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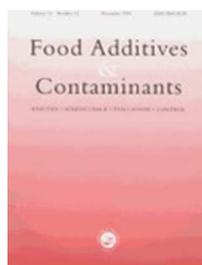
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Effect of household and industrial processing on levels of pesticide residues and degradation products in melons

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Abstract:	Two varieties of melons (<i>Cucumis melo</i>) were treated by two fungicides (carbendazim and maneb) and four insecticides (acetamiprid, cyromazin, imazalil and thiamethoxam) to quantify the effect of household processing on the pesticide residues. To ensure sufficiently high levels of residues in flesh and peels, the most concentrated formulations were applied pursuant to Good Agricultural Practices (GAPs). The peeling step decreased the concentration of pesticide residues for maneb, imazalil and acetamiprid by more than 90%. Cyromazin, carbendazim and thiamethoxam were reduced by ~50%. The reduction of the pesticides could not be fully explained by the systemic character of the pesticides. However, the agricultural practices (time of application), the solubility and mode of action (systemic vs. contact pesticide) of the pesticides allowed to make assumptions to explain the difference in processing factors for the studied pesticides. Degradation products (melamine and ethylenethiourea) were also investigated in this study but were not detected.

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3 **1 Effect of household and industrial processing on levels of pesticide residues**
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5 **2 and degradation products in melons**
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24 **Abstract**

25 Two varieties of melons (*Cucumis melo*) were treated by two fungicides (carbendazim and
26 maneb) and four insecticides (acetamiprid, cyromazin, imazalil and thiamethoxam) to
27 quantify the effect of household processing on the pesticide residues. To ensure sufficiently
28 high levels of residues in flesh and peel, the most concentrated formulations were applied
29 observing Good Agricultural Practice (GAP). The peeling step decreased the concentration of
30 pesticide residues for maneb, imazalil and acetamiprid by more than 90%. Cyromazin,
31 carbendazim and thiamethoxam were reduced by ~50%. The reduction of the pesticides could
32 not be fully explained by the systemic character of the pesticides. However, the agricultural
33 practices (time of application), solubility and mode of action (systemic vs. contact pesticide)
34 of the pesticides could be used to explain the difference in processing factors for the studied

1 pesticides. Degradation products (melamine and ethylenethiourea) were also investigated in
2 this study but were not detected.

3
4 **Keywords:** Pesticide residues, Processing factor, Fungicides, Insecticides, Degradation
5 products

6 7 **Introduction**

8 Melon (*Cucumis melo*) belongs to the same family as the cucumber, squash, pumpkin and
9 gourd and grows on the ground on a trailing vine. It is a sweet, juicy and very nutritious fruit.

10 The major producing countries are China (which produces more than 50 % of the world
11 production), Turkey, Iran, Spain, the United States, Rumania, Egypt and India (FAO, 2011).

12 This crop is susceptible to *fusarium* wilt disease (destructive vascular disease), downy mildew
13 (killing plants prematurely and reducing sugar content of melons) and gummy stem blight
14 (lesion on stems and leaves). To protect plants particularly during autumn growing seasons
15 and avoid these type of diseases, fungicide applications are necessary (Keinath et al. 2007,
16 Zhao et al. 2011). Furthermore, insecticides on melons are necessary to suppress high
17 whitefly populations and aphids (Tong-Xian 2004).

18 Pesticides have been linked to a wide spectrum of human health hazards, ranging from
19 short-term impacts such as headaches and nausea to chronic impacts like cancer, reproductive
20 harm, and endocrine disruption. Chronic health effects may occur years after even minimal
21 exposure to them in the environment, or result from their residues ingested through food and
22 water (Berrada et al. 2010, Claeys et al. 2011, Keikotlhaile et al. 2010). Research focuses on
23 the proper use of pesticides in terms of authorization and registration and on compliance with
24 Maximum Residue Limits (MRLs). Given the potential risk of pesticides for public health, the
25 use of pesticides in agriculture is subjected to constant monitoring. (Chen et al. 2011, Claeys

1 et al., 2011). It is important for the consumer to know the intake of pesticide residues. The
2 processing factors (PF: ratio between residues concentration in the processed commodity and
3 the same in the raw commodity) are useful to estimate the level of pesticide exposure at the
4 point of consumption after processing (Ling et al. 2011). Until now, no processing factors are
5 available for melons. However, melon consumption is increasing in the EU (AND
6 International 2010). Indeed, among the EU 27, the volumes of import of melons increased
7 twofold between 1999 and 2008.

8 It is well known that peeling plays a role in the reduction of residues (Holland et al. 1994,
9 Kaushik et al. 2009, Timme et al. 2004). Several studies of peeling have been done on
10 potatoes to measure some pesticides and minimum 90% reduction of pesticide residues were
11 observed (Kaushik et al. 2009, Lentza-Rizos et al. 2001, Lewis et al. 1996, Randhawa et al.
12 2007, Schattenberg et al. 1996). The peeling of apples, tomatoes, peppers, carrots, bananas,
13 oranges and lemons were also investigated in several studies (Balinova et al. 2006, Burchat et
14 al. 1998, Chavarri et al. 2005, Rasmussen et al. 2003, Timme & Walz-Tylla 2004). In these
15 experiments, peeling decreased residues (70 to 100%). However, some pesticides were not
16 influenced by this process because of their systemic activity (Krol et al. 2000).

