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The Occurrence and Analysis of Bisphenol A (BPA) in Environmental Samples – A Review

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ABSTRACT

This review paper briefly explains the meaning and characteristics of endocrine disrupting compounds (EDCs). EDCs comprise various types of natural and synthetic chemical compounds that can impede the reproductive action of the endocrine system in animals and humans. Further discussion is on bisphenol A (BPA), one of the examples of EDCs that is extensively used in industries nowadays. It acts as a monomer, which is desired in the production of polycarbonate plastics and epoxy resins. BPA later ends up in environmental compartments (air, water, sediment). In spite of this, BPA is not categorized as a persistent compound and it will be degraded either by photolysis or bacteria. It can only exist between three and five days in the environment. The concentration of BPA varies in different locations depending on the temperature, pH, source and time of sampling. BPA has been frequently debated due to its toxicity and carcinogenicity towards animals and humans. This paper also explains several extraction procedures and analytical methods concerning how to identify BPA in either aqueous or solid samples. However, an additional review is needed in respect of how to handle, reduce the level of BPA in the environment and understand the details concerning the existence of BPA.

INTRODUCTION

The growth of residents and world modernization have enhanced the total number of anthropogenic activities consequently led to the emission of toxic organic compounds in the environment, which include the endocrine disrupting compounds (EDCs). EDCs have been defined as exogenous materials or mixtures that appear during synthesis, secretion, transport, binding action or eradication of natural hormones and which cause harmful health effects in intact organisms or their progeny or (sub) population [1,2]. Rogers et al. [3] stated that the presence of EDCs in natural and synthetic compounds disrupts the endocrine system. Most EDCs are artificial compounds, which have been used for numerous purposes such as plasticizers, surfactants and pesticides [4].

Investigation of EDCs in Malaysia started in 1999 and became essential due to the difference in temperature, economic status and weather, which are totally different from other countries [5]. According to Razak et al. [6] the investigation of EDCs in environmental samples was initiated by reporting the existence of some compounds like chlorophenicol, sulphonamides, estrone, estradiol and paraquat in selected places. EDCs are believed to contaminate the environment via the discharge of industrial or domestic sewage effluent. Other studies also determined that the level of phthalates in river water and sediments were critical in the industrialized Klang Valley [7]. Numerous studies on EDCs have proven that the level of contamination has become worse despite the prohibition by governments of the usage of toxic chemicals [8].

The consequences of EDCs have affected almost all the environmental media (air, water, sediment and biota). Even at very low doses, EDCs can have negative side effects, while in worse case scenarios they may cause the propagation of human prostate cancer cells and cardiovascular disorders [9]. Researchers have studied the pathway of EDCs including the sources. The highest concentrations of this compound have been found in wastewater [10,11], sewage samples [12], leachate [13] and in potable or natural mineral water [14].

This review will briefly examine the examples of EDCs followed by a focus on bisphenol A (BPA), a type of EDC that is extensively used in manufacturing processes. This paper will also assess the sources, effects and analytical methods that have been studied globally.

Examples of the EDCs

The environment has already been contaminated with hazardous chemicals due to industrial and anthropogenic actions. In order to distinguish all the chemicals, a screening procedure were introduced by United States Environmental Protection Agency (USEPA) that considered the physical chemical properties, exposure and effect using toxicological methods. Nowadays, numerous categories of EDCs have been discovered. USEPA has updated a list of EDCs, which has nearly 10000 chemicals present in the environment. Thousands of chemicals have been designated based on different criteria and actions in binding activity to cellular response *in vitro* to *in vivo* [15]. Some of them have been identified as hormones, alkylphenols and phthalates.

Estradiol, estriol and progesterone are examples of steroid hormones that are known to be non-polar or weakly polar compounds [16]. The presence of hormones in in soils and sediment has been discussed [17]. Some of the hormones were used in contraceptive pills [18] and to control the onset of menopause [19]. In addition, phthalates were employed as plasticizers and mainly applied in medical stores, paints, cosmetics, perfumes, propellants and clothing [20].

