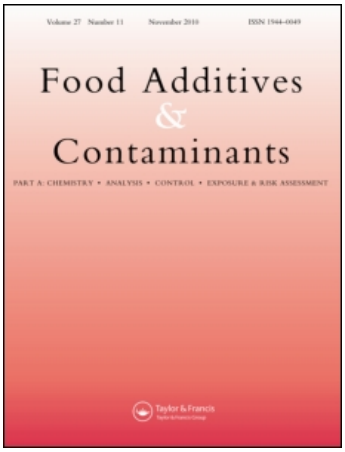

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Dietary risk assessment of organophosphorus and dithiocarbamate pesticides in a total diet study at a Brazilian university restaurant

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In this study ready-to-eat food samples were collected in the production line of the university restaurant of the University of Brasilia, Brazil, which serves non-vegetarian and vegetarian meals daily. Samples were analysed for the presence of ten organophosphorus insecticides (OPs) by GC/FPD, after extraction with ethyl acetate and anhydrous sodium sulfate ($LOQ = 0.002\,mg\,kg^{-1}$), and for dithiocarbamate fungicides, as CS_2, using the spectrophotometric method ($LOQ = 0.05\,mg\,kg^{-1}$). About 43% of the 175 samples analysed contained at least one OP compound at levels up to $1.83\,mg\,kg^{-1}$. Methamidophos was the compound most detected (37.7%), present in most of the soup, soybean and salad samples. No OP residues were found in fruit juice, beans and bran rice samples. The cumulative acute intake of OPs was estimated using methamidophos and acephate as index compounds (IC). The total cumulative intake represented 9.1% and 47.7% of the methamidophos ARfD for the non-vegetarian and vegetarian diets, respectively. When acephate was used as IC, the total intakes represented 20.7% and 116% of the ARfD for the non-vegetarian and vegetarian diets, respectively. Dithiocarbamates were detected in 70% of the 177 samples analysed, at levels up to $0.51\,mg\,kg^{-1}$ CS_2; all salad samples were positive and no residues were found in fruit juice. The chronic intake of dithiocarbamates represented 8.6 and 8.9% of the ADI (mancozeb) for the vegetarian and non vegetarian diets, respectively.

Keywords: gas chromatography; exposure assessment; risk assessment; total diet; pesticide residues; organophosphorous; vegetables; fruit; animal products; meat; beans

Introduction

The use of pesticides is still the most commonly used strategy for pest control in agricultural settings both during the pre- and post-harvest management of the crop. The toxicity of these compounds, however, is not always restricted to the target pest organism, having also been demonstrated in mammals (Belpoggi et al. 2002), including humans (Mendes et al. 2005).

Brazil has one of the largest pesticide markets in the world, with over 400 active ingredients registered for use in a variety of crops, including 31 organophosphorus insecticides (OP) and four dithiocarbamate fungicides (DC) (Ministry of Agriculture, Livestock and Food Supply (MALFS), Brazil 2010). These pesticides were the most frequently found in the Brazilian National Pesticide Residue Monitoring Program (PARA) between 2001 and 2004, detected in 13% (OP) and 21.6% (DC) of the 4001 samples of nine fruits and vegetables analysed (Caldas, Boon et al. 2006, Caldas, Tressou et al. 2006). Dithiocarbamates can result in neuropathology, thyroid toxicity and developmental toxicity in chronically exposed laboratory animals (Food and Agricultural Organization/World Health Organization (FAO/WHO) 1993; US Environmental Protection Agency (USEPA) 2001). Furthermore, the ethylene-*bis*-dithiocarbamate (EBDC) mancozeb was considered to be a multipotent carcinogenic agent in a long-term rat study (Belpoggi et al. 2002) and therefore human chronic intake of these pesticides may be a health concern.

The organophosphorus and the carbamates insecticides are inhibitors of acetyl cholinesterase (AChE), a process that can lead to an accumulation of the neurotransmitter acetylcholine at the nervous terminal after acute exposure, with the potential to alter neurological development in humans (Ahlbom et al. 1995; Ecobichon 2001). The dietary acute intake of some AChE inhibitors evaluated by the FAO/WHO Joint Meeting on Pesticide Residues (JMPR) indicated a possible risk to health, which has restrained the Codex Alimentarius Committee from setting a Codex Maximum Residue Level (MRL) for many of these compounds (Codex Alimentarius 2009). As these insecticides have a common mechanism of toxicity, acute exposure to more than one compound within the group in the diet can be evaluated in a cumulative

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manner (Mileson et al. 1998; USEPA 2006; Boobis et al. 2008). This approach assumes the additivity of the individual toxic effects, with the compound concentration being normalised to yield an equivalent concentration for one of the compounds: the index compound. This normalisation is achieved by applying the relative potency factor (RPF) to the individual residues. The RPF is defined as the ratio between the toxicological end-point of a compound and that of the index compound (Mileson et al. 1998).