17 Melons, frequently consumed in Belgium, were chosen in cooperation with the Belgian
18 Federal Agency for Safety of the Food Chain (FASFC). Pesticides were chosen according to
19 their frequency of MRL exceedance, frequency of detection and their toxicity (FASFC 2007,
20 FASFC 2008). Selected pesticides included acetamiprid, carbendazim, cyromazin, imazalil,
21 maneb and thiamethoxam.

22 To establish of processing factors for these pesticide residues, melons were grown,
23 sprayed, harvested, peeled, homogenized and analyzed. The selected pesticides and the
24 degradation products (ETU from maneb and melamine from cyromazin) were analysed before
25 and after peeling with several analytical methods (GC-MS/MS, GC-ECD, UHPLC-MS/MS).

1

2

3 **Materials and Methods**4 *Materials*5 *Pesticides*

6 Deuterated ethylenethiourea (d₄-ETU), ethylenethiourea, carbendazim and acetamiprid
7 were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) with certified purity of
8 99.0%. Thiram, cyromazin, melamine, imazalil and thiamethoxam were purchased from
9 Sigma-Aldrich (Seelze, Germany) with certified purity of 99.0%, 99.9%, 99.0%, 99.8% and
10 99.7%, respectively. Carbon disulfide (99.9%) was obtained from Merck (Darmstadt,
11 Germany).

12
13 *Chemicals for analysis*

14 Ultrapure water (< 8 MΩ·cm resistance) was supplied by a Millipore purification system
15 (Millipore Milli-Q Water System, Bedford, USA). Methanol, dichloromethane and
16 acetonitrile were of HPLC grade from Biosolve (Valkenswaard, The Netherlands). Iso-octane,
17 sodium hydroxide and ammoniac (25%) came from Merck (Darmstadt, Germany).
18 Trifluoroacetic acid (TFA) and acid acetic (with certified purity of at least 99% for both) as
19 well as ammonium acetate were purchased from Aldrich (Steinheim, Germany). Hydrochloric
20 acid (37%) and tin(II)-chloride were obtained from VWR (Fontenay sous Bois, France).
21 Ethanol (96%), ammonium chloride (99.5%), celite® 545, sodium sulphate (99%) and sodium
22 chloride (99%) were purchased from VWR (Leuven, Belgium).

23 The stock solution of carbon disulfide (CS₂), for analysis of maneb, was prepared at 4 mg
24 mL⁻¹ in iso-octane. Dilute standards at 40 µg mL⁻¹ were prepared by dilution of the stock

1
2
3 1 solution with iso-octane. A solution of thiram was prepared with ethanol to obtain an
4
5 2 equivalent concentration in CS₂ of 63.23 mg L⁻¹.
6

7 3 The stock solutions of acetamiprid, carbendazim, cyromazin, imazalil and thiamethoxam
8
9 4 for LC-MS/MS were prepared at 1 mg mL⁻¹ in acetonitrile containing 0.1% of acetic acid.
10
11 5 Dilute standards at 10 µg mL⁻¹, 1 µg mL⁻¹ and 100 ng mL⁻¹ were prepared by dilution of the
12
13 6 stock solution with methanol.
14

15
16 7 The stock solution of internal standard, ETU D4, was prepared at 100 µg mL⁻¹ in
17
18 8 methanol. The stock solution of ETU was prepared at 1 mg mL⁻¹ in methanol. Dilute
19
20 9 standards were prepared by dilution of the stock solution with water.
21

22
23 10 The stock solution of melamine was prepared at 1 mg mL⁻¹ in NaOH 0.1%. Dilute
24
25 11 standards at 10 µg mL⁻¹ and 1 µg mL⁻¹ were prepared by dilution of the stock solution with
26
27 12 water.
28

29
30 13 Solutions for calibration were prepared with spiking of diluted standard solution on blank
31
32 14 extract of melon. The blank extract came from melons previously tested in which no
33
34 15 pesticides were detected above the limit of detection. All solutions were stored at -18 °C.
35

36 16

37 38 17 **Produce**

39 40 18 *Cultivation*

41
42
43 19 The purpose of the field experiment was to produce in parallel two different melons
44
45 20 varieties, Mohican and Pancha, exposed to six selected pesticides.

46
47 21 Field melon was grown at Villers-Perwin, Belgium by Redebel sa. under greenhouse
48
49 22 conditions. Four applications of pesticides were performed on different crop growth stages as
50
51 23 shown in Table 1. The concentrations of the six active substances and the number of
52
53 24 applications were as high as possible, but following the GAPs (pre-harvest time, time between
54
55 25 two applications...), to ensure sufficiently high pesticide levels for the effects of processing
56
57

1 practices to be studied. It should be noted that some pesticides are not approved for the melon
2 crops in Belgium but are in other countries. The formulations were applied in two passing
3 using vertical spraying boom equipment at the proposed normal settings and timing.