Josefson [21] explained that this compound can be absorbed through the skin and reported high levels in human blood and urine. Meanwhile, alkylphenol is a phenolic compound, the application of which is similar to phthalates. Vom Saal and Welshons [22] reported that this compound causes infertility due to prostate cancer cells and reduced sperm production. One of the examples of alkylphenol is BPA, which is the most recently discussed.

BPA as a representation of EDC

Lately, BPA is the EDC that has caused most concern due to its high demand from manufacturers. It has been produced domestically with the highest volume to produce mainly polycarbonate plastics and epoxy resin [23–28]. There are two different methods of BPA manufacturing. The first method involves synthesizing the compound from the acid-catalysed condensation of phenol and acetone in the presence of a catalyst and applied with distillation technology [29]. The second method uses a different catalyst and employs purification technology [30].

Recently, BPA has been applied in digital media, medical tools, food storage containers and dental sealants [28,31]. BPA, also known as 4,4'-dihydroxy-2,2-diphenylpropane, exists in the form of crystals or flakes with a mild phenolic odour. More information on the physical and chemical properties of BPA is listed in **Table 1**. Wastes are being formed, especially during the process of heating, handling, washing and sterilizing [32].

Extreme levels of BPA have also been observed in food containers, especially cans with epoxy resin linings. Moreover, Brotons et al. [36] and Yoshida et al. [37] noted that a significant exposure of BPA leached out from food containers. Some retailers already addressed the problem by eliminating products containing BPA since they are known to have a negative effect and affect foetuses, infants and young children. Denmark for instance, has forbidden the usage of BPA in baby bottles followed by Canada which was the first to declare BPA a toxic compound followed by all European countries [3].

Table 1 Physical and chemical properties of BPA.

Synonym name	4,4'-Isopropylidenediphenol, 2,2-Bis(4-hydroxyphenyl)propane.			
	diphenylolpropane.			
	p'p-Isoprovlidenebisphenol ^a			
Appearance	white crystalline, granules and flakes solid			
	b,c			
Molecular Mass	228.29 g/mol			
Molecular Formula	C ₁₅ H ₁₆ O ₂			
Water Solubility	120-200 mg/L (20-25°C) ^b			
Density	1.20 g/cm ^{3 b}			
melting point	158-159°C °			
boiling point	398°C at 101.3 kPa °			
vapour pressure	87 Pa at 190°C b			
pKa	9.59-11.30 °			
strength	robustness, toughness, transparency and			
-	resistances to temperature ^d			
a LISEDA [33]				
^b Mohanatra at al. [0]				

° Cao [34]

^d Kang et al. [35]

According to The Star [38] BPA bottles in Malaysia have been banned as a safety measure. To date, no studies have reported BPA as being harmless and environmentally friendly. Tan and Mustafa [39] declared that polycarbonate plastics are not safe even if they are acknowledged to be tough and durable with high resistivity towards elevated temperature. Hydrolysis and BPA leaching are extremely high, especially when keeping boiling water inside or heating in the microwave [39,40]. The monitoring of BPA in environmental samples has also been done in water. Unfortunately, the concentration of BPA varies with time and month due to the inconsistent rainy and dry seasons in Malaysia [5].

Availability of BPA in the environment

BPA does not exist as a natural product. The availability in the environment is as a consequence of human activities. During the early 1990s, Krishnan et al. [41] accidently found that the BPA compound leached out from a polycarbonate flask during culture media autoclaving. Following that, the BPA level has also been investigated in landfill leachate, wastewater treatment plants, estuaries, lagoons [42], sewage, river and sea water, sediment [43], biota [44] and air [45]. The concentration of BPA in environmental compartments varies depending on the biotic and abiotic factors, source of samples, time of sampling, water pH and temperature, presence of bacteria and much more [46,47].

