



## Brazilian monitoring programs for pesticide residues in food – Results from 2001 to 2010

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### ABSTRACT

A total of 13,556 samples of 22 fruit and vegetable crops, rice, and beans were analyzed within two Brazilian pesticide residue monitoring programs between 2001 and 2010. Pesticide residues were found in 48.3% of the samples, and 13.2% presented some irregularity, mostly non-authorized active ingredient use. Less than 3% of the samples had residue levels above the MRL. Apple, papaya, sweet pepper and strawberry were the crops with the higher percentages of positive samples (about 80%). Dithiocarbamates and organophosphorus compounds were found in 41.6% and 30.8% of the samples, respectively. Carbendazim and chlorpyrifos were the pesticides most found (26.7 and 16.1% of positive samples, respectively). Almost half of the samples analyzed had multiple residues (up to 10 residues), with multiple residues most common in samples of apple, sweet pepper and tomato. About 8% of positive samples contained up to four residues of the same chemical class, mainly organophosphorus compounds (18.6%, mostly in apple) and triazoles (16.1%, mostly in papaya and grape). In general, the scenario of pesticide residues in foods investigated within the Brazilian governmental monitoring programs in the last decade is similar to what has been found in other countries. However, the use of non-authorized active ingredients is a common practice among the farmers in the country, a problem that the government authorities have been trying to solve. A preliminary cumulative acute exposure assessment for organophosphates and carbamates in apple has shown that the intake by individuals  $\geq 10$  years old accounts for 100% of the acephate ARfD, indicating a need to further investigate the exposure through the consumptions of other crops and group of pesticides, mainly for children.

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### 1. Introduction

Pesticide use is the most widely adopted pest management strategy to guarantee food supplies worldwide. In Brazil, one of the world's major food producers, over 90% of farmers rely on pesticide use (IBGE, 2006), and the country has ranked first in pesticide use worldwide in recent years, with over 673 million tons applied in 2008 (ANDEF, 2009).

The basis for pesticide regulation in Brazil was set by Federal Law No. 7802, enacted in 1989, and later by Acts 4074/2002 and 5981/2006 (ANVISA, 2011a). These legal standards regulate all aspects related to pesticides, including registration, use, production, storage, transport and disposal. The pesticide registration process involves the Ministry of Health, through the National Sanitary Surveillance Agency (ANVISA), which is responsible for

evaluating the impact of pesticide use on human health, and for the establishment of maximum residue levels (MRL); the Ministry of the Environment, which evaluates the impact on non-human species; and the Ministry of Agriculture, Livestock and Food Supplies (MAPA), responsible for evaluating pesticide pest control efficacy and approving the product label. Brazilian MRLs are established based on supervised pesticide residue trials conducted throughout the country, and reflect the good agricultural practices used nationally, specified in the approved product labels. As of June 2011, 343 active ingredients had MRLs established for a variety of food commodities in the country (ANVISA, 2011b).

Two monitoring programs for pesticide residues in food of vegetal origin are currently in place in Brazil, aimed at evaluating compliance with national MRLs: the Program on Pesticide Residue Analysis in Food (PARA), coordinated by ANVISA, and the National Residue and Contaminant Control Program (PNCRC), coordinated by the MAPA. The first results of the PARA program were published by Oliva, Gemal, Nóbrega, and Araújo (2003), and reported the residue findings from 350 samples of tomato and strawberry collected in

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four Brazilian states from July to December, 2001. Caldas, Tressou, and Boon (2006), Caldas, Boon and Tressou (2006) summarized the PARA results for the 2001–2004 period for organophosphorus, carbamates and dithiocarbamate pesticides in nine food commodities evaluated. Additionally, Mauricio, Lins and Alvarenga (2009) described the strategies implemented by the MAPA in 2006 to increase the analytical standards of the official laboratories under the PNCRC, including the updating of instrumentation facilities and the increase in capacity-building. The summary of the results obtained by the PARA program are periodically posted at the Agency website (ANVISA, 2011c), and those from the PNCRC were published in the official government gazette (Brasil, 2009a and 2010, p 3). These summaries are only available in Portuguese.

The objective of this paper is to present and discuss the results obtained by the PARA and the PNCRC pesticide residue monitoring programs for the period between 2001 and 2010.

## 2. Material and methods

### 2.1. The monitoring programs

From 2001 to 2007, the scope of the PARA program was to analyze 92 active ingredients (a.i.) in 9 food crops - apple, banana, carrot, lettuce, orange, papaya, potato, strawberry and tomato (ANVISA, 2011c). This scope was expanded in 2008 (to 167 a.i., with the inclusion of pineapple, rice, onion, bean, mango, sweet pepper, cabbage and grape), and in 2009 (to 234 a.i., with the inclusion of sugar beet, collard green and cucumber). The samples analyzed under the PARA were collected at local supermarkets and food distributors by the state sanitary surveillance agencies, and covered 24 of the 26 Brazilian states, and the Federal District. The samples were sent fresh for analysis and arrived at the laboratory within 24 h after collection.

The PNCRC program of products of vegetal origin initiated its activities in 2006, analyzing samples of apple and papaya for export, and samples of these crops from local markets in subsequent years. Its legal basis was established in 2009 (Brasil, 2009b), when pineapple, banana, grapes, lemon, melon, mango, strawberry, tomato, lettuce, and potato were included in the program. Potato data are not included in this paper due to problems in data reporting. Under the PNCRC, samples are collected by federal agriculture inspectors at packing houses in seven Brazilian states (Espírito Santo, Bahia, Pernambuco, Rio Grande do Norte, Santa Catarina, Rio Grande do Sul and Paraíba) and/or at the largest national distributor of fresh food, located in the city of São Paulo (CEAGESP - Companhia de Entrepósitos e Armazéns Gerais de São Paulo). Apple, mango, papaya and grape samples were collected from both the packing houses and CEAGESP, and the other crops only from the latter.

