

## Baby food production chain: Pesticide residues in fresh apples and products

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### Abstract

During 3 years of a monitoring programme, 522 samples of fresh apples, six brands of fruit purées and various types of fruit baby food prepared from these materials were analysed. Each sample was examined for the presence of 86 GC amenable pesticide residues. The reporting limits of the procedure employed for sample analyses were in the range 0.003–0.01 mg kg<sup>-1</sup>. Pesticide residues were detected in 59.5% of the samples of fresh apples. However, maximum residue levels (European Union MRLs) were exceeded only in 1.4% of samples. The levels of residues in 'positive' fruit purées were substantially lower, overall with residues detected in 33% of samples. Fruit baby food represented the commodity with the lowest incidence of residues being detected in only 16% of samples. The 0.01 mg kg<sup>-1</sup> MRL was exceeded in 9% of these products. Multiple residues were found in 25% of fresh apples and in 10% of fruit purées. None of fruit baby food samples contained more than a single residue. Organophosphorus insecticides and fungicides representing phthalimides, sulphamides and dicarboximides were the most frequently found residues. To obtain more knowledge on the fate of residues during fruit baby food production, processing experiments employing apples with incurred residues (fenitrothion, phosalone and tolylfluand) were conducted. Washing of apples did not significantly reduce the content of pesticides. Steam boiling followed by removal of peels/stems was identified as the most efficient steps in terms of residues decrease (phosalone) or complete elimination (fenitrothion and tolylfluand).

**Keywords:** *Pesticide residues, apples, fruit purée, baby food, monitoring programme, processing study*

### Introduction

The protection of food crops against pests and diseases by various pesticide sprays is a common approach in conventional farming. Under certain circumstances, in spite of applying these preparations in accordance with principles of good agricultural practice (GAP), residues of active ingredients may still occur in treated crops. Because of the potential health risk for consumers resulting from acute and/or chronic dietary exposure, maximum residue levels (MRLs) for many pesticide/commodity combinations have been established in the European Union. The MRL of 0.01 mg kg<sup>-1</sup> was established by Commission Directive 1999/39/EC for pesticide residues potentially occurring in

processed cereal-based foods and baby foods for infants and young children (European Communities 1999). The recent amendment (European Communities 2003) specifies compounds for which even lower MRLs are required. The reason for such strict regulations is obviously the vulnerability of this particular consumer group characterized by its immature physiological development and high food consumption rate per weight unit as compared with adults. In any case, pesticide residues represent food safety issues of high concern and on this account various surveillance/compliance programmes exist in all developed countries as a part of measures aimed at consumer protection. As shown in the available reports (Ripley et al. 2000; Andersen and Poulsen 2001; Dogheim et al. 2001;

2002; CAFIA 2003; NFA 2003; EU 2003, 2004; Poulsen and Andersen 2003; US FDA 2003; PSD 2004; USDA 2004) detectable residues were usually found in 30–60% of fruit samples.

It should be noted that significant changes of pesticide residues may occur during household/industrial processing of contaminated crop. As widely discussed by the scientific community (Holland et al. 1994; Cabras et al. 1998a–c; Hajšlová 1999; Krol et al. 2000; Zabik et al. 2000; Christensen et al. 2003; Rasmussen et al. 2003; Angioni et al. 2004) fruit processing (e.g. washing, peeling, cooking) usually results in some decrease of residues in products. However, in some cases (e.g. fruit drying or production of unrefined vegetable oil) increase of residues in product (expressed on its weight basis) may also occur. In principle, both chemical reactions (hydrolysis, oxidation, etc.) and physical processes (volatilization, adsorption, etc.) affect to some extent the levels of terminal residues in the final product. When considering residue changes during fruit processing, commodity-specific factors (e.g. character of surface: the occurrence of trichomes, the presence of cuticular waxes, etc.) should not be neglected. For the evaluation of residues changes, processing and/or production factors (i.e. residue level in processed product/residue level in the raw agricultural commodity; Hamilton et al. 1997; WHO 1997) are used.

The present study was focused on the determination of pesticide residues in the baby food production chain. During 3 years of the monitoring programme (2001–03), samples of fresh apples, fruit purées and fruit baby food were collected and analysed employing a validated multiresidue analytical method that enabled a reliable control of a wide range of GC amenable pesticides at levels  $0.01 \text{ mg kg}^{-1}$  and lower. To get more insight into the fate of residues during apple processing, the effects of individual technological operations such as washing, steam boiling, the removal of peels/stems and mixing the ingredients to obtain final products were evaluated on the basis of residue content determined in fresh apples, washed apples, apple purée, pomace and final product (baby food).

## Materials and methods

### Monitoring programme

The monitoring programme was carried out in collaboration with fruit baby food-producing company located in the Czech Republic. In total, 522 samples of apples, fruit purées and fruit baby food were collected during the monitoring

