Consumer risk assessment for conventional farming products taken from the Austrian market during the years 2003 to 2006 regarding pesticide residues

Risikoabschätzung für Pestizide von Produkten aus konventioneller Landwirtschaft der Jahre 2003 bis 2006 des österreichischen Marktes

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Summary

In this study, almost 4,300 conventional farming products of the Austrian market from 2003 to 2006 were tested for around 450 pesticides after extraction with the European Guidelines DIN EN 12393 and CEN/TC 275 with GC-MS and HPLC-MS/MS in order to establish a pesticide contamination database and estimate their toxicity. It was found that 46.4% of the samples presented residues below limit of detection (LOD), 15.1% one residue above LOD and 31.3% of the samples at least two residues above LODs. Furthermore, 47.9% of the samples presented residues between LODs and maximum residue levels (MRLs) and 5.7% of the samples contained residue concentrations exceeding one or more MRLs. Finally, it was shown that 15 pesticides in 29 pesticide product combinations, respectively, exceeded the acute reference dose (ARfD) for a two- to five-year-old child up to 22.6 times. Surprisingly, we observed exceedance of the ARfD for 26 of these 29 pesticide product combinations although the observed residues were below MRL. This should bring the authorities to reconsider the MRL values for the most vulnerable entities.

Keywords:
Pesticide, residues, food, fruit, vegetable, maximum residue limit, acute reference dose, risk assessment

Zusammenfassung

In dieser Studie wurden etwa 4300 Produkte aus konventioneller Landwirtschaft des österreichischen Marktes der Jahre 2003 bis 2006 auf 450 Pestizide nach den europäischen Normen DIN EN 12393 und CEN/TC 275 mit GC-MS und HPLC-MS/MS untersucht, um eine statistische Datenbasis zu erhalten, die eine Risikoabschätzung erlaubt. 46,4 % der Proben wiesen Rückstände unter der Bestimmungsgrenze auf, bei 15,1 % lag ein Rückstand darüber und bei 31,3 % mindestens zwei. 47,9 % der Proben wiesen Rückstände zwischen der Bestimmungsgrenze und dem Schädlingsbekämpfungsmittelhöchstwert auf und 5,7 % lagen über diesem. 15 Pestizide in 29 Pestizid-Produktkombinationen überschritten die akute Referenzdosis für ein 2- bis 5-jähriges Kind um das bis zu 22,6-fache. Diese Überschreitungen wurden bei 26 von 29 Pestizid-Produktkombinationen festgestellt, obwohl die Rückstände unter dem Schädlingsbekämpfungsmittelhöchstwert lagen. Eine Neubewertung des Höchstwertes seitens des Gesetzgebers wäre wünschenswert.

Kennwörter:
Pestizide, Rückstände, Lebensmittel, Obst, Gemüse, Höchstwert, akute Referenzdosis, Risikoabschätzung

1 Introduction

According to the directive 90/642/EEC [1], "*it is essential to protect plants and plant products against harmful organisms and weeds, not only to prevent a reduction in yield or damage to the products harvested but also to increase agricultural productivity. One of the most important methods of protecting plants and plant products from the effects of these organisms is the use of chemical pesticides.*" Pesticides are deliberately introduced all along the food chain in conventional farming from seeding to storage in order to kill or prevent the growth of insects (insecticides), unwanted plants (herbicides), fungi (fungicides), mites (acaracides) or nematodes (nematicides).

Unfortunately, pesticides are not only toxic to pests, they may be also harmful to animals and human beings. In 1993, the US EPA [2], in coordination with the International Agency for Research on Cancer (IARC) and the European Union (EU) listed 70 possible carcinogens [3]. In 2005, this list was extended to 160 potential pesticide carcinogens and published in a briefing paper of the Pesticide Action Network (PAN) UK [4]. Furthermore, some pesticides are suspected of being endocrine disruptors [5].

Since the discovery of the high-efficient properties and the introduction of DDT in the early 20th century, the worldwide utilisation of pesticides has incredibly increased. The pesticide use, which was already 50,000 tons a year around 1945, had raised by approximately a 50-fold to reach a total annual world pesticide use estimated at 2.5 million tons in 1997 [6]. Nowadays, the persistent organochlorine pesticides have been banned and substituted by short-lived compounds.

These facts and figures have made of pesticides a more and more discussed issue in the last years since some pesticides are persistent, accumulate in the food chain and contaminate the environment. In Europe, this forced the European Community to establish directives and maximum residue levels (MRLs) in foodstuff (directive 90/642/EEC [1]) in order to reduce the intake of pesticides by consumers.

