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EFFECTS OF STORAGE AND PROCESSING ON PESTICIDE RESIDUES IN PLANT PRODUCTS

(Technical Report)

Prepared for publication by

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Pesticides report 31: Effects of storage and processing on pesticide residues in plant products (Technical Report)

Abstract

Residues of pesticides in food are influenced by the storage, handling and processing that occurs between harvesting of raw agricultural commodities and consumption of prepared foodstuffs. Reviewing the extensive literature showed that in most cases these steps lead to large reductions in residue levels in the prepared food, particularly through trimming, washing and cooking operations. Residues of post harvest insecticide treatment on stored staples such as cereal grains and oil seeds generally decline only rather slowly. However processing into foods again results in large losses except for unrefined oils. The behaviour of residues in storage and processing can be rationalised in terms of the physico-chemical properties of the pesticide and the nature of the process. EBDC fungicides are examined in more detail as a class of fungicides of concern due to the formation of the toxic breakdown product ETU. Recommendations are provided for the conduct of storage or processing studies on fate of pesticide residues in food so that data obtained is relevant, comparable and may be extrapolated to other situations.

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1. INTRODUCTION

A large gap exists between consumer and scientific perceptions on the risks that pesticide residues in food pose to human health relative to other dietary risks. One cause of this misconception has been the emphasis placed on "worst case" evaluations and extrapolations of available data e.g. assuming that all crops are treated with pesticides and that the resulting residues in food as consumed are at maximum permitted levels (Ref. 1, 2, 3, 4, 5).

Controls on pesticide residues in crops are generally based on Maximum Residue Limits (MRL's) which are set using field trial data for a particular pesticide to arrive at the highest residue levels expected under use according to Good Agricultural Practice (GAP). Primary residue studies on food crops are mainly carried out on samples that have received minimal post harvest handling except for perhaps minor trimming and that have been stored deep frozen prior to analysis. Although MRL's are a credible and useful means of enforcing acceptable pesticide use, they are inadequate as a guide to human health risks from residues. Total diet studies have consistently shown that using MRL's as a basis for calculating human dietary consumption of pesticides over-estimate actual intakes by one to three orders of magnitude (Ref. 2, 3). A previous IUPAC report (Ref. 5) has recommended a stepwise approach to evaluating risks from pesticide residues in food which includes allowance for losses in processing.

An important factor leading to reduction of any residues left on crops at harvest are processing treatments such as washing, peeling, canning or cooking that the majority of foods receive prior to consumption. These can often substantially reduce the residue levels on or in food that has been treated with pesticides. For example, a study tracking chlorothalonil on crops from field to table showed that normal handling and processing of fresh cabbage, celery, cucumbers and tomatoes led to large reductions in residue levels (Ref. 6). The actual exposure of US consumers to chlorothalonil through diet was calculated to be only 2% of the maximum theoretical level estimated from MRL's. However in some special cases more toxic by-products or metabolites can be formed during processing. A much studied example is the formation of ethylenethiourea (ETU) from ethylene-bisdithiocarbamate fungicides (Ref. 7). Unit processes on food can also result in residues being redistributed or concentrated in various separated fractions of food or feed.

In principle, the magnitude of many of these effects can be predicted for particular pesticides from physico-chemical parameters such as solubility, hydrolytic rate constants, volatility, octanol-water partition coefficients and the actual physical location of residues. In practice lack of detailed data, particularly on the interactions with food components, means a more empirical approach has been followed. More research is required on some of these fundamental physico-chemical processes with pesticides in the context of food processing. However the general effects of processing may be rationalised by using these considerations.

Regulatory authorities are increasingly interested in such data. Studies into effects of storage and some commercial processing techniques on residues in food are a part of the registration requirements for pesticides in many countries. The Joint FAO/WHO meeting on pesticide residues (JMPR) considers effects of processing as part of their reviews of residue data for particular pesticides. Some member governments are also considering the introduction of formal protocols to evaluate effects of typical domestic food preparation. Data on processing is considered necessary to reassure consumers as to the actual versus hypothetical (from MRL's) exposure to residues in food. The Delaney amendment in the USA governing carcinogenic food additives also has had significant ramifications for registration of certain pesticides particularly where residues have been found to concentrate in particular food fractions (Ref. 1).

Several reviews have appeared over the last 15 years on the effects of processing on pesticide residues in food (Ref. 8, 9, 10). The emphasis has been mainly on the organochlorine insecticides. The US food industry has published some data showing large reductions in residue levels during commercial processing of vegetables (Ref. 11) and the industry has established a database for residues in processed foods (Ref. 12). The use of radiotracers in pesticide residue studies in stored products has been the subject of a conference proceedings (Ref. 13). Persistence and distribution of residues of post harvest applied agrochemicals in fresh fruits and vegetables have been the subject of a recent thorough review (Ref. 14).

This paper examines recent data on the effects of storage or processing on pesticide residues with a view to rationalising the information on modern pesticides. Relevant information has been extracted from the literature and from the in-depth reviews of pesticide residue data undertaken annually by JMPR and published by the Plant Production and Protection division of FAO. These reports contain detailed company data that is not otherwise readily accessible. However, there have been limitations

in the experimental designs or in the type of data collected from many processing studies. Recommendations are developed for approaches to research into effects of processing on residues.

2. MECHANISMS FOR POST-HARVEST ALTERATION OF RESIDUES IN FOOD

Basic processes acting on pesticide residues in the field can continue to operate after crops are harvested. These include:

- volatilisation
- hydrolysis
- penetration
- metabolism, enzymatic transformation
- oxidation

Photodegradation generally ceases or is greatly reduced once a crop is removed from the field situation.

The use of various physical unit processes on crops such as washing, trimming, peeling or juicing apportions residues between various processed food fractions. This often leads to direct reductions in the levels of residues in remaining edible portions. However lipophilic pesticides tend to concentrate in tissues rich in lipids and thus residue levels can increase in fractions such as vegetable oils. Processes involving heat or chemicals can increase volatilisation, hydrolysis or other chemical degradation and thus reduce residue levels. However drying processes may result in higher concentrations of residues due to loss of moisture.

3. EFFECTS OF STORAGE ON RESIDUES

3.1 Cereal Grains

Grains are frequently stored long term (3 - 36 months) at ambient temperatures in bulk silos where insecticides may be applied post-harvest to reduce losses from storage pests (Ref. 15, JMPR 1981). Grain based foods therefore have the potential to be a major source of residues in the diet for these insecticides. Analytical methods for residues in grains have been reviewed (Ref. 16).

