

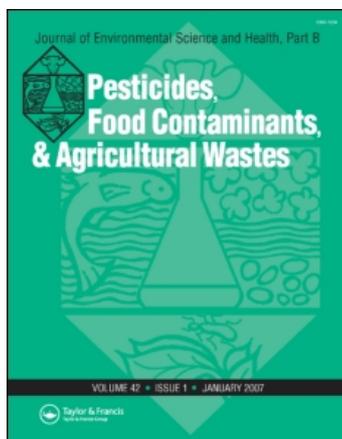
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Publisher Taylor & Francis

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Journal of Environmental Science and Health, Part B

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597269>

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First published on: 28 December 2010

To cite this Article Drouillet-Pinard, Peggy , Boisset, Michel , Périquet, Alain , Lecerf, Jean-Michel , Casse, Francine , Catteau, Michel and Barnat, Saida(2011) 'Realistic approach of pesticide residues and French consumer exposure within fruit & vegetable intake', Journal of Environmental Science and Health, Part B, 46: 1, 84 — 91, First published on: 28 December 2010 (iFirst)

To link to this Article: DOI: 10.1080/03601234.2011.534413

URL: <http://dx.doi.org/10.1080/03601234.2011.534413>

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Realistic approach of pesticide residues and French consumer exposure within fruit & vegetable intake

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The increase of fruit and vegetable (F&V) intake contributes to the prevention of chronic diseases, but could also significantly increase pesticide exposure and may thus be of health concern. Following a previous pesticide exposure assessment study, the present study was carried out to determine actual levels of pesticides within 400 g of F&V intake and to evaluate consumer risk. Forty-three Active Substances (AS) exceeding 10 % of the Acceptable Daily Intake (ADI) in balanced menus established for our previous theoretical study were considered. Fifty-six pooled food samples were analyzed: 28 fruit samples and 28 vegetable samples. Pesticide values were compared to Maximum Residue Levels (MRL) and to the “toxicological credit” derived from ADI. It was observed that 23 out of the 43 retained AS were never detected, 5 were detected both in F&V samples, 12 only in fruits and 3 only in vegetables. The most frequently detected AS were carbendazim, iprodione and dithiocarbamates. When detected, AS were more frequently found in fruit samples (74 %) than in vegetable samples (26 %). A maximum of 3 AS were detected at once in a given sample. Overall, we observed 8 and 14 overruns of the MRL in 1204 measures in pooled vegetable and fruit samples, respectively (0.7 % and 1.2 % of cases, respectively). Chronic exposure for adults was the highest for dithiocarbamates but did not exceed 23.7 % of the ADI in F&V. It was concluded that raising both F&V consumption up to 400 g/day (~5 F&V/day) according to recommendations of the national health and nutrition plan, does not induce pesticide overexposure and should not represent a risk for the consumer.

Keywords: Pesticide residue; exposure; fruit; vegetable; maximum residue level (MRL); acceptable daily intake (ADI)

Introduction

Increasing dietary intake of fresh Fruit and Vegetables (F&V) may significantly contribute to the prevention of major chronic diseases, such as diabetes,^[1,2] cardiovascular diseases^[3,4] osteoporosis^[5,6] and cancer.^[7,8] Nevertheless, on one hand the health benefits of F&V are recognized, on the other hand they represent a source of exposure to pesticides for the consumers. Such a change in increasing F&V intakes could induce a rise in pesticide exposure and thus may be of health concern.

A recent report from the European Commission Directorate General for Health and Consumers (DG SANCO) including national data sets showed that, in 8 % of unprocessed F&V sampled in France, Active Substances (AS)

levels exceeded Maximum Residue Levels (MRL).^[9] This report however, did not point out any chronic risk for the consumer.

In a previous theoretical study using deterministic approach (exposure assessment with AS levels set at MRL), we have shown that exposure in French adults consuming up to 800 g F&V per day should not lead to expose adults consumers above the Acceptable Daily Intake (ADI) for all the AS studied (except for cyhexatin and thiram).^[10] Residue levels of 10 AS should deserve particular attention because they exceeded 10 % of the ADI in menus containing only 200 g of F&V: carbaryl, cyhexatin, dicofol, ethoxyquine, flusilazole, iprodione, lambda-cyhalothrin, mancozeb, phosalone and thiram.

