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Analytical methods for antifouling booster biocides determination in environmental matrices: A review

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ABSTRACT

Since the discovery of their toxicity to aquatic environments, antifouling booster biocides (ABBs) have been widely researched and detected at trace levels in diverse environmental compartments including water, sediment, and, less frequently, biota. Hence, the reliable assessment of environmental risks posed by ABBs requires the development of analytical methods sufficiently robust, accurate, and precise for the simultaneous trace-level determination of ABBs. Herein, we summarize outstanding sample preparation procedures for the analysis of main ABBs in environmental matrices, describing techniques ranging from traditional extraction methods to novel miniaturized and micro-extraction ones, which have recently received much attention due to their reduced number of steps, low operational cost, and greater respect for the environment. The main applied chromatographic-based methods coupled to different detection techniques are also addressed. Despite the recent development of numerous ABBs determination methods, this topic continues to draw attention because of the lack of standardization among methods, despite legislation set up maximum standards levels for selected ABBs, and the need to monitor ABB transformation products for a reliable ecological risk assessment.

1. Introduction

Biofouling involves the attachment of organisms on (semi-)submerged surfaces such as boat/ship hulls, pipes, and underwater equipment, resulting in losses due to corrosion, ship performance deterioration, and the impairment of structures and systems [1]. Hence, the development of antifouling materials and coatings to remove or prevent biofouling is a task of high practical importance [2]. Antifouling coatings have a long-standing history and, according to some sources, have already been used by the Phoenicians and Carthaginians to protect their ships during expeditions [3]. However, antifouling coatings impact the environment because of their diffuse sources, ubiquitous distribution, and toxicity to non-target organisms across coastal areas [4,5].

Biocide-containing paints have been widely used to combat biofouling. The first regularly used antifouling paints (first-generation paints) contained copper oxide and zinc oxide as biocides. However, they quickly lost popularity because of their low durability and consequent rapid decrease in effectiveness. At the beginning of the 1960s, the naval industry developed and started using organotin compound (OT)-based antifouling paints (second-generation paints), e.g., those containing tributyltin (TBT) or triphenyltin (TPhT) as biocides. These paints were widely used in the 1980s, accounting for 90 % of ship hulls in operation around the world. However, as a setback to their efficiency and durability, such paints were found to be highly toxic to the marine environment [1]. One of the best-known biological effects of these paints is the so-called imposex, which is the imposition of male sexual characteristics onto female marine gastropods exposed to TBT/TPhT. The above phenomenon has been adopted worldwide as the best biomarker for assessing areas contaminated by this type of biocides [5,6]. In the 1980s, the use of TBT and TPhT has been banned on boats less than 25 m long given the toxic effects of these biocides on non-target species [4]. Moreover, in September 2008, the International Maritime Organization banned the use of TBT-based antifouling paints on vessels less than 25 m long through the Antifouling System Convention, which is currently ratified by 81 states [7].

In response to the increasingly strict regulations on the use of OT-based paints, third-generation antifouling paints were introduced in

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1987. These paints typically comprise inorganic biocides such as cuprous oxide in combination with up to four organic or organometallic biocides [5], being denoted as antifouling booster biocides (ABBs), novel antifouling biocides, booster biocides, or co-biocides. In the following, we will use the acronym ABB. At least 20 organic chemicals have been used as ABBs, namely diuron, irgarol 1051 (or simply irgarol), 4,5-dichloro-2-*n*-octyl-3-(2 H)-isothiazolin-3-one (DCOIT), 2-(thiocyanomethylthio)benzothiazole (TCMTB), chlorothalonil, dichlofluanid, tiram, TCMS pyridine, triphenylbornan pyridine, zinc pyrithione (ZnPT), copper pyrithione (CuPT), ziram, maneb, cuprous oxide, copper thiocyanate, and copper naphthenate [5] with some of them more widely used and more frequently reported than others. Table 1 summarizes the main physicochemical properties of the above biocides, which are considered in this review. This information helps to predict the worldwide occurrence and potential environmental behavior of these biocides, e.g., the short half-life of TCMTB and dichlofluanid in seawater indicates that the related transformation products are more readily generated than those of DCOIT and irgarol [8].

ABBs have been studied in many countries, including Spain [9–14], Brazil [15–18], Japan [19–21], China [22], Thailand [23], France [24], Korea [25,26], Greece [27,28], Sweden [29], United Kingdom (UK) [30], Vietnam [31], Southern England [32], Italy [33,34], Panama [35], the United States of America (U.S.A) [36], the Netherlands [37], and Iran [38], largely occurring in marinas with a large flow of vessels and poor maintenance system disposal. Therefore, the presence of these biocides in the marine ecosystem is increasing in terms of both frequency and concentration levels, as confirmed by analyses of sediments [11,14,31,39–41], water (including dissolved and particulate fractions) [9,13,20,35,42–44] and, less commonly, biota samples [20,45–48] which poses an environmental concern. Moreover, antifouling paint particles generated during the maintenance of vessels in shipyards, marinas, and fishing villages [16], can enter the aquatic environment and act as a source of metals (i.e., Cu and Zn) and antifouling biocides [49–52]. Furthermore, recent studies indicate that the presence of these particles constitutes a potential source of long-term ABBs [18].

Among the numerous ABBs used in antifouling paints, the ones most commonly employed, besides zinc/copper pyrithiones, zineb, and copper thiocyanate, are diuron, irgarol, chlorothalonil, dichlofluanid, DCOIT, and TCMTB. This review addresses the main sample preparation techniques and chromatographic-based analysis applied for the determination of the above contaminants in environmental matrices.

The occurrence of ABBs in environmental compartments (specifically, diuron and irgarol in water samples) has been studied starting from the 1990s [53,54]. Since then, different analytical techniques and methodologies have been developed, mostly involving steps such as pre-concentration, extraction, clean-up, and chromatographic separation and determination. In addition, previous works have dealt with historical contexts [1,5,55], toxicity effects [56–59], worldwide occurrence and geographical distribution [60–62], environmental fate and behavior [63,64], and degradation [19]. However, only two studies addressed sample preparation and analysis: one of them evaluated different mass spectrometry (MS) techniques for ABBs detection in marine samples [65], whereas the other reviewed the main procedures of sample preparation [66]. Thus, the present work aims to overview the updated information on sample preparation procedures and instrumental analysis for the determination of the main biocides detected in the aquatic environment, providing a brief fundamental of the employed analytical techniques and describing the advances in traditionally used and miniaturized methods in sample treatment.

