Salting-Out Assisted Liquid-Liquid Extraction Combined with HPLC for Quantitative Extraction of Trace Multiclass Pesticide Residues from Environmental Waters

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Abstract

In this study, salting-out assisted liquid-liquid extraction combined with high performance liquid chromatography diode array detector (SALLE-HPLC-DAD) method was developed and validated for simultaneous analysis of carbaryl, atrazine, propazine, chlorothalonil, dimethametryn and terbutryn in environmental water samples. Parameters affecting the extraction efficiency such as type and volume of extraction solvent, sample volume, salt type and amount, centrifugation speed and time, and sample pH were optimized. Under the optimum extraction conditions the method was linear over the range of 10 - 100 µg/L (carbaryl), 8 - 100 µg/L (atrazine), 7 - 100 µg/L (propazine) and 9 - 100 µg/L (chlorothalonil, terbutryn and dimethametryn) with correlation coefficients (R^2) between 0.99 and 0.999. Limits of detection and quantification ranged from 2.0 to 2.8 µg/L and 6.7 to 9.5 µg/L, respectively. The extraction recoveries obtained for ground, lake and river waters were in a range of 75.5% to 106.6%, with the intra-day and inter-day relative standard deviation lower than 3.4% for all the target analytes. All of the target analytes were not detected in these samples. Therefore, the proposed SALLE-HPLC-DAD method is simple, rapid, cheap and environmentally friendly for the determination of the aforementioned herbicides, insecticide and fungicide residues in environmental water samples.

Keywords

Environmental Waters, High Performance Liquid Chromatography, Salting-Out Assisted Liquid-Liquid Extraction, Southern Ethiopia, Trace Multiclass Pesticide Residues

1. Introduction

The use of agrochemical is becoming one of the preferred alternatives mainly because of their rapid actions on exterminating disease causing organisms, control insects, weeds and other pests. Extensive and frequent applications of these compounds, pesticides in particular, have greatly improved the quality and quantity of food, and advances in pesticide technology have increased the ability to sustain and improve the health and well-being of the ever growing human population [1]. Unfortunately, these compounds are potential pollutants having deleterious effects on human health, lives of the wild and aquatic animals and that of the inhabitants of the ecosystem in the environment mainly because of the undesirable risks caused from their eco-toxicity, bioaccumulation properties, hormone disrupting effects, etc. [2] [3].

The residues of applied pesticides are usually occurring in the environment at trace/ultra-trace levels [4] [5] [6]. In order to carry out trace enrichment, it is mandatory to search for fairly suitable and reliable sample preparation technique for selective and quantitative extraction of the target pesticide residues from complex sample matrices. To this end, quite a number of solventless and solvent-minimized sample preparation techniques have been developed, validated and applied in the analysis of trace level pesticide contaminants from various water systems and other matrices [7] [8] [9]. However, most of these techniques have their own limitations; for example, passive dosimetry [10] requires longer sample exposure times while membrane assisted solvent extraction (MASE) [11] uses longer extraction times to ensure quantitative analyte enrichment, typically 1 h; a non-selective characteristics of the extraction solvents in dispersive liquid-liquid microextraction (DLLME) [12]; limited applications of stir bar sorptive extraction (SBSE), not suiting for strongly polar compounds unless derivatized [13]. On the other hand, the apparatus needed for most of these techniques are expensive and may not easily be available in most laboratories of the developing countries.

