Review Article

Pesticides in water and the performance of the liquid-phase microextraction based techniques. A review

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ABSTRACT

The control of pesticides in surface, drinking and groundwater is nowadays a real necessity. In the European Community, their concentration must comply with the established parametric and environmental quality standards (EQSs). Regarding the new legislation, this article updates the information concerning the monitoring of pesticides and the technical specifications for their measurement in water samples where ultra-sensitive analytical methods are required. For some compounds, like pesticides, there is still a need to improve the performance of the existing methods. High sensitive techniques like gas chromatography tandem mass spectrometry (GC–MS/MS) and liquid chromatography coupled with mass spectrometry (LC–MS) have been developed. However, for most of the substances present at trace and ultra-trace levels the extraction and preconcentration steps are so far essential for their detection. Advances at a micro scale have been made and different types of microextractions are being developed. Liquid-phase microextraction (LPME) is an example. The study of this technique has increased in the last years and some innovations have been recently reported for pesticides water analysis. This article reviews the new developed LPME-based techniques and compares its performance with the analytical specifications established for pesticides water monitoring. The results show that LPME-based techniques can be a promising tool to improve the nowadays performance of methods used in pesticides water control.

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Contents

1. Introduction

It is well known that pesticides have the potential to prevent and control harmful organisms being a powerful tool to agricultural problems. It has been estimated that around one-third of the crop production would be lost if chemical substances were not applied against pests [1]. Pesticides have also been used in non-agricultural sectors such as wood preservation, disinfection or household uses. In spite of the several advantages, some pesticides can be toxic to humans and animals and their continuous application is causing serious problems of environmental and food contamination. The legislation in this area covers not only the conditions concerning the placing of pesticides on the market but also the levels of pesticide residues allowed in waters and food as well as the actions needed to promote sustainable use of pesticides [2–7]. In the European Community (EC), Directive 2000/60/EC [2] established a framework for the protection of waters. This Water Framework Directive (WFD) aims to reduce and to eliminate the presence of substances in the aquatic environment that have been considered by the Commission as toxic, persistent and liable to bio-accumulate. Such substances, named as priority substances and priority hazardous substances, are listed in Annex X of the WFD together with its permissible limits or environmental quality standards (EQSs) [2,8]. Not only the pesticides that are classified as priority substances are subject of control, other pesticides that are likely to be present in drinking and groundwater have also to be analyzed. The state of art in monitoring the priority substances in waters has been reviewed [9,10]. This article updates the information regarding the screening of pesticides in surface, drinking and groundwater. The data reviewed shows that ultra-sensitive analytical methods are mandatory since the water tolerable limits for most of the pesticides are in the low levels of parts per billion and in some cases parts per trillion [8,11–13]. To be detectable and quantified, the substances present at trace levels must be extracted and concentrated. Although environmental unfriendly, liquid–liquid extraction (LLE) is a classic preconcentration technique that has long been used in some standard analytical methods developed for routine analysis of pesticides [1,9,14–23]. Good recoveries and precision have been achieved with such methods. However, as pointed out by Lepom et al. [9] the existing standards for the analysis of some priority substances, where some pesticides are included, are not sensitive enough to conduct the actual compliance monitoring. The application of high sensitive analytical systems like gas chromatography tandem mass spectrometry (GC–MS/MS) and liquid chromatography coupled with mass spectrometry (LC–MS) has been a powerful option, nevertheless, a preconcentration of the compounds present mostly at trace levels prior to analysis is absolutely necessary. High recoveries and sample enrichments of the extracted substances have been obtained with new solvent microextraction techniques. Liquid-phase microextraction (LPME), solid-phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are examples. LPME is simple, rapid and inexpensive when compared with other extraction techniques. In addition, it can be applied to a wide range of compounds including pesticides. It is highly compatible with chromatographic methods and improvements have been made after its introduction in the mid-to-late 1990s [24–26]. LPME techniques seem to be a promising tool for the development of very sensitive standard procedures since the associated limits of detection (LOD) of the chromatographic methods can be at the levels of nanograms per liter (ng/L). Thus, the aim of this study is to review the recently innovations of liquid-phase microextraction (LPME) techniques applied to chromatographic water pesticides analysis and to compare its results with the performance method criteria established for water monitoring status [2,11–13]. Emphasis will be given to the LOD of pesticides classified as priority substances.

2. Control of pesticides and the performance criteria for their measurement

The presence of pesticides in the environment it is a reality and the control and monitoring of contaminants a matter of health protection. In the last decades there has been an enormous effort by companies and authorities to study and collect all possible information concerning the safe introduction of pesticides in the market and their release to the environment [1,27–29]. This sort of information has been valuable for monitoring water policy purposes [2,8,29,30]. Under the WFD, specific measures must be adopted against pollution of surface water and groundwater to attain "good water status" by the end of 2015. To reach this main objective, ecological and chemical parameters must be met and pollution sources controlled [2,11,31–45]. The presence of some substances classified as priority substances must be progressively reduced while for some other substances, which fall under the definition of priority hazardous substances, the occurrence in the aquatic environment must be eliminated. From the total of 33 priority substances listed by WFD, 11 were classified as priority hazardous substances [8]. Table 1 summarizes the pesticides that must be controlled in surface waters together with their EQSs. Some of them were not listed as priority substances, however, their monitoring was maintained since they fall under the scope of other Directives [8]. For health reasons, drinking and groundwater are also subject of control [2,11,12]. The list of individual pesticides to be monitored in those types of water is published every year by the competent authorities of each Member State. Only those pesticides which are likely to be present in a given water supply need to be supervised. For groundwater, and while a revision of the Drinking Water Directive is being prepared, the limits set for both type of waters are 0.5 µg/L for the sum of all pesticides and 0.1 µg/L for each compound [11,12,46,47]. Aldrin, dieldrin, heptachlor and the metabolite heptachlor epoxide are an exception. The limit is 0.03 µg/L [11]. These substances are highly toxic to humans. For aldrin and dieldrin the established EQS are even lower than the health safe limit. Heptachlor is not among the list of priority substances but is listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), among other pesticides, that are being restricted and will be banned in the next years [48–50]. To meet all the requirements of a good water chemical status, communities must have means of measure the undesirable substances in water samples. Rapid, sensitive and rigorous analytical methods are thus a valuable tool for quality assurance of aquatic ecosystems. To be comparable, the results must be precise, accurate and in agreement with official technical specifications for chemical analysis and monitoring of water status [13]. Even though the methods must be validated and well documented in accordance with EN/ISO 17025 or any equivalent standard, the analytical methods applied to quantify the priority substances must follow the recently established minimum performance criteria [13,51]. For a method to be approved, the limits of quantification (LOQ) must be equal or below a value of 30% of the

Table 1

Environmental quality standards (EQS) for pesticides in surface waters, their mandatory LOD and the standard methods applied (AA—annual average concentration or the arithmetic mean of the concentration measured at different times during the year for protection against long-term exposure; MAC—maximum allowable concentration at any representative monitoring point within the water body for protection against short-term exposure; n.a—not applicable) [8–13,49,50].