4 5 *Harvest*

6 Fruit specimens were taken manually. Sterile disposable (nitrile) gloves were worn for the
7 sampling. The first and the last plants of plot, diseased and undersized fruits were excluded
8 from sampling. To obtain more than 70 kg of melons, 67 melons Pancha and 103 melons
9 Mohican were randomly collected from the whole plot. A number identified each variety.
10 Melons were stored in a refrigerator room at 4 °C directly after the sampling. They were
11 transported in refrigerated condition to the laboratory on the day of harvest.

12 13 *Sample preparation and processing*

14 *Overview of processing and sampling steps*

15 Figure 1 shows the sampling flow diagram. To minimize the factor of variability, the two
16 melon varieties were each divided into two batches of 18 kg of raw melons, giving four
17 batches in total (Figure 1). As shown in Figure 1, part of melons did not undergo any
18 processing and was used as “positive control sample”. Peeling step for all batches was
19 executed on the same day.

20 At each step, melons were homogenized and 500 g were collected and stored at -20 °C
21 until pesticide residue analysis. Frozen samples were analyzed within one month.

22 23 *Unprocessed melon*

24 These melons, which did not undergo any processing are the “positive control sample”. It
25 is the raw melon used to calculate the PFs. The harvested melons (18 kg of melons taken

1 randomly) were cut into pieces and comminuted with the Robot Coupe® R23 (Mont-Saint-
2 Genevieve, Belgium). A sample was taken after a rough cut (~ 1 cm) and frozen for the
3 analysis of mancozeb. The rest was comminuted for a longer time and frozen until analysis.

4 5 *Peeling*

6 The peeling was realised with a knife with a blade of 10 cm and corresponded to the
7 peeling done by the consumer at home. We left the green part on the peels (< 0.5 cm). Melons
8 Mohican were smaller than melons Pancha but both varieties were highly variegated.

9 After removal of the peels, flesh (about 10 kg) and peels (about 7 kg) were comminuted
10 separately with the Robot Coupe® R23 (Mont-Saint-Genevieve, Belgium) and frozen until
11 analysis.

12 13 *Extraction and analysis of pesticides*

14 *Analysis of maneb by GC-ECD*

15 The analysis of maneb as CS₂ (compound obtained when dithiocarbamates are heated in
16 presence of acid and tin chloride) is based on methods normalized by the European
17 Committee for Standardization and modified by de Kok to replace the existing headspace
18 chromatography method by a liquid injection in GC-ECD (de Kok 2001, European
19 Committee for Standardization 1998).

20 The extraction of 25 g of matrix was done in presence of hydrochloric acid, iso-octane and
21 tin chloride. A closed vessel was stirred during 2 h in a water bath at 80 °C. After cooling, 1
22 µl of the supernatant containing 0.28 g matrix per mL was injected on a Varian 3400 gas
23 chromatographic system coupled with a ⁶³Ni Electron Capture Detector and a Varian 8200C
24 autosampler. The GC separation of CS₂ was achieved on a DB-5 column (60 m, 0.53 mm and
25 1.5 µm) from Grace (Deerfield, USA). The helium gas flow was at 2.6 mL min⁻¹ at 5 psi. The

1 injector and detector temperatures were 250 °C and 300 °C, respectively. The column
2 temperature was at 50 °C for 5 min, after that it increased by 50 °C per min until 250 °C. This
3 temperature was maintained for 5 min to obtain a total run time of 19 min. The retention time
4 of CS₂ was 3.3 min.

6 *Analysis of acetamiprid, carbendazim, cyromazin, imazalil and thiamethoxam by LC-MS/MS*

7 This method followed the Granby principle (Granby et al. 2004) with some adaptations. A
8 10 g sample of melons was extracted with a mixture of an extraction solvent (5mM
9 ammonium acetate, 90% MeOH-10% water), blended during 1 min with an ultra-turrax
10 homogenizer (Ultra-turrax IKA) and filtrated on büchner. Oxfendazole, the internal standard
11 was added to the filtrate. Mixture of extraction was used to give an extract volume of 60 mL.
12 The raw extract was diluted with mobile phase A (10% MeOH, 1% ammonium acetate 0.5 M
13 and 89% water) to a final concentration equivalent to 0.1 g matrix per mL and injected after
14 filtration on 0.2 µm. The LC separation was achieved on an Acquity UPLC BEH C₁₈ column
15 (1.7 µm, 2.1 × 100 mm) from Waters (Ireland). A gradient of mobile phase A and mobile
16 phase B (containing 10% water, 1% ammonium acetate 0.5M and 89% of methanol) supplied
17 at 0.45 mL min⁻¹ was applied. Starting from 99.9% of mobile phase A, the mobile phase was
18 linearly increased to 99.9% of mobile phase B in 10 min and maintained during two min. The
19 gradient was then returned to initial conditions in 0.1 min and held there for 2.9 min for
20 stabilization. The mass spectrometer operated in a positive electrospray ionization (ESI) mode
21 and acquired two transitions for each pesticide. Typical optimized ESI voltage settings are
22 presented in Table 2. Argon was used as the collision gas at a setting of 0.35 mL min⁻¹. The
23 dwell time was 10 ms per channel for quantifier ions and 5 ms for second transition.

