**Risk assessment of exposure to pesticides through dietary intake of
vegetables typical of the Mediterranean diet in the Basque Country**

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19 **ABSTRACT**

20 This study examined estimated dietary exposure among the Basque Country Autonomous
21 Community (northern Spain) to pesticides resulting from dietary intake of unprocessed
22 vegetables. Samples were collected according to a sampling plan established previously,
23 which was performed taking into account statistical factors, such as the population
24 distribution, the point of sale, (local shops or supermarkets), the season and the
25 consumption frequency of each vegetable. A total of 221 samples were analyzed using
26 gas chromatography tandem mass spectrometry (GC-MS/MS), and liquid
27 chromatography tandem mass spectrometry (LC-MS/MS). Results showed that 48.0% of
28 the samples contained no pesticide residues, while 52.0% contained pesticides, and 6.8%
29 of all samples showed residues above the maximum residue limit (MRL). As for the
30 pesticides detected, 56 different active substances were detected, including fungicides
31 and insecticides as the main pesticide types. All of the positive samples were collected in
32 local-area shops. The potential risk to the consumers through vegetable intake was
33 estimated by calculating the Hazard Quotient (HQ), showing ranges between 0.001–
34 0.214%. These results indicate that the exposure to pesticides from vegetable intake
35 among Basque consumers did not raise health concerns.

36 **Keywords:** Pesticides; Maximum residue limits; Vegetables; Risk assessment; Dietary
37 intake; Food safety; Food chain contamination; Food analysis; Food composition

38

40 1. Introduction

41 The perception of consumer risks related to pesticide use is a subjective issue. The Food-
42 Related Risk Eurobarometer places pesticide residues as the main risk for consumers
43 (European Food Safety Authority, 2010). Pesticides are increasingly viewed as non-
44 organic and industrially synthesized chemicals and the laws that govern their use are
45 considered to be unreliable and controlled by the agrochemical industry. Studies on risk
46 perception (Harris et al., 2002; Melnyk et al., 2011; Peres et al., 2006) often show that
47 consumers view pesticides as a high risk, whereas the actual risk turns out to be low when
48 examined scientifically, as has been demonstrated by numerous institutions and global
49 agencies (European Food Safety Authority, 2014a).

50 Dietary exposure to pesticide residues is assumed to be five orders of magnitude higher
51 than other exposure routes, such as from breathing air or drinking water (Juraske et al.,
52 2009). According to the World Health Organization (WHO), on average 30% of the diet
53 consists of fruits and vegetables (Martin Cerdeño, 2009), and fruits and vegetables are the
54 most frequently consumed food group. Because fruits and vegetables are consumed
55 mostly raw or semi-processed, it is expected that they contain higher pesticide residue
56 levels in comparison with other groups of food with plant origin. The FAO/WHO
57 recommends including this food group in the diet since their active compounds may
58 decrease the risk of cardiovascular diseases (Ivey et al., 2015; Woodside et al., 2013). On
59 the other hand, vegetables act as contaminant vehicles between nature and humans, and
60 they can also have potentially negative health effects (Alavanja and Bonner, 2012;
61 George and Shukla, 2011; Parron et al., 2014). Since the ingestion of pesticides from

vegetable intake presents potential risks for humans (Melnyk et al., 2011), widespread concerns about controlling and assessing vegetable food safety has arisen in recent years.

In addition, vegetable consumers can be simultaneously exposed to several active substances that may potentially contribute to a cumulative effect in the individual. The study of cumulative and synergistic effects of pesticides is a recommendation of the European Commission (European Community, 2005) and organizations such as EFSA propose possible methodologies for assessing the cumulative effects from exposure through food to different selected groups of pesticides (European Food Safety Authority, 2014a; Jensen et al., 2013). However, taking into account the current state of affairs, with more than 400 active pesticide substances permitted in the EU, it is practically impossible to quantify the risk of pesticide intake considering all of the cumulative and synergistic effects. The most widely used method for long-term risk assessment requires a comparison between the exposure calculated by means of the individual residue levels consumed and the acceptable daily intake (ADI).

