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Determination of processing factors, intake and risk
assessment**

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Survey of pesticide residues in table grapes. Determination of processing factors, intake and risk assessment

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Survey of pesticide residues in table grapes. Determination of processing factors, intake and risk assessment

Abstract

The differences in residue pattern between Italy and South Africa, the main exporters of table grapes to the Danish market, were investigated. The results showed no major differences with respect to the number of samples with residues, with residues being found in 54-78% of the samples. Exceedances of EU-MRL were found in five samples from Italy. A number of samples were rinsed to study possible reduction of residues. For copper, iprodione, procymidone and dithiocarbamates a significant effect of rinsing was found (20-49% reduction of residues). However, no significant effect was found for OPs and pyrethroids, whereas the number of samples with residues of benzilates, phenylamids and triazoles was insufficient to demonstrate any significant effects. Intake calculation showed that the average intake from Italian grapes was 3.9 µg/day for pesticides and 21 µg/day for copper. Correspondingly the intake from South African grapes was 2.6 and 5.7 µg/day. When the total exposure of pesticides from grapes were related to ADI, expressed as the sum of Hazard Quotients, the exposure were approx 0.5% for Italian samples and 1% for South African samples.

Keywords: pesticide residues, copper, monitoring programme, table grapes, processing factors, rinsing, intake calculations, Hazard Quotient

Introduction

Although pesticide residues in foodstuffs seldom exceed the maximum residue limits set by the Food authorities, consumer awareness of health issues due to pesticide residues as food contaminants is increasing. Food and health authorities around the world are continuously monitoring pesticide residues in fruit and vegetables, as well as many other agricultural products, to ensure that consumers are not exposed to any health risks (U. S. Food and Drug Administration 2005, The European Commission 2005).

In Denmark consumers are very concerned about the levels of pesticide residues in food, which often lead the NGO's to give the public advice on how to reduce pesticide intake, e.g. by buying fruit and vegetables from a specific country. These recommendations are often based on very small sets of data collected for other purposes and may therefore not be valid for the conclusions drawn.

It is well known that food processing may affect the level of pesticide residues (Zabik 1987). Processing has been defined as 'any action performed on a food product from the point of harvest to consumption' (Ritchey 1982). Typical household processing includes rinsing, boiling, peeling and juicing of fruits and vegetables. Effects of processing on pesticide residues in foods have been compiled in reviews by Liska and Stadelman (1969), Geisman (1975), Ritchey (1982), Zabik (1987) and Holland *et al.* (1994) and cover a wide range of processing practices. The effect of processing on residues has been seen to vary with both crop and pesticides (Burchat *et al.* 1998), and may be correlated with the physico-chemical parameters of a pesticide. In general, when investigating the effect of processing, it is important to use field-sprayed samples, since absorption, translocation and

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4 weathering of the pesticide might influence the effect of a processing practice (Krol *et al.* 2000).
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6 The processes acting on pesticide residues in the field such as volatilisation, hydrolysis, oxidation,
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8 metabolism and enzymatic transformation are relevant for reduction of pesticide residues during
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10 processing (Holland *et al.* 1994).
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16 Several studies have investigated the effect of washing (rinsing) on pesticide residue content, and
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18 found that washing (rinsing) had none or only limited effect on the residue content (Burchat *et al.*
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20 1998, Rasmussen *et al.* 2003, Boulaïd *et al.* 2005, Anderson *et al.* 1998, Christensen *et al.* 2003a).
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22 However, no studies could be found on rinsing of table grapes. The only type of processing
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24 investigated for grapes were the processing to wine (Cabras *et al.* 2000, Navarro *et al.* 1999).
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30 Prediction of exposure to pesticide residues through the diet is vital for approving the use of
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32 pesticides and for gaining official acceptance on pesticides residue levels, which occur in food
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34 commodities. Over the years more specific and detailed models have been developed to give an
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36 accurate risk assessment. When performing dietary risk assessment the changes of pesticide residue
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38 content during industrial and household processing should be taken into account, as it will produce
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40 more accurate estimates of the actual consumer exposures from fruit and vegetables (FAO/WHO,
41
42 2001) and consequently give a more accurate foundation for consumer guidance.
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49 In this study, pesticide residues and the essential element copper (Cu), have been monitored in
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51 grapes from the Danish market from 1998-2003. Copper was included, since copper sulfate is a
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53 vital ingredient of the Bordeaux and Burgundy mixture and has an estimated agricultural usage of
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55 approx. 140.000 tonnes per year worldwide (The Copper Development Association, 2007). The
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57 present study evaluates the levels of pesticides residues and copper in table grapes sampled and
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4 analysed during the period 1998-2003 of an on-going fruit and vegetable monitoring programme
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6 conducted by The Danish Veterinary and Food Administration.
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11 The results obtained here were used to evaluate potential differences in pesticide residues pattern
12 between the countries of origin of the grapes. Additionally, sub-samples from 1999 and 2001 were
13 rinsed with tap water in order to estimate processing factors from rinsing for the various pesticides.
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15 Grapes were chosen, as a representative sample type for the group of vegetables and fruits, as they
16 are eaten without any other processing than gentle rinsing. Table grapes have a large
17 surface/volume ratio and may therefore be difficult to rinse thoroughly. The intake is calculated
18 using the deterministic approach, as this method is widely used for calculation based on
19 commodity-by-commodity basis. Present study involves the intake calculation both before and after
20 processing. In order to evaluate multiple findings and the health hazard related to these, it is
21 possible to perform a cumulative risk assessment (Wilkinson *et al.* 2001, Jensen *et al.* 2003).. In
22 present study the cumulative risk assessment is performed in order to evaluate and compare the
23 findings of pesticide residues in table grapes from different countries.
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42 **Materials and methods**

