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Research Article

SIMULTANEOUS DETERMINATION OF NEONICOTINOID PESTICIDES IN TEA-TREE PLANTATION SOIL BY ULTRA-PERFORMANCE LIQUID CHROMATOGRAPHY TANDEM MASS SPECTROMETRY

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ABSTRACT

The quality of tea is influenced by many criteria related to farming methods, including soil characteristics and the use of chemical substances, typically pesticides or insecticides. The group of neonicotinoids (NEOs) is among the pesticides used in agriculture with the potential of accumulation in soils. In this study, the method for determining NEOs in tea-tree plantation soils was investigated and validated based on QuEChERS and UPLC-MS/MS as the sample preparation and measurement methods, respectively. The Acquity UPLC BEH C18 column (130 Å, 1.7 µm, 2.1 x 100 mm) (Waters Corporation) was used to serve the separation performed on the UHPLC System (UltiMate 3000, Thermo Fisher Scientific) coupled with tandem mass spectrometry (TSQ Endura, Thermo Fisher Scientific). The methods showed a proper linearity (R^2 > 0.995), an acceptable repeatability and reproducibility (%RSDs varied from 0.87-9.6 for both intra-day and inter-day), and high recoveries (81-102% for most of the spiked samples). The validated method was then applied to real soils collected from the tea plantations in the North (ancient tea plants) and South (organic and VietGAP), Vietnam. The results showed that undetected pesticide concentrations for northern soils and imidacloprid with its highest content (81.0 $\mu g\ kg^{-1}$) were recorded in the South.

Từ khóa: neonicotinoids; tea-tree plantation soils; QuEChERS; UPLC-MS/MS

1. Introduction

Tea is one of the most common non-alcoholic beverages consumed by many people around the world, especially in Asian countries. Tea tree is known with its scientific name as *Camellia sinensis* (L.) Kuntze, belonging to the family of Theaceae (Han, Mihara,

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Hashimoto, & Fujino, 2014). The properties of tea-tree plantation soils, especially the residues of pesticides in soils, have become a really important concern due to their influence on the quality of tea leaves and tea products. Moreover, the soils and underground water could be contaminated by long-term pesticide applications. Therefore, reliable and effective analytical techniques have been developed worldwide to identify, monitor, and assess the quantities of pesticide residues in agricultural soils in general and tea-tree plantation soils in specific.

The neonicotinoids have been used as an alternative to the organophosphates, N-methyl-carbamate, and pyrethroid insecticides. The neonicotinoids can be classified into three different varieties based on their functional groups of N-cyanamides (═N─CN), nitromethylenes (═CH─NO_2), and N-nitroguanidines (═N─ NO_2) (Schaafsma, Limay-Rios, Baute, Smith, & Xue, 2015). The popular commercially available neonicotinoids could be listed as imidacloprid, acetamiprid, nitenpyram, thiacloprid, thiamethoxam, clothianidin, and dinotefuran, in which imidacloprid currently accounts for approximately 41.5% of the total neonicotinoids used. Neonicotinoids have been registered for agricultural use in more than 120 countries and are widely applied in over 140 crop plants. Most neonicotinoids could be used as a foliar spray, seed treatment, and soil application (Jeschke, Nauen, Schindler, & Elbert, 2011).

For human beings, neonicotinoids can cause acute toxicity, which leads to diarrhea, watery eyes, urination, salivation, and central nervous system (CNS) irritation, and chronic toxicity that may cause allergies, loss of behavior control, nervous system poisoning, cancer, immune disorders, and reproductive disorders (Niaz et al., 2016). The neonicotinoid compounds also caused a serious decline in the number of bees (from 6 to 2.5 million between 1945 and 2008), which had a serious effect on agriculture. In 2013, the European Union (EU) implemented a ban on three types of neonicotinoids involving imidacloprid, clothianidin, and thiamethoxam for several crops such as corn, sunflower, canola, wheat, barley, oats, and flowering fruit (Wood, & Goulson, 2017). In 2018, the EU adopted a regulation that completely banned the outdoor use of imidacloprid, clothianidin, and thiamethoxam. In Vietnam, the number of studies related to neonicotinoids in general, and these compounds in tea-tree plantation soils are still limited.