Pesticide dietary assessments conducted so far in Brazil have used legal limits in raw commodities as parameters for residue concentration in food (Caldas and Souza, 2004), which probably overestimate exposure, or monitoring residue data for only a few food commodities (Caldas, Boon et al. 2006; Caldas, Tressou et al. 2006), underestimating exposure for not considering the complete diet. In total diet studies (TDS) the actual dietary exposure is assessed by analysing the chemical in all foods within a population diet in a ready-to-eat form, thus taking into consideration the impact of preparation and processing on the final chemical concentration (World Health Organization (WHO) 2005). TDS studies are normally conducted at the national level or for specific populations, such as vegetarians, and chemical classes (Food Standards Australia New Zealand 2003; New Zealand Total Diet Survey 2005; Falcó et al. 2004; Kumari and Kathpal 2009).

In the present study we conducted a dietary chronic risk assessment of dithiocarbamate fungicides and a cumulative acute risk assessment of organophosphorus insecticides using a TDS approach for the adult population of a university restaurant in the city of Brasilia, the capital of Brazil.

Materials and methods

Food consumption data

The university restaurant of the University of Brasilia serves daily approximately 3000 meals at lunchtime and 900 meals at dinner to university students, professors, staff and visitors. The normal lunch meal is composed of white rice, beans, raw vegetable salad (which include leafy vegetables, carrots, cabbage, tomato, cucumber, sweet pepper and/or onion) and a meat serving (beef, chicken or pork). The restaurant also serves an optional vegetarian meal during lunch in which the white rice is replaced by bran rice and the meat meal is replaced by a soybean meal (which can include vegetables), in addition to beans, a raw vegetable salad and a cooked vegetable portion. Daily dinner is vegetable soup. Dessert, served during both the lunch and dinner meals, includes fruit (banana, orange, pealed pineapple or watermelon) and fruit juice. The restaurant menu is nutritionally oriented and is typical of the diet of most regions in Brazil.

Food consumption data during lunchtime were obtained at the restaurant by a trained nutrition student according to the methodology described by Savio et al. (2005). Data were obtained during 6 non-consecutive days in May 2007 through direct observation of the food portions taken by 145 restaurant users eating the vegetarian meal, and 173 restaurant users eating the non-vegetarian meal. In this methodology the mean weight ($n = 3$) of the small, medium and large portions of each meal or food was used to transform each portion size into grams consumed. Age and body weight were reported by each participant. Soup (300 g) and fruit juice (200 ml) consumption data were provided by the university restaurant administration based on previous studies and were used for all participants. For each restaurant user and food the consumption per body weight was calculated.

Food samples

One hundred eighty-four ready-to-eat food samples were collected from the production line of the university restaurant during the second semester of 2005 and in February/March 2007. The number of samples in each food category collected for analysis was defined based on the higher incidence of pesticide residues expected in fruit and vegetables, as these commodities are the most treated with the pesticides investigated in this study. At least 700 g of each sample were collected each time in polystyrene plastic bags, and immediately taken to the laboratory for analysis. Control samples for method validation were provided by a local organic farmer or acquired at a local market. A control vegetable soup sample was prepared in the laboratory. Whenever samples were not immediately processed for analysis, they were kept frozen (−15°C) until analysed. Fruit with inedible peel was peeled before processing and frozen until analysis.

