Avrupa Bilim ve Teknoloji Dergisi
Sayı 31 (Ek Sayı 1), S. 539-544, Aralık 2021
© Telif hakkı EJOSAT'a aittir
Araştırma Makalesi

www.ejosat.com ISSN:2148-2683

European Journal of Science and Technology
No. 31 (Supp. 1), pp. 539-544, December 2021
Copyright © 2021 EJOSAT
Research Article

Determination of Chlorsulfuron and Pendimethalin Residues in Soil Using Modified QuEChERS Method by Liquid Chromatography-Tandem Mass Spectrometry

Tarık Balkan[1*]

[1*] Tokat Gaziosmanpaşa University, Faculty of Agriculture, Departmant of Plant Protection, Tokat, Turkey
(ORCID: 0000-0003-4756-4842), tarik.balkan@gop.edu.tr

(First received 16 October 2021 and in final form 15 December 2021)

(**DOI:** 10.31590/ejosat.1010792)

ATIF/REFERENCE: Balkan, T. (2021). Determination of Chlorsulfuron and Pendimethalin Residues in Soil Using Modified QuEChERS Method by Liquid Chromatography-Tandem Mass Spectrometry. *European Journal of Science and Technology*, (31), 539-544.

Abstract

Pesticides, which accumulate in the ecosystem at high concentrations, interfere with the food chain of life forms and cause significant damage to them. The continuous increase in weather, soil and water pollution due to the extensive use of pesticides has made it necessary to develop effective analytical methods to detect pesticides and to monitor continuously the level of residues with these methods.

In this study, an analytical method for the detection of chlorsulfuron and pendimethalin in soil matrix was developed and validated. The soil sample was fortified with a known quantity of pesticides at three different concentration levels (0.01, 0.05 and 0.1 mg kg^{-1}) and the analytes were extracted via a modified QuEChERS method.

Recovery studies were performed with 5 different modified QuEChERS methods. Better recoveries were obtained in T4 method (extraction with 266.6 mg MgSO4, 66.6 mg NaCl, 66.6 mg Trisodium citrate dehydrate (TSCD) and 33.3 mg Disodium hydrogen citrate sesquihydrate (DHS), dispersive -solid phase extraction tecnique (d-SPE) cleanup with 300 mg magnesium sulphate ($MgSO_4$) and 100 mg prime sekonder amine (PSA)). The recoveries were in the range 70–120%, with relative standard deviation (RSD) values lower than 15%. Chlorsulfuron and pendimethalin of limits of detection (LODs) were 0.96 and 1.30 µg kg^{-1} and limits of quantification (LOQs) were 3.19 and 4.34 µg kg^{-1}, respectively.

Keywords: dSPE, LC-MS/MS, Method validation, Pesticide residue, Soil

Sıvı Kromatografi-Tandem Kütle Spektrometrisi ile Modifiye QuEChERS Yöntemi Kullanılarak Chlorsulfuron ve Pendimethalin Kalıntılarının Toprakta Belirlenmesi

Öz

Ekosistemde yüksek konsantrasyonlarda biriken pestisitler, canlıların besin zincirine karışarak onlara önemli zararlar vermektedir. Pestisitlerin yaygın kullanımı nedeniyle hava, toprak ve su kirliliğinin sürekli artması, pestisitlerin tespiti için etkin analitik yöntemlerin geliştirilmesini ve bu yöntemlerle kalıntı düzeylerinin sürekli izlenmesini gerekli kılmaktadır.

Bu çalışmada, toprak matrisinde chlorsulfuron ve pendimethalin tespiti için analitik bir yöntem geliştirilmiş ve valide edilmiştir. Toprak numunesi bilinen miktarda pestisit ile üç farklı konsantrasyonda (0.01, 0.05 ve 0.1 µg kg^{-1}) fortifike edilmiş ve analitler modifiye QuEChERS yöntemi ile ekstrakte edilmiştir.

