fish, shrimp, and seabirds). Only few studies focus on the occurrence of phenolic EDCs in the human body. Thus, relevant research is urgently needed to fill this gap.
(3) Additional studies should be conducted on the relationship between phenolic EDC pollution in the environment and population diseases, and the corresponding guidelines and policies should be implemented. Although phenolic EDCs are known to cause damage to human health, few epidemiological studies on the pollution status and the relationship between pollution and environmental diseases are available; thus, further research is needed. At the same time, according to the situations above, formulating relevant policy restrictions to reduce the body's intake of phenolic EDCs are suggested for future studies.
(4) Promoting pretreatment techniques and detection methods efficiently and conveniently, inventing environmental-friendly raw materials, and establishing relevant criterion and legislation. Many food packaging and foods have been contaminated with phenolic EDCs. Strengthening detection and supervision by relevant laws and regulations and discovering additional eco-friendly raw materials to replace the traditional food packaging materials, such as plastics and phenolic resins, can reduce food pollution caused by phenolic EDCs to protect human health.

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