25 *Analysis of ethylenethiourea by LC-MS/MS*

8

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2
3 1 The method of analysis is described in a paper of Bonnechère *et al.* (Bonnechere et al.
4
5 2 2011). Briefly, ETU was extracted from the homogenized melon (10 g), after thawing of this
6
7 3 sample, by a 3:1 mixture of methanol-water. After 0.2 µm filtration, the extract containing
8
9 4 0.333 g matrix per mL was injected in LC-MS/MS (conditions in Table 2) on a Uptisphere
10
11 5 5MM1 mixed-mode chromatographic column (100 × 2.1mm, 5µm) with two different silanes
12
13 6 (C8/SCX) bonded on silica (Interchim, Montluçon, France), using an isocratic mobile phase
14
15 7 of 0.1% trifluoroacetic acid / methanol (95/5). The injection volume was 5 µL in full loop and
16
17 8 the run time was 2 min.
18
19

20 21 22 23 10 *Analysis of melamine by LC-MS/MS*

24
25 11 The method of analysis is described in a paper of Gosciny *et al.* (Gosciny et al. 2011).
26
27 12 The extraction of melamine is carried out using an acetonitrile-water-dichloromethane in an
28
29 13 acidic environment. After SPE and 0.2 µm filtration, the extract was injected in LC-MS/MS
30
31 14 (conditions in Table 2) on a Acquity HILIC column (100 × 2.1mm, 1.7µm) (Waters, Ireland),
32
33 15 using an isocratic mobile phase containing 2% ammonium acetate 0.5M, 8% water and 90%
34
35 16 of acetonitrile. The injection volume was 1 µL and the run time was 2 min.
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39

40 41 18 *Quantification and quality control*

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43 19 Limits of Quantification (LOQ) were estimated from the lowest calibration level. Based
44
45 20 on the signal-to-noise ratio upper or equal to 6, LOQs were at 40 µg kg⁻¹ for maneb, 2 µg kg⁻¹
46
47 21 for imazalil, 5 µg kg⁻¹ for cyromazin, 2 µg kg⁻¹ for thiamethoxam, and 1 µg kg⁻¹ for
48
49 22 acetamiprid and carbendazim, 50 µg kg⁻¹ for ETU and 25 µg kg⁻¹ for melamine. The linearity
50
51 23 of the instrument was evaluated with 5 or 6 points in the range of 50-1000 µg kg⁻¹ (wet
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53 24 weight basis) for ETU, 25-600 µg kg⁻¹ for melamine, 50-5000 µg kg⁻¹ for maneb and 10-1000
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1 $\mu\text{g kg}^{-1}$ for the pesticide residues analyzed by LC-MS/MS. In all cases, good linearity was
2 achieved with correlation coefficients > 0.995 .

3 For each batch of analysis, a control (a blank of melon) and a sample were spiked prior to
4 extraction and run. In the control, no pesticide must be found with a concentration greater
5 than the LOQ. If it is not the case that means a contamination and the analysis of the samples
6 must be redone. The spiked sample must have recovery of extraction between 70% and 120%
7 (SANCO/10684/2009) and the concentrations found in this sample were reported on the
8 control chart, which allows following the trend. Recoveries during the analysis of melon were
9 of 95.7% for ETU, 73.2% for maneb, 83.4% for melamine, 87.3% for cyromazin, 87.3% for
10 acetamiprid, 84.0% for carbendazim and 83.4% for imazalil. The calibration was checked
11 using a standard injected at the end of the sequence and could not deviate by more than 20%
12 from the injection of the same standard at the beginning of the sequence.

13 14 ***Calculation of processing factors***

15 Processing factors (PFs) were calculated for all transformation steps by a ratio between
16 the pesticide residue concentration (mg kg^{-1}) in the processed commodity and the pesticide
17 residue concentration (mg kg^{-1}) in the raw commodity.

18 19 **Results and discussion**

20 Sprayed pesticides were detected at various concentrations. In spite of the high
21 concentration of active substances applied on the raw melon, the concentrations for
22 thiamethoxam, carbendazim and imazalil were rather low. The lowest concentrations in the
23 raw product were observed for thiamethoxam and carbendazim (Table 3). Thiamethoxam was
24 applied at the lowest concentration in this study and carbendazim is the only which was
25 applied once, as early as the opening of the main stem (Table 1).