Geri kazanım çalışmaları 5 farklı modifiye QuEChERS yöntemi ile gerçekleştirilmiştir. T4 yönteminde (266.6 mg MgSO4, 66.6 mg NaCl, 66.6 mg TSCD ve 33.3 mg DHS ile ekstraksiyon, 300 mg $MgSO_4$ ve 100 mg PSA ile d-SPE clean up) daha iyi geri kazanımlar elde edilmiştir. Geri kazanımlar %70-120 aralığında olup, bağıl standart sapma (RSD) değerleri %15'ten düşük bulunmuştur. Chlorsulfuron ve pendimethalin'in sırasıyla LOD değerleri 0,96 ve 1,30 µg kg^{-1} ve LOQ değerleri 3,19 ve 4,34 µg kg^{-1} olarak belirlenmiştir.

Anahtar Kelimeler: dSPE, LC-MS/MS, Metod validasyonu, Pestisit kalıntısı, Toprak

---

[*] Corresponding Author: tarik.balkan@gop.edu.tr

1. Introduction

Pesticides are extensively used around the world, and pesticide demand is continues to increase for high agricultural yields and quality production (Sarkar et al., 2021). The most important advantages of pesticides are their ease of use, wide variety and faster results compared to other pest control methods. However, the negative effects of pesticides on ecology should also be taken into account. Pesticides have various effects on the beneficial microflora in the soil, such as inhibiting nitrification and reducing soil fertility (Diğrak et al. 1996; Sato 1987). In addition, pesticides that seep into rivers from cropland soils and reach lakes or the sea via surface and groundwater affect a variety of life forms. Pesticides are applied directly to the soil surface and into the soil, on the plant or on the seed in the form of seed spraying. A significant part of the pesticides thrown onto the plant surface falls into the soil and the pesticides falling on the soil can move in the soil over time depending on the soil type, solubility, permanence and climate factors (Kurutaş and Kılınç, 2013).

Pendimethalin is widely applied to soil as a selective preplant, preemergence and sometimes postemergence herbicide in variety of crop plants including cotton, sunflower, tobacco, maize, wheat, rice and vegetable crops to control annual grasses, certain broad leaf weeds of dryland crops and non-crop areas and also for plant growth promotion under tropical, subtropical, as well as temperate conditions (Jape et al. 2019).

Chlorsulfuron mainly utilize to control a large variety of grass and broad-leaved weeds as pre-emergence application on wheat or as a post-emergence application on wheat, barley, rye and oat crops (Alesso et al. 2016).

Pesticides, which accumulate in the ecosystem at high concentrations, interfere with the food chain of life forms and cause significant damage to them. The continuous increase in soil and water pollution due to the extensive use of pesticides has made it necessary to develop effective analytical methods to detect pesticides and to continuously monitor the level of residues with these methods (Taylor et al., 2002; Pinheiro and de Andrade, 2009; Park et al., 2010; Sharma et al., 2017).

A wide variety of chromatographic methods e.g., liquid chromatography (LC) (Navneet and Makhan, 2015), gas chromatography (GC) (Chopra et al., 2015), capillary electrophoresis (Han et al. 2008), electroanalytical (Andressa et al., 2011), colorimetric methods (Jigneshkumar and Suresh, 2017) and enzyme-linked immunoassay (Zeng et al. 2006) have been used till date for the determination of pesticide residues in many matrices. Today, Gas Chromatography/ Tandem Mass Spectrometry (GC-MS-MS) and Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS-MS) are more preferred for pesticide analysis. Equipped with ionization technique such as electrospray ionization (ESI) (Hernandez et al. 2006; Dolores et al. 2007; Wong et al. 2010; Bletsou et al. 2013; Islam et al. 2018) and atmospheric pressure chemical ionization (APCI) (Bonmatin et al. 2003; Xu et al. 2009; Botitsi et al. 2011), LC-MS/MS provides advanced sensitivity and selectivity compared to classic detectors (Saha et al., 2015.