2. Sample preparation

Sample preparation, one of the most important steps of analytical methods for the qualitative and quantitative analyte determination, aims to extract and enrich the analytes of interest from the matrix, remove co-extracted interferences, and, when necessary, transform the chemical structure of analytes to enhance their detectability. All these sample treatment stages help to improve method accuracy and precision [67]. Despite the advances in analytical instrumentation, the sample preparation step before instrumental analysis cannot be avoided. In short, the reliable analysis of biocides is dramatically affected by the selection of the extraction technique.

Traditional sample preparation techniques, including liquid-liquid extraction (LLE), solid-phase extraction (SPE), and soxhlet extraction [68] have been used for organic compounds isolation, such as ABBs [69–77]. Also, mechanical shaking [27,78–81], ultrasounds-assisted extraction (UAE) [11,38,82], or/and both (mechanical shaking and ultrasounds extraction) [78,79], but these techniques are usually time-consuming and require a large volume of organic solvent.

Subsequently, as a result of advances in analytical instrumentation, recent modifications, and the design of new devices, many analytical developments of the recent decades aimed at the use of auxiliary sources to achieve automatization and/or minimize the use of chemical reagents and solvents, and thus also reduce the waste generated in the proces. Techniques incorporating temperature and pressure control in extraction procedures include microwave-assisted extraction (MAE) [14,83,84], UAE [85], pressurized liquid extraction (PLE) [86–89], with more recent developments including inexpensive, simple, and non-automated sample preparation techniques such as matrix solid-phase dispersion (MSPD) [35,39,45,90], stir bar sorptive extraction (SBSE) [91,92], and supercritical fluid extraction (SFE) [80].

Table 2 lists the characteristics of the main sample preparation techniques used for ABBs determination in environmental matrices. Notably, no standard procedure exists, although LLE and SPE are the most frequently used techniques (despite being inferior to miniaturized methods in several aspects). Nonetheless, the exploration of miniaturized methods for the determination of ABBs along with their transformation products is a trending topic, as will be discussed in the following sections.

2.1. UAE

There are many sample treatment procedures based on UAE extraction of ABBs from solid samples. Overall, full extractions can be achieved in minutes with high reproducibility, simplifying manipulation and work-up, and providing high purity of the final extract. It is particularly useful when soil and sediments are to be analyzed considering the complexity of these two matrices with a large number of interferences [92].

UAE is a technique applied in several fields of chemistry since it presents different extraction mechanisms induced by ultrasound, besides the possibility of using combined mechanisms [93]. The main parameters to optimize for a proper ABBs extraction efficiency include the matrix nature and complexity, and physical parameters (solvent and temperature among others). Besides, as an ultrasound is a mechanical wave, some characteristics such as frequency, wavelength, and amplitude can also influence the extraction's performance [94].

Initially, the determination of ABBS using UAE was performed employing large volumes of solvent, where, typically, samples were sonicated in a heated water bath for some 15 min in the presence of 100–300 mL of extraction solvent [95]. UAE has been used for ABBs extraction from soil and sediment, with the most commonly used solvents being methanol [11] and acetone [38]. In these studies, some parameters

Table 1
Physicochemical properties of the most studied biocides and their transformation products. (MW: molecular weight; $t_{1/2}$: half-life; N.F.: information not found) [45–47].

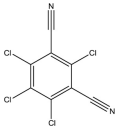
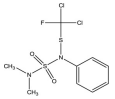
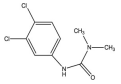
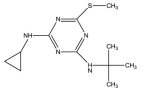
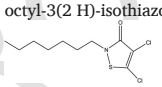
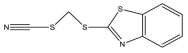
Biocide						
	Chlorothalonil	**Dichlofluanid**	**Diuron**	**Irgarol**	**DCOIT**	**TCMTB**
IUPAC name	2,4,5,6-tetrachlorobenzene-1,3-dicarbonitrile	*N*-[dichloro(fluoro)methyl]sulfanyl-*N*-(dimethylsulfamoyl)-4-methylaniline	3-(3,4-dichlorophenyl)-1,1-dimethylurea	2-(*tert*-butylamino)-4-(cyclopropylamino)-6-(methylthio)-*s*-triazine	4,5-dichloro-2h-octyl-3(2 H)-isothiazolone	2-(thiocyanatomethylthio)benzothiazole
Structure						
CAS number	1897–45-6	1085–98-9	330–54-1	28159–98-0	64359–81-5	21564–17-0
MW (g mol $^{-1}$)	265.9	333.2	233.0	253.3	282.2	238.3
Class	chloronitrile	sulfamide	phenylamide	*s*-triazine	thiazole	benzothiazole
log K_{ow}	2.9	3.6	2.7	3.9	2.8	3.1
log K_{oc}	N.F	3.1	2.3	3.3	4.2	2.7
Solubility in H_2O (25 °C, mg L $^{-1}$)	0.81	0.006	35	7.0	0.0065	10.4
$t_{1/2}$ in seawater (days)	1.8–8	0.12–0.75	31.4–365	24–365	0.004–3	31–36
$t_{1/2}$ in sediment (days)	N.F.	1.4	14	100–265	1.5	2.7
Main degradation products	benzamide; chloro-1,3-dicyanobenzene; dichloro-1,3-dicyanobenzene; trichloro-1,3-dicoanobenzene; 4-hydroxochlorothalonil; 2,5,6-trichloro-4-methoxyisophthalonitrile; 2,4,5-trichloroisophthalonitrile; isophthalonitrile	*N*,*N*-dimethyl-*N*'-phenylsulfamide (DMSA); *N*-dichlorofluoromethylthionaniline; aniline; dichlorofluoromethane	1-(3-chlorophenyl)-3,1-dimethylurea (CPDU); 1-(3,4-dichlorophenyl)-3-methylurea (DCPMU); 1-(3,4-dichlorophenyl)urea (DCPU); 3,4-dichloroanaline (3,4-DCA); *N*-(3-chlorophenyl)-*N*-methylurea (mCPMU)	2-methylthio-4-*tert*-butylamino-6-amino-*s*-triazine (M1); 3-[4-*tert*-butylamino-6-methylthiol-*s*-triazin-2-ylamino]-propionaldehyde (M2); *N*,*N*'-di-*tert*-butyl-6-methylthiol-*s*-triazine-2,4-diamine (M3)	*N*-(*n*-octyl)malonamic acid; *N*-(*n*-octyl)hydroxypropionamide; *N*-(*n*-octyl)acetamide; *N*-(*n*-octyl)oxamic acid; *N*-(*n*-octyl)carbamic acid	2-mercaptobenzothiazole (MBT); benzothiazole (BT); 2-(methylthio)-benzothiazole (MTBT)

Table 2
Summary of studies on ABB determination in different environmental matrices.