43 *Sampling*

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47 The samples were collected as part of the Danish Monitoring Programme on pesticide residues
48 (Poulsen and Andersen 2003) and the sampling procedure conformed to the EU directive
49 2002/63/EC (EU Commission 2002) on sampling for official control of pesticide residues.
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51 Sampling was performed year round by authorised personnel from food control units. A total of 563
52 samples of table grapes were collected from 1998 until 2003. From 2001-2003 the sampling
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4 programme for grapes were extended with 100 samples in order to elucidate the differences in
5 residues between the main producers of table grapes and to perform additional processing studies.
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7 For evaluation of differences between pesticide residues in samples from different countries al the
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9 563 samples were used. For calculation of processing factors by rinsing 120 of the 563 samples
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11 were used. These samples were collected in 1999 and 2001
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20 *Sample preparation.*

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22 Sample preparation prior to pesticide analysis was performed as described in Andersen and Poulsen
23
24 (2001). Samples for estimating processing factors were prepared as follows: Immediately after the
25
26 samples arrived at the laboratory, the samples were divided into three sub-samples of approximately
27
28 1 kg each. Each bunch of grapes was divided into an upper, middle and lower section of
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30 approximately equal size and the 3 sub-samples were made up of an equal number of the three
31
32 different sections and labeled A, B and C. The sub-samples C were rinsed thoroughly in running
33
34 cold tap water for 30 seconds and dried gentle with paper towels. Before the samples were
35
36 homogenised, representative test sample of 100g each were taken from all sub-sample for
37
38 immediate analysis of dithiocarbamates. All samples and sub-samples were then homogenized
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40 using a food processor until peel and pulp were cut to pieces smaller that 5 mm and put into sealed
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42 polyethylene bags and kept frozen at -20 degree Celsius until analysis.
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50 *Chemical analysis.* The Danish Institute for Food and Veterinary Research performed the analysis
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52 for Cu content. The pesticide analyses were carried out at the two Regional Food Control
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54 Laboratory in Copenhagen and Odense. All laboratories were accredited in accordance with
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56 ISO17025 by the Danish body of accreditation, DANAK.
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4 The grapes were analysed for approximately 150 pesticides and degradation products using 1) GC
5 multi-method with EC-, NP- and MS-detection (140 pesticides), 2) HPLC method with UV-
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7 detection (6 fungicides), 3) spectrophotometric method for the sum of dithiocarbamates and 4)
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9 inductively coupled plasma optical emission spectrometry (ICP-OES) method for the determination
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11 of copper.
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18 *GC multi-residue method.* The analytical procedure is detailed in Poulsen and Granby
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20 (2000). An analytical portion (25 g) was extracted by homogenisation with acetone, cyclohexan,
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22 ethyl acetate and anhydrous sodium sulfate. The extract was cleaned by gel-permeation
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24 chromatography. Approximately 140 pesticides (including isomers and metabolites) could be
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26 identified by retention time and quantified by capillary gas chromatography using 2 columns with
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28 different phase polarities and detection by ECD, NPD or MS.
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35 *HPLC multi method.* The analytical procedure is described in detailed in Juhler et al.
36
37 (1999). An analytical portion (25 g) was extracted by homogenisation with ethyl acetate in alkaline
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39 solution, cyclohexane and anhydrous sodium sulphate. Benomyl and thiophanat-methyl were
40
41 converted into carbendazim by heating with ethanolic hydrochloric acid. The extract was
42
43 fractionated on a silica cartridge. Residues of carbendazim and thiabendazole were determined by
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45 HPLC with UV detection (280 nm) using a C8 column and isocratic elution with methanol and
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47 triethylamin/phosphate buffer adjusted to pH 4.3 or 8.6 with phosphoric acid. Detected residues
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49 were determined using two different columns or two eluents with different pH.
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56 *Dithiocarbamate method.* An analytical portion of 100 g was boiled with hydrochloric
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58 stannous chloride to convert dithiocarbamates to carbon disulphide, which subsequently was
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4 distilled, cleaned and determined by spectrophotometry at 372 and 430 nm as described in Juhler et
5
6 al. (1999). The method cannot distinguish between the different dithiocarbamates.
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11 *Copper method.* Determination of copper was performed by wet-ashing followed by
12 detection ICP-OES. Details of the instrument and operating parameters are summarized in Table 2.
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14 Analytical portions of approximately 2.5 g were weighed into PTFE vessels of pressure digestion
15
16 system, and 3 ml of ultrapure, subboiled nitric acid was added. The vessels were then heated to 160
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18 degrees Celsius for 4 hours. After cooling, the resulting digests were diluted to a final volume of 40
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20 ml with laboratory water (18 M Ω) and stored in polyethylene vials until analysis.
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35 *Quality Assurance*