Sample preparation step before chromatographic analysis is very important to detect pesticide residues. For pesticide residue analysis in many matrices, liquid-liquid extraction (LLE), solid phase extraction (SPE) and combinations of both are the most commonly used sample preparation methods (Mohammad et al. 2018; Yang et al., 2019; Zhang et al. 2019). The QuEChERS (quick, easy, cheap, rugged, effective and safe) method developed by Anastassiades et al. (2003) is the most widely used sample preparation approach in the World. This method is simple and enables various modifications to be made at almost every process of the analysis (Rejczak and Tuzimski, 2015).

In this study, we aimed to develop methods with high sensitivity, accuracy, and precision to meet the SANTE/12682/2019 standard for determination of chlorsulfuron and pendimethalin pesticide residues in soil by modifying QuEChERS extraction and SPE clean-up using liquid chromatography- tandem mass spectroscopy (LC-MS/MS).

2. Material and Method

2.1. Standarts, reagents and sorbents

Chlorsulfuron (99.60% purity) and Pendimethalin (97.34% purity) reference standards were taken from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile (MeCN), methanol (MeOH), magnesium sulfate anhydrous (MgSO4), sodium acetate (NaOAc) and acetic acid (AcOH) were taken from Merck (Darmstadt, Germany). Primary secondary amine (PSA), graphitized carbon black (GCB) were taken from Supelco Analytical (Bellefonte, PA, USA). C18 was obtained from Agilent Technologies (Santa Clara, CA, USA).

2.2. Device and Tools

In the study, LC-MS/MS (Shimadzu LC-MS/ MS-8050), centrifuge (Hettich Rotina 380, 50 mL and Hettich Universal 320R, suitable for 15 mL centrifuge tube), analytical balance (Shimadzu AUW220D, ±0.0001 g), industrial cutter (Empero), Vortex (Ika) were used. Also, micropipette, 15 and 50 mL centrifuge tubes, washing bottle, ultrasonic bath, 2 and 12 mL glass vials with screw cap, 5 mL syringes, 45/25 mm syringe filters, balloon joje, disposable pipette and various materials such as weighing container were used in the analysis. Data was obtained and processed through LabSolution software provided with the instrument.

2.3. Extraction of samples, clean up

Extraction and clean up in residue analysis was performed with 5 different modified QUECHERS. Detailed information of the method is given in schematic diagram (Figure 1).

2.4. Chromatographic conditions

Chromatographic analysis were performed using LC-MS/MS (Liquid Chromatography/Tandem Mass Spectrometer). Chromatographic seperation were performed using a gradient elution program with eluent A consisting dH_2O + 5 mM ammonium formate and eluent B consisting of MeOH + 5 mM ammonium formate. Analysis started with 5% eluent B, which was increased linearly to 60% in 3 min, 70% in 4 min, 80% in 6 min, 95% in 7 min. This gradient was held for further 1.5 min before being returned to 5% eluent B in 8.51 min, , followed by re-equilibration time for 6.49 min, to give a total run time of 15 min. The flow rate was 0.40 mL min^{-1}. The injection volume was set to 10 µL. The column temperature was maintained at 40 ºC. For MS/MS detection, the electro spray ionization (ESI) interface was used positive polarity with the following; 400 ºC of heat block temperature, 250 ºC of desolvation line (DL) temperature, Nitrogen (N_2) as nebulizer gas of 2.9 L min^{-1} and drying gas of 10 L min^{-1}.

T0

15 g homogenate soil sample taken in a centrifuge tube (50 mL)

(Add spike solutions,wait 15 min)

Add 15 mL in acetonitrile (1% acetic acid) and shake vigorously by hand for 1 minute

Pour salts (266,6 mg $MgSO_4$,66,6 mg NaCl, 66,6 mg TSCD and 33,3 mg DHS per g of soil) into the extraction tube and shake vigorously by hand for 1 minute

Centrifuge 5 min at 5000 rpm

8 mL supernatant transfer to the 15 mL tube including 150 mg $MgSO_4$ and 50 mg PSA per mL of extract and shake vigorously by hand for 30 seconds

Centrifuge 5 min at 5000 rpm

By syringe filtered and transfer into 2 mL glass vials for LC-MS/MS.