Matrix	Biocide	Sample preparation	Instrumental analysis	Limit of detection (LOD)	Observations	Ref.
Water	Diuron and irgarol	SPE	LC-DAD LC-MS/MS	LC-DAD 0.05–0.10 ng mL^{-1} LC-ESI-MS/MS 0.004–0.02 ng mL^{-1}	–	[112]
Water and sediment	Diuron, irgarol, chlorothalonil, and dichlofluanid	Water: LLE; Sediment: Soxhlet	GC-MS	Water: 0.15–0.24 ng mL^{-1} Sediment: 3.1–4.9 ng g^{-1}	DCM	[65]
Marina water	OTs and irgarol	LLE	GC-MS	0.5 ng L^{-1}	–	[71]
Seawater	Irgarol and M1	LLE	GC-MS	0.6–0.7 ng g^{-1}	–	[64]
Seawater	Irgarol	LLE	GC-MS	N.R.	DCM	[67]
Seawater	Irgarol	LLE	GC-MS	2 ng L^{-1}	Hexane	[66]
Sediment	Diuron, irgarol, and DCOIT	LLE	LC-MS/MS	N.R.	–	[28]
Tap, river, and sea water	Chlorothalonil, dichlofluanid, and DCOIT	SDME	GC-ECD	0.25–3 ng L^{-1}	–	[100]
Seawater	Irgarol, chlorothalonil, dichlofluanid, DCOIT, and TCMTB	SPE	GC-MS/MS	0.05–50 ng L^{-1}	Polymeric cartridges	[10]
Sediment	Diuron and irgarol	MAE	LC-MS/MS	0.1–0.3 ng g^{-1}	SPE clean-up	[113]
Sediment	Diuron, irgarol, and DCOIT	UAE and SPE	LC-MS/MS	N.R.	–	[23]
Sediment	Irgarol	UAE and DLLME	GC-MS	N.R.	–	[33]
Seawater and sediment	Diuron, irgarol, and M1	Water: SPE Sediment: PLE	LC-MS/MS	Water: 1 ng L^{-1} (irgarol and M1) 2 ng L^{-1} (diuron) Sediment: 0.3 ng g^{-1}	–	[114]
Seawater	Irgarol	LLE	GC-MS	1 ng L^{-1}	DCM	[70]
Sediment	Diuron, irgarol, TCMTB, DCOIT, and dichlofluanid	VA-MSPD	LC-MS/MS	0.5–5 ng L^{-1} (LOQ)	–	[15]
Seawater and marine sediment	Dichlofluanid and DMSA	Water: SPE Sediment: LLE	GC-MS	Water: 10 ng L^{-1}; Sediment: 5 μg kg^{-1}	Degradation study	[26]
River and sea water	Irgarol, dichlofluanid, and 4-chloro-3-methylphenol	Online-SPE	GC-MS	10–200 ng L^{-1}	–	[92]
Seawater	Diuron, irgarol, TCMTB, dichlofluanid, and DCOIT	SPE	LC-MS/MS	0.3–2.7 ng L^{-1} (LOD) 0.8–8 ng L^{-1} (LOQ)	–	[30]
Marine sediment	Irgarol, TCMTB, DCOIT, dichlofluanid, and OTs	VA-MSPD	LC-MS/MS	0.08–0.75 ng L^{-1} (LOD) 0.25–2.5 ngg $^{-1}$ (LOQ)	Ethanol	[115]
Water, sediment, seaweed, and clams	Diuron	Water: SPE Biota: PLE and UAE	LC-MS/MS	Sediment: 0.003 ng g^{-1} Water: 0.2 ng L^{-1}	UAE with methanol-water followed by SPE clean-up	[88]
Seawater and marine sediment	Dichlofluanid and DMSA	Water: SPE; Sediment: LLE	GC-MS	Sea water: 10 ng L^{-1} (LOQ); Sediment: 10 ng g^{-1} (LOQ)	–	[25]
Marine sediment	Diuron, irgarol, and OTs	LLE and UAE	LC-MS/MS	0.001–0.1 μg g^{-1}	–	[36]
Marine sediment	Diuron and irgarol	PLE	GC-MS	12–17 ng L^{-1}	DCM:acetone (1:1, v/v)	[80]
Biota	Irgarol and its degradation products	Sonication	LC-MS/MS	0.005–0.183 ng g^{-1}	Acetone	[111]
Sediment and biota	Diuron, irgarol, M1, DCOIT, and OTs	LLE	LC-MS/MS	0.24–1 ng g^{-1}	Acetonitrile	[116]
Seawater	Diuron, irgarol, chlorothalonil, dichlofluanid, and TCMTB	On-line SPE	LC-DAD LC-MS	2–10 ng L^{-1}	–	[117]
Seawater	Dichlofluanid, diuron, and irgarol	On-line SPE	LC-MS	5–400 ng L^{-1}	–	[37]
Marine sediment	Diuron, irgarol, dichlofluanid, DCOIT, (dimethyldiuron-3,4(dichlorophenyl)urea, and M1	UAE	LC-MS	0.2–1.6 ng g^{-1}	SPE clean-up	[11]