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37 The quality assurance for the pesticide residues method are described in detail by Poulsen and
38
39 Andersen (2003). The analytical methods for pesticides were quality controlled by analysing two
40
41 spiked samples as well as randomly chosen replicate samples and blank determinations in each
42
43 analytical series of approximately 16 samples. Quality control for the analysis of copper included
44
45 the analysis of minimum one analytical blank, one certified reference material (NBS 1572 Citrus
46
47 leaves) (National Bureau of Standards, Washington DC, USA), and one double determination for
48
49 each batch of 10 unknown samples. All quality control samples were evaluated for accuracy and
50
51 precision, and in case of deviation from the quality criteria the analysis for the entire batch of
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53 samples was repeated.
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4 The uncertainties for all analytical methods were estimated according to the recommendations from
5 the ISO 'Guide to the expression of uncertainty in analytical measurements (International
6 Organization for Standardisation 1995) and the EURACHEM/CITEC Guide to quantifying the
7 uncertainty in analytical measurements (EURACHEM/CITAC 2000). A 4-step procedure, using
8 data from the in-house validation (top-down approach) was used in the quantification of the
9 uncertainty (Christensen *et al.* 2003b). Limits of determination were calculated as 6 times the
10 standard deviation of 7 spiked samples. The samples were spiked at concentration levels close to the
11 detection levels. The limits of determination and uncertainty estimates, for each individual
12 identified residue, are presented in Table 3.
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30 [insert Table 3 here]
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35 **Results and discussion**

36 *Pesticide residues*

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38 The 563 samples of table grapes analysed in the Danish Pesticide Monitoring Project from 1998-
39 2003 have been imported from 17 different countries. Italy and South Africa were the major
40 exporters to the Danish market, with approximately one third of the samples from Italy, one third
41 from South Africa and the last third from 15 other countries worldwide. Table 4 shows the number
42 of grape samples analyzed in the period 1998-2003 and the countries of origin.
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4 *Differences between the main exporters to the Danish market, Italy and South Africa.*