Priority substance	CAS[a] number	AA-EQS inland surface water (µg/L)	AA-EQS other surface water (µg/L)	MAC-EQS inland surface water (µg/L)	MAC-EQS other surface water (µg/L)	LOQ[b] (µg/L)	Uncertainty (±µg/L)	POPs	Standard methods
Alachlor Chloroacetanilide—Herbicide	15972-60-8	0.3	0.3	0.7	0.7	0.09	0.15	–	EN ISO 6468:1997 ISO1370:2000 EPA 8081B:2000
Atrazine Triazine—Herbicide	1912-24-9	0.6	0.6	2.0	2.0	0.18	0.3	–	EN ISO 1369:1997 EN ISO 0695:2000 ISO 11370:2000 EPA 527:2005 EPA 8141A:1994
Chlorofenvinphos Organophosphours—Insecticide	470-90-6	0.1	0.1	0.3	0.3	0.03	0.05	–	EN ISO 12918:2000 ISO 11370:2000 EPA 8270D:1998
Chloropyrifos Organophosphours—Insecticide	2921-88-2	0.03	0.03	0.1	0.1	0.009	0.015	–	EN ISO 12918:2000 EPA 257:2005 EPA 8141A:1994
Cyclodiene—Insecticides: Aldrin[c]	309-00-2	$\sum = 0.01$	$\sum = 0.005$	n.a	n.a	0.0015	0.0025	Yes	EN ISO 6468:1997 EPA 8081B:2000 EPA 8270D:1998 EPA 525.2: 1995
Dieldrin[c]	60-57-1							Yes	EN ISO 6468:1997 EPA 8081B:2000 EPA 8270D:1998
Endrin[c]	72-20-8							Yes	EN ISO 6468:1997 EPA 8081B:2000 EPA 8270D:1998
Isodrin[c]	465-73-6							–	EPA 525.2: 1995 EPA 8081B:2000 EPA 8270D:1998
DDT Total[c] Organochloride—Insecticide	n.a	0.025	0.025	n.a	n.a	0.0075	0.01	Yes	EN ISO 6468:1996 EPA 8081B:2000
p,p′-DDT[c] Organochloride—Insecticide	50-29-3	0.01	0.01	n.a	n.a	0.003	0.005	Yes	EN ISO 11369:1997 EPA 8325:1996 EPA 525.2: 1995
Diuron Urea—Herbicide	330-54-1	0.2	0.2	1.8	1.8	0.06	0.1	–	EN ISO 11369:1997 EPA 8325:1996
Endosulfan[d] Organochloride—Insecticide	115-29-7	0.005	0.0005	0.01	0.004	0.00015	0.00015	Nominated for addition	EN ISO 6468:1997 EPA 8081B:2000 EPA 525.2: 1995
Hexachlorobenzene[d] Organochloride—Fungicide	118-74-1	0.01	0.01	0.05	0.05	0.03	0.005	Yes	EN ISO 6468:1997 EPA 8270:1998 EPA 8081B:2000 EPA 8270:1998
Hexachlorobutadiene[d] Fungicide	87-68-3	0.1	0.1	0.6	0.6	0.03	0.005	–	EN ISO 10301:1998 EPA 8270:1998 EPA 8021B:1996
Hexachlorocyclohexane[d] Organochloride insecticide	608-73-1	0.02	0.002	0.04	0.04	0.0006	0.001	Yes	EN ISO 6468:1997 PA 8081B:2000 EPA 8270:1998
Isoproturon Urea—Herbicide	34123-59-6	0.3	0.3	1.0	1.0	0.09	0.15	–	EN ISO 11369:1997
Pentachlorophenol Insecticide, fungicide and herbicide	87-86-5	0.4	0.4	1	1	0.12	0.2	–	EN ISO 12673:1999 ISO 8165-1:1992 ISO 8165-2:1999 EPA 8270:1998
Simazine Triazine—Herbicide	122-34-9	1	1	4	4	0.3	0.50	–	EN ISO 10695:2000 ISO 11370:2000 EPA 8141A:1994
Trifluralin 2,6-dinitroanilide—Herbicide	1582-09-8	0.03	0.03	n.a	n.a	0.009	0.15	Yes	EN ISO 10695:2000 ISO 11370:2000 EPA 8081B:2000 EPA 8270:1998

DDT total comprises the sum of the isomers 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (CAS number 50-29-3; EU number 200-024-3); 1,1,1-trichloro-2-(o-chlorophenyl)-2-(p-chlorophenyl)ethane (CAS number 789-02-6; EU number 212-332-5); 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (CAS number 72-55-9; EU number 200-784-6); and 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (CAS number 72-54-8; EU number 200-783-0).

The term inland surface waters includes rivers, lakes and related artificial heavily modified water bodies where other surface waters include the transitional and coastal waters. The words 'not applicable' in the MAC-EQS column, means that the established AA-EQS values are also considered protective against short-term pollution.

[a] CAS—Chemical abstract service.

[b] LOQ—limit of quantification = 30% of minimum EQS value for each pesticide. POPs—persistent organic pollutants.

[c] This substance is not a priority substance but one of other pollutants for which the EQS are identical to those laid down in the legislation that applied prior to 13 January 2009 (entry into force of Directive 2008/105/EC).

[d] Priority hazardous substance.

relevant EQS, as summarized in Table 1, and the uncertainty of the results must be 50% or below the estimated EQS with a coverage factor of 2 ($k = 2$) corresponding to a level of confidence of approximately 95%. For drinking waters, the performance criterion is based on the limit of detection (LOD). This limit must be equal or lower than a value of 25% of the tolerable limit which means that for individual pesticides the LOD should be 25 ng/L [11]. In this study especially attention will be given to the LOD of methods. However, enforcements should be made at the scientific community to publish not only the LOD but also the LOQ and the uncertainty of methods since the established performance criteria for the analysis of the priority substances is essentially based on such parameters.

3. The analytical performance of the LPME-based techniques

The development of precise, accurate and ultra-sensitive analytical methods, associated to simplicity and celerity, is still a hard task to undertake. In method development several parameters must be tested and optimized and numerous difficulties can be found especially in the sample preparation step. Recently, Dömötörová and Matisováá [52] made a review where the particularities and difficulties of pesticide analysis in different matrixes by chromatographic processes are mentioned. The choice of the solvent is pointed out as an important parameter when liquid–liquid extraction (LLE) is applied to sample preparation. LLE is a classic preconcentration technique that has been applied to a wide range of compounds [14,15,23,53–55]. To overcome the shortcomings of LLE and to have simple, fast and green procedures microextraction techniques are being developed [26,56]. Liquid-phase microextraction (LPME) is a simple and low cost example. In LLE the analytes are extracted from an aqueous solution or donor phase into an organic solvent or acceptor phase. In a LPME the solvent can be a single microdrop suspended from a needle or it can be present in the pores of a hydrophobic membrane or separated from the donor phase by a membrane interface [57–59]. The dispersion of very fine droplets of organic solvents into the aqueous phase in a ternary solvent component system is another new option [26,57]. As illustrated in Fig. 1, the LPME processes are generally divided into three main groups: a) single-drop microextraction (SDME); b) membrane liquid-phase microextraction (MLPME) and c) dispersive liquid–liquid microextraction (DLLME). Their differences rely in the way the solvent contacts the aqueous phase. As for solid microextractions, like SPME and SBSE, the analyses can be automated or not and can be carried out by direct immersion or by headspace in a static or dynamic mode in conjunction with other extractions techniques such as solid-phase extraction (SPE) and supercritical fluid extraction (SFE). Based on these several characteristics many different configurations have been developed and some of them will be focused below. More details concerning the extraction principles and the historical developments

of LPME can be found in the recently review of Sarafraz-Yazdi and Amiri [57]. The chemical reactions involved in LPME and the developments of SDME have been pointed out by Li Xu's group [56,60]. Moreover, the developments of hollow-fiber liquid-phase microextraction (HF-LPME) and its application in the analysis of environmental and biological samples are well described by the teams of Rasmussen [61] and Lee [62], respectively. The applications and progresses of DLLME can be found in the reviews of Ojeda [63], Rezaee [26], and Zang et al. [64].