Our previous theoretical study led to gross overestimation of actual exposure of the consumer for two reasons: AS levels were set at MRL levels and we did not take into account processing and culinary practices. These treatments can cause losses of AS depending on their physicochemical properties and the nature of treatment. In a meta-analysis, Keikotlhaile et al.^[11] showed that processes which

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Received June 8, 2010.

Table 1. Toxicological reference values for active substances.

<i>Active substance</i>	<i>ADI mg/kg*</i>	<i>European MRL mg/kg^Δ</i>	<i>Active substance</i>	<i>ADI mg/kg*</i>	<i>European MRL mg/kg^Δ</i>
Captan	0.1	0.02	Fenitrothion	0.005	0.01
Carbaryl [§]	0.0075	0.05	Fluazifop- <i>p</i> -butyl	0.01	0.1
Carbendazim [§]	0.02	0.1	Fluazinam	0.01	0.05
Carbofuran	0.001	0.02	Flufenoxuron [§]	0.0035	0.05
Chlorfenvinphos [§]	0.0005	0.02	Flusilazole	0.002	0.02
Chlorothalonil	0.015	0.01	Formetanat	0.004	0.05
Chlorpyrifos Ethyl [§]	0.01	0.05	Iprodione [§]	0.06	0.02
Cyfluthrin	0.003	0.02	Iprovalicarb	0.015	0.05
Cyhexatin	0.0005	0.05	Lambda-cyhalothrin [§]	0.005	0.02
Cypermethrin [§]	0.05	0.05	Linuron	0.003	0.05
Deltamethrin [§]	0.01	0.05	Mepanipyrim	0.02	0.01
Dicofol	0.0025	0.02	Myclobutanil [§]	0.02	0.02
Difenoconazole [§]	0.01	0.05	Oxydemeton-methyl	0.0003	0.01
Diphenylamine [§]	0.02	0.05	Phosalone [§]	0.01	0.05
Dithianon	0.01	0.01	Phosmet	0.003	0.05
Dithiocarbamates [‡] as CS ₂ [§]	0.001	0.05	Procymidone [§]	0.025	0.02
<i>Mancozeb</i>	0.05		Propargite [§]	0.007	0.01
<i>Maneb</i>	0.05		Pirimicarb [§]	0.035	0.5
<i>Metam sodium</i>	0.001		Rotenone	0.001	0.01
<i>Thiram</i>	0.01		Tebufenozide [§]	0.02	0.05
<i>Ziram</i>	0.006		Tebufenpyrad	0.02	0.05
Endosulfan	0.006	0.05	Thiabendazole [§]	0.1	0.05
Ethoxyquin	0.005	0.05	Thiophanate-methyl [§]	0.08	0.10
Famoxadone	0.012	0.02	Vinchlozolin	0.005	0.05

[§] Active substances detected in the samples

* Data from Agritox base¹⁵

[‡] ADI value is the lowest within the group of dithiocarbamates

^Δ MRL collected from European Pesticide database¹⁶

mainly reduce pesticide residue levels were peeling, washing, blanching, cooking and frying.

The objective of the present study was to measure the levels of pesticide residues in the F&V prepared in the menu composed for the theoretical study with a realistic approach.^[10] Residue levels were compared to MRL then intakes of AS were compared to ADI to evaluate consumer risk.

Materials and methods

Active substances studied

The results of our theoretical study showed that no fewer than 183 AS could be present in the various F&V included in the menus created for the study. The AS exceeding 10 % of the ADI in our theoretical study were chosen for the laboratory measurements to be carried out on F&V. This cut-off 10 % level, which is not a toxicological reference value, was retained because it is admitted by expert committees that such a contamination level is unlikely to induce any effect in consumers. The set of AS to be determined is given in Table 1.

Composition of menus

Fresh F&V used in menus are presented in Table 2. Such an amount represents 2.5-fold the dietary intake of French adult consumers.^[12] Nutritional balance and adequacy of the various menus was assessed independently by the Nutrition Department of the Institut Pasteur-Lille. Table 3 gives an example of a balanced menu with 400 g of F&V.

F&V used in the study were all grown with conventional agricultural practice. They were purchased in accordance with French consumers habits: 60 % in superstores and variety shops (3 days of purchase per week), 20 % in open-air markets (2 days of purchase per week) and 20 % in F&V retail stores (2 days of purchase per week). More than 50 % of fruit samples and over 85 % of vegetable samples originated from metropolitan France (Fig. 1).