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7 Since a low number of samples were collected for most of the countries, it has only been possible to
8
9 compare results for the Italian and South African samples with regards to differences in number of
10
11 pesticide residues and risk assessment.
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16 *Percent of samples with pesticides residues.* During the year 2000 the laboratory structure at the
17
18 regional level changed and the two regional pesticide residues laboratories were merged.
19
20 Unfortunately, a lower number of samples were analyzed this year and the results seem to differ
21
22 from the other years. However, apart from 2000 no major differences were seen between the Italian
23
24 and South African samples with respect to the number of samples with residues, where residues
25
26 were found in 54-78% of the samples (data from 2000 not included). The residue level of the Italian
27
28 and South African samples is shown in Figure 1. A one-way analysis of variance shows no
29
30 differences for the whole period. However, from 2001-2003, the period where the majority of
31
32 samples were collected, a significant difference between the two countries ($p=0.04$) was found
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34 showing that a higher percentage of the Italian samples contained pesticide residues compared to
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36 South African samples.
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52 *Number of residue per sample.* Grapes from Italy had on average 1.65 residues per samples and the
53
54 frequencies increased significantly through the period. In 2003, the number of residues per sample
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56 was increased to 2.75 and one specific sample contained 11 different residues (See Figure 1).
57
58 Grapes from South Africa samples had 0.98 residues per sample, also slightly increasing during the
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4 period. A one-way analysis of variance showed no differences between the countries over the whole
5
6 period, but significant differences ($p=0.01$) from 2001-2003.
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11 *Exceedances of MRL and ARfD:* Only samples from Italy exceeded the MRL. Five samples (2.6%)
12 had residues above the EU-MRL. Two of these (phosalone and fenitrothion) were not significantly
13 exceeding the MRL considering the analytical uncertainty. Three samples with bromopropylate
14 were significantly exceeding the MRL (2-9 times). Two samples from South Africa had residues of
15 prothiofos (0.131 and 0.150 mg/kg), which were estimated to exceed the Acute Reference Dose,
16 ARfD. No international accepted ARfD for prothiofos is yet establish. The estimations are therefore
17 based on the manufacturer (personal communication, 2003) proposal at 0.00125 mg/kg bw. A
18 consumption of 225 g of grapes for an adult, would lead to exceedances of ARfD at 164-188%.
19 Corresponding, a consumption of 153 g for a child (19 kg) would lead to exceedances of ARfD at
20 422-483%.
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37 *Number of different pesticide residues.* Samples of Italian table grapes contained in total 34
38 different pesticide residues, whereas 21 were found in South African samples. Table 5 shows the
39 list of pesticide residues found in the grapes for the two countries together with their respective
40 values for acceptable daily intake (ADI). For further details on the listed ADI see Poulsen *et al.*
41 (2005)
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4 *Processing factors*
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7 To investigate any effect of processing it is important to have as identical sub-samples of each
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9 sample as possible, where one of the sub-samples is subjected to the processing. In this study the
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11 effect of rinsing with tap water was investigated. Prior to the experiment the grape samples in this
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13 investigation were carefully divided in 3 sub-samples (A, B and C) as described in Methods and
14
15 Materials.
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21 Sub-samples A and B were not rinsed in water and the results from the analyses were used to test
22
23 whether the sub-samples were comparable or not. The two sets of data for each pesticide group
24
25 were tested by a Paired Student's t-Test (Miller and Miller 1993) and the results showed no
26
27 difference between the concentrations in sub-samples A and B. Consequently, it was concluded that
28
29 the division of a sample into three identical sub-samples was successful.
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35 Only data which fulfilling the following criteria were included in the calculation: 1) For pesticide
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37 residues the processing factors were calculated for different classes of pesticides and a minimum
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39 number of results were needed to obtain statistical significant results. In order to include as many
40
41 results as possible the limit were set at $n \geq 5$. Therefore only results from the pesticide classes with
42
43 more than 5 samples entered the calculation. 2) Only result from samples where residues were
44
45 found in both sub-samples A and B were included in the calculations. 3) Result below the detection
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47 limits in sub-samples C were replaced with values of half of the detection limits in order to facilitate
48
49 the calculations. 4) Since copper occurs naturally in grapes only samples with a mean concentration
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51 of at least 10 times the detection limit were used for the calculation of the processing factor for
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53 copper. Following these criteria, 116 of 142 pesticide residues found in the 120 samples were
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55 analyzed and used for the calculation of the processing factors (see Table 6).
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7 The processing factor of rinsing was calculated for 8 pesticide classes; copper, benzilates,
8 dicarboximides, dithiocarbamates, organophosphorus pesticides (OPs), phenylamides, pyrethroids
9 and triazoles. However, since the dicarboximides iprodione and procymidone were frequently
10 found, the processing factor for these two pesticides was calculated individually.
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23 *Calculating of processing factor.* The processing factor for each pesticide or pesticide class were
24 calculated by the following equation:
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$$P = \text{avg} \left(\frac{\text{conc.} \overline{AB} - \text{conc.} C}{\text{conc.} \overline{AB}} * 100\% \right)$$

