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Streamlining sample preparation and gas chromatography–tandem mass spectrometry analysis of multiple pesticide residues in tea

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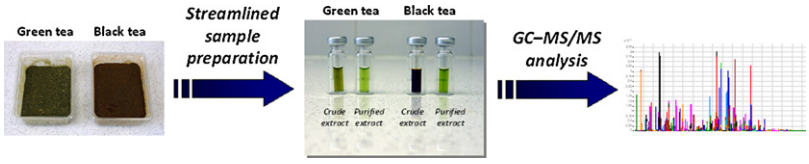
HIGHLIGHTS

- We developed a new sample preparation method for the rapid analysis of pesticide residues in tea.
- QuEChERS-based extraction followed by LLE cleanup enabled good recoveries and minimisation of matrix co-extracts.
- Hydration of matrix is crucial for efficient extraction of target analytes.
- GC–MS/MS enabled simultaneous determination of target analytes.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, a new rapid method for the determination of 135 pesticide residues in green and black dry tea leaves and stalks employing gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) with a triple quadrupole was developed and validated. A substantial simplification of sample processing prior to the quantification step was achieved: after addition of water to a homogenised sample, transfer of analytes into an acetonitrile layer was aided by the addition of inorganic salts. Bulk co-extracts, contained in the crude organic extract obtained by partition, were subsequently removed by liquid–liquid extraction using hexane with the assistance of added 20% (w/w) aqueous NaCl solution. The importance of matrix hydration prior to the extraction for achieving good recoveries was demonstrated on tea samples with incurred pesticide residues. For most of the analytes, recoveries in the acceptable range of 70–120% and repeatabilities (relative standard deviations, RSDs) ≤20% were achieved for both matrices at spiking levels of 0.01, 0.1 and 1 mg kg^{-1}. Under optimised GC–MS/MS conditions, most of the analytes gave lowest calibration level ≤0.01 mg kg^{-1}, permitting the control at the maximum residue levels (MRLs) laid down in Regulation (EC) No 396/2005. The developed method was successfully applied to the determination of pesticide residues in real tea samples.

1. Introduction

Tea is a popular beverage consumed worldwide and valued for its specific aroma and flavour as well as potential health-promoting properties [1]. As long as organic production is not considered, then the application of pesticides during tea cultivation and/or storage represents a common practice for pest and plant disease control [2]. Under certain circumstances, however, residues of active ingredients may occur in the 'final' product. Because of potential health risk for consumers, resulting from acute and/or chronic dietary exposure, maximum residue limits (MRLs) for many pesticides have been established in the EU. Currently, the EU Pesticides database [3] (based on Regulation (EC) No 396/2005 [4]) contains a list of 448 pesticide residues with respective MRLs for tea (dried leaves

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and stalks, fermented or otherwise of *Camellia sinensis*) ranging between 0.005 and 350 mg kg^{-1}. In recent years, several alerts concerning the presence of pesticide residues in tea—exceeding the MRLs—have been posted by the Rapid Alert System for Food and Feed (RASFF) [5].

Taking into account these facts, rapid and cost-effective multiple pesticide residue analysis represents an important task for both the tea producers and regulatory agencies. It should be noted, however, that the majority of until now published multiple pesticide residue methods were mainly dedicated to control of less complicated matrices such as fruit and vegetables [6]. The main reason might be the fact that tea represents a very complex matrix containing not only a high amount of caffeine, but also pigments, polyphenols, *etc.*, which make the analysis of multiple pesticide residues more difficult owing to matrix interferences and complicated extraction procedures, creating an analytical challenge [7]. Unfortunately, a current trend used in liquid chromatography–mass spectrometry (LC–MS), *i.e.* 'dilute-and-shoot' is not applicable in gas chromatography–mass spectrometry (GC–MS) since the analysed extracts typically contain—regardless of the dilution—many non-volatile co-extracts which can negatively affect the method performance characteristics. Repeated injections of non-volatile matrix components, which are gradually deposited in the GC inlet and/or front part of the GC column, can give rise to the successive formation of new active sites, which may be responsible for matrix-induced GC signal diminishment. Gradual decrease in analyte responses associated with this phenomenon, together with distorted peak shapes (broadening, tailing) and shifting the retention times towards higher values, negatively impact the ruggedness of the analytical method [8]. Despite of these limitations as compared to LC–MS, GC–MS remains an essential technique for comprehensive screening of pesticide residues and, for some analytes, this technique represents an irreplaceable tool (*e.g.* analysis of organochlorine pesticides).

Until now, published GC–MS-based methods for the analysis of pesticide residues in tea involve extraction (liquid–solid extraction; accelerated solvent extraction) employing acetonitrile (MeCN), ethyl acetate, acetone or mixtures of the solvents (*e.g.* cyclohexane-ethyl acetate, acetone-ethyl acetate-hexane, ethyl acetate-hexane, acetone-hexane, ethanol-toluene) [7,9–16] followed by typically a one- or two-step purification of the crude extract using gel permeation chromatography (GPC) and/or solid-phase extraction (SPE) with Carb-NH_2, Florisil or Envi-Carb cartridges [10,12–15]. Unfortunately, these procedures lead to increasing overall cost of the method, extending analysis time and requiring additional labour. Alternatively, dispersive-SPE with various sorbents such as primary-secondary amine (PSA), C_{18} silica, Florisil or graphitised carbon black (GPB) was employed for purification of the crude extracts [7,9,11,16]. Apart from these more common approaches, head-space solid-phase micro-extraction (SPME) and stir bar sorptive extraction (SBSE) were also successfully used in the analysis of some pesticide residues in tea [17,18]. Another possible simplification of the sample preparation procedure involves acetonitrile extraction/partitioning, which is the main concept of the QuEChERS (quick, easy, cheap, effective, rugged and safe) sample processing strategy, widely introduced in the control of pesticide residues in fruits and vegetables. The 'original' QuEChERS method involves initial extraction with acetonitrile, liquid–liquid partitioning after addition of a mixture of anhydrous $MgSO_4$ and NaCl, followed by a simple cleanup step in which the extract is mixed with PSA sorbent and anhydrous $MgSO_4$ (dispersive-SPE) [19]. Modification of this method was also used for the analysis of a limited number of pesticide residues (22) in tea. In that particular case, the tea sample was homogenised with water (forming 'puree') and pesticide residues were extracted with MeCN containing 1% acetic acid. After centrifugation, the crude extract was purified using dispersive-SPE with PSA and C_{18} sorbents followed by solvent exchange, after which a second dispersive-SPE step (with the same sorbents) was carried out to reduce matrix interference during GC–MS analysis. [7].

In this study, many types of pesticides possessing a wide range of different physico-chemical properties (volatility, polarity) were selected for the evaluation of a rapid analytical method for black and green tea. The sample preparation method was streamlined as much as possible to achieve acceptable recovery and repeatability of target analytes and, at the same time, reduce the amount of non-volatile and semi-volatile co-extracts. During the optimisation of sample preparation, gravimetric determination of co-extracts was employed. The use of gas chromatography coupled to tandem mass spectrometry (GC–MS/MS) with a triple quadrupole (QqQ) mass analyser was chosen for the analysis with the expectation of enhanced speed, high accuracy and improved selectivity. In the final phase, the developed method was applied to the determination of pesticide residues in real tea samples.

2. Materials and methods

2.1. Chemicals and materials

Pesticide reference standards, all 95% or higher purity, were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Sigma–Aldrich (Taufkirchen, Germany). A composite stock standard solution (5 μg mL^{-1}) of multiple pesticides (Table S-1 (Supplementary data)) was prepared in toluene. A stock internal standard solution containing triphenyl phosphate (TPP) at 2 μg mL^{-1} (Sigma–Aldrich), was also prepared in toluene.

MeCN and hexane were high purity solvents for pesticide residue analysis from Supelco (Bellefonte, PA, USA) and Merck (Darmstadt, Germany), respectively, and acetic acid was HPLC grade from Sigma–Aldrich. Anhydrous magnesium sulphate ($MgSO_4$) was from Fluka (Buchs, Germany), calcium chloride ($CaCl_2$), sodium chloride (NaCl) and sodium acetate tri-hydrate ($NaOAc{\cdot}3H_2O$) were obtained from Penta (Chrudim, Czech Republic). PSA sorbent was from Varian (Harbor City, CA, USA) and Bondesil C_{18} sorbent (40 μm) was obtained from Agilent Technologies (Santa Clara, CA, USA). Sodium citrate tri-basic dihydrate ($Na_3Citr{\cdot}2H_2O$) and sodium citrate dibasic sesqui-hydrate ($Na_2HCitr{\cdot}1.5H_2O$) were from Sigma–Aldrich. Deionised water (18 MΩ) was produced by a Milli-Q system (Millipore; Bedford, MA, USA).

2.2. Instrumentation

2.2.1. GC–MS/MS analysis

All GC–MS experiments were performed using a gas chromatograph Agilent 7890A GC (Agilent Technologies) coupled to a triple quadrupole mass spectrometer 7000B (Agilent Technologies) operated in electron ionisation mode (EI,−70 eV). The GC system was equipped with an Agilent 7693A autosampler (Agilent Technologies), a carbon dioxide cooled multimode inlet (MMI) and a 2 mm I.D. dimpled deactivated liner. For the separation, a coupling of an HP-5ms Ultra Inert column (15 m × 0.25 mm ID, 0.25 μm; Agilent Technologies) with a DB-5ms Ultra Inert column (0.50 m × 0.15 mm I.D., 0.15 μm; Agilent Technologies) *via* a pressure controlled tee (PCT) with pneumatics control module (PCM) was used. Optimised conditions of cold splitless (injection of hexane extracts) and solvent vent PTV (injection of MeCN extracts) methods are summarised in Table 1. The triple quadrupole was operated in multiple reaction monitoring (MRM) mode detecting 2–8 transitions per analyte as listed in Table S-1 (Supplementary data). The temperatures of the transfer line, the ion source, 1st and 2nd quadrupole were 280 °C, 280 °C, 150 °C and 150 °C, respectively.

Table 1
Optimised conditions for the injection and GC analysis of the pesticides.

Injection mode	Cold splitless	Solvent vent PTV
Injector temperature program	50 °C (0.1 min), 600 °C min^{-1} to 300 °C	30 °C (1.5 min), 600 °C min^{-1} to 300 °C
Vent time, flow and pressure	–	1.5 min, 30 mL min^{-1}, 5 psig
Carries gas pressure (He)	17.460 psig	17.460 psig
Injection volume	2 μL	2 μL
Splitless period	1 min	1 min
PCM pressure	2.0 psig	2.0 psig
Oven temperature program	50 °C (1.0 min), 50 °C min^{-1} to 150 °C, 6 °C min^{-1} to 200 °C, 16 °C min^{-1} to 280 °C (4.07 min)	70 °C (2.5 min), 50 °C min^{-1} to 150 °C, 6 °C min^{-1} to 200 °C, 16 °C min^{-1} to 280 °C (4.07 min)
Retention time locking compound	Trifluralin (locked to 6.219 min)	Trifluralin (locked to 7.318 min)
Post run time	2 min	2 min
Post run pressures inlet	1.0 psig	1.0 psig
Post run pressures PCM	60.0 psig	60.0 psig

The collision cell gases were nitrogen (1.5 mL min^{-1}) and helium (2.25 mL min^{-1}). The electron multiplier (EM) gain was set to 10 and both MS resolutions were 1.2 amu full width at half maximum. The dwell times were adjusted to 2–28 ms depending on the number of transitions per time window to achieve 5 cycles s^{-1} (Hz). Mass Hunter quantitative analysis software (v. B.04.04) (Agilent Technologies) was used for data processing.

2.3. Samples

Green and black tea samples were used for blanks, fortified samples for recovery assays and matrix-matched standards for calibration in the experiments. Before the recovery assays, the samples were tested for the absence of pesticide residues.

Samples (n = 37) for the monitoring study were purchased from the local markets and included black teas (n = 19), aromatised black teas (n = 6), green teas (n = 8) and aromatised green teas (n = 4).

The test material for Food Analysis Performance Assessment Scheme (FAPAS) proficiency test 19129 was supplied by the Food and Environmental Research Agency (FERA, York, UK). This test material (green tea) contained residues of chlorpyrifos (69.6 ± 15.3 μg kg^{-1}), fenpropathrin (63.5 ± 14.0 μg kg^{-1}), hexachlorobenzene (86.3 ± 19.0 μg kg^{-1}), phosalone (151 ± 32.2 μg kg^{-1}) and procymidone (62.9 ± 13.8 μg kg^{-1}). The assigned values and corresponding standard deviations for proficiency are given in brackets.

2.4. Sample preparation

2.4.1. Procedure I—Original (unbuffered) QuEChERS + LLE

The 'original' QuEChERS method [19] was used with modifications as follows: (1) weigh 2 g of homogenised tea sample into a 50 mL plastic centrifuge tube; (2) fortify the sample by appropriate volume to achieve 0.01–0.1–1 mg kg^{-1} spike and allow the sample to stand for 1 h at room temperature; (3) add 10 mL distilled water; (4) shake for 30 s; (5) leave the samples for 30 min for matrix swelling (hydration); (6) add 10 mL MeCN; (7) shake vigorously for 1 min by hand; (8) add 4 g anh. $MgSO_4$ and 1 g NaCl; (9) shake vigorously for 1 min by hand; (10) fortify the sample by appropriate volume to achieve 0.1 mg kg^{-1} for triphenyl phosphate (TPP) (internal standard); (11) centrifuge the tube at 10,000 rpm for 5 min; (12) transfer 1 mL of extract to a 15 mL plastic centrifuge tube containing 1 mL hexane and 5 mL 20% NaCl (w/w) solution; (13) shake vigorously for 1 min by hand; (14) centrifuge the tube at 10,000 rpm for 1 min; (15) transfer a part of (upper) hexane layer into a vial for GC–MS/MS analysis.

2.4.2. Procedure II—Acetate-buffered QuEChERS + LLE

The procedure was similar to original QuEChERS + LLE (Section 2.4.1) except for using 1% HOAc in MeCN (v/v) as an extraction solvent and the addition of 4 g anh. $MgSO_4$ and 1.7 g $NaOAc{\cdot}3H_2O$ during the partitioning step [20].

2.4.3. Procedure III—Citrate-buffered QuEChERS + LLE

The procedure was similar to original QuEChERS + LLE (Section 2.4.1) except for using 4 g anh. $MgSO_4$, 1 g NaCl, 1 g $Na_3Citr{\cdot}2H_2O$ and 0.5 g $Na_2HCitr{\cdot}1.5H_2O$ during the partitioning step [21].

2.4.4. Procedure IV—Extraction with pure MeCN + LLE

The extraction method [15] with pure MeCN (no matrix hydration) was used with modifications as follows: (1) weigh 5 g of homogenised tea sample into a 50 mL plastic centrifuge tube; (2) fortify the sample by appropriate volume to achieve 0.1 mg kg^{-1} spike and allow the sample to stand for 1 h at room temperature; (3) add 15 mL MeCN; (4) use an Ultra-turrax macerator at 15,000 rpm for 1 min; (5) centrifuge the tube at 10,000 rpm for 5 min; (6) transfer the MeCN layer into a 25 mL volumetric flask; (7) repeat the extraction with another 15 mL MeCN; centrifuge the tube at 10,000 rpm for 5 min; (8) combine the MeCN extracts; (9) fortify the extract by appropriate volume to achieve 0.1 mg kg^{-1} for TPP (internal standard); (10) make up to 25 mL MeCN. The MeCN extract was purified using LLE as described in Section 2.4.1.