MRL is defined by the WHO as "*the maximum concentration of a pesticide residue (expressed in mg/kg) legally permitted in or on food commodities and animal feed. MRLs are based on Good Agricultural Practice (GAP) data*" [7]. Since residues of pesticides and drugs may be broken down in tissue into various metabolites, MRLs are expressed either in terms of the amount of the parent compound remaining, or a metabolite that is representative of the residue of toxicological concern in the food.

In order to determine the damaging effect of pesticides on human beings, the acute and chronic toxicity have been defined for many pesticides through the Acute Reference Dose (ARfD) and the Acceptable Daily Intake (ADI) values, respectively.
The WHO defines the ARfD as "*the estimate of the amount of a substance in food, expressed on a body-weight basis, that can be ingested over a short period of time, usually during one meal or one day, without appreciable health risk to the consumer. It therefore reflects the acute (short-term) toxicity. At present, acute Reference Doses have been fixed for a limited number of pesticides* [8, 9]." On the same way the ADI is defined as "*the estimate of the amount of a substance in food, expressed on a body-weight basis that can be ingested daily over a lifetime without appreciable health risk to the consumer. The ADI is based on the no observed adverse effect levels (NOAEL) in animal testing. A safety factor, that takes into consideration the type of effect, the severity or reversibility of the effect, and the inter- and intra-species variability, is applied to the NOAEL. The ADI therefore reflects chronic (long-term) toxicity* [8, 9]*.*"

In order to check the pesticide residue situation on the market of the European Union and the three EFTA states (Norway, Iceland and Liechtenstein), the WHO has organised since 2003 national monitoring programmes and an EU-co-ordinated monitoring programme [8, 9]. In the national monitoring programme of the year 2004, 60,450 samples, including cereals, processed food and 50,428 fruit and vegetable samples, 135 substances were sought for [9].

Concerning the determination of pesticide residues in foodstuff nowadays principally two methods are used. Apolar and middle-polar pesticides are essentially analysed with gas chromatography (GC) coupled to mass spectrometry (MS) [10–15] whereas polar pesticides are in most of the case appraised with high-performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) [10, 16–23].

Traditionally, the extraction of pesticides from foodstuff was regulated by the European Guideline DIN EN 12393 part 1 to 3 [24–26] adapted from the German Guideline DFG S19 [27]. Since this method is time-consuming and environmentally unfriendly due to the large amount of solvent used as well as expensive, a new method known as the (modified) QuECheRS (Quick Easy Cheap Rugged and Safe) method has been developed in the last years [28] and drafted as the European Guideline CEN/TC 275 [29]. This method presents furthermore the advantage of being compatible with GC and LC whereas the DIN EN 12393 allows only the extraction of GC-amenable substances.

In this study we used the DIN EN 12393 as well as the CEN/TC 275 to extract and analyse around 450 pesticides from over 4,300 conventional farming fruit and vegetable samples within a period of four years (2003 to 2006). The goals were to establish a statistical database concerning the pesticide contamination in fruit and vegetable samples on the Austrian market and to examine the toxicological impacts of these samples.

2 Experimental

2.1 Materials

The pesticides chosen for this study have been selected based on their reported occurrence, health relevance and hazard risk as residue in foodstuff as well as according to their analytical feasibility with GC and HPLC [10]. Each analyte was provided either from Sigma-Aldrich or from Ehrenstorfer with the highest available purity. Single standard stock solutions were prepared dissolving 10 mg of standard in 10 mL acetonitrile and further diluted with acetonitrile to 10 µg/mL. GC/MS and HPLC/MS multicompound standard stock solutions were prepared dissolving 10 mg of each standard in 1,000 mL acetonitrile (10 µg/mL) and further diluted with acetonitrile to achieve concentrations of 5 µg/mL, 2 µg/mL, 0.5 µg/mL, 0.2 µg/mL and 0.05 µg/mL.

2.2 Sample preparation according to the European Guideline DIN EN 12393

Around 500 g of unwashed and unpeeled fruit or vegetable samples were homogenised with a chopper. 50 g of the previously chopped fresh sample were extracted according to the DIN EN 12393 [24–26]. This method consists of an extraction step with water/acetone (1:2, v/v) followed by partitioning with ethylacetate/cyclohexane (1:1, v/v), clean-up by gel permeative chromatography (GPC) and analysis with GC-MS. Aldrin, forbidden for use since over 20 years, was used as internal standard spiked at the partitioning step.