Traditional sample preparation techniques such as liquid-liquid extraction (LLE) [14] and solid-phase extraction (SPE) [5] are still popular, methods of choice and used commonly for quantitative extraction of trace multiclass pesticide residues from various environmental waters [15], despite their methodological drawbacks described in scientific literatures [16] [17]. The trace level analytes of interest, occurring in environmental waters and other matrices, are usually enriched in small volume of extracts and subsequently determined utilizing sensitive analytical instruments including HPLC [18], capillary electrophoresis (CE) [19], and Gas chromatography (GC) [20] coupled to different detectors [6]. In a conventional LLE, water immiscible organic solvents are commonly employed for facilitating efficient phase separation between the aqueous solution and non-polar organic solvents; the latter having low dielectric constant [21]. As a result, only non-polar contaminants, e.g., trace pesticide residues, may be extracted and concentrated in the non-polar organic solvents chosen. How-

ever, LLE procedure can be modified for further extending its applications for enabling efficient extraction of polar pesticide residues from various water samples [22] [23]. This can be achieved by addition of appropriate quantities of a salt to the mixture of the aqueous sample and water-miscible organic solvent, for causing formation of a two-phase system and simultaneous separation of the target analytes into the organic phase [24] [25]. The procedure can also be modified by adding an ion-pair agent, to form extractable ion-pairs, when efficient extraction of high polarity analytes is desired [15] [26]. The salting-out assisted liquid-liquid extraction (SALLE) technique was found to be simple, fast, cheap and environmentally safe and the resulting extracts could directly be introduced or evaporated and then reconstituted into suitable solvent before final instrumental analyses. During the years, merits and application potentials of the SALLE techniques were demonstrated in a number of studies [26], and on this basis this technique was selected as preferred alternative for establishing efficient extraction of pollutant pesticide residues, sampled from the various water samples of this study.

The sampling areas considered in this study, located around the Lake Ziway in Southern Ethiopia, are known for supplying sufficient quantities of agricultural crops including cereals, vegetables and fruits for local and central markets. However, attaining increased productivity, can't be realized without the frequent use of high yield varieties of agrochemicals; herbicides, insecticides, fungicides and fertilizers. This has also been associated with increased importation of pesticides in the recent years, which has raised to, on average, 2400 tons per annum, according the Pesticide Risk Reduction Programme in Ethiopia (PRRP) [27]. Consequently, application of the heavy doses of mixtures of different pesticides, causes accumulation levels the pesticide residues to increase with time [28]; possibly contaminate and pollute the various environmental compartments which enter the food chain and may be causing risk to human health. It was also noted that most of the farmlands are irrigated by pumped water from the Lake Ziway [29].

It was also known that different classes of pesticides including carbaryl, atrazine, propazine, chlorothalonil, dimethametryn and terbutryn were in use at least for the past three decades, and could leach into the water bodies of the surrounding areas. Therefore, the current study has focused on development of a simple, friendly and easy analytical method that enables selective and quantitative extraction of multiclass pesticide residues from different water samples obtained from the surroundings of the Ziway Lake. The technique thus was the SALLE, so as to perform efficient extraction residues of these pesticides from different water samples. Furthermore, experimental parameters influencing performances of the developed technique were optimized and validated. Based on the optimized conditions, the techniques was successfully applied for extraction of the water samples. The reliability of the technique was also evaluated and compared with other similar techniques reported in the literature.

2. Materials and Methods

2.1. Chemicals and Reagents

The pesticide standards considered in this study; namely, carbaryl, atrazine, propazine, chlorothalonil, dimethametryn and terbutryn were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Chemical structure and important physicochemical properties of the standards are provided in **Figure 1**. Both methanol, purchased from Carlo Erba (Rodano, Italy) and acetonitrile from Sigma Aldrich (Steinheim, Germany) were of HPLC grade solvents and used as mobile phase. Acetone was also purchased from Sigma Aldrich (Steinheim, Germany). All other chemicals, used in this study were of analytical grade reagents. The salts used as salting-out agents including NaCl and MgSO_4 were the products of Sigma Aldrich (Steinheim, Germany) while $(\text{NH}_4)_2\text{SO}_4$ was from BDH Chemicals Ltd (Poole, England). Hydrochloric acid (HCl) was the product of Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water was obtained by purifying with double distiller, A8000 Aquatron water Still (Bibby Scientific, Staffordshire, UK) and deionizer (EASYPure LF, Dubuque). It was filtered under vacuum through cellulose acetate filter papers ($0.45\ \mu\text{m}$, Micro Science) before use. The stock standard solution of 100 mg/L, containing each target analyte, was prepared in methanol. Intermediate standard solution of 10 mg/L was obtained from the stock solution. Both intermediate solution and other solutions, of lower concentrations, were prepared by diluting with reagent water.