Water

Rivers, lakes and estuaries are the major location sinks of BPA pollution. This compound could be found in wastewater from the factories due to inappropriate removal during the treatment process [35]. This is the main origin of contamination in aquatic life. Yamamoto et al. [13] found that leachate in landfills has a high level of BPA 1.3-17200 μ g/L, which is probably due to it leaching out from plastic debris. Suzuki et al. [48] discovered that the BPA level in the effluent is much higher because it is directly released to the environment without being treated, while, according to Huang et al. [28] BPA contamination is much higher in industrial and commercial areas compared to other regions. BPA is not suspected of being a persistent

compound. It could disappear and degrade within 2.5 and 4.7 days under aerobic conditions [30,46,47] but degrades more slowly in an anaerobic state [49]. The degradation of BPA within 3-5 days by bacteria will provide adequate time to have some impact on aquatic organisms [35]. Basheer et al. [50] found that the BPA concentration in biological samples is quite high, between 13.3-213.1 ppb particularly in *Portunus pelagicus*. However, if no degradation takes place within 30 days, the possibility of biota becoming contaminated could be higher [35].

Table 2 focuses on the level of BPA monitored worldwide in water, treatment plants, sewage and water bottles. The majority of concentrations of BPA detected in river water were lower than $0.01\mu g/L$, except for a study done in Taiwan, in which the concentration was much higher with levels up to $44\mu g/L$. In the meantime, the highest BPA concentration was found in bottled water in France. This is due to BPA migrating towards water, especially from polycarbonate drinking bottles when exposed to elevated temperatures [51]. BPA concentration in the leachate area before employing any treatment was detected up to 3000 $\mu g/L$.

Table 2 Concentration level of BPA measured in general sources.

BPA concentration (µg/l)	Sample	Location	Reference
0.0035 - 0.0598	tap water	Malaysia	[52]
0.0007 - 0.0059	bottled mineral water		
0.07 - 4.21	bottled water	France	[53]
< 0.01 - 149	wastewater	Ontario	[54]
49.9 - 0.031	sewage influent	Canada	[29]
0.0133 - 0.0192	sewage treatment plant - effluent	United Kingdom	[55]
0.8847 - 1.1052	sewage treatment plant - influent		
0.20 - 370	final effluent - waste paper recycling plants	Japan	[56]
0.07 - 228	leachate		[57]
0.009 - 3600			[58]
0.002 - 0.0297	drinking water treatment plant	France	[27]
0.009 - 0.776	river water	Germany	[59]
0.004 - 0.092		•	[60]
0.0009 - 0.044		United States	[61]
0.0191 - 0.106		China	[62]
0.01 - 44.65		Taiwan	[47]

Soil and sediment

The probability of BPA traces released from wastewater treatment and accumulates in sewage sludge is very high. **Table** 3 indicates the earlier studies that have been carried out. The sediment or soil has been recognized as a secondary source of EDCs rather than water due to its hydrophobic character, which tends to absorb more into the sediment [63].

Table 3 Environmental concentration of BPA measured in sediment and soil.

Location	BPA	Туре	Reference
	concentration		
	(µg/Kg)		
Germany- Baden-	0.5 - 15.0	river sediment	[64]
Württemberg			
Germany- Brandenburg and	10 - 190	river sediment	[65]
Berlin	4 - 1363	sewage sludge	
Germany- River Elbe	10 - 380	freshly deposited sediment	[60]
Canada- Ontario	7.01 – 74.38 up to 6.1	sewage sludge surface sediment	[66]
Italy- Venice Lagoon	2.1 – 118	lagoon sediment	[67]
Japan- Okinawa	< 1.2 - 22.0	urban river area	[68]
	nd – 6.8	rural river area	
Canada- Halifax Harbour	<0.09 - 9.50	surface sediment	[69]
Spain- Spanish Region,	0.7 - 4.6	agricultural soil	[70]

Bilbao Area	1.1 - 44.5	industrial soil
Iran- Anzali Wetland	10 - 6970	surface sediment

Staples et al. [30] found that around 50% of BPA will be absorbed into sediments or soils. The research on the occurrence of BPA in sediment is still limited [67]. A study by Bolz et al. [64] discovered that the availability of BPA in sediment is quiet high due to the discharge of sewage from treatment plants into water. Another study on BPA using soil adsorption has proven that this compound is unstable, mobile and bioavailable [72]. In order to understand the adsorption actions or mechanisms of BPA in sediment, a study was performed by Zeng et al. [73] using the Freundlich model. They found that the adsorption of BPA into the sediment decreases as the concentration of sediment increases.