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2
3 1 In this study, the peeling was done with a knife. Table 4 represents all processing factors
4
5 2 for the peeling step for the six detected pesticides for both varieties. The peeling removed an
6
7 3 important part of the pesticide residues between 62% and 95% for melon Mohican and
8
9 4 between 52% and 95% for melon Pancha.

10
11 5 Maneb and cyromazin are contact pesticides and form deposit on the surfaces of leaves
12
13 6 and fruits (Table 4). After the peeling step, in spite of an important reduction for the maneb
14
15 7 (91% for Mohican and 93% for Pancha), the decrease of cyromazin did not exceed 62% and
16
17 8 52% for Mohican and Pancha respectively. However this smaller reduction could be
18
19 9 explained by the higher solubility of cyromazin compared with the other pesticides (Table 4).
20
21 10 Compounds applied to the plants (leaves) do not have to cross the symplast to arrive in the
22
23 11 xylem contrary to compounds passing by roots. On the other hand, they have to cross the
24
25 12 more or less waxy cuticle according to the type of plant and the age. With the age, fractures in
26
27 13 the waxy coat form hydrophilic pores allowing the passage of the most hydrophilic molecules
28
29 14 as cyromazin (Al-Sayeda 2007). With this particularity, cyromazin could enter in the fruit by
30
31 15 the flow of xylem and be found in the flesh. As Krol *et al.* has also confirmed it is possible
32
33 16 that pesticide residues are incorporated into plant tissue proportional to the time they remain
34
35 17 on biologically active crops in the field. This may even be true of pesticides that are not
36
37 18 specifically labelled as systemic (Krol et al. 2000). The other four pesticides (acetamiprid,
38
39 19 carbendazim, imazalil and thiamethoxam) are systemic. Nevertheless, acetamiprid and
40
41 20 imazalil were strongly reduced by 91% for Mohican, 89% for Pancha and 91% for Mohican
42
43 21 and Pancha respectively. The reduction was somewhat less important for the thiamethoxam
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45 22 (67% & 58%) and carbendazim (63% & 47%) (Table 4). The difference of behaviour could
46
47 23 be explained by the time of application of these 4 active substances (Table 1). Indeed,
48
49 24 carbendazim was the first pesticide applied when the plant of melons had it's 5th flower open
50
51 25 on main stem. With this early application, carbendazim could enter in the plant and was

1 present in it before the apparition of fruit. The others were applied in the latest stage of
2 development when 10% of fruits showed typical fully ripe color (Table 1). Otherwise,
3 thiamethoxam has a good solubility and an octanol-water partition coefficient which allow
4 him at the same time to circulate in the phloem and in the xylem and consequently to be
5 present in the fruit (Table 4). On one hand, more than 90 % of acetamiprid, imazalil and
6 maneb, contact as well systemic pesticides, were removed with this process. On the other
7 hand, ~50% of carbendazim and thiamethoxam (systemic pesticide) and cyromazin (contact
8 pesticide) were eliminated. These 2 types of reduction could not be explained by the systemic
9 character of the pesticides. However, the agricultural practices (time of application) and the
10 water solubility could explain statistically these differences between the pesticides. The
11 octanol-water partition coefficient is also necessary to explain the behaviour of cyromazin. It
12 is a particular case, not shown in the statistical test which is a global approach. Indeed a
13 systemic pesticide applied late on the plants is found with a low concentration in the flesh.
14 Until now, several studies have explained processing factor with the physico-chemical
15 properties but they did not reflect the moments of application on the harvest (Rasmussen et
16 al. 2003, Burchat et al. 1998, Watts et al. 1974, Lee et al. 2009). These results show that it
17 really important to take into account the time of application of active substances for the risk
18 assessment. Indeed as Krol (2000) said, a systemic pesticide applied late could not act as a
19 systemic. For risk assessment, it is also necessary to be aware that the levels of residues in
20 melons depend on the time of application quite as the statistical test reflects it.

21 Reductions of 90% are consistent with previous studies on the peeling of various fruit and
22 vegetables (Balnova et al. 2006, Boulaid et al. 2005, Chavarri et al. 2005, Kaushik et al.
23 2009, Lentza-Rizos & Balokas 2001, Rasmussen et al. 2003, Schattenberg et al. 1996,
24 Timme & Walz-Tylla 2004, Fernandez-Cruz et al. 2006). It was indeed demonstrated that a
25 majority of the insecticides or fungicides applied directly to crops undergo very limited

1 movement or penetration of the cuticle. However, residues of these materials are confined to
2
3 the outer surfaces where they are amenable to removal by peeling (Holland et al. 1994,
4
5 Timme & Walz-Tylla 2004, Burchat et al. 1998).
6
7

8
9 In this study, we also investigated the degradation products of cyromazin and maneb,
10
11 being melamine and ethylenethiourea (ETU), respectively. In the unprocessed melon, these
12
13 two by-products were not detected (Table 3). In general, ETU is formed in an acidic, heated
14
15 environment and it is not the case with the peeling (Dubey et al. 1997, Hwang et al. 2003,
16
17 Kontou et al. 2001, Sottani et al. 2003).
18
19

