ORIGINAL ARTICLE

Modified QuEChERS Method for the Determination of S-Triazine Herbicide Residues in Soil Samples by High Performance Liquid Chromatography-Diode Array Detector

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Abstract

A modified QuEChERS method has been proposed for the quantitative determination of four s-triazine herbicides including atrazine, secbumetone, aziprotryne and terbutryn by high performance liquid chromatography with diode array detector (HPLC–DAD) from soil samples collected from different localities in Ethiopia. Different parameters affecting the chromatographic separations and extraction efficiency of the target analytes were studied and optimum conditions were obtained. Under the optimum conditions wide linearity range, i.e., from 7.2–200 ng g^{-1}, with coefficients of determinations of 0.995 or better were obtained. The limits of detections (LODs) and quantifications (LOQs) determined as 3 and 10 times the signal-to-noise ratio (S/N) were in the range of 2.2–8.3 ng g^{-1} and 7.2–27.8 ng g^{-1}, respectively. Intra- and inter-day precision studies of the proposed method, expressed as relative standard deviations (RSD) were in the range of 1.0–6.8% and 2.0–8.1%, respectively. The recoveries of the spiked soil samples collected from four different localities including Teji River, Ziway Lake, Atsebela River and Hawassa Lake area agricultural farmland soil samples, were in the range of 71–100% with the corresponding RSD ranging from 1.7–9.9%. The results of the study demonstrated that the developed method involves efficient sample preparation allowing the extraction of the target analytes, followed by the use of HPLC-DAD for quantitative analysis.

Keywords: *Modified QuEChERS; s-Triazine herbicides; Soil samples; HPLC-DAD*

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INTRODUCTION

One of the common uses of pesticides is for protection of agricultural yields before and after harvests, in gardening, household purposes and soil treatments. The pesticides most frequently used for these purposes fall into three major classes: insecticides, fungicides and herbicides (or weed killers) with other classes used in smaller quantities including rodenticides, nematicides, molluscicides, and acaricides (El-Shahawi et al., 2010). These compounds generally show a wide spectrum of beneficiary effects; improving plant health, maintaining agro-ecosystems, food supply, etc (Cserháti et al. 2004). On the other hand, their intensive use on large areas of agricultural farmland soils is reported to cause undesirable and deleterious effects to various environmental compartments (Carabias-Martínez et al., 2005). Trace level pesticide residues and their degradation products from contaminated soils can also be transported to the natural water resources and cause risks to human health, aquatic lives, inhabitants of the ecosystems, etc to various degrees (Mirbagheri and Monfared, 2009; and Wang et al., 2010)]. Their occurrences, in several matrices, at very low concentrations could significantly affect reliability of the scientific results obtained from their determinations unless standard and sensitive analytical methods are used or new ones are developed.

Selective and efficient analysis of trace level pesticide residues from complex matrices such as soil samples involves series of steps such as extraction, clean-up or interference removal, quantitative determination and confirmation of their identity. Sample extraction, i.e., isolation of the target analytes from the complex matrices is the primary step during chemical analysis. For solid samples, such as soils, extraction of the target analytes is a difficult task since the analytes may not easily be released from the matrices (Andreu and Picó, 2004). Therefore, extraction of the pesticide residues from soils generally requires use of efficient analytical techniques capable of extracting bound residues (Tor et al., 2006). Various sample preparation techniques such as soxhlet (Andreu and Picó, 2004), supercritical fluid extraction (SFE) (Anitescu and Tavlarides, 2006), pressurized liquid extraction (PLE) [Hussen et al, 2006; and Prestes et al., 2012), ultrasonic extraction (Tor et al., 2006; Yu, and Hu, 2007; and Ozcan et al., 2009) and microwave-assisted extraction (MAE) (Pateiro-Moure et al. 2008; and Merdassa et al., 2014) have been the most commonly used techniques for quantitative isolation of pesticide residues from soil samples. However, these techniques usually require long time, large volume of hazardous organic solvents and additional time for clean-up of the extract. Besides, techniques such as SFE and PLE also require expensive instruments that are not readily available in common analytical laboratories (Antonious et al. 2004; and Cavoski et al., 2008).

In the last couple of decades, development of analytical methods possessing characteristics——such as simplicity; preferably requiring a single step, low cost; reduced time; reduced sample size and use of small volume of toxic organic solvent, have gained considerable attentions (Flores-Ramírez et al., 2012). Among the several methods that have been proposed and successfully applied for analysis of pesticide residues in soil samples, QuEChERS, an acronym for quick, easy, cheap, effective, rugged and safe, is a typical example (Lesueur et al., 2008; Rashid et al., 2010; Shi et al., 2010).