In the matrix of soils, the pesticide residues are extracted by various methods, including liquid-liquid extraction, solid-phase dispersion, ultrasound-assisted solvent extraction, and QuEChERS. Several common solvents listed as methanol, acetone, and acetonitrile were employed for the extraction steps by different researchers. Among pesticides, neonicotinoids are characterized by low volatility and high polarity; moreover, their residue concentrations are adequate for the determination by HPLC or UPLC coupled with tandem mass spectrometry (Obana, Okihashi, Akutsu, Kitagawa, & Hori, 2003;

Sirtori, Aguera, Carra, & Sanchez Perez, 2014; Suganthi, Nikita, Kousika, Bhuvaneswari, & Sridharan, 2018).

The objectives of this study were to (i) investigate the sample preparation procedure (sample extraction and clean-up), (ii) validate the analytical method of neonicotinoids, and (iii) apply the validated method to several tea-tree plantation soils (Yen Bai and Lam Dong, Vietnam) to evaluate the levels of these pesticides.

2. Materials and methods

2.1. Chemicals and reagents

Deionized water (DI, Milli-Q, Merck, Germany) was used throughout this study. Solid chemicals, reagents, and solvents including formic acid (HCOOH), acetic acid (CH_3COOH), acetonitrile (ACN, HPLC grade), methanol (CH_3OH, HPLC grade), magnesium sulfate anhydrous ($MgSO_4$), ammonium formate ($HCOONH_4$), sodium chloride (NaCl), trisodium citrate dihydrate, and disodium citrate sesquihydrate, kit d-SPE (150 mg $MgSO_4$, 50 mg C18, 50 mg PSA) were of analytical grade and obtained from Merck, Germany. Acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, thiacloprid, thiamethoxam standards (> 99 %) were purchased from Sigma-Aldrich and used to prepare the stock solution of 1000 mg L^{-1} in methanol. Intermediate standard solutions of 50μg L^{-1} and working standard solutions of 0.50, 1.0, 2.0, 5.0, 10.0, 25.0, 50.0, 75.0, and 100 μL L^{-1} were prepared daily prior to use by diluting the stock standard solution.

2.2. Sample collection, pre-treatment, and storage

A total of 8 tea-tree plantation soil samples (0-30 cm in depth) were collected during the dry season (2019) from different regions in Vietnam (Table 1), followed by TCVN 5297:1995 (1995).

Table 1. *Tea-tree plantation soil codes and sampling locations*

No.	Sample code	Location	Brief description
1	YB-1 YB-2 YB-3	Yen Bai province (the North of Vietnam)	Ancient tea trees (Snow Shan Tea)
2	LD-1 LD-2 LD-3	Lam Ha, Lam Dong province (the South of Vietnam)	Organic cultivation (without inorganic fertilizers and crop protection chemicals)
3	LD-4 LD-5	Da Lat, Lam Dong province (the South of Vietnam)	VietGAP

In the pre-treatment steps, firstly, grass, leaves, roots, and stones were manually removed. All soil samples were dried in a thermostatic air-blower-driven drying closet at 40 °C to a constant mass. The samples were then ground, passed through a 200-mesh nylon sieve (0.074 mm), and carefully homogenized in the laboratory. Before being

analyzed, these samples were kept in polypropylene zipper locking bags and stored in a desiccator with silica gel as the moisture absorbent.

2.3. Sample preparation

The sample extraction and clean-up procedure (Figure 1) were carried out and modified based on the method presented in EN 15662:2018 (2018) and reference document from Michel and Pszczolinska (2016). The modifications proceeded in order to make the procedure possible with the available conditions and facilities of the laboratory.