20
21 If we compare the concentrations applied on the plants and the concentrations found in
22
23 melon, there is high variability between the active substances under investigation (Table 1).
24
25 For example, the concentration in maneb applied on plants was more than 50 times higher
26
27 than the concentration in cyromazin. The concentration retrieved in the melons (Table 3)
28
29 showed that the concentration in maneb is 1.5 times lower than for cyromazin. However, the
30
31 correlation of the results of both varieties was good.
32
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35 Mass balance recoveries were calculated to compare the total mg of each pesticide in the
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37 whole commodity to the residue in the flesh and peels after peeling. Measured concentrations
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39 available in Table 4 were corrected with the mass of the whole melons, the flesh and peels
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41 comminuted to obtain reconstituted samples. Taking account the measured uncertainties, the
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43 measured concentration and calculated concentration were close, as shown in Table 5, The
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45 Table 6 showed all corrected PFs. These PFs shows some difference between varieties. An
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47 explanation could be the difference of size between both varieties. The proportion peels/flesh
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49 is more important and engenders variations between the PFs of both varieties for certain
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51 pesticides.
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1 **Conclusion**

2 During this study, processing factors for peeling of melons were determined for
3 acetamiprid, carbendazim, cyromazin, imazalil, maneb and thiamethoxam. Mechanical
4 peeling, a typical household process, will remove 52 to 91% of the pesticides on the melon.
5 The reduction of the pesticides could not be fully explained by the systemic character of the
6 pesticides. However, the agricultural practices (time of application), the solubility and mode
7 of action (systemic vs. contact pesticide) of the pesticides allowed to make assumptions to
8 explain the difference in processing factors for the studied pesticides.

9 Two degradation products (melamine and ETU) with a higher toxicity than the parent
10 compounds were also studied and were not detected before and after peeling.

12 **Acknowledgement**

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14 and Environment (contract RT 08/3 PESTRANS). We extend our grateful thanks to Redebel
15 for setting up field trials to obtain commodities, to Martine Deridder and Marie-Anne Van
16 den Bergh for their help during the analysis of the samples.

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1 **Figure Caption**

2 Figure 1: Flow diagram of processing steps and sampling for one variety of melon.

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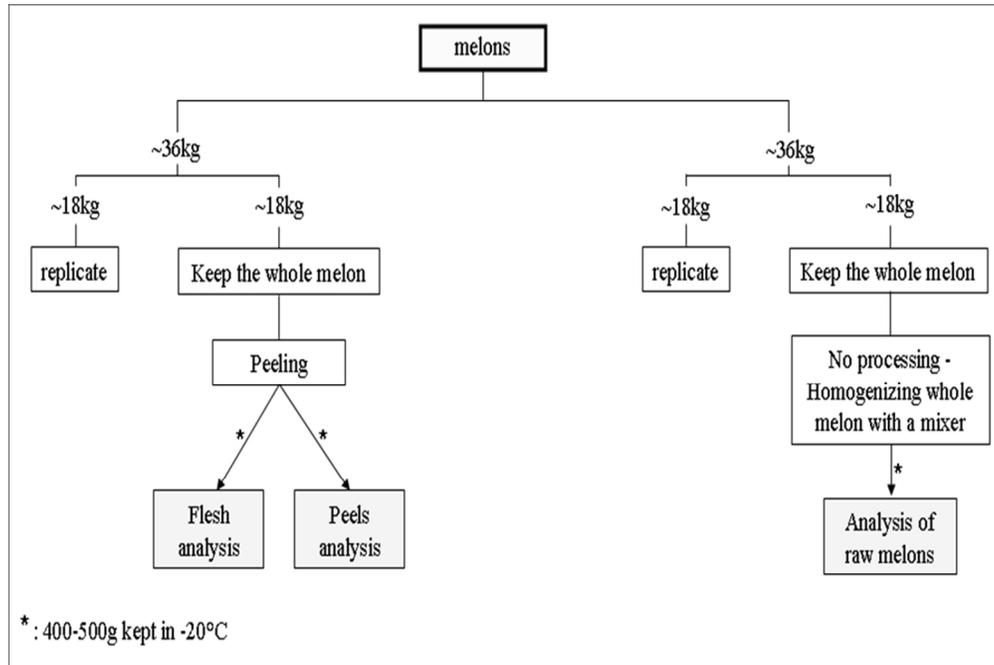


Figure 1: Flow diagram of processing steps and sampling for one variety of melon. 90x60mm (300 x 300 DPI)

Review Only

Table 1: Pesticides with their product name, rate of application and the crop stage at the moment of application