Sampling

The sampling period extended from August to November to afford maximal availability of all items included in the menus. Pooling preserves the proportions of each F&V as determined in the menus.

Table 2. Fruits and vegetables considered in the different menus.

Vegetables	
Bulbs*	shallott, garlic, onion
Leafy vegetables and herbs	
- Herbs	basil, dill, chives, mint, parsley
- Salad vegetables	batavia, corn salad, curly endive, lettuce, watercress,
- Others	endive, spinach,
Stem vegetables	celery, fennel, leek
Flowering vegetables	artichoke
Fruiting vegetables	
- Solanaceae	eggplant, pepper, tomato
- Cucurbitaceae with edible peel	zucchini, cucumber,
- Cucurbitaceae with no edible peel*	pumpkin, watermelon,
Roots & Tubers*	beet, carrots, turnip, celeriac
Cruciferous vegetables/Cabbages	broccoli, cauliflower, kale, Brussels sprout, green cabbage, red cabbage
Mushrooms	button mushroom
Pulses	butterbean, red and green bean, chickpea, lentil
Potatoes	
Fresh fruits	
Various	avocado*, grapes, banana*, fig*, kiwifruit*, pineapple*,
Citrus*	lemon, orange, pomelo
Pome fruits	apple, pear, quince
Berries & small fruits	strawberry
Stone fruits	nectarine, peach, plum

*peeled F&V.

F&V were washed and peeled as required depending on the menu. Every day of the four-week experimental period, one pooled fruit sample and one pooled vegetable sample were collected. All F&V were carefully rinsed with tap water and peeled only when necessary (Table 2). For vegetables, steam cooking was used throughout the study and oil or fat was added in minute amounts to prevent interference during pesticide extraction and determination steps. Thus, the total number of analyzed samples was 56 (28 of fruits and 28 of vegetables). Samples were kept at -20°C until analysis.

Determination of pesticide residues

All the samples were analyzed in the Laboratoire Central Atlantique, La Rochelle, France under ISO 17025 accreditation for such analyses. The laboratory used a multiresidue technique with solvent extraction known as "QuEChERS method" (Quick, Easy, Cheap, Effective, Rugged and Safe).^[13] Extracted samples were analyzed by

Table 3. Example of a balanced menu with 400 g of fruits and vegetables.

Breakfast	Lunch	Dinner
	Semolina: 150 g + Pepper: 50 g + Oil: 10 g	
Cereal bread: 130 g Butter: 20 g	Hake: 80 g Steamed spinach: 50 g	Batavia: 100 g + Oil: 15 g
Cottage cheese: 150 g Tea with milk: 100 g	White rice: 150 g + Oil: 10 g	Pasta: 200 g + Smoked Salmon: 50 g
Sugar: 15 g	Bread: 85 g	+ Parmesan cheese: 30 g
Kiwifruit: 100 g	Cottage cheese: 100 g + Sugar: 10 g Plum: 100 g	+ Fresh cream: 20 g Bread: 85 g

gas chromatography coupled with tandem mass spectrometry (GC/MS/MS).

This technique cannot be used for the dithiocarbamates, a group of AS which have a comparable chemical structure, but have different toxicological properties. The analytical method for dithiocarbamate residues is based on the evolution of CS_2 , and the particular AS applied cannot be identified. They were hydrolyzed by chlorohydric acid and determined, as hydrogen disulfide, by a spectrophotometric method according to the European norm EN 12936-1.^[14]

Validation tests have shown that analytical requirements set by the European Directive 97/57/CE^[15] were fulfilled.

Comparison of residue levels to reference values

ADI figures retained for risk evaluation were those valid for France at the time of the analysis (2009) and given in Tables 4 and 5.^[16]

MRL retained for calculations were those valid during analysis i.e. year 2009.^[17] They are in accordance with harmonized values established by European Food Safety Agency and placed under the Regulation 396/2005 CE^[18] in force since September 1st 2008.

Pooling different fruits on the one hand and several vegetables on the other hand induced dilution of AS and additionally prevented the identification of the couple fruit/AS or vegetable/AS. However, when different MRL values applied for the various vegetables or fruits in the same sample, the lowest value was selected.