Matrix	Biocide	Sample preparation	Instrumental analysis	Limit of detection (LOD)	Observations	Ref.
Marine sediment and water	Diuron, irgarol, M1, and DCOIT	LLE and SPE	LC-MS/MS	Water: 0.0003–0.0019 ng mL^{-1} Sediment: 0.04–0.18 ng g^{-1}	Monitoring study/ Acetonitrile	[21]
Marine sediment	Diuron, irgarol, dichlofluanid, and TCMTB	MAE	LC-MS/MS	0.1–0.3 ng g^{-1}	–	[35]
Fish tissue	Diuron and irgarol	MAE and SPE	LC-MS/MS	0.34–0.44 ng g^{-1}	Methanol	[39]
Fish tissue	Diuron and irgarol	VA-MSPD	LC-MS/MS	5–50 ng g^{-1} (LOQ)	Ethanol	[84]
Sediment, marine organisms, and water	Diuron and irgarol	LLE and SPE	HPLC-UV	0.6–1.4 ng g^{-1}	–	[18]
Marine sediment	Irgarol and M1	MAE and SPE	GC-MS	0.9–1.7 ng g^{-1}	MAE with water	[77]
Sediment	OTs, irgarol, DCOIT, chlorothalonil, and dichlofluanid	SPE	GC-FPD GC-NPD	1–10 ng g^{-1}	Florisil cartridges	[78]
Sediment	Irgarol	SFE	GC-MS	3 ng g^{-1}	Methanol and TFA	[74]
Fresh water, sediment, and biota	Irgarol	SPE	HPLC-UV-DAD GC-MS	HPLC: 1.7–3 ng g^{-1} GC-MS: 0.2–0.3 ng g^{-1}	Clean-up with florisil	[118]
Sediment and suspended particulate matter	DCOIT	SPE	GC-MS/MS	5 ng g^{-1}	–	[119]
Marine sediment	Diuron, irgarol, M1, DCPMU, DCPU, and DCA	LLE	LC-DAD	1.7–4 ng g^{-1}	SPE clean-up	[93]
Marine sediment	Irgarol, chlorothalonil, dichlofluanid, and DCOIT	SPME	GC-MS	0.5–25 ng g^{-1}	Water:acetone (5:95, v/v)	[100]
Seawater	Diuron, irgarol, M1, DCPMU, DCPU, and DCA	SPE	LC-DAD	0.005 ng mL^{-1} (DCPMU) 0.026 ng mL^{-1} (M1)	–	[38]
Green alga and seawater	Irgarol	LLE	GC-MS and GC-MS/MS	0.3 ng L^{-1}	Irgarol was detected at 9 of 10 sampled locations	[120]
Water and plant tissue	Irgarol	Water: LLE and SPE Plant tissue: LLE	GC-MS	Water: 1–5 ng mL^{-1} Plant: 2 ng g^{-1}	–	[121]
Sediment and mussel	Diuron, irgarol, M1, DCOIT, dichlofluanid, and pyrithiones	LLE	LC-MS/MS	0.24–1.1 ng g^{-1}	Many steps	[28]
Marine sediment	Diuron, irgarol, M1, dichlofluanid, dimethyldiuron, 1(3,4-dichlorophenyl)urea, and DCOIT	LLE	LC-MS	0.2–5 ng g^{-1}	Clean-up with Isolute ENV cartridges	[122]
Water	Irgarol, chlorothalonil, dichlofluanid, and terbutryn	SPE	GC-MS	1 ng L^{-1}	–	[123]
Seawater	Diuron and irgarol	ELISA and SPE	LC-DAD LC-MS	0.020 and 0.001 ng mL^{-1}	ELISA was compared with online-SPE	[9]
Water	Diuron, irgarol, chlorothalonil, dichlofluanid, TCMTB, and DCOIT	SPE	LC-MS GC-MS (EI and NCI mode)	5–25 ng L^{-1}	Different SPE adsorbents – Screening of pesticides	[10]
Seawater	Diuron, irgarol, TCMTB, and chlorothalonil	SPE	LC-DAD LC-MS	0.01–0.005 ng mL^{-1}	Polymeric cartridges	[117]
Sediment	Diuron, irgarol, M1, and OTs	LLE	GC-FPD and LC-MS	1000 ng g^{-1}	–	[36]
Natural waters (sea, river, and lake)	Chlorothalonil, chloro-1,3-dicyanobenzene, dichloro-1,3-dicyanobenzene, trichloro-1,3-dicyanobenzene, and benzamide	LLE and SPE	GC-ECD and GC-MS	5000 ng mL^{-1}	SDB extraction disks in SPE	[34]
Water	Chlorothalonil, chloro-1,3-dicyanobenzene, dichloro-1,3-dicyanobenzene, and trichloro-1,3-dicyanobenzene	SPE	GC-MS	N.R.	Photodegradation study and stability	[124]

Matrix	Biocide	Sample preparation	Instrumental analysis	Limit of detection (LOD)	Observations	Ref.
Soil and water	Chlorothalonil and its degradation products	SPE	GC and LC-MS	Water: 0.1–1 ng mL^{-1} Soil: 1000 and 2000 ng g^{-1}	Hydrophobic polymer for analyte isolation	[125]
Seawater and sediment	Irgarol and its degradation products	Online-SPE	LC-MS	0.002–0.005 ng mL^{-1}	Polymeric cartridges	[12]
Seawater	Irgarol	SPE	GC-MS GC-MS/MS	0.1–1 ng L^{-1}	SDB disks	[126]
Seawater and sediment	Diuron, irgarol, and others	Sea water: online-SPE Sediment: Soxhlet	LC-MS	Water: 0.03 ng mL^{-1} (irgarol), 0.05 ng mL^{-1} (diuron)	10-h extraction	[127]
Seawater and sediment	Irgarol and OTs	Water: SPE Sediment: Soxhlet	GC-FID GC-MS	Water: 0.4 ng L^{-1} (GC-FID) sediment: 0.05 ng g^{-1} (GC-FID), 0.55 ng g^{-1} (GC-MS)	SPE clean-up with C18 cartridges	[62]
Seawater	Chlorothalonil, dichlofluanid, DCOIT, irgarol, and TCMTB	SPE	GC-MS	1.5–20000 ng L^{-1}	Polymeric cartridges	[123]
Seawater	Dichlofluanid, diuron, dimethyldiuron, 1-(3,4-dichlorophenyl)urea, (2-thiocyanomethylthio)benzothiazole, chlorothalonil, DCOIT, irgarol, and one of its degradation byproducts (2-methylthio-4-tert-butylamino-s-triazine)	SPE	LC-MS	1–20 ng L^{-1}	Graphitized carbon black	[128]
Seawater	Irgarol	LLE	GC-MS	N.R.	DCM	[68]
Water and sediment	Irgarol and M1	Water: SPE Sediment: PLE	LC-MS/MS	Water: 1 ng L^{-1} Sediment: 1 ng g^{-1}	Exposure study	[83]
Water	Diuron and other classes of analytes	SPE	LC-MS	2 ng L^{-1}	Multiresidue analysis	[129]
Seawater	Diuron, irgarol, and other pesticides	SPE	LC-MS/MS	Diuron: 0.02 ng L^{-1} Irgarol: 0.05 ng L^{-1}	–	[13]

N.R.: not reported; ELISA - enzyme-linked immunosorbent assay; LC-DAD: liquid chromatography with diode array detection; GC–MS: gas chromatography with mass spectrometry detection; GC-FPD: gas chromatography with flame photometric detection; GC-ECD: gas chromatography with electron capture detection; GC-FID: gas chromatography with flame ionization detection; LC-UV: liquid chromatography with ultraviolet detection.

of extraction such as temperature enhancement due to the use of ultrasounds are rarely discussed.

However, nowadays the aim and trend of green analytical chemistry are to achieve good extraction efficiencies with a low solvent consumption. In this regard, the UAE can be combined with other extraction techniques to improve the determination of ABBs at increasingly lower concentrations, in environmental matrices. For example, the UAE has been reported, in combination with other techniques in organic contaminants extraction, including ABBs in wastewaters and filters residue [96].