3.1. Single-drop and membrane liquid-phase microextractions

Among the LPME-based techniques, SDME and MLPME were the first ones to be developed. Their differences relay in the way the acceptor phase is supported. In SDME the organic solvent contacts the aqueous phase through a suspended drop at the tip of a microsyringe. In MLPME the solvent can be present in the porosity of a membrane (HF-LPME) or it can be separated from the aqueous phase by a dense polymeric membrane (MASE). In 2007, Lambropoulou and Albanis [59] made a review of the application of SDME and MLPME to pesticide residue analysis. The optimization of LPME-based techniques as well as the advantages and disadvantages were described. From their study, the authors conclude that the LPME techniques have found many applications, the majority in environmental analysis. The review shows that a wide range of non-polar to moderate polar pesticides such as carbamates, chloroacetamide, chloroacetanilide, organochloride, organophosphorus, phenolic compounds, phenoxy acids, thiocarbamates and triazines have been extracted with SDME and MLPME from different matrices (water, soil, and food) and analyzed mainly by gas chromatography (GC) with mass spectrometry, electron capture or flame photometric detectors (GC–MS, GC–ECD, GC–FPD). High performance liquid chromatography with UV and MS detectors (HPLC–UV) has also been used. The results also illustrate that for most of the non-priority pesticides analyzed in water samples the performance of the methods is near or in agreement with the published technical specifications. Since this last review new studies have been published. An example is the application of SDME by Pinheiro and Andrade [65] in the analysis of organophosphorus and pyrethroids pesticides in water samples by GC–FID (flame ionization detector). An extraction time of 30 min with 1 μL of toluene was sufficiently to achieve recoveries between 73 and 104%, however, the LOD of the method is in the range of 300–3000 ng/L higher than the values acceptable for drinking water. A mixture of organophosphorus pesticides and carbamates was also analyzed by SDME coupled with GC–MS and GC–NPD [66,67]. Although the methods performance does not fulfill the European technical recommendations, improvements were made in the detection by MS especially for malathion (organophosphate pesticide). The same SDME technique was used by the group of Cortada [68] for the analysis of eighteen organochloride pesticides by GC–MS with selective ion monitoring (SIM) achieving limits of detection between 22 and 101 ng/L for extraction times of 37 min with 2 μL of toluene. These limits are well under the levels of sensitivity required by EPA methods. However, for the priority pesticides analyzed like aldrin, dieldrin, endosulfan, endrin, hexachlorocyclohexane (HCH) and p,p'-DDT, the LOD obtained do not comply with the statements of WFD. In the study of Wang et al. [69] a fast run time was obtained in the determination of chlorophenols by SDME–GC–MS. During the preconcentration step, derivatization and extraction took place simultaneously. High extraction efficiency was found with a mixture of toluene and hexane (1:1). The derivatization was done with 5% of N-(tert-butyldimethylsilyl)-N-methyl- trifluoroacetamide (MTBSTFA). Good recoveries (87.9–108.4%) and good precision (2.63–9.39%) together with low LOD were achieved (1.1–9.7 ng/L). For pentachlorophenol a LOD of 9.7 ng/L and a LOQ of 32.3 ng/L are considered a successful result. Comparing with other procedures, slightly lower LOD and LOQ were obtained under the
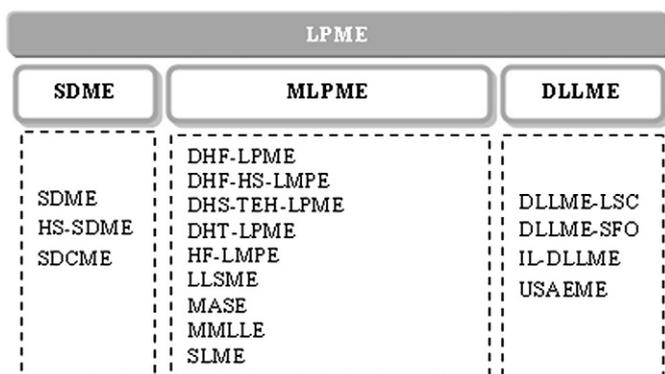
Fig. 1. Different configurations of LPME-based techniques applied to pesticide water analysis [26,57–61].

The figure shows a hierarchy chart. Top box: LPME. Below it three boxes: SDME, MLPME, DLLME.

SDME:
- SDME
- HS-SDME
- SDCME

MLPME:
- DHF-LPME
- DHF-HS-LMPE
- DHS-TEH-LPME
- DHT-LPME
- HF-LMPE
- LLSME
- MASE
- MMLLE
- SLME

DLLME:
- DLLME-LSC
- DLLME-SFO
- IL-DLLME
- USAEME

same conditions when solid-phase microextraction was used [69]. A less sensitive method was developed by Saraji and Bakhshi [70] when pentachlorophenol was analyzed by GC–MS after extraction with hexyl acetate and derivatization with *N*,*O*-bis(trimethylsilyl) acetamide.

SDME is highly compatible with GC but with LC the sensitivity decreases as a consequence of the incompatibility of the organic solvents with the LC mobile phase, where an extra step is needed for solvent evaporation and redissolution, and also as a consequence of the small volumes used. To overcome these apparent difficulties a new method based on the application of coacervates as extraction solvent of chlorophenols was developed by the research group of F. J. López-Jiménez [71]. Coacervation is defined by the IUPAC as the separation of colloidal systems into two liquid phases (one rich in colloid, i.e., the coacervate, and the other containing little colloid) [72]. Coacervates are thus colloid-rich liquids and seem to have unique properties to be adopted as solvents in SDME prior to LC analysis since they are non-volatile, which will restrict their evaporation, and can be compatible with LC mobile phases and with UV and MS detectors. Moreover, a larger volume drop can be used without disruption during the stirring of the solutions. In the work of López-Jiménez [71] the application of decanoic acid vesicle-based coacervates for the analysis of pentachlorophenol by LC–UV the derivatization step was eliminated which can be an advantage. In spite of the innovations, enforcements are still necessary to improve the sensitivity of the method. It is possible that the research in this area and their application to the analysis of other class of pesticides will increase in the next few years since new processes of coacervation are being developed for the extraction of a wide range of compounds with different polarities which is still a drawback of the LPME-based techniques [72]. In spite of the several advantages of SDME like simplicity, low cost and speediness of the runs, the application of this technique to routine analysis is not yet a reality. Progresses in the automation have been made, however, the high cost involved probably will make the technique not widely accessible [60]. Meanwhile, the application of membrane liquid-phase microextractions is growing. In the recent times, organochloride pesticides were analyzed by Chen et al. [73] using a headspace HF-LPME technique followed by GC–MS. The compounds were extracted with 1-hexanol by dynamic hook-type liquid-phase microextraction (DHT-LPME) where a long polypropylene hollow fiber, hook shape, was suspended at the top of the sample vial. With this type of configuration it was possible to achieve a higher contact solvent surface for enrichment of the compounds. The method was optimized and validated. The recoveries were found to be higher than 82%, the RSD was between 6.5 and 14% and the LOD of 2–5 ng/L were near the recommended European values. Dieldrin, endosulfan, heptachlor, *o*,*p*′-DDT and *p*,*p*′-DDE were the substances analyzed. Based on this study and also on their experience in the application of a solvent cooling system to decrease the solvent loss during extraction of pesticides with hollow fibers, the same research group developed a method where the same organochloride pesticides, plus aldrin, were extracted with a dynamic headspace time-extended helix liquid-phase microextraction (DHS-TEH-LPME) prior to analysis by GC–MS/MS [74,75]. A change in extracting solvent from 1-henaxol to 1-octanol, an increase in fiber length and a decrease in the temperature of the organic phase has improved significantly the LOD of the analytes, except for endosulfan and dieldrin. This type of procedure provided high enrichment factors along with excellent sample clean-up, however, as mentioned by the authors, the greatest weakness of the method was the unfeasibility to be fully automated and the poor precision obtained. HF-LPME was also applied to the analysis of carbamate pesticides by the researchers Hylton [76] and Yang et al. [77]. The results obtained in both studies, with a HPLC–UV system and without derivatization of the compounds, showed that the LOD are well comparable to the LOD of EPA methods which can be an indication that HF-LPME is a promising tool

