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Review

Multiresidue methods using solid-phase extraction techniques for monitoring priority pesticides, including triazines and degradation products, in ground and surface waters

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Abstract

The review describes the use of solid-phase extraction (SPE) techniques for monitoring priority pesticides in ground and surface waters. The focus is on triazine herbicides and their degradation products. Data concerning the fate, occurrence, properties and extraction of triazines and their degradation products using different SPE techniques are tabulated and discussed.

Keywords: Reviews; Solid-phase extraction; Extraction methods; Water analysis; Environmental analysis; Pesticides; Triazines

Contents

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1. Introduction

1.1. Pesticides

A pesticide is defined under the *Food and Environmental Protection Act* (FEPA) 1985 [1] as any substance, preparation or organism prepared or used for destroying any pest. It is a generic term that covers a wide spectrum of biologically-active compounds, including herbicides, fungicides and insecticides. Pesticide use has increased dramatically over the last four decades to reach an estimated $2.59 \cdot 10^9$ kg of active ingredient used worldwide in 1995 [2]. Global consumption of atrazine alone, one of the most widely used pesticides, is estimated at $70 \cdot 10^6$ kg/year, 90% of which is used for corn crops [3]. Worldwide pesticide consumption breaks down as follows: Asia (25%), Western Europe (25%), North and South America (40%), with the rest of the world sharing the remaining 10% [4]. The USA is the world's top consumer, at an estimated $380 \cdot 10^6$ kg of active ingredient. China, Italy, Australia and France follow, in that order, with an estimated 280, 160, 120 and $110 \cdot 10^6$ kg, respectively [5]. Canada, the second largest country in the world, consumed only $30 \cdot 10^6$ kg of pesticides [5]. However, these figures do not accurately reflect the true intensity of use of these chemicals on cultivated surface areas. In fact, when one considers the quantity of active ingredient of pesticides used per hectare, the ranking becomes as follows: Holland (19.95 kg/ha), Japan (18.07 kg/ha), Italy (7.66 kg/ha), France (4.51 kg/ha), USA (1.99 kg/ha), and, much further down, Canada (0.81 kg/ha) [6]. More than 1400 active ingredients are found worldwide in various commercial mixtures of pesticides [7]. The majority of this annual pesticide consumption takes the form of herbicides used to kill competing vegetation: they represent 81% of the compounds applied in Canada [8], 60% in the USA [9] and nearly 40% in France [10].

1.2. Priority pesticides

The criteria for including a contaminant on the Priority List consisted of determining whether the occurrence, or anticipated occurrence, of a given contaminant was likely at levels of concern to human health.

For the past 20 years, the European Union (EU) and Member States have implemented substance-specific controls through a range of directives and regulations aimed at protecting the aquatic environment from the effects of certain chemical pollutants. The first major legislation to control dangerous substances within the EU was the *Dangerous Substance Directive* (76/464/EEC) [11]. This directive identifies two broad categories of substances, List 1 and List 2, requiring effective control across the EU. List 1 substances are considered to be of greatest concern due to their toxicity, persistence and bioaccumulation, and ought to be eliminated from the aquatic environment. List 2 substances are considered to be less harmful and their entry into the aquatic environment ought to be minimized or reduced [12]. Atrazine and simazine are the only triazines, of 39 pesticides, to have been included on List 2 [13]. However, a recent European study recommends that a number of triazines (atrazine, cyanazine, metribuzin, propazine, simazine, terbutylazine, terbutryne and such degradation products as DEA, DIA and HA) ought to be added to a list of 38 priority pesticides [14].

In 1994, the US Environmental Protection Agency (EPA) criteria for analyte selection included consumption of at least 450 000 kg in 1982, a water solubility rate greater than 30 mg/l, and a hydrolysis half-life longer than 25 weeks. Parent pesticides and degradation products previously detected in groundwater, as well as pesticides regulated under the *Safe Drinking Water Act*, were automatically included on the list of survey analytes. An initial list of 161 chemicals, identified as ''priority'' analytes, was

developed in mid-1984 [15]. It was reduced by October 1986 to a total of 100 pesticides and their degradation products, including ametryn, atraton, atrazine, cyanazine, DAM, DEA, hexazinone, metribuzin, prometon, prometryn, propazine, simetryn, simazine, terbutryn. Atrazine, still widely used around the globe, was recently banned in Italy and Germany [16,17]. Propazine, another triazine herbicide, has been taken off the market in the United States [18].

The consequences of massive annual pesticide use remains poorly understood because most studies have focused primarily on parent compounds. There has been limited information on the environmental impacts of pesticide degradation products because the analytical methods used were either laborious, expensive, or unavailable. Some of these degradation products, however, are as toxic, or even more so, than their parent compounds [19]. Although the occurrence of a considerable number of potential degradation products has been reported, only a few of these products have been shown to be present in the environment (Table 1). The EPA has recently decided to include triazines and their degradation products as a group on the Contaminant Candidate List (CCL), in order to include all potential risks stemming from this class of compounds. Triazines and their degradation products have already been included on the Priority Group 1 list of pesticide tolerances that will be examined first under the *Food Quality Protection Act* (FQPA) tolerance reassessment (62 FR 42020).

1.3. Triazines and degradation products

Triazine herbicides were introduced to the market about 40 years ago and applied to a variety of crops. They represent a major group of pesticides. Symetric triazines can be divided into three groups: chloro-, methoxy- and methylthiotriazines. Metribuzin and metamitron are nonsymetric triazines known as triazinones, and hexazinone is known as a triazine dione.

The triazine herbicides are solids, with a low vapour pressure at room temperature, and water solubilities in the range of 5–750 ppm. The water solubility of each triazine compound is dependent on the substituent in the 2-position [20]. For example: Prometon ($-OCH_3$) 750 ppm; Prometryn ($-SCH_3$) 33 ppm; Propazine (–Cl) 5 ppm.

It should also be noted that, except for cyromazine (amine group), the ending of common names of symetric triazine herbicides is indicative of the substituent in the 2-position. For example:

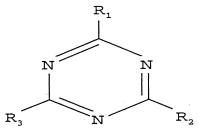
–azine chlorine atom;
–etryn alkylthio group (in general methylthio group);
–ton methoxy group.

The two most common triazines studied and detected in natural waters are atrazine and simazine. Since a large number of products are formed by the degradation of atrazine, the products were grouped into three major reaction types: dealkylation, oxidation, and dechlorination (Fig. 1) [21]. Chemical hydrolysis is considered to be the predominant degradation pathway for atrazine into the environment [22], HA being the major abiotic degradation product in water and soil [23].

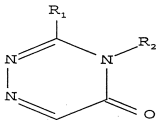
1.4. Contamination of ground and surface waters

Less than 0.1% of applied pesticides actually reaches the targeted pests, while the rest (99.9%) has the potential to move into other environmental compartments, including ground and surface waters [55]. Chemicals gain access to the water environment via both point sources, such as industrial effluents or accidental spillage, and diffuse sources such as agriculture or urban runoff. Runoff occurring within a few days of a pesticide application typically removes about 1% of the amount present in soil [56]. Studies of large agricultural watersheds have shown that the atrazine flux in rivers varies between 0.25 and 1.5% of the amount spread on the land [38,44]. The pollution of ground and surface waters by pesticide use depends upon several variables, including the type and quantity of pesticide used and possible exposure pathways. The factors affecting chemical transport from the field to surface water bodies include: inherent properties of the compound, such as water solubility, vapour pressure, organic carbon content/water partition coefficient (K_{oc}) and octanol–water partition coefficient (K_{ow}) of the soil; environmental conditions, including climate, soil texture and water content of the soil; landscape characteristics, including topography and presence of

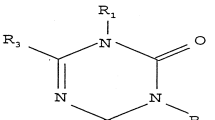
Table 1
Name, structure, physico-chemical properties and occurrence of triazine herbicides and their degradation products in ground and surface water [24–36][a]