2.2. Instrumentation

Chromatographic analyses were performed using Agilent Technologies 1200 series HPLC, equipped with quaternary pump, Agilent 1200 series Vacuum Degasser, Agilent 1200 series Autosampler and Agilent 1200 series diode array de-

Figure 1. Chemical structures, common names, log P (partition coefficient) and pK_a of the pesticides considered in this study [4] [30].

tector (DAD), all purchased from Agilent Technologies (Agilent Technologies, Germany). Chromatographic separation of the target compounds was performed on a ZORBAX Eclipse XDB-C₁₈ analytical column (150 × 3 mm i.d., 3.5 µm particle size) (Agilent technologies, USA). Data acquisition and processing were accomplished with LC Chemstation software (Agilent Technologies). A pH meter, Adwa, model 1020 (Romania) and centrifuge, Model 800 (China, Beijing) were used during sample preparation.

2.3. Chromatographic Conditions

Chromatographic separations were carried out using ternary mobile phase; consisting of reagent water (40%), acetonitrile (33%) and methanol (27%) in isocratic elution mode. The mobile phase flow rate, column temperature, injection volume and monitoring wavelength were 0.9 mL/min, 35°C, 10 µL and 230 nm respectively. Peak area was utilized as an instrumental response. Quantitative determination of the instrumental responses was based on the peak areas. Under this chromatographic condition, a good baseline separation was obtained for all the target analytes.

2.4. Sampling Sites and Sample Pretreatment

The representative environmental water samples were collected from different localities in the surrounding of Ziway town. Lake water samples were collected from Ziway Lake, ground water samples were from bore holes around Abine Garmama in the Ziway town and river waters from Buchesa River (outflow river from Ziway Lake). Geographical locations of the sampling sites are as follows: Lake Ziway is located at latitude of 8°00'21.94"N and longitude 38°50'31.78"E with elevation 1637.7 m above sea level. Ziway town is also located at latitude of 7°55'43.38"N and longitude 38°43'15.99"E with elevation 1648.7 m above sea level. All water samples were obtained in brown amber bottles and carried to the Analytical Laboratory of the Chemistry Department, Addis Ababa University, within 24 h. Each sample was then filtered through 0.45-µm membrane filter, before use, and then stored in a brown glass bottle, in a refrigerator at 4°C, for a maximum of 24 h [31]. The pH of each water sample was adjusted to the required value utilizing diluted solutions of HCl and NaOH.

2.5. Experimental Procedure for the SALLE

The sample solution of 5 mL was first spiked with predetermined volume of the standard solution containing mixture of the target analytes and quantitatively transferred to each of the 15 mL screw capped polyethylene test tubes. Then, 1.5 mL acetonitrile and 1.4 g NaCl were added. Thereafter, the solution was shaken gently for 1 min, to ensure complete dissolution of the salt. This was followed by centrifugation of the solution at 4000 rpm for 6 min, which resulted in phase separation. Then, the upper organic phase, was carefully withdrawn using 1 mL micro-syringe and quantitatively transferred to a vial, for subsequent injection to the HPLC system.

3. Results and Discussion

3.1. Optimization of the SALLE Procedure

In this study, vital parameters influencing the extraction and analyte separation were optimized in order to obtain maximum extraction efficiency and sensitivity [32] [33]. Experimental parameters studied and optimized include the type and volume of extraction solvent, sample volume and pH of the aqueous samples, type and concentration of the salt and centrifugation time and speed.