for routinely pesticides water analysis. To avoid the use of expensive microsyringes, the group of Berhanu [78] developed a new design of equilibrium in HF-LPME for the analysis of three organophosphorus pesticides (diazinon, chloropyrifos, and fenthion). In this new design the hollow fiber impregnated with *n*-undecane was connected to a copper wire and, at the end of the extraction time, the hollow fiber was removed with the help of the wire and soaked in ethyl acetate prior to GC–MS analysis. This type of configuration was found to be simple and of low cost. The LOD in reagent water using the GC–MS in the selected ion monitoring (SIM) were in the range of 15–80 ng/L. In spite of the good linearity and repeatability, for the priority substance chloropyrifos, a LOD of 15 ng/L does not meet the established performance criteria of the European legislation. In the study of Sanagi and Abidin [79] one triazole fungicide (hexaconazole) and two organophosphate insecticides (quinalphos and methidathion) were successfully analyzed by GC–ECD using toluene as HF-LPME solvent. The same insecticides quinalphos and methidation were investigated by Raharjo et al. [80]. The substitution of toluene by isooctanol and the separation and detection by HPLC–UV led to a considerably increase of the LOD. The same results were observed in the other study of Sanagi et al. [81] when a nylon cone shaped membrane was used to extract the organophosphates with hexane prior to their analysis by micro-LC–UV. Recently, Trtić-Petrović provided a different method for the analysis of sixteen pesticides with different polarities by HPLC–MS/MS with eletrospray ionization [82]. In this study, some innovations were made relatively to the organic acceptor solvent. Initially, the compounds were extracted with n-hexyl ether but, to increase the extractions of the more polar pesticides the addition of a binary mixture of other solvents like tri-*n*-octylphosphine oxide (TOPO), dichloromethane, di(2-ethylhexyl) phosphoric acid (DEHPA) and tri-*n*-butyl phosphate (TBP) was made. The results show that better extraction efficiency was achieved when a solvent mixture of 10% of TOPO and 10% of TBP diluted in *n*-hexyl ether was used. For ten of the sixteen pesticides analyzed, the LOD ranged from 26 to 237 ng/L and the LOQ to 94 ng/L to 793 ng/L. Good linearity and precision, with RSD from 0.8 to 11.8%, was achieved for these ten compounds extracted at pH 8.0. Atrazine and diuron had an extraction efficiency of more than 80%. For diuron the LOQ is above the recommended value of 60 ng/L. Even though for the 6 more polar compounds the method performance was not validated, since the lowest concentration that could be analyzed was above the legislated value, enforcements are being made to overcome the difficulties found in the simultaneous extraction of pesticides having different chemical properties by LPME techniques.

The combination of solid-phase microextraction with liquid-phase microextraction has been an advance in HF-LPME especially for complex matrices. Hu et al. [83] developed a novel liquid–liquid–solid microextraction (LLSME) technique based on membrane molecular imprinted polymer microfiber to extract and concentrate the triazines which were further analyzed by HPLC–UV. In this technique, a membrane molecular imprinted polymer (MIP) coated silica microfiber was protected with a toluene filled polypropylene hollow-fiber membrane. With this type of configuration the analytes were first extracted to the organic phase and then adsorbed on the MIP coated silica microfiber. After the extraction the hollow membrane was removed and the analytes were desorbed from the microfiber by the usual procedure of SPME–HPLC commercial devices. Good precision, low LOD between 6 and 20 ng/L and acceptable recoveries (81.7–108.7%) in sludge water were obtained. This innovation appears to be a promising analytical tool for the monitoring of triazines in complex environmental waters since the target analytes can be selective separated from complex and dirty samples.

Membrane-assisted solvent extraction (MASE) has been another type of MPLME applied to pesticide analysis [59]. This technique was introduced in 2001 by Hauser and Popp [84] for the extraction of organochloride compounds in combination with large volume

injection (LVI) gas chromatography electron capture detection (LVI–GC–ECD). In this study the use of a nonporous membrane was preferred to exclude any traces of water in the extracting solvent (heptane) which would adversely affected the injection system (LVI). The same research group worked on the extension of MASE to other environmental contaminates and developed a multiresidue/multi-class method for the analysis by LVI–GC–MS of 46 pesticides (30 organochlorides, 9 organophosphorous and 7 triazines) [85] extracted with 1 mL of cyclohexane. After the optimization of the extraction and detection conditions of the respective class of compounds, the fully automated MASE presented good precision with RSD less than 5% for organochloride and between 7 and 15% for organophosphorous and triazines. The LOD were in the range of 2–10 ng/L. Dimethoate was an exception with a RSD of 24% and a LOD of 50 ng/L. For the most polar and water soluble compounds LLE was superior in terms of recoveries. Recently, van Pinxteren et al. [86] applied the same extraction technique for the analysis of 10 pesticides from different classes by HPLC–MS/MS using toluene as the acceptor phase. To compare the results, the compounds were extracted by the traditional SPE. Good precision, established by a RSD of 7 to 13%, was obtained with both extraction techniques. Acceptable recoveries (71–105%) were found with MASE. For the priority substances like atrazine, diuron, isoproturon and simazine a better sensitivity was achieved with MASE in compliance with the mandatory limits. For more volatile compounds like pentachlorophenol the technique is not the best option [87]. This technique shows potential to be a good alternative to the conventional off-line SPE for the analysis of low to medium polar compounds. As referred by the authors, the application of MASE to more polar compounds is still limited due to the non-polar character of the membranes. Another disadvantage can be the time of extractions which is higher when compared to other liquid-phase microextraction techniques. To the best of our knowledge no additional innovations were found with MASE in the field of pesticides water analysis. This type of technique seems to be more applied to very complex matrices like soils [59]. Anyway, the application of MASE will probably increase with the development of new suitable membranes especially for the extraction of more polar compounds. From the studies reviewed herein it is clear that the innovations in the SDME and MLPME techniques are growing and their application in the analysis of non-priority pesticides have been successful evolved. What concern the priority pesticides MLPME seems to be a promising preconcentration technique. As summarized in Table 2, for aldrin, dieldrin, endrin, isodrin, chlorofenviphos, DDT and HCH, improvements should be made to increase the sensitivity of the methods. For endosulfan, the results were still substandard level. In the case of hexachlorobutadiene (HCB) and trifluralin no studies were found with reference to SDME or MLPME. For alachlor, atrazine, chloropyrifos, diuron, isoproturon and simazine the performance of the methods seem to fit the technical specifications for water pesticides monitoring.

3.2. Dispersive liquid–liquid microextraction

Dispersive liquid–liquid microextraction (DLLME) is another recent technique that has been successfully applied to the extraction and concentration of a wide variety of pesticides from water samples. DLLME was developed in 2006 by Rezaee and co-workers [26,89] and is based on a ternary solvent component system involving an aqueous phase, a non-polar water immiscible solvent (extracting solvent) and a polar water miscible solvent (disperser solvent). In this technique, fine droplets of the extracting solvent are dispersed into the aqueous phase when an appropriate mixture of both solvents is injected into water samples. Following mixing a cloudy solution is formed and after centrifugation or solidification after cooling, the fine particles of the extracting solvent containing the target analytes are separated from the aqueous phase. High recoveries and high enrichment factors can

be reached and the extraction time can be relatively short. The mixing of the three components ensures equilibration within a few seconds due to the large interface between the multiple fine extractor droplets and the aqueous solution. DLLME can be regarded as a multiple drop microextraction. Water insoluble and high density extracting solvents have been mostly used. Chlorobenzene, chloroform, carbon disulfide and carbon tetrachloride are some examples [26]. Acetone, acetonitrile, methanol and ethanol have been the main options as dispersive solvents. DLLME can be coupled with GC, HPLC and also with atomic absorption spectrometry (AAS) [26]. The non-selective characteristic of the extraction solvents can be sometimes a disadvantage. To overcome this difficulty and to eliminate the use of dispersive solvents, making the technique more environmental friendly, new alternatives are being developed like the use of ionic liquids (IL) and ultrasonic radiation. Due to its simplicity and low extraction time, DLLME is becoming an attractive preconcentration technique in pesticide water analysis. This extraction technique has been efficiently applied by Fattahi et. al [90] in the analysis of chlorophenols by GC–ECD. As before, derivatization and extraction were done simultaneously. Within a few seconds both steps were complete and after centrifugation the analytes were prepared to be injected into the GC. For pentachlorophenol recoveries of 98.7–101.3%, relative standard deviations (RSD) of 2.1–2.4% and a LOD of 10 ng/L were achieved. Equivalent results were obtained by Wang et al. [69] in the analysis by SDME–GC–MS. Since the recommended LOQ for pentachlorophenol is 120 ng/L, this means that the methods developed can be a competitive option to the standard methods applied for such classes of compounds that use the classic non-green LLE such as EN ISO 12673:1998 [91] or EPA 8270D:1998 [92]. Another group of pesticides, with LOD between 46 and 120 ng/L, analyzed by DLLME with GC–MS was the triazine herbicides [93]. Atrazine was also investigated by Zhou et al. [94] using a less sensitive method based on DLLME–HPLC–UV. For this class of compounds better sensitivity was achieved in the study of Hu et al. [81] when a membrane liquid-phase microextraction (MLPME) was used in the preconcentration step. Zhou et al. [95] also developed a method based on the same extraction technique to quantify the famous banned organochloride insecticide (p,p'-DDT) and its main metabolites (p,p'-DDE, p,p'-DDD) by HPLC–UV [92]. In spite of the acceptable values for the method repeatability and extraction efficiency the LOD are above the EQSs. The authors compared their method with other methods based on solid (SPE and SPME) as well as on liquid-phase microextractions (SDME and HF-LPME) and found out that for the compounds under investigation, the most sensitive was the SPE–HPLC–UV method (LOD of 4–13 ng/L). Supported on their experience on SDME, the group of Cortada [68,96] investigated the performance of the analysis of eighteen organochloride pesticides by DLLME–GC–MS. Considerable improvements were made in the method sensitivity when DLLME was applied relatively to SDME. The LOD of the compounds was more close to the LOD imposed by recent legislation. For DDT and its metabolites the DLLME–GC–MS method performance is comparable with the one developed by Zhou et al. [97] where SPE–HPLC–UV was used to quantify the same compounds. Like chlorophenols, organochloride and triazine herbicides, carbamates were also extracted by DLLME. In the study of Liu et al. [98] the pesticides were extracted with chloroform using acetonitrile as dispersive solvent. In spite of the good recoveries, linearity and precision, the LOD of the DLLME–HPLC–DAD method was in the μg/L range. A slightly different method was used by He et al. [99] in the analysis of the same class of pesticides. Similar outcomes were obtained when chlorobenzene was used as extracting solvent. Caldas et al. [100] analyzed by DLLME coupled with LC–ESI-MS/MS three different classes of pesticides, namely, the carbamate carbofuran, clomazone and tebuconazole. Acceptable recoveries (62.7–120%) associated to good precision (RSD between 1.9–9.1%) and low LOD (20 ng/L) meet the requirements for their determination in water samples. In the work of Fu et al. [101] the use of DLLME with HPLC–