Studies on grain following post-harvest treatments with insecticides have generally shown that residues only decline rather slowly (Ref. 15, 17, 18). Residues of the more lipophilic materials tend to remain on the seed coat although a proportion can migrate through to the bran and germ which contain high levels of triglyceride (Ref. 19). Storage fungi may assist in the degradation of insecticides (Ref. 19). Typical results are those for malathion and pirimiphos-methyl in rape seed (Ref. 20). Residues generally showed little decrease over 32 weeks at 20°C and 50-70% relative humidity. At 30°C malathion residues decreased by 30-40% while pirimiphos-methyl residues remained constant. Organochlorine and synthetic pyrethroid residues are also very stable under silo conditions (Ref. 18, 21). Data for insecticides in stored cereal grains have been reviewed (JMPR 1981). Quite a high proportion of the residues can be associated with the dust and other fine detritus which is removed when the wheat is cleaned before milling. For example deltamethrin levels on stored grain of 0.52 mg/kg were reduced to 0.42 mg/kg after cleaning (JMPR 1992).

Persistence of several insecticides in grains and beans stored under typical conditions have been studied in a number of countries using radiotracer techniques (Ref. 13). Extractable residues of parent malathion after storage periods of 3 - 9 months ranged from 16-65% of the applied doses. Considerable amounts of hydrolysis products were also present and bound residues (radioactivity unextractable by the solvent used) comprised 5-20% of the applied dose. Chlorpyrifos-methyl, fenvalerate and pirimiphos-methyl were generally more persistent than malathion. High proportions of the terminal residues of chlorpyrifos-methyl and fenvalerate were found to be in the bound form (ca 20% of the applied dose) compared to only 1-2% for pirimiphos-methyl. FAO/IAEA has published model protocols for conduct of studies on residues of protectant insecticides and methyl bromide fumigant in stored foods using radioactive tracer techniques (Annexes 1 & 2, Ref. 13).

Australian workers have developed predictive models for the rate of dissipation of residues of insecticides in grain stored under stable conditions of temperature and humidity (Ref. 22, 23). The first order rate constant for degradation of fenitrothion in various grains was dependent on temperature, following an Arrhenius equation, and was proportional to the water activity. The later parameter can be calculated from moisture contents using empirical equations for each grain type

(Ref. 24). The model has been extended to a variety of other insecticides of the O-P, carbamate and pyrethroid classes (Ref. 25, 26). The mechanism proposed was that insecticides adsorbed to the grain are desorbed by water and becomes available for degradation by enzymes, metal ions and other active molecules. Table 1 summarises the half-lives and temperature coefficients for degradation of protectants in wheat under reference conditions of 30°C and 50% relative humidity.

Table 1: Half lives and temperature coefficients for degradation of insecticides in wheat stored at 30°, 50% rel. humidity.
 $\ln(t_{0.5}) = K.T + C$

Insecticide	Half-life, $t_{0.5}$ (weeks)	Temperature coefficient, K (°C ⁻¹)
bioresmethrin	38	0.031
carbaryl	21	0.031
cyfluthrin	70	-
chlorpyrifos-methyl	19	0.040
deltamethrin	>50	-
dichlorvos	2	-
fenitrothion	14	0.036
fenvalerate	>50	-
malathion	12	0.050
permethrin	>50	-
pirimiphos-methyl	70	small
pyrethrins	55	0.022

- not established

From the work of Desmarchelier et al (Ref. 22, 23, 24, 25, 26).

3.2 Fruit and Vegetables

Most high moisture unprocessed foods must be held in chillers or refrigerators (0 to 5°C) for short to medium storage or deep frozen (-10 to -20°C) for longer periods. Studies on a variety of pesticides on whole food-stuffs under cool or frozen storage often have shown that residues are stable or decay only slowly (Ref. 14, 27, 28). For example a study of field incurred residues on kiwifruit stored at 0 to 1°C for 3 months found less than 20% decline in residues of chlorpyrifos, diazinon, permethrin, phosmet, pirimiphos-methyl, iprodione or vinclozolin (Holland and Malcolm, unpublished data). Similarly residues of several fungicides applied as dips to apples were relatively stable at storage temperatures of 0 - 2°C (Ref. 29). After 140-150 days residues of benomyl, carbendazim, methyl thiophanate and thiabendazole were 36% - 60% of the initial dose. Penetration of residues from the skin into the outer flesh was significant. However only traces of thiabendazole penetrated to the pulp in dipped citrus. Thiabendazole residues were highly stable in potatoes held at ambient temperature with less than 10% reduction after 56 days (JMPR 1977). The temperature of storage is important for less stable or more volatile compounds. For example residues of the carbamate thiodicarb were stable at -10°C but there were losses at 4.5°C. The highly volatile dichlorvos dissipated rapidly from kiwifruit or asparagus held at 1°C.

For the purpose of estimating dietary intake of pesticides through raw food, and in the absence of particular trial data, the conservative assumption must be that there is negligible reduction of incurred residues during storage of whole foodstuffs. Although there is little supporting data, particularly for non-frozen storage, the assumption also is that there is no change in residue composition.

4. PROCESSING

4.1 Processing Systems

A variety of unit operations are used in commercial or domestic food processing. These are summarised in Table 2.

Table 2: Representative unit operations used in food processing.

Process	Conditions	Process	Conditions
Washing	cold water hot water (blanching) chemical baths (caustic, acid, detergent, hypochlorite)	Pickling	
Peeling		Pasteurisation	
Husking		Oil Production	pressing
Hulling		Irradiation	solvent extraction clarification deodorisation hydrogenation
Shelling		Drying	oven solar spray freeze
Trimming		Grain Milling	hulling polishing grinding - whole flour - white flour - bran - germ
Comminution	blending chopping mincing	Infusion	tea, coffee
Juicing	pressing clarifying	Fermentation	beer wine soy products sauerkraut
Cooking	steaming boiling baking frying grilling microwave	Distillation direct	spirits steam - essential oils
Concentration	boiling vacuum reverse osmosis		
Jam Preserving			

In many cases a raw commodity will undergo a series of unit processes to form a food. For example, a range of specialised processes are used in canning tomatoes. The whole fruit is generally comminuted during production of canned juices, purees and ketchups whereas canned whole tomatoes are lye peeled. There may be intermediate storage periods before processed foods are finally consumed. The effects of various unit steps on residue levels of parent pesticide are likely to be additive although the quantitative effects on levels of any transformation products may not be so evident.