This extraction presents the advantage of providing clean samples concentrated by a factor 20 through the different extraction and cleaning steps.

2.3 Sample preparation according to the European Guideline CEN/TC 275

Around 500 g of unwashed and unpeeled fruit or vegetable samples were homogenised with a chopper. 10 g of the previously chopped fresh sample were extracted according to the CEN/TC 275 [29]. This method consists of an extraction with 10 mL acetonitrile and a pH stabilisation/salting-out effect with a mixture of four salts (magnesium sulfate anhydrous, sodium chloride, sodium citrate dihydrate and di-sodium hydrogen citrate sesquihydrate. The clean-up of the extracts is achieved through the use of the dispersive sorbent PSA (primary secondary amine) and magnesium sulphate anhydrous). The extracts are stabilised with a 5% formic acid solution for GC/MS and HPLC/MS analysis. Triphenylphosphate (TPP) was used as internal standard and spiked at the initial step.

2.4 Analyses with GC/MS

The analyses were performed on two Hewlett-Packard (Agilent Technologies, Waldbronn) GC/MS Model 6890N Series gas chromatography coupled to a 5973N mass selective detector and one Hewlett-Packard (Agilent Technologies, Waldbronn) GC/MS Model 6890N Series gas chromatography coupled to a 5975 mass selective detector. Details concerning the devices and operating conditions have already been published elsewhere [10, 11, 30]. The Agilent Chemstation Software G1701DA version D.02.00.237 was used for data analysis.

The identification and confirmation of the pesticides were realised like recommended by the European SANCO Guidelines [31, 32]. In its point system, the basic premise is that a correct identification by single quadropole-MS requires 3-ion criteria (one target ion and two qualifiers) for permitted substances and 4-ion criteria (one target ion and three qualifiers) for banned substances.

With the DIN EN 12393, limits of detection (LOD) and limits of quantification (LOQ) as low as 0.2 and 0.8 µg/kg product in full scan and 0.03 and 0.1 µg/kg product in SIM mode, respectively.

With the CEN/TC 275 LOD and LOQ ranged from 0.4 to 48.2 µg/kg and from 1.2 to161 µg/kg, respectively.

2.5 Analyses with HPLC/MS-MS

The analyses were performed on an Agilent Technologies HP-1100 Series (Agilent Technologies, Waldbronn) controlled with the Agilent Technologies Chemstation for LC 3D System Software coupled to an Agilent Technologies ion trap (IT) mass spectrometer LC/MSD trap XCT Plus (Agilent Technologies, Waldbronn) equipped with an electrospray ionisation (ESI) interface operated in positive mode and controlled with the Agilent Technologies LC/MSD trap software 5.3. Chromatographic separation was achieved using a Zorbax SB-C18 analytical column 2.1 x 150 mm, 3.5 µm particle size from Agilent Technologies at a flow rate of 300 µL/min. The mobile phases consisted of A: H_2O–MeOH, 90%–9.95% (v/v) with 0.05% HCOOH and B: H_2O–MeOH, 9.95%–90% (v/v) with 0.05% HCOOH. The gradient was 100% A at 0 min, 100% A at 1 min, 0% A at 10 min, 0% A at 17 min, 100% A at 20 min. The post time was 2 min with 100% A and the stop time 22 min. Details concerning the devices and operating conditions have already been published elsewhere [10, 16].

The identification and confirmation of the pesticides were, as already mentioned, realised as recommended by the European SANCO Guidelines [31, 32] implying thereby one precursor ion and two product ions with an IT mass detector.

With the CEN/TC 275 LOD and LOQ varied from 1.0 to 115 µg/kg and from 3.3 to 382 µg/kg, respectively.

2.6 Calculation

An acute risk estimation was carried out for adults and two- to five-year-old children on the basis of pesticide intake calculation models. The model used for adults was the NESTI model developed by the British Pesticide Safety Directorate [34] and the model used for two- to five-year-old children was the VELS model developed by the German Federal Institute for Risk Assessment [33]. Worksheets for both models are available online [33, 34] where percentile commodity intakes, body weights (76 kg for both adult males and females in the NESTI model and 16.15 kg for two- to five-year-old girls and boys in the VELS model), consumption data, unit weights and calculation cases are given. To take into consideration people with a higher consumption of a given product, a large portion value was introduced. Large portions are obtained from actual food consumption survey data for individuals identified as 97.5 percentile consumers of the commodity among eaters only [35].