### 2.2. Analytical methods

Five laboratories analyzed the samples collected within the PARA program, of which four are state laboratories. They were inspected and authorized by ANVISA to ensure compliance with ISO/IEC 17025 requirements; two laboratories are accredited by the competent Brazilian agency (INMETRO). Dithiocarbamates were determined as CS<sub>2</sub> either by spectrophotometry (LOQ of 0.08–0.4 mg/kg) or by gas chromatography (GC/FPD) (LOQ of 0.05–0.3 mg/kg). The multiresidue Mini Luke extraction method (The Netherlands, 1996) was used for the other pesticide classes, using GC/FPD, GC/ECD, CG/NPD, GC/MS/MS or LC/MS/MS. LOQs vary among laboratories, matrix and compound, being 0.01 mg/kg in most cases. The highest (0.4 mg/kg) was reported for carbendazim in apple and sweet pepper and cypermethrin in sweet

pepper, and the lowest (0.005 mg/kg) for carbendazim in pineapple, sugar beet, collard green, papaya, mango, cucumber, cabbage and grape, and tetraconazole in pineapple, sugar beet, mango, grape and cucumber.

Two ISO/IEC 17025 accredited laboratories analyzed the samples collected within the PNCRC program. Dithiocarbamates were determined as CS<sub>2</sub> by GC/FPD (LOQ of 0.01–0.07 mg/kg). Other pesticides were analyzed by multiresidue Mini Luke method using GC/ECD, GC/MS or LC/MS/MS. LOQ was 0.01 mg/kg in most cases, and the highest LOQ was 0.41 mg/kg for bifenthrin, captan, esfenvalerate and fenpropathrin in melon, strawberry and grape.

## 3. Results

A total of 13,556 samples were analyzed for pesticide residues between 2001 and 2010 (Table 1), of which 12,072 were from the PARA program (July 2001 to December 2009), and 1484 from the PNCRC (January 2006 to July 2010). Some samples collected between 2001–2002 and 2009–2010 did not contain the sampling data, so they were grouped. Laboratories that analyzed the samples in both programs used similar analytical methods with LOQs in the same range.

Prior to 2006, less than 50% of the samples analyzed contained pesticide residues (all samples from the PARA program), but from 2006 to 2010, the majority of the samples were positive for at least one pesticide ( $\geq$ LOQ) (Table 1). A total of 1790 samples (13.2%) were irregular (presence of a non-authorized a.i., or residue levels higher than the Brazilian MRL); irregular samples represented 27.3% of the positive samples. The periods of 2001/2002 and 2009/2010 had the higher percentages of irregular samples, representing 16.2 and 17.5% of the samples analyzed for each period, respectively, and 2005 the lowest (5.2%). When compared with the positive samples, higher percentages of irregularities were found in 2001/2002 (32%) and 2003 (43%).

The majority of the irregularities found for the period under study were related to the use of non-authorized a.i. (72.1%) (Table 1), mainly methamidophos (256 samples), chlorpyrifos (207 samples) and dithiocarbamates (138 samples). For 2001/2002, 2004 and 2005, over one third of the samples had at least one residue above the MRL. The pesticides most frequently found above the MRL for the whole period were dithiocarbamates (121 samples), carbendazim (99 samples) and iprodione (39 samples). Approximately 7% of the samples presented non-authorized a.i., and also residues above the MRL.

**Table 1**

Samples analyzed by the Brazilian monitoring programs from 2001 to 2010, as percent of positive and irregular samples.

Year	Samples analyzed	Positive samples, % <sup>a</sup>	Irregular samples				
			Total	% <sup>b</sup>	NA, % <sup>c,d</sup>	>MRL, % <sup>c</sup>	Both, % <sup>c,e</sup>
2001/2002	1278	41.5	207	16.2	51.2	38.2	10.6
2003	1369	28.6	168	12.3	83.9	7.1	8.9
2004	1208	47.1	130	10.8	64.6	31.5	3.8
2005	1195	37.4	62	5.2	67.2	32.8	—
2006	1049	57.3	118	11.2	74.6	16.9	8.5
2007	1373	57.0	175	12.7	76.6	16.6	6.9
2008	2194	51.4	250	11.4	83.1	12.4	4.4
2009/2010	3890	53.9	680	17.5	71.8	19.8	8.4
<b>Total</b>	<b>13556</b>	<b>48.3</b>	<b>1790</b>	<b>13.2</b>	<b>72.1</b>	<b>20.6</b>	<b>7.4</b>

<sup>a</sup> Presence of at least one pesticide residue at levels > LOQ.

<sup>b</sup> Related to the total of samples analyzed each year.

<sup>c</sup> Related to the total of irregular samples each year.

<sup>d</sup> Non-authorized active ingredient.

<sup>e</sup> Presence of both non-authorized active ingredient and residues above the MRL.

**Table 2**

Food commodities analyzed by the Brazilian monitoring programs from 2001 to 2010, as percent of positive and irregular samples.

Crop	Samples analyzed	Positive samples, % <sup>a</sup>	Irregular samples				
			Total % <sup>b</sup>	NA, % <sup>c,d</sup>	>MRL <sup>c</sup> , %	Both, % <sup>c,e</sup>	
Apple	1750	79.9	107	6.1	82.2	16.8	0.9
Papaya	1545	82.3	173	11.2	46.2	47.4	6.4
Potato <sup>f</sup>	1222	25.9	49	4.0	12.2	87.8	–
Orange <sup>f</sup>	1219	28.5	38	3.1	86.8	13.2	–
Tomato	1154	59.8	158	13.7	63.9	27.2	8.9
Carrot <sup>f</sup>	1021	15.5	83	8.1	48.2	51.8	–
Lettuce	1007	33.9	210	20.9	97.1	1.0	1.9
Strawberry	992	76.3	393	39.6	73.3	13.5	13.2
Banana	911	11.3	25	2.7	52.0	44.0	4.0
Beans <sup>f</sup>	301	55.1	6	2.0	50.0	50.0	–
Rice <sup>f</sup>	298	18.5	15	5.0	93.3	6.7	6.7
Grape	286	82.2	98	34.3	62.2	21.4	16.3
Mango	284	30.6	9	3.2	66.7	33.3	–
Pineapple	270	41.9	55	20.4	49.1	41.8	9.1
Cabbage <sup>f</sup>	268	18.3	43	16.0	100	–	–
S. pepper <sup>f</sup>	266	82.0	188	70.7	86.7	2.7	10.6
Onion <sup>f</sup>	263	1.1	3	1.1	100	–	–
Sugar beet <sup>f</sup>	172	32.0	37	21.5	100	–	–
Cucumber <sup>f</sup>	146	53.4	43	29.5	88.4	7.0	4.7
Collard <sup>f</sup> green	129	58.1	52	40.3	71.2	19.2	9.6
Lemon <sup>g</sup>	31	74.2	3	9.7	100	–	–
Melon <sup>g</sup>	21	28.6	2	9.5	100	–	–
<b>Total</b>	<b>13556</b>	<b>48.3</b>	<b>1790</b>	<b>13.2</b>	<b>72.1</b>	<b>20.6</b>	<b>7.4</b>

<sup>a</sup> Presence of at least one pesticide residue at levels  $\geq$ LOQ.