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35 where
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40 P: processing factor in percentage equal to the reduction by rinsing for each pesticide or
41 pesticide class
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45 conc. \overline{AB} : the mean concentration of pesticide residues in sub-sample A and B:
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48 conc. C: the concentration of pesticide residues in sub-sample C
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52 The results for the processing factors are shown in Table 7 and Table8. All the results were
53 evaluated by performing a Paired Student's t-Test where the adopted null hypothesis was
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57 '*concentration in sub-sample A = concentration in sub-sample C*'.
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4 For copper, iprodione, procymidone and dithiocarbamates a significant effect of rinsing was found
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6 (See Table 7). For copper, iprodione and dithiocarbamates almost half of the residues were rinsed of
7
8 with a significance level at 99% ($p < 0.01$). For procymidone the residue were reduced by one fifth at
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10 the significance level 95% ($p < 0.05$)
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23 No effect of rinsing with tap water was found for OPs, pyrethroids, benzilates, phenylamides and
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25 triazoles. However, this may be due to a high RSD value for the analytical method in combination
26
27 with only few samples. For that reason, the remaining results were subjected to statistical Power
28
29 Analysis (Zar 1984) in order to calculate the number of samples required to detect an effect, taking
30
31 the RSD of the analytical method into consideration. For OPs and pyrethroids the Power Analysis
32
33 demonstrated that the number of samples in the study was sufficient to conclude that rinsing had no
34
35 effect on these pesticides, see Table 8. However, the number of samples with residues of benzilates,
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37 phenylamides and triazoles were too low to demonstrate whether rinsing with tap water had an
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39 effect.
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Intake and risk assessment

The intake for residues of pesticides and cobber is calculated separately due to the big differences in intake. Furthermore, copper is also a naturally occurring element, which differ it from the other pesticide residues.

The average daily intake of pesticides was calculated for Italian and South African grapes based on consumption data from the Danish National Survey of Dietary Habits 2000-2002 (Danish Veterinary and Food Administration 2002). The survey was based on a combination of personal interviews about e.g. physical activities and a 7-day diary record. The consumption data were given for each individual as an average of the 7 days for each eaten food item together with information about gender, age and body weight. In total approximately 4000 persons from 4 to 75 years of age participated in the survey.

The intake of pesticides from grapes before rinsing was calculated by summing up the contribution from all the pesticides detected in the Italian or South African grapes. The contribution from each pesticide was calculated by multiplying the average concentration in Italian or South African grapes by the consumption of grapes. The average concentration for the individual pesticide residue were calculated by the following equation:

$$C_{agv} = C_{agv, pos} * n_{pos} + 50\% * RL * (N_{samples} - N_{pos})$$

Where

C_{agv} : Average concentration of the individual pesticides including correction by 50% of the Reporting Limit in the samples where the pesticide was not detected.

$C_{agv, pos}$: Average concentration of the pesticide in the samples where it has been detected.

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RL: Reporting Limit for the individual pesticide.

N_{samples}: Number of samples the analysed for the individual pesticide.

N_{pos}: Number of samples where the individual pesticide is detected.

The consumption was calculated for 6 different populations and results are shown in Table 9. The calculations of the intake of pesticides from the grapes after rinsing, was done in the same manner. For the pesticides showing potential for reduction by rinsing, the concentration was reduced by the processing factor shown in Table 7. The results for pesticides show that the intake in $\mu\text{g}/\text{day}$ from Italian grapes was 34% higher than from South African grapes. Additionally, it would be possible to reduce a higher percentage of the pesticide residues from the South African grapes by rinsing, 27% versus 10% from the Italian. After rinsing the intake from South African grapes was almost half of the intake from rinsed Italian grapes. The results are strictly correlated with the consumption and because women on average eat more grapes than men, their intake was higher. Equally, persons with high consumption of fruit and vegetables, grapes included, also have a higher intake of pesticides. The obtained data for copper clearly indicate, that the majority of the samples from Italy were exposed to the use of copper formulation, whereas only few indications of the use of copper formulation were seen in the rest of the samples including samples from South Africa. Therefore, the intake from Italian grapes was more the three times higher than from South African. The data also show that it was possible to reduce the intake of copper from rinsed Italian grapes to a larger extend, 42% versus 27% from the South African.