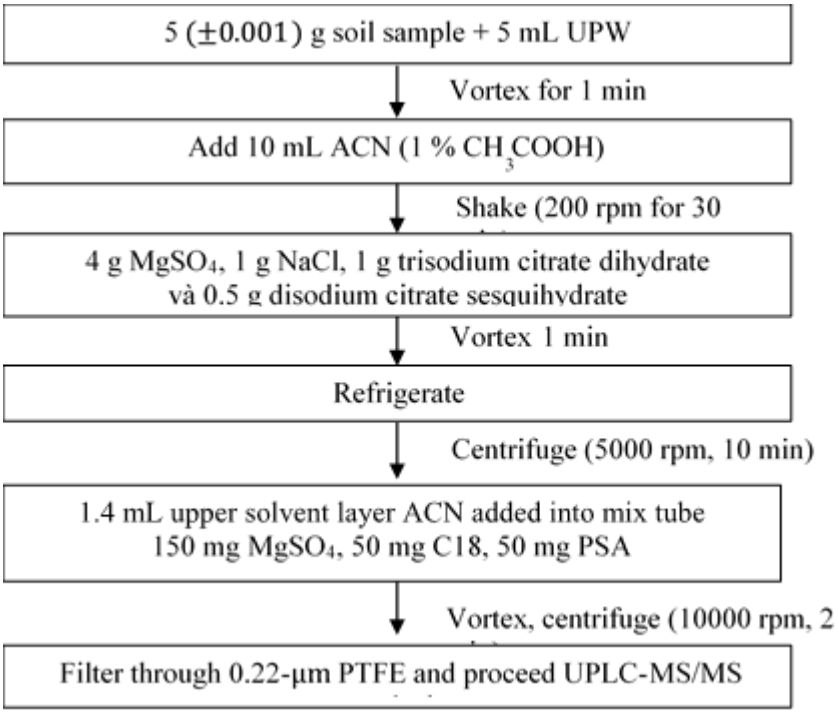

Figure 1. *Sample extraction and clean-up by QuEChERS*

A standard of 50 µg L^{-1} was spiked to the soil matrix, then followed by the sample preparation, as shown in Figure 1. The spiked samples were used to assess the matrix effects by changing the hydration volumes from 5 mL to 10 mL and also by the variation in the centrifuge velocity of 4000, 5000, and 10000 rpm. The matrix effects were evaluated by the calculation of ME (%) according to the following equation (del Mar Gómez-Ramos, Rajski, Lozano, & Fernández-Alba, 2016):

$$\text{ME (\%)} = \left(\left(\frac{\text{analyte signal spiked in the matrix}}{\text{analyte signal in pure solvent}}\right) - 1\right) \times 100$$

The following criteria were applied to assess the matrix effects:

- ME = 0: no matrix effects
- ME < 0: ion suppression matrix effects
- ME > 0: ion enhancement matrix effects
- Particularly, when ME in the range of 0-|20| %, it could be assumed that there are no matrix effects (Uclés et al., 2017).

2.4. The neonicotinoids compounds analysis by UPLC-MS/MS

The procedure for the determination of neonicotinoids in soil by UPLC-MS/MS includes sample extraction and clean-up (sample preparation) and UPLC-MS/MS analysis. The separation, detection, identification, and quantification of neonicotinoids were performed on an Ultra-High Performance Liquid Chromatography (UHPLC, UltiMate 3000) coupled with tandem mass spectrometry (MS/MS, TSQ Endura), Thermo Fisher Scientific. The LC separation was conducted in an ACQUITY UPLC BEH C18 column (130 Å, 1.7 µm, 2.1 × 100 mm) (Waters, Milford, MA, USA). A gradient program was used with mobile phase, consisting of solvent A (MeOH: H_2O = 2: 98 (+ 0.1 % HCOOH + 5 mM $HCOONH_4$) and solvent B (98 : 2 (+ 0.1 % HCOOH + 5 mM $HCOONH_4$), shown in Figure 2. A subsequent re-equilibrium time of 2 minutes was performed before the next injection, in which the injection volume was 2 µL by an autosampler. The flow rate was 0.3 mL min^{-1}. The column and autosampler temperatures were set at 40 and 15 ^oC, respectively.