For all the AS detected, the actual level of contamination was compared to MRL and chronic risk was assessed by comparison of intake to ADI values. Further, we

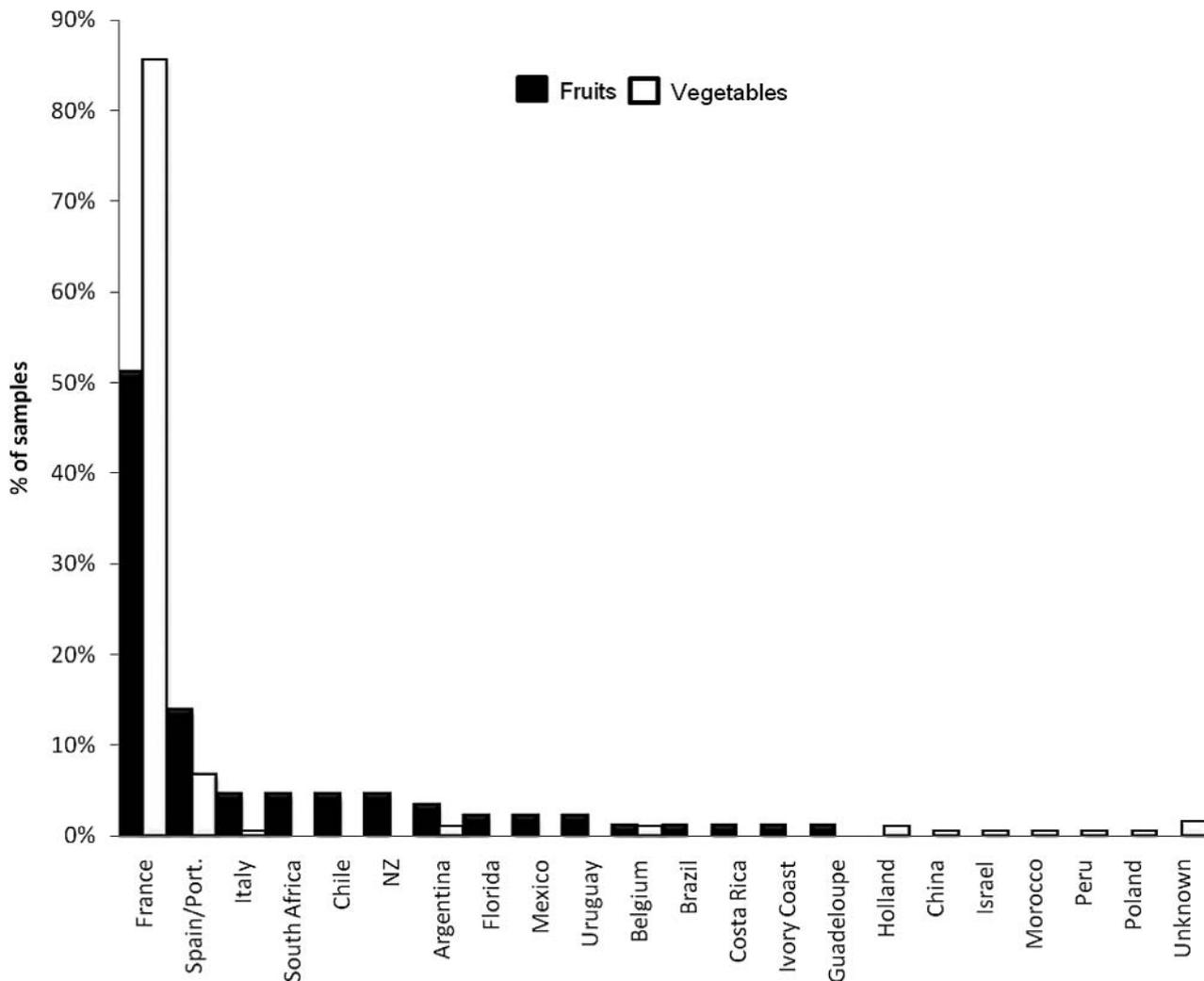


Fig. 1. Geographical origin of fruits and vegetables.

compared mean levels measured in the pooled F&V samples to the MRL. In a conservative approach, when an AS was not detected in a sample, value was set at the Limit of Quantification (LOQ) and not zero to calculate mean level.