An evaluation of the exposure to pesticides by means of vegetable intake seems to be essential to assess the risk caused by an elevated consumption of vegetables in the Mediterranean diet and because vegetables are often consumed raw. Therefore, members of the EU are committed to obtaining accurate results on food safety. Since the diet standards of Mediterranean countries depend on the consumption of specific foods (Tavani and La Vecchia, 1995), the so-called “Mediterranean diet” makes it necessary to take into account local diets that affect homogenous populations. In this sense, several studies have been carried out in countries and regions from the Mediterranean area bringing to light the specific characteristics of their population (Shen et al., 2015). In the case of the Basque Country (northern Spain), a study was carried out in 2007 that showed

a higher vegetable intake than for the rest of the country and neighboring countries in terms of unprocessed or raw food (Elika, 2008).

Thus, the objective of the present study, which has been applied to a community of about 2.5 million inhabitants, was to propose a model showing how to estimate the risks of pesticide intake from a diet with high vegetable content. In this study, pesticide residues were monitored in nine of the most-consumed vegetables in the Basque Country.

Analytical techniques based on chromatography coupled to mass spectrometry were used to determine pesticide residues during 2012–2014. The risk assessment was calculated according to the guideline provided by EFSA (European Food Safety Authority, 2014b).

2. Material and methods

2.1 Vegetable samples

A total of 221 samples from several supermarkets and local markets in the Basque Country were collected according to a sampling protocol established beforehand. The sampling consisted of 8 sampling times between 2012 and 2014: June 2012, October 2012, February 2013 and April 2013 for the first campaign; and June 2013, October 2013, February 2014 and April 2014 for the second campaign. The plan took into account the following criteria: (1) the particular province of the Basque Country (Araba, Biscay or Gipuzkoa); (2) the population within each province; (3) season; and (4) frequent consumption of individual vegetables. It was necessary to include the season as a factor because of seasonal differences in quantities and types of vegetables consumed. In spring and summer, mainly uncooked lettuce, tomatoes and peppers are consumed, while in autumn and winter boiled leeks, carrots, chard and courgettes are widely consumed and,

consequently, oil intake also is higher. Thus, 9 different vegetables were collected, including chard, courgettes, onions, beans, lettuces, peppers, leeks, tomatoes and carrots, representing the most-consumed vegetables in the Basque Country community. The commodities that were analyzed represent 82.3% of the vegetable intake of the Basque community diet (Elika, 2008). Samples were collected using the following criteria: (1) the origin and (2) the point of sale of the vegetable, noting whether collected in a large supermarket or a local shop. With respect to origin, only 11.7% of the collected samples were produced in the Basque Country (local origin); three-quarters of them, 74.9%, originated from outside of any of the production areas mentioned above. For 13.5% of the samples it was not possible to establish the origin.

The sampling procedure was in accordance with European regulation of sampling for official control for pesticide residues (European Community, 2002). Briefly, a sample size of 2 kg was taken, homogenized with a blender (Minipimer 7, Braun, Aschaffenburg, Germany) and then aliquots of 10 g were added to 50-mL Falcon tubes and stored in a freezer at – 42 °C until the analysis.

2.2 Chemicals and Pesticide Standards

Reagent-grade anhydrous sodium chloride (99.5%) and magnesium sulfate (97%) were purchased from Panreac (Barcelona, Spain). Primary secondary amine (PSA)-bonded silica (100 g, bulk) was supplied by Supelco (Bellefonte, PA). The mobile phase was prepared with HPLC-MS grade acetonitrile purchased from Scharlab (Barcelona, Spain) and with ammonium formate (99%) and ammonia solution (25%) for the pH adjustment from Sigma-Aldrich (Steinheim, Germany). All solutions were prepared in ultra-high

purity water (UHP) obtained from tap water pre-treated using Elix reverse osmosis cartridges and filtered by a Milli-Q system from Millipore (Bedford, MA).