Chemicals

All chemicals were of analytical grade, obtained from Vetec Quimica Fina Ltda (Rio de Janeiro, Brazil) or Merck (Darmstadt, Germany). Certified standards with known purity were kindly donated by Syngenta Crop Protection (Munchwilen, Switzerland) (mancozeb and profenophos), Bayer CropSciences (São Paulo, Brazil) (triazophos), Cheminova A/S (Lemvig, Denmark) (dimethoate, chlorpyrifos and acephate), BASF Corporation (New Jersey, USA) (monocrotophós) and IHARABRAS S.A Industrias Químicas (São Paulo, Brazil) (fenitrothion). Maneb and ethion were purchased from UltraScientific (Road Island, USA), methidathion and methamidophos from

ChemService (Pennsylvania, USA), and thiram from Uniroyal Chemical CO. INC (Connecticut, USA). Working solutions of mancozeb and maneb were prepared in lactose, and of thiram in acetone. A mixed organophosphorus working solution was prepared in ethyl acetate after dilution of primary stock solutions of $100\,\mu g\,ml^{-1}$. All glassware was washed with *n*-hexane or acetone, left in 10% alkaline Extran solution (Merck) and rinsed with distilled water before use.

Organophosphorus analysis

Food samples were analysed for the content of the ten OPs most detected in the PARA monitoring programme in previous years (Caldas, Boon et al. 2006) using the method reported by Caldas, Jardim et al. (2006), with some modifications. Briefly, samples were homogenised in a blender and extracted with ethyl acetate in the presence of anhydrous sodium sulfate in an ultra sonicator (Elma GmbH & Co KG, Singer, Germany). The extract (5 ml) was evaporated under nitrogen and dissolved in ethyl acetate for GC analysis. Fatty samples (soup, meat meals and cooked vegetables) were defatted with *n*-hexane before extraction. Sample extracts were analysed using a GC Finnigan 9001/FPD/AS-2000 and an OV 5% phenyl methyl syloxane capillary column (15.0 m, 250 μm diameter, film thickness = 0.25 μm). Hydrogen was used as the carrier gas and nitrogen as the make-up gas. The total run time was 15.7 min and 1 μl of the extracts was injected. The analyte concentration was determined using weighted linear regression calibration carried out with matrix-matched solutions of calibration standards at 8.0 to $1500\,pg\,\mu l^{-1}$ levels, prepared on the day of the analysis. The identity of the compounds in positive samples was confirmed by GC/MS (Agilent Technologies 6890N/5973) or by LC/MS/MS (Applied Biosystem 4000). The method was validated for cooked rice, beans, meat, soybean meal, soup, raw salad (tomato, lettuce, cabbage, sweet pepper and carrot) and fruit salad (banana, papaya, water melon and pineapple) at levels of $0.002\,mg\,kg^{-1}$ ($n = 5$); $0.02\,mg\,kg^{-1}$ ($n = 4$) and $0.2\,mg\,kg^{-1}$ ($n = 4$). Recoveries ranged from 70% to 120%; an LOQ of $0.002\,mg\,kg^{-1}$ was set for all compounds and matrices.

Dithiocarbamate analysis

Samples were analysed for DCs, as CS_2, using a spectrophotometric method (Caldas et al. 2001). In brief, the DC present in the sample was hydrolysed in an acid stannous chloride solution under heat and the formed CS_2 carried through a vertical reaction system to a sodium hydroxide solution and a copper (II) acetate monohydrate/diethanolamine solution (complexant). The resulting compound was quantified at 435 nm (Shimadzu UV 1650 PC) against a standard curve prepared with CS_2 and the complexant solution. The method was validated for lettuce, carrot, summer squash, soup, cooked beans, meat meal, soybean meal, raw salad and fruit salad. In each case triplicate control samples were fortified with a known amount of dithiocarbamate standard (thiram, mancozeb or maneb) at 0.05–$1.0\,mg\,kg^{-1}$ CS_2 levels. Recoveries ranged from 70% to 120% at all levels, with a coefficient of variation < 20%. The method LOQ was set at $0.05\,mg\,kg^{-1}$ CS_2 for all matrices.

Dietary risk assessment

The equivalent OP residue level in a sample, expressed as the index compound (IC) methamidophos or acephate, was calculated by multiplying the level detected by its relative potency factors (RPF) estimated by Caldas, Boon et al. (2006). For samples containing multiple residues, the equivalent residue levels were added and one concentration per sample, as the IC, was calculated (total equivalent residue). The deterministic approach to estimate the cumulative acute organophosphorus intake considered the highest total equivalent residue level found in each food category and the 97.5th percentile of food consumption by the university restaurant users. For each IC, risk characterisation was performed by comparing the total intake with the IC acute reference dose (ARfD), and expressed as percentage of the ARfD.