The MS/MS analysis was performed on a TSQ Endura triple-quadrupole mass spectrometer equipped with an ESI source (Thermo Fisher Scientific). The positive electrospray ionization (ESI+) mode was used for quantification with the parameters as the capillary voltage of 3500 V, cone voltage of 45 V, source block temperature of 120 ^oC, cone gas of 60 L h^{-1}, desolvation temperature of 350 ^oC, desolvation gas of 500 L h^{-1}, collision gas flow rate of 0.2 mL min^{-1}. Nitrogen gas was used as desolvation and cone gas, and the collision gas was argon. The tuning period was performed by direct injection of the individual and mixed standard pesticide solutions (10 mg L^{-1}) into the mass spectrometer using a syringe pump at the flow rate of 50 µL min^{-1}. The interface conditions were optimized for the highest intensities of the precursor ions. The chromatograms were recorded in full scan mode to discover the retention time. Neonicotinoids were identified according to their retention times, quantifier, and confirming ions in their MRM mode. Analytical instrument control, data acquisition, and treatment were performed by TraceFinder software version 5.1 (Thermo Fisher Scientific).

Figure 2. *UPLC gradient program*

The chromatographic analyses were run in triplicate to assure repeatability among runs. The performance characteristics of the method were evaluated, including the calibration curves, the limit of detection and quantification estimation, assessment of repeatability/intra-day and reproducibility/inter-day (% RSD_r and % RSD_R), and recovery based on the criteria shown in Appendix F AOAC (2016). The calibration curves (0.50-100 μL L^{-1} for all compounds) were established in the format of y = ax + b, whereas y and x represented the peak area and concentration (μg L^{-1}) of the analyte, respectively. The method accuracy and precision were assessed from the measurements during the recovery study conducted by samples spiked at levels of 2, 4, 10, 20, 50, 100, and 200 μg kg^{-1}.

3. Results and discussion

3.1. Optimization of MS/MS conditions

All the pesticides of interest were optimized in the positive electrospray ionization (ESI+) mode to select the proper ions based on the chemical ionization characteristics of neonicotinoids. The mass spectrometer was operated in full scan and MRM (multiple reaction monitoring) modes. The optimization of the precursor, product ions, cone voltage, and collision energy were recorded through the tuning period. The retention times and MRM transitions are shown in Table 2.

Table 1. *MRM transitions for ions of neonicotinoids in LC-MS/MS*

No.	Compound	Retention time (min)	Precursor (m/z)	Product (m/z)	Collision energy (V)	RF Lens (V)
1	Acetamiprid	3.30	223.088	126.071 (Q) 90.183 (C)	20.11 33.26	107.36
2	Clothianidin	3.60	250.062	169.071 (Q) 132.000 (C)	10.61 14.70	85.52
3	Dinotefuran	3.80	203.162	129.171 (Q) 157.100 (C)	11.26 10.25	66.40
4	Imidacloprid	4.10	256.062	209.000 (Q) 212.000 (C)	14.10 10.25	92.80
5	Nitenpyram	4.20	271.100	225.040 (Q) 189.111 (C)	12.78 10.25	102.51
6	Thiacloprid	4.50	253.088	126.040 (Q) 186.000 (C)	20.52 13.74	110.39
7	Thiamethoxam	4.90	292.000	211.000 (Q) 181.071 (C)	10.25 21.12	86.43

Q: quantifier ion; C: confirming ion

A total running duration for each sample is only about 5 minutes, indicating the ability to apply in routine analysis. The retention times of the analytes were relatively consistent with their $logK_{ow}$ values. However, dinotefuran was eluted first despite its lower

$logK_{ow}$ than nitenpyram. It might be because the pH of the mobile phase is approximately 2.5-3.0, and under this pH condition, dinotefuran (pKa = 12.6) existed dominantly in its ionic forms while nitenpyram (pKa = 3.1) exists both in ionic and neutral species. The similarity was also observed in the situation of happened clothianidin (pKa = 11.1 and $logK_{ow}$ = 0.905) and acetamiprid (pKa = 0.7 and $logK_{ow}$ = 0.8).

3.2. The matrix effects evaluation

The first step in the sample preparation procedure is to use a certain amount of water for sample hydration purposes. Moreover, the differences in the quantities of water for hydration might cause matrix effects along with the changes in centrifuge velocity. The ME values for each pesticide were calculated and performed in Figure 3.