3.1.1. Selection of the Organic Solvent

One of the critical parameters influencing the SALLE procedure is selection of appropriate extraction solvent. The organic solvent used for extraction in this technique should be highly polar, miscible in water in all proportions and induce phase separation upon addition of appropriate salt [23] [34]. In this study, extraction performances of the following solvents for trace multiclass pesticides were evaluated based on the polarity index given in parenthesis: acetonitrile (5.8), acetone (5.1) and methanol (5.1) [25]. Accordingly, series of experiments were performed using 5 mL water sample spiked at 50 µg/L level of the mixture containing the target analytes. It was observed that when acetonitrile was used as extraction solvent, the aqueous and organic phases were adequately separated while the other two solvents failed to cause the required phase separation. Use of acetonitrile, as the preferred extraction solvent in SALLE, for efficient isolation of polar organic compounds was reported in the literature [35]. In addition, acetonitrile is compatible with various types of instruments such as GC, HPLC, CE, inductively coupled plasma and AAS [25]. Furthermore, acetonitrile is less harmful than other organic solvents that are commonly used in conventional LLE as well as other LPME techniques and thus it is more favorable with a green chemistry context. Thus, acetonitrile was selected and used throughout this study.

3.1.2. Effect of the Extraction Solvent Volume

The extraction solvent volume also plays significant role on the extraction efficiency of the SALLE procedure. Generally, the optimum extraction solvent volume should offer high extraction efficiency as well as sufficient volume of the organic phase for the subsequent analysis [33]. The volume of acetonitrile, as extraction solvent, was varied over the range of 0.5 - 2.5 mL. With lower volumes of acetonitrile, *i.e.*, 0.5 and 1 mL, phase separation between the aqueous and organic phases was found to be insufficient. The peak areas of the target analytes decreased when volume of acetonitrile is greater than 1.5 mL which may be attributed to dilution of the organic phase, **Figure 2(a)**. The highest instrumental responses were obtained with 1.5 mL of acetonitrile and thus used as optimum extraction solvent volume.

3.1.3. Effect of Sample Volume

The study of the sample volume is the other important parameter that must be considered in order to establish standard experimental conditions. Accordingly,

Figure 2. (a) Effect of the extraction solvent volume; (b) effect of the amount of NaCl and (c) effect of pH on the SALLE efficiency. Extraction conditions (a): sample size, 5 mL spiked at 50 $\mu\text{g/L}$; amount of salt added, 1.5 g NaCl; shaking time, 1 min; centrifugation speed, 3500 rpm; centrifugation time, 3 min; pH = 7.0, $n = 3$, (b): volume of acetonitrile, 1.5 mL and other parameters are the same as in (a), (c): amount of salt added, 1.4 g NaCl; centrifugation speed, 4000 rpm; centrifugation time, 6 min and other parameters are the same as in (b).

volume of the reagent water was varied from 3 to 7 mL, to study the effect of sample volume on SALLE. At lower sample volume, phase separation was not observed, may be due to insufficient volume ratio of the sample to that of organic solvent. On the other hand, with increase in the sample volume, beyond 3 mL,

the peak areas of all the target analytes showed increasing tendencies. However, above 5 mL of the sample volume, the instrumental responses showed decreasing extraction tendencies which may be caused by the dilution effect caused by increased sample volume. Similar observations were also noted by other workers [23]. Therefore, 5 mL sample volume was selected as optimum and used for the subsequent experimental works.

3.1.4. Effect of the Salt Type and Amount

The addition of a salt into the sample solution cause increase in ionic strength of the sample solution and facilitates the transfer of target analytes from the aqueous phase to the organic solvent phase [36] [37]. In order to evaluate this effect, 1.5 g of each of the salts; *viz.*, sodium chloride (NaCl), magnesium sulphate (MgSO_4) and ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$), were added as potential salting-out agents. The results obtained revealed that NaCl is a suitable salting-out agent and used for further experiments.