4.2 Effects of Processing

4.2.1 Washing. The key elements in the effectiveness of washing in removing residues are:

- i) The location of the residue. Surface residues are amenable to simple washing operations whereas systemic residues present in tissues will be little affected. For example, the highly polar and systemic methamidaphos was the only pesticide of a number tested whose residues could not be removed from field tomatoes by washing (Ref. 31).

- ii) The age of the residue. There is evidence for a variety of crops and pesticides that the proportion of residue that can be removed by washing declines with time (Ref. 32, 33, 34, 35). This has been interpreted as being due to residues tending to move into cuticular waxes or deeper layers. For example the fractions of fenitrothion or methidathion residues on cauliflower that could be removed by washing or blanching were inversely proportional to the days after spray application (Ref. 34, 35). These post-harvest observations match those made on rain-fastness of pesticide deposits on fruit or leaves in the field.
- iii) The water solubility of the pesticide. Polar, water soluble pesticides such as carbaryl are more readily removed than low polarity materials (Ref. 11). This probably reflects not only their higher solubility in the wash but also their reduced propensity to move into waxy layers.
- iv) The temperature and type of wash. Hot washing and blanching are more effective than cold washing and the effectiveness may be further improved by detergent (Ref. 11, 31, 32). Blanching removed 82-87% of methidathion residues from cauliflower and did not show an effect of withholding period as compared to the lower proportion of residues removable by washing (Ref. 35). Domestic rinsing is less effective compared to thorough commercial washing. Hot caustic washes (Ref. 36) used in some commercial peeling operations can efficiently remove and degrade residues of hydrolysable pesticides.

A range of literature data is summarised in Table 3. Unfortunately many trials did not specify the age of the residue. In some cases where a high reduction in residue was achieved the pesticide had been applied by a post-harvest dip. Simple wash treatments are likely to be of lower effectiveness in reducing terminal residues on field sprayed crops harvested at common withholding periods of 7 - 28 days.

Table 3: Effect of washing or blanching on pesticide residue levels in fruit and vegetables.

Pesticide	Crop	Process	Residue reduction %	Reference
azinphos-methyl	lemon	wash	63	37
	orange	wash	84	37
carbaryl	broccoli	detergent wash	77	36
		blanch, wash	90	
	spinach	detergent wash	87	36
	tomatoes	detergent wash	97	36
carbosulfan	oranges	wash	50	JMPR, 1984
chlorothalonil	peaches	alkaline wash	97	JMPR, 1977
	tomatoes	wash	94	JMPR, 1977
cypermethrin	egg plant	detergent dip	50-60	38
	green gram	detergent dip	44-45	39
DDT	green beans	blanch	50	36
		wash	20	
		15% lye	90	
	spinach	detergent wash	48	36
	tomatoes	blanch	60	36
		wash	91	
peach	detergent wash	73	40	
	detergent wash	29		
diazinon	spinach	detergent wash	0	36
	tomatoes	wash	88	36
fenbutatin oxide	apples	wash	60	JMPR, 1977
fenvalerate	egg plant	detergent dip	50-60	38
		detergent dip	34-47	39
	green gram	blanch	50-51	

Table 3 (cont.)

Pesticide	Crop	Process	Residue reduction %	Reference
fenitrothion	apples	wash	9	41
	broccoli	wash, blanch	27-59	33, 34
	currants	wash	26	41
	okra	wash, blanch	24-49	33, 34
malathion	broccoli	blanch	9-34	42
	green beans	wash	96	10
		blanch	13-99	36, 42
	okra	wash	79-89	
	tomatoes	wash	95	11, 36
methidathion	cabbage	wash (day 0)	67-76	35
		wash (day 7)	24-30	
		blanch (day 0&7)	76-89	
	cauliflower	wash (day 0)	66-71	35
		wash (day 7)	20-24	
		blanch (day 0&7)	82-87	
parathion	broccoli	wash	0	36
		detergent wash	30	
		blanch	10	
	cauliflower	hand wash (30sec)	0-47	43
	cauliflower	wash/blanch	0-65	44
	cow-pea	hand wash (30 sec)	23-47	43
		wash/blanch	26-66	44
	green bean	soap wash	52	45
	mustard gr. spinach	soap wash	87	45
		wash	9-39	36, 10
		detergent wash	24	36
blanch, wash	58-71	36, 43		
permethrin	egg plant	detergent dip	50-60	38
		wash	31-36	39
	green gram	blanch	38-49	
		wash	20	46
		blanch	62	
permethrin	lettuce	water wash	64	JMPR, 1982
thiabendazole	potatoes	water wash	75-90	JMPR, 1977

4.2.2 Peeling, Hulling and Trimming A majority of the insecticides or fungicides applied directly to crops undergo very limited movement or penetration of the cuticle. It therefore follows that residues of these materials are confined to the outer surfaces where they are amenable to removal in peeling, hulling or trimming operations.

Peeling fresh fruits such avocado, bananas, citrus, kiwifruit, mango and pineapple achieves virtually complete removal of residues from the fruit. There is substantial data showing non-detectable residues in pulp of citrus and the edible portion of other fruits that support these conclusions. For example, supervised field trials of pirimiphos-methyl on various citrus crops gave non-detectable (< 0.03 mg/kg) residues in the pulp compared to residues in the peel at 21 - 28 days of 0.5 - 5 mg/kg (JMPR, 1985). Post harvest dipping trials have been conducted on pineapple with the fungicide triadimefon which has some trans-laminar action (JMPR, 1986). Residues in the flesh were consistently only 0.5 to 1% of those in the peel 1 to 11 days after dipping. Under Codex, MRL's are based on the whole fruit which is appropriate for assessing compliance with GAP. These MRL's are of limited significance in assessing exposure to pesticides from consumption of fresh fruits which are peeled or juiced. However some major crops such as apples and tomatoes may be consumed either whole or after peeling.

The skins from commercial peeling operations are often used for production of animal feeds or essential oils (citrus). These processes can result in a substantial increase in residue levels in the by-products over those determined on the whole fruit. For stable, non-systemic, pesticides the concentrations in the skins are determined by weight proportionality.

Residues of systemic pesticides can enter the flesh of crops. Following early season soil incorporation of phorate, residues in washed whole potatoes of 0.37 mg/kg (parent plus oxidation products) were only reduced by 50% through peeling (JMPR, 1992). Similarly disyston residues in potatoes were only reduced 35% by peeling (Ref. 47) whereas residues of the much more lipophilic chlorpyrifos were completely removed in the peels (Ref. 48).