2.2. MAE

The application of MAE to isolate and enrich ABBs from environmental samples, although not yet sufficiently exploited, appears to be an attractive alternative to the UAE. In short, MAE is based on the absorption of the microwave energy by extraction solvents increasing the pressure in combination with temperature, thus, the diffusion of the compounds from the matrix to the solvent can be achieved and improved [97].

In comparison with UAE, MAE presents some advantages, such as smaller solvent volume needed, less time consumption due to the direct heating of the solvents by microwaves, and the simultaneous extraction of up to 14 samples. However, there are also some drawbacks i.e. the extraction solvent must be able to absorb the microwave energy and an additional clean-up step could be needed depending on the complexity of the matrix [83].

The main variables to optimize in MAE, include the amount of the solid sample, solvent volume and, time and temperature. Although these variables were studied, they have been little discussed in the studies dealing with MAE isolation of ABBs, where the main variable of the technique remains the nature and volume of the solvent required. For ABBs extraction, the most common solvent used in MAE is methanol, due to the wide range of polarity of the ABBs of interest. However smaller volumes than those commonly used in UAE (10–50 mL) are needed [65].

Besides being used as an extraction technique, MAE was employed in combination with clean-up and SPE preconcentration steps for ABBs extraction from sediment samples. The combination of the two techniques enabled a considerable improvement in the results, demonstrating that the proposed procedure was a powerful tool in the determination of ABBs in environmental samples, such as harbor sediments [14], and sea mullets [46].

An interesting fact in this technique is that the water content of the samples can significantly benefit the MAE procedure because water improves the recoveries of the target compounds, helps non-polar organic solvents to absorb the microwave energy, and by itself can extract some organic compounds. Thus, water can be used as a potential extraction solvent (instead of the widely used organic solvents), further improving current trends in sample preparation methods, especially for ABBs [83].

2.3. PLE

In PLE, the extraction of organic contaminants, such as ABBs, from solid samples, is facilitated by the combined use of different organic solvents at high pressures and temperatures above the boiling point.

The main variables that can be optimized in PLE are temperature, pressure, number of extraction cycles, and extraction solvent volume. For ABBs, the solvents employed are usually the same as those used in

conventional liquid extraction techniques, e.g., methanol and acetonitrile [34]. However, following the current trend concerning the potential support of water in the extraction process, the methanol:water mixture has also been reported for diuron extraction from sediment [34].

Concerning temperature and pressure for ABBs isolation, generally, the studies employ about 100 °C and 1500 psi. Then, the resulting extracts are generally evaporated with N_2 and further reconstituted up to a few mL to preconcentrate the ABBs of interest. The whole extraction process lasts less than 15 min for 1–30 g of sample consuming a solvent volume 1.2–1.5 times lower than that of the PLE-extraction cell containing the solid sample [98].

Compared to UAE and MAE, the PLE technique features the benefits of a low sample amount, short extraction time, and automatization. However, the main drawbacks are the high cost of instrumentation/spare parts and the elevated energy consumption.

Supercritical fluid extraction (SFE) is another analytical technique of environmental samples preparation. It is quite similar to PLE, but employs a gas as the extraction agent, mainly CO_2, at the corresponding supercritical conditions. This technique is not as popular as PLE, but has found some application in environmental analysis. SFE was applied, for instance, for irgarol determination in Western Mediterranean sediments. The authors denoted the method developed for the analysis as SFE-Immunoaffinity chromatography, reporting a LOQ of 3 ng g^{-1} [80].

2.4. SPE

Among all techniques applied for the extraction of organic contaminants, SPE has become a common and effective method of extracting and enriching analytes from aqueous samples. SPE, first introduced in the 1970s and commercialized in 1978 [65], is a liquid-solid extraction technique based on the separation mechanisms of low-pressure liquid chromatography (LC) and mainly aiming to isolate analytes from a complex liquid matrix. Basic SPE instrumentation comprises a vacuum pump and a cartridge filled with a specific sorbent, with the main steps including sorbent activation, sample percolation/analyte sorption onto the sorbent, washing to remove matrix interferences, and, finally, analyte elution [99]. Given the wide variety of commercially available sorbents and operation simplicity, SPE is extensively used for the environmental analysis of organic compounds such as ABBs in aqueous matrices [9,12,13,35,42,66,77,100]. The main disadvantages of SPE are the need for sample pre-filtration to avoid the clogging of the solid-phase by particulate matter and the cost of disposable SPE cartridges [66]. Nevertheless, SPE remains one of the most widely used extraction techniques for liquid samples.

In the case of ABBs, SPE has been performed using C8 or C18 cartridges [42,43,77], polymeric materials [10,12,101], and, more recently, other materials such as graphitized carbon black [11] as the extracting sorbent.

SPE can also be coupled with chromatography to afford on-line SPE, which has been extensively used in studies on ABBs. Compared to previously described off-line SPE systems, on-line configurations feature the advantages of minimized adsorptive losses (which can occur during off-line sample transfer and sample handling procedures), automation, and higher reproducibility/sensitivity, as all extract is directly injected into the analytical LC column. To date, SPE cannot be coupled with gas chromatography (GC).

Besides, SPE has been frequently used to remove interferences and pre-concentrate the analytes from solid matrix extracts as a clean-up step, which is typically performed using florisil, Oasis HLB, and C18, among other types of cartridges [14,66,102].

2.5. SBSE

SBSE is a technique currently attracting the attention of the scientific community, since no solvent is needed during extraction. Classified as a solvent-free extraction, SBSE was developed by Baltussen et al. (1998) for aqueous samples, where a polydimethylsiloxane (PDMS) coating around a glass-coated magnetic stir bar was used. SBSE deserves attention because considerably increases absorption capacity and lowers the limits of detection of analytes. Several studies have been developed using SBSE to determine organic contaminants in matrices whether environmental or food. In general, when SBSE is used, all parameters of the analytical procedure, such as desorption and absorption steps in the SBSE are optimized [103].

For ABBs determination, some authors used SBSE in combination with further instrumental analysis by GC for chlorothalonil, dichlofluanid, DCOIT, irgarol, and TCMTB determination in 10 mL of seawater samples. In this study, the analytical validation parameters of the method were similar to those reported in previous studies; LOQs between 0.01 and 3 μg L^{-1} and linear dynamic ranges between 0.005 and 38 μg L^{-1} [91].