2.4.5. Matrix-matched standards preparation

For all procedures, matrix-matched standards were prepared similarly to fortified samples except for addition of a spike solution. For Procedure I, the concentrations of pesticides in matrix-matched standards were: 0.2, 0.5, 1, 2, 5, 10, 20, 30, 50, 100, 200 and 300 ng mL^{-1}, which correspond to 0.001, 0.0025, 0.005, 0.01, 0.025, 0.05, 0.1, 0.15, 0.25, 0.5, 1 and 1.5 mg kg^{-1} in the sample.

For Procedures II–IV, the concentrations of pesticides in matrix-matched standards were: 10, 20 and 30 ng mL^{-1}, which correspond to 0.05, 0.1 and 0.15 mg kg^{-1} in the sample.

Each matrix-matched standard also contained TPP (internal standard) at a concentration of 20 ng mL^{-1} (corresponding to 0.1 mg kg^{-1}).

2.4.6. Gravimetric determination of co-extracts

The crude MeCN extracts and purified hexane extracts, 5 mL and 15 mL, respectively, were evaporated until dryness using a vacuum evaporator (Büchi Rotavapor R-114 and Waterbath B-480, Switzerland) and the remaining co-extracts were gravimetrically

determined employing an analytical balance (GR-202-EC, A&D Instruments, Japan).

2.4.7. Determination of pH of tea matrices

Determination of the pH of tested matrices (green and black tea) was done by measuring the pH value of their water extracts. An amount of 2 g of the sample was weighed into a 50 mL plastic centrifuge tube followed by the addition of 10 mL of Milli-Q water. The content of the tube was mixed and the matrix was left to hydrate for 30 min. The pH of the water extracts and the deionised water was measured by a calibrated pH meter HI 991001 (Hanna Instruments Inc.; Woonsocket, RI, USA).

3. Results and discussion

In this study, 164 pesticides, mostly insecticides and fungicides, which may be found in tea were investigated. These target analytes, representing various structure classes are characterised by a wide variety of physico-chemical properties, including volatility, polarity, chemical and thermal stability *etc.* Combined with such a difficult matrix as tea, development of a simple and reliable analytical method was a real challenge. The way this challenge was addressed is described in detail in the following sections.

3.1. Optimisation of sample preparation

3.1.1. Purification of the crude extracts and checking of sample preparation efficiency

As mentioned in the Section 1, tea represents a complex matrix with high amounts of polyphenols, methyl xanthines such as caffeine, purines and phenolic acids, which might be co-isolated to some extent during sample extraction. These matrix co-extracts can impact the GC–MS/MS method performance in different ways. The non-volatile matrix components deposited at the inlet part of the GC system are typically responsible for formation of new active sites. On the other hand, the abundant (semi)-volatile matrix components can cause distortion of peak shapes and shifting of the retention times of target analytes. In addition, interfering ions (formed during the ionisation from the matrix co-extracts) with masses close to those of target residue and, even ion suppression, are the main factors that limit achieving low detection limits and reliable analyte identification.

Our preliminary experiments showed that the crude MeCN extracts of green and black tea contained a large amount of these matrix co-extracts (typically 40 mg mL^{-1} originated from 0.2 g of the sample equivalent). Whilst attempting to protect the GC–MS system as much as possible, we focused on reducing the level of co-extracted matrix. To this end, various strategies were investigated: (i) dispersive-SPE; (ii) dispersive-SPE followed by LLE; and (iii) LLE only.

For dispersive-SPE experiments, the following combinations of sorbents and desiccants were tested:

(i) 50 mg PSA + 150 mg $MgSO_4$ per 1 mL of crude MeCN extract.
(ii) 50 mg PSA + 50 mg $CaCl_2$ per 1 mL of crude MeCN extract.
(iii) 10 mg C_{18} + 50 mg PSA + 150 $MgSO_4$ per 1 mL of crude MeCN extract.
(iv) 10 mg C_{18} + 150 mg $MgSO_4$ per 1 mL of crude MeCN extract.

(*Note:* In all experiments the sample equivalent was 0.2 g per 1 mL of the crude MeCN extract.)

PSA represents a weak ion exchanger which mainly removes sugars, fatty acids, organic acids and some pigments, while C_{18} can be used for the reduction of lipids and non-polar interferences. During the course of our experiments, we omitted the use of graphitised carbon black (GCB), due to its high affinity to planar pesticides (*e.g.* hexachlorobenzene, phosalone, chlorothalonil). Also, anhydrous $MgSO_4$ or $CaCl_2$ were added to the extracts, since these salts were reported to have a positive impact on the removal of co-extracts [19,21]. It is assumed that drying with $MgSO_4$ or $CaCl_2$ removes water from the crude MeCN extracts (containing approx. 12% of water), thus, making the final MeCN extracts less polar and causing precipitation of certain polar matrix co-extracts [19].

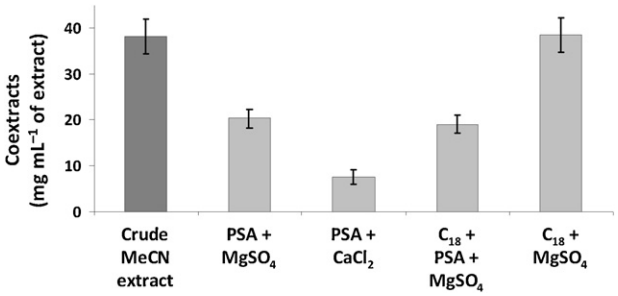

Fig. 1. Amount of matrix co-extracts determined gravimetrically in green tea extracts after purification employing various sorbents/desiccants for dispersive-SPE.

As Fig. 1 shows, the best efficiency for removing of matrix co-extracts was obtained when the combination of PSA and $CaCl_2$ was used. On the other hand, the other sorbent/desiccant mixtures, *i.e.* PSA/$MgSO_4$, C_{18}/PSA/$MgSO_4$, C_{18}/$MgSO_4$ only had a slight impact on the removing of matrix co-extracts. Nevertheless, the amount of co-extracts was still too high (7.5 ± 0.8 mg mL^{-1} originated from 0.2 g of the sample) taking into account that the content of co-extracts obtained by the QuEChERS method with dispersive-SPE (PSA/$MgSO_4$) for less problematic matrices (*e.g.* apple baby food, mixed fruit/vegetables, orange juice) was reported to be in the range of 0.2–1.7 mg mL^{-1} originated from 1 g of sample [19,20,22]. Therefore, we investigated further cleanup strategies to reduce the amounts of matrix co-extracts. To this end, we tested liquid–liquid extraction (LLE) using hexane with the aid of 20% aqueous NaCl (w/w) solution. For this experiment, the ratio of MeCN extract, hexane and 20% NaCl (w/w) solution was 1:1:5 (v/v/v). The addition of inorganic salt was used to enhance the transfer of target analytes into the hexane layer by means of the salting out effect.

As documented in Fig. 2, using this approach, the amount of matrix co-extracts determined gravimetrically reduced significantly (the extent of matrix co-extracts removal was almost the same for black and green tea). This can be explained by a decrease of solvent polarity (MeCN → hexane), which led to reduced solubility of polar co-extracts in the hexane extract, thus reducing their partition into this solvent. Considering such a discrimination effect, we also evaluated the possibility of purifying the crude MeCN extracts using LLE only, thus omitting the dispersive-SPE step. Surprisingly,

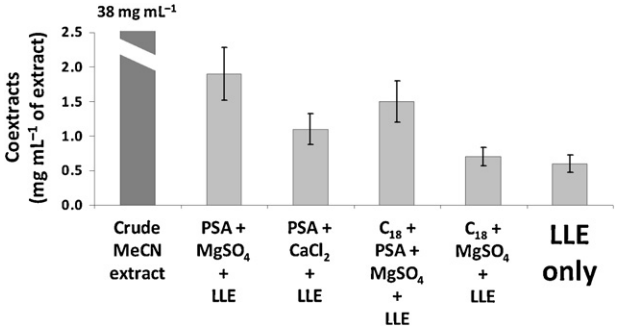

Fig. 2. Amount of matrix co-extracts determined gravimetrically in green tea extracts after purification employing various sorbents/desiccants for dispersive-SPE followed by LLE (hexane + 20% NaCl (w/w) solution).

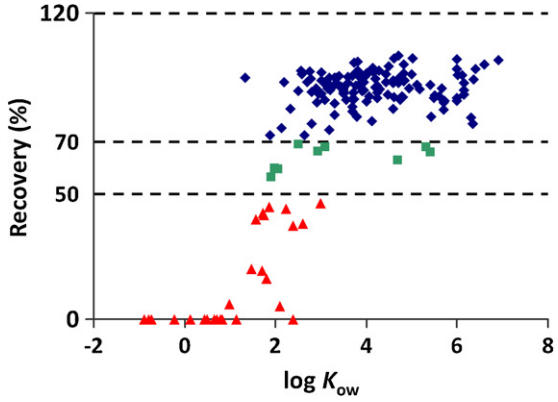

Fig. 3. Recoveries (%) of pesticides tested *vs.* their log K_{ow}. Data from the analysis of green tea spiked at a level of 1 mg kg^{-1}. The values of log K_{ow} were collected from [23,24].

the content of co-extractives was reduced to a level similar to that of a two-step purification employing a combination of dispersive-SPE and LLE. The efficiency of the cleanup procedure is also documented in Fig. S-1 (Supplementary data) showing the total ion current (TIC) for the mass range *m/z* 50–550 (full scan mode) for the crude MeCN extract and the extract after LLE.

Of course, not only the amount of co-isolated matrix compounds but also the recoveries of the target analytes represent an important performance characteristic of the analytical method. Therefore, in a follow up experiment, the combination of unbuffered QuEChERS extraction followed by LLE was investigated for the extraction of multiple pesticide residues (164) from green tea at a spiking level of 1 mg kg^{-1}. In general, the pesticides studied covered a wide range of polarities from the extremely polar methamidophos (log K_{ow} −0.9) to non-polar cyhalothrin-lambda (log K_{ow} 6.9). As Fig. 3 documents, pesticides with log K_{ow} <1.8 were poorly extracted using this method. Lower recoveries of these pesticides can be explained by the use of LLE with non-polar solvent (hexane) required for the elimination of most of the matrix co-extracts. On the other hand, the lipophilic pesticides (log K_{ow} >4) had a high tendency to partition into the hexane layer. For polar pesticides, however, LC–MS(/MS) analysis of the crude MeCN extract obtained by the QuEChERS method represents the best choice [25–27]; thus, we did no further experimentation to try and achieve higher recoveries of these analytes (29) which are troublesome to analyse by GC.

For these reasons, the dispersive-SPE was completely omitted from the sample preparation protocol and only LLE was used for cleanup of the crude MeCN extracts for subsequent experiments.

3.1.2. Comparison of various QuEChERS methods

At present, three main variations of the QuEChERS method are widely used in laboratories concerned with pesticide residue analysis: the original (unbuffered) method employing only aqueous acetonitrile for the primary extraction [19] and two buffered ones known as the AOAC Official Method 2007.01 (acetate-buffered) [20] and the CEN Standard Method EN 15662 (citrate-buffered) [21]. Buffers were introduced in order to achieve constant pH value during the extraction of different matrices to improve stability of base-sensitive compounds, which undergo hydrolysis at pH close to neutral. From 164 pesticides tested in this study, 125 provided acceptable recoveries (70–120%) at a spiking level of 0.1 mg kg^{-1} (green tea) regardless of which QuEChERS version was employed. Even for the troublesome (base-sensitive) pesticides, *i.e.* chlorothalonil and tolylfluanid, all three sample processing versions provided acceptable recoveries. Specifically, unbuffered, acetate-buffered and citrate-buffered QuEChERS enabled recoveries 84–88% for chlorothalonil and 81–89% for tolylfluanid. The reason for these comparable results might be due to the similar pH value (5.1 ± 0.1) of tea extracts (2 g + 10 mL of water) for both green and black tea. In addition, these two analytes are immediately transferred after the extraction from relatively polar MeCN into non-polar hexane, in which they are more stable. In order to investigate the purification process, the amounts of matrix co-extracts were determined in these extracts. Using green tea as the test matrix, gravimetrically determined co-extracts in crude MeCN extracts were in the range 35–38 mg mL^{-1}, whilst after LLE, their amounts were reduced to 0.5–0.6 mg mL^{-1} for all QuEChERS versions. In other words, all three QuEChERS extraction techniques provided comparable results in terms of recovery of target analytes and the amount of isolated matrix co-extracts.

3.1.3. Matrix swelling prior the extraction

Rather surprisingly, several recently published studies [15,16,28] dealing with the extraction of pesticide residues from tea used pure MeCN without any addition of water, which is generally recommended for the analysis of low-moisture matrices [29]. Cleaner extracts (less polar matrix components) are obtained when matrix hydration is omitted; however, the problem with lower recoveries of incurred residues might be, almost unavoidably, encountered [30]. To investigate this presumed issue in a greater detail, we compared the extraction efficiency of the streamlined sample preparation method, which uses matrix swelling (hydration) for 30 min prior to the extraction, and the method published by Pang et al. [15] that uses pure MeCN for the extraction without previous matrix hydration. Not only the recoveries obtained by these two methods using a common spiking procedure were compared, but also the results of the analysis of incurred residues from tea samples available in our laboratory.

Fig. 4 documents the results of the analysis of incurred residues in one black and one green tea sample. For most of the pesticides quantified in these samples, the method employing pure MeCN without any addition of water gave lower results (the underestimation ranging from 25% to 74%). However, for samples spiked with a pesticide standard (in toluene) prior to the extraction, the recoveries of 77–105% for QuEChERS + LLE with matrix hydration, and the recoveries of 78–110% for the extraction employing pure MeCN without matrix hydration were obtained. (*Note:* Similar results were also obtained for other tea samples with incurred pesticide residues analysed (data not shown here).) These results clearly documented that the addition of water to the tea sample is a key point to achieving maximum extraction yield (and therefore accurate results).

From the point of view of matrix co-extracts, the crude MeCN extract of green tea obtained by matrix hydration contained approximately 30-times more matrix co-extracts than without previous matrix hydration.

It is important to note that different extraction efficiencies of incurred residues in green and black tea samples were observed. For instance, bifenthrin was extracted from green tea to the same extent by both methods, while only 50% of incurred bifenthrin was extracted from black tea. In general, when using pure MeCN for the extraction without matrix hydration, the incurred residues were slightly better extracted from green tea than from black tea. The reason might be due to stronger binding to matrix components which originate during the fermentation processes.