QuEChERS method was first reported in 2003 as a simple, rapid and environmentally green sample preparation technique for analysis of pesticide residues in fruits and vegetables (Anastassiades et al., 2003). Its procedure involves an initial extraction of the target analyte utilizing acetonitrile followed by extraction/partitioning step after addition of a salt mixture. Aliquot of the extract is then cleaned-up by dispersive solid-phase extraction (d-SPE). This method is usually combined with gas or liquid chromatographic methods coupled to mass spectrometric (MS) detector (Paya et al., 2007; Diego et al., 2013; and Fenoll et al., 2012). The method has also been reported as a potential alternative technique for extraction and quantitative determination of pesticide residues from soil samples in combination with gas chromatography–mass spectrometry (GC-MS) and liquid chromatography–ion trap–mass spectrometry (LC-MS) (Lesueur et al., 2008, gas chromatography–tandem mass spectrometry (GC-MS/MS) (Rashid et al., 2010) and electron capture detector (GC-ECD) (Shi et al., 2010). However, based on the literature information, it has been learnt that the QuEChERS method has not been employed for extraction of s-triazine herbicides from soil samples. Furthermore, the technique has rarely been used in combination with HPLC-DAD.

S-triazine herbicides are one of the popular classes of pesticides types on worldwide scale and extensively utilized in the agricultural farmlands of Ethiopia, since early of 1970s (Megersa, et al., 2000). They are commonly employed for selective pre- and post-emergence control of broad-leaved and grassy weeds in maize, sorghum, soya beans and other field crops including green vegetables (Batissa, et al. 1989; and Malto, et al., 1989). Consequently, trace residues of these herbicides could significantly be accumulated in environmental samples such as soils (Megersa, et al., 2000). To determine the residual levels of these pesticides, in the soil matrices, use or development of simple and fast sample preparation technique is crucial. To this end, in this study, a modified QuEChERS method in combination with HPLC–DAD has been proposed for selective extraction and quantitative determination of four s-triazine herbicides; namely, atrazine (Atraz), secbumetone (Secb), aziprotryne (Azip) and terbutryn (Terb), from agricultural farmland soils. In the study, various parameters affecting the extraction efficiency of the technique as well as the chromatographic separation of the target analytes were investigated so as to establish the optimum conditions. Eventually, applicability of the optimized method has also been evaluated by analyzing four soil samples collected from different localities of agricultural farmlands, in Ethiopia, where intensive agricultural activities were in practice since several years.

MATERIALS AND METHODS

Chemicals and Reagents

Analytical standards of atrazine (Atraz), secbumetone (Secb), aziprotryne (Azip) and terbutryn (Terb) were purchased from Dr. Ehrenstorfer GmbH (Ausburg, Germany). The chemical structures, common names, abbreviations, the pK_a and log P of the target pesticides are given in Figure **1**. Individual stock standard solutions, 1000 mg L^{-1} and intermediate working solution containing 20 mg L^{-1} of each analyte, were prepared in acetonitrile. All these solutions were stored in dark, below 4 ^{o}C, when not in use.