<sup>b</sup> Related to the total of samples analyzed each year.

<sup>c</sup> Related to the total of irregular samples each year.

<sup>d</sup> Non-authorized active ingredient.

<sup>e</sup> Presence of both non-authorized active ingredient and residues above the MRL.

<sup>f</sup> Only PARA program.

<sup>g</sup> Only PNCRC program.

Table 2 shows the number and the percentage of positive and irregular samples for each crop analyzed under the programs. Apple and papaya were the crops with the highest number of samples analyzed, having also the higher percentages of positive samples (about 80%), with similar percentages found also for strawberry, grape and sweet pepper. Lemon and melon were analyzed only under the PNCRC program (2009/2010) (31 and 21 samples, respectively). Sweet pepper was the crop with the highest percentage of irregularity (70.7% of the samples analyzed), mainly due to non-authorized organophosphorus compound use (163 samples; Table 2), mostly methamidophos (103 samples). Strawberry represented 39.6% of irregular samples, from which 73.3% with non-authorized a.i., mostly captan, prochloraz and endosulfan. Over 60% of non-authorized use in lettuce was due to dithiocarbamates (withdrawn from the label in 2005). Only 4% of potato samples analyzed were irregular, mostly due to residues above the MRL (87.8%), a profile of irregularities clearly different from the other crops. Strawberry, grape and sweet pepper presented the highest percentages of irregular samples presenting both non-authorized use and residues above the MRL (>10%). Irregularities found in cabbage, sugar beet, onion, lemon and melon samples were due only to non-authorized use (Table 2). In cabbage, this was mostly due to the presence of procymidone (20 samples).

Data from the PNCRC program shown in Tables 1 and 2 only concern the period of 2006–2010. Table 3 shows the results of the PARA and the PNCRC for the crops analyzed in both programs during this period. In general, the PARA results showed a lower frequency of positive samples and a frequency of irregular samples over two times higher than the PNCRC program (17.9 and 8.0%, respectively). The number of samples analyzed in both programs was comparable only for apple and papaya, which showed similar

**Table 3**

Results obtained by the PARA and PNCRC monitoring programs from 2006 to 2010.

Crop	PARA 2006–2009			PNCRC 2006–jul 2010		
	Samples analyzed	Positive samples, % <sup>a</sup>	Irregular samples, % <sup>b</sup>	Samples analyzed	Positive samples, % <sup>a</sup>	Irregular samples, % <sup>b</sup>
Apple	560	84.1	2.7	690	87.8	5.7
Tomato	520	67.5	14.4	26	76.9	3.8
Strawberry	515	84.9	35.1	42	64.3	19.0
Lettuce	501	31.1	29.3	32	53.1	25.0
Banana	406	10.1	2.2	29	51.7	0.0
Papaya	396	89.4	19.4	540	92.0	9.1
Grape	266	84.2	36.8	20	55.0	0.0
Pineapple	240	43.3	20.4	30	30.0	20.0
Mango	261	27.6	2.3	23	65.2	13.0
<b>Total</b>	<b>3665</b>	<b>60.3</b>	<b>17.9</b>	<b>1432</b>	<b>85.0</b>	<b>8.0</b>

<sup>a</sup> Presence of at least one pesticide residue at levels > LOQ; Non-authorized active ingredient.

<sup>b</sup> Presence of non-authorized active ingredient and/or residues above the MRL.

frequencies of positive samples during the period. However, the frequency of irregular papaya samples collected by the PARA program was over 3 times higher than that from the PNCRC program (14.4 and 3.8% of the samples analyzed, respectively). In both programs, the majority of the irregular apple samples contained non-authorized a.i. (66.7 and 71.8%), while most of the irregular papaya samples contained residues above the MRL (55.8 and 59.2%) (data not shown). The number of samples analyzed by the PNCRC program for the other crops shown in Table 3 was much smaller than those from the PARA program (less than 10%, in general), and comparisons between the two data sets may be misleading.

Of the samples analyzed by the PNCRC, 934 samples (62.9%) were collected at packing houses (mostly commodities for export), and 550 samples at CEAGESP (for domestic consumption, including 8 samples of imported apples). The percentage of positive samples collected at CEAGESP (75.3%) was lower than that collected at packing houses (89%). However, only 2.9% of the packing house samples were irregular (2% non-authorized use), while 10.6% of the CEAGESP samples were in this situation (6.3% non-authorized) (data not shown).

Fig. 1 shows the percentage of residues that exceeded the national MRLs, considering all the positive samples. In about 25% of the cases, residues were up to 50% higher than the MRL, and in the majority of cases (65%), reached up to 2.5 times the MRL (15% exceedance of the MRL). The three highest residues above the MRL were triazophos in tomato (2075% MRL of 0.04 mg/kg), propiconazole in rice (3340% of MRL of 0.1 mg/kg), and chlorpyrifos in potato (3400% MRL of 0.01 mg/kg).

Most of the residues (51.3%) found in the positive samples analyzed were in the range of 0.01 to <0.1 mg/kg, and 5.8% had levels between 1 and 10 mg/kg Fig. 2 shows the residue levels found in the samples of the 10 crops with the highest percentage of positive residues (higher than 50% of the samples analyzed). The majority of the positive samples of cucumber and beans had residue levels <0.05 mg/kg. Over 40% of the sweet pepper and strawberry samples had residues in the range of 0.1 to <0.5 mg/kg, and about ¼ of the strawberry samples had residues above 0.5 mg/kg. Lettuce (33.9% of positive samples) presented the highest percentage of positive residues within the highest concentration range (1–<10 mg/kg) (27.5%; 122 residues) (not shown), of which over 70% were dithiocarbamates. One lettuce, one pineapple and 5 strawberries samples presented residues above 10 mg/kg, with the highest levels found in strawberry (14.7, 15.3 and 25.1 mg/kg of iprodione).