Triazine



Triazinone



Hexazinone

Common name	Nature	Position			Water solubility (mg/l)	Log K_{oc}	Log K_{ow}	Contamination levels (μg/l) [Ref.]	
		R_1	R_2	R_3				SW	GW
Ametryn	T	SCH_3	NHC_2H_5	NHC_3H_7 (iso)	185	2.5	3	0.005–0.13 [37,38]	0.005–0.35 [37]
Anilazine	T	Cl	Cl	NHC_6H_4Cl (aromatic)	Insoluble		3.0		
Dihydroxyanilazine	DP	OH	OH	NHC_6H_4Cl (aromatic)					
Dimetoxyanilazine	DP	OCH_3	OCH_3	NHC_6H_4Cl (aromatic)					
N-methyldimethoxy-anilazine	DP	OCH_3	OCH_3	$NCH_3C_6H_4Cl$ (aromatic)					
Atrazine	T	Cl	NHC_2H_5	NHC_3H_7 (iso)	30	2	2.6	0.003–136 [38–48]	0.003–10 [34,37,48–53]
ADHT	DP	OH	OH	NH_2					
AEHT	DP	OH	NHC_2H_5	NH_2					
AIHT	DP	OH	NHC_3H_7 (iso)	NH_2				0.86 [48]	
CAADT	DP	Cl	NH_2	$NHCOCH_3$					
CADEAT	DP	Cl	$NHCOCH_3$	NHC_2H_5					
CADIT	DP	Cl	NHC_3H_7	$NHCOCH_3$					
CAHT	DP	Cl	OH	NH_2					
CDADT	DP	Cl	$NHCOCH_3$	$NHCOCH_3$					
CDHT	DP	Cl	OH	OH					
Chlorodiamino-*s*-triazine	DP	Cl	NH_2	NH_2					
Cyanuric acid	DP	OH	OH	OH					
DAHT	DP	OH	NH_2	NH_2					
DEA	DP	Cl	NH_2	NHC_3H_7 (iso)	670	1.8	1.4	0.001–7.50 [43–45]	0.01–2.20 [37,54]
DIA	DP	Cl	NHC_2H_5	NH_2	3200	1.7	1.1	0.008–7.37 [43,48]	1.17 [54]
EDHT	DP	OH	OH	NHC_2H_5					
HA	DP	OH	NHC_2H_5	NHC_3H_7 (iso)	6 (pH 13) 230 (pH 2)			3.72 [48]	
Atraton	T				1800		2.4		
Aziprotryne	T	SCH_3	$NHCH(CH_3)_2$	N_3	55				
Chlorazine	T	Cl	$N(C_2H_5)_2$	$N(C_2H_5)_2$	10				
Cyanazine	T	Cl	$NHC(CN)(CH_3)_2$	NHC_2H_5	171	2.3	1.6	0.005–0.976 [37,38,43]	0.30 [34]
Cyanazine amide	DP	Cl	$NHC(CNHOH)(CH_3)_2$	NHC_2H_5				0.025–0.222 [38]	0.58 [34]
Deethylcyanazine amide	DP	Cl	$NHC(CNHOH)(CH_3)_2$	NH_2					
Deethylcyanazine	DP	Cl	$NHC(CN)(CH_3)_2$	NH_2					
Cyromazine	T	NHC_3H_5 (cyclo)	NH_2	NH_2	11000				
Desmetryn	T	SCH_3	$NHCH_3$	$NHCH(CH_3)_2$	580				
Dimethametryn	T	SCH_3	$NHCH_2CH_3$	$NHC_2H_4(CH_3)_2$	50		3.5		
Dipropetryn	T	SCH_2CH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	16				
Eglinazine	T	Cl	$NHCH_2CO_2H$	$NHCH_2CH_3$	300				
Hexazinone	H	CH_3	C_6H_{11} (cyclo)	$N(CH_3)_2$	33000	1.7		0.005–071 [38]	
DP-H1	DP	CH_3	C_6H_{10}-4-OH (cyclo)	$N(CH_3)_2$					
DP-H2	DP	CH_3	C_6H_{11} (cyclo)	$NHCH_3$					
DP-H3	DP	CH_3	C_6H_{10}-4-OH (cyclo)	$NHCH_3$					
DP-H4	DP	CH_3	C_6H_{11} (cyclo)	=O					
DP-H5	DP	CH_3	C_6H_{10}-4-OH (cyclo)	=O					
DP-H6	DP	CH_3	C_6H_{10}-2-OH (cyclo)	$N(CH_3)_2$					
DP-H7	DP	CH_3	C_6H_9-4-O (cyclo)	$N(CH_3)_2$					

Table 1 (continued)

Common name	Nature	Position			Water solubility (mg/l)	Log K_{oc}	Log K_{ow}	Contamination levels (μg/l) [Ref.]	
		R_1	R_2	R_3				SW	GW
Irgarol	T	SCH_3	$NHC(CH_3)_3$	NHC_3H_5 (cyclo)	7		3.6		
Metamitron	TO	CH_3	NH_2	C_6H_5 (aromatic)	1800				
Methoprotryne	T	SCH_3	$NHCH(CH_3)_2$	$NH(CH_2)_3OCH_3$	320		2.7		
Metribuzin	TO	SCH_3	NH_2	$C(CH_3)_3$	1220	1.8	1.9	0.005–0.174 [38]	0.27 [34]
DAM	DP	SCH_3	H	$C(CH_3)_3$					
DKM	DP	=O	NH_2	$C(CH_3)_3$					
DADKM	DP	=O	H	$C(CH_3)_3$					
Proglinazine	T	Cl	$NHCH_2CO_2H$	$NHCH(CH_3)_2$	750				
Prometon	TO	OCH_3	NHC_3H_7 (iso)	NHC_3H_7 (iso)	620	2.2	2.8	0.005–0.068 [38]	1.0 [34]
Prometryn	T	SCH_3	NHC_3H_7 (iso)	NHC_3H_7 (iso)	33	2.6	3.3	0.005–0.075 [38]	
Propazine	T	Cl	NHC_3H_7 (iso)	NHC_3H_7 (iso)	5		2.9	0.01–0.07 [46]	
Hydroxypropazine	DP	OH	NHC_3H_7 (iso)	NHC_3H_7 (iso)					
Sebuthylazine	T								
Secbumeton	T	OCH_3	NHC_2H_5	$NHCH(CH_3)C_2H_5$	600				
Simazine	T	Cl	NHC_2H_5	NHC_2H_5	5	2.1	2.2	0.002–1.1 [38,39,41–43,45–47]	0.01–1.12 [37]
Hydroxysimazine	DP	OH	NHC_2H_5	NHC_2H_5					
Simetryn	T	SCH_3	NHC_2H_5	NHC_2H_5	450		2.5		
Terbumeton	T	OCH_3	NHC_2H_5	$NHC(CH_3)_3$	130		3.0		
Terbuthylazine	T	Cl	NHC_2H_5	$NHC(CH_3)_3$	8.5		2.9	0.004–2.27 [45–47]	
Hydroxyterbuthylazine	M	OH	NHC_2H_5	$NHC(CH_3)_3$					
Deethylterbuthylazine	M	Cl	NH_2	$NHC(CH_3)_3$					
Terbutryn	T	SCH_3	NHC_2H_5	$NHC(CH_3)_3$	25		3.7	0.005–0.518 [37]	0.005–0.6 [37]
Trietazine	T	Cl	NHC_2H_5	NHC_2H_5	20		2.8		

[a] *Note*: T=Triazine, TO=Triazinone, H=Hexazinone, DP=Degradation product. For others, see List of abbreviations, Section 4.

tile-drainage and surface-runoff inlet network; and, management practices (tillage, crop selection and application method) [46]. Compounds having high water solubility and low soil adsorption will move easily to the groundwater. Table 2 shows the properties of pesticides and their high groundwater contamination potential [57].