T1

10 g soil homogenate soil sample taken in a centrifuge tube (50 mL)

(Add spike solutions,wait 15 min)

Add 10 mL in acetonitrile (1% acetic acid) and shake vigorously by hand for 1 minute

Pour salts (400 mg $MgSO_4$,10 mg NaCl, 10 mg TSCD and 33,3 mg DHS per g of soil) into the extraction tube and shake vigorously by hand for 1 minute

Centrifuge 5 min at 5000 rpm

6 mL supernatant transfer to the 15 mL tube including 200 mg $MgSO_4$ and 66.6 mg PSA per mL of extract and shake vigorously by hand for 30 seconds

Centrifuge 5 min at 5000 rpm

By syringe filtered and transfer into 2 mL glass vials for LC-MS/MS.

T2

15 g (2:1 soil: water) homogenate soil sample taken in a centrifuge tube (50 mL)

(Add spike solutions,wait 15 min)

Add 15 mL in acetonitrile (1% acetic acid) and shake vigorously by hand for 1 minute

Pour salts (266,6 mg $MgSO_4$,66,6 mg NaCl, 66,6 mg TSCD and 33,3 mg DHS per g of soil) into the extraction tube and shake vigorously by hand for 1 minute

Centrifuge 5 min at 5000 rpm

8 mL supernatant transfer to the 15 mL tube including 150 mg $MgSO_4$ and 50 mg PSA per mL of extract and shake vigorously by hand for 30 seconds

Centrifuge 5 min at 5000 rpm

By syringe filtered and transfer into 2 mL glass vials for LC-MS/MS.

T3

15 g (2:1 soil: water) homogenate soil sample taken in a centrifuge tube (50 mL)

(Add spike solutions,wait 15 min)

Add 15 mL in acetonitrile (1% acetic acid) and shake vigorously by hand for 1 minute

Pour salts (266,6 mg $MgSO_4$,66,6 mg NaCl, 66,6 mg TSCD and 33,3 mg DHS per g of soil) into the extraction tube and shake vigorously by hand for 1 minute

Centrifuge 5 min at 5000 rpm

8 mL supernatant transfer to the 15 mL tube including 150 mg $MgSO_4$, 50 mg PSA, 50 mg C18 and 50 mg GCB per mL of extract and shake vigorously by hand for 30 seconds

Centrifuge 5 min at 5000 rpm

By syringe filtered and transfer into 2 mL glass vials for LC-MS/MS.

T4

15 g homogenate soil sample taken in a centrifuge tube (50 mL)

(Add spike solutions,wait 15 min)

Add 15 mL in acetonitrile (1% acetic acid) and shake vigorously by hand for 1 minute

Pour salts (266,6 mg $MgSO_4$,66,6 mg NaCl, 66,6 mg TSCD and 33,3 mg DHS per g of soil) into the extraction tube and shake vigorously by hand for 1 minute

Centrifuge 5 min at 5000 rpm

4 mL supernatant transfer to the 15 mL tube including 300 mg $MgSO_4$ and 100 mg PSA per mL of extract and shake vigorously by hand for 30 seconds

Centrifuge 5 min at 5000 rpm

By syringe filtered and transfer into 2 mL glass vials for LC-MS/MS.

Figure 1. Analytical steps of modified QuEChERS for the analysis of chlorsulfuron and pendimethalin in soil samples

3. Results and Discussion

Sample preparation methods are important in the analysis of samples with complex matrices, especially in the simultaneous analysis of many pesticides. QuEChERS is the most widely used sample preparation method in pesticide residue analysis today (Gavel et al., 2019). This method enables various modifications to be made at every step of the analysis (Rejczak and Tuzimski, 2015).

Both the extraction and cleaning steps were modified to improve the efficiency of QuEChERS sample preparation in soil. Each extraction–clean-up combination has been tested by analyzing five soil samples spiked with all target pesticides at the level of 100 µg kg^{-1}. Among the modified methods recovery values were found at an acceptable level (70 to 120%) in the T4 method (Table 1). In summary of method optimization, extraction with 266.6 mg MgSO4, 66.6 mg NaCl, 66.6 mg TSCD and 33.3 mg DHS, d-SPE cleanup with 300 mg $MgSO_4$ and 100 mg PSA were selected for validation study.