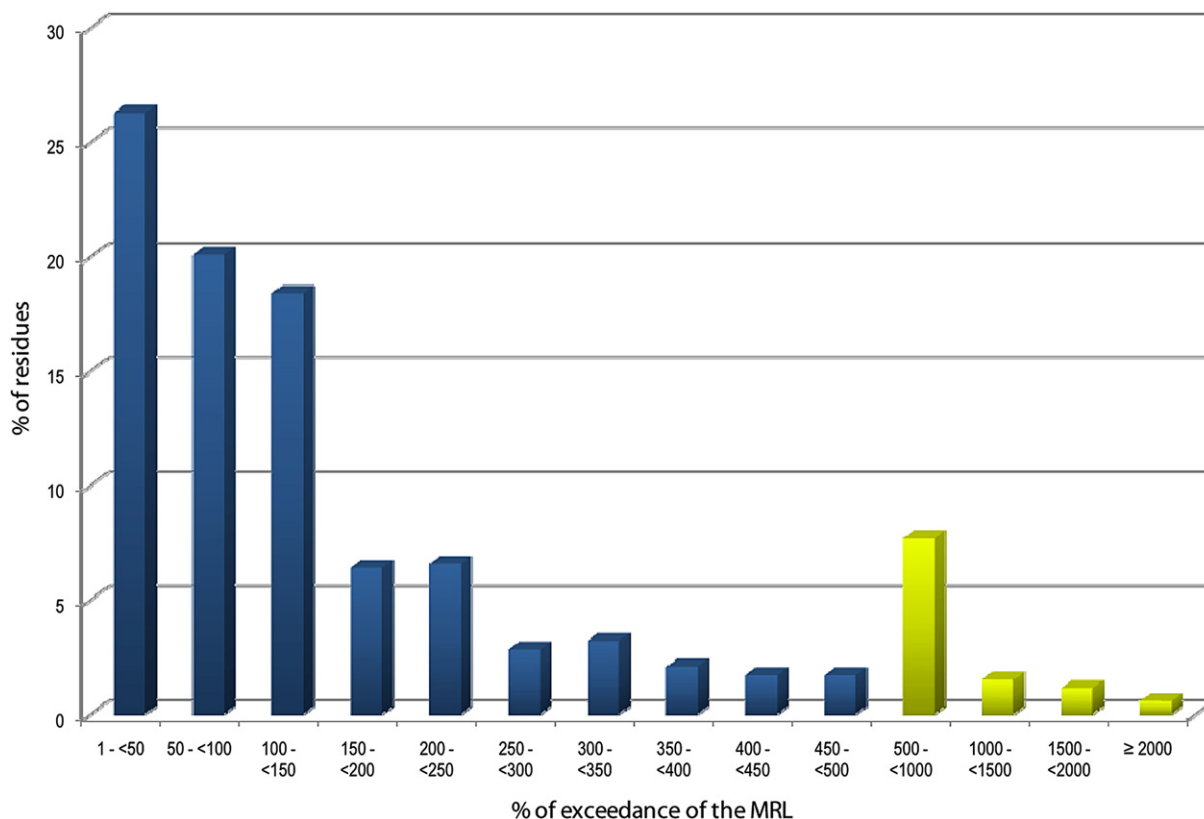


Fig. 1. Percentage by which the MRLs is exceeded in the samples analyzed of the Brazilian monitoring programs from 2001 to 2010. Dithiocarbamates had its LMR established as CS<sub>2</sub> only as of 2003.

Fig. 3 shows the crops presenting multiple residues (up to 7 different a.i.), which represent 47.8% of the positive samples. Sweet pepper was the crop with highest number of samples with multiple residues (73.9% of positive sweet pepper samples), followed by strawberry (71.6%) and grape (70.2%). With exception of grape, all the crop samples shown in Fig. 3 had mainly two residues. Eight grape samples had 8 residues, one had 9 residues and 2 had 10 different residues; one strawberry sample also had 8 different residues (data not shown).

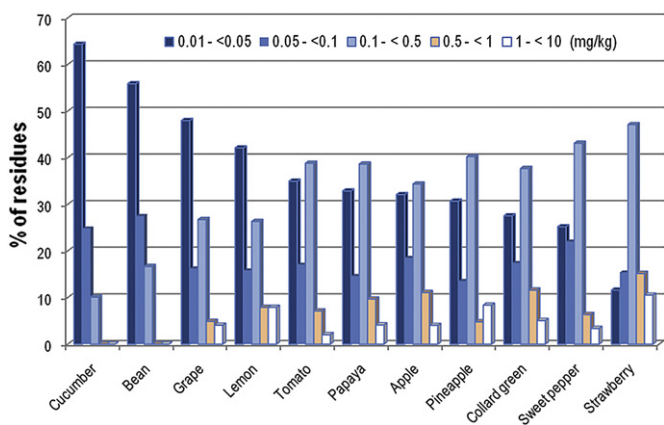


Fig. 2. Levels of pesticides found in the 11 highest positive crops samples analyzed by the Brazilian monitoring programs from 2001 to 2010.

Table 4 shows the five main pesticides classes found in each commodity, and Fig. 4 the main compounds found in all samples analyzed. Dithiocarbamates were the pesticides most frequently detected (41.6%, 2723 samples), mainly in lettuce, apple and tomato samples (Table 4). Carbendazim, a benzimidazole fungicide, was the single compound most frequently detected (26.7% of the samples) (Fig. 4).

All crops had at least one sample with one organophosphorus insecticide, a class of compounds found in 2017 samples, about one third of all positive samples (Table 4). Over 90% of the positive potato samples contained at least one organophosphorus compound, and the three positive onion samples analyzed contained only organophosphorus compounds (non-authorized use in all cases). The four organophosphorus compounds most frequently found in the samples analyzed were chlorpyrifos, methamidophos, acephate and dimethoate (Fig. 4), representing 15.4% of the residues.

Triazoles were present mostly in sugar beet, grape and rice (over 40% of the positive samples; Table 4), with tebuconazole and difenoconazole the most frequent compounds found within this class (Fig. 4). Pyrethroids, mainly fenprothrin (Fig. 4), were found in about 40% of positive collard green and sweet pepper samples (Table 4). Compounds from the carbamate class were found in 2.4% of the samples analyzed, being present in 10.7% of the banana samples (Table 4). Carbaryl was the carbamate most found (115 samples; 1.8% of positive samples), mainly in apples (89 samples).

