Analysis of Multiresidue Pesticides in Agricultural Paddy Soils Near Industrial Areas in Korea by GC–MS/MS and LC–MS/MS Using QuEChERS Extraction with dSPE Clean-Up

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Abstract: Pesticides have been used to control pests in agricultural fields and storage systems before circulating agricultural products to markets. A tandem mass spectrometry, equipped with gas chromatographic separation (GC–MS/MS) or ultra-performance liquid chromatographic separation (LC–MS/MS), was used to monitor residual pesticides in Korean rice paddy soils. Selective multiple reaction monitoring was employed during the analyses to achieve multiresidue pesticide analysis using GC–MS/MS and LC–MS/MS of 342 pesticides. In this study, QuEChERS extraction was employed with a dSPE clean-up to establish an effective pretreatment process. The limit of detection (LOD) and limit of quantification (LOQ) were set up for all pesticides, and method validation was performed for linearity and recovery at levels of 10 and 50 mg kg⁻¹ in the untreated soil sample. All pesticides satisfied the acceptable recovery range of 70–120%, within less than 20% RSD values, except for ametoctradin and gibberellic acid. In the paddy soil analyses, tricyclazole was the most frequently detectable pesticide, followed by oxadiazon, endosulfan, and chlorantraniliprole. Continuous monitoring of residual pesticides in paddy soils should be conducted due to the translocation of some systemic pesticides from soils to crop plants, and the impact of residual pesticides on the environment.

Keywords: multiresidue pesticide analysis; paddy soils; GC–MS/MS; LC–MS/MS; QuEChERS extraction

1. Introduction

Pesticides are used to improve crop productivity and isolate agricultural products from various pests, including insects and fungi. Crop production and farm household income may decrease if they are not used [1,2]. They are used before planting seeds of crops or after germination. In addition, they are sprayed when diseases or pests spread. In addition, they are used before agricultural product shipment [3–5]. Currently, pesticides include herbicides, insecticides, fungicides, and other ingredients to enhance pesticide activity. Depending on the cultivation pattern and primary crops in each country, the types of pesticides in use may be different, as well as the amounts of them used in the
fields [6,7]. In this respect, it has been reported that some countries, including Korea, use more pesticides than other countries to protect crops [8,9].

However, the use of these pesticides creates an indispensable situation that impacts the agricultural ecosystem; environmental destruction has been reported numerous times, and is recognized as a major cause of various human diseases [10]. Therefore, efforts to produce crops by limiting their use are of interest [11]. For example, the positive list system (PLS) collectively applies the level of 0.01 ppm for the maximum residue limit (MRL) to pesticides for which MRL is unset, and PLS has recently been passed in Korea [12]. Used pesticides evoke adverse effects on the ecosystem after spraying; they disrupt the terrestrial and aquatic ecosystems, and many of the endocrine-disrupting chemicals are from pesticides [13].

Therefore, it is inevitable to receive attention from the public regarding how high amounts of pesticides remain in cultivated crops, as well as agricultural soils and waterways, and monitoring of residual pesticides in agricultural products and environments contributes to the efficient safety management of pesticides [14,15]. However, in addition to this efficient management, it is necessary to maintain the agricultural environment safely when crops are not grown, because many pesticides remain in agricultural water and soil after cultivation, and the dynamics of these environments are not understood in some cases. For example, the kinetics and toxicity of the original pesticides and their metabolites are often not studied in detail [16].

Various kinds of pesticides may remain in agricultural soils for a long period, and studies have shown that they can be transferred to crops through roots when crops are growing [17,18]. The risk of migration of residual pesticides from the agricultural soil to crops can be prevented or predicted by monitoring residual pesticides in the agricultural soil.

Recently, monitoring of pesticide residues known as multiresidue pesticide analysis has been developed to analyze multiple pesticides simultaneously using GC–MS/MS and LC–MS/MS [19,20]. With this multiresidue analysis, the QuEChERS extraction method with the dSPE clean-up method also was introduced [19], and the analytical time should be shortened, with a reduction in the analysis cost. In this study, we developed a multiresidue pesticide analytical method using GC–MS/MS and LC–MS/MS with QuEChERS extraction and dSPE clean-up. We used the developed multiresidue analysis for monitoring 40 agricultural soils near the industrial areas in Pohang and Ulsan cities in Southern Korea. We analyzed 342 pesticides, including a pesticide banned by the Korean government due to its isomers and metabolites such as alpha-endosulfan, beta-endosulfan, and endosulfan sulfate. These chemicals are registered as persistent organic pollutants (POPs), and they also have been prohibited in Korean agriculture.

2. Materials and Methods

2.1. Chemicals

Acetonitrile, acetone, and methanol were purchased as HPLC grade from Burdick & Jackson Inc. (Muskegon, MI, USA). Formic acid (>98% purity) and ammonium formate (98% purity) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). D-(+)-Gluconic acid-δ-lactone, (-)-shikimic acid, 3-ethoxy-1,2-propanediol, and D-sorbitol, as analyte protectants, were purchased from Sigma-Aldrich. The tertiary distilled water was produced using a Milli-Q system (Millipore Co., Bedford, MA, USA).

2.2. Rice Paddy Soil Samples

The agricultural soil samples used in this study were collected from 40 rice paddy soils located in Ulsan and Pohang cities. The grid reference of the sampling site in Korea can be found in a previous report (Figure 1) [21]. The collected soil samples were passed through a 2 mm sieve after drying in the shade, and then stored frozen at −20 °C until analysis was performed. Pesticide standard solutions were made for a mixture containing 123 and 219 pesticides for the GC–MS/MS and LC–MS/MS analyses, respectively (Tables 1, S1, 2 and S2). Therefore, 342 pesticides were used to formulate a standard solution for the multiresidue pesticide analysis.
2.3. Preparation and Mixture of the Standard Solution

Standard pesticides used in this study were purchased from AccuStandard Inc. (New Haven, CT, USA) and were supplied as the liquid basis at concentrations of 1000, 500, and 100 mg kg\(^{-1}\). In a 20 mL volumetric flask, 1000, 500, and 100 mg kg\(^{-1}\) standard stock solutions were collected and combined. If the amount of solvent was large during pooling, it was left to dry using nitrogen. Finally, 20 mL of acetonitrile was added to resolve. A mixed standard solution for GC–MS/MS and LC–MS/MS was prepared. For the preparation of untreated samples, soil for the nondetection of 342 pesticides was selected after the first screening from among the analyzed samples. The untreated sample was prepared from the soil after grinding, and was stored frozen at \(-20^\circ\text{C}\) for validation analysis.

2.4. QuEChERS Sample Preparation

2.4.1. Extraction

For all tested samples, five grams (5.0 g ± 0.1 g) of the freeze-dried samples were weighed and transferred into 50 mL conical tubes. The weighed sample was activated in 2 mL of distilled water for 30 min and extracted in 2 mL of MeCN by shaking on a mechanical wrist shaker for 30 min. After extraction, samples were treated with 4 g anhydrous MgSO\(_4\), 1 g NaCl, 0.5 g Na\(_3\)citrate dihydrate, and 0.5 g Na\(_2\)Hcitrate sesquihydrate. Then, samples mixed with QuEChERS extraction salts were shaken for 1 min and centrifuged at 4000 rpm for 10 min. The supernatant after the centrifuge was reserved for further clean-up process.