[insert Table 9 here]

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4 Usually, risk assessments of the exposures are performed for the individual pesticides. A total risk
5 assessment of all the residues is strictly not possible, because the pesticides have different
6 toxicological end points. However, to provide an indication on the differences in exposure between
7 Italian and the South African grapes, the daily intakes have been normalised by the ADI values. The
8 method has been described in details in (Poulsen *et al.* 2005). Briefly, a so-called Hazard Quotient
9 (HQ) is calculated for all individual pesticide by dividing the intake with the relevant ADI. Then the
10 HQs are summed up (Σ HQ) which to give a Hazard Index. For copper the exposure is calculated
11 based on the Provisional Maximum Tolerable Daily Intake (PMTDI) at 0.5 mg/kg body weight
12 (WHO/FAO 1982).
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33 The results presented in Table 10 show that although the intake in $\mu\text{g}/\text{day}$ from Italian grapes was
34 higher than from South African grapes, the Σ HQ from the South African grapes was more than
35 double the Σ HQ compared to the Italian grapes. This indicates that the pesticides used in South
36 Africa were more toxicological problematic. Analogous to the intake in $\mu\text{g}/\text{day}$ the Σ HQ correlates
37 to the consumption. However, since women have, not only, a higher consumption but also a lower
38 bodyweight than men, the difference between males and females was even more conspicuous for
39 the Σ HQ than for the intake. Because the pesticides with the lowest ADI values were not between
40 the pesticides that can be reduced by rinsing it was only possible to reduce the Σ HQ for Italian
41 grapes with approximately 5% of the Σ HQ and the South African with only 2%. For copper the
42 'ΣHQ' was lower than for pesticides due to the relatively high PMTDI value.
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Conclusions

The main exporters of grapes to Denmark 1998-2003 were Italy and South Africa. The Italian grapes contained higher concentrations of pesticide residues and copper, higher number of pesticides residues per sample and more different pesticides compared to South African grapes. For copper, iprodione, procymidone and dithiocarbamates, a significant effect of rinsing was found, where up to half of the residues were removed by rinsing in tap water. No significant effect was found for OPs and pyrethroids, whereas for benzilates, phenylamides and triazoles the number of samples in the study was insufficient to demonstrate any significant effects. Because more Italian samples contained pesticides and copper with a potential for reduction by rinsing with tap water, the intake from Italian samples were reduced the most by rinsing. The exposure in relation to ADI for pesticides were higher for the South African samples, due to use of pesticides with lower ADIs.

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Table 1. ICP-OES Instrumentation and operating conditions for the determination of copper

Instrument	Perkin_Elmer 3300DV
Detector	Photo Multiplier
Spray Chamber	Scott Type (Ryton®)
Nebulizer	Cross Flow
RF Power	1300 kW
Plasma gas flow rate	15 l min ⁻¹
Auxiliary gas flow rate	0.5 l min ⁻¹
Nebulizer gas flow rate	-0.8 l min ⁻¹
Sample flow rate	1.0 l min ⁻¹
Plasma viewing mode	Axial
Wavelength	324.752 nm
Replicates	3
Read Time	Auto
Peak Algorithm	Peak Area
Points/Peak	3

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Table 2. Limits of determination and uncertainty estimates for copper and the pesticide residues detected in the samples.

Compound	Limit of determination, mg/kg ww	Uncertainty estimate, %
Bifenthrin	0.012	18
Bromopropylate	0.012	18
Captafol	0.004	16
Carbendazim	0.05	25
Chlorpyrifos	0.021	16
Chlorpyrifos-methyl	0.009	16
Copper	0.2	2.5
Cypermethrin	0.006	25
Deltamethrin	0.004	10
Diazinon	0.009	6
Dichlofluanid	0.003	8
Dimethoate	0.002	10
Dithiocarbamate	0.04	25
Endosulfan	0.004	11
Esfenvalerat	0.008	24
Fenarimol	0.007	19
Fenitrothion	0.01	19
Iprodione	0.004	10
Metalaxyl	0.004	13
Myclobutanil	0.005	19
Omethoate	0.004	28
Parathion	0.039	25
Phosalone	0.053	28
Phosmet	0.043	28
Procymidone	0.004	16
Pyrazophos	0.002	10
Tebuconazole	0.007	30
Tetradifon	0.052	23
Triadimenol	0.003	9
Vinclozolin	0.03	18

Table 3. Number of grape samples collected and analyzed from 1998-2003 and countries of origin.

	1998	1999	2000	2001	2002	2003	Total
Argentina					3		3
Australia					1		1
Brazil	1	9		5	10	12	37
Chile	7	2	10	9	10	7	45
Cyprus			1				1
France						1	1
Greece			2	2	6	2	12
India				1	3	5	9
Israel		1		4	1		6
Italy	32	24	8	49	45	33	191
Morocco						1	1
Namibia				1	1		2
Spain	2	11	1	8	11	7	40
South Africa	13	30	9	56	49	46	203
Turkey	1		1	3			5
USA				1			1
Egypt	1			1	2	1	5
Total	57	77	32	140	142	115	563

Table 4 Pesticide residues found in Italian and South African table grapes and their ADI.