For the risk assessment, the consumption data used for the predicted short-term intake (PSTI) calculations of adults (due to their representativity) and two- to five-year-old children (due to their sensitivity towards acute toxicity simulating the worst-case scenarios) were selected. The PSTIs were then compared to the corresponding ARfDs. Austrian i.e. German ARfDs were set as a reference [33]. Where German ARfDs were not available, the values from the WHO were used. For the pesticides found in this study, whose ARfD value is not available (biphenyl, bromopropylate, chlorthal-dimethyl, dieldrin, flufenoxuron, fluvalinate, omethoate, oxadizon, prothiophos, quinalphos, quintozene and triflumizole), no acute risk calculation was done.

For the acute risk calculation, three different cases were considered [36]:

Case 1: no variability is expected (average weight < 0.025 kg):

$$PSTI = \frac{LP * OR}{Bw}$$

Case 2a: weight of the unit (e.g. an apple) is lower than large portion (e.g. two apples) (U<LP):

$$PSTI = \frac{(U * OR * v) + (LP - U) * OR}{Bw}$$

Case 2b: weight of the unit (e.g. one watermelon) is higher or equal to large portion (e.g. half a watermelon) (U≥LP and U is replaced by LP):

$$PSTI = \frac{LP * OR * v}{Bw}$$

where:

- PSTI is the predicted short-term intake from sampling result,
- LP is the highest large portion reported,
- OR is the observed residue without measured uncertainty in mg/kg,
- Bw is the body weight (76 kg for adults and 16,15 kg for two- to five-year-old children),
- U is the unit weight (average weight of an edible portion) [37] and
- ν is the variability factor.

3 Results and discussion

From 2003 to 2006, 4,300 samples were analysed and partitioned as following: 360 samples in 2003, 950 in 2004, 1,330 in 2005 and 1,650 in 2006. 48 different residues were found in 2003, 80 in 2004 and 93 in 2005 and 2006.

Fig. 1 presents the pesticide residue findings for the years 2003 to 2006. On average from 2003 to 2006, it shows that 46.4% of the samples presented residues below LOD, 15.1% one residue above LOD and 31.3% of the samples multiple residues above LOD. It can be noticed that some samples showed up to 14 different pesticide residues.

Possible reasons for multiple residues are pesticide changes to avoid resistance, use of pesticide mix, use of different very selective pesticides to eliminate different pests, mix of product loads from different productions, use of more pesticides in lower concentration than less pesticides in higher concentration favoured to reduce the observed residue. The commonness of multiple residues varies between the different products. The most plausible explanation is the various single component origins of a seemingly homogeneous sample as shown with the so-called "mix peppers" (green, red and yellow) and "mix salad". The mix peppers, or mix salad, originate from different farming plants possibly using different fungicides and insecticides. Another example are grapes, that are on the one hand products with a long growing time and, on the other hand, generally produced in small plants, which lead to the gathering of product loads from more than one farmer.

Moreover, in total, 46.4% of the samples were with residues below LOD, 47.9% with residues between LOD and MRL and 5.7% with residues exceeding one or more MRLs. The amount of samples without residues, i.e. with residues below LOD, increased from 2004 to 2006 from 39.0 to 51.7% and the amount of samples presenting an exceedance of the MRL value decreased from 7.1 to 4.6%. This is possibly an effect of a monitoring programme that effectively started in the year 2004.

The results of the year 2004 were selected in order to compare the findings obtained in this study to the available European data (the reports for the year 2005 and 2006 are still not available). In 2004, 35% of the analysed samples in this study presented multiple residues against 23% in the EU national monitoring programme. In the seven groups (from two to eight and more pesticide residues), the percentage of pesticide-contaminated samples was equitable dispersed higher than in the EU national monitoring programme. With 39.0% of the samples without residues and 7.1% of the samples presenting an exceedance of the MRL value, the samples in this study were more contaminated than the samples analysed in the EU national monitoring programme (53% of the samples without residues and 5.0% of the samples with exceedance of MRL values) [9]. A possible explanation is that 20% of the samples analysed in this study were grapes and sweet peppers, samples that are traditionally higher pesticide-contaminated. Furthermore, on contrary to the EU national monitoring programme, this study contained follow-enforcement samples that already present a suspicion towards pesticide residues. Finally, an extended source of discrepancies can be differences in LODs since no data about the achieved LODs are accessible from the EU national monitoring programme.