2.4.2. Dilution for Clean-Up

Two mL of supernatant after centrifugation was dried under nitrogen gas and resolved in MeCN. Then, 300 μL aliquots of supernatant from resolved solvent were transferred to a microtube and mixed with 600 μL buffer solution (100 mM ammonium formate in distilled water, at pH 4.5) and 100 μL MeCN for the LC–MS/MS analysis. Then, 405 μL aliquots of supernatant from resolved solvent were transferred to a microtube and mixed with 20 μL AP and 75 μL MeCN for the GC–MS/MS. Sample solutions were passed through a 0.20 μm and 4 mm polytetrafluoroethylene (PTFE) syringe filter (Hyundai Micro, Seoul, Korea) before the GC–MS/MS and LC–MS/MS analyses.
2.4.3. GC–MS/MS Analysis

The GC–MS/MS analysis was conducted on a Shimadzu GCMS-TQ8040 triple quadrupole mass spectrometer coupled to a GC-2010 Plus equipped with an AOC-20S autoinjector and -20i autosampler (Shimadzu, Kyoto, Japan). For the mass spectrometer, the electron energy of the EI was 70 eV, and temperature values for the injection port and transfer line were 280 °C. Argon used with an AOC-20S in the collision inductive dissociation gas. For the gas chromatograph, a splitless GC glass liner with glass wool (Shimadzu, Kyoto, Japan) was inserted in the inlet.

The injection mode was splitless and the injection volume was 1 µL. The capillary column was an RxI-5Sil MS (20 m × 0.18 mm i.d., 0.18 µm df, Restek, Bellefonte, PA, USA). The oven temperature program (25 min) was initialized at 50 °C (held for 1 min), ramped up to 200 °C at 25 °C/min, and then to 300 °C at 10 °C/min (held for 5 min). Helium (≥99.999%) was used as the carrier gas, and total column flow was 1.0 mL/min (constant). For the multiresidue MRM data processing, the GC-MS solution (version 4.30) was used (Tables 1 and S1).

2.4.4. LC–MS/MS Analysis

A reverse-phase chromatographic separation and determination were used to analyze 231 pesticides using a Nexera X2 UHPLC system coupled with a Shimadzu LCMS-8050 triple quadrupole mass spectrometer (Kyoto, Japan). The UPLC system consisted of a solvent delivery module (LC-30AD), a column oven (CTO-20A), an autosampler (SIL-30AC), and a Kinetex C18 column (150 mm × 2.1 mm (i.d.), 2.6 µm) (Phenomenex, Torrance, CA). The mobile phase employed a time-programmed gradient system using solvents A and B. Solvent A consisted of 0.1% formic acid and 5 mM ammonium formate in water, whereas solvent B was 0.1% formic acid and 5 mM ammonium formate in methanol.

Gradient elution was initiated with 95% A for 1.0 min. Solvent B was then increased to 15% after 1.5 min and 60% within 2.4 min. Solvent B was linearly increased to 90% within 10 min and maintained until 12 min without a change in solvent B. Afterwards, solvent B was increased to 98% within 12.1 min, then kept constant for 18 min. Finally, solvent B was decreased linearly to 5% over 6 min and equilibrated for 6 min. The total analytical time was 24 min, and the injection volume was 10 mL. The flow rate was 300 µL/min.

The ESI–MS/MS was conducted under dynamic multiple reaction monitoring. Lab-solutions software (version 5.72) (Kyoto, Japan) was used to control the UPLC–MS/MS system. Interface temperature, heat block temperature, nebulizing gas flow, heating gas flow, and drying gas flow were set at 150 °C, 400 °C, 220 °C, 3 L/min, 10 L/min, and 10 L/min, respectively. Fragmentation and collision energy levels were optimized for each precursor and product ions. For each pesticide, at least one precursor ion with one product ion for setting identification (qualifier) and quantification (quantifier) purposes was determined, with a selection of the most abundant product ion for quantification, and the second one for confirmation. The precursor ion and optimized MS/MS parameters (fragment and collision energy) for each pesticide, using LC–MS/MS, are summarized in Tables 2 and S2.

2.4.5. Validation of Method Performance

The method validation was carried out using no-treatment soil samples previously checked to be free of pesticides. The parameters evaluated were: limits of detection (LOD), limits of quantification (MLOQ), linearity, recovery, and precision. The LOD and LOQs were calculated using signal-to-noise ratio (S/N) criteria; in all cases: LOD = 3 S/N and LOQ 10 S/N. Linearity was evaluated by preparing a calibration curve with five concentrations. For GC–MS/MS analysis, the calibration curve was obtained using an internal standard TPP, and all the equations of the calibration curve are represented in Tables 3, S3, 4 and S4. Matrix-matched calibration curves were prepared for soil matrices, and the evaluation of signal suppression/enhancement due to matrix effects was calculated with the equation from five-point calibration curves. Recovery was assessed with replicated spiking experiments...
(n = 3) with two levels (0.01 and 0.05 mg mL\(^{-1}\)) for the pesticides. Average recovery values were calculated, and standard deviations for repeatability from three replicates were obtained as a measure of precision. Retention times of pesticides in sample extracts corresponded to the average of the calibration standards measured in the same analytical sequence, with a tolerance of ±0.1 min.

3. Results and Discussion

3.1. Establishment of GC–MS/MS MRM Conditions

Precursor ions were determined through scan analysis of each pesticide, and retention time (RT) was found under the provided GC analysis conditions. Product ion scan analysis was conducted at various CE voltages (0–50 eV) using the determined precursor ions, and the optimal MRM conditions were set by comparing the sensitivity of the product ions generated at each CE value. Qualitative and quantitative ions were determined considering the sensitivity and surrounding disturbance ions or baseline. If the baseline on the chromatogram was poor or there were several interfering ions around the RT, ions were excluded from the quantitative ions, even if the signal was high, and they were only considered only as qualitative ions. GC–MS/MS MRM conditions are listed in Tables 1 and S1.

Table 1. MRM conditions for the first 40 pesticides in the GC–MS/MS analysis. MRM conditions for the other 83 pesticides are listed in Table S1.