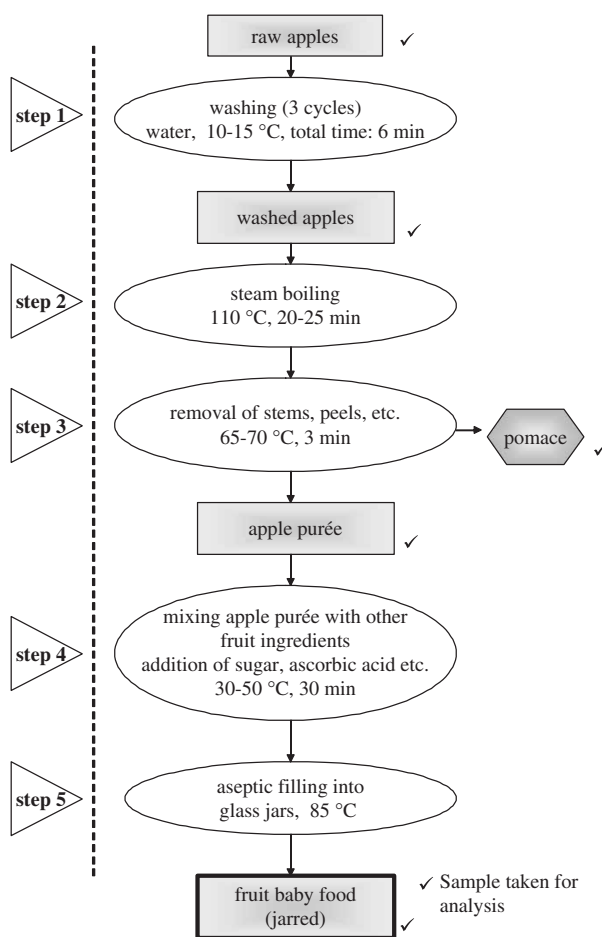


Figure 1. Flow chart of baby food production technology.

programme (2001–03). Apples (Golden Delicious, Idared and James Grieve varieties), which are the basic raw material for baby food production, were of local origin. After harvest, apples were stored in wooden boxes (weight of batch 350 kg) under controlled conditions (temperature  $10^{\circ}\text{C}$ ) for 2–3 weeks before industrial processing (for more details, see below) (Figure 1). Both fresh commodity and apple purée (an intermediate product) were checked for the presence of residues. For production of one batch of apple purée, fresh commodities from two to three farms were used.

Purées (processing ingredients) prepared from fruit other than apples were imported by our industrial partner from European Union countries. Those ingredients made from fresh fruit by similar procedures such as apple purée were supplied in sealed aseptic barrels (weight of content 200 kg) and stored at  $4^{\circ}\text{C}$  for a maximum of 1–2 weeks before processing (i.e. mixing with the apple purée to obtain the final products).

Table I. Details of field trials.

Field trial	Apple variety	Pesticide preparation <sup>a</sup>	Formulation type	Active ingredient <sup>b</sup>	Content of active ingredient	Application rate	Number of applications <sup>c</sup>	Pre-harvest interval (days)
F1	Golden Delicious	Euparen Multi.	Wettable powder	Tolylfluanid	50% (w/w)	2 kg ha <sup>-1</sup> <sup>d</sup>	2	7
F2	Idared	Sumithion Super	Emulsifiable concentrate	Fenitrothion	1000 g l <sup>-1</sup>	11 ha <sup>-1</sup> <sup>e</sup>	1	21
F3	Idared	Zolone 35 EC	Emulsifiable concentrate	Phosalone	350 g l <sup>-1</sup>	21 ha <sup>-1</sup> <sup>f</sup>	1	21

<sup>a</sup>Commercial name. <sup>b</sup>common name. <sup>c</sup>last application at the minimum permitted interval before harvest. <sup>d</sup>suspension: 2 kg Euparen Multi in 1000 litres water. <sup>e</sup>solution: 1 litre Sumithion Super in 1000 litres water. <sup>f</sup>solution: 2 litres Zolone 35 EC in 1000 litres water.

### Field work and processing

To get apples with incurred residues, three selected pesticide preparations were applied in one of the supplier's orchard during August 2003 (Table I). Application rates corresponded to label specifications; common spraying devices were employed for treatment. After the harvest, apples were stored at 10°C for 2 weeks. Intervals between pesticide application and processing were 3 weeks for apples obtained from field trial F1 and 5 weeks for apples from trials F2–3 (Table I). Apples were subjected to common technological operations, which are outlined in Figure 1. A total of 1000 kg fresh apples was processed yielding 940 kg apple purée and 60 kg pomace. Final products prepared from experimental apples (F1–3) differed in ingredients content. Apples treated with fenitrothion were used for the production of baby food containing 57% of apple purée. From apples treated with phosalone and tolylfluanid, final products containing 78 and 92% of apple purée, respectively, were produced. Two repeated series of processing experiments (each with the same initial amount of fresh apples obtained from trials F1–3) were performed.

### Sample collection and pre-analytical treatment

Sampling of fresh apples and fruit purées (except for apple purée) examined within the monitoring programme was performed about 1 week after their delivery to the industrial partner. Samples of washed apples, apple purée, pomace and fruit baby food (jarred products) obtained within the monitoring programme and/or processing study were collected during processing (see the sampling points in Figure 1).

After arrival in the laboratory, laboratory samples of fresh apples (about 2 kg) were subjected immediately to the following procedure. Whole apples were

chopped in the laboratory homogenizer and the pulp and peels were cut to pieces <5 mm. A total of 500-g portions of homogenized apples were stored in plastic bags at –18°C until analysed. Samples of fruit purée, pomace and fruit baby food obtained within the monitoring programme and/or processing study were stored in glass jars at –18°C until analysed.

### Pesticide standards and chemicals

Pesticide standards (purity ≥97%) were obtained from Dr Ehrenstorffer (Germany). The overview of analytes included in the monitoring programme together with reporting limits are summarized in Table II.

All organic solvents were of residue analysis grade; cyclohexane and toluene were supplied by Merck (Darmstadt, Germany); ethyl acetate was from Scharlau (Sentmenat-Barcelona, Spain). Sodium sulphate, anhydrous and sodium carbonate were obtained from Penta (Prague, Czech Republic).