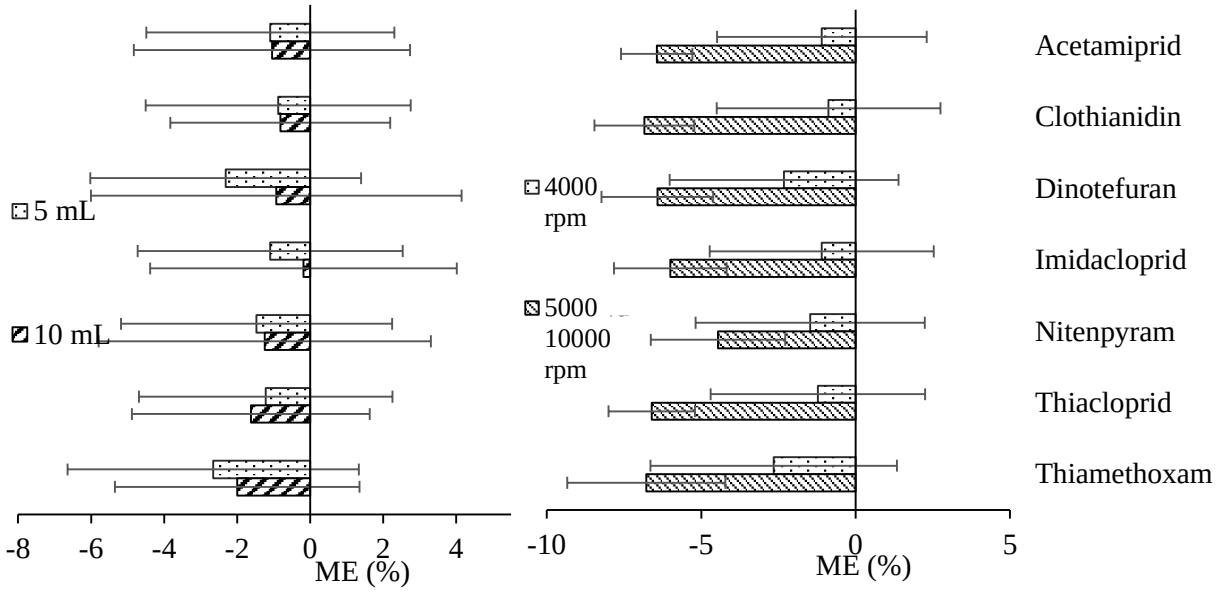

Figure 3. *The assessment of matrix effects (ME ± SD (%)) from the variations in hydration volumes (left) and centrifuge velocity (right)*

As can be seen from Figure 3, all ME values were mostly below zero (ion suppression effects). The MEs between 5-mL and 10-mL hydration were not remarkably different (–0.9 to –2.7% vs. –0.2 to –2.0%) and exhibited nearly the same ranges for all pesticides. The ion suppression effects could be explained because water-soluble released from the soil matrix during the hydration process might act as interferences. For the influences of centrifuge velocity, 4000 rpm showed smaller MEs than those of 5000 and 10000 rpm (–0.9 to 2.7% vs. –4.5 to –6.8%). However, all of the obtained MEs were in the range of 0-|20|%, considered as no matrix effects from the variations in hydration volumes and centrifuge velocities.

3.3. Method validation for the determination of neonicotinoids by UPLC-MS/MS

The validation parameters were calculated for the neonicotinoid concentration range from 2.0 to 200 $\mu g\ L^{-1}$ as performed in Table 3.