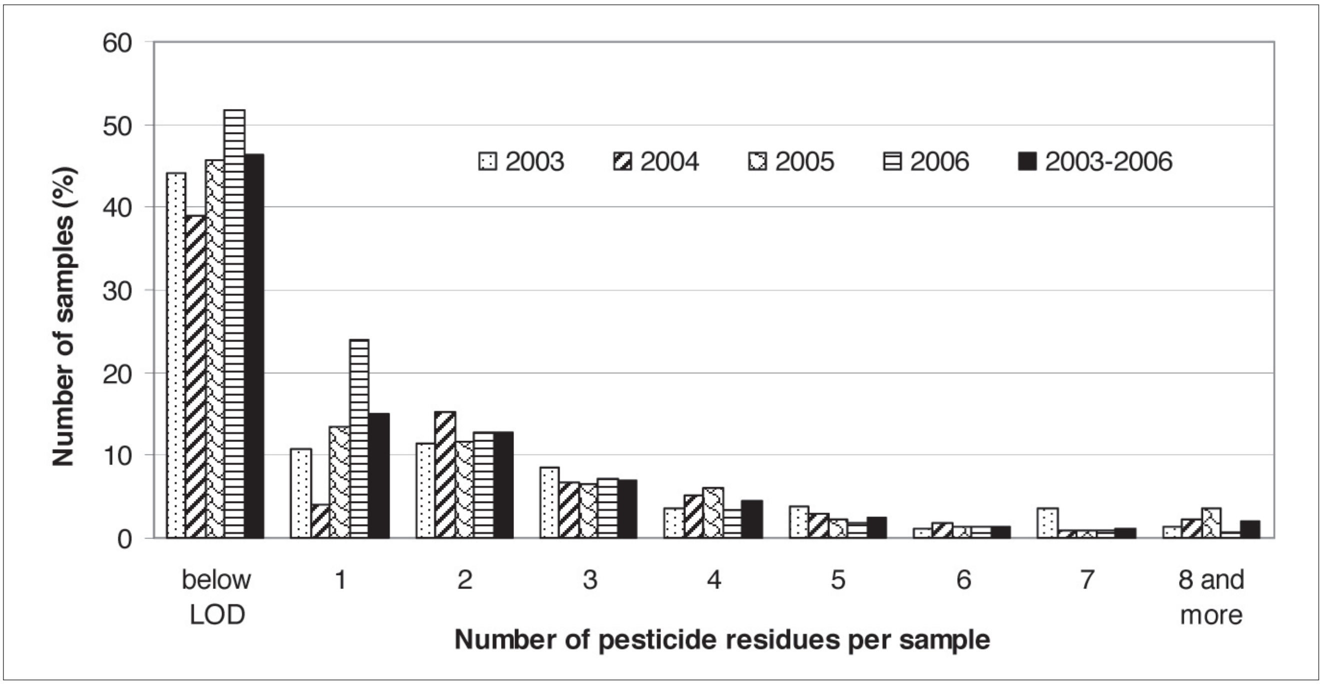

Fig. 1: Pesticide residues in conventional farming fruits and vegetables from 2003 to 2006 (total number of samples: 4,236; 2003: 362 samples; 2004: 949 samples; 2005: 1,334 samples; 2006: 1,643 samples).