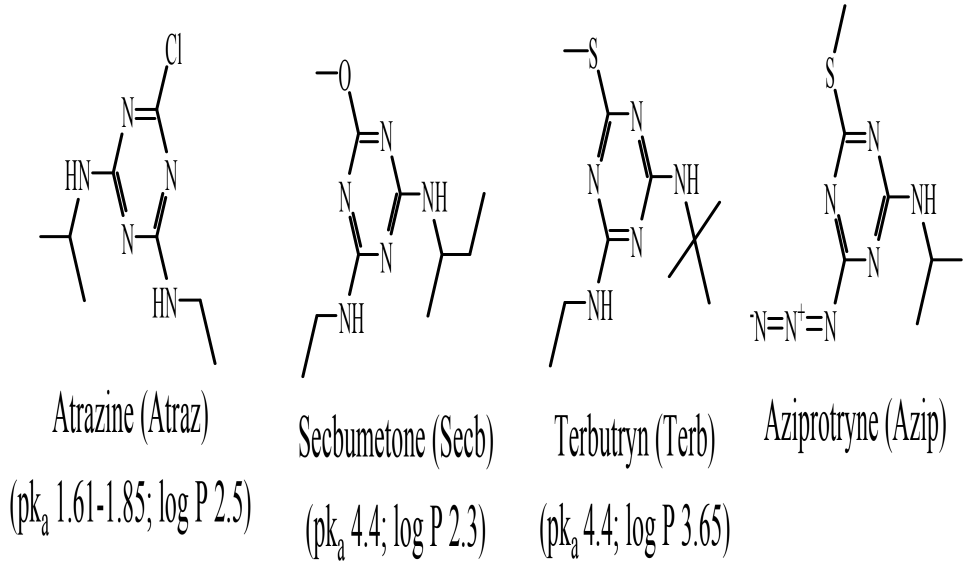

Figure 1: Chemical structures, common names, abbreviations, pK$_a$ and logP of the target analytes considered in the study.

All organic solvents utilized in this study were of HPLC grade and the chemicals were of analytical reagent grades. Acetonitrile and sodium chloride (NaCl) were obtained from Sigma Aldrich, Laborchemikalien GmbH (Seelze, Germany). Methanol and Anhydrous magnesium sulfate ($MgSO_4$) were from Carlo Erba Reagenti SpA (Ronado, Italy) and Fisher ChemAlert™ Guide (New Jersey, USA), respectively.

Instruments and Equipment

Chromatographic analyses were performed using Agilent Technologies® 1200 series HPLC equipped with Quaternary Pump (flow range 0.2–10 mL min^{-1}), Vacuum Degasser, thermostatted autosampler and multiple wavelength diode array detectors (DAD), purchased from Agilent Technologies (Waldbronn, Germany). Chromatographic separation of the target analytes was performed using a ZORBAX Eclipse XDB-C$_{18}$ analytical column (150 x 4.6 mm i.d., 5 µm particle size) (Agilent technologies). Sample processing and data acquisitions were performed using LC ChemStation B.02.01-SR1 from Agilent Technologies.

The d-SPE tube used for clean-up, Supel QuE PSA (EN) Tube (containing 150 mg primary secondary amine (PSA), 900 mg $MgSO_4$ and 150 mg Discovery DSC-18) was purchased from Sigma Aldrich, Laborchemikalien GmbH (Seelze, Germany). FW100 series grinder was purchased from Beijing Zhongxing Weiye Instrument Co., Ltd. (Beijing, China). A Centrifuge, model 800 from Jiangsu Zhenji insturuments Co., Ltd. (Jiangsu, China), an ultrasonic bath working at 50/60 Hz and 100 W from Selecta (Barcelona, Spain) and 15 mL centrifuge tube, Corning Inc. (NY, USA), were used for sample preparation.

Chromatographic Conditions

The mobile phase delivery was performed at the flow rate of 0.8 mL min^{-1} in isocratic mode. The mobile phase composition was water (solvent A) and methanol (solvent B), i.e., 40/60 (*v/v)*. The column temperature was maintained at 35 °C. The detection wavelength was adjusted at 230 nm with bandwidth of 4 in reference to wavelength 360 nm having bandwidth 100. For extract analysis, 15 µL was injected to the HPLC-DAD and eluted for a total of 20 min run time and peak area was utilized as instrumental response for quantitative analysis. Under these chromatographic conditions, a good baseline separation was obtained for all target analytes.

Soil Sampling

Four soil samples were collected from four representative areas of intensive horticultural farmlands in Ethiopia. Three of them were collected from Oromia Regional State: around Teji and Atsebela Rivers form South Western; Ziway Lake in the Easten Shoa Zones and Hawassa Lake in the Southern Nations, Nationalities, and Peoples' Region (SNNPR), respectively. A composite soil sample (five cores) was taken from each field. Five holes of 25 cm depth were made randomly for each sampling hole, using a small folding spade (Hussen, et al. 2006). All samples collected were pooled on a plastic sheet having an area of 3 m^2 and thoroughly mixed manually. To ensure further homogeneity, the soil samples were divided into six cores over the plastic sheet and then a small amount was taken from each portion to make a sub-sample of approximately 1 kg. The sub-sample of the soil was taken in a polyethylene plastic bag which was wrapped in methanol rinsed aluminum foil, and then transported to the laboratory in a chilled insulating box (Hussen, et al. 2006). The soil samples were air dried, grounded with a grinder and sieved with 150 µm sieve holes and then, the sieved sample was stored in a deep freezer below 4 °C until the time of analysis.