Table 3. *Method validation of NEOs by UPLC-MS/MS*

No.	Compounds	Regression equation	R^2	Recovery (%)	Intra-day (%RSD_r)	Inter-day (%RSD_R)
1	Dinotefuran	y = 3810.2x−1188	0.9994	81-94	1.0-4.9	0.87-6.2
2	Nitenpyram	y = 2507.3x−800.57	0.9994	71-82	2.0-9.6	5.5-7.9
3	Thiamethoxam	y = 7185.3x−3737.3	0.9990	91-102	1.5-2.4	1.5-5.1
4	Imidacloprid	y = 3055x−832.13	0.9992	89-100	1.1-3.7	1.3-5.9
5	Clothianidin	y = 2102.5x−609.74	0.9993	89-96	0.90-6.4	2.1-6.4
6	Acetamiprid	y = 14090x−7733.2	0.9995	86-95	1.7-4.0	2.7-5.4
7	Thiacloprid	y = 18097x−10287	0.9994	87-98	1.5-3.6	1.2-4.6

R^2: squared regression equation correlation coefficient calculated for the linear range of 2.0-200 μg L^{-1}; the confidence level p = 0.95.

In this study, the regression equations were established in the same concentration range for all of the analytes and showed acceptable linearity, according to Appendix F AOAC (2016) ($R^2 \geq 0.995$). The LOQ was defined as the minimum spiking level with RSD_r and RSD_R below 20% and the recoveries of 70-120%. In this study, the LOQs were 2.0 μg kg^{-1} for each compound. For trueness evaluation, the recoveries of spiked samples were ranged from 81-102%, except for nitenpyram exhibiting the lowest recoveries (71-83%). The reason might be due to the very short half-life of this pesticide in soils (only from 1 to 15 days), making nitenpyram in the spiked soils partly decomposed during experiments. The current method met the requirements of the repeatability and reproducibility presentd in the Appendix F AOAC (2016), CODEX, CXG 90-2017 (2017), and SANTE/11813/2017 (2017) standards for pesticide residues in food and feed.

3.4. Application of the validated method to real tea-tree plantation soil samples

The validated method was used to determine seven neonicotinoids in eight collected tea-tree plantation soil samples. The analytical results were performed in Table 4.

Table 4. *The analytical results of NEOs in soil samples (μg kg^{-1}), present as means (standard deviations)*

No.	Analytes	YB-1	YB-2	YB-3	LD-1	LD-2	LD-3	LD-4	LD-5
1	Acetamiprid	ND	ND	ND	ND	ND	ND	ND	ND
2	Clothianidin	ND	ND	ND	13.2 (0.60)	20.0 (0.28)	14.4 (0.44)	2.60 (0.10)	ND
3	Dinotefuran	ND	ND	ND	43.9 (3.9)	71.8 (2.1)	78.2 (3.9)	ND	ND
4	Imidacloprid	ND	ND	ND	18.9 (0.98)	81.0 (2.7)	6.56 (0.10)	15.2 (0.40)	ND
5	Nitenpyram	ND	ND	ND	ND	ND	ND	ND	ND
6	Thiacloprid	ND	ND	ND	ND	ND	ND	ND	ND
7	Thiamethoxam	ND	ND	ND	11.8 (0.29)	49.8 (0.99)	52.4 (1.5)	23.2 (0.54)	ND

ND: not detected

The concentrations of clothianidin, dinotefuran, imidacloprid, and thiamethoxam in soils varied in the ranges of were 2.60-20.0 µg kg^{-1}, 43.9-78.2 µg kg^{-1}, 6.56-81.1 µg kg^{-1}, and 11.8-52.4 µg kg^{-1}, respectively. The tea-tree plantation soils collected from Suoi Giang, Yen Bai Province (the North) presented "not detected" for all neonicotinoids. It might be because these regions were not cultivated by any inorganic fertilizers and pesticides for a very long time to make the ancient tea plants be able to grow and develop naturally without much intervention from human and farming activities. LD soil samples had relatively higher concentrations of neonicotinoids than the other samples, especially dinotefuran and thiamethoxam determined in LD-3 (78.2 and 52.4 µg kg^{-1}, respectively), imidacloprid in LD-2 was 81.0 µg kg^{-1}. Several pesticides, including acetamiprid, nitenpyram, and thiacloprid, were not detected with the current analytical method due to a much shorter half-life in soils compared to other compounds, in which clothianidin, dinotefuran, imidacloprid, and thiamethoxam had a relatively long half-life (50-545 days). The soils collected in Lam Dong Province which has just changed the farming methods from conventional to organic and VietGAP since nearly five years ago, without any use of these pesticides, could be in their decomposition process. Due to their stability in the environment, they, at the sampling time, still existed in soils. Therefore, the concentrations of clothianidin, dinotefuran, imidacloprid, and thiamethoxam were still found in these soils.