The hulls of cereal grains generally contain the majority of pesticide residues from any field treatments. Residues of parathion in oat or rice grains were reduced 8-10 fold on hulling (JMPR, 1991). Pirimiphos methyl residues in rice were reduced 70% and 90% by husking and polishing respectively (Ref. 25). Husking of corn (maize) removed 99% of the residues from field treatments with tetrachlorvinphos (Ref. 49).

Trimming operations also reduce residue levels in prepared food. The outer leaves of vegetables such as lettuce and crucifers contain a large proportion of the residues from pesticides applied during the growing season. For example, on cabbages one week after the last of eight weekly sprays of cyhalothrin, over 99% of the total residues were in the seven outermost leaves (Ref. 19). Standard sampling protocols for residue trials or enforcement (US-FDA, Codex) specify removal of soiled or withered outer leaves for these types of crop. Residue data and MRL's therefore sometimes reflect initial trimming. Domestic preparation of many foods often include further trimming operations. On the other hand the feeding of peelings or trimmings can result in higher exposure of animals such as pigs to residues.

4.2.3 Juicing Residues of parathion in apple juice were lower when fruit were first cored and peeled rather than pressed whole (JMPR, 1991); commercial juicing operations generally use whole fruit. The residue levels in juices from fruit or must from grapes will depend on the partitioning properties of the pesticide between the fruit skins/pulp and the juice (which generally contain some solids). The pulp or pomace by-products, which often include the skin, retain a substantial proportion of lipophilic residues. Thus moderately to highly lipophilic pesticides such as parathion, folpet, captan and synthetic pyrethroids are poorly transferred into juices and the residues are further reduced by clarification operation such as centrifugation or filtering (Ref. 50).

The relatively high residue levels in juicing by-products can undergo further increases on drying due to simple loss of moisture. For example apples treated post-harvest with bitertanol were processed giving concentration factors of 0.1, 2.5 and 7.5 in juice, wet pomace and dry pomace respectively over the residues on the whole fruit. Overall there was only an 11.4% absolute loss of bitertanol residue in drying the pomace (JMPR, 1986). Permethrin residues in apple juice were non-detectable while dry pomace showed a concentration factor of 25 over whole fruit (JMPR, 1979). Residues of the growth regulator paclobutrazol in apples were concentrated 12 fold in production of dry pomace and there was no loss of residue during the drying (JMPR, 1988). Similarly low level residues of abamectin on field treated tomatoes became non-detectable on the washed fruit (hot dip, pH 11) or in canned puree but were detectable on the wet pomace and concentrated 8 fold on drying (JMPR 1992). In contrast concentration factors for triadimefon residues in processed apples were 4 and 2 for wet and dry pomace respectively, showing losses were significant during drying (JMPR, 1981). Residue losses also were apparent for parathion on drying of apple or grape pomace (JMPR, 1991).

4.2.4 Comminution Disturbance of tissues in chopping, blending etc. leads to release of enzymes and acids which may increase the rate of hydrolytic and other degradative processes on residues that were previously isolated by cuticular layers. For example, fine chopping of crop samples leads to rapid degradation of EBDC fungicide residues (Ref. 51). However most pesticides are relatively stable in acidic tissue homogenates for the moderate periods of time involved in food preparation.

4.2.5 Cooking The processes and conditions used in cooking food are highly varied. The details of time, temperature, degree of moisture loss and whether the system is open or closed are important to the quantitative effects on residue levels. Rates of degradation and volatilisation of residues are increased by the heat involved in cooking or pasteurisation. For example in a study on radiolabelled chlorothalonil residues, cooking under open conditions resulted in 85 - 98% losses by volatilisation. Cooking under closed conditions resulted in hydrolysis with 50% of the chlorothalonil being recovered unchanged on the crop and the hydrolysis product being found in the liquor (JMPR, 1979). For compounds that are of low volatility and relatively stable to hydrolysis such as DDT and synthetic pyrethroids, losses of residues through cooking may be low and concentrations may actually increase due to moisture loss. However deltamethrin has been reported to have a half-life of 9 minutes in boiling water and residues were shown to be reduced by 15-66% in cooking of various vegetables (Ref. 17).

Table 4: Effect of cooking on pesticide residues in food.

Pesticide	Crop	Method	Reduction in residue concentration %	Reference
benomyl	green beans	boil, 30 min	50	JMPR 1978
carbaryl	tomatoes	boil, 30 min	69	52
cypermethrin	plums	boil, 30 min	10	JMPR, 1979
	cabbage	boil, 45 min	25	JMPR, 1979
	whole flour	bake	16-21	53
DDT	potatoes	boil	0	54
dimethoate	rice	boil	20	55
disyston	potatoes	fry	77-97	47
		boil, dehydr.	89-91	47
ethiofencarb	beans	boil, 15 min	>90 ^b	JMPR, 1977
	potatoes	fry	>50 ^b	JMPR, 1977
		bake	<5 ^b	JMPR, 1977
fenitrothion	rice, unpolished	boil	33-53	25
	rice, polished	boil	49-61	25
	whole flour	grill	52	56
	potatoes	boil or steam	7-16	57
		fry or bake	53-73	57
fenvalerate	whole flour	bake	12-13	53
malathion	broccoli	wash, boil	7-34	58
	spinach	boil	100	32
	whole flour	boil or grill	51	56, 59
	rice	boil	92	55
parathion me.	rice	boil	58	55
permethrin	apples	bake, 165 ^o , 45 min	0	JMPR, 1982
	tomatoes	fry, 2-3 min	0	JMPR, 1982
phenothrin	rice	boil	34-47	49
	wh.flour	bake	13-26	60
phorate	potatoes	microwave	43 ^b	JMPR, 1992
		fry	>90 ^b	
pirimiphos me.	rice	boil	18-25	25
thiabendazole	potatoes	baked	0	JMPR, 1977
deltamethrin	spinach	boil	20	17
	green bean	boil	50	17
	tea	infusion	>90	17

^a remaining 50% found as MBC in water

^b including metabolites

Table 4 summarises some trial data covering a range of crops, pesticides and cooking methods.