Pesticides were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Stock solutions were prepared in acetonitrile and stored at 4 °C. Standard working solutions were prepared by dilution of stock solutions in acetonitrile. Caffeine was used as an internal standard for a correct quantification in GC-MS.

2.3 Instrumentation

The liquid chromatographic analysis was performed on a 1200 Series HPLC system coupled to a 6410 triple quadrupole mass spectrometer from Agilent Technologies (Wilmington, DE) operating in dynamic multiple reaction monitoring mode (dMRM) and equipped with an electrospray ionization source (ESI) operating in positive ion mode. The data acquisition and analysis was carried out using Agilent MassHunter Workstation Data Acquisition software, B.02.01 version. The column used in the chromatographic separation was a Zorbax (Agilent) SB-C18 narrow bore column (2.1 mm × 100 mm, 3.5 µm) with a guard column with the same packing material, maintained at 60 °C. The mobile phase consisted of a mixture of ammonium formate (5 mM)/formic acid 0.01% (eluent **A**) and acetonitrile/water (ammonium formate (5 mM)/formic acid 0.01%) (95:5) (eluent **B**). Gradient separation of the analytes was performed, using a flow rate of 0.5 mL/min.

GC-MS analyses were performed with a Varian 3800 (Varian Instruments, Sunnyvale, CA) gas chromatograph (GC). A Varian 1200L triple quadrupole mass spectrometer (QqQ) was coupled to the GC. A FactorFour VF-5ms capillary column (30 m × 0.25 mm

i.d. , 0.25 μ m film thickness) from Varian was used. The QqQ mass spectrometer was operated using electron ionization (EI, 70 eV); and the MS/MS conditions were fixed for each compound, using an EI-MS/MS library specially created for the target analytes under the experimental conditions, trying to select as a precursor ion that with the highest m/z ratio (greater selectivity) and abundance (greater sensitivity).

The systems used to centrifuge the samples were a 5415 Eppendorf (Madrid, Spain) and AllegraTM X-22R centrifuge (Beckman Coulter, Pasadena, CA).

2.4 Pesticide analysis

The analysis of pesticide residues was performed at the Analytical Bioclinical Laboratory (LAB, SL., Almeria, Spain). Validated and accredited in accordance with UNE-EN ISO/IEC 17025:2005 by ENAC (National Accreditation Entity) methodologies were used. These methods consisted of gas chromatography/mass spectrometry (GC-MS/MS) (Fernandez Moreno et al., 2008) and liquid chromatography/mass spectrometry (LC-MS/MS) (Fenoll et al., 2010). A total of 151 active substances were screened by means of GC-MS/MS and 140 active substances in the case of LC-MS/MS including several pesticide action modes, such as herbicides, insecticides or fungicides. The glyphosate herbicide was individually analyzed using a method which combined the use of HILIC-type chromatography on an LC-MS/MS system to detect underivatized glyphosate (Lock and Unterluggauer, 2013).

So as to compare the data as an interlaboratory assay guaranteeing the reliability of the results, 10% of all samples were also analyzed in our laboratory (Central Service of Analysis of the University of the Basque Country UPV/EHU, SGIker, Alava, Spain). The 22 samples analyzed by means of this system were taken in duplicate and sent to both laboratories. The analytical method was based on internal validated procedures, similar to

the methods employed at the accredited laboratory and based on the QuEChERS method (Anastassiades et al., 2003). Briefly, the procedures involve initial single-phase extraction of 10 g sample with acetonitrile, followed by liquid–liquid partition aided by “salting out” process using NaCl (1 g) and MgSO₄ (4 g). Clean-up of the extracts (4 mL) was carried out by applying dispersive solid-phase extraction (d-SPE) with primary secondary amine (PSA, 150 mg) and MgSO₄ (900 mg). An aliquot of the supernatant extract (0.5 mL) was mixed with 0.2 mL initial mobile phase, centrifuged 5 min at 10000 rpm and transferred into auto-sampler vials and analyzed by LC–MS/MS. For the quantification, matrix-matched calibration method was employed. The limit of quantification (LOQ) for the studied pesticides varied from 0.002 to 0.050 mg kg⁻¹, except for a few cases where a lower LOQ value was established, 0.0005 mg kg⁻¹.