[71]

Air

Many studies have been conducted in water and sediment with the exclusion of air. However, the information on BPA spreading in the atmosphere is very limited and rarely reported [45,74,75]. BPA is an organic compound, which has low volatility [76]. This was proven when Staples et al. [30] determined that the distribution and movement of BPA in air is much lower than in water and sediment.

In addition, the half-life of this compound in air is much shorter compared to other environmental compartments. Based on Kang et al. [35] BPA in air will degrade somewhere between 0.74 and 7.4 hours. Thus, the possibility of inhaling this compound is much lower. However, a survey has shown that the BPA level in resin factories is much higher $(492\mu g/m^3)$ [28,77]. Hanaoka et al. [78] discovered that the concentration of BPA in the urine of workers was higher compared to workers who were not involved in BPA industries.

Surprisingly, BPA can also be emitted through the combustion of computer printed circuit boards in electronic waste [79] as well as in household products in the home and furnishing materials in the office [45]. Fu and Kawamura [80] contended that the presence of BPA in the air will have health consequences and therefore all sources of emission should be suitably controlled.

Threats of BPA on biological samples

Leaching of BPA is due to hydrolysis of the ester bond that binds them with polycarbonate or resin according to the temperature, acidity and basic condition [22]. The toxicity and carcinogenicity of BPA compounds are being studied due to the high production of BPA in industry. There have been many studies on the effects of consuming this compound [22,46,81]. Rogers et al. [3] claimed that EDCs interrupt the body system in numerous ways including binding to the nuclear and hormone receptors with sex and steroid hormones. The study conducted by Vom Saal and Welshon [22] suggested that BPA could have a considerable effect at very low doses in mice due to the limited binding of BPA to plasma binding proteins.

Table 4 indicates the previous studies that focused more on animal experiments. Rats or mice are frequently chosen as samples due to their high sensitivity to oestrogen during the examination of the mechanism of toxicity [82–85]. A kinetic test on the BPA metabolism in rodents, which requires giving small to relatively high doses of BPA has been done. The results show that the low dosage enhances the metabolism of BPA more and that it could be found shortly afterwards in the blood, urine and faeces [81].

Table 4 Biological effect of BPA on animal studies.

Species	Dose giver	n Dosing	Endpoint	References
	(µg/Kg)	technique		
mice – female	25, 250	Alzet osmotic pump	disorder of hypothalamic- pituitary-ovarian axis	[86]
mice – female	25, 250	Alzet osmotic	alters tissue organization in ovaries, mammary gland, disrupts cestrous cyclicity	[87]
rat – male	100, 50000	oral	raises Sertoli cell number per organ	[88]
mice – female	25, 250	osmotic pumps	alteration in genital tract of female offspring	[89]
rat – female	2.5, 25, 250 1000	, osmotic pump	stimulates the development of ductal hyperplasias, enhances number of tumour cells	[90]
rat – male	10, 5000	oral	proliferates sperm dna damage, reduces motility	[91]

These days, human exposure to BPA has become a topic in the media. The reference dose of taking BPA is $50\mu g/kg-d$ [92]. There are a few researchers who claim that food and water are the predominant routes of exposure [51,53,93–95]. Unfortunately, human biomonitoring of BPA has only been studied in urine (external exposure) and blood (internal exposure) [31,94]. BPA is completely excreted in urine within 24 hours and the value of concentration is expected to be reliable with a reference value [31,92].