Preparation of Target Analytes-Free Soil Samples

Target analytes-free soil sample was prepared for the study of different experimental parameters and validation of the proposed method. In order to prepare the target analytes-free soil sample, 150 g of the sample was dipped successively in 300 mL methanol, acetone, dichloromethane and *n*-hexane each for 12 h (Sun and Lee, 2003). The treated soil sample was then air-dried by spreading out on aluminum foil. Finally, the treated soil sample was analysed to confirm that there is no detectable levels of the target analytes before spiking.

Modified QuEChERS Extraction Procedure

Accurately weighed, 5 g, soil samples were placed into 50 mL centrifuge tube and was spiked with the required quantity of the working standard solution containing the mixture of the target analytes: Atraz, Secb, Azip and Terb. The content was then kept to stand for 30 min to allow aging and then, 5 mL ultrapure water was added to hydrate the sample. Afterwards, 5 mL acetonitrile was added and vigorously shaken manually for 3 min. This was followed by addition of 4 g $MgSO_4$ and 1 g NaCl to the sample mixture and further shaken vigorously for 2 min. Then, after sonicating for 5 min in ultrasonic bath, the content was centrifuged at 3000 rpm for 5 min. Then, 1.5 mL acetonitrile extract was transferred to the d-SPE tube for clean-up. The d-SPE tube was sealed, shaken vigorously for 1 min and centrifuged at 4000 rpm for 5 min. Finally, 150 µL was taken, from the upper layer, into a 200 µL insert vial and then 15 µL of the extract was injected into the HPLC system for analysis.

RESULTS AND DISCUSSION

Optimization of Chromatographic Conditions

In chromatographic analysis, efficient analyte resolution, in the shortest possible analysis time, is the preliminary experimental exercise usually considered. One of the procedures to achieve this intent is performing a series of experiments while changing composition of the mobile phases. Accordingly, the binary mobile phase utilized in the current study; namely, water (solvent A) and methanol (solvent B) were varied. In order to obtain efficient separation, in a reasonable analysis time, various ratios of the binary mobile phases were investigated in the isocratic mode at the flow rate of 0.8 mL min^{-1} and finally, a mobile phase composition of water: methanol, i.e., 40/60 v/v exhibited good signal separation of the target analytes in less than 20 min.

The effect of mobile phase flow rate was investigated in the range of 0.5–1.0 mL min^{-1}. It was observed that both retention times and peak widths were improved and found constant for all analytes with increasing flow rates. However, a flow rate of 0.8 mL min^{-1} was chosen as optimum throughout the analysis. The column oven temperature program and the DAD monitoring wavelength were set at 35 ºC and 230 nm, respectively.

Optimization of the Modified QuEChERS Method

Selection of the extraction solvent

The selection of appropriate extraction (organic) solvent is critical in QuEChERS procedure. The organic solvent must be highly polar, miscible in water and induce phase separation up on addition of the appropriate salt Gure et al., 2014). Accordingly, in this study, acetonitrile, methanol and methanol: acetonitrile i.e., 40/60 (v/v) were investigated. Figure 2 shows the variation of the peak areas of the target analytes as the function of the type of extraction solvents studied. It can be seen that for all target analytes, the highest peak areas were obtained with acetonitrile. As has also been reported, in QuEChERS procedures, acetonitrile has been considered as the solvent of choice for extraction of various classes of compounds from different matrices (Paya et al., 2007; and Correia-Sá et al., 2012). Thus, acetonitrile was chosen as the extraction solvent for further analysis.