Table 1. *Mean recovery of chlorsulfuron and pendimethalin (100 µg kg^{-1}) spiked in soil using the modified methods*

Pesticide	**Spiking level (µg kg^{-1}**	**Test Method** (% Mean recovery^{a})				
		T0	**T1**	**T2**	**T3**	**T4**
Chlorsulfuron	100	140.1	155.9	243.5	232.5	71.7
Pendimethalin	100	65.3	57.9	121.7	62.6	96.1

^{a} n=5.

3.1. Mass spectrometry

The optimization of mass spectrometric (MS) parameters were initially performed in precursor scan and product scan using direct flow injection. Multiple reaction monitoring (MRM) was performed in positive ion mode. MS/MS parameters for the two herbicides analyzed are given in Table 2. Chromatogram of Chlorsulfuron and Pendimethalin spiked (100 µg kg^{-1}) soil sample are given in Figure 2. Method validation parameters were evaluated including specificity, linearity, accuracy and method limits of detection (LOD) and quantification (LOQ).

Table 2. *Precursor ion, product ion, Q1/Q3 Pre Bias and collision energies of Chlorsulfuron and Pendimethalin (Multiple Reaction Monitoring (MRM) parameters)*

Pesticide	Precursor ion (g mol^{-1})	Product ion (g mol^{-1})	Q1 Pre Bias (V)	Collision energies (eV)	Q3 Pre Bias (V)
Chlorsulfuron	357.80	141.10/ 167.10	-17.0/ -17.0	-19.0/ -19.0	-26.0/- 17.0
Pendimethalin	282.00	212.05/ 194.00	-11.0/ -19.0	-10.0/ -18.0	-22.0/ -22.0

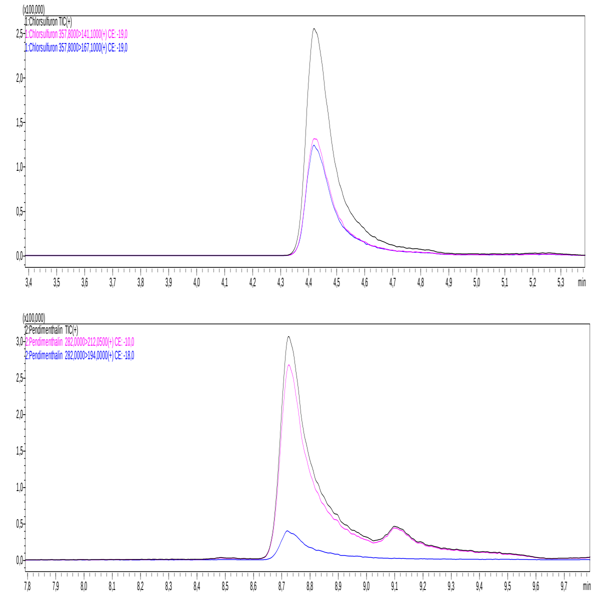

Figure. 2. Chromatograms obtained from soil samples spiked with standard solutions

3.2. Linearity and calibration curve

The linearity was evaluated using calibration curves at 5, 10, 25, 50 and 100 µg L^{-1} prepared in matrix blank extract (soil). Each calibration point was obtained by 3 repeated injections. Linear ranges and correlation coefficients are summarized in Table 3. It can be seen that correlation coefficient were all greater than 0.99. This result shows that the method was linear with a specified concentration ranges.

Table 3. *Calibration data*

Pesticide	Calibration matrix	Calibration range (µg mL^{-1})	Regression equation	Correlation coefficient (r^2)
Chlorsulfuron	soil	5-100	Y =(13490,1)X + (53892,8)	0.9907542
Pendimethalin	soil	5-100	Y =(31561,0)X + (-35780,7)	0.9981621

3.3. Accuracy

Accuracy is a parameter that covers the parameters of recovery and precision (repeatability and within-laboratory reproducibility). The repeatability studies were performed with 3 injections at 3 different concentrations (10, 50 and 100 µg kg^{-1}) on the same day. The within-laboratory reproducibility studies were performed with 3 injections at 3 different (10, 50 and 100 µg kg^{-1}) concentrations at five different times (Table 4). Data obtained during the validation process meet the criteria (Mean recovery; 70-120%, RSD% ≤ 20%) of the SANTE/12682/2019 guidance document (SANTE, 2019).