In the USA and in most European countries, groundwater is a major source of drinking water [58]. In Canada, 26% of the population relies upon groundwater for household use [59]. Herbicides can reach groundwater by leaching, thereby contaminating a source of drinking water. Herbicides were detected in about 50% of wells sampled in Iowa in 1996, with herbicide degradation products being detected in some 75% [19]. DEA, which is phytotoxic and considered to be as toxic as atrazine for both animals and humans [60], has often been detected in groundwater at concentrations of between 0.01 and 1 μg/l [61], and sometimes even at concentrations exceeding that of the parent product [62]. A seven-year study on the groundwater in the Paris region of France found DEA to be present at a concentration above that of its parent compound [63,64]. The atrazine degradation pathway and the higher solubility of DEA in water may explain this finding. These analyses demonstrate the importance of the routine monitoring of both parent and degradation products to obtain a clear picture of total pesticide residue in drinking (groundwater) and surface waters.

A recent EU directive states that the pesticide level must not exceed 0.1 μg/l for individual compounds, and some of their degradation products, (0.5 μg/l for all compounds) in water intended for human consumption, including groundwater [65]. In Canada and the USA, neither health advisory levels (HALs) nor maximum contaminant levels (MCLs) have yet been set for triazine degradation products, and the possibility of summing parent and degradation products to meet the health advisory limit is being considered. The EPA estimates that a drinking water exposure to 200 ppb of atrazine poses a one-in-a-million lifetime cancer risk and that, at the

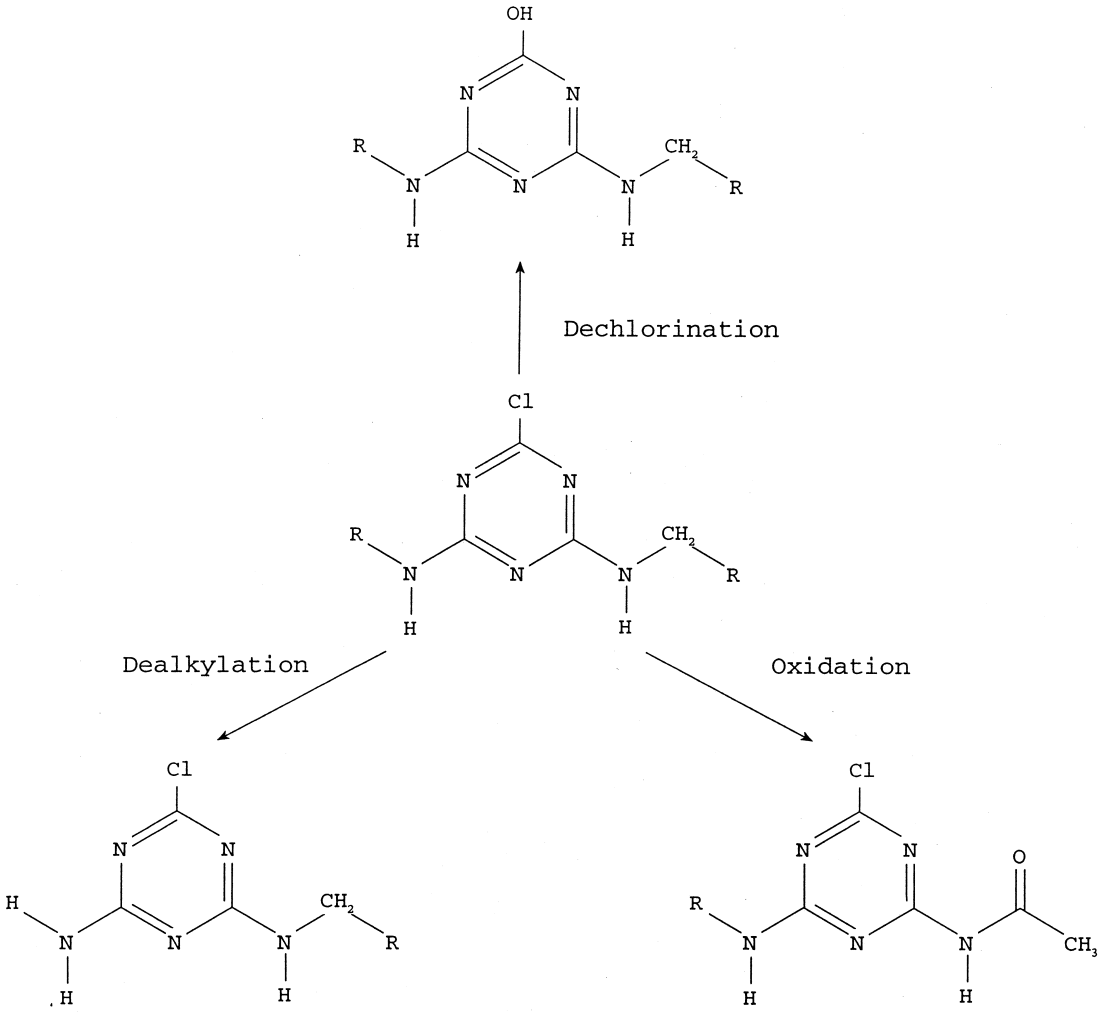


Fig. 1. Pathways for atrazine degradation. *R* is a CH_3 or C_3H_7 (iso) radical group.

proposed HAL of 3 ppb, consumption of atrazine in drinking water poses a risk of about one-in-one-hundred-thousand [66].

1.5. Multiresidue extraction techniques

The environmental impacts of pesticides are on the rise. Due to the large number of active ingredients used, trace analyses of these substances require techniques for the detection of the greatest number of compounds possible, with the fewest number of extraction and clean-up steps. Numerous techniques have been developed for the extraction of priority pesticides (including triazines and degradation products) from water. Of these, LLE [67–70], SPMD [71], SFE [72,73], SPE [74–79] and SPME [80–83] are the most widely employed.

It is important to consider the context of a particular study when developing a method. Further, the first targeted criterion is generally the detection limit (DL), which should be 25% of the recommended MCL values. The EU criteria (MCL) for pesticides in water, among the most stringent in the

Table 2
Properties of pesticides, indicating their high groundwater contamination potential

Parameter	Value
Water solubility	>30 mg/l
K_d	<5, usually <1
K_{oc}	<300
Henry's law constant	$<10^{-2}$ atm m^3 mol^{-1}
Speciation	Negatively, fully or partially charged at ambient pH
Hydrolysis half-life	>25 weeks
Photolysis half-life	>1 week
Field dissipation half-life	>3 weeks

world, are set at 0.1 ppb per pesticide, including certain degradation products. Thus, the majority of analytical methods have been designed around this criterion and were considered to be satisfied when 25% of this target figure was reached based on an accuracy rate of 25% [84]. Certain methods were developed to study the fate and transport of pesticides in rivers; these require the lowest possible DLs (ng/l or less) [85].

Most officially-sanctioned methods for the analysis of pesticides, including triazines, in water still use LLE techniques [68–70]. Conventional methods take samples of <1 l (up to 1 l and pH adjusted to 7), which are shaken with an immiscible organic solvent such as methylene chloride [86]. For pg or ng/l levels, larger sample volumes (up to 120 l) have been extracted using the Goulden large-sample extractor [85,87–89]. There are disadvantages to LLE techniques: they cannot extract polar pesticides like degradation products, they are laborious, time-consuming, expensive and subject to problems arising from the formation of emulsion, the evaporation of large solvent volumes, and the disposal of toxic or inflammable solvents [90]. Recent regulations pertaining to the use of organic solvents have made LLE techniques unacceptable [91]. However, several alternative methods which reduce or eliminate the use of solvents are now being employed to prepare samples for chromatographic analysis. These include supercritical fluid extraction, SPME and SPE. Currently, the emphasis is on automation of the whole SPE procedure. The ideal sample preparation methodology is fast, accurate, precise, and consumes little solvent. Furthermore, it is easily adapted for field work, and requires less costly materials. The SPE method may be the isolation technique that is capable of meeting all these expectations.