Table 5 shows the crops with samples containing up to four residues of the same chemical classes. Multiple residues of organophosphorus compounds were found in 18.6% of the samples positive for these compounds, followed by triazoles (16.1%). Apple

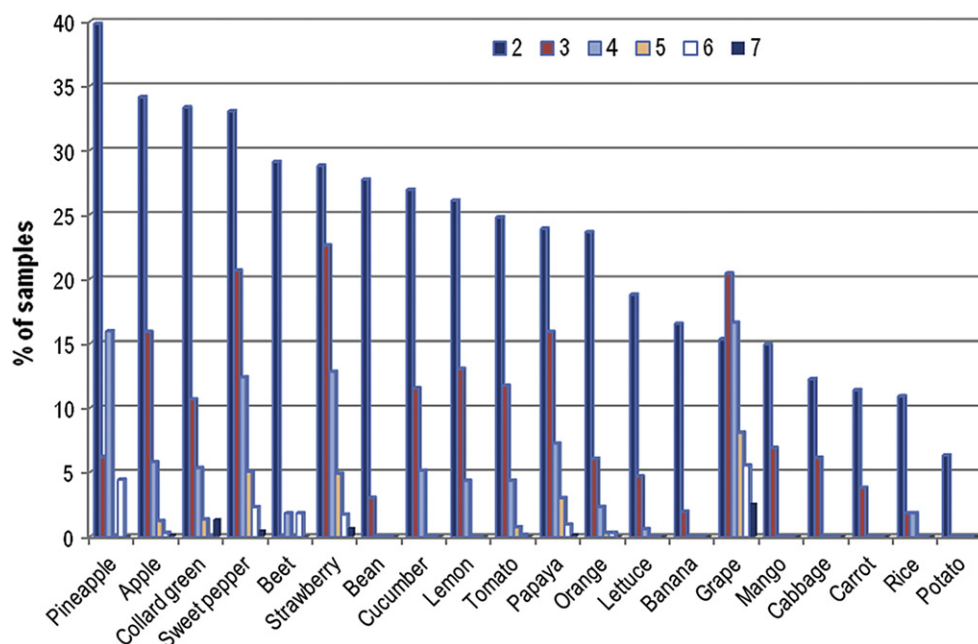


Fig. 3. Crops with multiple pesticide residues in the samples analyzed by the Brazilian monitoring programs from 2001 to 2010, s % of positive samples.

was the crop with the highest number of samples in this situation (154; 11% of the positive apple samples), followed by sweet pepper and tomato, with 91 and 89 samples, respectively. Papaya and grape were the main crops with samples with multiple residues from the triazole class (37 and 40 samples, respectively). Fifty four samples had residues of organophosphorus compounds plus carbamates, compounds known to be inhibitors of the enzyme acetylcholinesterase (AChE), mostly apple. No samples of potato, banana, mango, onion, cucumber, lemon and melon contained multiple residues of the same class.

**Table 4**  
Classes of pesticides most found in the Brazilian monitoring programs from 2001 to 2010, as % of positive samples.

Crop	DT	OP	TRI	PY	CB
Lettuce	71.3	18.5	3.5	7.6	2.3
Apple	67.7	51.7	4.0	0.7	6.7
Tomato	56.4	39.9	8.7	13.2	1.0
Collard green	46.7	21.3	5.3	40.0	0
Banana	45.6	6.8	3.9	3.9	10.7
Papaya	45.5	3.7	19.3	2.4	0
Carrot	36.1	23.4	24.1	0	0
Grape	29.8	11.1	44.7	23.4	0.4
Cucumber	29.5	16.7	6.4	17.9	2.6
Sweet pepper	26.1	67.4	5.0	40.4	5.0
Strawberry	25.2	15.1	5.9	18.4	1.1
Orange	14.4	56.5	0	5.2	0.9
Pineapple	11.5	3.5	6.2	19.5	0
Sugar beet	10.9	14.5	41.8	12.7	0
Rice	3.6	43.6	47.3	3.6	3.6
Potato	2.8	92.4	0	0	1.6
Beans	2.4	2.4	6.6	0.6	0
Mango	2.3	2.3	4.6	3.4	0
Cabbage	0	20.4	14.3	2.0	6.1
Lemon	0	17.4	8.7	8.7	4.3
Melon	0	16.7	0	16.7	0
Onion	0	100	0	0	0
<i>Total</i>	<i>41.6</i>	<i>30.8</i>	<i>10.2</i>	<i>8.3</i>	<i>2.4</i>

DT = dithiocarbamate; OP = organophosphorus; TRI = triazoles; PY = pyrethroids; CB = carbamates.

#### 4. Discussion

The Brazilian monitoring program data evaluated in this study show that 48.3% of the 13,556 samples analyzed from 2001 to 2010 were positive for at least one pesticide residue. Apple, papaya, grape and sweet pepper were the crops with the highest percentage of positive samples (around 80%). Irregularities found in 13.2% of the samples were mostly due to the presence of non-authorized a.i., and 2.7% of the samples analyzed had residue levels above the Brazilian MRL. Samples collected at farm packing houses within the PNCRC program were more likely to contain residues than those from food distributors, as expected, due to the degradation of residues that occurs between harvesting and sales. Packing house samples also had fewer irregularities, probably because most of the crops in these facilities are destined for export, and are likely to be subject to restricted pesticide use.

The high prevalence of non-authorized pesticide use in Brazil found in this study is in part due to the profile of the country's agricultural population and to the minimal phytosanitary support given to certain crops. Most Brazilian food growers have low levels of education (over 40% are illiterate) and receive limited technical support (IBGE, 2006, p. 1–777), do not read the pesticide labels or do not understand their content, and are economically vulnerable (Recena & Caldas, 2008; Recena, Caldas, Pires, & Pontes, 2006; Waichman, Ebeb, & Nina, 2007). In many cases, their decisions regarding which pesticides to use rely strongly on their previous experience, on costs, and on product availability on the farm (Recena & Caldas, 2008). For instance, over 100 a.i. are registered for use on tomato (8.7% of samples with non-authorized a.i.), including ten organophosphorus compounds and four dithiocarbamates (MAPA, 2011), which are the pesticides most found in the samples with irregularities. On the other hand, between 20 and 30 pesticides are registered for sweet pepper, collard green and lettuce (61, 28.7 and 20% of the samples analyzed with non-authorized a.i., respectively). It is likely that a farmer will use a pesticide registered for tomato in other crops also grown on the property, regardless of its registration status. In order to minimize non-authorized pesticide use on minor crops, the Brazilian Government has accepted, as