### Apparatus

A Foss Tecator 2094 homogenizer (Foss, Eden Prairie, USA) was used for chopping fresh apples. A Ultra-Turrax T-25 homogenizer (IKA, Staufen, Germany) was used for sample extraction.

A vacuum rotary evaporator Büchi Rotavapor (Büchi, Flawil, Switzerland) equipped with a vacuum controller was used for the removal of organic solvents from the extracts.

An automated high-performance gel permeation chromatography (HPGPC) system Aspec XL 231 (Gilson, Villiers le Bel, France) equipped with 600 × 7.5 mm PLgel high-performance column (Polymer Laboratories, Church Stretton, Shropshire, UK) was used for purification of crude extracts with ethyl acetate–cyclohexane (1:1, v/v) as a mobile phase at the flow rate 1 ml min<sup>-1</sup>.

Table II. Pesticides included in the monitoring programme.

Pesticide	Reporting limit <sup>a</sup> (mg kg <sup>-1</sup> )	Pesticide	Reporting limit <sup>a</sup> (mg kg <sup>-1</sup> )
Acephate	0.010	Heptachlor	0.003
Aldrin	0.003	Heptenophos	0.010
Azinphos-ethyl	0.008	Iprodione	0.010
Azinphos-methyl	0.008	Kresoxim-methyl <sup>b</sup>	0.005
Beta-cyfluthrin	0.008	Malathion	0.008
Bifenthrin <sup>b</sup>	0.005	Metalaxyl	0.010
Bitertanol <sup>b</sup>	0.010	Methacrifos	0.010
Bromopropylate	0.005	Methamidophos	0.010
Bupirimate	0.010	Methidathion	0.010
Captan <sup>b</sup>	0.010	Mevinphos	0.010
Carbaryl	0.010	Monocrotophos	0.010
Chlorfenvinphos	0.009	<i>o,p</i> -DDD	0.003
Chlorothalonil	0.003	<i>o,p</i> -DDE	0.003
Chlorpropham	0.010	<i>o,p</i> -DDT	0.003
Chlorpyrifos <sup>b</sup>	0.008	Omtoate	0.010
Chlorpyrifos-methyl <sup>b</sup>	0.008	<i>p,p</i> -DDD	0.003
Cyhalothrin- $\lambda$ <sup>b</sup>	0.006	<i>p,p</i> -DDE	0.003
Cypermethrin <sup>b</sup>	0.010	<i>p,p</i> -DDT	0.003
Cyprodinil <sup>b</sup>	0.010	Parathion	0.006
Deltamethrin <sup>b</sup>	0.006	Parathion-methyl	0.006
Diazinon	0.010	Penconazole <sup>b</sup>	0.010
Dichlofluanid	0.010	Permethrin	0.005
Dichlorvos	0.010	Phosalone <sup>b</sup>	0.009
Dieldrin	0.003	Phosmet	0.010
Difenoconazole <sup>b</sup>	0.010	Phosphamidon	0.010
Diphenylamine	0.006	Pirimicarb <sup>b</sup>	0.010
Dimethoate <sup>b</sup>	0.010	Pirimiphos-methyl <sup>b</sup>	0.008
Endosulfan- $\alpha$	0.003	Procymidone	0.005
Endosulfan- $\beta$	0.003	Propham	0.010
Endosulfan-SO <sub>4</sub>	0.003	Pyridaben <sup>b</sup>	0.010
Endrin	0.003	Quinalphos	0.010
Ethion	0.008	Tebuconazole <sup>b</sup>	0.010
Etrimfos	0.010	Tetraconazole <sup>b</sup>	0.010
Fenarimol <sup>b</sup>	0.010	Tetradifon	0.006
Fenitrothion <sup>b</sup>	0.005	Thiabendazole	0.010
Fenoxycarb <sup>b</sup>	0.010	Tolclofos-methyl	0.006
Fenthion	0.010	Tolyfluanid <sup>b</sup>	0.006
Fenvalerate	0.006	Triadimefon <sup>b</sup>	0.006
Folpet	0.006	Triazamate <sup>b</sup>	0.010
Hexachlorobenzene	0.003	Triazophos	0.010
HCH- $\alpha$	0.003	Trifloxystrobin <sup>b</sup>	0.006
HCH- $\beta$	0.003	Vinclozolin	0.006
HCH- $\gamma$	0.003		
HCH- $\delta$	0.003		

<sup>a</sup>Reporting limit corresponds to the practical limit of quantification (LOQ) of analytical method. <sup>b</sup>registered for use in apples in the Czech Republic.

A gas chromatograph HP 6890 Plus (Hewlett-Packard, Palo Alto, USA) equipped with an auto-sampler (HP 7683) and capillary column connected in parallel through a Y-piece to a nitrogen-phosphorus detector (NPD) and an electron capture detector (ECD) was used for the identification/quantification of pesticide residues in purified extracts.

A gas chromatograph HP 6890 II (Hewlett-Packard) equipped with an autosampler, capillary column and mass selective detector (quadrupole) HP 5973 was used for confirmation of the positive samples.

#### Multiresidue analytical method

*Preparation of pesticide solutions and matrix-matched calibration standards.* Stock solutions of individual pesticide standards in toluene were used for preparation of standard mixture, S<sub>m</sub>. Concentrations of individual analytes in standard mixture were in the range 3.1–15.7 µg ml<sup>-1</sup>.

The standard mixture, S<sub>m</sub>, was further diluted by toluene (10×, 20×, 100×, 200×, 1000× and 2000×, respectively) to obtain six standard solutions (S<sub>1</sub>–S<sub>6</sub>), which were used for the preparation of

matrix-matched calibration standards containing an aliquot corresponding to 1 g blank matrix. For validation experiments and a performance check, spiking solutions in ethyl acetate were prepared.