A steam distillation extraction procedure for triazines in aqueous media has been described by Janda and Martha [92]. However, a 3-h distillation period is required to recover 81% of the atrazine, with an appreciably lower recovery rate if shorter distillation times are employed. Some triazines, including atrazine and simazine, were extracted from water by supercritical fluid extraction (SFE) after freeze-drying of water samples [92] or their pre-concentration on solid-phase extraction disks [93–95]. The freeze-dried residue or SPE disk was then introduced into the extraction cell and eluted with either pure CO_2 or methanol or acetone-modified CO_2. Supercritical fluid chromatography has been applied in combination with on-line solid-phase extraction for pesticides, including triazines [96]. However, this technique is still used mainly on solid matrixes. The main limitation with aqueous matrixes remains the miscibility of water with supercritical carbon dioxide [97]. Recoveries of non-polar pesticides, extracted by SFE technique using octacedyl-bonded silica, are generally effective with CO_2 elution alone. This is not the case for semi-polar and polar compounds, such as triazines and their degradation products. For example, the addition of 10% methanol to CO_2 is necessary to reach acceptable recoveries for atrazine and some degradation products like HA and DAHT. Atrazine, simazine, DEA and DIA were extracted from cartridges filled with granular activated carbon (GAC) using the SFE technique [73]. Pure CO_2 was insufficient to elute these chemicals because of the interactions between GAC sites and the compounds. The addition of 50% of acetone was necessary to obtain acceptable recoveries.

Multiresidue methods using SPE and SPME techniques to extract priority pesticides, including triazines and degradation products, from water will be examined in the following paragraphs.

2. Solid-phase extraction

The SPE technique for sample preparation was

first introduced in the mid-1970s [98]. It became commercially available in 1978 as an alternative to LLE [99]. SPE cartridges and disks are now available from many suppliers and represent a variety of chemical matrixes.

In conventional SPE, a liquid is passed over a sorbent packed in a glass or polypropylene cartridge or embedded in a disk. As a result of the strong attraction between them, the analytes are retained on the sorbent. The sorbent is later washed with a small volume of solvent to disrupt the bonds between analyte and sorbent. The selection of an SPE method depends upon the pesticide under evaluation, expected concentrations, and the water volume being processed [100]. Disk extraction has been reported to use 90% less solvent than LLE and up to 20% less solvent than cartridges, and it eliminates the problem of channelling associated with cartridges [101]. This difference in solvent volumes may be attributed to the adsorption/desorption phenomenon occurring in the cartridge, which is not the case for the disk. However, the large diameter of the disk could act to compensate for this difference. Indeed, the volume of solvent used for disk elution may be similar to or even higher than the cartridge elution volume, depending upon the weight of the sorbent used in the cartridge and the disk's diameter. For standard methods, the SPE cartridge technique has been estimated to be 30 and 50%, respectively, less expensive per sample than disks and LLE [100]. This rate may be higher when extracting large volumes of water.

Methanol is usually utilized to pre-wet the C_{18} Bond-Elut columns and open the hydrophobic chains to increase the effective surface area and eliminate contamination by benzylsulphonic acid [102,103]. Water samples are also fortified with at least 1% methanol to continuously wet the stationary phase. This can improve recovery rates for a large number of pesticides, including triazines. By contrast, degradation products, which are often more polar than parent compounds, may not be retained as effectively in the presence of a modifier [104]. Varian recently developed a new sorbent for SPE techniques that requires no pre-extraction conditioning [105]. The application of this material, which saves time and is more practical for on-site extraction, is expected to gain ground in the coming years.

Ground and surface waters must always be filtered prior to the extraction of pesticides with the SPE technique. Pre-filtration through 0.45-μm PTFE filters has been recommended when using C_8 cartridges [106] or Empore extraction disks [107]. Prefiltering will not affect the determination of triazines and their degradation products, since these compounds exhibit a log K_{oc} near two and consequently they are largely (99.5%) distributed in water in the dissolved phase [108,109].

Table 3 presents numerous SPE and SPME techniques that have been used for multiresidue determinations of pesticides, including triazines and degradation products, in ground and surface waters.

2.1. Sorbents

Sorbent-analyte interactions fall into three categories: non-polar, polar and ionic. Non-polar sorbents are generally selected for extracting triazines from water. By contrast, degradation products, which contain very polar functional groups such as hydroxyl, carbonyls, amines, and sulfhydryls, need polar sorbents. Polar sorbents exhibit a strong tendency to form hydrogen bonds. The retention of polar compounds on polar sorbents is facilitated by non-polar solvents. Analytes that are capable of forming cations (positively-charged ions) include amines; analytes with the potential to form anions (negatively-charged ions) include carboxylic and sulfonic acids and phosphates. For retention to occur with ionic interactions, an anionic sorbent should be selected to retain cations, and a cationic sorbent to retain anions. For maximum retention, the pH of the matrix should be 2 pH units below the pK_a of the cation and 2 pH units above the pK_a of the anion [132].

Different types of sorbents have been employed in SPE techniques to extract triazines and their degradation products from water. The most widely used are C_8 and C_{18} chemically-bonded to silica [14,115,133–139], carbon black [119,140,141] and polymeric resins (such as PLRP-S) [133,142–145]. The most polar compounds, like DIA, DEA, HA and metribuzin, have low breakthrough volumes with these sorbents [133,143], except for carbon material [77,146] and some highly cross-linked styrene–di-

Table 3
SPE and SPME techniques for the multiresidue determination of triazines and degradation products in water[a]

Water	Pesticide	SPE–SPME	Recovery (R, %), detection limits and environmental levels (μg/l)	Ref.
GW (4 l) and SW (1 l)	Atrazine, DEA, DIA, DIHA, DEDIA, DEHA, HA	Cartridges filled with 500 mg of GCB material (Carbograph 4) followed by LC–MS	All chemicals in both matrixes: R=80–101%	[110]
Russian Arctic surface snow (0.004 l)	Sixty pesticides, including atrazine, hexazinone, metribuzin, propazine and simazine	SPME using 100-μm thick polydimethylsiloxane and 95-μm thick polyacrylate fibres, followed by GC–MS	Simazine: EL=2.5 μg/l	[111]
SW (4 l)	Twelve pesticides, including atrazine, DIA, DEA, cyanazine and simazine	C_{18} Empore extraction disk (47 mm I.D. and 0.5 mm thick, 500 mg C_{18} bonded silica), followed by LC-UV and -MS	Triazines: R=80–125% DIA: R=3% DEA: R=8–9%	[90]
SW (0.010–0.200 l)	Fourteen pesticides including atrazine and terbutryn, plus 41 unknown substances	Automated online SPE–LC–DAD, SPE–LC–MS and SPE-GC-MS	Atrazine and terbutryn detected	[75]
SW (0.100 l)	HA, DEHA and DIHA	Cartridges filled with propylenebenzene–sulfonic acid cation exchange (SCX), followed by LC-UV and LC-MS-MS detection	HA: EL=0.18–5.7 μg/l DEHA: EL=0.12–1.9 μg/l DIHA: EL=0.12–0.72 μg/l	[76]
GW (1 l)	Hexazinone and five metabolites	Cartridges filled with 500 mg of GCB (Envi-Carb) followed by capillary electrophoresis	Hexazinone: R=79–100% Metabolites: R=30–120%	[33]
SW (0.020 l)	Fourteen pesticides including atrazine, simazine, propazine, terbuthylazine, DIA, DEA and irgarol	On-line SPE–LC–MS. Cartridges filled with 80 mg silica and 2 mg of anti-atrazine and anti-chlortoluron immunosorbents	Triazines (except for DIA and HA): R=86–103% DIA: R=0%	[112]
Runoff water (0.100 l)	Atrazine, DEA, DIA, DEDIA, HA	Tandem SPE using two cartridges filled with 500 mg of C_{18} and SCX each, followed by LC–DAD and GC–NPD	Atrazine, DEA, DIA (C_{18}): R=96–99% DEDIA, HA (SCX): R=78–103%	[113]
SW (18 l)	Atrazine, ametryn, DEA, DIA, cyanazine, metribuzin, prometryn, propazine and simazine	Cartridges filled with 500 mg of GCB materia (Carbograph B 500–666 μm) followed by GC–NPD and LC-MS detection	Triazines (except metribuzin): R=51–84% Metribuzin: R=5% Atrazine, cyanazine, DEA, DIA and simazine: EL=0.003–0.052 μg/l.	[77,114]
SW (0.010–0.150 l)	Thirty pesticides including atrazine, DEA, DIA and simazine	On-line SPE using Empore 4.6 mm disk containing C_{18} or styrene–divinylbenzene, followed by LC–UV or LC-fluorescence detection	Atrazine: R=85–92% Simazine: R=84–87% DEA: R=48–55% DIA: R=17–22%	[115]
SW (0.250 l)	Atrazine, cyanazine, DEA, DIA, HA, hexazinone, prometon, propazine, sibuthylazine, simazine, simetryne and terbuthylazine	Automated on-line using Prospekt system. Cartridges (10×2 mm I.D.) prepacked with styrene–divinylbenzene copolymer (15–25 μm, PLRP-S) LC-UV detection	Determination below the 1 μg/l levels	[116]
GW (1 l)	Atrazine and simazine	Column filled with XAD-2 or C_{18} cartridges, followed by GC–NPD or GC–MS detection	Atrazine and simazine: R=74–85%	[117]
SW (0.500 l)	Phenylarea and triazine herbicides, including atrazine, simazine, propazine, terbuthylazine, DEA and DIA	Double-disk solid-phase extraction (47 mm I.D., 0.5 mm thick, containing each 500 mg of SAX and C_{18} materials); LC–DAD detection	Triazines: R=101–110% DIA: R=25%; DEA: R=85%	[78]
SW (0.250 l)	Thirty-four pesticides, including atrazine and metribuzin	Stability on cartridges filled with 500 mg of a small-particle-size GCB material (120–200 mesh); LC-UV detection	Atrazine and metribuzin, recovery after storage at −18°C for 21 days: R=94–95%	[118]
SW (4 l)	Eighteen herbicides, including ametryn, atrazine, DEA, DIA, cyanazine, metribuzin, prometryn, propazine and simazine	Stability on cartridges filled with 500 mg of a large-particle-size GCB material (60–80 mesh); LC–MS detection	Triazines, except metribuzin, recovery after storage at −20°C for 60 days: R=43–82%	[119]
SW (0.500–2 l)	Atrazine, cyanazine, DEA, DET, DIA, propazine, simazine and terbuthylazine	Cartridges filled with 500 mg of a non-ionic styrene–divinylbenzene copolymer resin (Envi-Chrom P, 80–160 μm spherical particles); LC-DAD	All triazines and degradation products: R=94–109%	[120]