4.2.6 Canning This commercial process in its various forms combines elements of washing, peeling, juicing, cooking and concentration. Processing whole tomatoes with vinclozolin residues of 0.73 mg/kg gave residues in canned juice, puree and ketchup of 0.18, 0.73 and 0.22 mg/kg respectively (JMPR, 1986). In this case the relatively stable fungicide vinclozolin was carried through the process in significant amounts. Only 13-14% of the parathion residues on tomatoes were found in canned juice or ketchup (Ref. 61) and no residues of malathion were carried into canned tomato products (Ref 36, 52). Several organophosphorus pesticides were shown to be unstable in canned products with residues becoming non-detectable after 1 year (Ref. 61, 62).

4.2.7 Milling and Other Processing of Grains Table 5 summarises some of the extensive literature on the effects of processing of wheat on residues. Although grains often contain residues of protectants (see Section 3.1) levels in the flour are greatly reduced. Most residues are present in the outer portions of the grain, and consequently levels in bran are consistently higher than in wheat, usually by a factor of about 2 to 6. For the herbicide glyphosate, which can enter the grain by translocation, residues are also higher in the bran than in the flour.

Table 5: Percentage reduction of residue concentrations during the milling of wheat and the baking of bread. Some decrease in residue concentrations can be attributed to dilution because the moisture level in bread is higher than in grain. Values are reported as mean and range (in parentheses), where the measured concentration in the commodity was higher than in the wheat the change is prefixed by "+". For bran, data recorded as the ratio of concentrations in the bran to concentrations in the wheat.

Pesticide	Wheat to wholemeal	Wheat to white flour	Wheat to wholemeal bread	Wheat to white bread	Bran/Wheat (concentration ratio)	Reference
bioresmethrin	5% (+50%-63%)	64% (30-89%)	43% (8-68%)	80% (69-91%)	4.0 (2.1-6.8)	JMPR, 1991
deltamethrin	29% (19-47%)	91% (88-93%)	69% (58-99%)	94% (91-96%)	3.3 (2.5-3.8)	JMPR, 1988
deltamethrin		63% (16-92%) ^b			3.5 (2.2-4.5) ^b	JMPR, 1992
diflufenzuron	31%, 14% ^b	83% 79% ^b	22% ^a 3% ^b	66% 58% ^b	2.2, 2.7 ^b	JMPR, 1988
fenitrothion	15%	78(72-85%)	60% (56-67%)	91% (90-92%)		JMPR, 1989
glyphosate	46%	55%	64%	93%	2.2	JMPR, 1987
methoprene	31% (11-57%)	77% (71-88%)	58% (43-86%)	89% (82-96%)	2.1 (1.4-3.0)	JMPR, 1988
permethrin	9% (5-13%)	65% (55-76%)	68% (38-79%)	84% (79-89%)	3.2 (2.0-3.8)	JMPR, 1991
phenothrin	15% (+6%-29%)	68% (61-75%)	48% (28-63%)	79% (69-91%)	3.6 (3.1-4.7)	JMPR, 1987
phenothrin	+20% (+100%-60%)	41% (+17%-70%)			3.9 (2.5-6.0)	JMPR, 1988
piperonyl butoxide	31% (15-42%)	83% (78-90%)	43% (11-63%)	93% (91-94%)	3.1 (2.6-3.7)	JMPR, 1988
piperonyl butoxide		39% (+20%-76%) ^b			2.0 (1.8-2.3) ^b	JMPR, 1992
triadimefon		40%		60%	2.6	JMPR, 1988
triadimenol		67%		72%	1.1	JMPR, 1988

^a % reduction in concentration, with concentration in bread expressed on a moisture-free basis.

^b cleaned grain.

The first process in a commercial flour mill is a cleaning process to remove dirt and debris which have been mixed with the wheat during harvesting. Some grain protectant residues are also removed in this process. It is not always clear from the literature if samples of wheat were taken for analysis before or after the cleaning process. Cleaning may be the most important part of the milling process in terms of removing residues.

Cooking further reduces residue levels (Ref. 55), but it is not always clear from data in the literature if the amount of residues has declined during cooking, or whether the levels are lower because of dilution; moisture levels in baked bread and boiled rice are much higher than in the grain.

The milling of rice substantially removes residues, which are mostly attached to the husk (Table 6). Residue levels are further depleted in the cooked rice.

The errors in calculating percentage reduction of residue concentrations are substantial, because they depend on dividing two residue concentrations both having typical residue level errors. The errors become quite large when one of the residue levels is near the limit of quantitation. Interpretation of percentage reduction comparisons must take into account likely errors.

4.2.8 Processing of Vegetable Oils and Fats The dominant feature in the processing of oil seeds is the retention of lipophilic pesticides in the oil or fat fraction. Residues in oil-seeds following husking are very low or non-detectable from field applications of most pesticides. However higher residues are produced by post-harvest treatments against storage pests which can lead to elevated residues in the oils. Processing seeds to recover oil using pressing or solvent extraction can concentrate lipophilic residues in the oil. Conversely highly polar pesticides such as dimethoate, oxamyl (JMPR, 1980) or thiodicarb (JMPR, 1985) are not transferred to the oil fraction. Dimethoate was specifically developed so residues would not remain in olive oil. Dimethoate and omethoate the oxygen analogue metabolite are largely removed during processing (Ref. 63). Table 7 lists the concentration ratios for residues of a number of pesticides in production of vegetable oils.

Concentration ratios are generally lower for cotton seed oil because of retention of much of the residue in the lint. High concentration ratios have been found for crops which give low yields of oil such as maize. Pressing of citrus peel led to concentrations of parathion in the oil 100-300 times those in the whole fruit (JMPR, 1991).

While some oils such as olive are sold unrefined, most crude vegetable oils receive some further processing. Steps such as alkali refining or deodorisation can be very effective at removing many pesticides from oils. For example 70 to 100% of residues of lindane or DDT plus metabolites were removed from a variety of vegetable oils by vacuum deodorisation at 230 to 260 C (Ref. 41). Methoprene residues of 50 to 150 mg/kg in crude maize oils were reduced to non-detectable levels after deodorisation (JMPR, 1988). Similarly residues from post harvest applications of dichlorvos, malathion, chlorpyrifos or captan to soyabeans were reduced to non-detectable levels in refined, deodorised oil (Ref. 65). However some stable, low vapour pressure pesticides such as synthetic pyrethroids seem to be less effectively removed by this treatment (Table 7).

4.2.9 Production of Alcoholic Beverages In principle residues on the barley or hops used in production of beers could be retained in the final product. In practice, a combination of the malting process, the high dilution with water and the filtering/fining processes generally result in non-detectable residues in beer. Malting of barley resulted in loss of about 80% of fenitrothion residues (Ref. 66). Synthetic pyrethroid residues underwent similar high losses during malting (Ref. 49). There is a high usage of EBDC fungicides on hops and ETU residues have been detected in beer (see section 4.2.10). Water-soluble compounds are more likely to transfer into the beer. Glyphosate residue levels in beer were about 4% of original levels in the barley (JMPR, 1987). Some glyphosate was lost during the washing, but most of the decrease could be attributed to dilution.