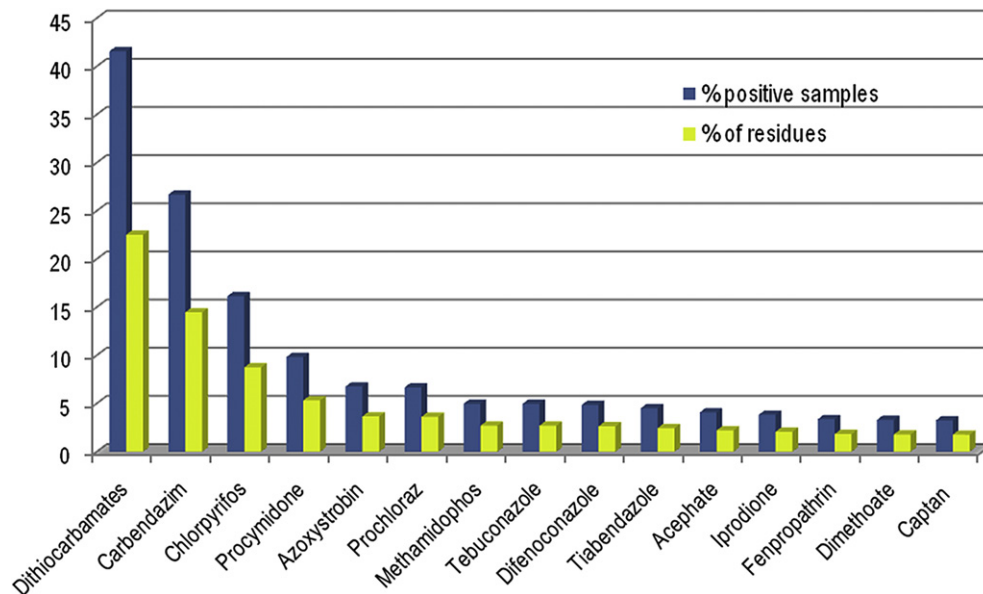


Fig. 4. The 15 pesticides most frequently detected in the samples analyzed by the Brazilian monitoring programs from 2001 to 2010.

of January 2010, the extension of the MRL to all crops within a group based on supervised residues analyses conducted only on representative crops for that group (INC ANVISA/IBAMA/MAPA 01/2010). For example, a MRL set for tomato could be extended to sweet pepper.

The results found in this study are within the range of those found for pesticide monitoring programs conducted elsewhere. The 2008 European Union (EU) program (78 active ingredients in 11,610 samples of nine crops from 29 countries) showed 35.9% of positive samples, and 2.2% of the samples exceeding the MRL (EFSA, 2010). In the Netherlands, 5.9% of the 4344 samples analyzed, mostly fruit and vegetables, had residues above the MRL (VWA, 2008). In Belgium, 65.7% of the 1413 fruit and vegetable samples were positive, and 6.1% had residues above the MRL (AFSCA, 2008). In Poland, 2.2% of the 5340 samples analyzed in 2004–2007 had residues exceeding the MRL (Góralczyk et al., 2009). Results from

the 2000–2008 Italian program showed 3.2% of the 6947 samples with residues above the MRL (Zicari, Soardo, Cerrato, & Rivetti, 2011). Pesticide analysis of 724 fruit and vegetables samples imported from South America to Denmark, Estonia, Finland, Norway and Sweden showed over 70% of positive samples, and 8.4% with residues above the MRL (Hjorth et al., 2011). About one third of these samples were from crops imported from Brazil, 9.2% of them having residues above the MRL. In the 2008 USFDA Program, 42.2% of the 3656 fruit and vegetable samples were positive and 3.5% were irregular, mostly for the presence of non-authorized a.i. in imported commodities (USFDA, 2008). In Australia, 98.9% of the 974 samples of five horticulture crops analyzed in 2009/2010 were in compliance with the relevant standards (DAFF, 2011).

Dithiocarbamates (MRLs from 0.1 to 3 mg/kg CS<sub>2</sub>) was the pesticide class most found in the Brazilian monitoring programs

**Table 5**  
Samples with multiple residues from the same class found in the Brazilian monitoring programs from 2001 to 2010.

Pesticide class	Number of samples <sup>a</sup>	Number of multiple residues, crop (number of samples)		
		2	3	4
OP	375 (18.6%)	Apple (131); tomato (59); sweet pepper (58); orange (28); strawberry (16); potato (10); papaya (6); lettuce (4); cabbage (4); carrot (4); pineapple (2); collard green (2); grape (1); bean (1)	Apple (17); sweet pepper (15); tomato (7); orange (3); carrot (1)	Sweet pepper (5); tomato (1)
TRI	107 (16.1%)	Papaya (36); grape (34); pineapple (6); strawberry (6); tomato (6); apple (4); rice (3); sugar beet (2); carrot (2);	Sugar beet (1); grape (5); papaya (1)	Grape (1)
PY	48 (8.8%)	pineapple (14); tomato (14); sweet pepper (13); strawberry (3); collard green (2); apple (1)	Collard green (1)	0
CB	4 (2.6%)	Tomato (2); lettuce (1); apple (1)	0	0
OP + CB <sup>b,c</sup>	54	Apple (29); strawberry (2); sweet pepper (2); tomato (2); lettuce (1); rice (1); cucumber (1); cabbage (1)	Apple (9); sweet pepper (4); strawberry (1)	Sweet pepper (1)

OP = organophosphorus compounds; TRI = triazoles; PY = pyrethroids; CB = Carbamates.

<sup>a</sup> % related to the number of positive samples within the class.

<sup>b</sup> The positive samples for OP and CB contained only one CB residue.

<sup>c</sup> One sweet pepper sample presented 4 OP residues and 1 CB.

(41.6% of positive samples). This incidence is much higher than that found in Canada (32.3%; Ripley, Lissemore, Leishman, Denommé, & Ritter, 2000) and the EU (7.6%; EFSA, 2010). Currently, five dithiocarbamate compounds are registered in the country. Mancozeb is the most used (about 3000 tons a.i. in 2009; Rebelo et al., 2010, 84 pp.), registered for 33 food crops (ANVISA, 2011b), being probably the main source of CS<sub>2</sub> detected in the samples. Metiram, the second most used (about 1000 tons in 2009, Rebelo et al., 2010, 84 pp.), and propineb are registered for 12 and 8 food crops, respectively. Metam sodium and tiram are used only in soil and/or seed treatment, modes of application that, in most cases, do not lead to residues in food.