Deviations between the content of active ingredients found in the 22 samples analyzed by both laboratories were in the range of 1.8–10.3%. With respect to the residue type, both laboratories detected the same active substances above the LOQ for the 22 samples.

2.5 Risk assessment

The dietary exposure to pesticides was estimated as a long-term exposure in order to assess the chronic health risk. For the calculation of long-term exposure the deterministic model was used, analogous to the calculation of the estimated daily intake (EDI). To achieve this purpose, the following values were taken into account: 1) the residue concentrations obtained from the analysis of commodities from 2012 to 2014; and 2) the daily consumption for each commodity, which was taken from the quantitative study of food consumption in the Basque Country (Elika, 2008). According to this study the consumption of each commodity by the adult population was: lettuce 16.35; chard 4.74;

pepper 21.74; tomato 46.92; courgette 4.67; bean 15.76; carrot 21.25; onion 23.27 and leek 10.46 g /day.

The total exposure was calculated by means of estimated daily intake (EDI) (World Health Organization, 1997) as follows:

$$EDI = \Sigma(F_i \times RL_i)/bw,$$

where EDI is estimated daily intake; F_i , consumption of food commodity; RL_i , median of the residue level in the vegetable; and bw , body weight of 65 kg.

The long-term risk assessment of vegetable intake compared to the pesticide toxicological data was estimated by means of the Hazard Quotient (HQ) by dividing the estimated daily intakes by the acceptable daily intake (ADI):

$$HQ = (EDI/ADI) \times 100$$

2.6 Data treatment

Concentrations of pesticide residues studied were represented by median rather than by average, because the median provides better robustness, and also because the value for the median of the concentrations was higher, so a worst-case scenario was assumed.

These values are given for each vegetable analyzed in the study. Moreover, a scaling graph is shown employing the sum of the medians of the residues detected. The LOQ of each active substance in each vegetable commodity was used in EDI calculations when pesticides were not detected.

3. Results and Discussion

3.1 Screening of pesticide residues

Chard, lettuce, tomato and carrot showed the highest percent of residue presence whereas others, namely onion, showed a lower frequency (Table 1). As for the pesticides detected, 56 different active substances were detected (Table 2), ranging between the LOQ to 1.60 mg kg⁻¹. Significantly high values (>>>MRL) were found for fenarimol, methomyl, cyproconazole, chlorpyrifos or methiocarb. Only 6.8% (15/221) of the samples contained pesticides above the MRL (positive samples). For the present study, in 52% (115/221) of the total samples, one or more pesticide residues were detected (Figure 1). In brief, 48.0% of the samples did not show the occurrence of any pesticide, and 20.4% had one single residue. As for the remaining 31.6% of the samples that showed pesticide presence, two or more residues were detected in the same sample; 8 samples contained more than 4 different active ingredients; and 13, 20 and 29 samples showed 4, 3 and 2 active substances, respectively. Tomato was the most frequent vegetable containing several active substances in the same sample and, in some cases, more than 4 pesticides were found together, with a frequency of occurrence as follows: cyprodinil, tebuconazole and triadimenol. Tomato was followed by pepper, lettuce and chard where 4 and 3 different active substances were detected in the same sample. Combinations of fungicides and insecticides with different action modes are usual in agriculture because some crops are sensitive to both fungal and insect attacks. Therefore, some commercial products have more than one active substance, so this may be the reason why several residues occurred in the same sample. As a result, around 34 different active substances were detected in tomato, 24 in pepper or 22 in lettuce.

Of the total samples 6.8% (15/221) contained pesticides above the MRL established for

each active ingredient. These limits, which are statutory limits for trade in food, are derived from studies/trials that establish the residues that remain in a commodity following the use of a plant protection product according to specified use conditions (Good Agricultural Practice, GAP). MRLs are not toxicological limits because they do not represent the maximum amount of the active substance that can be harmful to the health of consumers. That is, the surpassing of an MRL for a pesticide and commodity does not necessarily involve the existence of a health risk, which could be evaluated by other parameters such as ADI. However, in a study like this, with statistically significant samplings, a large number of samples exceeding the MRL could indicate a potential risk to health and the need to assess health risks.