Table 4*. Mean recovery, repeatability (RSDr) and within-laboratory precision (RSDwr) of the method for the mixture of the compounds in soil spiked at different levels*

Pesticide	Spiking level (µg kg^{-1})	% Mean recovery	SD	RSDr %	% Mean recovery	SD	RSDwr %
Chlorsulfuron	10	96.5	0.35	3.66	104.6	1.32	12.6
	50	104.4	3.46	6.75	98.4	2.47	5.02
	100	94.5	3.24	3.43	91.0	9.69	10.1
Pendimethalin	10	100.2	0.31	3.05	87.4	1.02	11.7
	50	91.5	6.19	13.5	78.3	3.65	9.32
	100	91.7	2.45	2.67	94.9	3.53	3.72

3.3. LOD and LOQ values

The studies were performed in 10 replicates at a single concentration (10 µg L^{-1}) and the standard deviation (SD) and relative standard deviation (RSD%) values of chlorsulfuron and pendimethalin were calculated. The LOD value is determined as 3 times the calculated standard deviation values for chlorsulfuron and pendimethalin. LOQ value was calculated as 10 times the standard deviation values for chlorsulfuron and pendimethalin (Table 5). The LOQ was obtained lower than EU-MRL values (EC, 2008; EC, 2019).

Table 5*. Mean, SD, RSD%, LOD, LOQ and MRL values (µg kg^{-1})*

	Mean	SD	RSD %	LOD	LOQ	MRL
Chlorsulfuron	9.69	0.32	0.03	0.96	3.19	50*
Pendimethalin	10.1	0.43	0.04	1.30	4.34	50*

* EU-MRL lowest residual value for plant products (EU, 2008; EU, 2019)

4. Conclusions and Recommendations

In this study an analytical method based on modified QuEChERS extraction combined with LC-MS/MS analysis was developed for determination of residues of chlorsulfuron and pendimethalin in soil. The developed method demonstrated appropriate validation parameters in terms of linearity, limit of detection and quantification, high accuracy and precision. Owing to the MS/MS detection, the method gave a good sensitivity and selectivity for chlorsulfuron and pendimethalin. The LOQs assessed by the method were below than the MRL values prescribed by European Union (EU). Interfering peaks were not observed in the chromatograms of the analyzed soil samples. This method is suitable for chlorsulfuron and pendimethalin analysis in soil.

References

Anastassiades, M., Lehotay, S. J., Stajnbaher, D., & Schenck, F. (2003) Fast and easy multiresidue method employing acetonitrile extraction/partitioning and “dispersive solid-phase extraction” for the determination of pesticide residues in produce. J AOAC Int 86:412–431.

Alesso, M., Escudero, L.A., Talio, M.C., & Fernández, L.P. (2016). Monitoring of chlorsulfuron in biological fluids and water samples by molecular fluorescence using rhodamine B as fluorophore, Talanta, Volume 160, Pages 431-436. https://doi.org/10.1016/j.talanta.2016.07.053.

Andressa, G., Djenaine, D. S., & Sergio A. S., M., (2011). Pendimethalin determination in natural water, baby food and river sediment samples using electroanalytical methods. Microchemical Journal, 98(1), 9–143.

Bletsou, A. A., Hanafi, A. H., Dasenaki, M.E., & Thomaidis N.S. (2013). Development of specific LC-ESI-MS/MS methods to determine bifenthrin, lufenuron and iprodione residue levels in green beans, peas and chili peppers under Egyptian field condition. Food Anal Methods 6:1099–112.