In contrast, wine-making involves no dilution and therefore residues are more likely to be found. The residual characteristics of the major fungicides used in viticulture have been reviewed (Ref. 50). In addition to transfer of residues from the grapes into the must, stability of residues to the fermentation and fining processes are important factors. Fermentation on the skins as carried out in red wine production is likely to lead to higher residues in raw wine.

Residues in must may be absorbed to the solids produced during fermentation and thus be lost in the fining processes. However, a range of pesticides with suitable solubilities and stabilities can give rise to residues in wine. Table 8 summarises available data on the reductions in residues that have been found during processing of grapes into wine. Further degradation of residues can occur during storage. The half lives for dimethoate, methidathion and dialiflor residues in bottled wine stored at 24°C were 30, 7 and 7 days respectively (Ref. 67).

Table 6: Percentage reduction of residue concentrations during the processing and cooking of rice. Some decrease in residue concentrations can be attributed to dilution because the moisture level in cooked rice is higher than in the raw grain. Values are reported as mean and range (in parentheses).

Pesticide	Rice in husk to husked rice	Rice in husk to polished rice	Rice in husk to cooked rice	Reference
bioresmethrin	93%	97%	>98% ^a	25
carbaryl	86%	98%	98% ^a	25
deltamethrin	92% (55-99%)		97% (93-100%)	JMPR, 1987
fenitrothion	82%	92%	96% ^a	25
d-phenothrin	89%	97%	>97% ^a	25
methacrifos	80%	97%	>98% ^a	25
parathion		>93%		JMPR 1991
pirimiphos-methyl	70%	94%	98% ^a	25

^a % reduction in residues, with allowance for weight change during cooking.

Table 7: Pesticide residues in vegetable oils.

Crop	Pesticide	Residue concentration ratio oil/seed		Residue loss on deodorisation %	Reference
		crude oil	refined oil		
Cotton seed	chlordimefon	0.8	0.6	100	JMPR, 1979
	cypermethrin	0.8	0.7	60	JMPR, 1979
	diazinon	-	1.7	-	64
	l-cyhalothrin	0.2	0.1	-	JMPR, 1986
Maize	methoprene	10-20	-	100	JMPR, 1988
	parathion	1.3-3.4	1.3-3.4	-	JMPR, 1991
Olives	parathion	4.5	-	-	JMPR, 1991
Peanuts	pirimiphos-methyl	1.7	1.2	-	JMPR, 1985
Soyabean	fenvalerate	1.1	-	-	JMPR, 1979
	dichlorvos ^a	5.3	0.07	100	65
	chlorpyrifos ^a	4.1	2.85	100	65
	malathion ^a	3.9	0.43	100	65
Sunflower	diazinon	-	1.5	-	64
	permethrin	0.7	-	17	JMPR, 1982
Rape	etrimfos	2.7	1.7	98	JMPR, 1986

- data not reported

^a from dry flake

Table 8: Effects of juicing and vinification on pesticide residues from grapes.

Pesticide	% Reduction in residue from field grape			Reference
	Must	Clarified juice	Wine	
benomyl	0	0	0, 75 ^a	68
captafol	50	95	100	69
chlorothalonil	12-33	-	-	JMPR, 1979
dialiflor	-	-	90	67
dimethoate	-	-	15	67
folpet	50	95	100	69
iprodione	45-70	60-80	70-87	JMPR, 1977
metalaxyl	0	30-50	66	51
methidathion	-	-	54	67
methiocarb	0-10	-	40-70	JMPR, 1981
procymidone	40	-	70	JMPR, 1981
propiconazole	70	-	100	JMPR, 1987
triadimefon + triadimenol	50	-	50-100	JMPR, 1979
vinclozolin	59-88	80	89-93	JMPR, 1986

- not determined

^a bentonite fining

5. METABOLITES

Degradative or transformation processes leading to formation of metabolites will often be increased by unit processes used in food processing, particularly those involving use of heat or chemicals. Although no examples are available of pesticides where food processing has resulted in the production of new metabolites, the proportions of various metabolites may change from those found in field or laboratory studies on whole plants. As metabolites are generally more polar than parents, changes in proportions between processing fractions also can be expected. It is therefore prudent in preliminary processing studies to monitor all residues of concern as guided by plant metabolism studies. Use of radio-labelled parent simplifies the tracking of residues through processing. FAO-IAEA conferences have covered use of radio-labelled pesticides in storage studies (Ref. 13). Studies of malathion on rice (Ref. 70) and phenothrin on wheat (Ref. 60) have also been reported.

Detailed studies on the fate of metabolites during food processing are lacking for most pesticides. Some studies on parathion have included measurements on paraoxon or the p-nitrophenol hydrolysis product. Paraoxon behaved similarly to parent in processing of field treated citrus, apples and grapes (JMPR, 1991). Exaggerated rates of application were required to produce sufficient paraoxon to track through the trials. Blanching or canning operations on vegetables containing parathion residues did not result in accumulation of p-nitrophenol (Ref. 43, 61). Conjugated metabolites of benzoylprop in wheat were found to concentrate 5 fold in the bran after milling (Ref. 71).

Bound residues can be a major proportion of terminal residues for some grain protectants (see Section 3.1). The nature and significance of bound residues remain ill defined (Ref. 13). Bound tetrachlorvinphos residues in faba beans caused significant decreases in weight gain and plasma cholinesterase when fed to mice (Ref. 13). Further research is required on fate of bound residues during food processing and on their bioavailability.

6. DITHIOCARBAMATE FUNGICIDES

The ethylene bis-dithiocarbamates (EBDC) fungicides form a useful example of a pesticide class where processing studies have formed an important part of research and evaluation. This group of pesticides have come under particular scrutiny because of their ability to form the metabolite or breakdown product ethylenethiourea (ETU), a putative carcinogen. A similar problem exists for formation of propylenethiourea from propylene bis-dithiocarbamates e.g. propineb.