Table 3 (continued)

Water	Pesticide	SPE–SPME	Recovery (R, %), detection limits and environmental levels (μg/l)	Ref.
SW (0.002 l)	Atrazine, cyanazine, DEA, DIA, HA, simazine, terbuthylazine and terbutryn	On-line coupled-column-LC–UV containing C_{18} sorbent with large volume injection	Atrazine, DEA, DIA and HA: R=96–104%	[28]
SW (0.010–0.100 l)	Eleven pesticides, including atrazine and DEA	On-line SPE–GC–MS–MS using cartridge (10×2 mm I.D.) packed with 15–25 μm PlRP-S co-polymer	Atrazine and DEA: DLs=0.2–0.5 μg/l	[121]
SW (0.100–0.500 l)	Twelve pesticides, including ametryn, atrazine, cyanazine, prometryn, simazine and terbutryn	On-line and off-line SPE in combination with LC–DAD using styrene–divinylbenzene membrane disks	Triazines: R=74–92% Off-line mode: DLs=0.05–0.1 μg/l On-line mode: DLs=0.03 μg/l	[122]
SW (0.004 l)	Twelve pesticides, including atrazine, prometon and terbutryn	SPME–GC–NPD using 65 μm CW–DVB coated fibre	Triazines: DLs=0.03–0.10 μg/l	[81]
GW (0.004 l)	EPA method 507 (39 organonitrogen and organophosphorus pesticides), including ametryn, atraton, atrazine, propazine, prometon, prometryn, simazine, simetryn and terbutryn	SPME–GC–NPD and SPME–GC–MS using 100 μm PDMS	Triazines: GC–MS: DLs=0.010–0.030 μg/l GC–NPD: DLs=0.010–0.400 μg/l	[82]
GW (0.004 l)	Fourteen pesticides, including atrazine, ametryn and terbutryn	SPME–GC–MS (in full scan and under SIM mode) using 85 μm polyacrylate coated fibre	Triazines: Full scan mode: DLs=0.01 μg/l SIM mode: DLs=0.002 μg/l	[83]
SW (0.05 l)	Atrazine, DEA, DIA, propazine, simazine, terbuthylazine and hydroxylated derivative hydroxyatrazine	On-line (LC–DAD) configuration using two-step preconcentration: an SDB precolumn coupled with a cation-exchanger precolumn	Triazines: DLs=0.1 μg/l Hydroxylated derivative: DLs=0.1 μg/l	[123,124]
SW (1 l)	Thirty-two pesticides including atrazine, metribuzin, prometryn, simazine and terbuthylazine	Cartridges filled with C_{18} bonded silica, followed by GC–ECD, GC–NPD and GC–MS	Triazines: R=58.3–90.7% DLs=0.005–0.02 μg/l	[125]
SW (2 l)	Seventeen pesticides including atrazine, DEA and simazine	C_{18} bonded silica phase and polystyrene–DVB followed by GC–MS, GC–NPD and GC–ECD	Triazines: DLs=0.002–0.005 μg/l	[126]
GW (0.2 l)	Fifteen pesticides including atrazine, ametryn, prometryn and terbutryn	On-line LC–MS. Cartridges filled with 10 μm lichrospher Si 100 RP-18	Triazines: DLs=0.0008 μg/l	[127]
SW (0.004 l)	Atrazine, cyanazine, propazine, sebuthylazine, simazine, terbuthylazine	On-line LC–MS–MS. Enrichment on a short column (10×2 mm I.D.) filled with 8 μm C_{18} bonded silica	DLs=0.1 μg/l	[128]
Water containing 20 ppm humic acid (0.200 l)	Atrazine, propazine, simazine and terbuthylazine	On-line SPE–LC–UV using a coupled column system, consisting of a combination of a molecularly-imprinted polymer (MIP) and a C_{18}-silica column molecularly-imprinted polymer (MIP) and a C_{18}-silica column	Triazines: R=74–77% Enrichment factor: 100	[129]
SW (0.050 l)	Atrazine, cyanazine, DEA, DIA, HA, prometon, propazine, sebuthylazine, simazine, simetryn, terbuthylazine	On-line LC–DAD using an anti-atrazine immunosorbent	Triazines: R=60–101%; DIA: R=0% DLs=0.1 μg/l	[130]
SW (0.010 l)	Seven triazines: atrazine, dipropetryn, prometryn, terbuthylazine, terbutryn, sebuthylazine and simetryn	On-line immuno-affinity-based SPE–GC–NPD	Atrazine, terbuthylazine and sebuthylazine: R=64–88% The others were not recovered DLs=0.0015 μg/l with GC–NPD	[131]

[a] *Note*: R: Recovery; DL: Detection limit; EL: Environmental level.

vinylbenzenes (Envi-Chrom P) [133,144]. In recent years, chemically-modified polymeric resins with a polar functional group have been developed and used in the SPE of these compounds, and the break-through volumes were higher than those obtained with their unmodified analogues [146–149]. New cross-linked styrene–divinylbenzene packing materials, such as LiChrolut EN [147,150–152], Styrosob and Macronet Hypersol [153], Isolute ENV [150] and HYSphere-1 [154] are now available. These sorbents have a higher degree of cross-linking and, thereby, an open structure (high-porosity materials)

that increases their specific area [155] and allows greater π–π interactions between analytes and sorbent. This means that the breakthrough volumes will be higher than those obtained when the cross-linked sorbents are used [156]. The three sorbents allowed for the same percent recoveries for atrazine and simazine (80–86%) in water [156].