Product	Number of samples analysed	Pesticide residues (% of the products)
Apple	124	Chlorpyrifos (38%), diphenylamine (9%), fenoxycarb (9%), carbaryl (9%)
Apricot	36	Lambda-cyhalothrin (8.3%), carbendazim (5.6%)
Banana	30	Imazalil (40%), thiabendazole (27%)
Blueberry	29	Iprodione (14%), pyrimethanil (7%)
Cherry	55	Fenhexamid (27%), dimethoate (18%), fludioxonil (7%)
Clementine	45	Imazalil (67%), chlorpyrifos (62%), o-phenylphenol (36%), malathion (29%), dicofol (24%), thiabendazole (20%), methidathion (13%)
Grape	425	Procymidone (54%), cyprodinil (35%), fludioxonil (27%), lambda-cyhalothrin (26%), quinoxyfen (23%), metalaxyl (20%), azoxystrobin (19%), triadimenol (17%), propargite (12%)
Grapefruit	7	Imazalil (43%), chlorpyrifos (43%)
Kiwi	49	Iprodione (18%), vinclozoline (16.3%), fenhexamid (6%)
Lemon	60	O-phenylphenol (27%), bromopropylate (22%), chlorpyrifos (22%), imazalil (18%)
Lime	17	Imazalil (12%)
Mango	1	Thiabendazole (21%)
Melon	69	Endosulfan (16%), procymidone (7.2%), bromopropylate (5.8%), buprofezin (5.8%)
Nectarine	72	Fenbuconazole (13%), iprodione (11%), procymidone (11%), chlorpyrifos (9.7%)
Orange	78	Imazalil (47%), chlorpyrifos (38%), o-phenylphenol (12%), thiabendazole (12%)
Papaya	15	Prochloraz (53%)
Peach	67	Chlorpyrifos (18%), iprodione (9%), tebuconazole (6%)
Pear	145	Procymidone (15%), carbaryl (11.7%), kresoxim-methyl (9.7%), tolclofos-methyl (9%)
Pineapple	37	Triadimenol (86%), triadimefon (84%), piperonyl butoxide (22%), prochloraz (22%)
Plum	40	Fenhexamid (7.5%)
Raspberry	41	Procymidone (22%), cyprodinil (15%), iprodione (15%)
Redcurrant	31	Fenhexamid (48%), fludioxonil (35%), cyprodinil (16%)
Strawberry	154	Cyprodinil (29%), fludioxonil (25%), azoxystrobin (14%), fenhexamid (14%), myclobutanil (14%)

Tab. 1: Typical pesticide product combinations (% of the product sample amount) in fruits for the years 2003–2006.

Product	Number of samples analysed	Pesticide residues (% of the products)
Asparagus	19	No residues found
Broccoli	31	Lambda-cyhalothrin (6.5%)
Cabbage	22	Chlorpyrifos (9.1%), iprodione (9.1%), difenoconazole (9.1%)
Carrot	45	Azoxystrobin (4.4%), chlorpyrifos (4.4%), difenoconazole (4.4%)
Cauliflower	40	Chlorpyrifos-methyl (2.5%), cypermethrin (2.5%), cyprodinil (2.5%), folpet (2.5%)
Chives	56	Difenoconazole (21%), azoxystrobin (10.7%), propamocarb (7.1%)
Chinese cabbage	36	Chlorpyrifos (8.3%), iprodione (8.3%)
Corn salad	70	Iprodione (36%)
Courgette	41	Procymidone (10%), endosulfan (7.3%)
Cucumber	116	Cyprodinil (25%), metalaxyl (15%), procymidone (8%)
Dill	51	Chlorpyrifos (24%), pendimethalin (20%), cypermethrin (12%)
Eggplant	39	Cyprodinil (13%), procymidone (7.7%), fludioxonil (5.1%)
Endive	74	Endosulfan (16%), metalaxyl (10.8%), iprodione (8.1%)
Iceberg lettuce	120	Metalaxyl (10%), procymidone (5.8%)
Kohlrabi	19	Chlorpyrifos (11%), iprodione (11%)
Leek	31	Lambda-cyhalothrin (6.5%)
Lettuce	217	Iprodione (36%), propamocarb (22%), cyprodinil (18%), metalaxyl (15%), procymidone (13%), deltamethrin (10%)
Lollo rosso	21	Procymidone (38%), azoxystrobin (14%)
Onion	37	No residues found
Sweet pepper	412	Procymidone (17%), pirimiphos-methyl (14%), endosulfan (12%), cypermethrin (8.5%)
Parsley	56	Difenoconazole (34%), cypermethrin (8.9%)
Pole bean	28	Difenoconazole (11%), procymidone (11%)
Potato	168	Chlorpropham (40%)
Radish	25	Chlorpyrifos (8%), propamocarb (16%), iprodione (12%)
Ruccola	100	Deltamethrin (19%), dicloran (14%), iprodione (13%)
Spinach	22	Azoxystrobin (14%), dicloran (14%)
Succory	16	Metalaxyl (44%)
Tomato	243	Procymidone (35%), cyprodinil (13%), chlorothalonil (8.2%), fludioxonil (7.0%), iprodione (7.0%), endosulfan (7.0%)
White cabbage	27	Iprodione (11%)

Tab. 2: Typical pesticide product combinations (% of the product sample amount) in vegetables for the years 2003–2006.

Furthermore, *Tab. 1* and *Tab. 2* show the main typical pesticide product combinations in fruits and vegetables, respectively, for the years 2003–2006. It was noticed that products like onions, garlic, apricots, courgettes, eggplants, leeks, carrots and broccoli were rarely contaminated. It was also pinpointed that some products, when contaminated, contain just one characteristic pesticide like potatoes, only contaminated with chlorpropham, a post-harvest sprout inhibitor.