Pesticide	Italian	S. Africa n		ADI Mg/ kg body weight
	samples ¹	Mean concentration mg/kg	Number of residues	
Total number of residues sample analyzed	315		198	
Azoxystrobin ²	3	0.065		0.1
Bifenthrin	4	0.031		0.02
Bromopropylate	19	0.437		0.03
Captan+folpet			7	0.307
Carbendazim (benomyl group)	2	0.135		0.03
Chlorpyrifos	11	0.052	2	0.035
Chlorpyrifos-methyl	30	0.039		0.01
Cyfluthrin	11	0.025		0.02
Cypermethrin	10	0.044	5	0.035
Cyprodinil ³	14	0.240	4	0.029
Deltamethrin	6	0.014		0.1
Dichlofluanid	4	0.079		0.3
Dimethoate	1	0.035	8	0.039
Endosulfan	2	0.020	1	0.021
Esfenvalerat	1	0.031		0.02
Fenarimol	1	0.045	1	0.007
Fenitrothion	12	0.120		0.005
Fenson	1	0.430		
Flucythrinate	1	0.047		0.02
Fludioxonil ³	12	0.115		0.33
Iprodione	5	0.504	77	0.457
Maneb-group	29	0.459	23	0.253
Metalaxyl	31	0.044	1	0.008
Myclobutanil	5	0.042	1	0.014
Omethoate			4	0.024
Parathion	2	0.015		0.0006
Penconazole	9	0.029	1	0.009
Permethrin	1	0.042	2	0.103
Phosalone	4	0.357		
Phosmet			1	0.008
Procymidone	60	0.269	37	0.405
Prothiofos			4	0.175
Pyrimethanil ³	10	0.120	1	0.037
Tebuconazole	3	0.050	6	0.036
Tetradifon	1	0.070		0.02
Triadimefon+triadimenol	8	0.054		0.03
Trichlorfon	1	0.016		0.02
Trifloxystrobin ²	1	0.009	2	0.009
Vinclozolin			10	0.078

¹ 191 Italian samples and 203 South African samples are analysed for the majority of the pesticide found.² Only analysed in 2002 and 2003 in 78 Italian samples and 95 South African samples

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³ Only analysed in 203 in 33 Italian samples and 46 South African samples

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Table 5 Number of residues included in calculations of processing factors per pesticides and class as well as for copper.

Class	Pesticide	Number of residues includes in calculations	Number of residues includes in calculations per pesticide class
Benzilate	Bromopropylate	7	7
Dicarboximide	Iprodione	19	19
	Procymidone	21	21
Dithiocarbamate	Dithiocarbamate	19	19
OP-pesticides	Chlorpyrifos	6	
	Chlorpyrifos-methyl	5	
	Diazinon	1	
	Dimethoate	1	
	Phosalone	2	
	Phosmet	1	16
Phenylamide	Metalaxyl	11	11
Pyrethroid	Bifenthrin	3	
	Cypermethrin	5	
	Deltamethrin	1	
	Esfenvalerat	1	
	Fenitrothion	7	17
Triazole	Tebuconazole	4	
	Triadimenol	2	6
<i>Pesticide residues In total</i>		<i>116</i>	<i>116</i>
Inorganic	Copper content	120	27

Table 6 The concentration range, RSD for the analytical method, number of samples, probability for reduction and the reduction in % for pesticide residues and copper by rinsing with tap water. Significant reduction are marked by single asterisks ($p < 0.05$) and double asterisks ($p < 0.01$).

Pesticide class	Conc. range	RSD for the analytical method %	Measured samples, n	Probability	Reduction %
Copper	0.2-179	8	12	<0.001	47**
Dicarbimide - iprodione	0.01-0.55	13	19	<0.001	49**
Dicarbimide – procymidone	0.01-0.95	13	21	0.017	22*
Dithiocarbamates	0.011-0.62	20	19	<0.001	41**

Table 7. The concentration range, RSD for the analytical method, number of samples, observed effect, probability for reduction and the required sample size.