N-Alkyl silica sorbents are usually appropriate in the framework of multiresidue extraction for log $K_{ow}>3$ of analysed substances [14]. The performance of *N*-alkyl silica was improved by increasing the hydrophobic interactions and using high silica surface areas. However, these measures were insufficient for the retention of polar compounds, which are better retained with SDB polymers.

A multiresidue method based on off-line SPE mode with GC–MS, LC–UV–DAD and LC–MS was developed in Europe for monitoring pesticides on the priority list. Various sorbents were tested: Isolut C_{18}, LiChrolut, Envi 18, SDB, OASIS, Envichrom and Envi-carb. The SDB, OASIS, Envi-chrom and Envi-carb appear to be the most promising for extracting polar compounds, including triazines and their degradation products [139].

Knutsson et al. [157] have reported on the supported liquid membrane (SLM) extraction technique; it seems to be more selective than SPE using C_{18}. The supported liquid membrane in question consists of a PTFE membrane impregnated with a water-immiscible solvent. Two channels, a donor channel (sample) and an acceptor channel (sorbent), are formed at either side of the membrane through which the analytes are carried. An acidic acceptor has been used for propazine and simazine, which have low pK_a values [157], but the method still needs improving. Although the SLM technique can extract very polar compounds, it is nonetheless limited to those that form ionized species.

The performances of the different sorbents used in SPE techniques for the multiresidue determination of pesticides, including triazines and degradation products, in ground and surface waters are shown in Table 3.

2.2. Cartridges

SPE cartridges are available in a wide range of sizes, with volumes ranging from less than 1 ml to over 50 ml. When selecting the optimum cartridge size for a particular application, factors to be considered are ability to retain all analytes in a sample, volume of original sample, and final volume of the purified sample after elution. In general, the mass of the analytes and interfering compounds retained by the sorbent should be less than 5% of the mass of the sorbent. A good rule of thumb is that the elution volume should be 2–5 times the bed volume of the cartridge [132]. This volume may be higher, however, depending on the properties of the selected pesticides, the nature of the adsorbent, the type of eluant, and the analytical technique used [77,114].

The various SPE techniques using cartridges for the multiresidue determination of pesticides, including triazines and degradation products, in ground and surface waters, have been described and are presented in Table 3.

2.3. Disks

A variation on the extraction cartridge is the disk in which the sorbent (on a polymer or silica substrate) is embedded in a web of PTFE or glass fibre. Glass fibre disks are thicker and more rigid, providing higher flow-rates than with PTFE membranes, as illustrated by the high throughputs used with laminar extraction disks. The sorbent particles embedded in the disks are smaller than those found in the cartridges (8-μm diameter rather than 40 μm). The short sample path and small particle size allow efficient trapping of analytes with a relatively high flow-rate through the sorbent, as compared to the cartridges. The disks are primarily used to reduce analysis time when handling large volumes of aqueous environmental samples. Disks are available in several different diameters (4.6 mm, 47 mm and 93 mm), with the larger volumes allowing faster flow-rates. The most frequently used disk size is the 47 mm, which is suitable for standard methods (0.5–1 l water sample volumes). Small-diameter SPE disks (4.6 mm) were coupled on-line with an LC system [90].

Barceló et al. [90] showed that the recoveries on C_{18} Empore disks (1–4 l) were very high for a large number of pesticides, including atrazine, simazine

and cyanazine: 80–125%, compared to 3–17% for degradation products (DEA and DIA). The extraction disks allowed for relatively high flow-rates, compared to cartridges using this same material because of the absence of channelling and the faster mass transfer provided by the smaller particle sizes [90]. Viana et al. [158] have demonstrated that C_8 disks allow better recoveries for atrazine, prometryn and propazine (87–93%) than do C_{18} disks (66–67%). Pichon et al. [159] employed a multiresidue method using a new laminar extraction disk in combination with LC and a Baker Speedisk DVB for polar compounds and a C_{18} silica disk for non-polar compounds. They achieved rapid handling of one-litre sample volumes, with DLs ranging from 0.01 to 0.05 μg/l.

2.4. Solid-phase microextraction

Solid-phase microextraction (SPME) first became available to analytical researchers in 1989 [160]. The technique consists of two steps: first, adsorption of analytes from an aqueous matrix by dipping the SPME fibre into the matrix, and second, desorption of analytes from a polymeric layer into the carrier gas stream of a heated GC injector. SPME is easily coupled with gas chromatography and liquid chromatography using a special device. The heated split/splitless injector, septum programmable injector (SPI) or the on-column port of the gas chromatograph can be used for the thermal desorption of the analytes from the fibre. The thermal desorption in the GC injector facilitates use of the SPME technology for thermally-stable compounds. Otherwise, the thermally-labile analytes can be determined by SPME–LC or SPME–GC (e.g., if an in-situ derivatization step in the aqueous medium is performed prior to extraction). Different types of commercially-available fibres are now being used for the more selective determination of different classes of compounds: 100 μm polydimethylsiloxane (PDMS), 30 μm PDMS, 7 μm PDMS, 65 μm Carbowax–divinylbenzene (CW–DVB), 85 μm polyacylate (PA), 65 μm PDMS–DVB, and 75 μm Carboxen–polydimethylsiloxane (CX–PDMS) [81,132,161]. PDMS, which is relatively non-polar, is used most frequently. For triazines, however, a 85-μm polyacylate coating is more suitable since it is a more hydrophilic fibre [162]. With this technique, DLs can be as low as 0.1 μg/l (limit set by the EU for individual pesticides in drinking water) if combined with GC with selective nitrogen-phosphorus detection [162]. Since SPME is an equilibrium extraction rather than an exhaustive extraction technique, it is not possible to obtain 100% recoveries of analytes in samples, nor can it be assessed against total extraction. Method validation may thus include a comparison of the results with those obtained using a reference extraction technique on the same analytes in a similar matrix. Surrogates and standard additions are needed to control for the matrix effect [163].

In evaluating the performance of a 65-μm CW–DVB fibre combined with SPME–GC–NPD, it was shown that this fibre is most sensitive to twelve pesticides, including atrazine, prometon and terbutryn [81]. PDMS–DVB, CW–DVB and PA are more appropriate for polar, nitrogen-containing herbicides. An inter-laboratory trial involving the analysis of triazines and their degradation products demonstrated the validity of SPME using CW–DVB fibre in association with added NaCl and in combination with a GC system [164]. The results obtained with these methods demonstrated that SPME is a robust and reproducible method for the analysis of several pesticides. But use of this technique for extracting the more polar pesticides is limited by the types of fibre available.

Advancements are being made in the refinement of the SPME technique. The LC–SPME interface has been improved, and new mixed phases based on solid/liquid sorption (e.g. CW–DVB and PDMS–DVB) have been developed in recent years for the analysis of compounds by LC. A new, modified accessory to the LC system, called in-tube SPME, was recently developed. It aspirates and dispenses samples from vials with the syringe in the inject position, then desorbs with aspirated solvent in the load position. Returning the valve to the inject mode will transfer analytes to the analytical column [165].

2.5. Immuno-extraction

The immuno-extraction technique consists of using SPE cartridges filled with antibody materials

bonded onto silica-based sorbents. These materials, called immuno-affinity sorbents, have been used to extract triazines from water samples [130]. They are specific to the target compounds; thus, DIA is not recovered with anti-atrazine immunosorbents, while HA and prometon are not recovered with anti-simazine immunosorbents [130].

The comparison of an anti-atrazine immunosorbent and a PLRP-S sorbent for the extraction of triazine from the Seine River (50 ml) using the SPE technique has demonstrated the high selectivity and efficiency of the immunosorbent [130]. Recently, Dallüge et al. [131] reported on the use of an on-line coupling of immuno-affinity-based solid-phase extraction and gas chromatography for the determination of *s*-triazines in aqueous samples. These sorbents are expected to undergo further refinement for other classes of pesticides. This would allow for the extraction of some very polar compounds from water because the antigen-antibody interaction is not based on the hydrophobic process [166].