| Pesticides                  | RT (min) | Precursor > Product Ion (CE, eV) | Qualifier Ion | Qualifier Ion |
|-----------------------------|----------|----------------------------------|---------------|---------------|
| Acrinathrin                 | 13.525   | 181.00 > 152.10                  | 24            | 208.00 > 181.10 | 9             |
| Alachlor                    | 8.572    | 188.00 > 160.10                  | 9             | 188.00 > 131.10 | 21            |
| Aldrin                      | 9.143    | 263.00 > 192.90                  | 30            | 263.00 > 190.90 | 30            |
| Ametoctradin                | 13.88    | 246.00 > 188.20                  | 27            | 246.00 > 174.10 | 30            |
| Anilofos                    | 12.748   | 226.00 > 157.00                  | 15            | 184.00 > 157.00 | 9             |
| Azaconazole                 | 10.647   | 217.00 > 173.00                  | 15            | 173.00 > 109.10 | 27            |
| Benfuresate                 | 8.399    | 163.00 > 121.10                  | 9             | 256.00 > 163.10 | 9             |
| BHC-alpha                   | 7.55     | 181.00 > 145.00                  | 15            | 219.00 > 183.00 | 9             |
| BHC-beta                    | 7.891    | 181.00 > 145.00                  | 18            | 219.00 > 183.00 | 9             |
| BHC-delta                   | 8.226    | 181.00 > 145.00                  | 15            | 219.00 > 183.00 | 9             |
| BHC-gamma                   | 7.891    | 181.00 > 145.00                  | 15            | 219.00 > 183.00 | 12            |
| Bifenox                     | 12.784   | 341.00 > 310.00                  | 9             | 310.00 > 189.00 | 9             |
| Bifenthrin                  | 12.448   | 166.00 > 164.10                  | 21            | 183.00 > 76.10  | 27            |
| Bromobutide                 | 8.487    | 232.00 > 176.20                  | 27            | 237.00 > 160.20 | 15            |
| Bromopropylate              | 12.514   | 341.00 > 183.00                  | 21            | 237.00 > 160.20 | 15            |
| BIFACHLOR                   | 10.036   | 176.00 > 147.10                  | 15            | 237.00 > 160.20 | 15            |
| Butachlor                   | 14.426   | 331.00 > 180.00                  | 21            | 331.00 > 152.10 | 30            |
| Carbophenothion             | 11.51    | 342.00 > 157.10                  | 15            | 342.00 > 199.10 | 6             |
| Chlorantraniliprole         | 12.676   | 278.00 > 249.00                  | 20            | 280.00 > 251.00 | 20            |
| Chlordane-cis               | 9.988    | 377.00 > 267.90                  | 27            | 377.00 > 266.00 | 24            |
| Chlordane-trans             | 10.168   | 377.00 > 267.90                  | 27            | 377.00 > 266.00 | 24            |
| Chlorfenapyr                | 10.699   | 247.00 > 227.20                  | 15            | 247.00 > 200.00 | 27            |
| Chlorfenvinphos (E)         | 9.472    | 267.00 > 159.00                  | 18            | 323.00 > 266.90 | 18            |
| Chlorfenvinphos (Z)         | 9.625    | 267.00 > 159.00                  | 18            | 323.00 > 266.90 | 18            |
| ChlorfImurazone             | 7.291    | 213.00 > 171.10                  | 9             | 171.00 > 127.00 | 15            |
| Chlorobenzilate and chloropropylate | 10.959 | 251.00 > 111.10                  | 27            | 139.00 > 75.10  | 27            |
| Chlorpropopham              | 7.292    | 127.00 > 65.10                   | 21            | 213.00 > 171.00 | 9             |
| Chlorpyrifos-methyl         | 8.492    | 286.00 > 93.10                   | 24            | 286.00 > 270.90 | 18            |
| Cyfluthrin-1                | 14.632   | 163.00 > 127.00                  | 6             | 226.00 > 206.10 | 15            |
| Cyfluthrin-2                | 14.731   | 163.00 > 127.00                  | 6             | 226.00 > 206.10 | 15            |
| Cyfluthrin-3                | 14.786   | 163.00 > 127.00                  | 6             | 226.00 > 206.10 | 15            |
| Cyfluthrin-4                | 14.83    | 163.00 > 127.00                  | 6             | 226.00 > 206.10 | 15            |
Table 1. Cont.

| Pesticides       | RT (min) | Precursor > Product Ion (CE, eV) | Quantifier Ion | Qualifier Ion |
|------------------|---------|---------------------------------|----------------|---------------|
| Cyhalothrin-1    | 13.196  | 197.00 > 141.10 12 197.00 > 161.10 6 |                |               |
| Cyhalothrin-2    | 13.365  | 197.00 > 141.10 12 197.00 > 161.10 6 |                |               |
| Cypermethrin-1   | 14.938  | 163.00 > 127.10 9 163.00 > 109.00 24 |                |               |
| Cypermethrin-2   | 15.042  | 163.00 > 127.10 9 163.00 > 109.00 24 |                |               |
| Cypermethrin-3   | 15.092  | 163.00 > 127.10 9 163.00 > 109.00 24 |                |               |
| Cypermethrin-4   | 15.138  | 163.00 > 127.10 9 163.00 > 109.00 24 |                |               |
| Cyprodinil       | 9.527   | 224.00 > 208.10 21 225.00 > 210.10 18 |                |               |
| DDD-p,p<sup>′</sup> | 11.121  | 235.00 > 165.10 24 235.00 > 199.00 18 |                |               |
| DDE-p,p<sup>′</sup> | 10.466  | 246.00 > 176.10 27 218.00 > 246.00 21 |                |               |
| DDT-o,p<sup>′</sup> | 11.12  | 235.00 > 165.10 24 235.00 > 199.10 18 |                |               |
| DDT-p,p<sup>′</sup> | 11.702  | 235.00 > 165.10 24 235.00 > 199.00 18 |                |               |
| Deltamethrin     | 16.511  | 253.00 > 172.00 0 253.00 > 174.00 0 |                |               |
| Diclofop-methyl  | 11.925  | 253.00 > 162.10 21 206.00 > 124.10 27 |                |               |
| Dicloran         | 7.704   | 206.00 > 176.00 12 206.00 > 124.10 27 |                |               |
| Dicofol          | 9.289   | 139.00 > 111.10 15 250.00 > 139.10 15 |                |               |
| Dieldrin         | 10.565  | 279.00 > 206.90 27 263.00 > 192.90 30 |                |               |

3.2. Establishment of LC–MS/MS MRM Conditions

The precursor ion was determined using a full scan analysis of 0.1 mg mL<sup>−1</sup> of each pesticide without an LC column. By comparing the ionization intensities in the positive and negative modes, at the same time, ions with optimal sensitivity, such as [M + H]<sup>+</sup>, [M − H]<sup>−</sup>, and [M + NH<sub>4</sub>]<sup>+</sup> were set as precursor ions. Using the determined precursor ions, product ions at various CE voltages were searched using the MRM optimization tool, and ions suitable for double quantification/qualification were determined. Using the established MRM conditions, the RT of the pesticides was measured using an analysis method optimized in this study. LC–MS/MS MRM conditions are listed in Tables 2 and S2.

Table 2. MRM conditions for the first 40 pesticides in the LC–MS/MS analysis. MRM conditions for the other 179 pesticides are listed in Table S2.

| Pesticides          | RT (min) | Ionization     | Precursor > Product Ion (CE, eV) | Quantifier Ion | Qualifier Ion |
|---------------------|---------|----------------|---------------------------------|----------------|---------------|
| Abamectin B1        | 12.987  | M + NH<sub>4</sub><sup>+</sup> | 890.6 > 305.25 29 890.6 > 567.3 15 |                |               |
| Acephate            | 3.990   | M + H<sup>+</sup> | 184 > 143 10 184 > 95.15 24 |                |               |
| Acetamiprid         | 4.636   | M + H<sup>+</sup> | 223.1 > 126.15 21 223.1 > 99.05 38 |                |               |
| Aldicarb            | 5.143   | M + NH<sub>4</sub><sup>+</sup> | 207.9 > 89.1 16 207.9 > 70 15 |                |               |
| Amisulbrom          | 9.993   | MCl<sub>35</sub> + H<sup>+</sup> | 465.8 > 226.95 18 467.8 > 228.85 21 |                |               |
| Azimsulfuron        | 6.131   | M + H<sup>+</sup> | 424.9 > 182.1 17 424.9 > 156.05 34 |                |               |
| Azinphos-methyl     | 6.592   | M + H<sup>+</sup> | 317.9 > 132 13 317.9 > 159.9 7 |                |               |
| Azoxyystrobin       | 6.840   | M + H<sup>+</sup> | 404.1 > 372.2 15 404.1 > 344.2 25 |                |               |
| Benidicarb          | 5.430   | M + H<sup>+</sup> | 224.1 > 109.15 16 224.1 > 161.7 9 |                |               |
| Bensulfuron-methyl  | 6.644   | M + H<sup>+</sup> | 411 > 149.15 21 411 > 119.1 39 |                |               |
| Benthiavalicarb-isopropyl | 7.474 | M + H<sup>+</sup> | 382.2 > 180.1 30 382.2 > 116.15 21 |                |               |
| Benzoicvyclon       | 7.433   | M + H<sup>+</sup> | 446.9 > 257.2 25 446.9 > 229.05 36 |                |               |
| Benoximate          | 9.386   | M + H<sup>+</sup> | 364 > 199.1 9 364 > 105.1 22 |                |               |
| Bitertanol          | 9.381   | M + H<sup>+</sup> | 338.1 > 70.1 9 338.1 > 99.1 15 |                |               |
| Boscald             | 7.198   | M + H<sup>+</sup> | 343 > 307.2 20 343 > 140.1 21 |                |               |
| Bromacil            | 5.574   | M + H<sup>+</sup> | 261 > 205.05 14 261 > 188 28 |                |               |
| Buprofezin          | 10.702  | M + H<sup>+</sup> | 306.2 > 201.2 12 306.2 > 116.1 15 |                |               |
| Cadusafos           | 9.912   | M + H<sup>+</sup> | 271.1 > 159.05 12 271.1 > 97.05 34 |                |               |
| Cafenstrole         | 7.699   | M + H<sup>+</sup> | 351.1 > 100.15 10 351.1 > 72.2 28 |                |               |
| Carbaryl            | 5.677   | M + H<sup>+</sup> | 202.1 > 145.2 13 202.1 > 127.15 25 |                |               |
Table 2. Cont.