The analytical method to analyse DC fungicides in food determines the CS_2 derived from any DC present in the sample, and therefore does not discriminate among the compounds applied to the crops. In order to estimate the chronic intake of DC, it was assumed that all CS_2 detected in the sample came from the use of mancozeb (scenario 1) or that 30% came from the use of propineb (scenario 2). This approach was proposed by Caldas, Tressou et al. (2006) based on the use profile of DC in Brazil, mostly mancozeb products. For the first scenario, risk characterisation was performed by comparing the total chronic dietary intake (as CS_2) with the accepted daily intake (ADI) of mancozeb ($30\,\mu g\,kg^{-1}\,bw\,day^{-1}$; FAO/WHO 1993), calculated as CS_2 ($16.9\,mg\,kg^{-1}\,bw\,day^{-1}$; 1 mole of mancozeb hydrolyses to 2 mole of CS_2). In the second scenario, the percentage of CS_2 coming from propineb was transformed to mancozeb by applying a relative toxicity factor of 1.92 (propineb in relation to mancozeb) to the total intake (Caldas, Tressou et al. 2006). The exposure to mancozeb and propineb can be assessed together as both share the same mechanism of action (FAO/WHO 1993; Hamilton 1998). In both scenarios the total intake was expressed as the percentage of the mancozeb ADI.

Table 1. Description and food consumption of the surveyed population eating non-vegetarian and vegetarian meals at the university restaurant in Brasilia, Brazil.

	Non-vegetarians		Vegetarians	
Population description	($n = 173$)		($n = 145$)	
Percentage men	67.6		50.3	
Body weight (kg), mean (range)	67.6 (39–100)		63.6 (43–95)	
Age (years), mean (range)	23.3 (18–67)		24.0 (17–58)	
Food consumption ($g\,kg^{-1}$ bw)	Mean	97.5 P	Mean	97.5 P
Rice, polished or bran	1.4	3.1	1.5	4.1
Beans	1.9	4.5	1.8	5.2
Meat or soybean	2.5	4.4	2.5	5.2
Cooked vegetables[a]	–	–	1.2	4.6
Salad[b]	1.0	2.9	0.98	2.0
Fruit[c]	1.4	5.2	2.7	9.7
Fruit juice[d]	3.0	4.4	3.2	4.3
Vegetable soup[e]	4.6	6.6	4.8	6.4
Total ($g\,kg^{-1}$ bw)	$15.9^{f} \pm 4.5$	24.3	$18.8^{f} \pm 4.3$	28.4

Notes: [a]Includes brassicas, fruiting vegetables, root and tuber vegetables.
[b]Includes leaf vegetables, brassicas and fruiting vegetables.
[c]Banana, pineapple, papaya, watermelon or clementine.
[d]Consumption of 200 ml.
[e]Consumption of 300 g.
[f]Significantly different ($p < 0.001$).

Results and discussion

Food consumption

Most of the interviewed university restaurant users eating non-vegetarian meals were men; about half of the vegetarians were women (Table 1). Mean body weights were 67.6 and 63.6 kg for individuals eating non-vegetarian and vegetarian meals, respectively; on average, they were 23–24 years of age. Individuals who ate the vegetarian meal had a higher total mean daily food consumption/bw than those eating the non-vegetarian meal ($p < 0.001$). This is mainly due to the additional cooked vegetable portion consumed by the vegetarians, which is not available to the non-vegetarians (Table 1).

Residues in food

One hundred and seventy-five of the 184 prepared food samples collected at the university restaurant were analysed for the presence of the OP compounds; of these, 42.8% contained at least one compound investigated, at or above the LOQ ($0.002\,mg\,kg^{-1}$) (Table 2). No residues were detected in any sample of bran rice, beans and fruit juice. Vegetable soup, soybean, cooked vegetables, and salad had the highest percentage of positive samples (89.5%, 70.0%, 58.8% and 60%, respectively) (Table 2). The distribution of the residue levels found in this study was sharply left skewed, with 71.4% of the positive samples containing residues lower than $0.01\,mg\,kg^{-1}$, 94.2% lower than $0.05\,mg\,kg^{-1}$, and only three samples containing residues higher than $1\,mg\,kg^{-1}$. Very low pesticide residues are expected in processed food, as washing, peeling and cooking can significantly reduce the residues present in the raw commodity (Holden et al. 2001; Keikotlhaile et al. 2010).