3.2. Optimisation of GC–MS/MS conditions

For the injection of hexane extracts, a cold splitless mode using 2 μL was used. Higher volumes required the PTV to be operated in solvent vent mode since peak distortions of early eluting pesticides were observed during cold splitless injection. For the separation, a coupling of a 15 m narrow bore non-polar

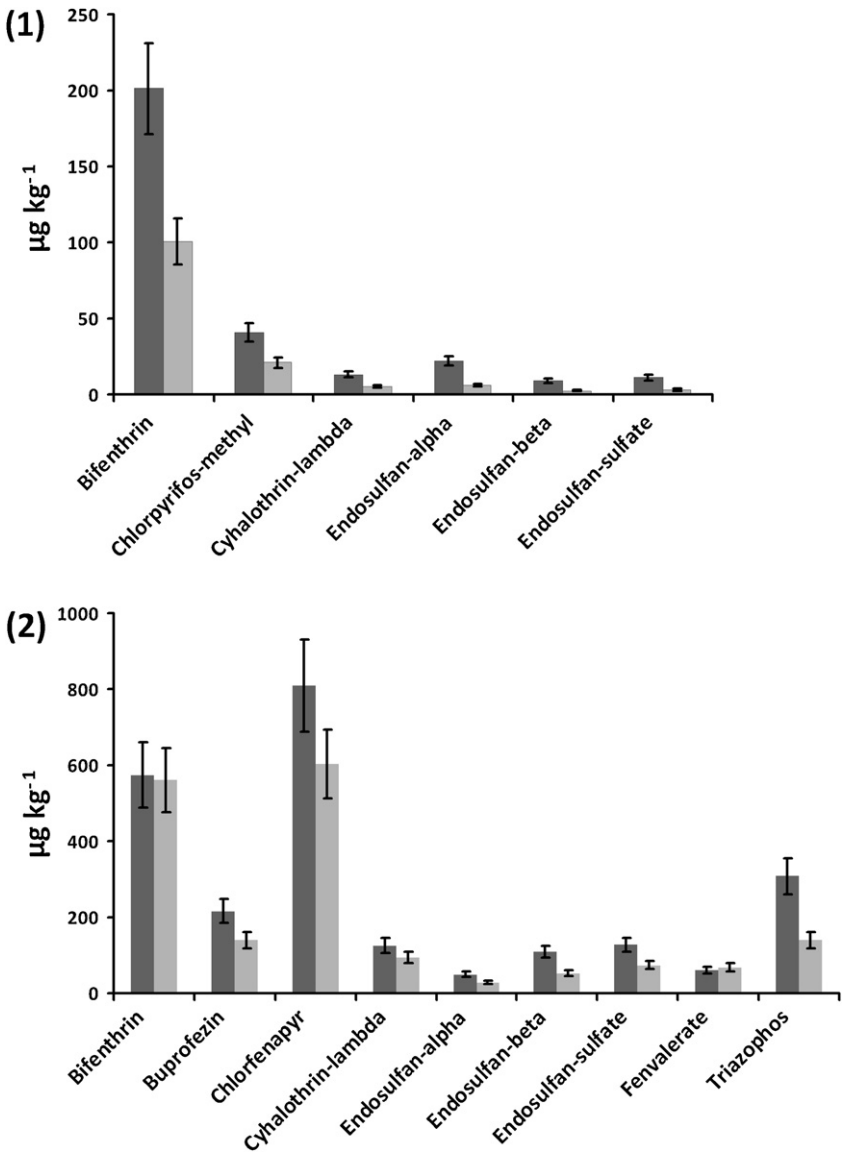

Fig. 4. Comparison of results obtained by the analysis of incurred residues in (1) black tea and (2) green tea employing (■) QuEChERS + LLE with previous matrix hydration and (■) extraction with pure MeCN without previous matrix hydration.

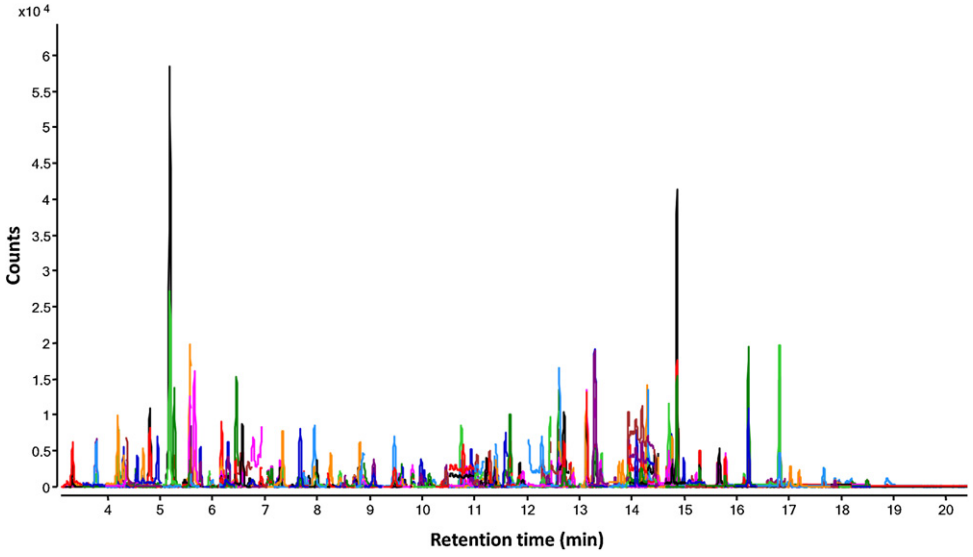

Fig. 5. An overlay of MRM chromatograms of the 164 pesticides in the matrix-matched standard (0.1 mg kg^{-1}) acquired using the optimised MS/MS method.

Table 2
Results of the validation study [mean recoveries (%), relative standard deviations (RSDs, %), lowest calibration levels (LCLs, mg kg^{-1})].

	Green tea							Black tea						
	Level (0.01 mg kg^{-1})		Level (0.1 mg kg^{-1})		Level (1 mg kg^{-1})			Level (0.01 mg kg^{-1})		Level (0.1 mg kg^{-1})		Level (1 mg kg^{-1})		
Analyte	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	LCL (mg kg^{-1})	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	LCL (mg kg^{-1})
Aldrin	62	10	66	5	79	5	0.0025	76	12	69	8	83	4	0.005
Ametryn			77	7	72	6	0.025			42	23	58	4	0.05
Azinphos-ethyl	96	8	95	5	95	4	0.0025	89	18	88	5	97	2	0.0025
Azinphos-methyl	89	10	88	3	89	5	0.01	82	20	74	8	83	6	0.005
Azoxystrobin	68	14	64	3	69	4	0.005	55	14	50	6	65	3	0.005
BHC-alpha	90	7	92	4	90	5	0.0025	91	8	83	5	91	4	0.0025
BHC-beta	88	8	88	4	91	4	0.005	81	10	85	4	92	3	0.005
BHC-delta	82	9	90	3	89	6	0.0025	95	9	83	5	91	3	0.0025
Bifenthrin	76	3	79	3	98	5	0.0025	86	6	79	4	97	2	0.005
Bromophos-methyl	77	7	85	5	92	4	0.001	91	12	84	3	94	3	0.001
Bromophos-ethyl	77	6	80	4	90	5	0.01	86	9	80	5	92	3	0.0025
Bromopropylate	84	12	88	3	92	4	0.001	89	13	83	4	93	2	0.001
Bupirimate	84	13	95	3	89	4	0.001	78	11	73	4	83	3	0.001
Buprofezin	82	9	90	4	90	4	0.005	89	5	84	3	91	3	0.01
Cadusafos	94	6	101	4	95	4	0.01	94	4	89	4	96	3	0.01
Carbophenothion	102	16	80	4	95	4	0.01	85	11	79	6	96	2	0.01
Chinomethionat	72	6	76	6	79	5	0.001	77	9	73	4	83	2	0.001
Chlordane, *cis*-	59	5	74	8	87	5	0.0025	90	6	75	6	88	3	0.0025
Chlordane, *trans*-	67	6	73	5	86	5	0.005	86	11	74	6	88	3	0.005
Chlorfenapyr	102	28	99	4	96	5	0.0025	109	24	91	7	94	2	0.001
Chlorfenvinphos	98	5	100	4	95	5	0.0025	95	10	89	2	96	3	0.0025
Chlorobenzilate	87	4	95	3	93	5	0.001	94	4	87	3	94	3	0.001
Chlorothalonil	79	11	85	4	85	5	0.005	88	13	76	4	86	4	0.005
Chlorpropham	94	6	96	2	92	5	0.001	91	10	88	3	93	3	0.001
Chlorpyrifos	91	10	88	4	93	5	0.001	90	6	86	3	95	3	0.005
Chlorpyrifos-methyl	85	11	93	4	92	5	0.0025	88	13	90	6	95	3	0.005
Chlozolinate	98	18	99	5	93	4	0.01	95	9	90	3	94	4	0.01
Cyfluthrin (sum)	79	7	90	4	102	4	0.005	87	9	86	5	100	2	0.005
Cyhalothrin-lambda	90	13	85	4	102	4	0.0025	91	11	85	6	101	2	0.001
Cypermethrin (sum)	80	3	83	3	100	4	0.005	72	20	74	17	101	2	0.005
Cyprodinil	73	3	85	3	85	5	0.001	76	5	74	4	82	2	0.0025
DDD, *o,p*'-	74	4	73	3	88	5	0.001	82	6	75	4	90	3	0.001
DDD, *p,p*'- + DDT, *o,p*'-	71	4	73	3	88	5	0.001	82	6	75	4	90	3	0.001
DDE, *o,p*'-	65	4	71	5	85	5	0.001	81	8	74	4	88	3	0.001
DDE, *p,p*'-	57	8	66	6	82	5	0.001	75	4	71	5	86	3	0.001
DDT, *p,p*'-			85	13	93	15	0.05			75	4	90	3	0.05
Deltamethrin	95	23	82	5	102	4	0.005	85	17	84	5	97	2	0.01
Diazinon	96	8	101	4	95	5	0.0025	94	9	89	4	96	3	0.0025
Dichlobenil	88	4	98	4	93	5	0.001	90	5	84	3	92	3	0.001
Dichlofluanid	68	10	72	3	86	5	0.01	93	12	83	5	96	3	0.01
Dichlorvos	54	16	56	4	56	4	0.001	52	8	49	5	56	3	0.001
Diclofop-methyl	85	7	96	2	93	5	0.001	94	7	85	3	93	3	0.001
Dicloran	74	14	76	4	77	3	0.0025	74	13	69	4	77	2	0.005
Dieldrin	70	14	82	5	87	6	0.0025	90	18	79	7	89	4	0.0025
Difenoconazol (sum)	93	5	88	5	91	4	0.005	74	12	79	4	88	2	0.005
Diphenylamine	93	4	96	3	93	5	0.001	91	3	85	3	94	3	0.001
Disulfoton	64	7	73	6	90	5	0.005	74	7	70	4	96	3	0.005
Disulfoton-sulfone	76	4	69	5	72	5	0.005	65	17	59	3	72	3	0.005
Endosulfan-alpha	77	18	81	6	86	5	0.0025	101	18	80	6	88	4	0.01
Endosulfan-beta	84	18	81	3	88	5	0.005	79	16	77	7	89	3	0.01
Endosulfan-sulfate	88	7	93	3	92	5	0.0025	90	8	85	3	91	3	0.0025
Endrin	66	17	81	7	87	6	0.005	98	12	78	7	89	4	0.005
Ethion	98	4	87	4	98	4	0.0025	88	9	85	5	98	2	0.0025
Ethoprophos	93	5	100	2	95	6	0.001	96	5	89	4	97	4	0.001
Etrimfos	95	13	96	3	92	5	0.0025	96	6	89	3	95	3	0.001
Fenamidone	83	9	90	3	89	4	0.001	82	7	77	2	90	2	0.001
Fenamiphos	69	16	74	6	80	5	0.0025	68	9	69	4	83	3	0.0025
Fenarimol	73	10	85	4	83	4	0.001	76	8	74	2	83	3	0.001
Fenchlorphos	83	7	86	4	90	5	0.005	93	2	84	5	92	3	0.01
Fenitrothion	97	9	92	6	91	4	0.001	98	13	88	6	95	3	0.001
Fenoxycarb	100	5	99	4	87	6	0.005	82	22	84	9	82	5	0.0025
Fenthion	80	9	92	4	94	4	0.005	92	5	85	4	95	3	0.005
Fenvalerate (sum)	83	9	81	4	102	4	0.005	84	10	84	6	100	2	0.005
Flucythrinate (sum)	90	4	93	4	103	4	0.0025	91	8	90	3	102	2	0.0025
Fludioxonil	61	22	68	7	78	4	0.0025	60	22	56	6	73	2	0.0025
Fluvalinate (sum)	98	18	93	4	101	9	0.01	93	19	92	9	89	5	0.01
Fonofos	84	5	92	3	93	5	0.0025	90	4	86	5	96	3	0.0025
Haloxyfop-ethoxyethyl	94	6	105	4	99	4	0.001	95	8	93	2	98	2	0.001
Haloxyfop-methyl	94	11	101	2	95	4	0.001	97	5	90	3	95	3	0.001
Heptachlor	67	13	73	5	86	6	0.005	84	13	73	7	90	4	0.005
Heptachlor-epoxide (endo)			81	7	87	5	0.025			80	8	90	4	0.025

Table 2 (*Continued*)

	Green tea							Black tea						
	Level (0.01 mg kg^{-1})		Level (0.1 mg kg^{-1})		Level (1 mg kg^{-1})			Level (0.01 mg kg^{-1})		Level (0.1 mg kg^{-1})		Level (1 mg kg^{-1})		
Analyte	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	LCL (mg kg^{-1})	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	Rec. (%)	RSD (%)	LCL (mg kg^{-1})
Heptachlor-epoxide (exo)			87	6	89	5	0.025			79	9	90	3	0.025
Heptenophos	79	7	86	4	83	5	0.001	79	5	75	4	83	3	0.001
Hexachlorobenzene	53	8	61	8	68	6	0.001	72	9	64	8	75	3	0.001
Iprodione	91	14	93	5	89	4	0.005	98	20	82	6	86	2	0.005
Isofenphos	91	6	98	4	97	4	0.005	99	8	92	3	99	2	0.005
Isofenphos-methyl	94	4	99	4	97	4	0.005	97	11	92	4	99	3	0.01
Kresoxim-methyl	91	8	102	5	95	4	0.001	90	7	87	4	95	2	0.001
Lindane	85	5	90	2	89	6	0.0025	85	11	80	5	91	4	0.0025
Malaoxon			95	10	90	11	0.025			82	25	91	4	0.025
Malathion	98	5	102	3	97	5	0.01	99	7	91	3	99	3	0.005
Mecarbam			98	3	97	5	0.025			91	8	100	4	0.025
Metazachlor	78	20	71	3	75	4	0.005	81	17	66	11	76	4	0.005
Methacrifos	96	6	102	3	97	5	0.001	100	7	89	3	97	3	0.001
Methidathion	89	4	93	4	93	4	0.005	91	8	87	3	94	3	0.0025
Methiocarb			87	3	86	5	0.025	87	14	81	3	86	4	0.01
Methoxychlor	112	9	111	11	100	12	0.01			58	22	89	14	0.025
Myclobutanil	61	5	64	3	66	4	0.0025	55	8	52	3	65	3	0.0025
Naled			74	15	80	22	0.025			74	37	74	36	0.05
Nitrofen	86	14	77	5	88	4	0.0025	83	10	81	5	92	2	0.0025
Nuarimol	71	5	73	4	74	4	0.0025	64	8	64	4	73	3	0.0025
Oxychlordane			77	7	87	5	0.025			75	13	90	3	0.025
Oxyfluorfen			94	11	88	4	0.025			88	4	92	2	0.025
Paraoxon			64	7	59	5	0.1			61	6	64	3	0.1
Parathion-ethyl	89	19	92	7	92	4	0.01	100	12	91	7	96	2	0.005
Parathion-methyl	96	11	95	5	89	4	0.025	106	15	90	4	92	3	0.025
Penconazole	93	15	88	4	89	5	0.005	81	11	78	4	88	4	0.0025
Pencycuron			79	8	62	3	0.025			58	22	73	6	0.01
Pendimethalin	87	10	85	13	90	5	0.005	105	10	85	7	93	2	0.01
Permethrin (sum)	73	5	80	3	96	5	0.0025	88	4	81	3	96	2	0.005
Phenothrin (sum)			80	4	96	4	0.025			82	5	95	3	0.025
Phenthoate	95	8	94	6	95	4	0.005	94	5	88	2	98	3	0.01
Phenylphenol, *o*-	84	6	89	2	85	4	0.001	85	4	76	2	87	4	0.001
Phosalone	92	9	93	4	97	4	0.001	96	13	88	4	96	2	0.001
Phosmet	92	14	88	3	88	4	0.0025	81	13	78	5	86	4	0.0025
Pirimiphos-ethyl	91	17	94	5	96	4	0.0025	82	20	88	6	97	2	0.0025
Pirimiphos-methyl	93	6	97	5	94	4	0.0025	95	9	89	5	97	3	0.0025
Procymidone	93	5	97	4	92	5	0.0025	97	5	86	3	92	3	0.0025
Profenofos	97	13	97	3	93	5	0.005	98	14	86	5	94	3	0.005
Propargite	92	10	96	4	101	5	0.005	90	15	89	3	96	4	0.005
Propham	96	12	93	5	89	6	0.01	90	9	85	2	93	6	0.01
Prothiofos	71	10	75	5	90	5	0.001	82	9	79	4	91	3	0.001
Pyrazophos	93	9	94	5	98	4	0.001	87	11	90	5	98	2	0.001
Pyridaben	79	11	83	4	94	4	0.0025	110	13	84	3	95	2	0.0025
Pyridaphenthion	92	16	88	5	90	3	0.005	85	7	81	3	90	2	0.0025
Quinalphos	101	15	100	4	96	5	0.0025	88	14	91	5	97	3	0.005
Quintozene	74	14	77	6	83	5	0.0025	83	8	77	5	88	3	0.0025
Resmethrine (sum)			80	4	77	4	0.05			68	10	74	2	0.025
Sulfotep	99	9	98	5	95	5	0.001	94	8	87	7	96	3	0.001
Tebuconazole	77	18	84	5	81	4	0.001	74	11	70	5	80	2	0.001
Tecnazene	81	8	85	5	86	5	0.001	85	8	81	5	91	3	0.001
Tefluthrin, *cis*-	81	5	88	3	98	5	0.001	90	4	83	5	96	3	0.001
Terbufos	85	5	90	5	94	4	0.001	91	5	85	5	96	3	0.001
Terbufos-sulfone			103	6	96	4	0.01			97	5	99	2	0.01
Tetraconazole	87	21	89	6	86	4	0.005	76	9	74	6	84	3	0.005
Tetradifon	71	9	83	4	87	5	0.001	87	12	81	4	89	3	0.001
Thiometon	62	9	72	6	91	5	0.0025	75	8	68	5	94	3	0.005
Tolclofos-methyl	87	7	94	4	93	5	0.001	95	11	87	4	95	3	0.0025
Tolylfluanid	90	9	84	3	92	5	0.0025	90	8	83	5	98	3	0.005
Triadimefon	90	6	96	3	92	5	0.0025	88	10	84	3	91	3	0.001
Triadimenol			65	20	68	4	0.05			57	6	68	3	0.025
Triazophos	95	9	96	6	95	4	0.001	94	9	90	2	96	2	0.001
Trifloxystrobin	101	9	104	3	99	4	0.01	96	6	89	3	98	2	0.01
Trifluralin	81	8	89	4	93	5	0.001	90	6	83	6	95	3	0.001
Vinclozolin	91	11	100	3	94	5	0.005	97	14	88	4	95	3	0.005