*Extraction.* Aliquot portion (25 g) of homogenized sample was weighed into a glass beaker. Before extraction of strawberry and raspberry purée, the pH of the matrix was adjusted by the addition of 1 ml  $\text{Na}_2\text{CO}_3$  solution ( $c = 1 \text{ mol l}^{-1}$ ). A total of 100 ml ethyl acetate and 75 g anhydrous sodium sulphate was added and the mixture homogenized (2 min) using an Ultra-Turrax. The suspension was filtered through a layer of anhydrous sodium sulphate. The filtrate was vacuum evaporated and the residue dissolved in an ethyl acetate–cyclohexane mixture (1:1, v/v) and made up to 50 ml.

*Clean-up.* Crude extract (2 ml) containing 0.5 g original matrix in 1 ml was automatically loaded onto a gel column via the sample loop. The first portion of eluate was discarded; the second one (15.0–31.0 ml) was collected. This ‘pesticide’ fraction was vacuum concentrated and the residual solvent removed with a gentle stream of nitrogen. The residue was dissolved in 1 ml toluene and analysed by gas chromatography.

*Separation, detection and quantification.* All the gas chromatographic (GC) separations (regardless of the GC instrument used) were carried out under the same operating conditions: the injection (1  $\mu\text{l}$  sample or standard solution) was carried out by the pulsed splitless technique (injector temperature  $250^\circ\text{C}$ , injection pulse 60 psi, injection pulse period 2 min); capillary column DB5-MS (60 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ; J&W Scientific, Folsom, USA) was used for separation; temperature programme: initial temperature  $90^\circ\text{C}$  (2 min),  $5^\circ\text{C min}^{-1}$  to  $180^\circ\text{C}$  (0 min),  $2^\circ\text{C min}^{-1}$  to  $280^\circ\text{C}$  (5 min); helium was used as the carrier gas: programmed flow:  $0.5 \text{ ml min}^{-1}$  (35 min),  $0.05 \text{ ml min}^{-1}$  to  $2 \text{ ml min}^{-1}$  (0 min),  $0.5 \text{ ml min}^{-1}$  to  $3 \text{ ml min}^{-1}$ ; detectors: (1) NPD: temperature  $300^\circ\text{C}$ , hydrogen flow  $3 \text{ ml min}^{-1}$ , air flow  $60 \text{ ml min}^{-1}$ , nitrogen flow (make-up)  $10 \text{ ml min}^{-1}$ ; (2) ECD: temperature  $300^\circ\text{C}$ , anode gas flow (nitrogen)  $6 \text{ ml min}^{-1}$ , make-up gas flow (nitrogen)  $60 \text{ ml min}^{-1}$ ; (3) MSD-quadrupole analyser (operated in SIM mode), interface temperature  $280^\circ\text{C}$ , ion source temperature  $230^\circ\text{C}$ , ionization technique: electron ionization (EI).

All chromatographic data were processed using ChemStation (A.04.05, Hewlett-Packard) software. A six-point matrix-matched calibration (compensation of matrix effects) was used for quantification of target analytes. For each peak areas were plotted against the concentration and a linear calibration curve was constructed. The peak area of each calibration point represented the average obtained from two matrix standards analysed before and after the particular batch of test samples. The calculated results were not corrected for recovery.

#### *Quality control*

A validated multiresidue method was employed for sample analyses (compliance with ISO/IEC 17025 (1999) was accredited by the Czech Accreditation Institute). Experiments aimed at the assessment of accuracy (trueness and precision) were performed within the validation scheme. Two series of six replicates spiked before extraction on two different concentration levels (concentration range of target pesticides was in the first set  $0.155\text{--}0.785 \text{ mg kg}^{-1}$ , in the second one  $0.031\text{--}0.157 \text{ mg kg}^{-1}$ ) were analysed. For all compounds, recoveries in the range 70–110% were obtained. To improve the recovery of extraction, an increase of pH of strawberry and raspberry purée up to 7 by the addition of  $\text{Na}_2\text{CO}_3$  solution ( $c = 1 \text{ mol l}^{-1}$  in distilled water) was first carried out. The limit of detection (LOD) was evaluated from a chromatogram of the matrix-matched standard ( $S_6$ ) and it represented the concentration of the analyte that generated a response for which the average signal-to-noise ratio  $S/N = 3$  was achieved. LOQ represents the minimum concentration of the analyte that can be quantified with acceptable precision (European Union guidelines for quality control procedures; European Union 2004). The LOQ of each analyte was calculated as  $3 \times \text{LOD}$ . The reporting limits (Table II) corresponded to the practical limits of quantification (LOQ), i.e. LOQs that were achievable throughout the whole monitoring period.

Within each batch of samples, a spiked sample (identical matrix, concentration of target analytes  $0.031\text{--}0.157 \text{ mg kg}^{-1}$ ) was analysed to check the performance of the analytical method. Samples that contained residues above the MRLs were re-analysed to confirm that the limit was exceeded.

Over the years, laboratory has successfully participated in proficiency testing schemes organized by either the Central Science Laboratory (York, UK), i.e. FAPAS® (CSL 2001, 2002, 2003), or by the National Food Administration Uppsala, Sweden (European Commission 2002, 2003).