Bonmatin, J. M., Moineau, I., Charvet, R., Fleche, C., Colin, M. E., & Bengsch, E. R. (2003). A LC/APCI-MS/MS method for analysis of imidacloprid in soils, in plants, and in pollens. Anal Chem 75:2027–2033.

Botitsi, H. V., Garbis, S. D., Economou, A., &Tsipi D. F. (2011). Current mass spectrometry strategies for the analysis of pesticides and their metabolites in food and water matrices. Mass Spectrom Rev 30:907–939.

Chopra, I., Chauhan, R., & Kumari, B. (2015). Persistence of pendimethalin in/on wheat, straw, soil and water. Bulletin of Environmental Contamination and Toxicology, 95(5), 694–699.

Diğrak, M., Kirbağ, S. & Özçelik, S. (1996). Bazı Pestisitlerin Toprak Mikroorganizmaları Üzerine Etkisi. Turkish Journal of Agriculture and Forestry, TÜBİTAK, 20, 165-173.

Dolores, B. M., María, M. G., Piedad, P. V., & Dolores, M., G. G (2007). Simple and rapid determination of benzoylphenylurea pesticides in river water and vegetables by LC–ESI-MS. Chromatographia, 66(7-8), 533–538.

EU (European Union). (2008). Commission Regulation (EC) No 149/2008 of 29 January 2008 amending Regulation (EC) No 396/2005 of the European Parliament and of the Council by establishing Annexes II, III and IV setting maximum residue levels for products covered by Annex I thereto. Official Journal of the European Union L, 51, 1-398.

EU (European Union). (2019). Commission Regulation (EU) 2019/1791 of 17 October 2019 amending Annexes II, III and IV to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for 1-decanol, 2,4-D, ABE-IT 56, cyprodinil, dimethenamid, fatty alcohols, florpyrauxifen-benzyl, fludioxonil, fluopyram, mepiquat, pendimethalin, picolinafen, pyraflufen-ethyl, pyridaben, S-abscisic acid and trifloxystrobin in or on certain products. Official Journal of the European Union L, 62, 1-66.

Han, L., Guo, B. Y., Feng, J. H., Lu, X. M., & Lin J.M. (2008). Study on the enantioselective degradation of imazethapyr in soil by CE. Chromatographia 68:1071–1073.

Hernandez, F., Pozo, O. J., Sancho, J. V., Bijlsma, L., Barreda, M., & Pitarch, E. (2006) Multiresidue liquid chromatography tandem mass spectrometry determination of 52 non gas chromatography-amenable pesticides and metabolites in different food commodities. J Chromatogr A 1109:242–252.

Islam, A. K. M. M., Hong, S. M., Lee, H. S., Moon, B. C., Kim, D., & Kwon, H., (2018). Identification and characterization of matrix components in spinach during QuEChERS sample preparation for pesticide residue analysis by LC-ESI-MS/MS, GC-MS and UPLC-DAD. Journal of Food Science and Technology, 55(10), 3930–3938.

Jape P., Maheshwari V., & Chaudhari A. (2019) Microbial Degradation of Nitroaromatic Pesticide: Pendimethalin. In: Singh D., Gupta V., Prabha R. (eds) Microbial Interventions in Agriculture and Environment. Springer, Singapore. https://doi.org/10.1007/978-981-13-8391-5_20

Jigneshkumar, V. R., & Suresh, K. K. (2017). Simple and selective detection of pendimethalin herbicide in water and food samples based on the aggregation of ractopamine dithiocarbamate functionalized gold nanoparticles. Sensors and Actuators B: Chemical, 245, 541–550.

Kurutaş, E. B., & Kılınç, M. (2003). Pestisitlerin Biyolojik Sistemler Üzerine Etkisi. Arşiv Kaynak Tarama Dergisi, 12 (3).

Mohammad, F., Roya, N., Hooshang, S., & Mohammadkazem, R. (2018). Determination of acetamiprid, imidacloprid, and spirotetramat and their relevant metabolites in pistachio using modified QuEChERS with liquid chromatography-tandem mass spectrometry. Food Chemistry, 240, 634–641.