For the evaluation of chronic risk, several parameters were considered: ADI, “toxicological credit” taking into account body weight of consumer ($ADI \times 57.5 \text{ kg}$),^[19] the amount of F&V ingested (400 g/d: 200 g fruits + 200 g vegetables) and the mean AS level measured. The “toxicological credit” allows to adapt the ADI by taking into account the bodyweight of the consumer according to Equation 1 and is a useful parameter to evaluate the relative contribution of F&V as pesticide residues vectors in the diet. Exposure was calculated deterministically according to Equation 2 by multiplying the mean value of AS and the amount of fruits or vegetables consumed. Comparison of the exposure to the “toxicological credit”

allowed us to evaluate the consumer risk.

$$\text{Toxicological credit} = \text{ADI} \times \text{bodyweight} \quad (1)$$

$$\text{Exposure} = \text{Mean value AS} \times \text{Amount of fruits (or vegetables) consumed} \quad (2)$$

Results and discussion

Active substances (AS)

Forty-three AS were measured on 56 samples (28 fruit samples and 28 vegetable samples), which means a total of 2408 measures performed from which: 2347 ended without any detection and 61 (2.5 %) had detectable AS.

Of the 43 AS analyzed, 23 were never detected. Five were detected both in F&V samples, 12 were detected only in fruits and 3 only in vegetables. The most frequently

Table 4. Pesticide residues and exposure through vegetable consumption.

Active substances (<i>N</i> detections on 28 samples)	Mean value (mg/kg) [†]	MRL			Toxicological credit (mg/d)	Intake = 200 g of vegetables		Intake = 400 g of vegetables	
		European MRL ^{Δ*} (mg/kg)	% of MRL	ADI (mg/kg/d)		Exposure 1* (mg/kg/d)	Used Toxicological credit (%)	Exposure 2 [§] (mg/kg/d)	USED Toxicological Used
Difenoconazole (4)	0.012	0.05	24 %	0.01	0.575	0.0024	0.42 %	0.0048	0.84 %
Iprodione (3)	0.011	0.02	53 %	0.06	3.450	0.0021	0.06 %	0.0042	0.12 %
Carbendazim (2)	0.010	0.1	10 %	0.02	1.150	0.0020	0.18 %	0.0041	0.35 %
Deltamethrin (2)	0.01	0.05	20 %	0.01	0.575	0.0020	0.35 %	0.0040	0.70 %
Lambda-cyhalothrin (2)	0.014	0.02	69 %	0.005	0.288	0.0020	0.71 %	0.0041	1.42 %
Dithiocarbamates (1)	0.068	0.05	136 %	0.001	0.0575	0.0136	23.73 %	0.0273	47.45 %
Thiophanate-methyl (1)	0.01	0.1	10 %	0.08	4.600	0.0021	0.05 %	0.0041	0.09 %
Chlorfenvinphos (1)	0.011	0.02	54 %	0.0005	0.0288	0.0021	7.45 %	0.0043	14.91 %

[†]calculated on 28 samples, when active substance (AS) not detected, value was set at the LOQ

^ΔMRL collected from European Pesticides database¹⁶

^βAdult with bodyweight of 57.5 kg: Toxicological credit = ADI*57.5

* For a daily consumption of 200 g of vegetables in 400 g of F&V menus: Exposure 1=Mean value*0.2

[§]Exposure 2 = 2* Exposure 1

detected AS were carbendazim, iprodione and dithiocarbamates; and the AS detected were more often in fruits (74 %) than in vegetables (26 %).

Sixty-four percent of the samples ($n = 36$) showed at least one AS and 36 % none. No more than 3 AS were detected in the daily pooled samples of fruits or vegetables. A single AS was detected in two-thirds of samples.

As already mentioned, it was not possible to identify which fruit or which vegetable could be responsible for the detected AS; but the aim of the study was to evaluate intake of AS and not to identify vectors of specific AS. There was no difference in the number of AS detected between F&V purchased in different shops.

Comparison of residue levels with MRL

In vegetables

Table 4 describes the value of pesticide residue detected in vegetables as a percentage of the MRL.

Of the 43 AS we were looking for, 8 were detected in vegetable samples: difenoconazole, iprodione, carbendazim, deltamethrin, lambda-cyhalothrin, dithiocarbamates, thiophanate-methyl and chlorfenvinphos. The mean level of dithiocarbamates was the only one to be over MRL, and this was due to a single sample with measured level reaching 11 times the MRL.

Regarding the other pesticide residues, mean level compared to MRL reached for instance 24 % for difenoconazole, 53 % for iprodione, 69 % for lambda-cyhalothrin and 54 % for chlorfenvinphos (Table 4). However some samples showed levels exceeding MRL value: 2 samples from 4 where difenoconazole was detected, showed levels of 180 % and 300 %, the 3 samples where iprodione was de-

tected showed levels of 150 % and 400 %, 1 sample from 2 where lambda-cyhalothrin was detected showed level of 150 % and the only sample where chlorfenvinphos was detected showed level of 150 %.