## Results and discussion

### Residues in apples supplied for baby food production

Similar to growing other food crops, a wide range of pesticide preparations might be applied in conventional farms during the pre-harvest period and/or storage of apples. Organophosphates, carbamates and pyrethroids are the most common active ingredients of formulations used for the protection of apple trees against insects such as codling moth (*Cydia pomonella*), apple sawfly (*Hoplocampa testudinea*) and others. The occurrence of residues may also result from the use of preparations containing sulphamides, triazoles or strobilurines that are widely used to protect apples against fungal diseases such as scab (*Venturia inaequalis*), powdery mildew (*Podosphaera leucotricha*) and other rots.

Altogether, 72 modern pesticides that may occur in apples and/or other fruit ingredients were controlled in our study. In addition, 15 persistent organochlorine pesticides and related compounds that can be transported through atmosphere were included in the monitoring. Note that while only compounds amenable to GC were included in current experiments, in the follow-up study that was finished at the end of 2004, more polar pesticides were also monitored employing LC/MS-MS procedure.

Considering the data obtained within the whole monitoring period (2001–03), pesticide residues were detected in 59.5% of samples (LODs = 0.001–0.005 mg kg<sup>-1</sup>). Nevertheless, only 1.4% samples (i.e. 3/220) exceeded the European Union MRLs established for fresh commodity. In all these cases, fenoxycarb residues (MRL = 0.05 mg kg<sup>-1</sup>) were responsible for the violation. The contamination of samples obtained in this study is in line with findings reported for apples in many other recent national monitoring programmes; the percentage of apple samples containing detectable pesticide residues ranged from 16 to 75% (Akiyama et al. 2002; EU 2003; US FDA 2003). Figure 2 shows the comparison of the present data with surveillance results reported by the Czech Agriculture and Food Inspection Authority (CAFIA). Note that not only fruit from the local production chain, but also imported apples are involved in the CAFIA report. The apparently higher contamination rate found in the present study was due to very low reporting limits (their values were 0.01 mg kg<sup>-1</sup> and lower; Table II). The MRLs for fresh apples targeted by CAFIA were in many cases higher than 0.01 mg kg<sup>-1</sup>. Hence, even less sensitive measurements (higher LODs) still allow the reliable control of legislative requirements. In spite of that,

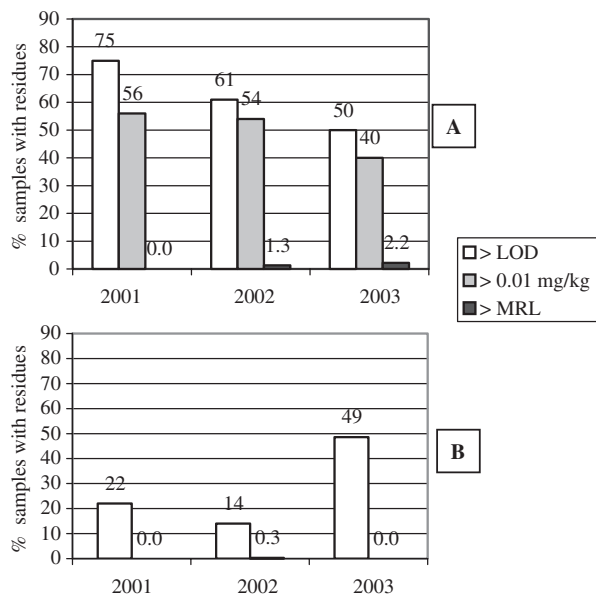


Figure 2. Occurrence of pesticide residues in fresh apples found within monitoring programme presented in this study (A), and monitoring data for fresh apples reported by Czech Agriculture and Food Inspection Authority (B, CAFIA 2002–04).

an industrial partner insisted on low LOQs to avoid any problem resulting from the transfer of residues into processed product.

Generally, comparison of the incidence rate of pesticide residues recognized in this study with information obtained in other national monitoring programmes is rather difficult because of differences in the detection/quantification limits of analytical procedures employed for sample examination as well as due to only a partial overlap of the spectrum of pesticides involved in various reports (in most cases only summary data are available, hence it is not always possible to obtain the detailed information needed for comprehensive comparison). Under these circumstances, comparison of the present data with results published by CAFIA can be considered as the most relevant. The list of monitored pesticides analysed was almost identical.

As shown in Figure 2A, the highest contamination rate, when expressed as the percentage of samples containing detectable residues, was found at the beginning of the monitoring study. At that time the discussion of strategy suitable for apple treatment with respect to specific requirements for minimal residues in crops used for baby food production was initiated. In terms of levels/frequency of residues, the most problematic occurrence was mainly with captan, chlorpyrifos-methyl, fenitrothion, phosalone and tolylfluanid. Figures 3A–C shows the response of farmers to the request for the minimal use of preparations leaving high residues in