Furthermore, some positive samples were detected where the residue content exceeded twice or more the MRL, such as pepper or carrot. Within the samples of pepper containing pesticides (16/28), methiocarb and methomyl exceeded the MRL by around 205% and 445%, respectively. Endosulfan also appeared in one case for pepper. For carrot, a similar situation was observed. Nearly all the samples of carrots had metalaxyl presence, and for a few carrot samples (2/28) the MRL was 220% exceeded. On the other hand, around one-third of the chard samples (3/9) were also classified as positive samples. Cypermethrin, cyproconazole and chlorpyrifos were detected above the MRL for chard samples, while fenarimol exceeded 5-times the MRL in beans. In addition, chlorpyrifos-methyl and tebuconazole also appeared above MRL in two samples of lettuce together with pyraclostrobin in tomato. Chlorpyrifos was one of the most common organophosphorus compounds detected in carrot behind metalaxyl. This observation also appeared in the study carried out by (Jensen et al., 2009) in Denmark.

As far as legality terms are concerned, four forbidden pesticides were detected such as carbendazim and procymidone in onions, endosulfan in peppers, fenarimol and

procimidone in beans and carbendazim in tomatoes. Moreover, endosulfan and fenarimol, which are chlorinated substances, exceeded the MRL. These chlorinated compounds are seen as threatening toxicants in part because they persist in the environment.

3.2 Scale grouped data and origin

A scaling plot was performed to rank all vegetables studied according to the sum of their median concentrations. The highest values in the total residues content were found in samples of lettuce (Figure 2) followed by chard, with the lettuce residues contents ($0.0038 \text{ mg kg}^{-1}$) twice as high as for chard ($0.0021 \text{ mg kg}^{-1}$). The total residue content in pepper ($0.0019 \text{ mg kg}^{-1}$) was a bit lower than in chard ($0.0021 \text{ mg kg}^{-1}$). However, 24 different active substances contributed to the total residue content in pepper, while there were fewer active substances in the case of chard with only 15 different active substances. Different than expected, carrot was one of the vegetables with the lowest residues content ($0.0001 \text{ mg kg}^{-1}$), even though it was the vegetable with the second highest percent of positive samples. Of the samples with pesticide presence, 77.4% of them (89/115) were collected in local shops. In terms of positive samples, all of them belonged to local shops.

3.3 Risk assessment

The risk assessment from vegetable intake was estimated, in order to plot the degree of pesticides present in the diet of the Basque population. To do this, the median of the concentrations was used rather than the average of the concentrations because it was higher and, consequently, a decision to assume a worst-case scenario was made. The

long-term risk was estimated in adults by means of the hazard quotient. For this, the estimated daily intake (EDI), together with the acceptable daily intake (ADI), was taken into account. Table 3 shows the hazard quotient (HQ) that was calculated for each pesticide, indicating that the exposure ranged between 0.001–0.214%. The pesticides found with the lowest HQ were chlorantraniliprole (0.001%), kresoxim-methyl (0.001%), metalaxyl (0.008%) and trifloxystrobin (0.004%); and those found with the highest HQ were methomyl (0.134%) procymidone (0.214%) or difenoconazole (0.129%). Overall, the potential risk associated with pesticide consumption for Basque consumers does not raise health concerns, since it represents very low percentages of HQ. Similar results were reported by (Łozowicka et al., 2012) in Brassica vegetables, the consumption of which is greatly increasing.

Our calculations would suppose the worst scenario, because we assumed that all commodities were treated with the 56 pesticides detected in this study, even though it is known that this situation does not represent reality, and thus the risk was overestimated.