Pesticides with recoveries <50%: Acephate, Bendiocarb, Carbaryl, Carbosulfan, Cyanazine, Desmetryn, Dicrotophos, Dimethoate, Fenamiphos-sulfone, Fenthion-sulfone, Fenthion-sulfoxide, Fensulfothion, Formothion, Metalaxyl, Metamitron, Methamidophos, Mevinphos, Monocrotophos, Omethoate, Oxadixyl, Paraoxon-methyl, Phosphamidon (sum), Pirimicarb, Prometon, Propoxur, Simetryn, Thiabendazol, Trichlorfon, Vamidothion.

(5%-phenyl)-methylpolysiloxane GC column to a 0.5 m microbore column with the same stationary phase (required for backflush operation) was employed. A total cycle run time of 29 min included a 1 min pre-injection step, a 21 min GC run, a 2 min post-run, post-column backflush and a 3 min cool-down of the GC oven and injection port.

The optimisation of the MS/MS method consisted of (i) acquisition of MS spectrum in full scan mode; (ii) selection of precursor ions; (iii) product ion scans at 5, 10, 15, 20, 25, 30, 35 and 40 eV; and (iv) fine tuning of collision energies in multiple reaction monitoring (MRM) mode. Fig. 5 shows an overlay of MRM chromatograms of the 164 pesticides in a matrix-matched standard (0.1 mg kg^{-1}) acquired using the optimised MS/MS method (Table S-1 (Supplementary data)). Typically, two MRM transitions per analyte are used in laboratories to meet identification criteria (1 precursor ion + 2 product ions earn 4 identification points) [29]. However, the presence of background interferences in a complicated matrix such as tea (even after careful optimisation of sample preparation) can cause serious problems, so therefore this identification criterion is not met. Under such conditions, an additional analysis employing either more selective MRM transitions or the use of an orthogonal MS technique (*e.g.* high-resolution TOFMS) are required. In order to avoid the latter scenario, we used more than two transitions per analyte whenever suitable precursor/product ions were available (Table S-1 (Supplementary data)). For example, Fig. S-2 (Supplementary data) illustrates the lower selectivity of some transitions of buprofezin (MW = 305). During the MRM optimisation, 4 transitions were optimised using a standard of this pesticide in pure solvent: m/z 105 → 77 (100%); m/z 105 → 104 (82%); m/z 172 → 57 (19%); m/z 175 → 132 (16%). However, when analysing tea extracts, we found that the software-based automatically selected quantification transition m/z 105 → 77 (the most intense) was not selective enough, thus, this transition had to be replaced by a more selective one (m/z 105 → 104) and the remaining two transitions were used for confirmation purposes.

3.3. Method validation

The combination of the streamlined unbuffered QuEChERS method with LLE and the optimised GC–MS/MS method was evaluated in a validation study, involving analysis of six replicates of green and black tea samples, each spiked at 0.01, 0.1 and 1 mg kg^{-1} with 164 pesticides.

Table 2 provides mean recoveries, relative standard deviations (RSDs) and lowest calibration levels (LCLs) obtained from the analysis of the extracts of both matrices. For most pesticides (about 125) with log K_{ow} >1.8, average recoveries were in line with criteria that set acceptable mean recovery to be between 70 and 120% with RSD ≤20% [29].

For another 10 pesticides, lower recoveries between 50 and 70% were obtained (*e.g.* azoxystrobin, hexachlorobenzene). Since consistent results (≤20% RSD) were achieved for these pesticides, the results could be corrected for the known recovery factors from the analyses.

Very low (or even zero) extraction efficiencies were obtained for several polar analytes (see Table 2), which are better suited for analysis by LC–MS/MS and their analysis by GC–MS has always been considered to be troublesome.

In terms of sensitivity, for the majority of the analytes the LCLs were in the range of 0.001–0.01 mg kg^{-1} (corresponding to 0.2–2 ng mL^{-1}), thus, unbiased identification and reliable quantification of target analytes at MRLs, which are in most cases well above these levels, was possible. The LCL had to provide signal-to-noise ratio (S/N) >10 for the quantitative transition and at least one confirmation transition had to provide S/N >3.

In order to verify method trueness, a proficiency testing material (black tea) was used. Calculated z-scores were for determined pesticide residues within the acceptable range of $-2 \leq z \leq 2$ (chlorpyrifos: +1.2; hexachlorobenzene: −0.5; phosalone: +1.1; procymidone: +0.9).

3.4. Long-term stability of responses

Co-extracted non-volatile matrix compounds may cause serious problems in routine trace GC analysis for a large sequence of samples for pesticide residues [31]. The long-term stability of analytes in the extracts and instrument robustness of the developed method were evaluated by repeated injections of matrix-matched standards/blanks. Fig. S-3 (Supplementary data) shows the long-term stability of selected pesticides after several injections of the extracts prepared using the streamlined sample preparation method. In this experiment, 160 injections of extracts were carried out. After the first five injections of tea extracts (required to stabilise the responses of analytes when a new liner was used, so called priming the GC system with the matrix), no further significant fluctuations of analyte responses were observed during this period. It should be noted that post-run, post-column backflush was used between each injection. The use of backflush ensured that any high-boiling matrix material remaining in the column at the end of each run was quickly and efficiently removed (*via* the split vent) prior to the next injection in a sequence. Thus elimination/reduction of these non-volatiles improved the ruggedness of the GC–MS/MS method. In general, we recommend that after the injection of 20 samples, a matrix-matched standard of constant concentration is injected to monitor possible deviation of analyte responses.

3.5. Monitoring study

In the final phase of this work, the validated method was used to analyse 37 samples in a pilot study to further evaluate its performance and applicability. The analysed samples included green and black teas, some of them aromatised. The test results are presented in Table S-2 (Supplementary data). In total, 81% of the samples were tested 'positive' (≥0.01 mg kg^{-1}) containing at least one pesticide residue. Cypermethrin (68%), endosulfans (41%), propargite (38%), bifenthrin (38%), cyhalothrin-lambda (24%) and buprofezin (24%) were the most frequently found pesticides. Also, it was found that some samples contained residues around the MRLs and that in one sample, two residues (buprofezin and triazophos), exceeded the MRLs. It was observed that green tea resulted in more positive hits than black tea. The higher occurrence of pesticide residues was observed for aromatised green teas, in which case essential oils and flower petals might introduce pesticides to those teas. This indicates that to reduce consumers' dietary exposure, tea represents one of the food commodities worthy of frequent monitoring for pesticide residues.

4. Conclusions

In this work, we presented a novel solution for the rapid analysis of multiple pesticide residues in dry tea leaves. The features of a new analytical strategy together with benefits resulting from its application can be summarised as follows:

(i) The new procedure enables a substantial simplification of sample processing prior to quantification by GC–MS/MS. After addition of water to a homogenised tea sample, transfer of analytes into the MeCN layer is facilitated by the addition of inorganic salts. Bulk matrix components can be subsequently removed by liquid–liquid extraction using hexane with the aid of 20% NaCl (w/w) solution. Compared to existing GC–MS

methods employed for the analysis of pesticide residues in tea, this newly developed simple sample preparation procedure avoids the use of GPC and/or (dispersive-)SPE cleanup steps, which increase the overall cost of the method, extend the analysis time and require additional labour.

(ii) Employing tea samples containing incurred residues for the analysis, it was clearly demonstrated that the addition of water to the sample matrix is a key point to achieving maximum extraction yield. Although MeCN is a relatively polar solvent, when used for direct extraction, penetration into the matrix is obviously not efficient enough.

(iii) For most of the target analytes, performance characteristics were in line with the SANCO/12495/2011 document, *i.e.* recoveries were within the acceptable range of 70–120% and repeatabilities of the analytical procedure were $\leq$20% at all three spiking levels (0.01, 0.1 and 1 mg/kg). The LCLs were low enough to allow reliable control of pesticide residues in tea at the MRLs set in the EU (Regulation (EC) No 396/2005).

Disclaimer

Mention of brand or company names in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the Institute of Chemical Technology, Prague.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.aca.2012.06.051.

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Supplementary data

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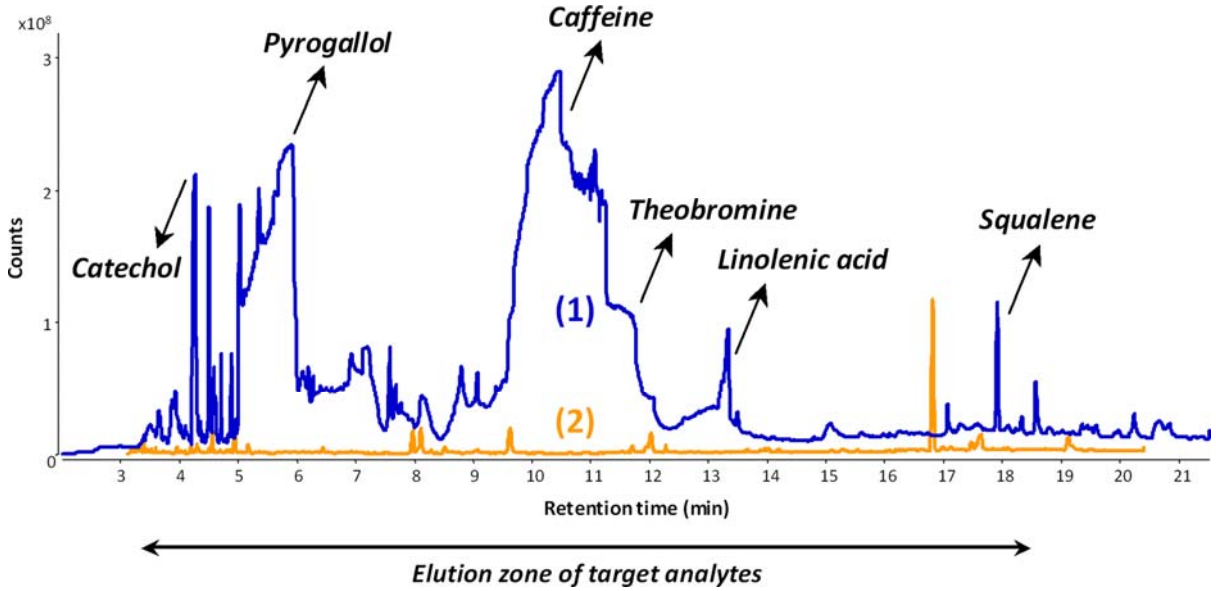

Supplementary Fig. S-1: Total ion current (TIC) of the mass range *m*/*z* 50–550 acquired in full scan mode of the crude MeCN extract (1) and the extract after LLE (2).

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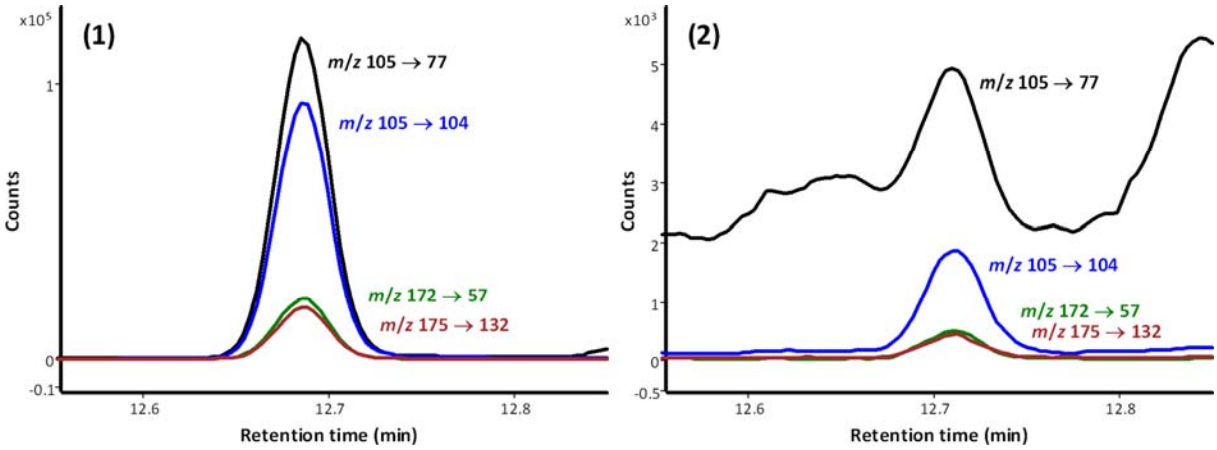

Supplementary Fig. S-2: Selectivity of buprofezin detection in MS/MS. (1) Analysis of analyte in pure solvent (hexane) at a concentration level of 200 ng mL^{-1}; (2) analysis of analyte in hexane extract of tea spiked at a concentration level of 0.025 mg kg^{-1} (corresponding to 5 ng mL^{-1}).

