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Pesticide Residues in some Commodities: Dietary Risk for Children

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Abstract The objective of this study was to identify pesticides found in infants' and children's diets. Fruits and vegetables were collected from 2004 to 2007 and analyzed using a multiresidue method. The most frequently detected residues were procymidone, captan, chlorpyrifos and chlorothalonil. Twenty-eight percent of the samples contained pesticide residues. Strawberry, pear, apple, peach and tomato contained pesticide levels of concern. Twenty-one pesticides were found with the estimated total mean daily intake greater than the acceptable daily intake for four of the pesticides. Residues of carbaryl, diazinon and methidathion exceeded regulatory levels in (apple, strawberry, and orange).

Keywords Pesticide residues · Dietary intake · Health risk · Fruits and vegetables

The world food production involves the pesticide usage; in Brazil, more than 800 different pesticide formulations have been commercialized, and the most important commodities in such market are soybean, cotton, sugar cane, corn, wheat, coffee, citrus and rice. Commodities such as vegetables and fruits have an 11% share of the total in the pesticide market. The uses of such substances have a great toxicological importance, despite of the fact they may cause health hazard, especially to infants and children due to the immaturity of their body systems. An infant's and a child's diet is usually quite the same of an adult's, but the vulnerability to chemical compounds should be considered due to their metabolic rates, which are different, and the food and liquid intake, which is proportionally higher if compared to an adults. In such way, the consumption of food contaminated food by pesticides should contribute to a risk of early exposure.

Infant's and children's nutritional data show that vegetables and fruits consumption are supported by the pesticide legislation, which is established to adults. These days developed countries have started working to protect infants and children, and some Maximum Residues Limits (MRL) have been established; usually at 0.01 or 0.005 mg/kg. In Brazil, no such work has been done yet. Nutritionists and experts suggested that a 6 months old breast fed infant should be introduced to different food items, such as: *1* Bread, cereals and tubercles, *2* fruits (apple, banana, papaya, pineapple), *3* vegetables (carrot, zucchini, broccoli, chayote), *4* beans (soybean, bean, lentil, chick-pea), *5* meat and egg (fish, chicken, calf), *6* milk, cheese and yogurt, *7* oil and fatty matter, *8* sugar and sweet.

The objective of this study is to evaluate the MRL accomplishment to Brazilian legislation, of fruit and vegetable samples analyzed by Pesticide Residues Laboratory from Biological Institute (Instituto Biologico, Sao Paulo State) and also an evaluation of the infant's and children's dietary intake.

Materials and Methods

During the period from 2004 to 2007 the LRP analyzed samples of: apple (62), banana (245), bean (582), broccolis (32), carrot (32), chayote (72), orange (72), papaya (138),

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peach (125), pear (41), potato (149), strawberry (170), rice (206) and tomato (141).

The samples were collected from the local market and analyzed immediately. The samples were conditioned and identified correctly. No treatments, such as washing or removing the peel, were applied to the samples. Almost 140 active ingredients were studied. The multiresidue method (DFG 1999) were employed and the pesticide residues were extracted by acetone; partitioning step with sodium chlorine and ethyl acetate + cyclohexane (1:1); organic phase was concentrated in rotary evaporator and the final extract reduced in gentle nitrogen stream; purification step with GPC (Bio Beads S-X3 support); an aliquot of concentrated extract were used for chromatographic analysis with LC and GC (NPD and FPD detectors), and further purifying step was carried out with silica gel deactivated 1.5% for ECD detection.

Gas and liquid chromatographic analyses were used to identification and quantification of the pesticides. The compounds identities were confirmed using columns with different polarities, different injection systems and different techniques. The LC MS/MS was used especially to pesticide residues confirmation and quantification.

The electron capture detector conditions were: megabore column SPB^{TM}1, column program from 200 to 215°C, splitless system, detector temperature: 300°C; capillary column SPB^{TM} 608; column program from 90 to 250°C; splitless system at 220°C; detector temperature: 300°C. Nitrogen/phosphorus detector conditions were: capillary column PTE^{TM} 5; column program from 80 to 250°C; splitless injection, detector temperature: 300°C; capillary column SPB^{TM} 20; colunm program from 90 to 220°C; SPI injection system at 95 to 225°C; detector temperature: 300°C. Flame photometric detector conditions were: megabore column DB1701^{TM}; column temperature 200°C/10 min; on column injection at 220°C; detector temperature 220°C; megabore column DB5; column temperature of 170°C; on column injection at 190°C; detector temperature 220°C.

The LC systems used were: UV–Vis, injection of 100 µL, RP C18 column (5 µm), and mobile phase: acetonitrile, water and methanol, some salts related to the substance analyzed were used, wavelength from 150 to 280 nm. The MS/MS system used a Phenomenex C18 column (5 µm), mobile phase: methanol and water (1:1) and 5 mM of ammonium phormiate as salt, the ESI positive mode was employed.