The amount of NaCl was also varied from 1 to 1.7 g, at five points. It was observed that when smaller amounts, *i.e.*, 1 g and 1.2 g salt were added, phase separation was not observed. On the other hand, with larger amounts of NaCl, 1.6 and 1.7 g, dissolution of the salts added was not complete [36]. Addition of 1.4 g NaCl provided the well resolved chromatogram and the highest peak areas, **Figure 2(b)**, for all the analytes and thus chosen as the optimum quantity of the salt.

3.1.5. Effect of Centrifugation Speed and Time

Centrifugation of the sample solution obviously influences kinetics of the extraction and enhances contact between the organic solvent and aqueous solution and thus facilitates formation of the two-phase system in the SALLE technique [34]. In this study, the effect of centrifugation speed was varied in the range of 2000 to 4000 rpm, with interval of 500 rpm while the centrifugation time is kept at 5 min. It was found that the peak area of all target analyte increases with increasing centrifugation speed. However, centrifugations speed of higher than 4000 rpm were not conducted due to the instrumental limitations. As a result, 4000 rpm was utilized as optimum centrifugation speed for further experiments.

Optimizing the time required for phase separation is also important analytical step, in order to obtain a clear extract [33]. To this end, time of centrifugation was varied from 4 to 8 min, at five points, within 1 min interval, keeping the centrifugation speed at the optimum of 4000 rpm. The experimental results revealed that centrifugation time of 6 min to be the optimum and used throughout this study.

3.1.6. Effect of the Sample pH

In this study, the effect of pH of sample solution was studied over the range of 3 to 7. Based on the experimental results showed that, the peak areas of all the target analytes increased with rise in the sample solution pH, up to pH 6. This may be due to the enhanced stability of the pesticide compounds, both in weakly acidic and alkaline environments [38]. However, beyond pH 6, the peak areas

started to decrease mainly because of degradation or ionization of the analytes in strongly alkaline conditions [4], **Figure 2(c)**. Therefore, sample solution of pH 6 was selected for subsequent experiments.

3.2. Evaluation of the Proposed Method

3.2.1. Calibration Curves and Analytical Performance Characteristics

The proposed SALLE technique coupled to the HPLC-DAD detection was evaluated at different concentration levels of the standard solution ranging from 7 µg/L to 100 µg/L. Utilizing the optimized parameters, each concentration level was extracted and injected in triplicate. Then, the calibration curves were constructed by plotting the peak areas as instrumental responses versus the target pesticide concentrations. The correlation coefficient (R^2) of the calibration curves were 0.990 or better, for all the analytes considered, confirming good linearity over the studied concentration range. The limits of detection (LOD) and quantification (LOQ), defined as the minimum analyte concentrations yielding 3 and 10 times the signal-to-noise ratio (S/N), were in the range of 2.0 - 2.8 µg/L and 6.7 - 9.5 µg/L, respectively. The figures of merit of the proposed technique are given in **Table 1**.

3.2.2. Precision Study

Evaluation of the precision of the proposed method was based on the results obtained from intra-day (repeatability) and inter-day (reproducibility) studies applying the optimized conditions. This was performed by extracting the water samples which were spiked with the standard solution, at concentration level of 25 µg/L, for both studies. For intra-day precision, the spiked concentration was extracted and injected in triplicate on the same day, under the same experimental conditions. Similarly, inter-day precision of the method was also assayed during three consecutive days, at the same concentration level with that spiked for intra-day study. The results of both the intra- and inter-day precisions, expressed as relative standard deviations (%RSD) of the peak areas, are shown in **Table 1**. The results of the precision studies for the proposed SALLE technique have demonstrated acceptable precision [39], and thus can reliably be utilized

Table 1. Statistical and performance characteristics and precision of the proposed SALLE technique