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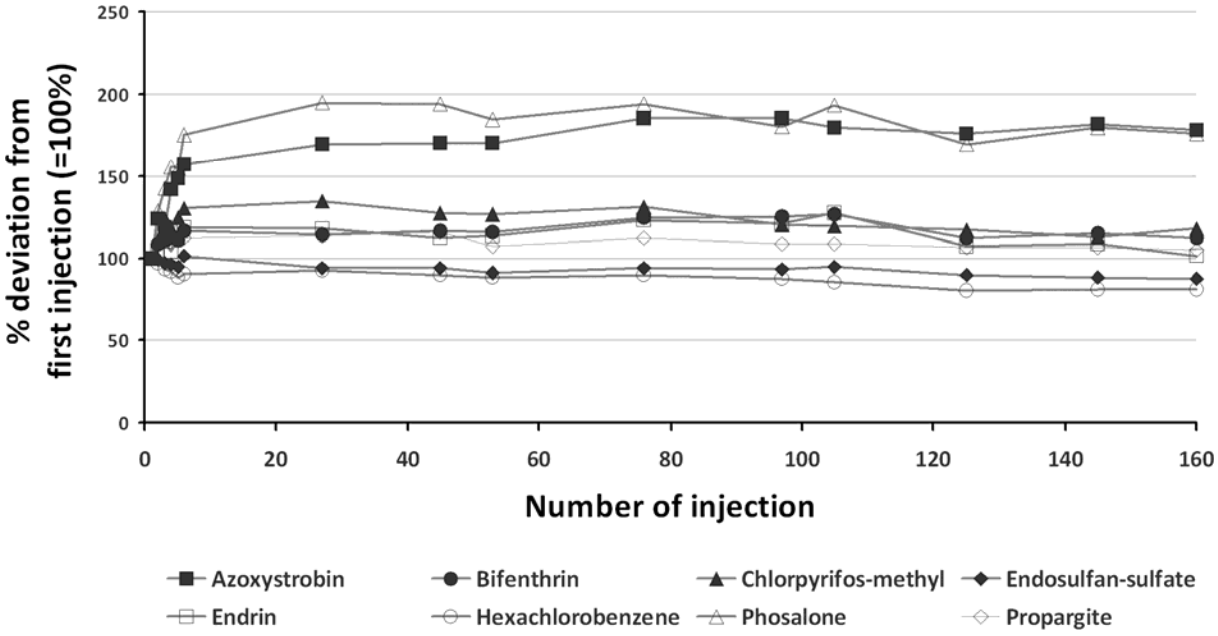

Supplementary Fig. S-3: Long-term stability of GC–MS/MS system with injection of extracts prepared employing unbuffered QuEChERS+LLE. Each point corresponds to the injection of a matrix-matched standard at 0.1 mg kg^{-1} concentration in a sequence.

Table S-1 (Supplementary data)

Optimised conditions of GC–MS/MS method

Compound Name	RT	ISTD	Precursor ion	MS1 resolution	Product ion	MS2 resolution	Dwell	CE	RT Window
Methamidophos	3.30	FALSE	126	Wide	96	Wide	10	8	0.3
Methamidophos	3.30	FALSE	141	Wide	95	Wide	10	6	0.3
Methamidophos	3.30	FALSE	141	Wide	79	Wide	10	18	0.3
Methamidophos	3.30	FALSE	141	Wide	64	Wide	10	16	0.3
Dichlorvos	3.33	FALSE	109	Wide	79	Wide	10	5	0.3
Dichlorvos	3.33	FALSE	109	Wide	47	Wide	10	15	0.3
Dichlorvos	3.33	FALSE	185	Wide	109	Wide	10	15	0.3
Dichlorvos	3.33	FALSE	185	Wide	93	Wide	10	15	0.3
Dichlobenil	3.79	FALSE	173	Wide	138	Wide	10	12	0.3
Dichlobenil	3.79	FALSE	171	Wide	136	Wide	10	15	0.3
Dichlobenil	3.79	FALSE	173	Wide	136	Wide	10	12	0.3
Dichlobenil	3.79	FALSE	173	Wide	100	Wide	10	28	0.3
Mevinphos	4.20	FALSE	127	Wide	109	Wide	10	10	0.3
Mevinphos	4.20	FALSE	127	Wide	95	Wide	10	15	0.3
Mevinphos	4.20	FALSE	192	Wide	127	Wide	10	10	0.3
Mevinphos	4.20	FALSE	193	Wide	127	Wide	10	10	0.3
Acephate	4.30	FALSE	136	Wide	94	Wide	10	14	0.3
Acephate	4.30	FALSE	136	Wide	94	Wide	10	10	0.3
Acephate	4.30	FALSE	142	Wide	96	Wide	10	8	0.3
Acephate	4.30	FALSE	136	Wide	42	Wide	10	6	0.3
Propham	4.36	FALSE	93	Wide	66	Wide	10	15	0.3
Propham	4.36	FALSE	93	Wide	65	Wide	10	25	0.3
Propham	4.36	FALSE	179	Wide	92	Wide	10	30	0.3
Trichlorfon	4.43	FALSE	109	Wide	93	Wide	10	5	0.3
Trichlorfon	4.43	FALSE	145	Wide	109	Wide	10	8	0.3
Trichlorfon	4.43	FALSE	109	Wide	79	Wide	10	5	0.3
Methacrifos	4.68	FALSE	208	Wide	180	Wide	10	4	0.3
Methacrifos	4.68	FALSE	240	Wide	180	Wide	10	8	0.3
Methacrifos	4.68	FALSE	208	Wide	93	Wide	10	14	0.3
Phenylphenol, o-	4.81	FALSE	170	Wide	169	Wide	10	20	0.3
Phenylphenol, o-	4.81	FALSE	169	Wide	115	Wide	10	35	0.3
Heptenophos	5.27	FALSE	124	Wide	89	Wide	10	15	0.3
Heptenophos	5.27	FALSE	124	Wide	63	Wide	10	35	0.3
Omethoate	5.44	FALSE	110	Wide	79	Wide	10	10	0.3
Omethoate	5.44	FALSE	156	Wide	110	Wide	10	20	0.3
Omethoate	5.44	FALSE	156	Wide	79	Wide	10	15	0.3
Tecnazene	5.52	FALSE	215	Wide	179	Wide	10	8	0.3
Tecnazene	5.52	FALSE	203	Wide	143	Wide	10	22	0.3
Tecnazene	5.52	FALSE	203	Wide	83	Wide	10	34	0.3
Propoxur	5.58	FALSE	110	Wide	92	Wide	10	10	0.3
Propoxur	5.58	FALSE	110	Wide	82	Wide	10	8	0.3
Propoxur	5.58	FALSE	152	Wide	110	Wide	10	6	0.3
Propoxur	5.58	FALSE	110	Wide	64	Wide	10	16	0.3
Propoxur	5.58	FALSE	110	Wide	63	Wide	10	32	0.3
Diphenylamine	5.66	FALSE	169	Wide	168	Wide	10	15	0.3
Diphenylamine	5.66	FALSE	169	Wide	167	Wide	10	20	0.3
Ethoprophos	5.78	FALSE	158	Wide	114	Wide	10	5	0.3
Ethoprophos	5.78	FALSE	158	Wide	97	Wide	10	15	0.3

Ethoprophos	5.78	FALSE	158	Wide	81	Wide	10	15	0.3
Chlorpropham	5.94	FALSE	213	Wide	171	Wide	10	5	0.3
Chlorpropham	5.94	FALSE	213	Wide	127	Wide	10	5	0.3
Naled	6.01	FALSE	145	Wide	113	Wide	10	19	0.3
Naled	6.01	FALSE	145	Wide	109	Wide	10	13	0.3
Naled	6.01	FALSE	185	Wide	93	Wide	10	14	0.3
Naled	6.01	FALSE	185	Wide	109	Wide	10	18	0.3
Dicrotophos	6.16	FALSE	127	Wide	109	Wide	10	12	0.3
Dicrotophos	6.16	FALSE	127	Wide	95	Wide	10	17	0.3
Dicrotophos	6.16	FALSE	193	Wide	127	Wide	10	8	0.3
Bendiocarb	6.18	FALSE	166	Wide	151	Wide	10	10	0.3
Bendiocarb	6.18	FALSE	151	Wide	109	Wide	10	10	0.3
Bendiocarb	6.18	FALSE	151	Wide	107	Wide	10	15	0.3
Bendiocarb	6.18	FALSE	151	Wide	81	Wide	10	10	0.3
Pencycuron	6.25	FALSE	209	Wide	180	Wide	10	6	0.5
Pencycuron	6.25	FALSE	125	Wide	89	Wide	10	20	0.5
Pencycuron	6.25	FALSE	125	Wide	63	Wide	10	35	0.5
Pencycuron	6.25	FALSE	209	Wide	125	Wide	10	16	0.5
Trifluralin	6.22	FALSE	306	Wide	264	Wide	10	10	1
Trifluralin	6.22	FALSE	264	Wide	160	Wide	10	15	1
Monocrotophos	6.33	FALSE	127	Wide	109	Wide	10	5	0.3
Monocrotophos	6.33	FALSE	127	Wide	95	Wide	10	15	0.3
Monocrotophos	6.33	FALSE	192	Wide	127	Wide	10	20	0.3
Cadusafos	6.30	FALSE	159	Wide	131	Wide	10	5	0.3
Cadusafos	6.30	FALSE	159	Wide	97	Wide	10	20	0.3
Cadusafos	6.30	FALSE	159	Wide	79	Wide	10	35	0.3
Sulfotep	6.31	FALSE	322	Wide	294	Wide	10	2	0.3
Sulfotep	6.31	FALSE	322	Wide	266	Wide	10	4	0.3
Sulfotep	6.31	FALSE	322	Wide	202	Wide	10	6	0.3
Sulfotep	6.31	FALSE	322	Wide	174	Wide	10	15	0.3
Sulfotep	6.31	FALSE	322	Wide	146	Wide	10	28	0.3
BHC-alpha	6.44	FALSE	219	Wide	183	Wide	10	10	0.3
BHC-alpha	6.44	FALSE	181	Wide	145	Wide	10	15	0.3
BHC-alpha	6.44	FALSE	181	Wide	109	Wide	10	30	0.3
BHC-alpha	6.44	FALSE	219	Wide	145	Wide	10	20	0.3
Thiometon	6.58	FALSE	88	Wide	60	Wide	10	6	0.3
Thiometon	6.58	FALSE	125	Wide	79	Wide	10	10	0.3
Thiometon	6.58	FALSE	125	Wide	47	Wide	10	20	0.3
Thiometon	6.58	FALSE	246	Wide	88	Wide	10	6	0.3
Hexachlorobenzene	6.59	FALSE	284	Wide	249	Wide	10	25	0.3
Hexachlorobenzene	6.59	FALSE	284	Wide	214	Wide	10	35	0.3
Hexachlorobenzene	6.59	FALSE	284	Wide	142	Wide	10	50	0.3
Dicloran	6.71	FALSE	178	Wide	150	Wide	10	14	0.3
Dicloran	6.71	FALSE	206	Wide	176	Wide	10	5	0.3
Dicloran	6.71	FALSE	208	Wide	178	Wide	10	8	0.3
Dicloran	6.71	FALSE	206	Wide	124	Wide	10	28	0.3
Dimethoate	6.76	FALSE	143	Wide	111	Wide	10	10	0.3
Dimethoate	6.76	FALSE	125	Wide	79	Wide	10	5	0.3
Dimethoate	6.76	FALSE	125	Wide	47	Wide	10	20	0.3
Dimethoate	6.76	FALSE	229	Wide	87	Wide	10	10	0.3
Prometon	6.93	FALSE	210	Wide	168	Wide	10	5	0.3
Prometon	6.93	FALSE	210	Wide	112	Wide	10	10	0.3
Prometon	6.93	FALSE	210	Wide	94	Wide	10	15	0.3
Prometon	6.93	FALSE	210	Wide	75	Wide	10	20	0.3

BHC-beta	7.09	FALSE	219	Wide	183	Wide	10	10	0.3
BHC-beta	7.09	FALSE	181	Wide	145	Wide	10	15	0.3
BHC-beta	7.09	FALSE	181	Wide	109	Wide	10	30	0.3
BHC-beta	7.09	FALSE	219	Wide	145	Wide	10	20	0.3
Lindane	7.13	FALSE	219	Wide	183	Wide	10	5	0.3
Lindane	7.13	FALSE	181	Wide	145	Wide	10	12	0.3
Lindane	7.13	FALSE	181	Wide	109	Wide	10	30	0.3
Quintozene	7.25	FALSE	295	Wide	237	Wide	10	20	0.3
Quintozene	7.25	FALSE	237	Wide	143	Wide	10	30	0.3
Quintozene	7.25	FALSE	237	Wide	119	Wide	10	30	0.3
Terbufos	7.29	FALSE	231	Wide	175	Wide	10	10	0.3
Terbufos	7.29	FALSE	288	Wide	231	Wide	10	4	0.3
Terbufos	7.29	FALSE	231	Wide	129	Wide	10	25	0.3
Fonofos	7.34	FALSE	137	Wide	109	Wide	10	5	0.3
Fonofos	7.34	FALSE	246	Wide	137	Wide	10	5	0.3
Fonofos	7.34	FALSE	246	Wide	109	Wide	10	16	0.3
Phosphamidon I	7.64	FALSE	127	Wide	109	Wide	10	10	0.3
Phosphamidon I	7.64	FALSE	193	Wide	127	Wide	10	8	0.3
Phosphamidon I	7.64	FALSE	264	Wide	193	Wide	10	6	0.3
Phosphamidon I	7.64	FALSE	227	Wide	127	Wide	10	8	0.3
Phosphamidon I	7.64	FALSE	264	Wide	127	Wide	10	15	0.3
Diazinon	7.64	FALSE	199	Wide	93	Wide	10	15	0.3
Diazinon	7.64	FALSE	304	Wide	179	Wide	10	15	0.3
Diazinon	7.64	FALSE	199	Wide	135	Wide	10	10	0.3
Paraoxon-methyl	7.71	FALSE	247	Wide	230	Wide	10	5	0.3
Paraoxon-methyl	7.71	FALSE	230	Wide	200	Wide	10	5	0.3
Paraoxon-methyl	7.71	FALSE	230	Wide	136	Wide	10	5	0.3
BHC-delta	7.75	FALSE	219	Wide	183	Wide	10	10	0.3
BHC-delta	7.75	FALSE	181	Wide	145	Wide	10	15	0.3
BHC-delta	7.75	FALSE	181	Wide	109	Wide	10	30	0.3
BHC-delta	7.75	FALSE	219	Wide	145	Wide	10	20	0.3
Disulfoton	7.68	FALSE	88	Wide	60	Wide	10	5	0.3
Disulfoton	7.68	FALSE	88	Wide	59	Wide	10	25	0.3
Disulfoton	7.68	FALSE	186	Wide	142	Wide	10	5	0.3
Disulfoton	7.68	FALSE	274	Wide	88	Wide	10	5	0.3
Chlorothalonil	7.84	FALSE	267	Wide	232	Wide	10	30	0.3
Chlorothalonil	7.84	FALSE	266	Wide	231	Wide	10	20	0.3
Chlorothalonil	7.84	FALSE	267	Wide	168	Wide	10	35	0.3
Tefluthrin, cis-	7.94	FALSE	177	Wide	137	Wide	10	15	0.3
Tefluthrin, cis-	7.94	FALSE	177	Wide	127	Wide	10	15	0.3
Etrimfos	7.99	FALSE	181	Wide	153	Wide	10	8	0.3
Etrimfos	7.99	FALSE	292	Wide	181	Wide	10	6	0.3
Etrimfos	7.99	FALSE	292	Wide	153	Wide	10	16	0.3
Etrimfos	7.99	FALSE	277	Wide	125	Wide	10	14	0.3
Formothion	8.20	FALSE	198	Wide	170	Wide	10	0	0.3
Formothion	8.20	FALSE	198	Wide	170	Wide	10	4	0.3
Formothion	8.20	FALSE	224	Wide	155	Wide	10	8	0.3
Formothion	8.20	FALSE	170	Wide	93	Wide	10	2	0.3
Formothion	8.20	FALSE	125	Wide	47	Wide	10	15	0.3
Formothion	8.20	FALSE	224	Wide	125	Wide	10	16	0.3
Formothion	8.20	FALSE	198	Wide	93	Wide	10	6	0.3
Pirimicarb	8.26	FALSE	152	Wide	96	Wide	10	10	0.3
Pirimicarb	8.26	FALSE	166	Wide	96	Wide	10	15	0.3
Pirimicarb	8.26	FALSE	238	Wide	166	Wide	10	10	0.3