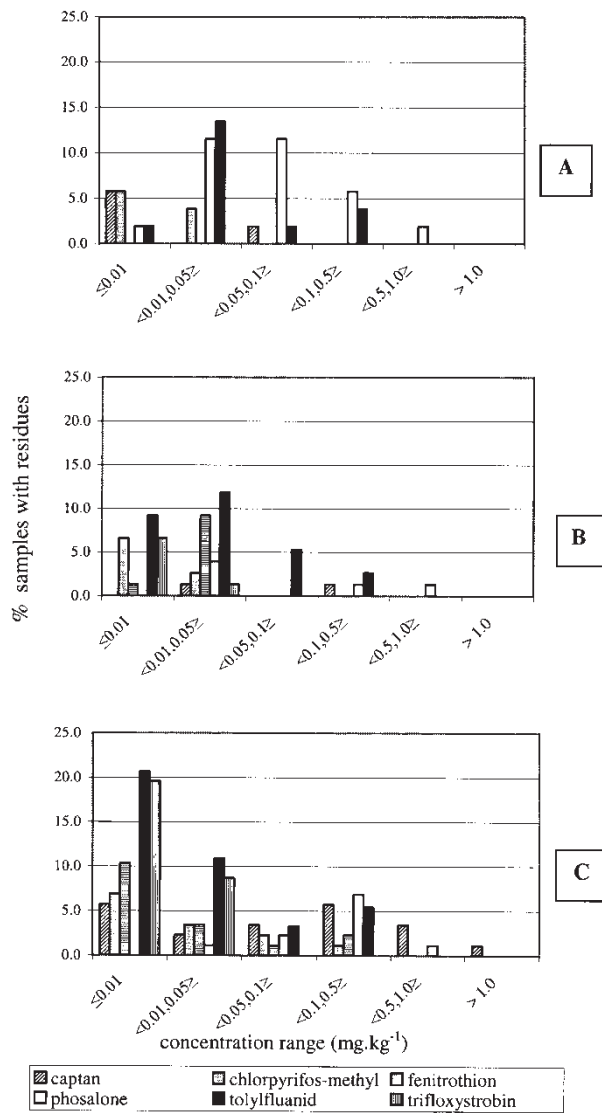


Figure 3. Frequency distribution of selected pesticide residues in fresh apples: A, 2001; B, 2002; and C, 2003.

treated apples. The most pronounced change in treatment practices occurred in case of preparations containing phosalone as an active ingredient. In the first monitoring year, 19% of apple samples contained residues of phosalone exceeding  $0.05 \text{ mg kg}^{-1}$ ; in the next year this was only 3%. However, in 2003, some increase of phosalone residues occurred again (11% samples contained residues of this insecticide). This result might be attributed to different weather conditions that were probably less favourable for post-treatment residue dissipation. Note that in none of apple samples was the  $2 \text{ mg kg}^{-1}$  MRL exceeded. Actually, the residues were far below this level. The changes of frequency distribution among individual years were also found for fenitrothion. Its residues were not detected in 2001. However, in 2002–03 this insecticide was found quite frequently.

Farmers probably started to use this insecticide as a substitute for the more persistent phosalone. As shown in Figures 3A–C, residues of fenitrothion were detected in a lower concentration range as compared with phosalone.

The summary information on residues in fresh apples is given in Table III. Several pesticides leaving residues only in the lowest concentration range were identified (e.g. bifenthrin, trifloxystrobin).

#### *Residues in baby food ingredients (fruit purées)*

As shown in Table IV, pesticide residues were found in less than 50% of samples of fruit ingredients (except for raspberry purée). When considering the whole data set, only 19% of samples contained residues above  $0.01 \text{ mg kg}^{-1}$ . The lower extent of contamination of fruit ingredients is obviously due to the partial elimination of residues during the processing (washing, boiling) of fresh fruit. Similar trends in the residue levels across the production chain were reported by several authors (Holland et al. 1994; Christensen et al. 2003; Rasmussen et al. 2003). Chemical reactions (hydrolysis) and/or physical processes (volatilization) are responsible for the elimination of residues.

From a comparison of results for apple purées shown in Table IV with the list of pesticides found in the respective fresh commodities, it can be seen that only 30% of compounds were transferred into this processing intermediate. Fenitrothion and especially phosalone represent the only residues in apple purée that were found in concentrations above  $0.01 \text{ mg kg}^{-1}$ .

As regards other types of pureés, those products prepared from pears, peaches and apricots were contaminated mainly by organophosphorus and carbamate insecticides. Strawberry and raspberry purées frequently contained residues of dicarboximide fungicides represented by procymidone and vinclozolin. The concentration of most of residues was less than  $0.05 \text{ mg kg}^{-1}$ . Nevertheless, several compounds (carbaryl, iprodione, procymidone, thiabendazole) were present at relatively high levels.

#### *Residues in final products (fruit baby food)*

Pesticide residues were detected in 16% samples of fruit baby food ( $\text{LODs} = 0.001\text{--}0.005 \text{ mg kg}^{-1}$ ). In 9% of them the content of residues exceeded the MRL ( $0.01 \text{ mg kg}^{-1}$ ). A low percentage of 'positive' fruit baby food samples was also found in reports summarizing results of monitoring programmes realized in various countries (NFA

Table III. Results of monitoring programme 2001–03: fresh apples (220 samples).

Pesticide	MRL (mg kg <sup>-1</sup> )	Frequency distribution of pesticide residues <sup>a</sup> (%)					>1.0 (mg kg <sup>-1</sup> )
		≤0.01 <sup>b</sup> (mg kg <sup>-1</sup> )	<0.01, 0.05 ≥ (mg kg <sup>-1</sup> )	<0.05, 0.1 ≥ (mg kg <sup>-1</sup> )	<0.1, 0.5 ≥ (mg kg <sup>-1</sup> )	<0.5, 1.0 ≥ (mg kg <sup>-1</sup> )	
Azinphos-methyl	0.5	1.4	0.5	–	–	–	–
Bifenthrin	0.05	0.9	0.9	–	–	–	–
Bitertanol	2.0	0.5	0.5	0.5	–	–	–
Bromopropylate	2.0	1.4	0.5	–	0.5	–	–
Captan	3.0	3.7	1.4	1.9	2.8	1.4	0.5
Chlorpyrifos	0.5	0.5	0.9	–	–	–	–
Chlorpyrifos-methyl	0.5	6.5	3.3	0.9	–	–	–
Cypermethrin	1.0	–	–	0.5	–	–	–
Cyhalothrin-lambda	0.1	0.5	–	–	–	–	–
Cyprodinil	1.0	0.5	–	–	–	–	–
Deltamethrin	0.1	–	1.9	–	–	–	–
Fenitrothion	0.5	4.7	4.7	0.5	0.9	–	–
Fenoxycarb	0.05	–	–	1.4	–	–	–
Kresoxim-methyl	0.2	0.5	1.9	–	–	–	–
Penconazole	0.1	0.9	0.9	–	–	–	–
Permethrin	1.0	0.5	–	–	–	–	–
Phosalone	2.0	0.5	4.7	3.7	4.7	1.4	–
Pirimicarb	0.5	2.3	0.5	–	–	–	–
Pirimiphos-methyl	2.0	0.5	–	–	–	–	–
Tebuconazole	0.5	0.5	–	–	–	–	–
Tetraconazole	0.5	3.3	1.4	–	–	–	–
Tolyfluanid	1.0	12.3	11.8	3.6	4.1	–	–
Trifloxystrobin	0.5	10.7	1.2	–	–	–	–
Triazamate	0.1	0.9	0.9	–	–	–	–