| Pesticides                  | RT (min) | Ionization       | Precursor > Product Ion (CE, eV) |
|-----------------------------|---------|------------------|---------------------------------|
|                             |         |                  | Quantifier Ion | Qualifier Ion |
| Carbendazim                 | 4.484   | M + H*           | 192.1 > 160.1 | 192.1 > 132  |
| Carbofuran                  | 5.519   | M + H*           | 222 > 123.05 | 222 > 165.2  |
| Carboxin                    | 5.723   | M + H*           | 236 > 143.05 | 236 > 87.15  |
| Carfentrazone-ethyl         | 8.661   | M + H*           | 411.9 > 346.05| 411.9 > 366.1|
| Carprofamide                | 8.907   | M + H*           | 334 > 138.95 | 334 > 103.1  |
| Chlorpyrifos                | 11.021  | M + H*           | 349.9 > 198.05| 349.9 > 97   |
| Chlorsulfuron               | 5.563   | M + H*           | 357.9 > 141.2 | 357.9 > 167.2|
| Chromafenozide              | 7.974   | M + H*           | 395.2 > 175.15| 395.2 > 147.1|
| Clefenthine                 | 9.297   | M + H*           | 302.8 > 138.1 | 302.8 > 102.05|
| Clothianidin                | 6.884   | M + H*           | 240.1 > 125.15| 240.1 > 99.1 |
| Cyazofoamid                | 4.535   | M + H*           | 250 > 169.1   | 250 > 132.1  |
| Cyhalofop-butyl             | 9.940   | M + H*           | 375.0 > 256.0 | 375.0 > 120.1|
| Cyanoxanil                 | 4.801   | M + H*           | 292.1 > 70.2  | 292.1 > 125.15|
| Cyproconazole(I)            | 7.539   | M + H*           | 269.2 > 151.2 | 269.2 > 119.2|
| Cyproconazole(II)           | 7.832   | M + H*           | 269.2 > 151.2 | 269.2 > 119.2|

3.3. Method Validations

3.3.1. LOD, LOQ, and Linearity of the Calibration Curve

The LODs were 3 μg kg⁻¹ and LOQs were 10 μg kg⁻¹ for each pesticide. Linearity refers to the ability of an experimental method to obtain a linear measurement value for the amount or concentration of an analyte in a sample within a certain range. The results of the GC–MS/MS (Tables 3 and S3) and LC–MS/MS (Tables 4 and S4) analyses of the soil samples were evaluated by calculating correlation coefficients, y-intercepts, and bracket calibration curves of matrix-matched standard solutions.

Table 3. LOD, LOQ, and linearity of the first 40 pesticides using GC–MS/MS. LOD, LOQ, and linearity of the other 83 pesticides are listed in Table S3.

| No. | Pesticides                  | Limit of Detection (μg kg⁻¹) | Limit of Quantification (μg kg⁻¹) | Linearity (r²) |
|-----|-----------------------------|-----------------------------|-----------------------------------|----------------|
| 1   | Acrinathrin                 | 3                           | 10                                | 0.9998         |
| 2   | Alachlor                    | 3                           | 10                                | 0.9999         |
| 3   | Aldrin                      | 3                           | 10                                | 0.9995         |
| 4   | Aminopterin                 | 3                           | 10                                | 0.9974         |
| 5   | Anilofos                    | 3                           | 10                                | 0.9999         |
| 6   | Azinphosethyl               | 3                           | 10                                | 0.9999         |
| 7   | Benfuresate                 | 3                           | 10                                | 0.9985         |
| 8   | BHC(Lindane)-gamma         | 3                           | 10                                | 0.9984         |
| 9   | BHC-alpha                   | 3                           | 10                                | 0.9993         |
| 10  | BHC-beta                    | 3                           | 10                                | 0.9994         |
| 11  | BHC-delta                   | 3                           | 10                                | 0.9978         |
| 12  | Bifenox                     | 3                           | 10                                | 0.9986         |
| 13  | Butachlor                   | 3                           | 10                                | 0.9993         |
| 14  | Butanilamide                | 3                           | 10                                | 0.9999         |
| 15  | Butenylacetate              | 3                           | 10                                | 0.9999         |
| 16  | Butefenacil                 | 3                           | 10                                | 0.9996         |
Table 3. Cont.

| No. | Pesticides           | Limit of Detection (µg kg⁻¹) | Limit of Quantification (µg kg⁻¹) | Linearity ($r^2$) |
|-----|----------------------|-----------------------------|----------------------------------|------------------|
| 18  | Carbophenothion      | 3                           | 10                               | 0.9998           |
| 19  | Chlorantraniliprole  | 3                           | 10                               | 0.9991           |
| 20  | Chlordane-cis        | 3                           | 10                               | 0.9997           |
| 21  | Chlordane-trans      | 3                           | 10                               | 0.9999           |
| 22  | Chlorfenapyr         | 3                           | 10                               | 0.9993           |
| 23  | Chlorfenzinphos      | 3                           | 10                               | 0.9999           |
| 24  | Chlorfluazuron       | 3                           | 10                               | 0.9997           |
| 25  | Chlorobenzilate      | 3                           | 10                               | 0.9999           |
| 26  | Chlorpropham         | 3                           | 10                               | 0.9993           |
| 27  | Chlorpyrifos-methyl  | 3                           | 10                               | 0.9996           |
| 28  | Cyfluthrin           | 3                           | 10                               | 0.9999           |
| 29  | Cyhalothrin          | 3                           | 10                               | 0.9990           |
| 30  | Cypermethrin         | 3                           | 10                               | 0.9998           |
| 31  | Cyprodinil           | 3                           | 10                               | 0.9996           |
| 32  | DDD-p,p′             | 3                           | 10                               | 0.9764           |
| 33  | DDE-p,p′             | 3                           | 10                               | 0.9999           |
| 34  | DDT-o,p′             | 3                           | 10                               | 0.9904           |
| 35  | DDT-p,p′             | 3                           | 10                               | 0.9998           |
| 36  | Deltamethrin         | 3                           | 10                               | 0.9994           |
| 37  | Diclofop-methyl      | 3                           | 10                               | 0.9999           |
| 38  | Dicloran             | 3                           | 10                               | 0.9992           |
| 39  | Dicofol              | 3                           | 10                               | 0.9996           |
| 40  | Dieldrin             | 3                           | 10                               | 0.9995           |