Desmetryn	8.44	FALSE	213	Wide	198	Wide	10	10	0.3
Desmetryn	8.44	FALSE	213	Wide	141	Wide	10	15	0.3
Desmetryn	8.44	FALSE	213	Wide	58	Wide	10	10	0.3
Phosphamidon II	8.55	FALSE	127	Wide	109	Wide	10	10	0.3
Phosphamidon II	8.55	FALSE	193	Wide	127	Wide	10	8	0.3
Phosphamidon II	8.55	FALSE	264	Wide	193	Wide	10	6	0.3
Phosphamidon II	8.55	FALSE	227	Wide	127	Wide	10	8	0.3
Phosphamidon II	8.55	FALSE	264	Wide	127	Wide	10	15	0.3
Chlorpyrifos-methyl	8.72	FALSE	288	Wide	273	Wide	10	15	0.3
Chlorpyrifos-methyl	8.72	FALSE	286	Wide	271	Wide	10	16	0.3
Chlorpyrifos-methyl	8.72	FALSE	288	Wide	93	Wide	10	26	0.3
Parathion-methyl	8.72	FALSE	263	Wide	246	Wide	10	2	0.3
Parathion-methyl	8.72	FALSE	233	Wide	124	Wide	10	10	0.3
Parathion-methyl	8.72	FALSE	233	Wide	109	Wide	10	14	0.3
Parathion-methyl	8.72	FALSE	263	Wide	109	Wide	10	15	0.3
Parathion-methyl	8.72	FALSE	263	Wide	79	Wide	10	30	0.3
Vinclozolin	8.74	FALSE	212	Wide	172	Wide	10	15	0.3
Vinclozolin	8.74	FALSE	212	Wide	145	Wide	10	15	0.3
Vinclozolin	8.74	FALSE	212	Wide	145	Wide	10	20	0.3
Vinclozolin	8.74	FALSE	285	Wide	213	Wide	10	10	0.3
Vinclozolin	8.74	FALSE	212	Wide	109	Wide	10	40	0.3
Heptachlor	8.80	FALSE	274	Wide	239	Wide	10	20	0.3
Heptachlor	8.80	FALSE	272	Wide	237	Wide	10	25	0.3
Heptachlor	8.80	FALSE	272	Wide	117	Wide	10	40	0.3
Carbaryl	8.86	FALSE	144	Wide	116	Wide	10	15	0.3
Carbaryl	8.86	FALSE	144	Wide	114	Wide	10	30	0.3
Tolclofos-methyl	8.82	FALSE	265	Wide	250	Wide	10	15	0.3
Tolclofos-methyl	8.82	FALSE	265	Wide	220	Wide	10	25	0.3
Tolclofos-methyl	8.82	FALSE	265	Wide	215	Wide	10	25	0.3
Tolclofos-methyl	8.82	FALSE	265	Wide	93	Wide	10	25	0.3
Simetryn	8.87	FALSE	213	Wide	185	Wide	10	6	0.3
Simetryn	8.87	FALSE	213	Wide	170	Wide	10	8	0.3
Simetryn	8.87	FALSE	213	Wide	155	Wide	10	20	0.3
Malaoxon	8.87	FALSE	195	Wide	125	Wide	10	10	0.3
Malaoxon	8.87	FALSE	195	Wide	109	Wide	10	16	0.3
Malaoxon	8.87	FALSE	268	Wide	127	Wide	10	4	0.3
Malaoxon	8.87	FALSE	268	Wide	99	Wide	10	4	0.3
Ametryn	9.01	FALSE	227	Wide	170	Wide	10	30	0.3
Ametryn	9.01	FALSE	227	Wide	152	Wide	10	20	0.3
Fenchlorphos	9.08	FALSE	285	Wide	270	Wide	10	12	0.3
Fenchlorphos	9.08	FALSE	287	Wide	272	Wide	10	12	0.3
Fenchlorphos	9.08	FALSE	270	Wide	240	Wide	10	12	0.3
Fenchlorphos	9.08	FALSE	285	Wide	240	Wide	10	25	0.3
Fenchlorphos	9.08	FALSE	125	Wide	79	Wide	10	4	0.3
Metalaxyl	9.09	FALSE	160	Wide	130	Wide	10	20	0.3
Metalaxyl	9.09	FALSE	206	Wide	162	Wide	10	20	0.3
Metalaxyl	9.09	FALSE	206	Wide	132	Wide	10	5	0.3
Metalaxyl	9.09	FALSE	249	Wide	146	Wide	10	20	0.3
Paraoxon	9.11	FALSE	149	Wide	119	Wide	10	10	0.3
Paraoxon	9.11	FALSE	149	Wide	102	Wide	10	20	0.3
Methiocarb	9.47	FALSE	168	Wide	153	Wide	10	10	0.3
Methiocarb	9.47	FALSE	153	Wide	109	Wide	10	10	0.3
Methiocarb	9.47	FALSE	225	Wide	168	Wide	10	6	0.3
Methiocarb	9.47	FALSE	168	Wide	109	Wide	10	12	0.3

Methiocarb	9.47	FALSE	225	Wide	153	Wide	10	18	0.3
Fenitrothion	9.47	FALSE	277	Wide	260	Wide	10	5	0.3
Fenitrothion	9.47	FALSE	277	Wide	125	Wide	10	15	0.3
Fenitrothion	9.47	FALSE	277	Wide	109	Wide	10	20	0.3
Pirimiphos-methyl	9.57	FALSE	305	Wide	290	Wide	10	10	0.3
Pirimiphos-methyl	9.57	FALSE	305	Wide	276	Wide	10	25	0.3
Pirimiphos-methyl	9.57	FALSE	290	Wide	233	Wide	10	10	0.3
Pirimiphos-methyl	9.57	FALSE	305	Wide	180	Wide	10	5	0.3
Pirimiphos-methyl	9.57	FALSE	290	Wide	125	Wide	10	25	0.3
Dichlofluanid	9.62	FALSE	167	Wide	124	Wide	10	5	0.3
Dichlofluanid	9.62	FALSE	167	Wide	97	Wide	10	15	0.3
Dichlofluanid	9.62	FALSE	224	Wide	123	Wide	10	8	0.3
Dichlofluanid	9.62	FALSE	224	Wide	77	Wide	10	10	0.3
Aldrin	9.67	FALSE	298	Wide	263	Wide	10	8	0.3
Aldrin	9.67	FALSE	257	Wide	222	Wide	10	12	0.3
Aldrin	9.67	FALSE	263	Wide	193	Wide	10	30	0.3
Aldrin	9.67	FALSE	263	Wide	191	Wide	10	30	0.3
Malathion	9.83	FALSE	158	Wide	125	Wide	10	8	0.3
Malathion	9.83	FALSE	173	Wide	127	Wide	10	4	0.3
Malathion	9.83	FALSE	173	Wide	117	Wide	10	5	0.3
Malathion	9.83	FALSE	173	Wide	99	Wide	10	15	0.3
Fenthion	9.99	FALSE	278	Wide	169	Wide	10	18	0.3
Fenthion	9.99	FALSE	278	Wide	151	Wide	10	12	0.3
Fenthion	9.99	FALSE	278	Wide	125	Wide	10	15	0.3
Fenthion	9.99	FALSE	278	Wide	109	Wide	10	22	0.3
Chlorpyrifos	10.04	FALSE	314	Wide	286	Wide	10	5	0.3
Chlorpyrifos	10.04	FALSE	314	Wide	286	Wide	10	5	0.3
Chlorpyrifos	10.04	FALSE	314	Wide	258	Wide	10	14	0.3
Parathion-ethyl	9.99	FALSE	291	Wide	109	Wide	10	10	0.3
Parathion-ethyl	9.99	FALSE	291	Wide	81	Wide	10	10	0.3
Cyanazine	10.21	FALSE	225	Wide	189	Wide	10	10	0.3
Cyanazine	10.21	FALSE	212	Wide	151	Wide	10	10	0.3
Cyanazine	10.21	FALSE	212	Wide	123	Wide	10	22	0.3
Cyanazine	10.21	FALSE	225	Wide	136	Wide	10	16	0.3
Triadimefon	10.15	FALSE	208	Wide	181	Wide	10	5	0.3
Triadimefon	10.15	FALSE	208	Wide	127	Wide	10	15	0.3
Triadimefon	10.15	FALSE	210	Wide	113	Wide	10	20	0.3
Tetraconazole	10.39	FALSE	336	Wide	218	Wide	10	20	0.3
Tetraconazole	10.39	FALSE	336	Wide	204	Wide	10	34	0.3
Tetraconazole	10.39	FALSE	336	Wide	164	Wide	10	35	0.3
Tetraconazole	10.39	FALSE	336	Wide	156	Wide	10	34	0.3
Tetraconazole	10.39	FALSE	336	Wide	141	Wide	10	35	0.3
Bromophos-methyl	10.46	FALSE	331	Wide	286	Wide	10	34	0.3
Bromophos-methyl	10.46	FALSE	331	Wide	93	Wide	10	34	0.3
Bromophos-methyl	10.46	FALSE	329	Wide	314	Wide	10	16	0.3
Bromophos-methyl	10.46	FALSE	331	Wide	316	Wide	10	16	0.3
Cyprodinil	10.75	FALSE	225	Wide	224	Wide	10	10	0.3
Cyprodinil	10.75	FALSE	224	Wide	208	Wide	10	20	0.3
Pirimiphos-ethyl	10.76	FALSE	333	Wide	318	Wide	10	5	0.3
Pirimiphos-ethyl	10.76	FALSE	333	Wide	304	Wide	10	5	0.3
Pirimiphos-ethyl	10.76	FALSE	304	Wide	168	Wide	10	10	0.3
Pirimiphos-ethyl	10.76	FALSE	318	Wide	166	Wide	10	12	0.3
Pirimiphos-ethyl	10.76	FALSE	318	Wide	109	Wide	10	35	0.3
Pirimiphos-ethyl	10.76	FALSE	318	Wide	97	Wide	10	35	0.3

Heptachlor-epoxide (endo)	10.78	FALSE	183	Wide	155	Wide	10	20	0.3
Heptachlor-epoxide (endo)	10.78	FALSE	263	Wide	191	Wide	10	40	0.3
Heptachlor-epoxide (endo)	10.78	FALSE	217	Wide	182	Wide	10	15	0.3
Heptachlor-epoxide (endo)	10.78	FALSE	263	Wide	193	Wide	10	37	0.3
Heptachlor-epoxide (endo)	10.78	FALSE	183	Wide	119	Wide	10	30	0.3
Heptachlor-epoxide (endo)	10.78	FALSE	353	Wide	282	Wide	10	15	0.3
Heptachlor-epoxide (endo)	10.78	FALSE	353	Wide	263	Wide	10	10	0.3
Isofenphos-methyl	10.79	FALSE	199	Wide	121	Wide	10	11	0.3
Isofenphos-methyl	10.79	FALSE	241	Wide	199	Wide	10	5	0.3
Isofenphos-methyl	10.79	FALSE	199	Wide	167	Wide	10	5	0.3
Isofenphos-methyl	10.79	FALSE	241	Wide	121	Wide	10	21	0.3
Oxychlordane	10.81	FALSE	185	Wide	149	Wide	10	4	0.3
Oxychlordane	10.81	FALSE	187	Wide	151	Wide	10	4	0.3
Oxychlordane	10.81	FALSE	387	Wide	263	Wide	10	14	0.3
Oxychlordane	10.81	FALSE	389	Wide	263	Wide	10	14	0.3
Metazachlor	10.85	FALSE	133	Wide	117	Wide	10	25	0.3
Metazachlor	10.85	FALSE	209	Wide	132	Wide	10	20	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	353	Wide	282	Wide	10	15	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	353	Wide	282	Wide	10	20	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	353	Wide	263	Wide	10	15	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	353	Wide	263	Wide	10	25	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	253	Wide	218	Wide	10	27	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	253	Wide	183	Wide	10	40	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	289	Wide	253	Wide	10	12	0.3
Heptachlor-epoxide (exo)	10.91	FALSE	289	Wide	219	Wide	10	26	0.3
Pendimethalin	10.94	FALSE	281	Wide	252	Wide	10	2	0.3
Pendimethalin	10.94	FALSE	252	Wide	208	Wide	10	2	0.3
Pendimethalin	10.94	FALSE	252	Wide	191	Wide	10	4	0.3
Pendimethalin	10.94	FALSE	252	Wide	162	Wide	10	10	0.3
Pendimethalin	10.94	FALSE	252	Wide	161	Wide	10	20	0.3
Penconazole	10.97	FALSE	248	Wide	192	Wide	10	15	0.3
Penconazole	10.97	FALSE	248	Wide	157	Wide	10	25	0.3
Terbufos-sulfone	10.95	FALSE	153	Wide	125	Wide	10	2	0.3
Terbufos-sulfone	10.95	FALSE	199	Wide	143	Wide	10	10	0.3
Terbufos-sulfone	10.95	FALSE	153	Wide	97	Wide	10	10	0.3
Terbufos-sulfone	10.95	FALSE	199	Wide	171	Wide	10	3	0.3
Thiabendazol	11.08	FALSE	174	Wide	130	Wide	10	13	0.6
Thiabendazol	11.08	FALSE	201	Wide	174	Wide	10	19	0.6
Thiabendazol	11.08	FALSE	174	Wide	103	Wide	10	24	0.6
Tolylfluanid	11.05	FALSE	181	Wide	138	Wide	10	6	0.3
Tolylfluanid	11.05	FALSE	137	Wide	91	Wide	10	18	0.3
Tolylfluanid	11.05	FALSE	137	Wide	65	Wide	10	30	0.3
Tolylfluanid	11.05	FALSE	238	Wide	137	Wide	10	8	0.3
Chlozolinate	11.14	FALSE	331	Wide	186	Wide	10	14	0.3
Chlozolinate	11.14	FALSE	331	Wide	259	Wide	10	6	0.3
Chlozolinate	11.14	FALSE	259	Wide	188	Wide	10	14	0.3
Chlozolinate	11.14	FALSE	188	Wide	147	Wide	10	15	0.3
Chlorfenvinphos	11.23	FALSE	267	Wide	159	Wide	10	20	0.3
Chlorfenvinphos	11.23	FALSE	267	Wide	81	Wide	10	40	0.3
Isofenphos	11.24	FALSE	213	Wide	185	Wide	10	5	0.3
Isofenphos	11.24	FALSE	255	Wide	121	Wide	10	25	0.3
Isofenphos	11.24	FALSE	213	Wide	121	Wide	10	15	0.3
Quinalphos	11.27	FALSE	157	Wide	129	Wide	10	15	0.3
Quinalphos	11.27	FALSE	146	Wide	91	Wide	10	30	0.3