Methamidophos was the most frequently detected compound (37.7% of the samples) present in the majority of the soup, soybean and salad samples, and in half of the cooked vegetables samples; acephate was present in 22.3% of the samples, mainly in soybean meal (Figure 1). Methidathion and profenofos were not detected in any sample ($<0.002\,mg\,kg^{-1}$). Methamidophos and acephate (Figure 2) were the compounds found in seven of the eight samples that had residues $\geq 0.05\,mg\,kg^{-1}$, with acephate present at levels above $1\,mg\,kg^{-1}$ (1.05 and $1.83\,mg\,kg^{-1}$; Table 2). In Brazil these compounds are registered, among other crops, for potato, soybean and tomato; acephate can also be used in cabbage, broccoli and bell pepper, crops that are commonly present in the food samples collected at the university restaurant, including the soybean meals.

Multiple OP residues occurred in 40 samples (22.8% of those analysed), of which 19 were salad samples, one containing six different compounds (Table 3). Thirty samples contained residues of methamidophos and acephate, with or without other compounds, with acephate always being present at higher levels than methamidophos. Methamidophos is a plant metabolite of acephate, and is also formed

Table 2. Organophosphorus residues in food served at the university restaurant in Brasilia, and their highest total equivalent residues (HTER) expressed as methamidophos and acephate.

Food	Samples analysed/ ≥ LOQ	Maximum residues (mg kg^{-1})	HTER as (mg kg^{-1})	
			Methamidophos	Acephate
Polished rice	14/1	0.004	0.004	0.050
Bran rice	7/0	<0.002	<0.002	<0.002
Beans	10/0	<0.002	<0.002	<0.002
Meat	11/3	0.006	0.006	0.072
Soybean	10/7	0.008	0.031	0.272
Cooked vegetables	20/12	1.83	0.788	9.77
Salad	51/30	1.05	0.142	1.52
Fruit	28/5	0.177	0.054	0.671
Fruit juice	5/0	<0.002	<0.002	<0.002
Vegetable soup	19/17	0.026	0.026	0.320
Total	175/75			

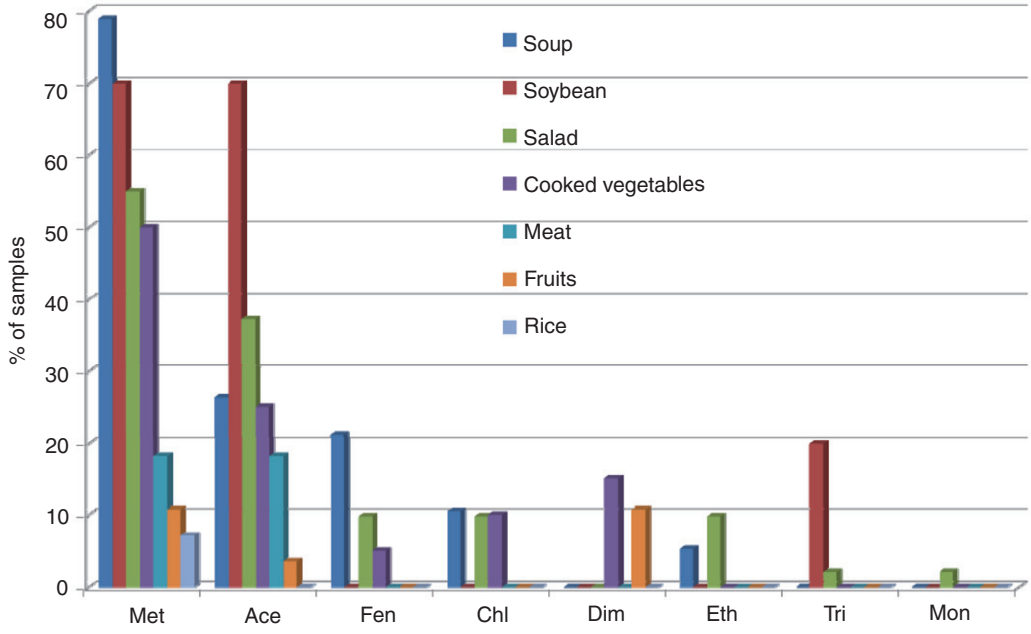

Figure 1. Organophosphorus compounds detected in the samples collected at the university restaurant in Brasilia (university restaurant), Brazil. ace, Acephate; met, methamidophos; chl, chlorpyrifos; mon, monocrotophos; eth, ethion; fen, fenitrothion; tri, triazophos; and dim, dimethoate.