Table 4. LOD, LOQ, and linearity for the first 40 tested pesticides using LC–MS/MS. LOD, LOQ, and linearity for other 179 pesticides are listed in Table S4.

| No. | Pesticides            | Limit of Detection (µg kg⁻¹) | Limit of Quantification (µg kg⁻¹) | Linearity ($r^2$) |
|-----|-----------------------|-----------------------------|----------------------------------|------------------|
| 1   | Abamectin B1          | 3                           | 10                               | 0.9999           |
| 2   | Acephate              | 3                           | 10                               | 0.1000           |
| 3   | Acetamiprid           | 3                           | 10                               | 0.9933           |
| 4   | Aldicarb              | 3                           | 10                               | 0.9904           |
| 5   | Amisulbrom            | 3                           | 10                               | 0.9979           |
| 6   | Azimsulfuron          | 3                           | 10                               | 0.9974           |
| 7   | Azinphos-methyl       | 3                           | 10                               | 0.9985           |
| 8   | Azoxystrobin          | 3                           | 10                               | 0.9918           |
| 9   | Bendiocarb            | 3                           | 10                               | 0.9982           |
| 10  | Bensulfuron-methyl    | 3                           | 10                               | 0.9978           |
| 11  | Benthiavalicarb-isopropyl | 3                   | 10                               | 0.9969           |
| 12  | Benzobicyclon         | 3                           | 10                               | 0.9932           |
| 13  | Benzoic acid          | 3                           | 10                               | 0.9963           |
| 14  | Bitertanol            | 3                           | 10                               | 0.9995           |
| 15  | Boccalid              | 3                           | 10                               | 0.9971           |
| 16  | Bromacil              | 3                           | 10                               | 0.9963           |
| 17  | Buprofezin            | 3                           | 10                               | 0.9911           |
| 18  | Cadusafos             | 3                           | 10                               | 0.9974           |
| 19  | Cafenstrole           | 3                           | 10                               | 0.9904           |
| 20  | Carbaryl              | 3                           | 10                               | 0.9905           |
| 21  | Carbendazim           | 3                           | 10                               | 0.9977           |
| 22  | Carbofuran            | 3                           | 10                               | 0.9935           |
| 23  | Carpoxylin            | 3                           | 10                               | 0.9913           |
| 24  | Carfenpenta-ethyl     | 3                           | 10                               | 0.9901           |
| 25  | Carpropame            | 3                           | 10                               | 0.9917           |
| 26  | Chlorpyrifos          | 3                           | 10                               | 0.9991           |
Table 4. Cont.

| No. | Pesticides          | Limit of Detection (µg kg\(^{-1}\)) | Limit of Quantification (µg kg\(^{-1}\)) | Linearity \((r^2)\) |
|-----|---------------------|--------------------------------------|------------------------------------------|------------------|
| 27  | Chlorsulfuron       | 3                                    | 10                                       | 0.9998           |
| 28  | Chromafenozide      | 3                                    | 10                                       | 0.9968           |
| 29  | Clethodim           | 3                                    | 10                                       | 0.9989           |
| 30  | Clofentezine        | 3                                    | 10                                       | 0.9961           |
| 31  | Clomazone           | 3                                    | 10                                       | 0.9941           |
| 32  | Clothianidin        | 3                                    | 10                                       | 0.9999           |
| 33  | Cyazofamid          | 3                                    | 10                                       | 0.9938           |
| 34  | Cyclosulfamuron     | 3                                    | 10                                       | 0.9959           |
| 35  | Cyfluifenamid       | 3                                    | 10                                       | 0.9953           |
| 36  | Cyhalofop-butyl     | 3                                    | 10                                       | 0.9915           |
| 37  | Cyflufenamid        | 3                                    | 10                                       | 0.9924           |
| 38  | Cyproconazole(I)    | 3                                    | 10                                       | 0.9937           |
| 39  | Cyproconazole(II)   | 3                                    | 10                                       | 0.9923           |
| 40  | Daimuron            | 3                                    | 10                                       | 0.9922           |

3.3.2. Recovery Rates

Analytical recovery is a test that measures an analysis error related to the analysis process within the preparation of a sample and extraction of an analyte from the sample before quantitation. The results of the GC–MS/MS and LC–MS/MS analyses of the soil are reported in Tables 5, S5, 6 and S6, and the recovery rates had values ranging from 70 to 120% and <20% RSD, which are effective recovery rates.

In the recovery test in the soil using GC–MS/MS, all pesticides except ametoctradin out of 123 pesticides had three repeated tests at the two spiked levels of 10 and 50 µg kg\(^{-1}\), and all recovery rates for pesticides satisfied the effective recovery range of 70–120% (Tables 5 and S5). In addition, the coefficient of variation (% RSD) was confirmed to be less than 20% for all pesticides (Tables 5 and S5).

Table 5. Recoveries of the first 40 pesticides in the untreated soil using GC–MS/MS \((n = 3)\). Recoveries of the other 83 pesticides are listed in Table S5.

| No.  | Pesticides            | Soil       | Low (10 µg kg\(^{-1}\)) | High (50 µg kg\(^{-1}\)) |
|------|-----------------------|------------|--------------------------|--------------------------|
|      |                       |            | Rec. | RSD   | Rec. | RSD   |
| 1    | Acrinathrin           | 106.58     | 10.9 | 94.65 | 3.7  |
| 2    | Alachlor              | 113.99     | 9.8  | 96.30 | 1.9  |
| 3    | Aldrin                | 97.53      | 2.2  | 99.01 | 4.3  |
| 4    | Ametoctradin          | -          | -    | -     | -    |
| 5    | Anilofos              | 105.35     | 2.9  | 96.05 | 2.5  |
| 6    | Azaconazole           | 98.77      | 2.2  | 95.97 | 1.0  |
| 7    | Benfuresate           | 98.77      | 6.6  | 95.14 | 7.0  |
| 8    | BHC(Lindane)-gamma   | 89.30      | 9.2  | 99.92 | 5.6  |
| 9    | BHC-alpha             | 93.00      | 8.0  | 100.41| 3.6  |
| 10   | BHC-beta              | 104.12     | 6.1  | 98.60 | 3.0  |
| 11   | BHC-delta             | 88.07      | 5.7  | 98.44 | 4.1  |
| 12   | Bifenox               | 110.70     | 3.4  | 89.14 | 0.7  |
| 13   | Bifenthrin            | 110.70     | 1.7  | 95.64 | 1.4  |
| 14   | Bromobutide           | 100.82     | 4.3  | 95.89 | 2.6  |
| 15   | Bromopropylate        | 108.64     | 1.1  | 95.31 | 1.2  |
| 16   | Butachlor             | 104.94     | 7.3  | 100.49| 5.9  |
| 17   | Butafenacil           | 111.11     | 2.2  | 95.72 | 1.4  |
| 18   | Carbophenothion       | 104.94     | 4.1  | 96.13 | 3.4  |
Table 5. Cont.