FLD (fluorescence detector) was successfully applied in the simultaneous analysis of one carbamate pesticide (carbaryl) and one organophosphorous insecticide (triazophos) in waters and fruit juices. Good precision and recoveries of 80–114% and LOD ranging from 12.3 to 16.0 ng/L were well achieved. In the study of Tsai and Huang [102] a new adaptation of the DLLME was investigated. Dispersive liquid–liquid microextraction with little solvent consumptions (DLLME-LSC) was applied to the extraction of priority substances aldrin, dieldrin, endosulfan and heptachlor from river, tap and seawater. The separation and detection were done by GC–MS and the results were acceptable for river and tap water. A high enrichment factor and high recoveries (90.5–109.4%) were achieved in the extraction step of the compounds using as extraction solvent a mixture of *tert*-butyl methyl ether and tetrachloroethylene (6:4). Associated to these results are good repeatability and sensitivity (LOD of 0.4–2.5 ng/L) which makes the method a promising for routine analysis. Another DLLME configuration, named partitioned dispersive liquid–liquid microextraction (PDLLME), was studied by Chou et al. [103] in the analysis of the phenylurea herbicides by HPLC–UV. Although the authors agree that in PDLLME the extraction efficiency of polar compounds seems to increase, since the polar compounds, depending on their partition coefficients, can be extracted into the dispersive solvent (tetrahydrofuran) as well as into the extracting solvent (dichloromethane), the sensitivity of the method is still beyond the desirable European values. Better results were obtained in the work of Saraji and Tansazan [104], especially for linuron, when the conventional DLLME was applied using acetone and carbon disulfide as dispersive and extracting solvent, respectively.

An innovative configuration of DLLME based on ultrasound-assisted emulsification-microextraction (USAEME) has been developed by Regueiro et al. [105] for the analysis of emergent contaminates and pesticides in environmental waters by GC–MS. Musk fragrances, phthalate esters and lindane (γ-HCH) were the compounds under investigation. With USAEME the mass transfer process between the aqueous phases and the extraction solvent is accelerated by ultrasonic radiation speeding up the extraction efficiency and the time of the analysis (10 min). Although the LOD is at the ng/L level for most of the compounds, for lindane (γ-HCH) a LOD of 21 ng/L and a LOQ of 71 ng/L does not meet the requirements recommended by the WFD. The same extractive technique was applied by Ozcan et al. [106] in the analysis of eighteen organochloride pesticides by gas chromatography with micro-electron capture detection (GC-μECD) achieving LOD between 2 and 16 ng/L. The compounds evaluated were hexachlorocyclohexane (4 isomers), heptachlor epoxide, dieldrin, aldrin, endrin, endrin aldehyde, endrin ketone, endosulfan (2 isomers), endosulfan sulphate, o,p'-DDT, p,p'-DDE, p,p'-DDD and methoxychlor. The method seems to be more selective for lindane than the one developed by Regueiro et al. [105], nevertheless, the sensitivity for all the compounds is still below the limits imposed by the EC Directives. Ultrasound-assisted emulsification–extraction was also investigated by Feo et al. [107] in the analysis of fourteen pyrethroid insecticides by gas chromatography with negative ion chemical ionization mass spectrometric detection using ammonia as reagent gas (GC-NCI-MS). Acceptable recoveries (63–105%) and good repeatability with RSD of 2–5% were achieved using 1 mL of chloroform as extracting solvent. The LOD of 0.03 to 35.8 ng/L makes the procedure a potential method for pyrethroids insecticides water monitoring. Another class of pesticides that has been isolated by ultrasound-assisted microextraction was the carbamates. In the work developed by Wu et al. [108] a surfactant (Tween 20) was used to accelerate the ultrasound emulsion formation decreasing the compounds extraction time. The separation and detection was done by HPLC–DAD and the recoveries in the spiked river, reservoir and well water were satisfactory. The authors compared the precision and sensitivity of their method with other earlier studies and found out that the LPME-based techniques showed better sensitivity in comparison to solid-phase microextraction technique (SPME) [76,109]. The results also show that when the new DLLME technique was applied the extraction time was significantly reduced from 120 min with SPME to 3 min with DLLME.

To overcome the problems associated to the use of highly toxic solvents in the usual process of DLLME, new procedures are being published using low density organic compounds which can be further solidified to increase the precision and accuracy of the methods. The group of Leong et al. [110] applied the technique of solidification of a floating organic drop (SFO) with DLLME in the analysis, by GC–ECD and GC–MS, of some halogenated organic compounds like 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, tetrachloroethylene, hexachlorobutadiene and 4-bromodiphenyl ether. Better LOD was obtained with the electron capture detector. For hexachlorobutadiene a LOD of 3 ng/L can be an acceptable value since its mandatory LOQ is ten times higher. Organochloride pesticides were also analyzed with the same method by the same research group [111]. In spite of the good recoveries (82.9–102.5%) and precision (RSD of 5.8–8.8%), the LOD of heptachlor, aldrin, α-endosulfan, β-endosulfan, o,p-DDT and p,p'-DDE stood between 11 and 110 ng/L well above the recommended limits. The same organochloride compounds, plus dieldrin, endrin, lindane, p,p'-DDD and p,p'-DDT, were evaluated by Farahani et al. [112] using a similar method. A change in the extracting solvent from hexadecane to 1-dodecanol and an increase of the temperature and extraction time led to a better precision and lower LOD (7–19 ng/L) for most of the eleven pesticides analyzed. SFO combined with DLLME was also used by Faraji et al. [113] in the investigation of phenolic compounds where the toxic pentachlorophenol was included. Once more, derivatization and extraction were done in one step. Acetic anhydride and 1-undecanol were sequential mixed with water samples and after approximately 17 min the organic solvent was solidified in an ice bath, transferred to a clean vial and finally injected in the GC–MS. Precision and recoveries were lower than the method applied by Fattahi et al. [90] but the sensitivity was improved especially for pentachlorophenol. Extractions with 1-undecanol followed by drop solidification were also used by the group of Khalili-Zanjani [114] in the quantification of organophosphorous pesticides by GC–FPD. The results suggest that the method seems to be less sensitive than the one applied by Berijani et al. [115] who used the traditional high solvent density DLLME procedure achieving LOD in the ng/L range. A slightly different method was presented by Farajzadeh et al. [116] in the determination of the same class of pesticides by GC–FID and GC–MS. In this study cyclohexane was used as low density extracting solvent. Better LOD, in the range of ng/L, was achieved with mass spectrometric detection. The results were similar to ones by Berijani et al. [114]. Chen et al. [117] also used the same low density microextraction solvent based technique in the analyses of 4 carbamates by GC–MS/MS. An extraction time of 10 min with toluene and acetonitrile as dispersing solvent provided, in conjunction with the detection system, good repeatability with RSD in the range of 2.7–6.8%, efficient recoveries (94.5–104%) and better LOD (1–50 ng/L) than the method of Hylton [76] and Wu et al. [109].