Although it has many extraction advantages, SBSE can still be combined with other techniques to improve ABBs determination. In this direction, recently García et al. (2020), employed a focused ultrasound-assisted extraction (FUSE) followed by SPE clean-up and an SBSE pre-concentration, and further thermal desorption (TD) coupled to GC–MS/MS for chlorothalonil, dichlofluanid, DCOIT, irgarol and TCMTB determination in marine sediments. The SPE step was included in the method because the samples had a high organic matter and low sand contents. ABBs were sampled using stir bars (20 mm length, 0.5 mm film thickness) coated with PDMS. The stir bars were stirred at 900 rpm for 3 h. at room temperature [92]. Overall, the proposed method was simple, allowed ABBs determination in marine sediments up to very low concentration levels, and provided good recovery rates. Summarizing, the main advantages of SBSE is its simplicity, absence of any preliminary sample pretreatment steps, small sample volume required, high throughput, and the absence of toxic solvents.

According to literature, the current/near future trend in environmental ABBs trace analysis is the application in combination of different techniques, such as the FUSE-SPE-SBSE and, when possible, at miniaturized size, as will be discussed in the next sections.

2.6. Micro-extraction techniques

According to a literature search, for ABBs determination in environmental matrices, miniaturization and micro-extraction have recently received much attention. Its main advantages include low organic solvent volume, low reagent amount, low energy consumption, as well as high throughput, and potential automation [104,105]. Micro-extraction methods including single-drop micro-extraction (SDME) [106], solid-phase micro-extraction (SPME) [40,107], and, matrix solid-phase dispersion (MSPD) [39,90] have been employed to investigate the presence of ABBs in solid and semi-solid samples.

Besides the aforementioned advantages, miniaturized techniques are characterized by minimal waste production due to the reduced consumption of solvents and reagents, also in line with the recent trend in the development of methods to study biocides in environmental matrices. However, to be practically valuable in biocide analysis, miniaturized techniques should achieve the same sensitivity and selectivity as traditional extraction techniques.

Multi-residue analytical studies have recently been developed, to simultaneously extract ABBs and other organic contaminants in a single method. This is yet considered a challenge since these contaminants of-

ten have a wide range of physical-chemical properties which makes their co-extraction difficult.

2.6.1. SDME

SDME is considered an advanced liquid-liquid extraction technique. Due to the enhancement of the micro-extraction techniques in recent years, solvent micro-extraction (SME), liquid-phase microextraction (LPME) and SDME, hve attracted increasing attention for organic contaminants determination in water samples [108]. SDME has become a popular technique because of its ease of operation, nearly solvent-free nature (and hence, increased environmental friendliness), and the potential to improve analytical sensitivity.

Essentially, SDME combines extraction, clean up (eventually), and concentration in a minimum number of steps, followed by direct extract introduction into the instrumental analytical system. As with the other above-mentioned techniques, SDME can be optimized through the selection of solvents, extraction time, agitation period, organic drop volume, and salt concentration. However, in addition to the lack of automation, the other main disadvantage of SDME is the cost of the fibers [109].

For ABBs determination, the only work found in literature applying SDME used toluene as extraction solvent due to the polarity of the target analytes (chlorothalonil, dichlofluanid, and DCOIT), 1.5 mL of drop size, and 15 min. of extraction time. Although little explored, SDME demonstrates to be a technique with great potential; as it is fast, accurate, and effective for the extraction of these contaminants from water samples [106]. In any case, other organic solvents can be used for ABBs extraction with SDME, such as methanol and ethanol for irgarol and diuron extraction. However, to date, the potential of SDME has yet been fully exploited, in both methodology and application.

2.6.2. SPME

Compared to other sample preparation techniques, SPME is an alternative miniaturized method featuring the advantages of low disposal cost and potential for sensitivity improvement, as already discussed for SDME [65]. Most studies dealing with the SPME extraction of ABBs focused on water or seawater samples [107,111,112].

The wide and successful application of SPME relays on the fact that it is considered a truly solvent-free technique, or that dramatically reduces the use of solvents because of the adsorbing fibers are directly employed in the sample extraction step, and thus reducing the time required for the extraction, from several hours to less than 1 h [110]. When a solvent is used in SPME for ABBs extraction, acetone, and, recently, water were employed, such for instance in the analysis of marine sediments [110]. Notably, even in samples with high organic matter content, the use of these solvents provides several advantages, in particular, the solvent volume reduction over conventional techniques such as LLE with subsequent clean up by SPE.

SPME has been compared with SPE for selected ABBs (irgarol 1051, dichlofluanid, chlorothalonil, and DCOIT) determination in seawater samples. Although both techniques achieved very low limits of detection (0.4–20 ng L^{-1}), SPME was found to be more efficient than SPE, which requires the use of different adsorbents for ABBs extraction [112].

As an advance of the SPME technique, the use of Headspace Solid Phase Microextraction (HS-SPME) to DCOIT, irgarol 1051, and diuron extraction from water samples has been reported [113]. However, the optimization parameters of this proposed technique were hardly discussed.

2.7. MSPD

Although it was developed in 1989, MSPD is considered a current technique. It has proved to be most useful in the analysis of emerging contaminants in viscous, solid, and semi-solid samples. The original technique was developed for drug residue extraction from bovine tissues and, since then, it has been extensively applied to the simultaneous extraction of several organic contaminants with a wide range of physicochemical properties. The basic principle of MSPD is the physical blending of the sample with an abrasive solid support. The obtained blend is placed into an SPE cartridge, and elution is performed with a suitable organic solvent. However, given the difficulty of properly placing the mixture in the cartridge, the original MSPD has undergone several modifications to improve efficiency and reproducibility [114]. To the authors' knowledge, there are no studies in the literature reporting applications of the original MSPD technique in ABBs determination.

As a result of a modification of the original technique, the elution step as in SPE, has been replaced by agitation with the eluent in propylene tubes to afford the so-called vortex-assisted MSPD (VA-MSPD) [115]. In general, this modification has been used in the extraction of some organic contaminants from sediment [116,117], soil [118,119], sludge [120,121], and fish [122,123].

As well as in the extraction techniques mentioned so far, the major challenge in VA-MSPD is the selection of the main variables that can be optimized, such as the solid support and organic solvent type/quantity. For ABBs extraction from sediment samples, most studies used around 2 g. of the sample, C18 as the solid support, and ethanol [35] or methanol [39] as extraction solvent.