<sup>a</sup>Total number of contaminated samples = 100%. <sup>b</sup>interval includes both quantified and non-quantified (<reporting limit) results.

2003; US FDA 2003; PSD 2004). For instance, the US FDA found pesticide residues in 6% samples of fruit baby food.

Organophosphorus insecticides chlorpyrifos and phosalone together with dicarboximide fungicide procymidone were the only analytes found in analysed samples within the presented monitoring programme (Table V). The latter compound was not detected in fresh apples. However, it was transferred into the final product from fruit ingredients. The highest residue concentration in examined baby food samples was found for phosalone (0.034 mg kg<sup>-1</sup>).

#### Multiple residues

Most of 'positive' fruit samples contained the residue of only one pesticide. Nevertheless, as shown in Figure 4, the occurrence of multiple residues was also found in some samples. Overall, multiple residues were detected in 25% of fresh apples, in 4% of apple purée and in 8% of the other fruit purées used as ingredients. The proportion of samples of fresh apples that contained multiple residues is comparable with results from European Union countries (EU 2003).

#### Processing study

A processing study was carried out to investigate the effect of particular technological steps on the content of pesticide residues in fruit baby food. As described above, three lots of apples (each treated with different pesticide formulation) were available. Before performing the experiments, 'critical' technological operations that might result in a change of residues content were identified as important for sampling.

The decrease of residues due to their washing off from the apple surface was expected in step 1 of Figure 1. A further decrease of residue levels was expected in step 2 as the result of residue thermal breakdown, volatilization, etc. Sampling of fresh apples, the production intermediates, waste products (pomace) and final products was performed to document the distribution of residues.

As shown in Table VI, none (phosalone) or only a negligible (fenitrothion, tolyfluanid) decrease of residues occurred during the washing step, although all of these compounds represent contact pesticides and their residues are primarily deposited on the surface of the treated crop. However, all these pesticides are relatively



Table IV. Results of monitoring programme 2001–03: fruit purée.

Commodity	Number of samples	Samples with residues above LOD (%)	Samples with residues above the MRL 0.01 mg kg <sup>-1</sup> (%)	Pesticide	Frequency distribution of pesticide residues <sup>a</sup> (%)			
					≤0.01 <sup>b</sup> (mg kg <sup>-1</sup> )	<0.01, 0.05 ≥ (mg kg <sup>-1</sup> )	<0.05, 0.1 ≥ (mg kg <sup>-1</sup> )	<0.1, 0.5 ≥ (mg kg <sup>-1</sup> )
Apple purée	119	29	12	Chlorpyrifos	2.9	–	–	–
				Chlorpyrifos-methyl	5.7	–	–	–
				Fenitrothion	5.7	5.7	–	–
				Phosalone	40.0	31.4	–	–
				Pirimicarb	14.3	–	–	–
				Tolyfluanid	8.6	–	–	–
				Triazamate	5.7	–	–	–
Pear purée	20	20	15	Trifloxystrobin	8.6	–	–	–
				Azinphos-methyl	25.0	–	–	–
				Bromopropylate	25.0	–	–	–
				Chlorpyrifos	25.0	–	–	–
				Chlorpyrifos-methyl	25.0	–	–	–
				Phosalone	–	25.0	–	–
				Procymidone	–	50.0	–	–
Peach purée	30	47	37	Carbaryl	–	–	7.1	–
				Cypermethrin	–	7.1	–	–
				Chlorpyrifos	7.1	7.1	7.1	–
				Fenarimol	13.3	–	–	–
				Iprodione	–	–	–	7.1
				Phosalone	7.1	42.9	–	–
				Pirimicarb	–	21.9	–	–
				Procymidone	–	–	–	7.1
				Tebuconazole	14.3	–	–	–
				Triazophos	7.1	–	–	–
				Bromopropylate	50.0	25.0	–	–
Apricot purée	29	14	14	Phosalone	–	50.0	–	–
				Thiabendazole	–	–	25.0	–
				Triazophos	–	25.0	–	–
				Bromopropylate	7.7	–	–	–
				Chlorpyrifos-methyl	7.7	–	–	–
Strawberry purée	41	32	12	Iprodione	7.7	–	–	–
				Malathion	–	7.7	–	–
				Procymidone	53.8	23.1	–	–
				Vinclozolin	7.7	7.7	7.7	–
				Bifenthrin	14.3	–	–	–
				Bromopropylate	7.1	–	–	–
Raspberry purée	19	74	58	Carbaryl	–	–	–	7.1
				Procymidone	21.4	35.7	21.4	14.3
				Vinclozolin	21.4	7.1	–	–

<sup>a</sup>Total number of contaminated samples = 100%. <sup>b</sup> interval includes both quantified and non-quantified (<reporting limit) results.