There have been numerous studies that have clarified that BPA has a wide range of effects. These include learning defects, increased aggression, immune deficiency syndrome, multiplying of the growth rate, abnormalities in liver-enzyme, chronic kidney and respiratory disease, diabetes and obesity [9,32,96]. Due to these impacts, BPA has been declared a noxious compound that must be taken seriously in respect of human health. More work is needed to further explore the toxicity and carcinogenicity of BPA and its effects on human health.

Method analysis of BPA

Sample preparation

The sample preparation is the most important stage prior to the analytical method. This technique can enhance the sensitivity and reduce the interference by cleaning and concentrating the samples [97]. The sample preparation for liquid and solid samples is different. For liquid samples, liquid-liquid extraction is commonly used (LLE) [98], solid phase extraction (SPE) [99] and solid phase microextraction (SPME) [100]. Meanwhile, the type of extraction for solid samples includes soxhlet extraction (SE) [12], accelerated solvent extraction (ASE) [59] and microwave extraction system (MAE) [47].

Extraction of analyte from environmental samples

Generally, samples need to be filtered to eliminate the suspended and organic materials. They can either be filtered by normal filter paper or a membrane filter as long as the size is in microns. Cai et al. [101] and Liu et al. [102] contend that a millipore cellulose membrane or pre-combusted GF/F filter paper can also be used in water analysis. Usually, filtration is followed by the extraction process.

The pre-treatment for solid samples necessitates many steps due to the complexity of the matrices. Samples first need to be extracted before being injected into the instrument. In this case, a few techniques have been introduced. SE is a conventional method for extraction, which even though it consumes a lot of solvent and time, researchers still use it in the extraction of solid samples. The latest known techniques are ASE and MAE, both of which give a better outcome and require less solvent in the extraction. The time required for the extraction is also much faster compared to SE. For liquid samples, LLE is one of the traditional methods used in the analysis of BPA. Nevertheless, it uses a large amount of solvent, increases the extraction time, requires a huge volume of sample and the formation of emulsion frequently occurs [97].

Recently, the SPE method has often been used in sample preparation. The optimization of SPE is crucial to make sure the sample is totally concentrated and clean. It involves a few steps including conditioning of the sorbent, elution, volume of sample and type of sorbent used during extraction [97]. Different sorbents have different selectivity and recoveries. Examples of the sorbents that are mainly used include Oasis HLB, RP-C18, Strata X-AW and polymeric cartridges. Gros et al. [103] determined that both Oasis HLB and Strata X are capable of extracting analyte with a wide range of pH. However, Strata X is mostly employed in multi-group analysis even though it does not always achieve better recoveries. RP-C18 is essential for pH adjustment on a sample by referring to the characteristics of the compound prior to extraction.

The volume of sample also plays an important part in obtaining a better recovery. Commonly, 1L of sample is taken and extracted using an appropriate solvent. Although a small volume of sample will reduce the extraction time it will not fully concentrate [97]. Hence, small recoveries will be acquired after being analysed. SPE consists of two types: (i) disks [69] and (ii) sorbent cartridge [104]. Disks seem to have more benefit compared to the sorbent cartridge because they have the ability to minimize sample clogging and have a large surface area. However disks tend to use a large volume of solvent for sample elution hence more interference will emerge in the chromatogram [9].

The SPME technique is the newest method, which is a process for the adsorption of the analyte onto the surface of the coated silica fibre. Different types of fibre have a different selectivity. According to Chang et al. [105] the amount of analyte adsorbed onto the fibre during equilibrium time is directly related to the sample concentration. The fibre is acknowledged to have sensitivity to organic compounds. Mohapatra et al. [9] stated that SPME is more effective compared to other techniques. It has the ability to reduce the time required and the amount of solvent while giving better recovery during analysis. However, this technique has not been fully utilised by other researchers and SPE still remains the most extensively used.