In the analysis of the tissues of *Mugil liza, Cynoscion guatucupa,* and *Micropogonias furnieri*, VA-MSPD was employed for chlorothalonil, dichlofluanid, DCOIT, and TCMTB extraction using 0.2 g of sample, 2 g of C18 support, 0.2 g of sodium sulfate, and 5 mL of ethyl acetate as extraction solvent [45]. In another work, the authors employed 0.5 g of mussel shell as solid support, 0.5 g of sodium sulfate, and 5 mL of ethanol for diuron and irgarol extraction from fish tissue [90]. The main differences between these two studies, besides the differences in target ABBs, corresponded to the compatibility of the analyte's physical-chemical properties and the organic solvent needed as the mobile phase in the further chromatographic separation. Due to the extremely wide range of these properties, the most polar ABBs were extracted with ethanol and analyzed by LC, while the least polar and thermally stable ones were extracted with ethyl acetate and analyzed by GC.

A recent multiresidue method developed by Soares et al. (2020) to analyze simultaneously 59 organic contaminants including pharmaceuticals, personal care products, and ABBs in marine sediments of Brazil [124] employed VA-MSPD as extraction technique. The performance of the method was very satisfactory affording low LOQs, from 0.4–37 ngg^{-1} dw. Besides the good performance, when compared with methods relying on traditional techniques, the developed method demonstrated to be more environmentally friendly, simpler, faster, and cheaper.

Although only few studies employed VA-MSPD for ABBs extraction, these previous results revealed that the technique is suitable for the extraction of ABBs from environmental samples and holds great promise for environmental studies, featuring a performance on par with that of traditional techniques.

2.8. Biota samples

In contrast to water and sediment samples, studies on ABBs determination in biota are only a few. Generally, the methods used for ABBs biota extraction are identical to those used for sediment samples and include traditional techniques such as MAE [46], mechanical shaking with organic solvent [20,31,125], and VA-MSPD [45,90,124].

When the analytical purpose of ABBs includes the potentially formed transformation products, another important factor to consider is the stability of the environmental samples. It is known that the concentration of the target ABBs in certain samples may change with time

through biological and/or chemical degradation processes. This is the case when metabolites of ABBs are investigated in biota samples. Regardless of the method selected to analyze ABBs in environmental samples, some precautions can be adopted to preserve the integrity of the sample, thus avoiding not only degradation but also cross-contamination [126–130]. Although these measures are useful as guidance to information regarding storage vessels, these documents are based on validated stability studies and in best practice that can be based in a general way. Also and to the authors' knowledge, no specific document that guarantees the stability of environmental samples in ABBs and metabolites determination has been published.

3. Chromatographic separation and detection techniques

Table 3 compiles the most outstanding analytical methodologies followed in studies on ABBs determination in marine sediment, seawater, biota, and other environmental matrices.

The LC and GC chromatographic techniques are applied in ABBs determination. Both can be coupled to different detectors depending on the characteristics of the analyzed biocides.

3.1. GC-based analysis

GC is suitable for the analysis of non-polar and thermally labile compounds such as chlorothalonil, dichlofluanid, irgarol, DCOIT, TCMTB, and diuron, although the latest requires a pre-derivatization step. Among the detection techniques used for the GC-based analysis of biocides, the most common are flame thermionic detection (FTD) [40], electron capture detection (ECD) [40,106,110], flame ionization detection (FID) and nitrogen-phosphorus detection (NPD) [84]. Still, MS [28,70,71,101] remains the most applied detection technique, providing analyte identification, high selectivity and sensitivity in two monitoring modes and a sequential mode (or tandem – MS/MS).

GC–MS methods predominantly employ electron impact ionization (EI) and chemical ionization (CI) [66]. For chlorothalonil, dichlofluanid, DCOIT, and TCMTB, negative chemical ionization (NCI) has shown greater sensitivity than EI [66]. For example, Voulvoulis et al. developed a method for the simultaneous determination of four ABBs, including diuron, in water and sediment samples by GC-EI-MS. To this end, trimethylanilinium hydroxide was used as a derivatization reagent [71]. To avoid derivatization, diuron can be analyzed by LC because of its large polarity.

Instrumental parameters such as analytical column type, injection mode, injection volume, and temperature used in GC separation have been optimized in many works on ABBs determination. The splitless injection has been identified as the most suitable for the analysis of biocides at trace-level [74,101]. Regarding injection volume, 1 and 2 μL have been employed [38,70,71].

Nonpolar GC capillary stationary phases, such as methylpolysiloxane, and injection, interface, and detector temperatures of 280–320 °C are typically used for ABB determination [8,71], with the exact parameter value depending on the physicochemical features of the target compounds. Temperature gradients are commonly used [71] as exemplified by PVT [60].

3.2. LC-based analysis

LC is well suited for the analysis of more polar ABBs, such as diuron, but it is also applicable to the determination of irgarol, dichlofluanid, TCMTB, and DCOIT, additionally allowing the analysis of related transformation products, including metabolites (which are usually more polar than the parent compounds, but still can be accumulated in biota tissues), without the need for derivatization. LC with absorbance (diode-array) detection [9,12,43,102,131] and UV detection (UV) [20,132] can be implemented by comparing the obtained chromatographic retention times and UV spectra, although coupling with linear ion-trap [124] and single [14] or triple quadrupole [133] MS increases sensitivity and thus provides better detectability of both parent biocides and products of their (a)biotic degradation [19,39].

Despite the notorious differences in sensitivity, linear dynamic range, and selectivity among the different types of MS detectors, MS is the detection technique of choice for ABBs determination by LC. Electrospray ionization (ESI) and atmospheric pressure chemical ionization techniques (APCI) [41], both in negative-ion (NI) and positive-ion (PI) modes, have been widely applied to ABBs determination by LC–MS. Higher sensitivity was achieved for dichlofluanid and TCMTB using NI ionization, whereas irgarol, diuron, and DCOIT are commonly determined by PI-mode [11,66]. While the corresponding GC injection volumes vary from 1 to 2 μL, LC commonly uses a volume of 10 μL [39]. The LC mobile phases employed usually contain water, acetonitrile, and methanol as organic solvents, and ammonium acetate and formiate as buffers, with pH adjustment using ammonium hydroxide, acetic, or formic acid [134,135].

Although most studies cited herein are multi-residue methods, it is important to note that no standard analytical method is currently available for ABBs analysis. Thus, it is essential to optimize the chromatographic separation and detection conditions to find a sample preparation procedure best suited for the analysis of ABBs in real environmental samples. The establishment of a standard protocol would allow comparison among studies.

Table 3
Main characteristics of sample preparation techniques used for ABB determination in the environment (adapted from [130]).