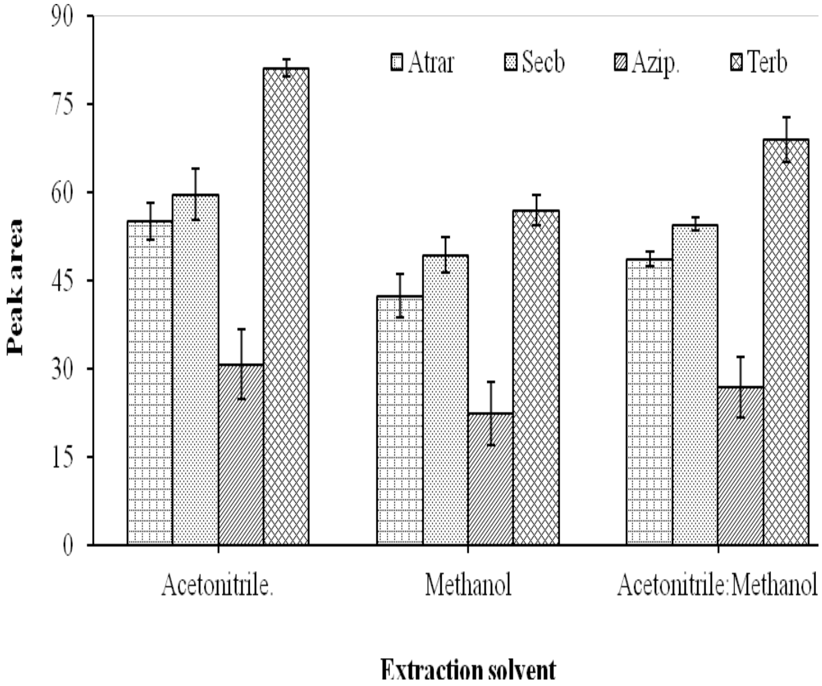

Figure 2: Selection of the extraction solvent. Extraction conditions: soil sample, 5 g; spiked concentration level, 50 ng g^{-1}; extraction solvent volume, 10 mL; volume of water added, 5 mL; 4 g $MgSO_4$, 1 g NaCl; sonication time, 5 min; centrifugation rate and time before d-SPE, 3000 rpm and 5 min, respectively; shaking time of d–SPE, 1 min; centrifugation rate and time after d–SPE, 4000 rpm and 5 min, respectively.

Effect of the volume of extraction solvent

The volume of extraction solvent is also the other important parameter that could influence the extraction performance of QuEChERS method. In the present study, in order to obtain the optimum volume, various volumes of acetonitrile, in the range of 5.0–10.0 mL, were investigated, keeping other experimental parameters constant. As it can be seen from Figure 3, variations of the peak areas of the target analytes were observed with change in the volumes of acetonitrile. The peak areas of the target analytes were found to decrease as the volume of acetonitrile increases. The observed decrease in the peak areas of the analytes at higher volumes of acetonitrile may be attributed to the dilution effect, resulting from the higher volume of the organic phase separated after extraction (Gure et al., 2014). Therefore, 5 mL of acetonitrile was chosen for further experiments.

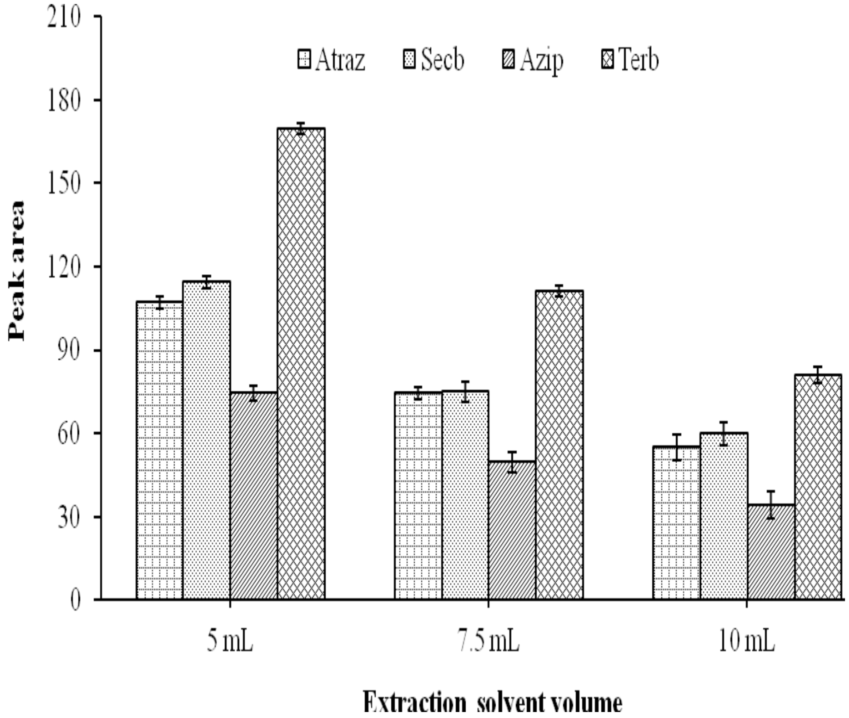

Figure 3: Effect of acetonitrile volume. Extraction conditions were earlier described in Fig. 2.