Pesticides	Product Name	Active ingredient (g ha ⁻¹)	Application date	Crop Stage (BBCH ^a)	Number of days before harvest	MRL (mg/kg)
Acetamiprid	Gazelle SP	105	9/08/2010	BBCH 83 = 30% of fruits show typical fully ripe colour (FTRC)	10	<i>0.01*</i>
		98	16/08/2010	BBCH 87 = 70% FTRC	3	
Carbendazim	Punch SE	319	5/07/2010	BBCH 65 = 5th flower open on main stem	45	<i>0.1*</i>
Cyromazine	Trigard 100 SL	58	2/08/2010	BBCH 81 = 10% FTRC	17	<i>0.3</i>
		63	9/08/2010	BBCH 83 = 30% FTRC	10	
		59	16/08/2010	BBCH 87 = 70% FTRC	3	
Imazalil	Fungaflor EC	97	2/08/2010	BBCH 81 = 10% FTRC	17	<i>2</i>
		105	9/08/2010	BBCH 83 = 30% FTRC	10	
		98	16/08/2010	BBCH 87 = 70% FTRC	3	
Maneb	Trimangol 75 WG	1950	2/08/2010	BBCH 81 = 10% FTRC	17	<i>1</i>
		2108	9/08/2010	BBCH 83 = 30% FTRC	10	
		1971	16/08/2010	BBCH 87 = 70% FTRC	3	
Thiamethoxam	Actara 25 WG	5	2/08/2010	BBCH 81 = 10% FTRC	17	<i>0.2</i>
		5	9/08/2010	BBCH 83 = 30% FTRC	10	
		5	16/08/2010	BBCH 87 = 70% FTRC	3	
			19/08/2010	BBCH 89 = fully ripe: fruit have typical fully ripe colour	HARVEST	

^a The BBCH-scale is a system for a uniform coding of phenologically similar growth stages of all mono- and dicotyledonous plant species.

* Indicates lower limit of analytical determination (Reg. (EU) No 600/2010)

Italics characters indicate that these substances are not authorized on melon in Belgium

Table 2

MS detection and selected ion for multi-residues analysis by LC-MS/MS. Quantifier daughter ions are in bold.

MS detection								
Extractor (V)	4							
RF Lens (V)	0.2							
Cone Gas Flow (L/Hr)	50							
Desolvation Gas Flow (L/Hr)	800							
Selected Ion	Parents (m/z)	Daughter (m/z)	Capillary (kV)	Source Temperature (°C)	Desolvation Temperature (°C)	Cone (V)	Collision (V)	Retention time (min)
Cytromazin	167.01	84.9 60.3	0.6	130	400	28	16 18	1.53
	292.3	211.0				19	12	
	294.3	180.9 211.0	0.6	130	400	19	24 12	2.49
Acetamiprid	223.0	125.8 89.9	0.6	130	400	26	21 35	3.65
Carbendazim	192.1	160.1 132.1	0.6	130	400	25	18 30	3.92
Oxfendazole	316.0	159.0	0.6	130	400	34	28	5.35
Imazalil	297.1	159.0	0.6	130	400	30	20	8.67
		69.1					20	
ETU	102.9	44.3 85.9	0.3	130	450	31	15 15	0.91
ETU D4	106.9	45.1 48.2	0.3	130	450	31	15 15	0.89
Melamine	126.9	84.8 67.8	0.8	150	400	42	22 17	0.91

Table 3

Concentrations (mg kg^{-1}) of pesticides and degradation products for the two melon varieties after peeling step. Mean values (\pm SD, $n = 2$) of two melon batches are depicted.

Variety 1: Mohican				
Pesticides	LOQ (mg/kg)	Raw Mean values (\pm SD)	Flesh Mean values (\pm SD)	Peels Mean values (\pm SD)
Acetamiprid	0.001	0.042 (\pm 0.00057)	0.0039 (\pm 0.00007)	0.081 (\pm 0.0087)
Carbendazim	0.001	0.0014 (\pm 0.00049)	< LOQ	0.0042 (\pm 0.0018)
Cyromazin	0.005	0.078 (\pm 0.0022)	0.029 (\pm 0.0031)	0.110 (\pm 0.0024)
Imazalil	0.002	0.0092 (\pm 0.00085)	< LOQ	0.017 (\pm 0.0039)
Maneb	0.040	0.48 (\pm 0.075)	0.043 (\pm 0.032)	0.82 (\pm 0.086)
Thiamethoxam	0.002	0.0045 (\pm 0.0000)	< LOQ	0.0074 (\pm 0.0003)
ETU	0.050	< LOQ	< LOQ	< LOQ
Melamine	0.025	< LOQ	< LOQ	< LOQ
Variety 2: Pancha				
Pesticides	LOQ (mg/kg)	Raw Mean values (\pm SD)	Flesh Mean values (\pm SD)	Peels Mean values (\pm SD)
Acetamiprid	0.001	0.046 (\pm 0.0029)	0.0051 (\pm 0.0018)	0.083 (\pm 0.00092)
Carbendazim	0.001	0.0012 (\pm 0.00021)	< LOQ	0.0034 (\pm 0.00014)
Cyromazin	0.005	0.081 (\pm 0.013)	0.039 (\pm 0.0026)	0.084 (\pm 0.00064)
Imazalil	0.002	0.011 (\pm 0.00014)	< LOQ	0.017 (\pm 0.0032)
Maneb	0.040	0.55 (\pm 0.050)	< LOQ	0.91 (\pm 0.062)
Thiamethoxam	0.002	0.0036 (\pm 0.0003)	< LOQ	0.0074 (\pm 0.0001)
ETU	0.050	< LOQ	< LOQ	< LOQ
Melamine	0.025	< LOQ	< LOQ	< LOQ

Table 4: Mean values (\pm SD, n = 2) of processing factors (PF) for peeling step for six pesticides in two varieties of melons.