About 30% of the positive samples contained organophosphorus compounds, a higher percentage in comparison with the 2003–2005 Dutch program on 11,873 fruit and vegetable samples (15%, Boon, van der Voet, van Raaij, & van Klaveren, 2008). Chlorpyrifos was the second single compound most frequently detected in the Brazilian programs (7.8% of the samples), and the main organophosphorus compound detected. Chlorpyrifos was also the main organophosphorus compound detected in the 2004–2007 Danish monitoring (7.4% the samples; Jensen, Petersen, & Christensen, 2009), and was found in 8.6% of the samples in Europe (EFSA, 2010), 16.9% of samples of food imported to Europe (Hjorth et al., 2011), and in 42.7% of the 1150 peach samples analyzed in 2002–2007 in Greece (Danis, Karagiozoglou, Tsakiris, Alegakis, & Tsatsakis, 2011). Organophosphorus compounds are among the most acute toxic pesticides on the market worldwide, and their registration is being phased out or has been canceled in many countries, including Brazil. The use of methamidophos, the second most found organophosphorus compound in this study and the most used in the country in 2009 (5000 tons a.i.; Rebelo et al., 2010, 84 pp.), was prohibited in the country in July 2012 (RDC 1/2011; ANVISA, 2011a).

Among the triazole pesticides, tebuconazole and difeconazole were the main compounds found in the Brazilian monitoring programs. In Belgium, difenoconazole was the fifth pesticide most frequently found (Claeys et al., 2011), and tebuconazole and/or myclobutanil were the main triazoles detected in the European program (EFSA, 2010), in Canada (Ripley et al., 2000) and in Greek peaches (Danis et al., 2011). Fenpropratin was the main pyrethroid compound found in the Brazilian monitoring program (3.4% of positive samples). In Egypt (Dogheim, El-Marsafy, Salama, Gadalla, & Nabil, 2002), Denmark (Poulsen & Andersen, 2003), and Canada (Ripley et al., 2000), cypermethrin was the main pyrethroid found in the food samples analyzed. Although detected in less than 3% of the positive samples in Brazil, cypermethrin was the second a.i. most used in the country in 2009 (over 50,000 tons), following glyphosate (Rebelo et al., 2010, 84 pp.).

Almost half of the positive samples (47.8%) had multiple residues, with grape being the crop with the highest number of residues in a single sample (of up to 10). Grape samples were also found to have over seven different pesticide residues in Egypt (Dogheim et al., 2002), Europe (Hjorth et al., 2011), and Canada (Ripley et al., 2000). In the EU Program, a single table grape sample had 26 pesticides (EFSA, 2010). Over 8% of the positive samples had at least two residues from the same chemical class, mainly from the organophosphorus and triazole classes. About 19% of the samples containing organophosphorus compounds had at least two residues of this class, a lower percentage than what was found in the Netherlands (22.2%) (Boon et al., 2008). Multiple residues are expected in some crops since the application must alternate among pesticide classes to prevent pest resistance. However, the presence of multiple residues may also suggest that principles of good agriculture practice are not being respected (EFSA, 2010).

The use of pesticides is necessary for pest management and the presence of their residues in food is unavoidable. However, these compounds are toxic to humans at certain levels and their presence in the diet may be a health concern to humans (Bjørning-Poulsen, Andersen, & Grandjean, 2008; Breckenridge et al., 2009; CODEX, 2009; Mendes, Mendes, Cipullo, & Burdmann, 2005; Menegola, Broccia, Di Renzo, & Giavini, 2006; USEPA, 2001). In addition to providing data to assess whether the product is being applied to the crop according to the instructions on the approved labels (compliance with MRL), pesticide residue monitoring program data can also be used to assess the human health risk from exposure to pesticide through the diet (Claeys et al., 2011; Caldas & Souza, 2004; Jensen et al., 2009; Katz & Winter, 2009). Furthermore, the cumulative exposure to multiple residues with the same mechanism of action (organophosphate and carbamates, AChE inhibitors, and triazoles, sterol 14-demethylase inhibitors) can lead to unsafe intake of these compounds in the diet (Caldas, Boon et al., 2006; Caldas, Tressou et al., 2006, EFSA, 2010; USEPA, 2001).

We conducted a preliminary cumulative acute exposure assessment for the AChE inhibitors in apple, the commodity with the highest number of samples analyzed by the monitoring programs, one of the crops with the highest frequencies of positive samples and the one with the highest number of samples with multiple organophosphate and organophosphate plus carbamates residues. In this estimation, we calculated the equivalent residue levels in a sample, expressed as the index compound (acephate), by multiplying the level of the AChE inhibitor compound detected by its relative potency factor (RPF) calculated by Caldas, Boon, and Tressou (2006) and Boon et al. (2008, for fenitrothion only). The cumulative acute exposure was estimated using the FAO/WHO Joint Meeting on Pesticide Residues methodology to estimate the short-term intake of pesticides at the international level (FAO, 2003). The highest equivalent residue found in apple in the monitoring programs during the period of 2005–2010 was used as the HR (0.387 mg/kg, as acephate). The large portion (600 g; 97.5 P of apple consumer days, mean body weight of 70 kg) was estimated from a dietary survey for individuals 10 years or older conducted by IBGE in 2008/2009 (34003 respondents on two non-consecutive days, 4426 apple consumer days; data not published). The calculated cumulative acute intake of AChE inhibitors by individuals  $\geq 10$  years was 50  $\mu\text{g}/\text{kg}$  bw, representing 100% of the acephate ARfD (50  $\mu\text{g}/\text{kg}$  bw; FAO, 2002). This result indicates the need for expanding the assessment to other crops and pesticide classes, and to assess the exposure by children. Dietary risk assessments have been conducted previously in our laboratory on cumulative acute exposure to AChE inhibitors, and on chronic exposure to dithiocarbamates (Caldas, Boon et al., 2006; Caldas & Souza, 2004; Caldas, Tressou et al., 2006). The latest data (2005–2010) from the Brazilian monitoring programs will be used to update the previous assessments, and also to estimate the cumulative exposure to the triazole fungicides, which were found as multiple residues in 16.1% of the samples containing these compounds.