Effect of the volume of water

The QuEChERS method involves addition of water to dry matrices; e.g., for soil samples to make the pores in the sample more accessible to the extraction solvent and thus to increase the extraction efficiency of the method (Koesukwiwat et al., 2010; and Pinto et al., 2010). In this study, the effect of the moisture content of the sample on the extraction performance of the method was investigated by adding different volumes of water from 0.0–7.5 mL to the soil samples. As it can be observed from Figure 4, the peak areas of all the target pesticides increased with the volumes of water of hydration up to 5 mL and then started to decline up on addition of higher volumes. The obtained lower peak areas at higher volumes of water may most probably be due to the increase in the solubility of acetonitrile in water (Gure et al. 2014). Therefore; 5 mL water was selected for the subsequent experiments.

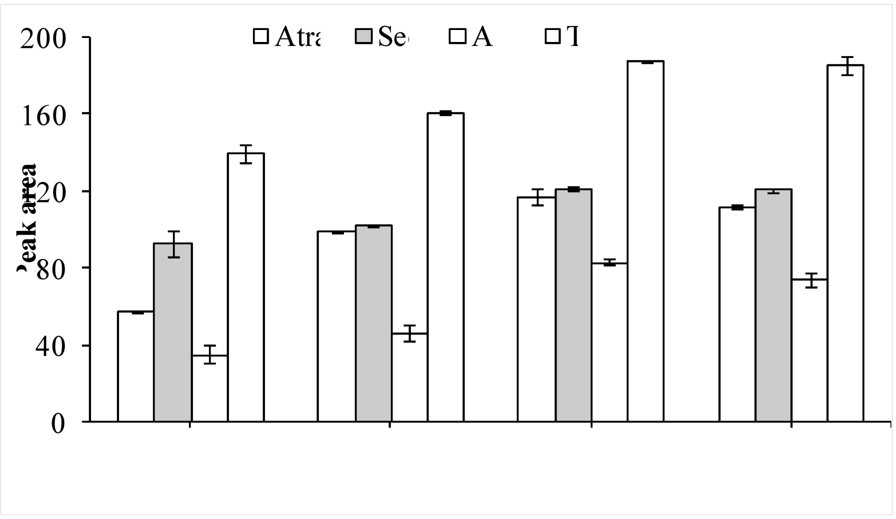

Figure 4: Effect of the volume of water. Extraction conditions: acetonitrile volume, 5 mL; other conditions were as given in Fig. 2.

Validation of the Proposed Method

Calibration curves and analytical performance characteristics

The proposed modified QuEChERS combined with HPLC–DAD method was evaluated using matrix-matched calibration curves, which were established using the previously prepared analyte-free soil sample. The calibration curves were constructed by spiking the mixture of four target pesticides at five concentration levels, ranging from 20–200 ng g^{-1}. Each concentration level was extracted in duplicate and each extract was also injected in triplicate. The calibration curves were constructed by plotting the peak areas as instrumental responses versus the target pesticide concentrations. For all analytes, the coefficients of determination (R^2) of the calibration curves were 0.995 or better, confirming good linearity over the studied concentration range. The limits of detection (LOD) and quantification (LOQ) which were considered as the minimum analyte concentrations yielding 3 and 10 times the signal-to-noise ratio (S/N), were in the range of 2.2–8.3 ng g^{-1} and 7.2–27.8 ng g^{-1}, respectively. The figures of merit of the proposed method are in Table 1.

Table 1: Performance characteristics of the proposed method

Analyte	Linear range (ng g^{-1})	R^2	LOD (ng g^{-1})	LOQ (ng g^{-1})
Atraz	7.2–200	0.999	2.2	7.2
Secb	11.9–200	0.995	3.6	11.9
Azip	27.8–200	0.995	8.3	27.8
Terb	13.5–200	0.996	4.1	13.5

Precision study

The precision of the method was evaluated in terms intra- and inter-day precision studies by applying the optimized conditions to analytes-free soil sample. The intra-day precision of the method was investigated by extracting spiked soil samples at two concentration levels: 50 and 100 ng g^{-1} of each analytes. Each concentration level was prepared in duplicates and then injected in triplicates on the same day, under the same experimental conditions. Similarly, the inter-day precision of the method was also assayed by spiking the analytes-free soil sample at the same concentration levels, indicated earlier for intra-day precision study, during three consecutive days and each concentration level was injected in triplicate. The results of both intra- and inter-day precisions, expressed as relative standard deviations (RSD) of peak areas, are shown in Table 2. The proposed method has demonstrated acceptable precision, i.e., RSD less than 8.1%, and thus can be utilized for monitoring of the target analytes in soils and other related matrices.