Triadimenol	11.32	FALSE	128	Wide	65	Wide	10	20	0.3
Triadimenol	11.32	FALSE	168	Wide	70	Wide	10	5	0.3
Triadimenol	11.32	FALSE	168	Wide	70	Wide	10	10	0.3
Phenthoate	11.29	FALSE	274	Wide	246	Wide	10	4	0.3
Phenthoate	11.29	FALSE	246	Wide	121	Wide	10	4	0.3
Phenthoate	11.29	FALSE	274	Wide	125	Wide	10	16	0.3
Phenthoate	11.29	FALSE	274	Wide	121	Wide	10	10	0.3
Phenthoate	11.29	FALSE	274	Wide	93	Wide	10	14	0.3
Mecarbam	11.30	FALSE	159	Wide	131	Wide	10	10	0.3
Mecarbam	11.30	FALSE	329	Wide	131	Wide	10	10	0.3
Chinomethionat	11.40	FALSE	234	Wide	206	Wide	10	10	0.3
Chinomethionat	11.40	FALSE	206	Wide	148	Wide	10	15	0.3
Procymidone	11.43	FALSE	283	Wide	255	Wide	10	10	0.3
Procymidone	11.43	FALSE	283	Wide	96	Wide	10	10	0.3
Procymidone	11.43	FALSE	283	Wide	67	Wide	10	40	0.3
Chlordane, trans-	11.45	FALSE	272	Wide	237	Wide	10	16	0.3
Chlordane, trans-	11.45	FALSE	373	Wide	337	Wide	10	4	0.3
Chlordane, trans-	11.45	FALSE	373	Wide	266	Wide	10	25	0.3
Chlordane, trans-	11.45	FALSE	373	Wide	266	Wide	10	25	0.3
Chlordane, trans-	11.45	FALSE	375	Wide	268	Wide	10	25	0.3
Chlordane, trans-	11.45	FALSE	373	Wide	264	Wide	10	25	0.3
Chlordane, trans-	11.45	FALSE	375	Wide	266	Wide	10	25	0.3
Methidathion	11.59	FALSE	145	Wide	85	Wide	10	5	0.3
Methidathion	11.59	FALSE	145	Wide	58	Wide	10	15	0.3
Methidathion	11.59	FALSE	302	Wide	145	Wide	10	0	0.3
Methidathion	11.59	FALSE	302	Wide	85	Wide	10	16	0.3
DDE, o,p'-	11.68	FALSE	246	Wide	211	Wide	10	20	0.3
DDE, o,p'-	11.68	FALSE	246	Wide	176	Wide	10	30	0.3
DDE, o,p'-	11.68	FALSE	248	Wide	176	Wide	10	30	0.3
Bromophos-ethyl	11.70	FALSE	359	Wide	331	Wide	10	4	0.3
Bromophos-ethyl	11.70	FALSE	358	Wide	303	Wide	10	14	0.3
Bromophos-ethyl	11.70	FALSE	359	Wide	303	Wide	10	14	0.3
Bromophos-ethyl	11.70	FALSE	359	Wide	285	Wide	10	35	0.3
Endosulfan-alpha	11.74	FALSE	239	Wide	204	Wide	10	15	0.3
Endosulfan-alpha	11.74	FALSE	229	Wide	194	Wide	10	10	0.3
Endosulfan-alpha	11.74	FALSE	241	Wide	206	Wide	10	15	0.3
Endosulfan-alpha	11.74	FALSE	195	Wide	159	Wide	10	5	0.3
Vamidothion	11.88	FALSE	87	Wide	58	Wide	10	10	0.3
Vamidothion	11.88	FALSE	169	Wide	125	Wide	10	5	0.3
Vamidothion	11.88	FALSE	145	Wide	87	Wide	10	5	0.3
Vamidothion	11.88	FALSE	145	Wide	58	Wide	10	25	0.3
Chlordane, cis-	11.84	FALSE	272	Wide	237	Wide	10	16	0.3
Chlordane, cis-	11.84	FALSE	373	Wide	337	Wide	10	4	0.3
Chlordane, cis-	11.84	FALSE	373	Wide	266	Wide	10	25	0.3
Chlordane, cis-	11.84	FALSE	373	Wide	266	Wide	10	25	0.3
Chlordane, cis-	11.84	FALSE	375	Wide	268	Wide	10	25	0.3
Chlordane, cis-	11.84	FALSE	373	Wide	264	Wide	10	25	0.3
Chlordane, cis-	11.84	FALSE	375	Wide	266	Wide	10	25	0.3
Haloxyfop-methyl	11.87	FALSE	316	Wide	91	Wide	10	22	0.3
Haloxyfop-methyl	11.87	FALSE	316	Wide	272	Wide	10	24	0.3
Haloxyfop-methyl	11.87	FALSE	375	Wide	288	Wide	10	23	0.3
Haloxyfop-methyl	11.87	FALSE	375	Wide	316	Wide	10	12	0.3
Disulfoton-sulfone	11.92	FALSE	213	Wide	125	Wide	10	7	0.3
Disulfoton sulfone	11.92	FALSE	186	Wide	97	Wide	10	15	0.3

Disulfoton sulfone	11.92	FALSE	186	Wide	81	Wide	10	20	0.3
Disulfoton sulfone	11.92	FALSE	213	Wide	97	Wide	10	16	0.3
Fenamiphos	12.28	FALSE	303	Wide	217	Wide	10	20	0.3
Fenamiphos	12.28	FALSE	303	Wide	180	Wide	10	15	0.3
Fenamiphos	12.28	FALSE	303	Wide	154	Wide	10	20	0.3
Fenamiphos	12.28	FALSE	303	Wide	80	Wide	10	40	0.3
Prothiofos	12.32	FALSE	267	Wide	239	Wide	10	5	0.3
Prothiofos	12.32	FALSE	162	Wide	98	Wide	10	20	0.3
Prothiofos	12.32	FALSE	309	Wide	239	Wide	10	15	0.3
Prothiofos	12.32	FALSE	162	Wide	63	Wide	10	40	0.3
Prothiofos	12.32	FALSE	267	Wide	221	Wide	10	23	0.3
Prothiofos	12.32	FALSE	309	Wide	221	Wide	10	9	0.3
Dieldrin	12.36	FALSE	263	Wide	193	Wide	10	30	0.3
Dieldrin	12.36	FALSE	263	Wide	191	Wide	10	30	0.3
Profenofos	12.40	FALSE	337	Wide	309	Wide	10	6	0.3
Profenofos	12.40	FALSE	337	Wide	267	Wide	10	16	0.3
Profenofos	12.40	FALSE	208	Wide	98	Wide	10	25	0.3
Profenofos	12.40	FALSE	208	Wide	63	Wide	10	38	0.3
Profenofos	12.40	FALSE	337	Wide	188	Wide	10	34	0.3
Profenofos	12.40	FALSE	339	Wide	188	Wide	10	32	0.3
DDE, p,p'-	12.45	FALSE	246	Wide	211	Wide	10	20	0.3
DDE, p,p'-	12.45	FALSE	246	Wide	176	Wide	10	30	0.3
DDE, p,p'-	12.45	FALSE	248	Wide	176	Wide	10	30	0.3
Fludioxonil	12.58	FALSE	248	Wide	154	Wide	10	25	0.3
Fludioxonil	12.58	FALSE	248	Wide	127	Wide	10	30	0.3
DDD, o,p'-	12.62	FALSE	235	Wide	200	Wide	10	8	0.3
DDD, o,p'-	12.62	FALSE	235	Wide	199	Wide	10	15	0.3
DDD, o,p'-	12.62	FALSE	235	Wide	165	Wide	10	20	0.3
DDD, o,p'-	12.62	FALSE	237	Wide	165	Wide	10	20	0.3
Myclobutanil	12.69	FALSE	179	Wide	152	Wide	10	6	0.3
Myclobutanil	12.69	FALSE	179	Wide	125	Wide	10	14	0.3
Metamitron	12.78	FALSE	104	Wide	77	Wide	10	20	0.3
Metamitron	12.78	FALSE	202	Wide	174	Wide	10	4	0.3
Metamitron	12.78	FALSE	202	Wide	104	Wide	10	17	0.3
Metamitron	12.78	FALSE	174	Wide	104	Wide	10	16	0.3
Metamitron	12.78	FALSE	174	Wide	77	Wide	10	36	0.3
Buprofezin	12.71	FALSE	105	Wide	104	Wide	10	8	0.3
Buprofezin	12.71	FALSE	105	Wide	77	Wide	10	20	0.3
Buprofezin	12.71	FALSE	175	Wide	132	Wide	10	10	0.3
Buprofezin	12.71	FALSE	172	Wide	57	Wide	10	12	0.3
Oxyfluorfen	12.80	FALSE	252	Wide	196	Wide	10	20	0.3
Oxyfluorfen	12.80	FALSE	361	Wide	300	Wide	10	12	0.3
Oxyfluorfen	12.80	FALSE	300	Wide	223	Wide	10	20	0.3
Oxyfluorfen	12.80	FALSE	252	Wide	170	Wide	10	32	0.3
Oxyfluorfen	12.80	FALSE	252	Wide	146	Wide	10	32	0.3
Endrin	12.80	FALSE	281	Wide	245	Wide	10	20	0.3
Endrin	12.80	FALSE	345	Wide	281	Wide	10	10	0.3
Endrin	12.80	FALSE	263	Wide	193	Wide	10	35	0.3
Endrin	12.80	FALSE	263	Wide	191	Wide	10	35	0.3
Bupirimate	12.85	FALSE	273	Wide	193	Wide	10	5	0.3
Bupirimate	12.85	FALSE	316	Wide	208	Wide	10	5	0.3
Bupirimate	12.85	FALSE	273	Wide	108	Wide	10	15	0.3
Nitrofen	12.88	FALSE	283	Wide	253	Wide	10	10	0.3
Nitrofen	12.88	FALSE	285	Wide	255	Wide	10	14	0.3

Nitrofen	12.88	FALSE	283	Wide	202	Wide	10	35	0.3
Nitrofen	12.88	FALSE	283	Wide	202	Wide	10	14	0.3
Nitrofen	12.88	FALSE	283	Wide	162	Wide	10	22	0.3
Kresoxim-methyl	12.88	FALSE	206	Wide	131	Wide	10	10	0.3
Kresoxim-methyl	12.88	FALSE	206	Wide	116	Wide	10	5	0.3
Endosulfan-beta	13.02	FALSE	239	Wide	204	Wide	10	15	0.3
Endosulfan-beta	13.02	FALSE	229	Wide	194	Wide	10	10	0.3
Endosulfan-beta	13.02	FALSE	241	Wide	206	Wide	10	15	0.3
Endosulfan-beta	13.02	FALSE	195	Wide	159	Wide	10	5	0.3
Chlorfenapyr	13.08	FALSE	247	Wide	227	Wide	10	15	0.3
Chlorfenapyr	13.08	FALSE	247	Wide	200	Wide	10	25	0.3
Chlorfenapyr	13.08	FALSE	247	Wide	197	Wide	10	20	0.3
Chlorfenapyr	13.08	FALSE	408	Wide	59	Wide	10	10	0.3
Chlorobenzilate	13.14	FALSE	139	Wide	111	Wide	10	15	0.3
Chlorobenzilate	13.14	FALSE	139	Wide	75	Wide	10	30	0.3
Chlorobenzilate	13.14	FALSE	253	Wide	141	Wide	10	10	0.3
Chlorobenzilate	13.14	FALSE	251	Wide	139	Wide	10	12	0.3
Fenthion-sulfoxide	13.24	FALSE	279	Wide	169	Wide	10	15	0.3
Fenthion-sulfoxide	13.24	FALSE	279	Wide	109	Wide	10	20	0.3
Fensulfothion	13.24	FALSE	293	Wide	141	Wide	10	10	0.3
Fensulfothion	13.24	FALSE	293	Wide	125	Wide	10	10	0.3
Fensulfothion	13.24	FALSE	292	Wide	109	Wide	10	20	0.3
Fensulfothion	13.24	FALSE	293	Wide	97	Wide	10	25	0.3
DDD, p,p'-	13.30	FALSE	235	Wide	200	Wide	10	8	0.3
DDD, p,p'-	13.30	FALSE	235	Wide	199	Wide	10	15	0.3
DDD, p,p'-	13.30	FALSE	235	Wide	165	Wide	10	20	0.3
DDD, p,p'-	13.30	FALSE	237	Wide	165	Wide	10	20	0.3
Fenthion-sulfone	13.24	FALSE	310	Wide	109	Wide	10	20	0.3
Fenthion-sulfone	13.24	FALSE	310	Wide	105	Wide	10	10	0.3
DDT, o,p'-	13.35	FALSE	235	Wide	199	Wide	10	20	0.3
DDT, o,p'-	13.35	FALSE	235	Wide	165	Wide	10	20	0.3
DDT, o,p'-	13.35	FALSE	237	Wide	165	Wide	10	20	0.3
Oxadixyl	13.40	FALSE	132	Wide	117	Wide	10	16	0.3
Oxadixyl	13.40	FALSE	163	Wide	132	Wide	10	15	0.3
Oxadixyl	13.40	FALSE	163	Wide	117	Wide	10	25	0.3
Oxadixyl	13.40	FALSE	233	Wide	146	Wide	10	20	0.3
Oxadixyl	13.40	FALSE	278	Wide	146	Wide	10	8	0.3
Ethion	13.44	FALSE	231	Wide	175	Wide	10	5	0.3
Ethion	13.44	FALSE	231	Wide	129	Wide	10	25	0.3
Triazophos	13.69	FALSE	161	Wide	134	Wide	10	5	0.3
Triazophos	13.69	FALSE	161	Wide	106	Wide	10	10	0.3
Triazophos	13.69	FALSE	257	Wide	162	Wide	10	5	0.3
Carbophenothion	13.76	FALSE	157	Wide	121	Wide	10	25	0.3
Carbophenothion	13.76	FALSE	153	Wide	97	Wide	10	10	0.3
Carbophenothion	13.76	FALSE	153	Wide	79	Wide	10	30	0.3
Carbophenothion	13.76	FALSE	157	Wide	75	Wide	10	40	0.3
Endosulfan-sulfate	13.83	FALSE	272	Wide	237	Wide	10	20	0.3
Endosulfan-sulfate	13.83	FALSE	387	Wide	253	Wide	10	5	0.3
Endosulfan-sulfate	13.83	FALSE	272	Wide	117	Wide	10	40	0.3
Endosulfan-sulfate	13.83	FALSE	387	Wide	217	Wide	10	25	0.3
DDT, p,p'-	13.94	FALSE	235	Wide	199	Wide	10	20	0.3
DDT, p,p'-	13.94	FALSE	235	Wide	165	Wide	10	20	0.3
DDT, p,p'-	13.94	FALSE	237	Wide	165	Wide	10	20	0.3
Trifloxystrobin	14.09	FALSE	131	Wide	116	Wide	10	15	0.3