during the processing of food treated with acephate (FAO/WHO 2003). The presence of multiple OP residues in the samples analysed in this study can be the result of different products being applied to one crop that is a component of the food (such as tomato in salad or soup) and/or, most likely, the result of single residues present in the different crops used to prepare the food. Results from the PARA programme (Caldas, Boon et al. 2006) have shown that 19.8% of the 540 tomato samples and 26% of the 529 potato samples analysed were positive for OPs, mainly chlorpyrifos and methamidophos; 19 tomato samples and three potato samples had multiple residues. In this programme only 4.4% of the lettuce samples and less than 1% of the carrot samples were positive, none containing multiple residues.

Table 2 also shows the highest total equivalent residues (HTER) calculated for single and multiple residue samples expressed as either IC. The highest levels were found when the HTER was expressed as acephate. All HTERs ≥ 0.002 mg kg^{-1} were related to samples containing methamidophos, and with the exception of a cooked vegetable sample, all contained multiple residues. This cooked vegetable sample had

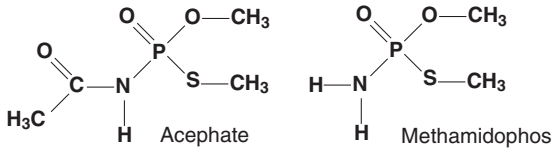

Figure 2. Chemical structures of methamidophos and acephate.

the highest single residue of methamidophos, $0.788\,mg\,kg^{-1}$. Methamidophos is more toxic than acephate, with an RPF of 12.4 when acephate is used as IC (Caldas, Boon et al. 2006), the same estimated by Boon et al. (2008), leading to a HTEC of $9.77\,mg\,kg^{-1}$ expressed as acephate (Table 2). The presence of triazofos in multiple residue samples (soybean and salad; Table 3) also contributed to the HTER, as this compound has RPFs of 5.58 and 48.3 for methamidophos and acephate as IC, respectively (Caldas, Tressou et al. 2006).

Approximately 70% of the 177 samples analysed were positive for DC (Table 4). All salad samples were positive, having also the second highest mean and the highest residue levels of all samples analysed (0.14 and $0.51\,mg\,kg^{-1}$ CS_2, respectively). Results from the PARA programme in raw commodities show that about 45% of the tomato samples and 34% of the lettuce samples analysed were positive for DC, with means of 0.20 and $0.36\,mg\,kg^{-1}$ CS_2, respectively (Caldas, Tressou et al. 2006). These crops were present, alone or in combination with other crops, in most of the salad samples analysed in this study.

Dietary risk assessment

The cumulative acute risk assessments of OP pesticides for both non-vegetarian and vegetarian populations at the university restaurant using methamidophos and acephate as IC are shown in Table 5. For non-vegetarians the consumption of salad and fruit contributed most to the total cumulative intake (means of 45.4% and 32.2%, respectively). The total cumulative intake for vegetarians was over five times higher than for non-vegetarians, with the consumption of cooked vegetables alone contributing 76–77% of the total intake. The intake from the consumption of cooked vegetable (Table 5) was estimated using the residues of methamidophos found in one sample ($0.788\,mg\,kg^{-1}$), hence having the greatest impact on the total cumulative intake for vegetarians.

Caldas, Boon et al. (2006) conducted a cumulative acute exposure assessment of organophosphorus and carbamates using monitoring residue data for nine food crops analysed in the PARA programme. The consumption of tomato contributed with over 60% of the total intake, with methamidophos, monocrotophos and/or triazophos present in the samples which yielded the top ten equivalent residue levels in this crop, expressed as methamidophos or acephate. In a similar study conducted in Denmark the consumption of apples contributed with almost half of the total cumulative intake through the consumption of 43 fruits, vegetables and cereals commodities (Jensen et al. 2009). Both studies applied processing factors to the residues found in the raw commodities to account for the reduction of residues during processing, such as peeling of fruits with inedible peel.