| No. | Pesticides          | Soil Low (10 µg kg⁻¹) | Soil High (50 µg kg⁻¹) |
|-----|---------------------|-----------------------|-----------------------|
|     |                     | Rec. | RSD | Rec. | RSD |
| 19  | Chlorantraniliprole | 100.41 | 16.0 | 97.45 | 3.9 |
| 20  | Chlordane-cis       | 112.76 | 7.1  | 96.46 | 3.4 |
| 21  | Chlordane-trans     | 102.47 | 10.7 | 96.54 | 3.3 |
| 22  | Chlorfenapyr        | 98.35  | 9.6  | 101.48 | 2.1 |
| 23  | Chlorfenvinphos     | 107.00 | 1.8  | 97.45 | 0.9 |
| 24  | Chlorfluazuron      | 96.71  | 11.8 | 98.19 | 2.3 |
| 25  | Chlorobenzilate     | 106.17 | 2.0  | 95.97 | 1.3 |
| 26  | Chlorpropam         | 98.77  | 6.6  | 96.71 | 3.9 |
| 27  | Chlorsulfuron-methyl| 97.53  | 5.8  | 98.77 | 4.3 |
| 28  | Cyfloxin           | 110.29 | 2.8  | 96.13 | 1.6 |
| 29  | Cyhalothrin         | 112.76 | 1.7  | 92.68 | 0.6 |
| 30  | Cypermethrin        | 106.58 | 1.8  | 93.91 | 2.4 |
| 31  | Cyprodinil          | 101.24 | 5.6  | 93.66 | 3.2 |
| 32  | DDD-p,p'            | 116.05 | 1.1  | 105.76 | 1.2 |
| 33  | DDE-p,p'           | 101.65 | 4.9  | 98.68 | 2.9 |
| 34  | DDT-o,p'           | 113.17 | 2.7  | 103.13 | 1.1 |
| 35  | DDT-p,p'           | 106.17 | 3.1  | 94.90 | 1.0 |
| 36  | Deltamethrin (Tralomethrin deg.) | 109.47 | 1.3 | 90.78 | 4.1 |
| 37  | Diclofop-methyl     | 102.47 | 1.2  | 95.72 | 2.3 |
| 38  | Dicloran           | 112.35 | 4.0  | 93.75 | 8.2 |
| 39  | Dicofol            | 114.82 | 2.8  | 99.18 | 1.6 |
| 40  | Dieldrin           | 99.59  | 10.5 | 96.30 | 8.1 |

In the recovery test of the soil using LC–MS/MS, all pesticides except for gibberellic acid out of 219 pesticides had three repeated tests at the two spiked levels of 10 and 50 µg kg⁻¹, and all recovery rates for pesticides satisfied the effective recovery range of 70–120% (Tables 6 and S6). In addition, the coefficient of variation (% RSD) was confirmed to be less than 20% for all pesticides (Tables 6 and S6).

Table 6. Recoveries of 40 pesticides in the untreated soil using LC–MS/MS (n = 3). Recoveries for the other 179 pesticides are listed in Table S6.

| No. | Pesticides          | Soil Low (10 µg kg⁻¹) | Soil High (50 µg kg⁻¹) |
|-----|---------------------|-----------------------|-----------------------|
|     |                     | Rec. | RSD | Rec. | RSD |
| 1   | Abamectin B1        | 82.5 | 4.4 | 82.3 | 4.3 |
| 2   | Acephate            | 103.6 | 4.9 | 101.6 | 9.5 |
| 3   | Acetamiprid         | 82.3  | 4.6 | 99.9  | 1.3 |
| 4   | Aldicarb            | 96.7  | 3.2 | 101.3 | 2.3 |
| 5   | Amisulbrom          | 91.8  | 8.5 | 93.8  | 4.4 |
| 6   | Azimsulfuron        | 76.5  | 2.3 | 91.8  | 5.0 |
| 7   | Azinphos-methyl     | 79.0  | 8.1 | 89.1  | 6.6 |
| 8   | Azoxydrostrobine    | 96.1  | 4.0 | 114.2 | 2.2 |
| 9   | Benidicarb          | 80.9  | 1.5 | 86.1  | 2.1 |
| 10  | Bensulphon-methyl   | 78.2  | 4.8 | 84.0  | 2.0 |
| 11  | Benthiavalcab      | 83.9  | 6.2 | 88.7  | 0.6 |
| 12  | Benzobicyclon       | 86.1  | 4.7 | 91.9  | 2.9 |
MeCN was selected to use as the extraction solvent for residual pesticides in soil samples, as other studies used MeCN for soil extraction [22,23]. In our study, MeCN was properly used to extract multiresidue pesticides from soil samples. In addition, to obtain better efficiency in extraction and recoveries of multiresidue pesticides from soil samples, the QuEChERS procedure was employed in our study, as all recovery rates were in the range considered effective and promising. As a pressurized liquid extraction failed to obtain a satisfactory recovery rate within the range of 65.1% to 122.2% for 25 pesticides in the soil samples, the QuEChERS procedure provided better recoveries, with the extraction recovery in the range of 79.4 to 113.3% with RSDs of 1.0 to 12.2% [24]. On the other hand, the QuEChERS procedure may have caused strong salting-out effects, as the mean recoveries of paclobutrazol (125%) and fenvalerate (122%) treated at the level of 5 µg kg\(^{-1}\) were observed to be higher than for other pesticides [25]. However, such salting-out effects were not observed in our study. Therefore, the recoveries of multiresidue pesticides were generally between 70 and 120% with RSDs below 20%, indicating that the proposed method in this study was feasible to analyze 340 pesticides in soil samples.

3.4. Residual Pesticides in 40 Korean Agricultural Soils

Table 7 shows the results of the multiresidue pesticide analysis of each soil sample. Based on these results, the pesticide with the highest detection frequency in Korean paddy soils (40 sites) was tricyclazole, and the detection range was 0.003–0.034 mg kg\(^{-1}\). The pesticide was detected in 30 out of 40 soil samples, thus, the detection frequency reached 75% (Table 7). Tricyclazole [5-methyl-1,2,4-triazolo(3,4-b)(1,3)benzothiazole] is a triazole-typed systemic fungicide that is absorbed by foliage and roots, and is translocated to xylem.
and apoplasts in plants [26]. In Korea, it is only registered and used for controlling southern corn-leaf blight and rice blast diseases [27]; however, there is no domestic allowable standard for its residue in other crops. According to the risk assessment of pesticide residues in the soil, it has been reported that tricyclazole was mostly detected in soil samples in agricultural cultivated lands [28].

Tricyclazole in the residual pesticides was most frequently detected in Korean paddy soils because it is a fungicide that is used quite often, as 46,915 kg was released in 2017 in Korea, accounting for 5.6% of the fungicide used for paddy rice [29]. With this large consumption, tricyclazole has a long mean half-life (DT50) value of 305 days in surface soil, while the DT50 value of difenoconazole in paddy soil ranged from 2.82 days to 23.26 days [30,31]. These two factors can be attributed to extended tricyclazole presence in the paddy soil.