In fruits

Table 5 describes the value of pesticide residues detected in fruits as a percentage of the MRL.

Of the 43 AS, 17 were actually detected in fruit samples: carbendazim, dithiocarbamates, iprodione, thiophanate-methyl, phosalone, myclobutanil, chlorpyrifos Ethyl, lambda-cyhalothrin, carbaryl, cypermethrin, procymidone, pirimicarb, thiabendazole, flufenoxuron, propargite, diphenylamine and tebufenozide.

The mean level of pesticide residues compared to MRL reached 89 % for dithiocarbamates, 63 % for iprodione, 31 % for carbaryl, 88 % for procymidone, 24 % for thiabendazole and 100 % for propargite (Table 5). However some samples showed residue levels exceeding MRL value: the 7 samples where dithiocarbamates were detected showed levels of 200 % and 860 %, 4 samples from 5 where iprodione exceeded the MRL with a maximum level of 1250 % in one of the samples and the only samples where carbaryl, procymidone and myclobutanil were detected showed level of 340 %, 1100 % and 120 %, respectively.

Comparison of the daily intake of pesticide residues with ADI

In vegetables

Chronic exposure for adults, as assessed from the selected menus, represents 23.7 % of the ADI for dithiocarbamates (Table 4), which means an available toxicological credit of 76 % for this class of AS. Nevertheless, in the single

Table 5. Pesticide residues and exposure through fruit consumption.

Active substances (<i>N</i> detections on 28 samples)	Mean value (mg/kg) [†]	MRL			Toxicological credit (mg/d) ^β	Intake = 200 g of fruits		Intake = 400 g of fruits	
		European MRL ^{Δ*} (mg/kg)	% of MRL	ADI (mg/kg/d)		Exposure 1* (mg/kg/d)	Used Toxicological credit (%)	Exposure 2 [§] (mg/kg/d)	Used Toxicological Used
Carbendazim (13)	0.015	0.1	15 %	0.02	1.15	0.0017	0.15 %	0.0034	0.30 %
Dithiocarbamates (7)	0.044	0.05	89 %	0.001	0.0575	0.0089	15.47 %	0.0180	30.95 %
Iprodione (5)	0.013	0.02	63 %	0.06	3.45	0.0025	0.07 %	0.0050	0.14 %
Thiophanate-methyl (3)	0.0096	0.1	10 %	0.08	4.6	0.0019	0.04 %	0.0039	0.08 %
Phosalone (3)	0.0094	0.05	19 %	0.01	0.575	0.0019	0.33 %	0.0038	0.65 %
Myclobutanil (2)	0.01	0.02	52 %	0.02	1.15	0.0021	0.18 %	0.0041	0.36 %
Chlorpyrifos Ethyl (2)	0.01	0.05	20 %	0.01	0.575	0.0020	0.35 %	0.0040	0.70 %
Lambda-cyhalothrin (1)	0.01	0.02	50 %	0.005	0.288	0.0020	0.70 %	0.0040	1.39 %
Carbaryl (1)	0.016	0.05	31 %	0.008	0.46	0.0031	0.68 %	0.0063	1.37 %
Cyperméthrin (1)	0.01	0.05	21 %	0.05	2.875	0.0021	0.07 %	0.0041	0.14 %
Procymidone (1)	0.018	0.02	88 %	0.025	1.438	0.0035	0.24 %	0.0070	0.49 %
Pirimicarb (1)	0.011	0.5	2 %	0.035	2.013	0.0022	0.11 %	0.0044	0.22 %
Thiabendazole (1)	0.012	0.05	24 %	0.1	5.75	0.0024	0.04 %	0.0047	0.08 %
Flufenoxuron (1)	0.011	0.05	21 %	0.0035	0.201	0.0021	1.06 %	0.0043	2.13 %
Propargite (1)	0.01	0.01	100 %	0.007	0.403	0.0020	0.50 %	0.0040	0.99 %
Diphenylamine (1)	0.01	0.05	20 %	0.02	1.15	0.0020	0.17 %	0.0040	0.35 %
Tebufenozide (1)	0.01	0.05	20 %	0.02	1.15	0.0020	0.17 %	0.0040	0.35 %

[†]calculated on 28 samples, when active substance not detected, value was set at the LOQ

^ΔMRL collected from European Pesticides database¹⁶

^βAdult with bodyweight of 57.5 kg: Toxicological credit = ADI*57.5

*For a daily consumption of 200 g of fruits in 400 g of F&V menus: Exposure=Mean value*0.2

[§]Exposure 2 = 2* Exposure 1

sample where dithiocarbamates were detected, 195 % of the toxicological credit was used.