Analyte	Linear range (µg/L)	R^2	LOD (µg/L)	LOQ (µg/L)	Regression equation	Intra-day (%RSD)	Inter-day (%RSD)
Carbaryl	10 - 100	0.991	2.8	9.5	$Y = 8.24x + 23.05$	3.37	3.15
Atrazine	8 - 100	0.992	2.3	7.7	$Y = 8.99x + 34.31$	1.55	2.41
Propazine	7 - 100	0.995	2.0	6.7	$Y = 10.00x + 28.94$	2.45	1.97
Chlorothalonil	9 - 100	0.991	2.7	8.9	$Y = 16.44x + 41.85$	1.44	1.7
Terbutryn	9 - 100	0.990	2.3	8.3	$Y = 13.12x + 24.59$	1.69	3.03
Dimethametryn	9 - 100	0.999	2.6	8.5	$Y = 11.47x + 26.92$	2.15	1.38

for monitoring of the target analytes in different water samples that could be obtained from varied sources and localities.

3.2.3. Application of the Developed Method to the Real Samples

The applicability of the proposed method was evaluated by extracting all the three water samples; river, ground and lake water samples following the optimized SALLE analytical technique. The results obtained revealed that there were no target analytes detected in any one of the water samples analyzed. This could be either the water samples analyzed were free from the residues of target pesticides or contained concentrations below the detection limits. Consequently, the applicability of the technique was further investigated by extracting the three water samples spiked at concentration level of 50 µg/L, the peak areas of which compared with those obtained from the spiked reagent water at the same concentration levels, in order to assess the matrix effects. The relative recovery (%RR), defined as the ratios of the peak areas of spiked real water extracts to the peak areas of spiked reagent water extracts [40] was used to evaluate the matrix effect. The calculated %RR and % RSD obtained for the extracts of both real water samples and reagent water were in the acceptable ranges [39], **Table 2**. Typical chromatograms for water samples from Ziway Lake, before and after spiking with 50 µg/L using the optimized SALLE technique are provided in **Figure 3**.

3.2.4. Comparison with Other Reported Methods

The extraction efficiency of the proposed SALLE procedure has been compared with similar analytical techniques reported in the scientific literatures. On the basis of the parameters indicated in **Table 3**, it was noted that the technique de-

Table 2. %RR and %RSD of the environmental water samples (n = 3), analyzed for residues of the target analytes by SALLE technique.

Pesticides	Spiked level, µg/L	Lake water		Ground water		River water	
		%RR	%RSD	%RR	%RSD	%RR	%RSD
Carbaryl	0	nd	-	nd	-	nd	-
	50	106.6	7.8	92.7	6.4	89.1	2.3
Atrazine	0	nd	-	nd	-	nd	-
	50	98.1	3	92.5	2.9	86.8	1.6
Propazine	0	nd	-	nd	-	nd	-
	50	96.5	1.6	93.6	0.8	85.7	2
Chlorothalonil	0	nd	-	nd	-	nd	-
	50	75.5	6.4	87.1	1.5	86.9	10.1
Terbutryn	0	nd	-	nd	-	nd	-
	50	99.8	4.6	85.2	3.8	83.3	1.6
Dimethametryn	0	nd	-	nd	-	nd	-
	50	98.9	1	83.4	5.9	83.8	4.9

nd = not detected.

Figure 3. Typical representative chromatograms for water samples from blank (a) and spiked (b) Ziway Lake. Extraction conditions: 5 mL spiked at 50 µg/L; volume of acetonitrile, 1.5 mL; amount of salt added, 1.4 g NaCl; shaking time, 1 min; centrifugation speed, 4000 rpm; centrifugation time, 6 min; $n = 3$. Peaks: 1, Carbaryl; 2, Atrazine; 3, Propazine; 4, Chlorothalonil; 5, Terbutryn; 6, Dimethametryn.

veloped in this study was found to use shorter extraction time and smaller or comparable sample volume than the other methods. Moreover, the technique utilizes classical laboratory equipments as well as less toxic organic solvent (acetonitrile), which can be found in common research laboratories, e.g., in the developing countries. It also offered similar or better LODs and comparable linearity ranges with others cited for comparison. Based on the experimental findings the proposed technique can be considered as one of the preferred alternative,

Table 3. Comparison of the proposed SALLE method with related reported techniques.