A review of toxicological data and environmental health criteria for the dithiocarbamates and ETU has been published (Ref. 7). The toxicology of ETU, the formation of ETU and decontamination processes for crops were recently reviewed (Ref. 72). Earlier monitoring data showed that ETU residues could be found in raw agricultural commodities but the levels were generally less than 1% of parent EBDC and seldom exceeded 0.05 mg/kg. For comparison, the national limits in four countries are between 0.01 and 0.1 mg ETU/kg for different commodities. However EBDC's are rather unstable compounds and elevated levels of ETU have been found in food after certain processes. Conditions that favour the conversion of EBDC's to ETU are high pH and heat.

Table 9 summarises available data on residues of ETU derived from processing some crops containing incurred EBDC residues. Up to 50% of the EBDC residues on the raw crop were converted to ETU during some processes involving heat such as blanching, cooking and canning.

The recent review of EBDC fungicide registrations in the USA included very large residue monitoring studies on crops and some of their processed products. Improved HPLC technology for detection of ETU was used to achieve lower detection limits than in previous surveys. Monitoring of 300 processed food samples covering 14 commodities including juices, sauces and frozen vegetables showed mean EBDC and ETU residues for each group of 0.001 - 0.21 mg/kg and 0.001 - 0.006 mg/kg respectively (Ref. 73).

Efforts have been made to find techniques for commercial processing which reduce the EBDC levels in crops or prevent the formation of ETU. A summary of these studies is shown in Table 10. Although the polymer/metal complex powder formulations of EBDC's are virtually insoluble in water, they also are not very lipophilic and so largely remain on the surface of the crop at harvest. Commercial washing techniques reduced the EBDC levels on crops to a great extent. Warm acid washing was more effective than a cold water wash only. Hypochlorite washing followed by rinsing with sodium sulfite or detergent solution was even more effective.

ETU is moderately water soluble and thus washing techniques have been shown to be effective at reducing ETU levels on fresh foods, although small amounts often still could be detected. The stability of ETU was studied in canned products from tomatoes (Ref. 87), and in canned apples (Ref. 81). ETU was sometimes found to have a slow decomposition rate, with the majority of residues still remaining after several weeks. It was least persistent at low pH. However addition of ascorbic acid reduced formation of ETU during sterilisation but resulted in higher stability of ETU during storage due to the anti-oxidative effect.

ETU can also be formed in the brewing process from hops containing EBDC. Suggested techniques to reduce the ETU levels were not successful (Ref. 88). Low levels of ETU residues have been found in concentrated grape juice and in must but residues have not been detected in wine (Ref 51, 89). Zineb and ETU have been reported to be completely adsorbed to grape solids and wine suspended solids (Ref. 51, 89).

There is a lack of information in the literature about the levels of ETU residues left in prepared food after home-cooking of raw crops containing EBDC residues. It seems important to gather more information on this topic.

7. RECOMMENDED APPROACHES TO STUDIES FOR REGULATORY PURPOSES ON RESIDUES IN PROCESSED FOOD

7.1 Scope of Studies

Codex has recognised the need for better estimates of residue levels in food as consumed (Ref. 2) and has prepared draft guidelines for developing suitable residue data. The large number of pesticides and crops plus the very diverse range of commercial or domestic processes used to produce foods, make it impractical to gather residue data on all the possible combinations. Residue data requirements for a particular crop can be classified at 3 levels: the raw commodity, as it moves in trade, and as it is

Table 9: Residues of ETU and conversion rates of EBDC's after various food processings of crops with incurred residues of EBDC's.

EBDC's in raw commodity, mg/kg	Treatment	ETU level, mg/kg	% conversion of EBDC, mean	Reference
mancozeb, 3.2 - 11	Cooking tomatoes with reflux 10 min	0.9 - 1.3	49%	74
manzate D, 3.1 - 12	"	0.5 - 1.4	38%	74
metiram, 1.1 - 5.1	"	0.2 - 0.8	47%	74
zineb, 1.3 - 5.2	"	0.1 - 1.0	40%	74
mancozeb, 0.3 - 7.1	Washing and canning, tomato juice	0.03 - 0.1	49%	75
mancozeb, 0.1 - 0.8	Washing, peeling, dicing, canning, carrots	<0.01 - 0.05	10%	75
mancozeb, 2 - 219	Washing, blanching, chopping, canning spinach	0.2 - 2.7	20%	75
maneb, 2.4, 8.0 (ETU: <0.01, 0.02 mg/kg)	Washing and canning whole tomatoes	0.02, 0.07	-	75
"	Evaporating tomato juice to sauce with heat	0.1, 0.2	-	75
"	Evaporating tomato juice to paste with heat	0.4, 0.5	-	75
maneb, 87. 187 (ETU: 0.2, 0.7 mg/kg)	Washing and canning spinach	1.8, 2.5	-	75
"	Blanching and freezing spinach	0.8, 1.4	-	75
mancozeb, 2.8 - 18	Cooking spinach for 15 min	0.2 - 1.7	18%	76
maneb, 1.6 - 10	"	0.2 - 0.9	19%	76
zineb, 8.6 - 19	"	0.4 - 0.8	13%	76
maneb, 0.1 - 0.4	Washing and canning, tomato juice	<0.01 - 0.04 ¹	-	77
"	Washing and canning, tomato fruit	<0.01 - 0.02 ¹	-	77
mancozeb, 0.09 - 0.8	Washing and canning, tomato juice	<0.01 - 0.07 ¹	-	77
"	Washing and canning, tomato fruit	<0.01 - 0.02 ¹	-	77
mancozeb, 0.03 - 0.6	Washing and canning, tomato juice	<0.01 - 0.07 ¹	-	77
"	Washing and canning, tomato fruit	<0.01 - 0.05 ¹	-	77
mancozeb, Metiram (ETU: 0.01 mg/kg)	Canning, apple juice	0.05	-	78
"	Drying 145°C, apple pomace	0.2	-	78
mancozeb, <0.1 - 21	Cooking in water 30 min, grain	<0.01 - 0.09	30%	79
zineb, 0.4 - 46 (herb tea)	Infusion 15 min	<0.1 - 10 mg/l (tea water)	1.5%	80
Mancozeb, (spiked 10 mg/kg)	Boiling 15 - 60 min, apples	-	7%	81

¹ One raw sample 0.03 mg ETU/kg, the others <0.01.

Table 10: Techniques to decontaminate ETU from EBDC's in commercial processes.