In terms of co-occurrence, some samples contained more than 2 or 3 different residues. The results showed a no-zero risk due to the very large number of samples containing pesticides. This percent was similar to the values found by (Knežević et al., 2012). Other authors (Arienzo et al., 2013) also found similar values in terms of number of residues in an individual sample. With respect to the positive samples in the European Union, some of the pesticides exceeding the legal limit were pesticides with fungicide and/or insecticide action like endosulfan, methiocarb, metalaxyl or pyraclostrobin. The use of these kinds of pesticides is widespread, especially in northern Spain due to the environmental conditions of high humidity and low temperatures, which can encourage the proliferation of several fungal diseases. Despite this, in a recent study about the

genotoxicity of pesticide mixtures present in the diet of the French population (Graillot et al., 2012) it was demonstrated that the effect of a 5-pesticide cocktail in food showed a potential toxicity when they act all together rather than when one individually damages the DNA of human cells. In this context, an exhaustive study of the combinatory effect of pesticides would be required, in order to have a more objective vision of this problem.

Conclusions

Among 221 analyzed samples during 2012 and 2014, pesticide residues were detected in 52% of the samples involving 9 types of vegetables, and 6.8% of the samples exceeded the MRL. The most common pesticide types found were fungicides and insecticides. However, these types often appear together, and 2, 3, 4 and more than 4 residues were detected simultaneously for some samples. All of the positive samples were locally sourced (produced in the Basque Country). Lettuce was the commodity with the highest total pesticide content. Some banned substances were detected whose toxicity may be attributed with a risk for health. Furthermore, the risk assessment performed revealed that the Basque community seems not to be negatively affected, since HQ index for occurring residues was very low in all cases.

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433 **Figure and Table Captions**

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435 Figure 1. Frequency of occurrence of pesticides

436 Figure 2. Total pesticide content for nine different vegetables

437

438 Table 1. Number of samples containing one or more residues in several vegetables.

439 Table 2. Pesticide residues concentrations (mg/kg) for nine different vegetables (values
440 are the medians of the detected concentrations).

441 Table 3. Long-term risk assessment of vegetable intake

442

Table 1. Number of samples containing one or more residues in several vegetables.

Vegetable	nº samples	Presence (>LOQ)	% presence	Positive (>MLR)	% positive
Lettuce	24	16	66.7	2	8.3
Chard	9	8	88.9	3	33.3
Pepper	28	16	57.1	2	7.1
Tomato	72	47	65.3	3	4.2
Courgette	10	3	30.0	0	0.0
Bean	18	4	22.2	1	5.6
Carrot	28	18	64.3	4	14.3
Onion	23	1	4.3	0	0.0
Leek	9	2	22.2	0	0.0

Table 2. Pesticide residues concentrations (mg/kg) for nine different vegetables (values are the medians of the detected concentrations)

[illegible]

Table 2 (continued)

Active substance	Chard	Courgette	Onion	Bean	Lettuce	Pepper	Leek	Tomato	Carrot	Min-Max (mg/kg)
Flutriafol						0.06		0.02		0.01-0.20
Imidacloprid	0.04	0.06			0.03	0.05		0.03		0.02-0.15
Iprodione		0.04		0.043	1.60			0.04		0.02-1.60
Kresoxim-methyl						0.25				0.01 -0.25
Lambda cyhalothrin	0.05				0.02					0.01-0.06
Lufenuron	0.02									0.01 -0.02
Mepanipirim								0.09		0.03-0.15
Metaflumizone								0.02		0.01 -0.02
Metalaxyl					0.02				0.03	0.01-0.22
Methiocarb					0.08	0.41				0.08-0.41
Methomyl						0.09				0.01 -0.09
Methoxyfenozide						0.04				0.01 -0.04
Myclobutanil						0.02		0.01		0.01-0.02
Pymetrozine						0.08		0.05		0.02-0.14
Pyraclostrobin					0.03	0.02		0.01		0.01-0.36
Pyridaben						0.02				0.01 -0.02
Pyrimethanil					0.15	-		0.04		0.02-0.87
Pirimicarb	0.24					0.03				0.03-0.24
Pyriproxyfen						0.15		0.11		0.02-0.15
Procymidone			0.02	0.04						0.02-0.04
Propamocarb	0.59	0.53			0.12			0.01		0.01-0.67
Spinosad	0.02				0.03					0.02-0.03
Spiromesifen						0.04		0.02		0.01-0.04
Tebuconazole					0.70	0.03	0.021	0.02		0.01-0.70
Tebufenpyrad								0.02		0.01 -0.02
Thiacloprid								0.01		0.01 -0.01
Thiamethoxam		0.04			0.09					0.04-0.09
Thiophanate-methyl								0.20		0.01 -0.20
Triadimenol						0.02		0.03		0.02-0.06
Trifloxystrobin	0.01					0.07				0.01-0.08