Table V. Results of monitoring programme 2001–03: fruit baby food (44 samples).

Pesticide	Frequency distribution of pesticide residues <sup>a</sup> (%)		
	≤0.01 (mg kg <sup>-1</sup> )	<0.01, 0.02 ≥ (mg kg <sup>-1</sup> )	<0.02, 0.04 ≥ (mg kg <sup>-1</sup> )
Chlorpyrifos	0.0	0.0	14.3
Phosalone	42.9	14.3	14.3
Procymidone	0.0	14.3	0.0

<sup>a</sup>Total number of contaminated samples = 100%.

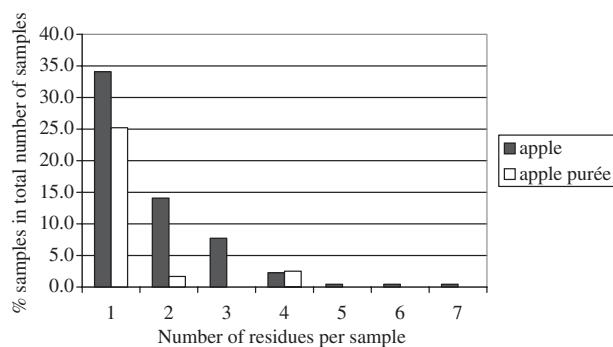


Figure 4. Multiple residues in apples and apple purée.

lipophilic compounds (the *n*-octanol–water partition coefficients,  $\log K_{ow}$ , for fenitrothion, phosalone and tolylfluanid are 3.43, 4.01 and 3.90, respectively; Tomlin 2002). Consequently, the penetration of these pesticides into the deeper layers of surface waxes may occur during the period following the application. This phenomenon, characterized as ‘ageing of the residue’ and observed during fruit storage, was considered by Holland et al. (1994) when explaining the low efficiency of the washing of stored products. On the other hand, in some studies, the reduction of residues by washing was achieved. For instance, Cabras et al. (1998a) obtained some decontamination of plums in this way (e.g. residues of iprodione decreased after 5 min of washing to about 40% of the initial concentration in fresh plums). The discrepancy in the effectiveness of washing was in the latter case attributed to the adsorption of residues onto dust particles deposited on the fruit surface. The extent of penetration into epicuticular wax was limited. Hence, most of the residues could be mechanically removed by the water stream together with solid particles.

In our experiments, substantial reduction of residues was observed after steam boiling, which was followed by the removal of peels/stems. As mentioned above, various physico-chemical

factors might be responsible for the reduction of residues in processed fruit. Considering the conditions employed in the steps identified above as ‘critical’ and the values of calculated processing factors, the fate of target pesticides can be characterized as follows.

Washing is ineffective in terms of the removal of phosalone. When considering its total amount in the final product and waste, only 6% of residues originally contained in fresh apples were lost. Most of the residues (81%) were transferred into pomace, obviously because of their retention in waxes contained in peels. Note that the apparent decrease of the phosalone level in final baby food is not caused by its breakdown but only by ‘dilution’ of apple purée by the addition of other fruit ingredients (Figure 1, step 4).

Volatilization (specifically in the case of fenitrothion, which has the highest vapour pressure among studied pesticides, 18 mPa at 20°C; Tomlin 2002) and breakdown (especially for tolylfluanid, which is known to be prone to hydrolysis) at elevated temperatures were probably the main processes causing elimination of these compounds. While no detectable residues were found in apple purée, only 19 and 30% of the original content of fenitrothion and tolylfluanid, respectively, were determined in pomace.

## Conclusions

A monitoring study employing a highly sensitive multiresidue method documented extensive contamination of apples from conventional farming. Although the residues in fresh crops treated in accordance with principles of good agriculture practice usually do not exceed MRLs established for fresh commodity, their occurrence in the baby food supply chain is of concern. Considering the strict regulation (0.01 mg kg<sup>-1</sup>) applied for pesticides potentially contained in processed cereal-based foods and baby foods for infants and young children, producers need to identify preparations leaving (relatively) high residues to avoid any contamination problem.

Processing factors determined experimentally under specific production conditions provide important information. Although a substantial decrease of residues during baby food production may be expected, pesticide residues (as observed in the monitoring study) may be still found in fruit baby food. Therefore, baby food producers should take appropriate measures (especially for careful quality checking of fresh fruit) to minimize pesticide residues in the final products.

Table VI. Residues in fresh apples and experimental processing factors.

Pesticide	Technological operation								
	Fresh apples	Washing		Steam boiling followed by removal of peels/stems				Baby food <sup>a</sup>	
		Washed apples		Apple purée		Pomace			
	Concentration (mg kg <sup>-1</sup> )	Concentration (mg kg <sup>-1</sup> )	Processing factor	Concentration (mg kg <sup>-1</sup> )	Processing factor	Concentration (mg kg <sup>-1</sup> )	Processing factor	Concentration (mg kg <sup>-1</sup> )	Processing factor
Fenitrothion	0.016	0.014	0.86	<LOD (LOD = 0.001)	–	0.053	3.31	<LOD (LOD = 0.001)	–
Phosalone	0.059	0.057	0.97	0.011	0.18	0.775	13.14	0.008	0.13
Tolylfluanid	0.029	0.025	0.86	<LOD (LOD = 0.002)	–	0.142	4.89	<LOD (LOD = 0.002)	–

<sup>a</sup>Content of phosalone in the product was expressed as content in apple purée. Because two series of processing experiments were performed, the concentration represents the mean of two determinations.

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