2.6. Molecularly-imprinted polymer

The concept of this technique was inspired by Pauling's antibody formation theory, in which an antigen is used as a template to aid in the rearrangement of antibody polypeptide chains so that the antibody having a three-dimensional configuration complements the antigen molecule [167]. The first experimental attempt at molecular imprinting was made in 1949 by imprinting a dye on silica gel [168]. However, it was not until the early 1970s that successful imprints on synthetic organic polymers were achieved [169–173]. The MIP technique has become increasingly popular in recent years. It has already been used in different applications as a drug retaining matrix, in the enantioseparation of drugs, and as a solid-phase extraction material for hydroxycoumarin extraction, showing its considerable potential for selective extraction. It is expected to be beneficial for the extraction and clean-up of various polar pesticides from complex matrixes. Certain applications have already been performed, mainly on triazines, using an off-line system [174–176]. By coupling an MIP–SPE column on-line with a C_{18} column, Bjarnason et al. [129] distinguished triazines from humic acid, reaching an enrichment factor of up to 100 with satisfactory recoveries of 74–77%. Lanza and Sellergren [177] tested six functional monomers of MIPs — methacrylic acid (MAA), methyl methacrylate (NMA), hydroxyethyl methacrylate (HEMA), *N*-vinyl-a-pyrrolidone (NVP), (trifluoromethyl)acrylic acid (TFM), and 4-vinylpyridine — and found that MAA was more suitable for the extraction of chlorotriazines.

Further optimization of MIPs may lead to more efficient matrix discrimination and allow for the extraction of some very polar compounds from water as polymer-molecule interaction is not based on the hydrophobic process.

2.7. On-line and off-line procedures

On-line SPE–GC (equipped with electron-capture, thermo-ionic, flame photometric or mass spectrometer detectors) and SPE–LC (equipped with DAD, fluorescence, atomic emission or mass spectrometric detection) are the methods of choice for the trace-level determination of pesticides. The feasibility of SPE–GC was first demonstrated in 1987 [178]. A great deal of effort has since been put into developing interfacing for the on-line coupling of aqueous sample treatment by SPE and analysis by GC. In general, the combination of SPE (using pre-column or disk) and LC is an important improvement over GC applications [179–181], since it is not necessary to remove all residual water from cartridges or disks, and because elution solvents (e.g. methanol and acetonitrile) are compatible with the final separation method [90]. The recent development of a large-volume injection system in GC (10–250 μl) has partly closed this gap, however. There have been a number of reports in the literature of methods employing on-line and off-line procedures for determining priority pesticides, including triazines and degradation products, in water [182–186]. Some of them are summarized in Table 3. Several studies, using pre-column (10–20 mm length×1–4.6 mm I.D., 5–10 μm packing gradually replaced by 15–40 μm packing with C_8, C_{18} and silica–divinylbenzene [S–DVB] and membrane disks (diameter, 3–4.6 mm packing with C_{18} and S–DVB) have compared different sorbent materials for on-line SPE–LC. SPE methods can now be easily converted into fully automated on-line systems coupled to LC or GC

techniques. With these methods, small sample volumes (0.001–0.010 l) are sufficient to obtain 0.01–0.1 μg/l for a large variety of compounds, including triazines and their degradation products [182,187,188]. This is an enormous advantage over off-line procedures. Regardless, on-line procedures benefit from the absence of contamination or loss of analytes during solvent evaporation, while off-line procedures are favourable for their applicability to on-site sampling and the opportunity to inject the same extract twice.

The reproducibility, sensitivity and robustness of a fully on-line SPE and LC–DAD (SAMOS) system have been demonstrated for monitoring pesticides in surface waters [123]. The relative standard deviation (RSD) values for retention times ranged from 0.2 to 1.5% ($n=20$). The repeatability of the method using 100 ml of surface water spiked with 1 μg/l was in the range of 3.8–8.9% for atrazine and propazine and 10.0–23.8% for DEA and simazine. The method's reproducibility was in the range of 2.3–3.5% for DEA and atrazine, and 13.1–49% for propazine and simazine. DLs were around 15 ng/l for triazines [159]. The robustness of the SAMOS system was illustrated by the fact that no major problem was encountered in the course of over 1000 determinations.

2.8. Breakthrough volumes

The breakthrough volume is one of the most important characteristics in determining the use of an adsorbent in a particular analysis. It can occur in SPE techniques due to insufficient retention of analytes (depending on their physico–chemical properties) or by exceeding the capacity of the sorbent. Many studies have focused on this subject, particularly with regard to triazines and their degradation products [115,139,189].

Pichon and Hennion [116] reported that the breakthrough volumes of simazine, atrazine and cyanazine (at μg/l levels), when using on-line pre-concentration, were approximately five times higher on PLRP-S pre-columns than on C_{18} silica. In another study, these same authors recommended the use of C_{18} cartridges for analytes with log $K_{ow}>2.5–3$ and SDP polymers for those with log $K_{ow}<2.5$ [139]. Mills and Thurman [190] have shown that C_{18} resin has the lowest capacity for DIA, with approximately 80% retention from the 100-ml sample volume commonly used in environmental analyses. DEA had 100% retention from a 100-ml sample, but breakthrough began at approximately 200 ml. The parent herbicides atrazine, propazine and simazine had 100% retention from the same volume, with initial breakthrough beginning at 750 ml for simazine, 1250 ml for atrazine, and 2500 ml for propazine. These authors concluded that the retention of selected pesticides and degradation products on C_{18} resin from aqueous solutions increases with increasing alkyl-chain length: DIA, DEA, simazine, atrazine, and propazine, in that order.

2.9. Nature and volume of elution

After a sorbent is selected for use with either cartridges or disks, depending on its retention efficiency for the target pesticides, the second step consists of determining the best solvent or mixture of solvents to disrupt this link and to evacuate the analytes from the SPE materials. Several studies have been conducted to select the most suitable solvent for the elution of priority pesticides, including triazines and degradation products, from different sorbents [77,191]. In general, an eluant is chosen based on its high-performance, low volume, weak toxicity, non-interference with compounds, and compatibility with the chromatographic system used (GC or LC).

Di Corcia and Marchetti [191] showed that 5 ml of CH_2Cl_2–MeOH (80:20, v/v) was only efficient for the elution of ten pesticides, including triazines and some degradation products, from cartridges filled with small-particle-size GCB material (120–400 mesh). High polar chemicals (e.g., degradation products of atrazine: DEA, DEDIA, DEHA, DIA, DIHA) could be eluted after enrichment of this mixture by 5 mmol/l HCl. In the same context, Sabik [77], has shown that the use of GC techniques for analysis can influence the choice of eluant. Ethyl acetate was thus preferred, even though tens of millilitres of this solvent were necessary to elute the same pesticides from cartridges filled with large-particle-size GCB material (60–80 mesh). The desorption of compounds strongly bonded with GCB material can prove quite difficult, and sometimes involves the use

of selective eluants or an increase in the volume of whatever solvents are being used (e.g., methanol, acetonitrile or ethyl acetate). Thus, a back-flush desorption of analytes with THF solvent is reported to be more efficient than elution with methanol or acetonitrile [139,182].

Iijima et al. [24] found good correlation between elution profiles of a macroporous diatomaceous earth (MDE) column and a silica gel cartridge and the log K_{ow} values of several pesticides, including ametryn, anilazine, atrazine, cyanazine, metribuzin, prometryn, simazine and simetryn. Non-polar and slightly polar compounds (log $K_{ow}>1.1$) [e.g., ametryn (log $K_{ow}=2.4$), anilazine (log $K_{ow}=3.0$), atrazine (log $K_{ow}=2.0$), metribuzin (log $K_{ow}=1.6$), prometryn (log $K_{ow}=2.9$), and simetryn (log $K_{ow}=1.8$)] were completely eluted from the MDE column with 70 ml of hexane. By contrast, under the same conditions, cyanazine (log $K_{ow}=1.1$) and simazine (log $K_{ow}=1.6$), which are considered more polar, were eluted only at about 70%. High polar compounds (log $K_{ow}<1.1$) require a more polar solvent such as ethyl acetate for elution.