Table 2: Intra- and inter-day precisions of the proposed method (RSD) for the spiked soil samples

	Intra–day RSD (n = 6)		**Inter–day RSD (n = 9)**	
Analyte	**50 ng g^{-1}**	**100 ng g^{-1}**	**50 ng g^{-1}**	**100 ng g^{-1}**
Atraz	3.6	1.4	7.5	2.9
Secb	3.6	1.2	7.2	2.2
Azip	6.8	6.1	8.1	6.6
Terb	1.6	1.0	2.2	2.9

Applications and recovery studies

The applicability of the proposed method was evaluated by performing recovery studies utilizing soil samples collected from four different intensified horticulture farmlands in Ethiopia. For recovery studies each of these samples was spiked at two concentration levels, earlier used for precision studies. Each concentration level was extracted in duplicates and each was injected in triplicate. In all cases, unspiked soil samples were also extracted and analyzed by the proposed method, but, none of the target analytes were detected in these samples. Recoveries were calculated by comparing the concentration of the analyte obtained utilizing the proposed method with the initial concentration of the target analytes, spiked to the soil samples (Burns et al., 2002). Recoveries and the corresponding RSD of each of the target analytes in the soil samples are shown in Table 3. The observed recoveries were in the range of 71–100%, with RSD less than 10.0 in all the studied samples. These results are in good agreement with the acceptable recovery range, i.e., 70%–120%, established by the European Commission for pesticide residue analysis (Drożdżyński and Kowalska, 2009). Thus, the obtained results demonstrated that proposed modified QuEChERS combined with HPLC-DAD method could be used as attractive alternative for monitoring of s-triazine herbicides in the soil samples.

Table 3: Recoveries (% R, n = 6) and their corresponding RSD, in bracket, for each herbicide in the soil samples

Soil sample	**Spiked (ng g^{-1})**	**Average recoveries; % R, n = 6 (RSD)**			
		Atraz	**Secb**	**Azip**	**Terb**
Teji River area	50	72 (5.6)	88 (6.9)	73 (6.5)	73 (7.5)
	100	72 (6.4)	88 (4.3)	74 (4.9)	72 (5.4)
Ziway Lake area	50	79 (8.4)	97 (5.2)	76 (5.8)	71 (4.8)
	100	76 (4.9)	100 (2.40	75 (6.4)	72 (1.7)
Atsebela River area	50	82 (4.8)	94 (6.2)	76 (7.8)	73 (7.1)
	100	90 (5.6)	95 (8.0)	78 (5.3)	73 (2.7)
Hawassa Lake area	50	88 (5.0)	72 (7.9)	71 (8.6)	96 (4.6)
	100	85 (9.9)	76 (5.3)	77 (6.2)	91 (4.3)

Typical chromatogram of the unspiked soil sample, collected from Atsebela River area, and of the sample spiked with 100 ng g^{-1} of the target analytes, analyzed by the proposed QuEChERS-HPLC-DAD method under the optimum conditions are shown in Figure 5.