For non-vegetarians the total cumulative intake was lower than the ARfD for both IC scenarios (9.1% and 20.7%, respectively) (Table 5). For vegetarians it reached almost half of the ARfD for methamidophos, and exceeded the ARfD for acephate by 16%, indicating in this case a potential health risk to consumers. These results show the impact of the IC choice on the cumulative acute risk assessment of OPs. The USEPA (2006) considered methamidophos to be the appropriate IC to conduct the cumulative acute assessment of organophosphorous in the United States. In the Netherlands, Boon et al. (2008) chose acephate in their assessment for the Dutch population, and Bosgra et al. (2009) estimated RPFs using both methamidophos and acephate as IC. Jensen et al. (2009) conducted their studies in Denmark using methamidophos and chlorpyrifos as IC. In Brazil, Caldas, Boon et al. (2006) estimated the RPFs using both methamidophos and acephate as IC based on practically the same toxicological database used by the USEPA and Boon et al. (2008). In the Brazilian study, which also included the carbamate insecticides, the associated risk was about two times higher when acephate was used as the IC. In the present study, the percentage ARfD using acephate as IC was over two times higher than when methamidophos were used, for both non-vegetarian and vegetarian populations. Caldas, Boon et al. (2006) found exceedance of the ARfD for both ICs at the P99.99 for the adult population and for acephate at P99.9 for children (0–6 years old). Boon et al. (2008) also found an exceedance of the acephate ARfD for the Dutch children exposed to OPs (134% of ARfD at P99.9).

The selected index compound in a cumulative assessment should have the largest available toxicological data of acceptable quality (USEPA 2002). The USEPA has selected methamidophos as IC for their cumulative assessments for the large AChE inhibition data to support the modelling of a benchmark dose by different routes of exposure (USEPA 2002). However, these data are not available for all AChE inhibitors considered in other studies. Caldas, Boon et al. (2006) have chosen acephate for the well-performed toxicology studies for the inhibition of AChE in rat, which were evaluated by the JMPR. In any case, the available toxicological database used to estimate RPFs have

Table 3. Samples collected at the university restaurant containing multiple OP residues.

Food	Number of samples	Pesticides (number of samples)
Salad	19	ace/met (12); ace/met/chl (2); ace/met/mon (1); met/fen/eth (2); ace/met/fen/eth (2); met/fen/eth/chl/mon/tri (1)
Soybean	8	ace/met (2); met/tri (2); met/fen (1); ace/met/chl (1); ace/met/fen (1);
Soup	6	ace/met (3); met/fen (2); ace/met/chl/eth (1)
Cooked vegetables	6	ace/met (3); ace/met/ chl (1); ace/met/fen (1); met/dim/chl (1)
Meat	1	ace/met (1)

Note: ace, Acephate; met, methamidophos; chl, chlorpyrifos; mon, monocrotophos; eth, ethion; fen, fenitrothion; tri, triazophos; and dim, dimethoate.

Table 4. Residue data and dietary risk assessment of dithiocarbamate fungicides through the food consumption at the university restaurant.

Food category	Samples analysed/≥LOQ	Mean residues[a] (range) (mg kg^{-1} CS_2)	Intake non-vegetarian meal (μg kg^{-1} bw day^{-1})	Intake vegetarian meal (μg kg^{-1} bw day^{-1})
Polished rice	10/6	0.15 (<0.05–0.40)	0.210	–
Bran rice	11/3	0.04 (<0.05–0.08)	–	0.06
Beans	10/4	0.06 (<0.05–0.13)	0.114	0.180
Meat meal	10/6	0.08 (<0.05–0.20)	0.200	–
Soya meal	11/6	0.05 (<0.05–0.08)	–	0.125
Cooked vegetables	20/15	0.12 (<0.05–0.40)	–	0.144
Salad	51/51	0.14 (0.06–0.51)	0.140	0.137
Fruit	29/22	0.08 (<0.05–0.19)	0.112	0.216
Fruit juice	6/0	0.025 (<0.05)	0.000	0.000
Vegetable soup	19/10	0.08 (<0.05–0.25)	0.368	0.384
Total intake (μg kg^{-1} pc day^{-1}, CS_2)			1.144	1.174
Percentage ADI,[b] 100% mancozeb			6.8	6.9
Percentage ADI,[b,c] 30% propineb			8.6	8.9

Notes: [a]Residues were considered at 0.5 LOQ for the intake calculation.
[b]ADI of mancozeb, expressed as CS_2 (16.9 μg kg^{-1} bw day^{-1}).
[c]Calculated as [(total intake*0.7) + (total intake*0.3*1.92)]/ADI.