Analytical method

In order to detect the existence of BPA, an instrument with high sensitivity and that is also reliable and accurate should be selected. However, with a low concentration of sample, noise would probably interfere with the analysis. Hence, quality assurance and method validation must be done to establish better results. The determination of BPA is mostly measured in the river as it receives the effluent from industrial and municipal waste [9]. This part will emphasize the techniques to quantitate low levels of BPA. In the beginning of the process, various steps including sample collection, clean-up, extraction and much more must be deliberated. BPA is mostly analysed using the chromatographic method. Gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) are the most common instruments in the determination of BPA [98,106]. **Table** 5 represents the details concerning the determination of BPA in different countries using various analytical and extraction skills.

Although GC-MS is the most common instrument used, it still has a few drawbacks in the analysis of BPA. Before the sample injection, a derivatizing agent should be added, which, generally requires a whole day to derivatize due to inadequate volatility for direct analysis [9,107]. In addition, even though the percentage of sample lost during derivatizing is high, researchers use this instrument to detect the presence of BPA even though it has been classified as time consuming. Yasuhara et al. [108] employed GC-MS to determine the occurrence of organic components in leachate. Nonetheless, this method was slightly modified to obtain a virtuous chromatographic diagram [10,29].

Krishnan et al. [41] detected the existence of BPA released from a polycarbonate flask during autoclaving using the reversedphase HPLC. Nevertheless, this method has been superseded by a more sensitive instrument, the LC-MS and later the LC-MS-MS which is considered to be a more sensitive, fast and simple instrument that does not require a derivatizing agent [109]. Currently, Dorival-García et al. [110,111] used LC-MS-MS to analyse BPA, including chlorinated derivatives in sewage sludge and obtained a highest recovery rate from 97.7% to 103.1%. This proved how sensitive this instrument is.

An internal standard is essential when sample monitoring. This standard is to compensate the potential loss of analyte during analysis and for any variations in instrument performance [107]. Different analyses will apply different internal standards. Bisphenol A d-16 is commonly used for BPA studies [52,67,112]. Dekant and Völkel [107] mentioned that an ordinarily stable isotope was used because of the physicochemical characteristics, which are almost comparable to the unknown analyte.

CONCLUSION

BPA is produced during the condensation process of phenol and acetone and is needed in the manufacturing of resin and polycarbonate plastics. The BPA compound has already demonstrated the signs of oestrogenic performance and has acute toxicity to aquatic life due to their discharge into the surroundings (water, air, soil). An elevated concentration of BPA can be found in effluent and leachate, while moderate levels of BPA can be obtained in seawater, river water and bottled water. The toxicity and carcinogenicity of BPA has been disputed by many researchers. The reference dose (RfD) of BPA is 0.05 mg/kg/day and only has an effect when the dosage is more than 50mg/kg bw/day. BPA has been recognized as a toxic compound due to the reaction that can have an adverse effect on the endocrine system. More research must be done to determine the carcinogenicity and toxicity of BPA. Sensitive and selective procedures have been developed and applied to detect traces of BPA. SPE is known to be a simple, clean and concentrated technique for sample preparation, while MAE is a newer approach that has been applied for the extraction of solid samples. GC-MS and LC-MS-MS are considered to be convenient analytical techniques that are selective and sensitive for perceiving low amounts of BPA.

Table 5 Various determination of BPA in different country.