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#### ANNEX. Compounds analyzed by the Brazilian monitoring programs from 2001 to 2010

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2,4-D Acid  
 Abamectin  
 Acephate  
 Acetamiprid  
 Acibenzolar-S-methyl  
 Alachlor  
 Aldicarb  
 Aldrin<sup>2</sup>  
 Allethrin  
 Ametryn  
 Aminocarb  
 Asulam  
 Atrazine  
 Azaconazole<sup>1</sup>  
 Azinphos-ethyl<sup>2</sup>  
 Azinphos-methyl<sup>1</sup>  
 Azoxystrobin  
 Benalaxyl  
 Bendiocarb<sup>1</sup>  
 Beta-cyfluthrin  
 Beta-cypermethrin  
 Bifenthrin  
 Bioallethrin  
 Bitertanol  
 Boscalid  
 Bromacil  
 Bromopropylate  
 Bromuconazole  
 Bupirimate<sup>1</sup>  
 Buprofenzin  
 Cadusafos  
 Captan  
 Carbaryl  
 Carbendazim  
 Carbofenotion<sup>2</sup>  
 Carbofuran  
 Carbosulfan  
 Carboxin  
 Chlordane<sup>1</sup>  
 Chlorfenapyr  
 Chlorfenvinphos<sup>2</sup>  
 Chlorpyrifos-methyl  
 Chlorthiophos<sup>1</sup>  
 Clethodim  
 Clofentezine  
 Clomazone  
 Clothianidin  
 Coumafos<sup>1</sup>  
 Cyanazine  
 Cyanofenphos<sup>1</sup>  
 Cyazofamide  
 Cyfluthrin  
 Cymoxanil  
 Cypermethrin  
 Cyproconazole  
 Cyprodinil  
 Cyromazine  
 Dazomet  
 DDT total<sup>2</sup>  
 Deltamethrin  
 Demeton-S-methyl  
 Diafenthiuron  
 Diallyl<sup>1</sup>  
 Diazinon  
 Dichlofluanid  
 Dichlorvos  
 Dicofol

#### ANNEX (continued)

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Dicrotophos<sup>1</sup>  
 Dieldrin<sup>1</sup>  
 Difenconazole  
 Diflubenzurom  
 Dimethoate (dimethoate +omethoate)  
 Dimethomorph  
 Diniconazole<sup>1</sup>  
 Disulfoton  
 Dithiocarbamate  
 Diurom  
 Dodemorph<sup>1</sup>  
 Endosulfan  
 Endrin<sup>2</sup>  
 Epoxiconazole  
 Esfenvalerate  
 Etefon  
 Ethiofencarb<sup>2</sup>  
 Ethion  
 Ethoprophos  
 Etofenprox  
 Etrimfos<sup>2</sup>  
 Famoxadone  
 Fenamiphos  
 Fenarimol  
 Fenazaquin<sup>1</sup>  
 Fenbuconazole<sup>1</sup>  
 Fenhexamid<sup>1</sup>  
 Fenitrothion  
 Fenoxycarb<sup>1</sup>  
 Fenpropathrin  
 Fenpropimorph  
 Fenpyroximate  
 Fenthion  
 Fenvalerate  
 Fipronil  
 Flazasulfuron  
 Fluasifop-p-buthyl  
 Flufenoxuron  
 Fluquinconazole  
 Flusilazole<sup>1</sup>  
 Flutriafol  
 Folpet  
 Fonofos<sup>1</sup>  
 Forchlorfenuron<sup>1</sup>  
 Fosthiazate  
 Furathiocarb  
 Halosulfuron  
 HCH(alfa+beta+delta)  
 Heptachlor  
 Heptachlor – epoxide<sup>1</sup>  
 Heptenophos<sup>1</sup>  
 Hexachlorobenzene (HCB)  
 Hexaconazole  
 Hexazinone  
 Hexythiazox  
 Imazalil  
 Imibenconazole  
 Imidacloprid  
 Indoxacarb  
 Iprodione  
 Iprovalicarb  
 Kresoxim methyl  
 Lambda-cyhalothrin  
 Malaixon  
 Malatione  
 Metalaxyl  
 Metamitron  
 Metconazole  
 Methamidophos  
 Methidathion  
 Methiocarb  
 Methomyl  
 Methoxychlor<sup>2</sup>  
 Methoxyfenozide  
 Metolachlor  
 Metribuzin  
 Mevinphos



## ANNEX (continued)

Mirex  
 Monocrotophos<sup>2</sup>  
 Monuron  
 Myclobutanil  
 Neburon  
 Nitenpyram  
 Nuarimol  
 Oxadixyl<sup>2</sup>  
 Oxamyl<sup>2</sup>  
 Oxyfluorfen  
 Paclobutrazol  
 Paraoxon-methyl  
 Parathion-ethyl  
 Parathion-methyl  
 PBO (piperonyl – butoxide)  
 Penconazole<sup>1</sup>  
 Pencycuron  
 Pendimethalin  
 Permethrin  
 Permethrin  
 Phenothrin  
 Phenthoate  
 Phorate  
 Phosalone  
 Phosmet  
 Phosphamidon<sup>2</sup>  
 Picloram  
 Picoxystrobin  
 Pirifenox<sup>2</sup>  
 Pirimicarb  
 Pirimiphos-ethyl<sup>1</sup>  
 Pirimiphos-methyl  
 Prochloraz  
 Procymidone  
 Profenofos  
 Prometryn  
 Propamocarb  
 Propargite  
 Propiconazole  
 Propoxur  
 Prothiofos  
 Pyraclostrobin  
 Pyrazophos  
 Pyridaben  
 Pyridaphenthion  
 Pyrimethanil  
 Pyriproxyfen  
 Quintozene  
 Quizalofop-p-ethyl  
 Rotenone<sup>1</sup>  
 Spinosad  
 Spirodiclofen  
 Spiromesifen  
 Spiroxamine<sup>1</sup>  
 Sulfentrazone  
 Sulfometuron-methyl  
 Sulfosulfuron<sup>1</sup>  
 Sulfotep<sup>1</sup>  
 Tebuconazole  
 Tebufenozide  
 Tebufenpyrad<sup>1</sup>  
 Tebuthiuron  
 Temephos  
 Terbufos  
 Tetraconazole  
 Tetradifon  
 Thiabendazole  
 Thiacloprid  
 Thiamethoxam  
 Thiobencarb  
 Thiodicarb  
 Thionazin<sup>1</sup>  
 Tolyfluanid  
 Tralkoxydim  
 Triadimefon  
 Triadimenol  
 Triazophos

## ANNEX (continued)

Trichlorfon  
 Trifloxystrobin  
 Trifloxysulfuron  
 Triflumizole  
 Trifluralin  
 Vamidothion<sup>2</sup>  
 Vinclozolin  
 Zoxamide

<sup>1</sup> Active ingredient never authorized in Brazil

<sup>2</sup> Active ingredients previously authorized in Brazil

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