Table 7. Residual amounts of pesticides in soils at 20 sites in Ulsan city and 20 sites in Pohang city as analyzed by GC–MS/MS and LC–MS/MS.

| Ulsan Soils | Determined Pesticides | Determined Amounts (µg kg⁻¹) | Pohang Soils | Determined Pesticides | Determined Amounts (µg kg⁻¹) |
|-------------|-----------------------|-----------------------------|--------------|-----------------------|-----------------------------|
| Ulsan 1     | Tricyclazole          | 0.013                       | Pohang 1     | *                     | 0.005                       |
|             |                       |                             |              |                       |                             |
| Ulsan 2     | Tricyclazole          | 0.001 *                     | Pohang 2     | Dimethomorph          | 0.016                       |
|             |                       |                             |              | Imidacloprid          |                             |
|             |                       |                             |              | Mandipropamid         | 0.003 *                     |
|             |                       |                             |              | Endosulfan            | 0.040                       |
|             |                       |                             |              | Chlorantraniliprole   | 0.038                       |
|             |                       |                             |              | Thifluzamide          | 0.002                       |
| Ulsan 3     | Tricyclazole          | 0.004 *                     | Pohang 3     | Alachlor              | 0.009                       |
|             |                       |                             |              | Procymidone           | 0.004 *                     |
| Ulsan 4     | Carpropramide, Tricyclazole | 0.003 *                   | Pohang 4     | Oxadiazon             | 0.057                       |
|             |                       |                             |              | Tricyclazole          | 0.005 *                     |
|             |                       |                             |              | Thifluzamide          | 0.005 *                     |
| Ulsan 5     | Tricyclazole          | 0.019                       | Pohang 5     | Carbendazim           | 0.002 *                     |
|             |                       |                             |              | Oxadiazon             | 0.016                       |
|             |                       |                             |              | Thiadinil             | 0.004 *                     |
|             |                       |                             |              | Tricyclazole          | 0.002 *                     |
|             |                       |                             |              | Procymidone           | 0.003 *                     |
|             |                       |                             |              | Thifluzamide          | 0.141                       |
| Ulsan 6     | Tricyclazole, Butachlor | 0.020                      | Pohang 6     | *                     | *                           |
|             |                       |                             |              |                       |                             |
| Ulsan 7     | Chlorantraniliprole, Methoxyfenozide, Endosulfan | 0.008, 0.003 * | Pohang 7 | *                     | *                           |
|             |                       |                             |              |                       |                             |
| Ulsan 8     | Tricyclazole          | 0.136                       | Pohang 8     | Carbendazim           | 0.001 *                     |
|             |                       |                             |              | Oxadiazon             | 0.029                       |
|             |                       |                             |              | Tricyclazole          | 0.009                       |
|             |                       |                             |              | Thifluzamide          | 0.014                       |
|             |                       |                             |              | Fenoxanil             | 0.008                       |
| Ulsan 9     | Tricyclazole          | 0.007 *                     | Pohang 9     | Mandipropamid         | 0.012                       |
|             |                       |                             |              | Procymidone           | 0.004 *                     |
|             |                       |                             |              | Chlorfenapyr          | 0.051                       |
|             |                       |                             |              | Endosulfan            | 0.009                       |
|             |                       |                             |              | Bifenthrin            | 0.004 *                     |
| Ulsan 10    | Tricyclazole          | 0.004 *                     | Pohang 10    | Oxadiazon             | 0.020                       |
|             |                       |                             |              | Tricyclazole          | 0.010                       |
|             |                       |                             |              | Thifluzamide          | 0.007 *                     |
| Ulsan Soils | Determined Pesticides | Determined Amounts (µg kg\(^{-1}\)) | Pohang Soils | Determined Pesticides | Determined Amounts (µg kg\(^{-1}\)) |
|------------|-----------------------|--------------------------------------|--------------|-----------------------|--------------------------------------|
| Ulsan 11   | Tricyclazole          | 0.012                                | Pohang 11    |                       | 0.052                               |
|            |                       |                                      |              | Benzbicyclon          | 0.008                               |
|            |                       |                                      |              | Isoprotiolane         | 0.005 *                             |
|            |                       |                                      |              | Oxadiazone            | 0.016                               |
|            |                       |                                      |              | Tricyclazole          | 0.023                               |
|            |                       |                                      |              | Thifluzamide          | 0.020                               |
|            |                       |                                      |              | Fenoxanil             | 0.024                               |
| Ulsan 12   | Tricyclazole, Butachlor | 0.018, 0.006 *                      | Pohang 12    |                       | 0.010                               |
|            |                       |                                      |              | Flubendiamide         | 0.002 *                             |
|            |                       |                                      |              | Isoprotiolane         | 0.001                               |
|            |                       |                                      |              | Oxadiazone            | 0.004                               |
|            |                       |                                      |              | Tricyclazole          | 0.011                               |
|            |                       |                                      |              | Thifluzamide          | 0.011                               |
|            |                       |                                      |              | Fenoxanil             | 0.032                               |
| Ulsan 13   | - **                  | - **                                 | Pohang 13    |                       | 0.001 *                             |
|            |                       |                                      |              | Carpropamide          | 0.003 *                             |
|            |                       |                                      |              | Flubendiamide         | 0.001 *                             |
|            |                       |                                      |              | Iprobenfos            | 0.002                               |
|            |                       |                                      |              | Isoprotiolane         | 0.001                               |
|            |                       |                                      |              | Oxadiazone            | 0.004                               |
|            |                       |                                      |              | Tricyclazole          | 0.007                               |
|            |                       |                                      |              | Fenoxanil             | 0.009                               |
| Ulsan 14   | - **                  | - **                                 | Pohang 14    |                       | 0.002 *                             |
|            |                       |                                      |              | Carbendazim           | 0.013                               |
|            |                       |                                      |              | Flubendiamide         | 0.001                               |
|            |                       |                                      |              | Iprobenfos            | 0.002                               |
|            |                       |                                      |              | Isoprotiolane         | 0.002                               |
|            |                       |                                      |              | Oxadiazone            | 0.070                               |
|            |                       |                                      |              | Tricyclazole          | 0.020                               |
|            |                       |                                      |              | Thifluzamide          | 0.029                               |
|            |                       |                                      |              | Fenoxanil             | 0.057                               |
| Ulsan 15   | Tricyclazole          | 0.032                                | Pohang 15    |                       | 0.002 *                             |
|            |                       |                                      |              | Flubendiamide         | 0.004 *                             |
|            |                       |                                      |              | Isoprotiolane         | 0.011                               |
|            |                       |                                      |              | Oxadiazone            | 0.016                               |
|            |                       |                                      |              | Thifluzamide          | 0.003 *                             |
|            |                       |                                      |              | Fenoxanil             | 0.022                               |
| Ulsan 16   | Carbendazim, Tricyclazole, Endosulfan | 0.004 *, 0.003 *, 0.006 * | Pohang 16    |                       | 0.003 *                             |
|            |                       |                                      |              | Carbendazim           | 0.002 *                             |
|            |                       |                                      |              | Flubendiamide         | 0.002 *                             |
|            |                       |                                      |              | Iprobenfos            | 0.002                               |
|            |                       |                                      |              | Isoprotiolane         | 0.002                               |
|            |                       |                                      |              | Oxadiazone            | 0.022                               |
|            |                       |                                      |              | Tricyclazole          | 0.008                               |
|            |                       |                                      |              | Thifluzamide          | 0.006                               |
|            |                       |                                      |              | Fenoxanil             | 0.008                               |
| Ulsan 17   | Tricyclazole          | 0.007 *                              | Pohang 17    |                       | 0.002 *                             |
|            |                       |                                      |              | Carbendazim           | 0.001 *                             |
|            |                       |                                      |              | Flubendiamide         | 0.005 *                             |
|            |                       |                                      |              | Iprobenfos            | 0.005                               |
|            |                       |                                      |              | Isoprotiolane         | 0.002                               |
|            |                       |                                      |              | Oxadiazone            | 0.034                               |
|            |                       |                                      |              | Tricyclazole          | 0.022                               |
|            |                       |                                      |              | Thifluzamide          | 0.020                               |
|            |                       |                                      |              | Fenoxanil             | 0.015                               |
In addition, tricyclazole was detected in unregistered crops, which could result in the unintentional generation of unsuitable agricultural products. According to the PLA system, an MRL value of 0.01 mg kg\(^{-1}\) is applied to nonregistered crops. A factor for detecting unused tricyclazole is the possibility that pesticides remaining in the soil will be absorbed into the crops [18,32]. Recently, Hwang et al. [18] reported that up to 38.50% of tricyclazole used in the soil during lettuce cultivation remained in the lettuce, proving that tricyclazole is transferred to crops. Therefore, the residue of tricyclazole in paddy soil can be transferred to crops. Further research on this translocation using rice cultivation is needed.