Table 5. Dietary risk assessment of organophosphorus through food consumption at the university restaurant using methamidophos and acephate as index compounds.

	Intake as (μg kg^{-1} bw)			
	Metamidophos, ARfD = 10 μg kg^{-1} bw[a]		Acephate, ARfD = 50 μg kg^{-1} bw[a]	
Food category	Non-vegetarian	Vegetarian	Non-vegetarian	Vegetarian
Polished rice	0.012	–	0.012	–
Bran rice[b]	–	0.004	–	0.004
Beans[b]	0.004	0.005	0.004	0.005
Meat meal	0.026	–	0.317	–
Soybean	–	0.161	–	1.414
Cooked vegetables	–	3.625	–	44.94
Salad	0.412	0.284	4.408	3.040
Fruit	0.281	0.529	3.489	6.576
Fruit juice[b]	0.004	0.004	0.004	0.004
Vegetable soup	0.172	0.166	2.112	2.0480
Total intake	0.912	4.774	10.347	58.034
% ARfD	9.1	47.7	20.7	116

Notes: [a]Food and Agricultural Organization/World Health Organization (FAO/WHO) (2002).
[b]Residues were considered at 0.5 LOQ for the intake calculation.

uncertainties (Bosgra et al. 2009), and the outcome of the assessments using both ICs should be considered when evaluating the possible health impact from the exposure to these pesticides.

The chronic dietary risk assessment of DC is shown in Table 4. The total intakes from the consumption of non-vegetarian and vegetarian meals were similar, with vegetable soup contributing with over one-third of the total intake in both cases. The total intake represented less than 10% of the ADI when 30% of the CS_2 residues found in the samples were considered to have originated from the use of propineb in the field, the most critical exposure scenario. These results confirm previous studies using monitoring data conducted in Brazil (Caldas et al. 2004; Caldas, Tressou et al. 2006) and Denmark (Jensen et al. 2008) that concluded that the dietary exposure to dithiocarbamate does not represent a health risk to consumers. Studies that assess the dietary exposure to the dithiocarbamate are always subject to the inherent limitation of the method used to analyse this class of pesticide. In addition to not discriminating among the DCs applied to the crop, the method based on the measurement of the CS_2 formed during the hydrolysis can give false-positive results due to the natural presence of sulfur compounds in the food, mainly brassicas (FAO/WHO 1993; Caldas et al. 2004). Hence, the results can reflect an overestimation of the real exposure.

An additional limitation of this study is that the food consumption data obtained at the university restaurant, as well as the food that was collected and analysed for the presence of the pesticides, did not include information on the food eaten outside the restaurant, such as breakfast, which is not served at the restaurant. Although this lack of information can underestimate the exposure, we believe that this is only important when the missing data are related to fruits and vegetables. We also did not have individual consumption data for soup, assuming a standard consumption level for all university restaurant users. This might have underestimated the exposure for high soup consumers, which is relevant in the acute exposure estimation to OPs, mainly for non-vegetarians, for whom soup contributed with up to 20% of the intake.

Conclusion

The outcome of a dietary risk assessment of pesticides will depend on both the data and the methodology used to estimate the exposure and assess the risk. This paper presented the results of a pesticide dietary risk assessment using residue data on ready-to-eat meals, individual consumption data and a deterministic estimation of the exposure within a TDS approach. TDSs are considered to have a high level of refinement compared with assessments that use monitoring residue data and are recommended by the WHO to be conducted by governments at a national level (WHO 2005).

The results show that the chronic intake of dithiocarbamates through the consumption of meals at the university restaurant in Brasilia, Brazil, does not pose a health risk to consumers. Although the cumulative acute intake of organophosphorus pesticides for vegetarians indicated a small exceedance of the acephate ARfD, this result needs to be considered in light of all the uncertainties involved in the estimation, including those associated with the consumption and residue data, and with the choice of the IC in the cumulative approach. Organophosphorus pesticides are the most toxic compounds currently used in agriculture in Brazil and in several other countries, which has led to governmental actions aimed at eliminating or restricting their use. Recently, the registration of monocrotophos was cancelled in Brazil, and a similar action was proposed by the Brazilian Health Surveillance Agency (ANVISA) regarding methamidophos (ANVISA 2010). Lastly, the government should implement and maintain actions to enforce the correct use of pesticides in the field, so consumers are not exposed to unsafe levels of these compounds in their diets.

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