Characteristic	Soxhlet extraction	UAE	LLE	PLE	MAE	SPE	SPME	MSPD
Matrix type	S/L	S/L	L	S	S	S/L	S/L/G	S
Sample pre-treatment	Yes	No	No	Yes	Yes	No	Yes	Yes/No
Automatic cleaning between two samples	No	No	No	Yes	No	No	No	No
Pressure	No	No	No	Yes	No	Yes	No	No
Temperature	Yes	Yes	No	Yes	Yes	No	Yes	No
Sample volume (mL)	200–500	100–300	50–500	N.A.	25–50	50–100	2–10	N.A.
Sample mass (g)	N.A.	N.A.	N.A.	15–45	N.A.	N.A	N.A	5–100
Extraction time	4–48 h	0.5–1 h	12–48 h	12–20 min	0.5–1 h	1–4 h	5–90 min	0.5–2 h
Solvent extraction and simultaneous filtration	No	No	No	Yes	No	No	No	No
Sequential extraction	No	No	Yes	Yes	No	No	No	No
On-line extraction with clean-up	No	No	No	No	No	Yes	No	No
Automatic solvent change	No	No	No	Yes	No	No	No	No

N.A.: not applicable; S: solid, L: liquid, G: gas.

4. Legislation

Although the global ban of TBT was proclaimed as a major environmental success, the increasing use of substitute antifoulants, despite there being limited knowledge about the potentially deleterious effects associated with their use, pose risks to the environment [57]. Assessing risks in complex ecosystems is a difficult task and thus, there are still many gaps to be filled. However, studies have been carried out in order to contribute to real information on ABBs [136] In this sense, Environmental Risk Assessments (ERAs), predicted no-effect concentrations (PNECs), environmental quality standards (EQS) and Environmental Risk Limits (ERLs) have driven decision-makers for regulating ABBs use [57].

In general, Irgarol 1051 and diuron are the most detected in water and sediment samples worldwide and they are among the most persistent ABBs increasing the risk to the aquatic ecosystems [1,78,137,138]. Published ERAs have identified irgarol 1051 and its metabolite M1 as hazardous to coastal waters under the influence of maritime activities [139,140]. Some countries from Asia, North America, Europe, and Oceania have already restricted or banned the use of irgarol 1051 and/or diuron [1,141,142]. The current European water framework directive (WFD) established annual average EQS of 0.2 $\mu g L^{-1}$ and maximum allowable concentration EQS of 1.8 $\mu g\ L^{-1}$ for diuron, which is considered a priority substance (Directive 2013/39/ EU) [143], while Martins et al. (2018) estimated EQS of 2.2×10^{-2} $\mu g\ L^{-1}$ for diuron and 1.4×10^{-3} $\mu g\ L^{-1}$ for irgarol 1051 [57]. ERLs of 2.4×10^{-2} ng L^{-1} and 0.97×10^{-2} ng L^{-1} were also established for irgarol 1051 and ziram, respectively, in seawater. For soil and sediment, ERLs are the same for irgarol 1051 and ziram, with values of 1.4 $\mu g\ kg^{-1}$ and 0.011 $\mu g\ kg^{-1}$, respectively [144,145].

Chlorothalonil is not registered for use as antifouling in the Europe, but it is authorized in Australia and some Asian countries. This ABB has restricted use in Canada, with established water quality criteria (WQCs) for fresh and marine waters of 0.18 $\mu g L^{-1}$ and 0.36 $\mu g L^{-1}$, respectively [1,146,147]. Conversely, dichlofluanid has been regarded as a low-risk ABB, being approved in the UK, Oceania, Asian countries, and the EU. The estimated values of EQS in seawater (0.2 $\mu g\ L^{-1}$) and ERL in sediment (190 $\mu g\ kg^{-1}$) for this ABB are higher than the EQS (8.5×10^{-2} $\mu g\ L^{-1}$) and ERL (50.6 $\mu g\ kg^{-1}$) established for chlorothalonil. An ERL of 0.38 $\mu g\ L^{-1}$ in seawater was established for TCMTB [57,144,145], but no EQS/ERLs were found for sediment.

Indeed, despite the relatively low EQS of 6.7×10^{-4} $\mu g\ L^{-1}$ for seawater, aquatic ecosystems are at risk since DCOIT concentrations above these threshold limits have already been measured in the environment. Even so, the use of this ABB in paint formulations is still authorized in many countries (including Australia, Japan, China, the UK, and European countries). However, currently, DCOIT is under review in the USA [57].

Since many ABBs appear to be toxic at concentrations below those already detected, they pose a real risk to the aquatic ecosystems. Thus, as depicted by the semi-persistent behavior of DCOIT [148], the more frequently an antifoulant is used, the more likely it is to cause negative environmental impacts due to its occurrence associated with continuous inputs (pseudo-persistence). Despite their widespread use, regulations addressing the issue of ABBs in the aquatic environments are still restricted to a few countries. It is within the environmental policies of some regions, especially Oceania, some Asian countries, and in Europe, but Latin America, for instance, has no regulation concerning ABBs, except for organotin-based antifouling paints [57].

5. Final remarks and future trends

Several organic chemicals have been used as ABBs, namely diuron, irgarol 1051, DCOIT, TCMTB, chlorothalonil, dichlofluanid, tiram, TCMS pyridine, triphenylbornan pyridine, ZnPT, CuPT, ziram, maneb, cuprous oxide, copper thiocyanate, and copper naphthenate. Since some of them are more widely used and/or more frequently reported than others, the present study focused on diuron, irgarol 1051, TCMTB, DCOIT, chlorothalonil, and dichlofluanid.

Despite the abundance of studies on ABBs determination using a wide range of sample preparation procedures, as addressed by the present review, no standard and/or official method of analyzing these compounds in environmental samples is available. The ultimate selection of the most suitable analytical method depends on the physicochemical properties of the target analyte, type of matrix, conditions available at the laboratory, limits of detection and quantification to be achieved, as well as the specific chromatographic and MS requirements of the instrumentation. Most analytical methods have been developed for water and sediment analysis, whereas less attention has been paid to biota samples, which are typically analyzed using the same methods as those employed for sediment samples. Despite their worldwide extended use, regulations establishing annual average discharges and/or maximum allowable concentration for ABBs in the aquatic environments are still restricted to a few countries.

The perspectives and future trends rely on the use of analytical methods that are preferably based on miniaturized sample preparation techniques, environmentally friendly, fast, and coupled with modern chromatographic techniques (e.g., the use of different ionization sources) replacing traditional techniques and ensuring reliable information on the occurrence and partitioning of ABBs in the environment.

Finally, one should acquire reliable data and fill the knowledge gap regarding the fate and worldwide occurrence of major ABBs and their transformation products. Even though this development is still in its infancy, one should note the feasible combination of progress in analytical instrumentation technology with the determination of transformation products.

Declaration of Competing Interest

There are no conflicts of interest to declare.

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