Consequently *Tab. 3* shows a comparison for the ten most frequently found pesticides between our study and the EU national monitoring programme for the year 2004. This list was established by calculating the percentages of the findings of each pesticide in relation to the total number of samples analysed for this specific pesticide and classified in decreasing order. The maneb group, the benomyl group, chlormequat and bromides were not analysed in the present study. Consequently three of the remaining pesticides (chlorpyrifos, iprodione and procymidone) were present in

Rank	Present study[a]	EU national monitoring programme[b]
1	Procymidone	Maneb group
2	Cyprodinil	Chlorpyrifos
3	Chlorpyrifos	Imazalil
4	Iprodione	Procymidone
5	Fludioxonil	Benomyl group
6	Metalaxyl	Iprodione
7	Pyrimethanil	Thiabendazole
8	Azoxystrobin	Chlormequat
9	Triadimenol	Bromide
10	Cypermethin	o-Phenylphenol

[a] *Based on the same amount of samples for each product.*
[b] *The results from all reporting states were combined and are summarised inhere. A breakdown of the results from each state is provided in Annex 1 of the Report 2004 [9].*

Tab. 3: Comparison of most frequently found pesticides for the year 2004 between the present study and the EU national monitoring programme.

both lists. The most frequent pesticide residues were found in grapes and sweet peppers that represented 20% of the analysed samples. As far as no data are available concerning the ratio of the different samples analysed in the EU national monitoring programme, a direct comparison of the results is not applicable.

Finally, *Tab. 4* presents, for all the pesticides with an available ARfD value, the ARfD exhaustion for adults and two- to five-year-old children, respectively. It shows that 15 pesticides (bifenthrin, cyfluthrin, dimethoate, endosulfan, fenitrothion, folpet, imazalil, lambda-cyhalothrin, methidathion, methiocarb, methomyl, procymidone, triadimefon, triadimenol, and vinclozolin) gathered in 29 pesticide product combinations exceeded the ARfD for a two- to five-year-old child. These numbers were reduced to eight pesticides (dimethoate, endosulfan, imazalil, methidathion, methiocarb, methomyl, procymidone, and triadimenol) in eleven pesticide product combinations, respectively, when considering the acute toxicity towards adults.

In 18 of the 29 pesticide product combinations, exceedances of the ARfD were observed for two- to five-year-old children but not confirmed for adults. The highest exceedance was observed for procymidone in grapes with a factor of 22.6 times the ARfD for two- to five-year-old children and 6.8 times the ARfD for adults, respectively. It is noticeable that 73 samples i.e. 17.2%, of the total grape samples exceeded the ARfD for a chosen age group of children. This number was decreased but still significant with 31 samples representing 7.3% of the total grape samples as far as adults are concerned. Remarkable were also procymidone in lettuce (exceedance of the ARfD for adults in 1.5% of the total lettuce samples and 2.0% for two- to five-year-old children, respectively) and imazalil in oranges (exceedance of the ARfD for adults in 7.7% of the total lettuce samples against 12.8% for two- to five-