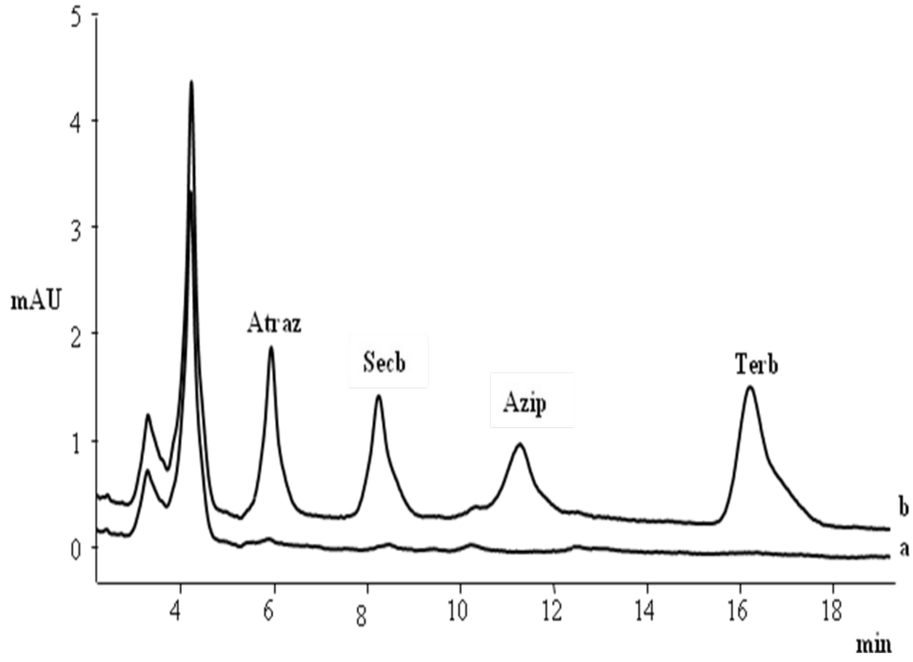

Figure 5: Typical chromatograms of (a) a blank (unspiked) and (b) a spiked soil samples collected from Atsebela River area, with 100 ng g^{-1} of the target pesticides.

Matrix effects

The matrix effect is generally recognized as suppression or enhancement of the analytical signal due to co-eluting matrix components (Asensio-Ramos et al., 2010). To minimize errors related to matrix-induced signal enhancement or suppression effect, matrix-matched calibration is commonly employed (Paya et al., 2007). In the current study, matrix effects were evaluated by comparing the slopes obtained from the calibration curves constructed in matrix matched-standards with those obtained in the standards diluted in pure solvent, acetonitrile (Zhang et al., 2009; and Romero-Gonzalez et al., 2011). The overall results of matrix effects are shown in terms of percentage (%ME), demonstrating either signal enhancement or suppression. Percentage matrix effect can be calculated using the following formula and the observed results are presented in Figure 6. As can be seen, for all the target analytes, except for Atraz, the matrix effects were found to be below ± 20%, indicating insignificant effect on the analysis of these compounds in the soil samples (Gilbert-López et al., 2010).

$$\%ME = [(\text{Slope of matrix matched/Slope of the standard in solvent}) \times 100] - 100$$

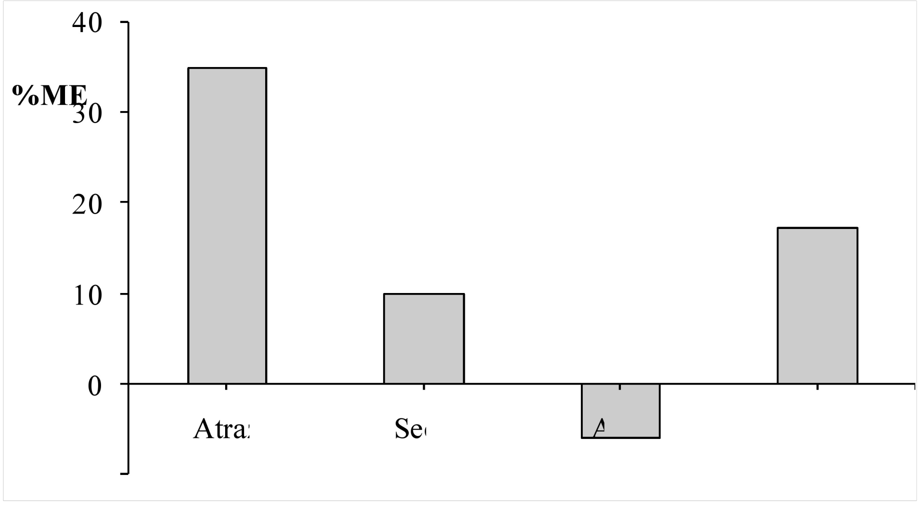

Figure 6: Matrix–induced signal enhancement or suppression effects in the soils samples.

CONCLUSION

In present study, the modified QuEChERS method, in combination with HPLC–DAD, has been proposed for extraction and quantitative analysis of four s-triazine herbicides in the soil samples. Various parameters affecting the chromatographic separations and extraction efficiencies of the target analytes were investigated and the optimum conditions were established. Under the optimum conditions, matrix-matched calibration curves constructed in analytes-free soil samples have coefficient of determinations of 0.995 or better with wide linearity ranges. The method has also demonstrated its usefulness for determination of the target pesticides with LODs and LOQs varying from 2.2–8.3 ng g^{-1} and 7.2–27.8 ng g^{-1}, respectively. The precisions of the method were also in acceptable range (lower than 10%) and satisfactory recoveries over the range 71–100% were obtained. Generally, the observed results indicated that the developed method could effectively be used as attractive alternative for rapid sample extraction, preconcentration and determination of the target pesticides in the soil samples and other related matrices.

Conflict of Interest

The authors confirm that this article has no conflicts of interest.

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