Analytical methods	Analyte studied	Sample type and its volume (mL)	LDR ($\mu\text{g/L}$)	LODs ($\mu\text{g/L}$)	%RDS	Extraction time (min)	Ref.
SALLE-capillary LC-DAD	Cephoperazone, cefquinome, cephalixin, cephapirin, cephaloniun, cephamandole, cephasolin and cephadroxile	Water (4)	1.3 - 100	0.4 - 1.3	0.6 - 9.9	<10	[26]
SALLE-capillary LC-DAD	Cephoperazone, cefquinome, cephalixin, cephapirin, cephaloniun, cephamandole, cephasolin and cephadroxile	Banana juice (2.5)	10 - 500	3 - 13	1.2 - 9.9	<10	[26]
CPE-HPLC-DAD	Thiamethoxam, imidacloprid, acetamiprid, thiachloprid	Water (18)	4 - 2000	0.8 - 1.2	-	17	[41]
IL-MNPs based SPE-capillary LC-DAD	Thifensulfuron methyl, metsulfuron methyl, triasulfuron, tribenuron methyl and primisulfuron methyl	Water (50)	5 - 100	5 - 100	2.3 - 4.9	-	[42]
Au-TEOS based SPE-capillary LC-DAD	Bensulfuron-methyl, metsulfuron-methyl, pyrazosulfuron-methyl, thifensulfuron-methyl and triasulfuron	Water (10)	50 - 1000	2 - 9	2.1 - 4.5	-	[43]
Au-NP-IL-silica based SPE-capillary LC-DAD	Bensulfuron-methyl, metsulfuron-methyl, pyrazosulfuron-methyl, thifensulfuron-methyl and triasulfuron	Water (10)	50 - 1000	2 - 6	2.8 - 4	-	[43]
SPE-CE-UV	Triasulfuron, rimsulfuron, flazasul-furon, metsulfuron-methyl and chlorsulfuron	Aqueous extract of grapes (250)	0.97 - 200 ($\mu\text{g/kg}$)	0.97 - 8.3 ($\mu\text{g/kg}$)	5.2 - 21.4	>120	[44]
SPE-HPLC-MS	Amidosulfuron, Aimsulfuron, Nicosulfuron, Thifensulfuron Methyl, Tribenuron Methyl and Azoxystrobin	Water (1000)	15 - 150	5 - 8.1	-	> 60	[45]
SALLE-HPLC-DAD	Carbaryl, atrazine, propazine, chlorothalonil, dimethametryn and terbutryn	Lake water (5)			1 - 7.8		Current study
		River water (5)	7 - 100	2 - 2.8	1.6 - 10	<8	
		Ground water (5)			0.67 - 6.42		

having promising future for selective and quantitative extraction of trace level pesticide pollutants considered in this study and others having polar chemical natures and/or ionizable pollutants contaminating various environmental water systems.

4. Conclusion

The analytical technique, SALLE combined with HPLC-DAD, was developed for the analysis of fungicide, herbicides and insecticide in environmental waters. The consumption of the extraction solvent (acetonitrile) was reduced to a very

low level compared to convective extraction procedures while ensuring operational convenience as well as benign extraction/cleanup performance. It provides a green, fast, economical and simple method for the analysis of multiclass pesticides residue in water sample matrices. Under the optimum extraction condition the method has large linear range with correlation coefficients (R^2) between 0.99 and 0.999, low limits of detection and quantification, and satisfactory extraction recoveries for ground, lake and river water. Therefore, the developed method is a powerful tool for quality control of multiclass pesticides residue in environmental water samples.

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