Bold- pesticides exceeding the established MRL

Empty boxes: values below the LOQ of each active substance in each vegetable commodity

Table 3. Long-term risk assessment of vegetable intake.

Active materia	EDI (x10 ⁻⁵) (mg/kg bw/day)	ADI (mg/kg bw/day)	HQ(%)	Active substance	EDI (x10 ⁻⁵) (mg/kg bw/day)	ADI (mg/kg bw/day)	HQ(%)
Acetamiprid	1.380	0.070	0.020	Iprodione	1.288	0.060	0.021
Acrinathrin	0.324	0.010	0.032	Kresoxim-methyl	0.334	0.400	0.001
Azoxystrobin	1.361	0.200	0.007	Lambda cyhalothrin	0.361	0.005	0.072
Boscalid	1.381	0.040	0.035	Lufenuron	0.334	0.015	0.022
Bupirimate	0.334	0.050	0.007	Mepanipyrim	0.722	0.020	0.036
Carbendazim	1.080	0.020	0.054	Metaflumizone	0.722	0.010	0.072
Cymoxanil	0.334	0.013	0.026	Metalaxyl	0.611	0.080	0.008
Cypermethrin	0.901	0.050	0.018	Methiocarb	0.586	0.013	0.045
Cyproconazole	0.400	0.020	0.020	Methomyl	0.334	0.003	0.134
Cyprodinil	1.308	0.030	0.016	Methoxyfenozide	0.334	0.100	0.003
Cyromazine	0.964	0.060	0.005	Myclobutanil	1.056	0.025	0.042
Chlorantraniliprole	0.722	1.560	0.001	Pymetrozine	1.056	0.030	0.035
Chlorothalonil	0.722	0.015	0.048	Pyraclostrobin	1.308	0.030	0.044
Chlorpyrifos	0.400	0.020	0.020	Pyridaben	0.334	0.010	0.033
Chlorpyrifos-methyl	0.973	0.010	0.097	Pyrimethanil	0.973	0.170	0.006
Diethofencarb	0.722	0.430	0.002	Pirimicarb	0.407	0.035	0.012
Difenoconazole	1.289	0.010	0.129	Pyriproxyfen	1.056	0.100	0.011
Dimetomorf	0.973	0.050	0.019	Procymidone	0.600	0.003	0.214
Endosulfan	0.334	0.006	0.056	Propamocarb	1.118	0.290	0.004
Famoxadone	0.722	0.012	0.060	Spinosad	0.324	0.024	0.014
Fenarimol	0.242	0.010	0.024	Spiromesifen	1.056	0.030	0.035
Fenhexamid	0.973	0.200	0.005	Tebuconazole	1.134	0.030	0.038
Flonicamid	0.794	0.025	0.032	Tebufenpyrad	0.722	0.010	0.072
Flubendiamide	0.722	0.017	0.042	Thiacloprid	0.722	0.010	0.072
Fludioxonil	1.635	0.370	0.004	Thiametoxam	0.323	0.026	0.012
Flupicolide	0.072	0.080	0.001	Thiophanate-methyl	0.722	0.080	0.009
Flutriafol	1.056	0.010	0.106	Triadimenol	1.056	0.050	0.021
Imidacloprid	1.453	0.060	0.024	Trifloxystrobin	0.407	0.100	0.004

Figure 1

Figure 2