Pesticides	PF peeling (\pm SD)		Action mode	log-octanol-water-partitioning coefficients	Water solubility at 20 °C (mg/L)
	Mohican	Pancha			
Acetamiprid	0.091 (\pm 0.002)	0.11 (\pm 0.040)	Systemic	0.8	2950
Carbendazim	0.37 (\pm 0.14)	0.43 (\pm 0.08)	Systemic	1.48	8
Cyromazin	0.38 (\pm 0.04)	0.48 (\pm 0.08)	Non systemic	0.069	13000
Imazalil	0.11 (\pm 0.010)	0.093 (\pm 0.001)	Systemic	3.82	22.4
Maneb	0.088 (\pm 0.068)	0.073 (\pm 0.007)	Non systemic	-0.45	178
Thiamethoxam	0.33 (\pm 0.16)	0.42 (\pm 0.20)	Systemic	-0.13	4100

Table 5: Active substances (mg) accounting for mass balance of pesticides and degradation products for the two melon varieties after peeling step. Mean values (\pm SD, n = 2) of two melon batches are depicted.

Variety 1: Mohican				
Pesticides	Raw (measured)	Flesh	Peels	Raw (calculated)
	Mean values (\pm SD)			
Acetamiprid	0.75 (\pm 0.058)	0.037 (\pm 0.0001)	0.57 (\pm 0.084)	0.60 (\pm 0.084)
Carbendazim	0.024 (\pm 0.0073)	0.048 (\pm 0.0001)	0.029 (\pm 0.014)	0.034 (\pm 0.014)
Cyromazine	1.38 (\pm 0.049)	0.281 (\pm 0.026)	0.77 (\pm 0.014)	1.05 (\pm 0.04)
Imazalil	0.16 (\pm 0.026)	0.010 (\pm 0.0001)	0.12 (\pm 0.032)	0.13 (\pm 0.032)
Maneb	8.60 (\pm 1.88)	0.41 (\pm 0.31)	5.78 (\pm 0.84)	6.19 (\pm 1.15)
Thiamethoxam	0.080 (\pm 0.0051)	0.010 (\pm 0.013)	0.052 (\pm 0.0001)	0.061 (\pm 0.013)
ETU	< LOQ	< LOQ	< LOQ	< LOQ
Mélamine	< LOQ	< LOQ	< LOQ	< LOQ
Variety 2: Pancha				
Pesticides	Raw	Flesh	Peels	Raw (calculated)
	Mean values (\pm SD)			
Acetamiprid	0.86 (\pm 0.0016)	0.065 (\pm 0.025)	0.59 (\pm 0.077)	0.653 (\pm 0.10)
Carbendazim	0.022 (\pm 0.0052)	0.0063 (\pm 0.0002)	0.024 (\pm 0.0019)	0.030 (\pm 0.0021)
Cyromazine	1.50 (\pm 0.15)	0.49 (\pm 0.050)	0.59 (\pm 0.067)	1.086 (\pm 0.12)
Imazalil	0.20 (\pm 0.015)	0.013 (\pm 0.0004)	0.12 (\pm 0.037)	0.13 (\pm 0.037)
Maneb	10.17 (\pm 0.31)	0.50 (\pm 0.017)	6.46 (\pm 1.21)	6.97 (\pm 1.23)
Thiamethoxam	0.067 (\pm 0.0012)	0.019 (\pm 0.0095)	0.051 (\pm 0.0066)	0.070 (\pm 0.016)
ETU	< LOQ	< LOQ	< LOQ	< LOQ
Mélamine	< LOQ	< LOQ	< LOQ	< LOQ

Table 6: Mean values (\pm SD, n = 2) with mass balance of processing factors (PF) for peeling step for six pesticides in two varieties of melons.

Pesticides	PF peeling (\pm SD)	
	Mohican	Pancha
Acetamiprid	0.049 (\pm 0.0038)	0.075 (\pm 0.030)
Carbendazim	0.20 (\pm 0.062)	0.29 (\pm 0.072)
Cyromazine	0.20 (\pm 0.020)	0.33 (\pm 0.046)
Imazalil	0.058 (\pm 0.0091)	0.063 (\pm 0.0051)
Maneb	0.048 (\pm 0.038)	0.050 (\pm 0.0023)
Thiamethoxam	0.12 (\pm 0.16)	0.29 (\pm 0.14)