Pesticide class	Conc. range	RSD for the analytical method %	Measured samples, n	Observed Effect %	Probability	Required sample size, n
OP-pesticides	0.01-1.13	20	16	20	0.313	16 ¹
Pyrethroids	0.01-0.63	17	17	16	0.119	17 ¹
Benzilates	0.19-0.79	16	7	-23 ³	0.084	9 ²
Phenylamides	0.01-0.15	28	11	11	0.193	87 ²
Triazoles	0.02-0.085	28	6	14	0.472	55 ²

¹ Significant no-effect

² Number of samples in the study was insufficient to demonstrate a significant effect

³ The negative reduction represents an increase in pesticide. However, the effect is not significant

Table 8 Intake of pesticides and copper in $\mu\text{g}/\text{day}$ from Italian and South African grape before and after rinsing. Copper results are shown in brackets. The calculations are performed for 6 populations

Intake, $\mu\text{g}/\text{day}$	Consumption g/day	Italy		South Africa	
		Before rinsing Intake, $\mu\text{g}/\text{day}$	After rinsing Intake, $\mu\text{g}/\text{day}$	Before rinsing Intake, $\mu\text{g}/\text{day}$	After rinsing Intake, $\mu\text{g}/\text{day}$
All, 4-70 years	5.2	3.9 (21)	3.5 (12)	2.6 (5.7)	1.9 (4.2)
Male, 15-75 years	3.5	2.6 (14)	2.3 (8.1)	1.8 (3.9)	1.3 (2.8)
Female, 15-75 years	7.6	5.7 (31)	5.2 (17)	3.8 (8.4)	2.8 (6.1)
Children, 4-14 years	3.6	2.7 (15)	2.5 (8.3)	1.8 (4.0)	1.3 (2.9)
High F&V, Male: 15-75 years 1)	13	9.8 (53)	8.9 (30)	6.5 (14)	4.8 (10)
High F&V, Female: 15-75 years 1)	23	17 (93)	16 (53)	11 (25)	8.4 (19)

1) High consumer of fruit and vegetables

Table 9 The total exposure of pesticides expressed as Σ HQ for Italian and South African grape before and after rinsing calculated for 6 different populations. The calculated exposure of copper (in brackets) was based on the PMTDI.

	Body weight, kg	Italy		South Africa	
		Before rinsing Σ HQ,%	After rinsing Σ HQ,%	Before rinsing Σ HQ,%	After rinsing Σ HQ%
All, 4-70 years	66.4	0.50 (0.06)	0.47 (0.04)	1.14 (0.02)	1.11 (0.01)
Male, 15-75 years	82.4	0.27 (0.03)	0.26 (0.02)	0.62 (0.01)	0.60 (0.01)
Female, 15-75 years	67.3	0.59 (0.09)	0.56 (0.05)	1.64 (0.02)	1.61 (0.02)
Children, 4-14 years	35.1	0.28 (0.08)	0.26 (0.05)	1.49 (0.02)	1.46 (0.02)
High F&V, Male: 15-75 years	82.4	1.00 (0.13)	0.95 (0.07)	2.30 (0.03)	2.24 (0.03)
High F&V, Female: 15-75 years	66.9	1.77 (0.28)	1.69 (0.16)	5.01 (0.08)	4.89 (0.06)

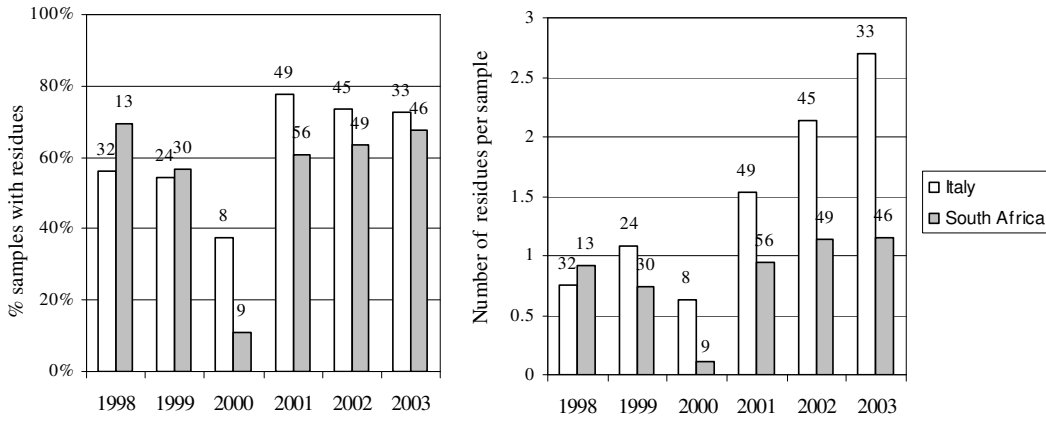


Figure 1 Percent of samples with residues and number of residues per sample found in Italian and South African grapes. Numbers above the columns are number of samples analyzed.

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