In DLLME the association with solid-phase extractions techniques is becoming a usual procedure. In the work of Zhao et al. [118] chloroacetanilide herbicides were extracted and concentrated by SPE-DLLME prior to GC–MS injection. The herbicides were adsorbed from a large volume of water samples onto a multi-walled carbon nanotube, eluted with acetone and then concentrated by DLLME. With this hyphenated technique a better precision was achieved when compared with the work of Zhao et al. [119] where SDME was used to extract the same compounds. In both studies the LOD are below the European recommendations. The combination of stir bar sorptive extraction (SBSE) and DLLME has been another approach made by the group of Farajzadeh [120] for the determination of triazole fungicide by GC–FID and GC–MS. For hexaconazole the method seems more precise and sensitive than the one applied by Sanagi et al. [81] which

Table 2
The LPME-based techniques applied to pesticides classified as priority substances and the performance of the associated methods. To compare the results the LOQ established by legislation were also included.

Priority Substance	Type of water	Type of LPME	Analysis	LOD (ng/L)	Recovery (%)	RSD (%)	EF	Mandatory LOQ (ng/L)	Ref.
Alachlor	Distilled water, river, lake, tap water	SDME	GC–ECD	2.5	88–102	6.8–7.9	–	90	[59]
	Milli-Q, drinking water	MASE	GC–MS (SIM)	10	72.3	10.7	–		[59]
Atrazine	Deionized water	HF-LPME	HPLC–MS/MS	26	–	4.3–8.9	–	180	[82]
	Water, sludge water	HF-LPME	HPLC–UV	300	–	–	–		[83]
	River, groundwater	MASE	HPLC–MS/MS	1	–	7	–		[86]
	Bidistilled water	MASE	LVI–GC–MS	10	–	9.1	–		[85]
	Water, sludge water	LLSME	HPLC–UV	15	94.3	3.1	–		[83]
	Water, tap, river water	DLLME	GC–MS	60		151	4.33		[93]
	Ultrapure, tap, reservoir groundwater	DLLME	HPLC–UV	600	99.5	6.4	–		[94]
Chlorofenvinphos	Ultrapure water	SDME	GC–NPD	200	–	–	–	30	[67]
Chloropyrifos	Farm, river, well water	SDME	GC–FPD	4	–	8.6–13.4	552	9	[59]
	Ultrapure water	SDME	GC–NPD	800	–	–	–		[67]
	Ultrapure water	HF-LPME	GC–MS (SIM)	15	–	14.8	–		[78]
	Doubly-distilled, tap, well, rain water	DLLME (IL)	HPLV–UV	5000	101.8–113.4	2.4–4.0	–		[126]
Cyclodienes								1.5	
Aldrin	Water, tap, reservoir water	SDME	GC–ECD	20	90.9	3.7	20		[59]
	Water, wastewater	SDME	GC–MS	53	90 ± 8	9.9	–		[68]
	Rainwater	HF-LPME	GC–MS (SIM)	59	79.3–98.7	2.01	105		[59]
	Water and seawater	HF-LPME	GC–MS (SIM)	6	–	8.6	–		[59]
	Seawater	HF-LPME	GC–MS (SIM)	59	83.6–89.5	2.01	105		[59]
	Water, river water	DHS-TEH-LPME	GC–MS/MS	0.33	106 ± 17	15.4	1112		[74]
	Bidistilled water	MASE	LVI–GC–MS	5	–	10.9	–		[85]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	7	–	5.4	708		[112]
	Tap, lake water	DLLME-SFO	GC–ECD	21.6	90.2–94.8	8.5	37		[111]
	Distilled, river tap, surface water	DLLME	GC–MS	9	81–97	7	–		[96]
	River, reservoir water	DLLME-LSC	GC–MS (SIM)	0.6–1.2	93.9–104.5	4.1–7.1	–		[102]
	Distilled, tap, well, surface water	USAEME	GC–μECD	2–16	90–98	–	–	–	[106]
Dieldrin	Water, tap, reservoir water	SDME	GC–ECD	5	96.7–96.1	5.7	60		[59]
	Water, wastewater	SDME	GC–MS	53	90 ± 8	9.9	–		[59]
	Water, wastewater	SDME	GC–MS	22	78 ± 8	6.3	–		[68]
	Water and seawater	HF-LPME	GC–MS (SIM)	1	–	5.7	–		[59]
	Rainwater	HF-LPME	GC–MS (SIM)	47	74.9–87.3	2.32	92		[59]
	Seawater	HF-LPME	GC–MS (SIM)	47	91.4–97.1	2.32	92		[59]
	Water, river water	DHS-TEH-LPME	GC–MS/MS	25	106 ± 12	16.3	1184		[74]
	Deionized, rainwater	DHT-LPME	GC–MS	2	84.2	14.4	328		[73]
	Deionized, rainwater	Static-LPME	GC–ECD	5	–	5.7			[73]
	Bidistilled water	MASE	LVI–GC–MS	2	–	7.3	–		[85]
	Distilled, river tap, surface water	DLLME	GC–MS	4	82–100	9	–		[96]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	19	–	6.4	1290		[112]
	River, reservoir water	DLLME-LSC	GC–MS (SIM)	0.4–1.1	93.6–100.5	8.2–8.9	–		[102]
	Distilled, tap, well, surface water	USAEME	GC–μECD	2–16	83–94	–	–	–	[106]
Endrin	Water, wastewater	SDME	GC–MS	68	78 ± 6	9.8	–		[68]
	Water and seawater	HF-LPME	GC–MS (SIM)	8	–	4.7	–		[59]
	Rainwater	HF-LPME	GC–MS (SIM)	33	85.6–93.1	1.93	92		[59]
	Rainwater	HF-LPME	GC–MS (SIM)	31	82.9–102.2	5.50	69		[59]
	Seawater	HF-LPME	GC–MS (SIM)	33	77.3–93.7	1.93	98		[59]
	Seawater	HF-LPME	GC–MS (SIM)	31	89.3–90.0	5.50	69		[59]
	Bidistilled water	MASE	LVI–GC–MS	2	–	7.0	–		[85]
	Distilled, river tap, surface water	DLLME	GC–MS	4	81–102	8	–		[96]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	14	–	7.2	1337	–	[112]
	Distilled, tap, well, surface water	USAEME	GC–μECD	2–16	94–103	–	–	–	[106]
Isodrin	Bidistilled water	MASE	LVI–GC–MS	10	–	8.1	–		[85]
DDT total[a]								7.5	
p,p′-DDT	Water, tap, reservoir water	SDME	GC–ECD	200	90.5–92.6	9.6	55	3	[59]
	Water, wastewater	SDME	GC–MS	101	50 ± 10	7.8	–		[68]
	Rainwater	HF-LPME	GC–MS (SIM)	17	81.6–97.6	1.66	68		[59]
	Seawater	HF-LPME	GC–MS (SIM)	17	81.7–94.7	1.66	68		[59]
	Water, seawater	HF-LPME	GC–MS (SIM)	1	–	7.4	–		[59]
	Bidistilled water	MASE	LVI–GC–MS	2	–	9.5	–		[85]
	Distilled, river tap, surface water	DLLME	GC–MS	4	75–93	11	–		[96]
	Water, melted snow, river water	DLLME	HPLC–UV	320	95.67–110.0	4.10	100		[95]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	16	–	5.5	1190		[112]
	Distilled, tap, well, surface water	USAEME	GC–μECD	2–16	75–83	–	–		[106]
o,p′-DDT	Water, river water	DHS-TEH-LPME	GC–MS/MS	0.37	98 ± 15	17.4	1520		[74]
	Deionized, rainwater	DHT-LPME	GC–MS	4	94.4	6.5	370		[73]
	Bidistilled water	MASE	LVI–GC–MS	2	–	7.9	–		[85]