Chronic exposure for adults, as assessed from the selected menus, represents 7.5 % of the ADI for chlorfenvinphos, which corresponds to an available toxicological credit of 92.5 %. Moreover, in the single sample where chlorfenvinphos was detected, only 21 % of the toxicological credit was used.

For the remaining AS, exposure (mean value x amount of vegetable consumption) is lower than 5 % of toxicological credit.

In fruits

Chronic exposure for adults represents 15.5 % of the ADI for dithiocarbamates (Table 5), which means an available toxicological credit of 84.5 % for this class of AS. Nevertheless, in 1 sample of the 7 in which dithiocarbamates were detected, 150 % of the toxicological credit was used.

For the remaining AS, exposure (mean value x amount of fruit consumption) is lower than 7 % of toxicological credit.

This study shows, with a realistic approach, that intake of pesticides via F&V for French adult population is far

beyond the ADI. Further, raising both F&V consumption up to 400 g/day (~5 F&V/day) according to recommendations of the national health and nutrition plan^[20] should not lead to ADI overrun in consumers. Except for dithiocarbamates, more than 90 % of the toxicological credit remained available for vegetables as well as for fruits. Moreover, in the present study, we studied AS found in the menu with 800 g of F&V of our previous study to consider larger variety of F&V, so that we can extrapolate from our results with 400 g of F&V. Based on these results, increasing F&V consumption up to 800 g/day will not result in ADI exceedance (Tables 4 and 5).

Regarding exceeding MRL, we should remind that MRL is the maximum concentration of a pesticide residue legally permitted in or on food commodities. MRL are based on Good Agricultural Practice data, so that exceeded MRL are indicators of violations of Good Agricultural Practice, but cannot be interpreted as risk for the consumers.

Moreover, it should be kept in mind that other components of the French diet, such as cereals and wine can bear additional amounts of AS such as organophosphate and carbamates.^[21] The use of LOQ values instead of zero, when no AS was detected, increased mean levels of AS and

estimates of daily intake. Nevertheless using mean values is more appropriate than using single values for evaluation of chronic risk.

Although the number of menus and determinations in this study were small, this reassuring statement may also be relevant to the general population since fresh F&V in the menu were chosen not only to respect nutritional balance and also to mimic French dietary habits. Bias in the choice of F&V analyzed was kept minimal by randomization of the menus. Sampling period was large enough to minimize any seasonal variation in F&V availability and both AS selection and use.

Every day, pooling all the fruits or all the vegetables of the menu in one sample may have caused dilution, rendering detection of minor AS residues unachievable. This solution seemed the most suitable for feasibility, due to the number of samples to be analyzed.

Regarding the dithiocarbamates, in a conservative approach, the ADI value for this group was the ADI for ziram, the lowest within this group. However, a final conclusion regarding the potential health risk related to the observed CS₂ residues cannot be drawn, since the origin of CS₂ remains unknown. Residue risk evaluation is obscured by the fact that some food commodities are known to give false positive results as natural precursors of CS₂ are present in some crops such as *Brassica oleracea*.^[22] Therefore the appropriate toxicological reference value could not be identified^[19] and results should be interpreted with caution regarding this group of AS.

Conclusion

This study shows that the most frequently detected AS were carbendazim, iprodione and dithiocarbamates and that AS were detected more often in fruits than in vegetables. Furthermore, never more than 3 AS were detected in the same sample. Overall, we observed 8 and 14 MRL's overruns on the 1204 measures in vegetables and the 1204 measures in fruits respectively, which indicates MRL exceedance in 0.7 % and 1.2 % of cases, respectively.

Chronic exposure for adults was the highest for dithiocarbamates but did not exceed 23.7 % of the ADI in vegetables and fruits. It means that consumption of the recommended daily intake of F&V does not represent a risk for the consumer.

Acknowledgments

The work was partially supported by a research grant from Aprifel, a French non-profit organization of fresh food and vegetables producers.

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