Trifloxystrobin	14.09	FALSE	116	Wide	89	Wide	10	20	0.3
Trifloxystrobin	14.09	FALSE	190	Wide	130	Wide	10	6	0.3
Trifloxystrobin	14.09	FALSE	222	Wide	130	Wide	10	8	0.3
Tebuconazole	14.19	FALSE	250	Wide	125	Wide	10	25	0.3
Tebuconazole	14.19	FALSE	252	Wide	127	Wide	10	25	0.3
Nuarimol	14.18	FALSE	314	Wide	139	Wide	10	5	0.3
Nuarimol	14.18	FALSE	235	Wide	139	Wide	10	18	0.3
Nuarimol	14.18	FALSE	235	Wide	123	Wide	10	16	0.3
Diclofop-methyl	14.27	FALSE	340	Wide	254	Wide	10	14	0.3
Diclofop-methyl	14.27	FALSE	340	Wide	253	Wide	10	14	0.3
Diclofop-methyl	14.27	FALSE	253	Wide	162	Wide	10	22	0.3
Diclofop-methyl	14.27	FALSE	281	Wide	120	Wide	10	12	0.3
Triphenyl phosphate	14.31	TRUE	326	Wide	233	Wide	10	10	0.3
Triphenyl phosphate	14.31	TRUE	326	Wide	169	Wide	10	30	0.3
Triphenyl phosphate	14.31	TRUE	326	Wide	77	Wide	10	30	0.3
Propargite	14.30	FALSE	135	Wide	107	Wide	10	15	0.3
Propargite	14.30	FALSE	135	Wide	77	Wide	10	25	0.3
Resmethrin (sum)	14.43	FALSE	171	Wide	143	Wide	10	4	0.3
Resmethrin (sum)	14.43	FALSE	123	Wide	95	Wide	10	6	0.3
Resmethrin (sum)	14.43	FALSE	123	Wide	81	Wide	10	8	0.3
Haloxyfop-ethoxyethyl	14.50	FALSE	302	Wide	77	Wide	10	36	0.3
Haloxyfop-ethoxyethyl	14.50	FALSE	316	Wide	288	Wide	10	10	0.3
Haloxyfop-ethoxyethyl	14.50	FALSE	302	Wide	274	Wide	10	23	0.3
Haloxyfop-ethoxyethyl	14.50	FALSE	316	Wide	91	Wide	10	21	0.3
Iprodione	14.67	FALSE	187	Wide	159	Wide	10	15	0.3
Iprodione	14.67	FALSE	314	Wide	271	Wide	10	5	0.3
Iprodione	14.67	FALSE	187	Wide	124	Wide	10	25	0.3
Iprodione	14.67	FALSE	314	Wide	245	Wide	10	10	0.3
Iprodione	14.67	FALSE	314	Wide	56	Wide	10	20	0.3
Phosmet	14.71	FALSE	160	Wide	133	Wide	10	15	0.3
Phosmet	14.71	FALSE	160	Wide	133	Wide	10	20	0.3
Phosmet	14.71	FALSE	160	Wide	105	Wide	10	15	0.3
Phosmet	14.71	FALSE	160	Wide	77	Wide	10	30	0.3
Pyridaphenthion	14.71	FALSE	204	Wide	203	Wide	10	10	0.3
Pyridaphenthion	14.71	FALSE	340	Wide	199	Wide	10	8	0.3
Pyridaphenthion	14.71	FALSE	340	Wide	109	Wide	10	22	0.3
Pyridaphenthion	14.71	FALSE	340	Wide	97	Wide	10	35	0.3
Fenamiphos-sulfone	14.72	FALSE	292	Wide	196	Wide	10	15	0.3
Fenamiphos-sulfone	14.72	FALSE	320	Wide	292	Wide	10	10	0.3
Fenamiphos-sulfone	14.72	FALSE	292	Wide	213	Wide	10	10	0.3
Fenamidone	15.00	FALSE	238	Wide	103	Wide	10	22	0.3
Fenamidone	15.00	FALSE	238	Wide	237	Wide	10	22	0.3
Fenamidone	15.00	FALSE	268	Wide	180	Wide	10	22	0.3
Bromopropylate	14.77	FALSE	183	Wide	155	Wide	10	15	0.3
Bromopropylate	14.77	FALSE	183	Wide	76	Wide	10	35	0.3
Bromopropylate	14.77	FALSE	341	Wide	185	Wide	10	20	0.3
Bromopropylate	14.77	FALSE	341	Wide	183	Wide	10	20	0.3
Carbosulfan	14.78	FALSE	164	Wide	149	Wide	10	10	0.3
Carbosulfan	14.78	FALSE	164	Wide	103	Wide	10	25	0.3
Carbosulfan	14.78	FALSE	149	Wide	77	Wide	10	32	0.3
Fenoxycarb	14.81	FALSE	255	Wide	186	Wide	10	10	0.3
Fenoxycarb	14.81	FALSE	186	Wide	109	Wide	10	15	0.3
Bifenthrin	14.87	FALSE	166	Wide	165	Wide	10	16	0.3
Bifenthrin	14.87	FALSE	182	Wide	167	Wide	10	12	0.3

Bifenthrin	14.87	FALSE	181	Wide	166	Wide	10	25	0.3
Bifenthrin	14.87	FALSE	181	Wide	165	Wide	10	25	0.3
Methoxychlor	14.88	FALSE	227	Wide	212	Wide	10	16	0.3
Methoxychlor	14.88	FALSE	212	Wide	169	Wide	10	15	0.3
Methoxychlor	14.88	FALSE	227	Wide	169	Wide	10	28	0.3
Methoxychlor	14.88	FALSE	227	Wide	141	Wide	10	40	0.3
Tetradifon	15.15	FALSE	354	Wide	159	Wide	10	10	0.3
Tetradifon	15.15	FALSE	356	Wide	159	Wide	10	10	0.3
Phenothrin (sum)	15.23	FALSE	183	Wide	168	Wide	10	15	0.5
Phenothrin (sum)	15.23	FALSE	183	Wide	153	Wide	10	15	0.5
Azinphos-methyl	15.29	FALSE	160	Wide	132	Wide	10	5	0.3
Azinphos-methyl	15.29	FALSE	160	Wide	102	Wide	10	15	0.3
Azinphos-methyl	15.29	FALSE	160	Wide	77	Wide	10	20	0.3
Phosalone	15.30	FALSE	182	Wide	138	Wide	10	5	0.3
Phosalone	15.30	FALSE	182	Wide	111	Wide	10	15	0.3
Phosalone	15.30	FALSE	182	Wide	75	Wide	10	40	0.3
Phosalone	15.30	FALSE	367	Wide	182	Wide	10	10	0.3
Cyhalothrin-lambda	15.65	FALSE	197	Wide	141	Wide	10	15	0.5
Cyhalothrin-lambda	15.65	FALSE	181	Wide	152	Wide	10	30	0.5
Cyhalothrin-lambda	15.65	FALSE	197	Wide	161	Wide	10	5	0.5
Cyhalothrin-lambda	15.65	FALSE	181	Wide	127	Wide	10	35	0.5
Fenarimol	15.67	FALSE	139	Wide	111	Wide	10	15	0.3
Fenarimol	15.67	FALSE	139	Wide	75	Wide	10	35	0.3
Fenarimol	15.67	FALSE	219	Wide	107	Wide	10	10	0.3
Fenarimol	15.67	FALSE	251	Wide	139	Wide	10	15	0.3
Azinphos-ethyl	15.79	FALSE	160	Wide	132	Wide	10	0	0.3
Azinphos-ethyl	15.79	FALSE	132	Wide	104	Wide	10	4	0.3
Azinphos-ethyl	15.79	FALSE	132	Wide	77	Wide	10	12	0.3
Azinphos-ethyl	15.79	FALSE	160	Wide	104	Wide	10	8	0.3
Pyrazophos	15.80	FALSE	221	Wide	193	Wide	10	10	0.3
Pyrazophos	15.80	FALSE	232	Wide	204	Wide	10	10	0.3
Pyrazophos	15.80	FALSE	221	Wide	149	Wide	10	15	0.3
Pyridaben	16.23	FALSE	147	Wide	132	Wide	10	10	0.3
Pyridaben	16.23	FALSE	147	Wide	117	Wide	10	20	0.3
Permethrin (sum)	16.24	FALSE	183	Wide	168	Wide	10	15	0.5
Permethrin (sum)	16.24	FALSE	183	Wide	153	Wide	10	15	0.5
Permethrin (sum)	16.24	FALSE	163	Wide	127	Wide	10	5	0.5
Permethrin (sum)	16.24	FALSE	183	Wide	115	Wide	10	25	0.5
Permethrin (sum)	16.24	FALSE	183	Wide	77	Wide	10	38	0.5
Cyfluthrin (sum)	16.67	FALSE	206	Wide	151	Wide	10	25	0.5
Cyfluthrin (sum)	16.67	FALSE	163	Wide	91	Wide	10	15	0.5
Cyfluthrin (sum)	16.67	FALSE	227	Wide	77	Wide	10	30	0.5
Cypermethrin (sum)	16.93	FALSE	181	Wide	152	Wide	10	25	0.5
Cypermethrin (sum)	16.93	FALSE	163	Wide	127	Wide	10	5	0.5
Cypermethrin (sum)	16.93	FALSE	181	Wide	127	Wide	10	35	0.5
Flucythrinate (sum)	17.03	FALSE	199	Wide	157	Wide	10	5	0.5
Flucythrinate (sum)	17.03	FALSE	157	Wide	107	Wide	10	15	0.5
Flucythrinate (sum)	17.03	FALSE	199	Wide	107	Wide	10	30	0.5
Fenvalerate I	17.67	FALSE	167	Wide	125	Wide	10	10	0.3
Fenvalerate I	17.67	FALSE	167	Wide	89	Wide	10	40	0.3
Fenvalerate I	17.67	FALSE	225	Wide	119	Wide	10	15	0.3
Fluvalinate (sum)	17.92	FALSE	250	Wide	200	Wide	10	22	0.5
Fluvalinate (sum)	17.92	FALSE	252	Wide	200	Wide	10	18	0.5
Fluvalinate (sum)	17.92	FALSE	209	Wide	141	Wide	10	16	0.5

Fluvalinate (sum)	17.92	FALSE	209	Wide	77	Wide	10	32	0.5
Fluvalinate (sum)	17.92	FALSE	250	Wide	55	Wide	10	18	0.5
Fenvalerate II	17.89	FALSE	167	Wide	125	Wide	10	10	0.3
Fenvalerate II	17.89	FALSE	167	Wide	89	Wide	10	40	0.3
Fenvalerate II	17.89	FALSE	225	Wide	119	Wide	10	15	0.3
Difenoconazol (sum)	18.18	FALSE	323	Wide	265	Wide	10	15	0.5
Difenoconazol (sum)	18.18	FALSE	325	Wide	267	Wide	10	16	0.5
Difenoconazol (sum)	18.18	FALSE	267	Wide	204	Wide	10	16	0.5
Difenoconazol (sum)	18.18	FALSE	265	Wide	202	Wide	10	20	0.5
Deltamethrin	18.50	FALSE	181	Wide	152	Wide	10	25	0.5
Deltamethrin	18.50	FALSE	253	Wide	174	Wide	10	15	0.5
Deltamethrin	18.50	FALSE	253	Wide	172	Wide	10	10	0.5
Deltamethrin	18.50	FALSE	253	Wide	93	Wide	10	20	0.5
Azoxystrobin	18.88	FALSE	344	Wide	329	Wide	10	15	0.3
Azoxystrobin	18.88	FALSE	344	Wide	210	Wide	10	30	0.3
Azoxystrobin	18.88	FALSE	344	Wide	183	Wide	10	20	0.3
Azoxystrobin	18.88	FALSE	344	Wide	156	Wide	10	25	0.3

Legend

RT	Retention time (min)
ISTD	Internal standard (False/True)
Dwell	A default value of dwell time 10 ms is present. The respective values for each time segment are based on the number of transitions.
CE	Collision energy (eV)
RT Window	Retention time window (min)

Table S-2 (Supplementary data)

Overview of pesticide residues determined in tea samples (results expressed in mg kg^{-1})

		Bifenthrin	Buprofezin	Chlorfenapyr	Chlorpyrifos	Cyfluthrin (sum)	Cyhalothrin-lambda	Cypermethrin (sum)	Deltamethrin	Endosulfan-alpha	Endosulfan-beta	Endosulfan-sulfate	Ethion	Fenvalerate (sum)	Permethrin (sum)	Propargite	Triazophos
	MRL (*mg kg*$^{-1}$)	**5**	**0.05**	**50**	**0.1**	**0.1**	**1**	**0.5**	**5**		**30**		**3**	**0.05**	**0.1**	**5**	**0.02**
Black tea	*Sample 1*							0.119									
	Sample 2	0.012						0.046			0.012	0.022				0.014	
	Sample 3																
	Sample 4										0.013	0.019	0.026			0.022	
	Sample 5												0.017				
	Sample 6	0.048						0.116		0.011	0.015	0.033				0.043	
	Sample 7																
	Sample 8							0.060		0.022	0.048	0.113				0.010	
	Sample 9																
	Sample 10																
	Sample 11	0.054						0.131		0.011	0.018	0.036				0.039	
	Sample 12																
	Sample 13	0.025						0.048	0.021	0.039	0.085	0.160				0.018	
	Sample 14							0.095									
	Sample 15															0.046	
	Sample 16							0.055									
	Sample 17																
	Sample 18							0.026					0.025				
	Sample 19							0.037								0.023	
Black tea, aromatized	*Sample 1*	0.013						0.155									
	Sample 2							0.067									
	Sample 3		0.036														
	Sample 4																
	Sample 5	0.139	0.012				0.038	0.112		0.011	0.018	0.015					0.010
	Sample 6															0.258	

Table S-2 (Supplementary data) (continued)

Overview of pesticide residues determined in tea samples (results expressed in mg kg^{-1})

		Bifenthrin	Buprofezin	Chlorfenapyr	Chlorpyrifos	Cyfluthrin (sum)	Cyhalothrin-lambda	Cypermethrin (sum)	Deltamethrin	Endosulfan (alpha)	Endosulfan (beta)	Endosulfan sulfate	Ethion	Fenvalerate (sum)	Permethrin (sum)	Propargite	Triazophos
	MRL (mg kg^{-1})	**5**	**0.05**	**50**	**0.1**	**0.1**	**1**	**0.5**	**5**		**30**		**3**	**0.05**	**0.1**	**5**	**0.02**
Green tea	*Sample 1*	0.285	0.035	0.168	0.021		0.083	0.324		0.031	0.064	0.080		0.025		0.011	0.014
	Sample 2							0.299							0.014	0.015	
	Sample 3							0.052	0.012								
	Sample 4							0.082									
	Sample 5	0.085					0.023	0.099		0.017	0.029	0.030		0.028			
	Sample 6	0.207	0.059	0.168			0.084	0.262		0.021	0.043	0.047		0.018		0.015	0.010
	Sample 7	0.187	0.013	0.080			0.018	0.073		0.011	0.014	0.041					
	Sample 8							0.037	0.010								
Green tea, aromatized	*Sample 1*	0.462	0.179	0.650	0.029	0.011	0.093	0.325		0.050	0.058	0.115		0.070		0.015	0.214
	Sample 2	0.127	0.028	0.063	0.020		0.063	0.325		0.016	0.028	0.032		0.025			0.034
	Sample 3	0.148	0.021	0.239	0.023		0.065	0.207	0.021	0.030	0.076	0.132		0.018		0.059	0.018
	Sample 4	0.147	0.018	0.064			0.028	0.115		0.010	0.013	0.018		0.032			

Legend

(*no value*)	<0.01 mg kg^{-1}
(*value*)	Result±*U* < MRL
(*value*)	Result < MRL but MRL within *U*
(*value*)	Result > MRL but MRL within *U*
(*value*)	Result±*U* > MRL

Note: A default value of 50% as expanded measurement uncertainty (*U*) was applied (according to SANCO/12495/2011, Appendix C [29]).