Fungicide/ processed product	EBDC's in processed product, mg/kg		ETU in processed product, mg/kg		Treatment (to reduce EBDC/ETU)	Reduction (%, mean value)	Reference
	Untreated ^a	Treated	Untreated ^a	Treated			
mancozeb/ canned tomato juice	0.17	0.11	0.033	0.017	Water wash 10 min	38 % 65 % (EBDC)	82 82
	0.54	0.19	0.065	0.019			
"	0.17	0.04	0.033	n.d.	Hot acid wash (1.0 M HCl)	76 % 82 % "-	82
	0.54	0.10	0.065	0.012			
"	0.30-1.03	0.09-0.71	n.d.-0.02	n.d.-0.03	Water wash 2-10 min	49 % 51 % "-	81
	0.73-1.40	0.26-0.88					
"	0.30-1.03	n.d.-0.13	n.d.-0.02	n.d.-0.02	0.1% sodium hypochlorite wash 2-6 min, dip 0.1% sodium sulfite	91 % 79 % "-	81
	0.73-1.40	0.09-0.45					
maneb/green beans	1.5±0.1	0.82±0.05	0.03±0.009	0.02±0.005	2 min cold water wash + 2 rinses	Small EBDC re- duction, ETU left	83
"	1.5±0.1	<0.02	0.03±0.009	0.14±0.03	Boiling water for 3 min	Ca 100 % (EBDC), ETU formation	83
"	1.5±0.1	0.04±0.03	0.03±0.009	0.06±0.01	Blanching in 1.0 M HCl 2 min, rinsing in cold water	95 % (EBDC)	83
"	1.5±0.1	<0.02	0.03±0.009	<0.01	0.1 % alkaline hypochlorite 2 min, dip in 0.1% sodium sulfite	Ca 100 % (EBDC), no ETU left	83
maneb/frozen or juiced tomatoes	0.36-2.15	0.15-0.25	-	-	Cold water wash 10 min	30-77 % (EBDC)	83
maneb/frozen or juiced tomatoes	0.36-2.15	<0.02-0.17	-	-	2-4 min alkaline hypochlorite wash 2-4 min, dip in 0.1% sodium sulfite	>30 % (EBDC)	83
mancozeb/ canned apple puree	10 ^b		-	-	Addition of citric acid (lowering pH from 4.0 to 3.0)	Formation of ETU lowered from 9% to 3%	81
mancozeb/ canned spinach			1.2-18.7	0.08-0.64	Water wash 3 min and rinsing	80-98% (ETU)	84
"			1.2-18.7	0.02-0.38	Washing in sodium hypochlorite - detergent at pH = 9	Further reduction of ETU, but not signifi- cant different from water wash only	84
mancozeb/ canned spinach			21	0.7-4.3	Washing with water 1-3 min, and rinsing	High reduction of ETU, no difference 1 and 3 min wash	85
"			21	0.5-1.6	Washing in sodium hypochlorite - 0.1 % basic detergent	Highest reduction	85
mancozeb, manzate 200/ canned spinach			6.9-7.5	0.1-5.8	Different washings compared: water, sodium, hypochlorite detergents, different pH	Highest removal of EBDC's at high pH and high degree of detergent	86

^a Untreated = processed as the "treated" samples, except for the decontamination process described below "treatment".

^b Spiked samples.

consumed. The following points should be considered in determining the scope of processing studies that maybe required for registration of a pesticide on a crop.

1. Whether the crop is major (>0.5% diet) and whether residues at harvest are significant (amount and toxicology). These are over-riding prerequisites for most processing studies although "major" or "significant" may be difficult to assess. Post-harvest applications of pesticides will definitely require processing studies e.g. protectants on stored grain. National or local dietary habits will influence the choice of crops. The diets of infants and children should receive special attention due to the lack of data that has been identified as a particular deficiency to risk assessment for this population group (Ref. 90).
2. Whether the pesticide is likely to concentrate in a food fraction e.g. vegetable oil. Even very low residues may become significant if they become more concentrated.
3. Which portion of the treated crop is consumed. Identifying situations where normal processing leads to large reductions in residue levels in food items is also important.
4. Whether the food is a processed commodity commonly moving in international trade.
5. Which processes are commonly applied to the crop:
 - a) Simple commercial, leading to a traded commodity
e.g. washing of fruit or vegetables
solar drying of fruit
 - b) Complex commercial - large scale multi-step food manufacturing processes:
e.g. milling/baking of grains
vegetable oil production
juicing
canning
 - c) Typical domestic trimming, washing and cooking. More information is required on the effects of domestic cooking practices on residues.

Even within these guidelines the range of possible experiments to define the effects of processing on residues in a particular pesticide / crop combination could be large. Careful consideration needs to be given to the most plausible scenarios for processing to affect particular residues in food so the primary question on the likely residue intake by consumers can be economically answered.

7.2 Study protocols

The following recommendations are made for conducting processing trials in order that residue data can be produced which is relevant, comparable and may be extrapolated to other situations. A key requirement is the quantitative accounting for changes in residue levels in processed foods due to losses, redistribution amongst food fractions and concentration or dilution from changes in moisture content.

1. Studies generally should be conducted on crops with incurred residues harvested at recommended pre-harvest intervals. Initial residue levels should be near the MRL's, if necessary by the use of exaggerated field rates.
2. Careful attention should be given to obtaining crop lots that are large enough and of adequate uniformity to establish significant differences in residue levels during processing.
3. Codex guidelines (Ref. 91) should be followed in sampling and sample preparation for determination of initial residue levels in the lots.
4. Commercial processing facilities should be used where possible. If laboratory studies are conducted then the conditions should simulate the commercial process as closely as possible with particular attention to the problems of scale.
5. All relevant information regarding the particular process and operating conditions used should be recorded. Particular attention needs to be given to cooking studies where there are a large range of possibilities within both domestic and commercial processes. For example important differences in residue behaviour can arise between closed and open systems.

6. Residue results should be reported so that the reasons for changes in concentrations can be identified (loss versus redistribution versus change in moisture content). This normally will involve tracking amounts of residue on a dry weight basis.
7. Metabolites should be included where possible, particularly if they may be of toxicological significance.
8. Major fruit or vegetable crops which are frequently peeled before consumption should have residue measurements made on both flesh and peelings. This can be economically incorporated into standard residue trials.
9. Due to the potential major contribution of grain protectants to residues in the diet, milling and associated studies on treated grain always should be carried out and commercial scale facilities used. The Codex description of cereal grain milling fractions should be used (Ref. 91).
10. Vegetable oil studies should cover all fractions including seed, meal, crude oil and refined oil.
11. Juicing studies should include whole fruit and skinned fruit where applicable. The unclarified / clarified juice and wet / dry pomace fractions should be analysed.

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