Oxadiazon is used as an herbicide to control annual weeds in rice farming [27]. In this study, it was detected at a level of 0.002–0.070 mg kg\(^{-1}\). The detection frequency was at 15 points in 40 soil samples, reaching 38% (Table 7). This pesticide was detected in the range of 0.028–0.359 mg kg\(^{-1}\) in 8 samples out of 80 paddy soils, and the detection rate was 10% [14]. However, Noh et al. [14] did not report residual oxadiazon in soil samples from Gyengsang Province, located in Pohang and Ulsan. Our results were different from the results of Noh et al. [14]. Park et al. [33] found that oxadiazon was detected in the range of 0.001–0.836 mg kg\(^{-1}\) after residual pesticide analysis using 150 points in Korean paddy soil. The detection frequency reached 19.3%. The authors demonstrated that this higher detection frequency was related to the use of a larger amount of oxadiazon in 2006 than other pesticides, and the half-life of the pesticide in the soil was relatively long (31–91 days). Lee et al. [34] reported that oxadiazon had a high adsorption rate in soil with high organic matter content, and exhibited a lower desorption rate in comparison to the lower organic-matter-possessing soils.

In this study, we focused on the detection of endosulfan, which has been banned in Korea since 2012. Currently, endosulfan is registered as a POP, and most countries around the world have banned it. In our study, it was detected at a level of 0.006–0.040 ppm, and the detection frequency was 7.5% (Table 7). For endosulfan, a report on the translocation from soil to rice farming has been reported [35], and two concentrations, 3 and 10 mg kg\(^{-1}\), were found in paddy soils, showing 0.546 and 1.258 mg kg\(^{-1}\) of endosulfan in the rice straw, respectively. However, endosulfan was not found in brown rice. For cucumbers grown in

### Table 7. Cont.

| Ulsan Soils | Determined Pesticides | Determined Amounts (µg kg\(^{-1}\)) | Pohang Soils | Determined Pesticides | Determined Amounts (µg kg\(^{-1}\)) |
|-------------|-----------------------|--------------------------------------|--------------|-----------------------|--------------------------------------|
| Ulsan 18    | Tricyclazole          | 0.001 *                              | Pohang 18    | Carbendazim           | 0.001 *                              |
|             |                       |                                      |              | Carpropamide          | 0.003 *                              |
|             |                       |                                      |              | Flubendiamide         | 0.005 *                              |
|             |                       |                                      |              | Iprobenfos           | 0.014 *                              |
|             |                       |                                      |              | Isoprotiolane        | 0.002 *                              |
|             |                       |                                      |              | Oxadiazon            | 0.002 *                              |
|             |                       |                                      |              | Tricyclazole         | 0.020                                |
|             |                       |                                      |              | Butachlor            | 0.006 *                              |
|             |                       |                                      |              | Thifluzamide         | 0.020                                |
|             |                       |                                      |              | Fenoxanil            | 0.034                                |
| Ulsan 19    | Tricyclazole          | 0.004 *                              | Pohang 19    | Carbendazim           | 0.001 *                              |
|             |                       |                                      |              | Carpropamide         | 0.002 *                              |
|             |                       |                                      |              | Iprobenfos           | 0.002 *                              |
|             |                       |                                      |              | Isoprotiolane        | 0.008                                |
|             |                       |                                      |              | Oxadiazon            | 0.013                                |
|             |                       |                                      |              | Tricyclazole         | 0.006 *                              |
|             |                       |                                      |              | Fenoxanil            | 0.010                                |
| Ulsan 20    | Tricyclazole          | 0.034                                | Pohang 20    | Carpropamide         | 0.003 *                              |
|             | Mefenacet             | 0.002 *                              |              | Iprobenfos           | 0.005 *                              |
|             |                       |                                      |              | Oxadiazon            | 0.006 *                              |

* Indicates that the determined value was lower than the limit of quantification. ** Indicates that there were no pesticides determined by the analytical methods used in this study.
endosulfan-treated soils with two levels, 20 and 40 mg kg$^{-1}$, its residual amount reached 7.8 and 14.5 mg kg$^{-1}$, respectively, after 15 days of growth [17]. Recently, Kim et al. [16] reported that they found the highest endosulfan residues near farmland, and an endosulfan metabolite, endosulfan sulfate, was dominant in most soil samples. Endosulfan and its sulfate were found in the soils at an average of 0.8 mg kg$^{-1}$ [16]. Therefore, it is necessary to monitor endosulfan and its metabolites in agricultural soils on a regular periodic basis, even if banned in Korea.

Chlorantraniliprole is an anthranilic-acid-related insecticide that shows a selective activator on insect ryanodine receptors, interfering with muscle contraction [36]. This pesticide presents a half-life ranging from 12.6 to 23.1 days in soil [37]. In this study, chlorantraniliprole was detected at a concentration of 0.008–0.038 mg kg$^{-1}$, and the detection frequency was 5% (Table 7). Although there have been no reports on the residual pattern of this pesticide in paddy soil in Korea, it was detected in perilla leaf, brassica leafy vegetables, and spinach from 2010 to 2012 at a level of 0.129–0.805 mg kg$^{-1}$ [13]. In addition, carbendazim (8/40) and carpropanid (7/40) were found as pesticides detected below the LOQ, but with high detection frequency.

4. Conclusions

In this study, we developed a multiresidue pesticide analysis using GC–MS/MS and LC–MS/MS to monitor 342 pesticides in paddy soils. MRM values for each pesticide, LOD and LOQ, linearity of the calibration curve, and recoveries were validated for the instrumental analyses of the paddy soils. With this validated method, four pesticides, including tricyclazole, oxadiazon, endosulfan, and chlorantraniliprole, were detected among the 40 paddy soils near the industrial area in Pohang and Ulsan cities, Korea. Even with the ban of endosulfan use due to its classification as a POP, its detection in paddy soils might still be needed for continuous monitoring of paddy soils nationwide when considering the mapping of other banned pesticides.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/app11188415/s1, Table S1: MRM conditions for the other 83 pesticides in the GC–MS/MS analysis, Table S2: MRM conditions for the other 179 pesticides in the LC–MS/MS analysis, Table S3: LOD, LOQ, and linearity of the other 83 pesticides using GC–MS/MS, Table S4: LOD, LOQ, and linearity for the other 179 tested pesticides using LC–MS/MS, Table S5: Recoveries of the other 83 pesticides in the untreated soil using GC–MS/MS ($n = 3$), Table S6: Recoveries of the other 179 pesticides in the untreated soil using LC–MS/MS ($n = 3$).

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