Navneet, K., & Makhan, S. B. (2015). Harvest time residues of pendimethalin and oxyfluorfen in vegetables and soil in sugarcane-based intercropping systems. Environmental Monitoring and Assessment, 187(5), 221–230.

Park, J. H., Mamun, M. I., Choi, J. H., Abd El-Aty, A. M., Assayed, M. E., Choi, W. J., Yoon, K. S., Han, S. S., Kim, H. K., Park, B. J., Kim, K. S., Kim, S. D., Choi, H. G., & Shim, J. H., (2010). Development of a multiresidue method for the determination of multiclass pesticides in soil using GC. Biomedical chromatography: BMC, 24(8), 893–901. https://doi.org/10.1002/bmc.1383

Pinheiro, A., & de Andrade, J. B., (2009). Development, validation and application of a SDME/GC-FID methodology for the multiresidue determination of organophosphate and pyrethroid pesticides in water. Talanta, 79(5), 1354–1359. https://doi.org/10.1016/j.talanta.2009.06.002

Rejczak, T., & Tuzimski, T. (2015). A review of recent developments and trends in the QuEChERS sample preparation approach. Open Chemistry, 19, 980–1010. https://doi.org/10.1515/chem-2015-0109

Saha, A., Shabeer T P, A., Banerjee, K., Hingmire, S., Bhaduri, D., Jain, N. K., & Utture, S. (2015). Simultaneous analysis of herbicides pendimethalin, oxyfluorfen, imazethapyr and quizalofop-p-ethyl by LC-MS/MS and safety evaluation of their harvest time residues in peanut (Arachis hypogaea L.). Journal of food science and technology, 52(7), 4001–4014. https://doi.org/10.1007/s13197-014-1473-9

SANTE. (2019). Document No Sante/12682/2019 Method validation & quality control procedures for pesticide residues analysis in food & feed. European Commission: Brussels, Belgium

Sarkar, S., Berbardes, D.J., Keely, J., Möhring, N. & Jansen, K. (2021). The use of pesticides in developing countries and their impact on health and the right to food. EU publications. https://doi.org/10.2861/28995

Sato, K. (1987). Penthaclorophenol (PCP) Tolerance of Bacteria Isolated from Soil Percolated with PCP. Journal of Pesticide Science, 12, 582-589.

Taylor, M. D., Klaine, S. J., Carvalho, F. P., & Barcelo, D. (2002). Pesticide residues in coastal tropical ecosystems: distribution, fate and efects. CRC Press, Boca Raton.

Sharma, A., Kumar, V., Bhardwaj, R., & Thukral, A.K. (2017). Seed presoaking with 24-epibrassinolide reduces the imidacloprid pesticide residues in green pods of Brassica juncea L. Toxicol Environ Chem 99(1):95–103.

Wong, J., Hao, C., Zhang, K., Yang, P., Banerjee, K., Hayward, D., Iftakhar, I., Schreiber, A., Tech, K., Sack, C., Smoker, M., Chen, X., Utture, S. C. & Oulkar D.P., (2010). Development and interlaboratory validation of a QuEChERS-Based liquid chromatography-tandem mass spectrometry method for multiresidue pesticide analysis. J Agric Food Chem 58: 5897–5903.

Yang, Q., Ai, X., Li, S., Liu, H., & Liu, Y. (2019). Determination of pendimethalin in water, sediment, and Procambarus clarkii by high performance liquid chromatography-triple quadrupole mass spectrometry. Environ Monit Assess 191, 621. https://doi.org/10.1007/s10661-019-7794-4

Zhang, Z. H., Dong, M. F., Hao, X. H., Han, L. J., Song, S. Y., & Yao, W., (2019). Evaluation of cleanup procedures in pesticide multi-residue analysis with QuEChERS in cinnamon bark. Food Chemistry, 276, 140–146.

Zeng, D. Y., Shi H. Y., Li, B., Wang, M., & Song, B. A. (2006). Development of an enzyme-linked immunosorbent assay for quantitative determination of quizalofop-p-ethyl. J Agric Food Chem 54: 8682–86