Table 2 (*continued*)

Priority Substance	Type of water	Type of LPME	Analysis	LOD (ng/L)	Recovery (%)	RSD (%)	EF	Mandatory LOQ (ng/L)	Ref.
	Tap, lake water	DLLME-SFO	GC–ECD	25.1	85.1–90.0	8.8	181		[111]
	Water, melted snow, river water	DLLME	HPLC–UV	510	91.00–106.2	2.80	100		[95]
p,p′-DDE	Water, tap, reservoir water	SDME	GC–ECD	50	94.2–98.3	5.4	55		[59]
	Water, wastewater	SDME	GC–MS	25	43 ± 5	9.0	–		[68]
	Water and seawater	HF-LPME	GC–MS (SIM)	1	–	10.6	–		[59]
	Water, river water	DHS-THE-LPME	GC–MS/MS	0.27	104 ± 15	17.8	2121		[74]
	Deionized water, rainwater	DHT-LPME	GC–MS	4	99.6	10	445		[73]
	Bidistilled water	MASE	LVI–GC–MS	2	–	4.7	–		[85]
	Water, melted snow, river water	DLLME	HPLC–UV	350	86.56–119.6	7.50	100		[95]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	10	–	6.3	986		[112]
	Tap, lake water	DLLME-SFO	GC–ECD	28.3	86.3–102.5	7.2	872		[111]
	Distilled, river tap, surface water	DLLME	GC–MS	2	81–99	7	–		[96]
	Distilled, tap, well, surface water	USAEME	GC–µECD	2–16	98–100	–	–	–	[106]
p,p′-DDD	Water, wastewater	SDME	GC–MS	22	47 ± 7	6.9	–		[68]
	Rainwater	HF-LPME	GC–MS (SIM)	28	85.0–108.4	2.28	67		[59]
	Seawater	HF-LPME	GC–MS (SIM)	28	92.1–95.2	2.28	67		[59]
	Water and seawater	HF-LPME	GC–MS (SIM)	1	–	7.4	–		[59]
	Bidistilled water	MASE	LVI–GC–MS	2	–	6.8	–		[85]
	Water, melted snow, river water	DLLME	HPLC–UV	40	85.58–103.5	6.13	100		[95]
	Distilled, river tap, surface water	DLLME	GC–MS	4	84–96	8	–		[96]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	8	–	4.9	884		[112]
	Distilled, tap, well, surface water	USAEME	GC–µECD	2–16	95–100	–	–	–	[106]
Diuron	Deionized water	HF-LPME	HPLC–MS/MS	64	–	5.2–9.6			[82]
	River and groundwater	MASE	HPLC–MS/MS	0.5	–	9	–	60	[86]
	Deionized, river, tap well water	DLLME	HPLC–DAD	70	89.108	6.4	60		[104]
Endosulfan[b]	Rainwater	HF-LPME	GC–MS (SIM)	28	79.4–90.1	3.13	155	0.15	[59]
	Seawater	HF-LPME	GC–MS (SIM)	28	92.0–93.3	3.13	155		[59]
α-Endosulfan	Water, tap and reservoir water	SDME	GC–ECD	200	83.3–90.4	4.6	70		[59,73]
	Ultrapure, tap, surface water	SDME	GC–ECD	10	90–100	1.7–5.5	4.9		[59]
	Water, wastewater	SDME	GC–MS	64	47 ± 6	7.6	–		[68]
	Water, river water	DHS-TEH-LPME	GC–MS/MS	19	109 ± 15	12.5	633		[74]
	Deionized water, rainwater	DHT-LPME	GC–MS	5	85.8	12.2	275		[73]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	16	–	5.5	1267	–	[112]
	Tap, lake water	DLLME-SFO	GC–ECD	12.1–19.7	87.0–96.2	7.6	808		[111]
	Distilled, river tap, surface water	DLLME	GC–MS	5	83–95	6	–		[96]
	River and reservoir water	DLLME-LSC	GC–MS (SIM)	0.4–0.8	99.5–102.0	5.6–9.7	–		[102]
	Distilled, tap, well, surface water	USAEME	GC–µECD	2–16	94–101	–	–	–	[106]
β-Endosulfan	Ultrapure, tap, surface water	SDME	GC–ECD	10	90–100	4.9	–		[59]
	Water, wastewater	SDME	GC–MS	71	52 ± 5	7.9	–		[68]
	Bidistilled water	MASE	LVI–GC–MS	10	–	7.4	–		[85]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	9	–	5.9	1091	–	[112]
	Tapr lake water	DLLME-SFO	GC–ECD	12.9	85.5–93.5	5.8	286		[111]
	Distilled, river tap, surface water	DLLME	GC–MS	25	85–103	15	–		[96]
	River, reservoir water	DLLME-LSC	GC–MS (SIM)	1.3–2.5	93.1–101.6	6.0–8.2	–		[102]
	Distilled, tap, well, surface water	USAEME	GC–µECD	2–16	90–101	–	–	–	[106]
Hexachlorobenzene	Milli-Q, drinking water	MASE	GC–MS (SIM)	0.02	47.3	2.6	–		[59]
	Reagent water, groundwater	MASE	LVI–GC–ECD	10	93	9	–	30	[84]
	Reagent water	MASE	LVI–GC–MS	2	–	6.0	–		[85]
Hexachlorobutadiene	Water, tap, lake water	DLLME-SFO	GC–ECD	3	93–98	8.7	219	30	[110]
	Water, tap, lake water	DLLME-SFO	GC–MS	45	100–102	1.3	283		[110]
Hexachlorocyclohexane[c]:								0.6	
α-HCH	Water, wastewater	SDME	GC–MS	87	103 ± 8	6.7	–		[68]
	Rainwater	HF-LPME	GC–MS (SIM)	17	86.1–106.7	13.72	139		[59]
	Seawater	HF-LPME	GC–MS (SIM)	17	91.8–93.6	13.72	139		[59]
	Water, seawater	HF-LPME	GC–MS (SIM)	1	–	6.6	–		[59]
	Milli-Q, drinking water	MASE	GC–MS (SIM)	0.01	81.8	15.5	–		[59]
	Deionezed, river, drinking water	MASE	GC–MS (SIM)	10–25	107.6	5.2	–		[59]
	Reagent water, groundwater	MASE	LVI–GC–ECD	10	89	6	–		[84]
	Bidistilled water	MASE	LVI–GC–MS	5	–	5.7	–		[85]
	Distilled, river, tap, surface water	DLLME	GC–MS	3	101–113	7	–		[96]
	Distilled, tap, well, surface water	USAEME	GC–µECD	2–16	100–103	–	–		[106]
β-HCH	Water, wastewater	SDME	GC–MS	93	100 ± 8	6.5	–		[68]
	Rainwater	HF-LPME	GC–MS (SIM)	29	87.4–111.6	10.29	83		[59]
	Seawater	HF-LPME	GC–MS (SIM)	29	85.3–91.3	10.29	83		[59]
	Water and seawater	HF-LPME	GC–MS (SIM)	5	nr	5.5	nr		[59]
	Milli-Q, drinking water	MASE	GC–MS (SIM)	0.02	73.8	16.7	–		[59]
	Reagent water, groundwater	MASE	LVI–GC–ECD	10	–	–	–		[84]
	Bidistilled water	MASE	LVI–GC–MS	10	–	4.8	–		[85]
	Distilled, river, tap, surface water	DLLME	GC–MS	5	96–112	25	–		[96]
	Distilled, tap, well, surface water	USAEME	GC–µECD	2–16	98–100	–	–	–	[106]
γ-HCH	Water, tap, reservoir water	SDME	GC–ECD	20	97.2	3.2	95		[59]

(continued on next page)

Table 2 (*continued*)