2.10. Parameters affecting solid-phase extraction

Several studies have been conducted to determine the parameters affecting pesticide extraction with SPE techniques [77,139,186,188,192–195]. Baez et al. [192] have evaluated the type of sorbent, sorbent mass, and flow-rate in the extraction process, in the sample concentration of the different compounds, and in sample volume, pH, and ionic strength [192]. They found that percent recoveries of simazine, atrazine and propazine at pH 9 were lower than those at pH 4; an increase in the ionic strength of aqueous samples led to increasing recoveries for mainly prometon and prometryn; and that neither sample volume (250–1000 ml) nor flow-rate (8–16 ml/min) factors significantly affected the recovery of most compounds.

Other studies have shown that humic and fulvic interference can be eliminated with the use of polymeric sorbents at pH 7 instead of C_{18} at pH 3 when extracting pesticides from water. This allows for the simultaneous extraction and analysis of acidic pesticides and triazines such as cyanazine, simazine and atrazine without any interference [139,186,188].

In a recent study, Sabik [77] examined the effect of several parameters on the percent recoveries of 20 pesticides, including triazines and degradation products, from SPE cartridges filled with GCB material. The author showed that parameters like the addition of sodium sulfite and sodium chloride to the sample; the acidification of Carbopack B; the interval between spike and extraction; the method of cartridge elution (forward- vs. back-flush technique); and dissolved organic material can affect percent recoveries of selected pesticides. Senseman et al. [193] have demonstrated the influence of dissolved humic acid and calcium-Montmorillinite clay on pesticide extraction efficiency in water using solid-phase extraction disks. Johnson et al. [194] have pointed out the possibility of interference from dissolved organic material in the solid-phase extraction of pesticides from water. Lastly, Choudhury et al. [195] have tested the influence of varying ionic strength, pH, methanol content, and temperature on the SPME extraction.

2.11. On-site extraction and stability of pesticides on solid-phase extraction materials

Very few studies have reported on the stability of pesticides, including triazines and degradation products, on SPE materials [118,119,196]. In addition to time and space savings, the stabilization of pesticides on these materials makes it possible to use SPE techniques for on-site extraction. Sabik et al. [119] demonstrated the stability of 20 urea and triazine herbicides, including four degradation products, on GCB material over a two-month period. Liška and Bilikova [196] studied the stability of 16 polar pesticides including triazines, carbamates, and phenylureas sorbed onto a polymer sorbent; they found that most remained stable over a seven-week period. Crescenzi et al. [118] studied the stability of 34 pesticides, including atrazine, metamitron and metribuzin, on C_{18} and GCB materials, reporting that selected triazines and triazinone remained stable on both materials during the test period (three weeks). Columns filled with XAD-2 and XAD-4 sorbents have been widely used for the on-site sampling and extraction of several pesticides from surface waters [197]. However, the extensive extraction and manipulation required of these sorbents to obtain a

clean resin is a major disadvantage. Other on-site pre-concentration techniques have been reported on, including those involving cartridges, disks, and SPMD [198]. An automated on-line SPE–LC–DAD method for on-site pesticide monitoring in surface water has also been used in the basin of the Rhine River [199].

3. Conclusion

The intensive use of pesticides results in the contamination of ground and surface waters. Several multiresidue methods have thus been developed to monitor priority pesticides, including triazines and degradation products, in these matrixes. The SPE technique has proven to be the best technique for isolating these chemicals in water. It is fast, accurate, precise, consumes little solvent, is easily adapted for field work, and does not involve costly material. The work of pesticide analysis has greatly benefited from the extensive use of this technique. Many sorbents are now available in cartridge or disk systems, including non-polar, polar, ionic, immunosorbent and MIP. Automated methods using SPE techniques in conjunction with various sorbents are now gaining considerable acceptance, leading to smaller sample volumes (a few ml) and reaching lower DLs (ng/l). With the use of SPE techniques, a large number of priority pesticides, including triazines and degradation products, are now being easily and efficiently monitored using lower quantities of water samples and less toxic solvent.

4. Nomenclature

ADHT	Aminodihydroxy-*s*-triazine
AEHT	6-Amino-4-ethylamino-2-hydroxy-*s*-triazine
AIHT	6-Amino-4-isopropylamino -2-hydroxy-*s*-triazine
CAADT	6-Amino-4-acetamido-2-chloro-*s*-triazine
CADEAT	4-Acetamido-2-chloro-6-ethylamino-*s*-triazine
CADIT	4-Acetamido-2-chloro-6-isopropylamino-*s*-triazine
CAEAT	6-Amino-2-chloro-4-ethylamino-*s*-triazine
CAHT	6-Amino-2-chloro-4-hydroxy-*s*-triazine
CAIPT	6-Amino-2-chloro-4-isopropylamino-*s*-triazine
CCL	EPA contaminant candidate list
CDADT	2-Chloro-4,6-diacetamido-*s*-triazine
CDHT	2-Chloro-4,6-dihydroxy-*s*-triazine
CW	Carbowax
CX	Carboxen
DAD	Diode array detection
DADKM	Deaminateddiketometribuzin
DAHT	Diaminohydroxy-*s*-triazine
DAM	Deaminatedmetribuzin
DEA	Deethylatrazine
DEC	Deethylcyanazine
DEHA	Deethylhydroxyatrazine
DET	Deethylterbutylazine
DIA	Deisopropylatrazine
DIHA	Deisopropylhydroxyatrazine
DKM	Diketometribuzin
DL	Detection limit
DP-H1	3-(4-hydroxycyclohexyl)-6-9-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione
DP-H2	3-cyclohexyl-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione
DP-H3	3-(4-hydroxycyclohexyl)-6-(methylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione
DP-H4	3-cyclohexyl-1-methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione
DP-H5	3-(4-hydroxycyclohexyl)-1-methyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione
DP-H6	3-(*trans*-2-hydroxycyclohexyl)-6-9-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione
DP-H7	3-(4-cyclohexanone)-6-9-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)- dione
DVB	Divinylbenzene
ECD	Electron-capture detection
EL	Environmental level
EDHT	6-Ethylamino-2,4-dihydroxy-*s*-triazine
EPA	US Environmental Protection Agency
EU	European Union
FEPA	Food and Environmental Protection Act
FQPA	Food Quality Protection Act

GAC	Granular activated carbon
GC	Gas chromatography
GCB	Graphitized carbon black
GW	Ground water
HA	Hydroxyatrazine
HAL	Health advisory levels
HP	Hydroxypropazine
HS	Hydroxysimazine
HT	Hydroxyterbutylazine
K_d	Solid-water distribution ratio
K_{oc}	Soil organic carbon sorption coefficient
K_{ow}	Octanol–water partition coefficient
LC	Liquid chromatography
LLE	Liquid–liquid extraction
MAA	Methyl methacrylic acid
MCL	Maximum contaminant level
MIP	Molecularly-imprinted polymer
MS	Mass spectrometry
MMA	Methyl methacrylate
NPD	Nitrogen-phosphorus detection
NVP	*N*-Vinyl-a-pyrrolidone
PA	Polyacrylate
PDMS	Polydimethylsiloxane
PTFE	Poly(tetrafluoroethylene)
R	Recovery
S	Silica
SAX	Strong anion exchanger
SCX	Strong cation exchanger
SFE	Supercritical fluid extraction
SIM	Selected ion monitoring
SLM	Supported liquid membrane
SPE	Solid-phase extraction
SPI	Septum programmable injector
SPMD	Semi-permeable membrane device
SPME	Solid-phase microextraction
SW	Surface water
THF	Tetrahydrofuran
THT	Trihydroxy-*s*-triazine

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