Pesticide	**Product**	**ARfD (mg/kg Bw)**	**Maximum residue (mg/kg)**	**Total number of analysed samples**	**% ARfD of an adult resulting from maximum residue concentration**	**Absolute number of samples (relative frequency in %) with ARfD exceedance for an adult**	**% ARfD of a two- to five-year-old child resulting from maximum residue concentration**	**Absolute number of samples (relative frequency in %) with ARfD exceedance for a 2 to 5 year old child**
Bifenthrin	Grapes	0.01	0.19	425	38	0 (0%)	124	1 (0.24%)
Cyfluthrin	Lettuce	0.02	1.39	542	68	0 (0%)	112	1 (0.18%)
Dimethoate	Grapes	0.01	0.98	425	193	1 (0.24%)	321	1 (0.24%)
	Sweet peppers	0.01	0.34	412	45	0 (0%)	107	1 (0.24%)
Endosulfan	Apples	0.015	1.26	124	126	1 (0.81%)	690	2 (1.6%)
	Melons	0.015	0.45	69	118	1 (1.4%)	218	2 (2.9%)
	Sweet peppers	0.015	0.88	412	77	0 (0%)	369	7 (1.7%)
	Tomatoes	0.015	0.39	243	27	0 (0%)	120	1 (0.41%)
Fenitrothion	Grapes	0.04	1.51	425	75	0 (0%)	247	1 (0.24%)
Folpet	Pears	0.1	1.44	145	23	0 (0%)	131	1 (0.69%)
Imazalil	Grapefruits	0.05	0.97	7	33	0 (0%)	173	1 (14.3%)
	Lemons	0.05	1.57	60	12	0 (0%)	171	1 (1.7%)
	Mandarines	0.05	4.83	4	107	1 (25.0%)	404	2 (50.0%)
	Melons	0.05	0.96	69	76	0 (0%)	140	1 (1.5%)
	Oranges	0.05	2.83	78	128	6 (7.7%)	439	10 (12.8%)
	Pears	0.05	1.68	145	54	0 (0%)	307	1 (0.69%)
Lambda-cyhalothrin	Grapes	0.0075	0.28	425	7.4	0 (0%)	244	21 (5.0%)
	Lettuce	0.0075	0.47	542	6.2	0 (0%)	101	1 (0.18%)
Methidathion	Oranges	0.01	0.7	78	159	2 (2.6%)	543	2 (2.6%)
	Satsumas	0.01	0.75	16	83	0 (0%)	313	1 (6.3%)
Methiocarb	Sweet peppers	0.01	0.8	412	106	1 (0.24%)	252	2 (0.49%)
Methomyl	Sweet peppers	0.01	6.68	412	882	1 (0.24%)	2,103	1 (0.24%)
Procymidone	Grapes	0.035	12.1	425	682	31 (7.3%)	2,264	73 (17.2%)
	Pears	0.035	0.94	145	43	0 (0%)	245	2 (1.4%)
	Sweet peppers	0.035	0.8	412	30	0 (0%)	144	2 (0.49%)
	Lettuce	0.035	15.9	542	448	8 (1.5%)	732	11 (2.0%)
Triadimefon	Pineapples	0.08	3.4	37	97	0 (0%)	197	3 (8.1%)
Triadimenol	Pineapples	0.08	3.76	37	107	1 (2.7%)	218	3 (8.1%)
Vinclozolin	Kiwis	0.06	5.64	49	73	0 (0%)	378	5 (10.2%)

Tab. 4: ARfD exhaustion from pesticides for adults and two- to five-year-old children (obtained from the VELS and NESTI worksheets).

year-old children, respectively). Finally, methidathion in oranges with a residue of 0.70 mg/kg fresh product was exceeding the ARfD of both adults and kids in two samples i.e. 2.6% of the total orange samples.

26 of the 29 pesticide product combinations presented an exceedance of ARfD for two- to five-year-old children although the observed residues were below MRL. This significantly demonstrates that MRLs should be reduced to protect also the more vulnerable persons against acute toxicity.

4 Conclusions

In this study, we figured out that the situation of the pesticide contamination in conventional farming products on the Austrian market improved between 2003 and 2006. The amount of samples with residues below LOD, i.e. without residues, decreased from 51.7 to 39.0%, the amount of samples with residues exceeding MRL from 7.1 to 4.6% and the amount of samples with multiple residues from 35.0 to 27.8% between 2003 and 2006. This might be due on the one hand to monitoring programmes and on the other hand to the yearly updated MRL values.

The most commonly found pesticides were procymidone, cyprodinil, chlorpyrifos, iprodione, fludioxonil, metalaxyl, pyrimethanil and azoxystrobin. Apart from the organophosphorus insecticide chlorpyrifos, seven of the eight most common pesticides were organochlorine and organonitrogen fungicides. The pesticides most commonly presenting a residue above MRL value were pyridaben, dichloran, iprodione, etofenprox and chlorpropham. Pyridaben, dichloran and etofenprox are not regulated in Austria although they are authorised in other countries like Spain and the Netherlands for instance.

Furthermore, the samples analysed in this study were more pesticide-contaminated than the samples of the EU national monitoring programme, which might be explained by the higher amount of grape and sweet pepper samples in this study and by the absence of follow-enforcement samples in the EU national monitoring programme.

Finally, concerning the risk assessment, samples containing pesticides with extremely high exceedance of the ARfD of adults (up to 8.8 times the ARfD) and two- to five-year-old children (up to 23 times the ARfD) were pinpointed. These exceedances were even observed with residues ranging below the different MRL values. Therefore, the authors recommend the MRL values for pesticides, whose measured amounts lead to exceedances of specific ARfD values following the PSTI approach, to be reconsidered and eventually lowered in order to protect the most sensitive and vulnerable collectives of the population.

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