4. Conclusions

In this study, a QuEChERS method presented in EN 15662:2018 (2018) was investigated and modified to determine the concentration of seven neonicotinoid pesticides in tea-tree plantation soils collected from the North and South (Vietnam) using UPLC-MS/MS as the measurement method. The analytical method was validated according to the criteria performed in Appendix F AOAC (2016) and allowed seven neonicotinoid compounds to be separated within 5 minutes. Good analytical recovery, repeatability, reproducibility, and linearity were obtained. The LOQs were estimated as 2.0 µg kg^{-1} for all of the analytes. The recoveries of most samples were in the range of 81-102%, and %RSDs varied from 0.87-9.6 for both intra-day and inter-day. The validated method was then applied to determine the contents of these seven pesticides in real tea-tree plantation soil samples collected from Yen Bai (the North) and Lam Dong (the South). Among these regions, Yen Bai had undetected concentrations of neonicotinoids due to the long-term growth and development of ancient tea plants. The soils in Lam Dong exhibited certain contents for several compounds with longer half-life such as clothianidin, dinotefuran, imidacloprid, and thiamethoxam despite the current practices of using organic and VietGAP farming. The presence of these pesticides might be in their decomposition process. Therefore, more soil samples should be collected, and the sampling activities should be carried out for a longer time to obtain a better understanding and conclusions.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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XÁC ĐỊNH ĐỒNG THỜI CÁC HỢP CHẤT THUỐC BẢO VỆ THỰC VẬT NEONICOTINOID TRONG ĐẤT TRỒNG TRÀ BẰNG PHƯƠNG PHÁP SẮC KÍ LỎNG SIÊU HIỆU NĂNG GHÉP NỐI ĐẦU DÒ KHỐI PHỔ HAI LẦN

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ABSTRACT

Chất lượng của trà bị ảnh hưởng bởi nhiều yếu tố liên quan đến phương thức canh tác trồng trọt, bao gồm các đặc tính của đất cũng như việc sử dụng những hợp chất hoá học, đặc biệt là hợp chất thuốc bảo vệ thực vật. Nhóm hợp chất neonicotinoid (NEO) được xem là một trong các loại thuốc bảo vệ thực vật sử dụng trong nông nghiệp và có khả năng tích lũy trong đất. Trong nghiên cứu này, phương pháp xác định các hợp chất NEO trong đất trồng trà được khảo sát và thẩm định sử dụng QuEChERS và UPLC-MS/MS lần lượt là phương pháp xử lí mẫu và phương pháp đo. Cột sắc kí lỏng Acquity UPLC BEH C18 (130 Å, 1.7 µm, 2.1 x 100 mm) (Waters) được sử dụng để tách các hợp chất trên hệ máy UHPLC (UltiMate 3000) ghép nối với đầu dò khối phổ hai lần (TSQ Endura) của hãng Thermo Fisher Scientific. Phương pháp cho độ tuyến tính phù hợp (R^2 > 0.995), độ lặp lại và độ tái lặp tốt (%RSD dao động trong khoảng 0.87-9.6%), hiệu suất thu hồi cao (81-102% đối với hầu hết các mẫu thêm chuẩn). Phương pháp đã thẩm định được áp dụng vào mẫu đất được thu thập từ các vùng trà ở miền Bắc (nơi trồng cây trà cổ thụ) và miền Nam (canh tác theo phương thức hữu cơ và VietGAP). Kết quả cho thấy các mẫu đất ở miền Bắc không phát hiện các hợp chất neonicotinoid và hợp chất imidacloprid có hàm lượng cao nhất (81.0 $\mu g\ kg^{-1}$) được ghi nhận trong mẫu đất ở miền Nam.

Keywords: các hợp chất neonicotinoid; đất trồng trà; QuEChERS; UPLC-MS/MS