Country	Sample	Extraction method	Analytical method	l Derivati- zing agen	BPA range	Reference
Spain	Water Seawater	LLE DLLME	GC-MS LC-ESI-	_	2.50 – 10.0 μg/L Nd – 0.035 μg/L	[106] [112]
	River water	LiChrolut	MS-MS LC-MS	_	0.065 - 0.295	[113]
	Sewage	RP-18 Sep-Pak Vac C18 SPE	LC-ESI- MS-MS	-	μg/L 0.0134 μg/L (primary treatment), 0.00636 μg/L	[12]
	Urban wastewater	LLE	GC-MS	BSTFA	(final effluent) 0.01 - 2.5µg/L	[114]
Japan	Wastewater Environmental water	LLE MIP	GC-MS HPLC	BSTFA -	$\begin{array}{c} 0.02-0.5\mu g/L \\ 0.002-0.07\mu g/L \end{array}$	[115] [116]
	Seawater, River water	Oasis HLB	LC-MS	-	1.6 – 11μg/L, 0.2 – 4.8μg/L	[117]
	Seawater	SPE disk (EMPORE) octadecyl silica	GC-MS	BSTFA+ 10% TMCS	0.0061 – 1.07 μg/L	[118]
	River water	SBSE	TD-GC- MS	Acetic acid	39.0 – 47.0µg/L	[119]
	River water	LPME	GC-MS	Sodium hydroxide (in-situ derivatizat	<0.6-700.0 μg/L	[120]
	River water	PS-2 SPE	GC-MS	BSTFA	Nd – 0.23 µg/L	[48]
	Waste plastic Leachate	LLE	GC-MS GC-MS		0.149 – 12.3 μg/L	[121] [108]
C1.'	Leachate	LLE	GC-MS	-	1.3 – 17200 μg/L	[13]
China	container	SPINE	GC-MS	%TMCS	0.7 – 78.5 μg/L	[122]
	River water, Sediment River water, Sediment	HLB SPE, UASE LiChrolut RP-18 SPE	GC-MS LC-ESI- MS-MS	-	0.7556 μg/L, 33.8 ng/g 0.01 – 44.65 μg/L, 0.37 – 491.54	[123]
	River water	LLE	GC-MS	Trifluoroa cetic acid	ng/g 0.0191 – 0.106 μg/L	[62]
	River water	EN sorbent	HPLC	-	0.16 – 1.02 μg/L	[99]
	Lake water	Oasis HLB	UHPLC	-	0.00395 - 0.01453	[124]
	WWTP effluent,	Oasis HLB SPE	GCMS	BSTFA	μg/L 0.013 – 0.044 μg/L,	[125]
	water				0.004 – 0.059 μg/L	
Germany	River water, Sediment	LLE, ASE	HPLC	HFBA	0.009 – 0.776 μg/L,	[59]
	River water, Sewage effluent, Sewage sludge, Sediment	LiChrolut RP-18 and EN SPE, SE	GC-MS	Sylon BTZ	0.0005 - 0.41 µg/L, 0.018 - 0.702 µg/L, 0.004 - 1.363 ng/g, 0.01 - 0.19 ng/g	[65])
Canada	Sewage effluent, Sludge	C-18 SPE	GC-MS	PFPA	49.9 – 0.031 μg/L 36700 – 104 ng/g	, [29]
	Seawater, Sediment	EMPORE SDB-XC disk SPE, Sonication	LC-MS- MS	-	Nd – 0.0026 μg/L <0.090 – 9.5 ng/g	, [69]
Italy	Water lagoon	Envi-C18 SPE	HPLC- ESI-IT- MS	_	0.0022 - 0.03 μg/L	[42]
	Water lagoon, Sediment	Envi-C18 SPE,	HPLC- ESI-MS	-	< 0.001 – 0.145 µg/L, < 2.0 – 118.0 pc/c	[67]

DLLME: dispersive liquid-liquid microextraction; PS-2: styrenedivinyl polymer; Vac: vacuum; SDB-XC: polystyrenedivinylbenzene; MIP: molecular imprinted polymer; SBSE: stir bar sorption extraction; PRP: polymeric reversed phase; LPME: liquid phase microextraction; SPME: solid phase microextraction; UASE: ultrasonic-assisted solvent extraction; EE-SPME: electro-enhance solid phase microextraction; MASE: microwave assisted solvent extraction; HLB: hydrophilic/lipophilic balanced; GC-MS: gas chromatographic-mass spectrometry; LC-MS: liquid chromatographic-mass spectrometry; UHPLC: ultra high performance liquid chromatography; BSTFA: N,O-bis(trimethylsilyl)trifluoroacetamide; TMCS: Trimethylchlorosilane; PFBOCI: pentafluorobenzoyl chloride; HFBA: heptafluorobutyric anhydrid; PFPA: pentafluorpropionic.

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