Priority Substance	Type of water	Type of LPME	Analysis	LOD (ng/L)	Recovery (%)	RSD (%)	EF	Mandatory LOQ (ng/L)	Ref.
	Water, wastewater	SDME	GC–MS	45	102 ± 8	6.5	–		[68]
	Rainwater	HF-LPME	GC–MS (SIM)	13	93.4–112.6	14	74		[59]
	Seawater	HF-LPME	GC–MS (SIM)	13	84.1–86.52	14	74		[59]
	Water, seawater	HF-LPME	GC–MS (SIM)	3	–	6.5	–		[59]
	Milli-Q, drinking water	MASE	GC–MS (SIM)	0.04	98.5	16.0	–		[59]
	Reagent water, groundwater	MASE	LVI–GC–ECD	10	93	9	–		[84]
	Bidistilled water	MASE	LVI–GC–MS	10	–	6.0	–		[85]
	Distilled, river tap, surface water	DLLME	GC–MS	8	96–111	5	–		[96]
	Deionized, tap, river, agriculture water	DLLME-SFO	GC–ECD	11	–	5.8	1311		[112]
	Ultrapure, tap water	USAEME	GC–MS	21	103–109	6–9	–		[105]
	Distilled, tap, well, surface water	USAEME	GC-μECD	2–16	100–103	–	–		[106]
δ-HCH	Water, wastewater	SDME	GC–MS	66	101 ± 8	8.2	–		[68]
	Water, seawater	HF-LPME	GC–MS (SIM)	2	–	5.5	–		[59]
	Milli-Q, drinking water	MASE	GC–MS (SIM)	0.01	68.7	17.1	–		[59]
	Reagent water, groundwater	MASE	LVI–GC–ECD	25	105	8	–		[84]
	Bidistilled water	MASE	LVI–GC–MS	2	–	5.4	–		[85]
	Distilled, river, tap, surface water	DLLME	GC–MS	6	86–109	8	–		[96]
	Distilled, tap, well, surface water	USAEME	GC-μECD	2–16	100–102	–	–		[106]
Pentachlorophenol	Purified, river water	SDME	GC–MS	61	–	9.3–10.7	138	120	[70]
	Distilled, river water	SDME	GC–MS	9.7	94.7	4.61	–		[69]
	Distilled, superficial, reservoir, groundwater	SDCME	HPLC–UV	300	92–105	4.8	–		[71]
	Reagent water, groundwater	MASE	LVI–GC–MS	595	95.4	12.7	–		[87]
	Reagent water, groundwater	MASE	LVI–GC–ECD	10	93	9	–		[84]
	Water, tap, well, river water	DLLME	GC-ECD	10	98.7–101.3	2.1–2.4	710		[90]
	Water, tap, mineral, river water	LMPE-SFO	GC–MS	5	89.2–93	8.3	1035		[113]
Isoproturon	River and groundwater	MASE	HPLC–MS/MS	0.5	–	7	–	90	[86]
	Water, river water	PDLLME	HPLC–UV	100–280	91–104	1.5–5.9			[103]
Simazine	Deionized water	HF-LPME	GC–MS (SIM)	10	94.3–104.5	0.78–2.68	190	300	[59]
	Deionized water	HF-LPME	HPLC–MS/MS	61	–	3.6–10.8	–		[83]
	Surface water	SLME	HPLC–UV	100	85	–	–		[59]
	Deionized water	MASE	GC–MS (SIM)	5–100	–	10.4	–		[59]
	River, groundwater	MASE	HPLC–MS/MS	2.5	–	10	–		[86]
	Bidistilled water	MASE	LVI–GC–MS	10	–	7.2	–		[87]
	Water, tap and river water	DLLME	GC–MS	120	109.7–115.9	151	4.31		[93]

[a]   DDT total comprises the sum of the isomers: *p,p′*-DDT; *o,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD.

[b]   Endosulfan is a mixture of two sterioisomers: α-endosulfan or endosulfan I comprises 64–67% of the tech. grade and β-endosulfan or endosulfan II, comprises 29–32% tech. grade [88].

[c]   Hexachlorocyclohexano (HCH) is a mixture of four sterioisomers: α-HCH, β-HCH, γ-HCH, δ-HCH. For material containing ≥ 99% of γ-HCH the common name is lindane [88].

was based on a MLPME extraction. Another advance in DLLME has been the use of ionic liquids (IL). Their immiscibility in water and the high capacity to dissolve organic compounds make them suitable for analytical extraction purposes [121–125]. Some applications have been made to pesticide analysis by HPLC–UV, but the LOD is above the environmental limits [126–129]. An exception was published by Xie et al. [130] in the analysis of three organophosphorous pesticides (phorate, parathion, and phoxim) where LOD between 1 and 10 ng/L was obtained using the IL 1-butyl-3-methylimidazolium hexafluorophosphate as extracting solvent ([C4MIM][PF6]). Until now the most applied IL in pesticide analysis has been 1-octyl-3-methylimidazolium hexafluorophosphate ([C8MIM][PF6]) and 1-hexyl-3-methylimidazolium hexafluorophosphate ([C6MIM][PF6]). It is quite sure that advances will be made in this area. The application of other IL and the synthesis of new ones specially designed for the analysis of multiple classes of pesticides will be an option in the next years. Moreover, as column contamination by IL is the main difficulty found in GC analysis, it is likely that in the future the GC and LC analytical system will be design to overcome such problems. From the data published one can see that the main advantage of DLLME seems to be the low extraction time which is sometimes associated to good method performance. With this type of preconcentration technique improvements were made in the analysis of some of the priority pesticides. Aldrin, dieldrin, endrin, α-endosulfan, and β-endosulfan are examples when USAEME was used. As before, no data was found for the analysis of trifluralin by DLLME. Among all the LPME techniques summarized in Table 2, MASE seems to be associated to more sensitive methods for the described pesticides, except for alachlor (SDME), aldrin, *o,p′*-DDT and *p,p′*-DDE (HF-LPME).

4. Future perspectives

From the studies related herein it is clear that LPME-based techniques seem to be a potential extraction procedure for the analysis of pesticides in water samples. Several organic solvents have been used and more options will appear in the future. The application of the LPME-based techniques to standard multiresidue/multiclass methods will probably be a reality soon. In the study of Mamun et al. [15] a method for the screening of 82 multiclass pesticides by GC with electron capture detection (GC–ECD) was developed based on the EPA extraction procedures. Recoveries from water samples were found to be between 82% and 120% and the LOD ranged from 20 to 2000 ng/L. Since the extraction of the compounds was done by LLE with dichloromethane it is expected that in the future the application of LPME-based techniques will be an alternative to LLE standard analytical procedures [18,19,21,46,92]. Moreover, the association of LPME-based techniques to modern chromatographic methods like gas chromatography high resolution mass spectrometry (GC–HRMS), fast GC, two-dimensional chromatography (GC×GC) and ultra high performance liquid chromatography (UHPLC) will be most likely a powerful option for the development of rapid and ultra-sensitive analytical methods. Moreover, the isolation of the target analytes with hyphenated extraction techniques seems to be an advance especially for complex matrices. It is possible that soon this type of devices will

appear as an integral part of the actual hyphenated chromatographic and detection systems.

5. Conclusions

Pesticides are present in everyday life of any community. Depending on their toxicity, the acceptable values imposed by European legislation in water samples are mostly at trace and ultra-trace levels. To have low LOD and LOQ in compliance with the technical specifications special attention has been paid to the extraction and concentration of the target analytes. All authors agree that LPME-based techniques are simple, time-saving and of low cost when compared to other microextraction techniques. Several methods have been developed based in the methodologies of SDME, MLPME and DLMME. For some priority pesticides like alachlor, aldrin, atrazine, chloropyrifos, DDT and its metabolites, dieldrin, diuron, hexachlorobenzene, hexachlorobutadiene, isoproturon, pentachlorophenol and simazine the LPME-based techniques can probably offer a valid and reliable alternative to the well established but non-green LLE. For endrin, isodrin, hexachlorocyclohexane (HCH), and especially endosulfan future efforts shall be addressed to increase methods sensitivity. For the other non-priority pesticide, the LPME-based techniques are a promising tool to develop very sensitive analytical methods in compliance with the established threshold limits set up by the European Community.

Acknowledgments

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