The validation study accomplished with the criteria for analytical performance (Thompson et al. 2002). It was used the representative matrices and analytes concept. The parameters of accuracy, precision, repeatability and reproducibility were obtained from the recoveries results of validation studies. The recoveries testing have been applied regularly in the laboratory since the method has been introduced and the results from the proficiency testing schemes have been satisfactory performances. The calibration curve was made with different standards concentrations. Some points from the curve were injected simultaneously to determinate the linearity of the detector response to the different concentrations. The quantification limits for organochlorine pesticides is 0.001 mg/kg and 0.01–0.05 for organophosphorus, carbamates, pyrethroids some herbicides and fungicides. The recoveries generally ranged from 70% to 110%. The Laboratory employed external standards to calculate the results.

The contributions of these commodities on ADI were calculated employing the Theoretical Maximum Dietary Intake (TMDI) and it is calculated by computing the total MRLs in mg/kg established for a pesticide versus the food consumption of the commodity in kg/day and to the national values, it was considerate as NTMDI (National Theoretical Maximum Dietary Intake).

$$\mathrm{TMDI} = \sum \mathrm{MRL} \times \mathrm{F_I}$$

MRL = Maximum Residue Limit established by legislation or the quantity of pesticide residue found at the food analysis, F_1 = consumption *per capita* of each food/day, according to data consumption from IBGE 2004 and GEMS/FOOD 2003 to regional diet, The TDMI, in mg/person/day or mg/body weight/day, uses the body weight of 15 kg.

The pesticide residues values found in the analysis were used to calculate the TMDI which values are applied to know the contribution of the pesticide residue in the percent of ADI (%ADI < 100), comparing the values from the TDMI with the ADI it was possible to verify the food contribution to ADI.

$$\%\mathrm{ADI} = \frac{\mathrm{TMDI} \times 100}{\mathrm{ADI}}$$

Results and Discussion

About 28% of the evaluated samples presented detectable levels of pesticide residues and the products were: acephate, amethryn, azinphos methyl, bifenthrin, captan, carbaryl, carbendazim, chlorpyrifos, chlorothalonil, lambda cyhalothrin, cypermethrin, deltamethrin, diazinon, dimethoate, endosulfan, ethion, fenitrothion, fenpropathrin, fenthion, fluazinam, folpet, alpha HCH, imidacloprid, iprodione, malathion, methamidophos, methidathion, omethoate, parathion methyl, permethrin, phenthoate, phosalone, procymidone, profenofos, pyridaphenthion, pyrimiphos methyl, quintozene, tetradifon, thiabendazole and triazophos. Those substances were found combined or not with other molecules and the main groups were organophosphorus and

Table 1 Findings of pesticide/commodities and MRL established by the Brazilian legislation

Pesticides	Commodities	Number of findings, number of findings/sample and MRL (mg/kg)
Acephate	2, 9, 12, 13	8 = 3 (2, 9, 12)/NPC; 5 (7, 13)/MRL = 0.5
Amethryn	14	1 = NPC
Azinphos methyl	9	16 = All NPC
Bifenthrin	12	2 = NPC
Captan	1, 9, 10, 12, 13	78 = 8 (9, 13)/MRL = 15.0; 30 (1, 10)/MRL = 25.0 and 40 (12)/NPC
Carbaryl	1, 9, 10	32 = 15 (9, 10)/NPC; 17 (1)/MRL = 2.0
Carbendazim	8, 9, 12	26 = 9 (9)/NPC; 14 (8)/MRL = 0.5; 3 (12)/MRL = 5.0
Chlorpyrifos	1, 3, 5, 7, 9, 10, 11, 12, 13	98 = 30 (5, 9, 10. 12, 13)/NPC; 49 (10, 11)/MRL = 1.0; 5 (7)/MRL = 2.0; 4 (3)/MRL = 0.1
Chlorothalonil	3, 4, 8, 12, 13, 14	66 = 13 (4, 12, 14)/NPC; 20 (3, 8)/MRL = 0.1; 33 (13)/MRL = 1.0
Lambda cyhalothrin	2, 10, 12	3 = 2 (2, 10)/NPC; 1 (12)/MRL = 0.05
Cypermethrin	10, 13	8 = 1 (10)/NPC; 7 (13)/MRL = 0.1
Deltamethrin	13	1 = MRL = 0.03
Diazinon	3, 11, 12, 14	8 = All NPC
Dimethoate	6, 7, 9, 12	12 = 11 (6, 9, 12)/NPC and 1 (7)/MRL = 2.0
Endosulfan	3, 9, 12, 13	40 = All NPC
Ethion	7	5 = MRL = 2.0
Fenitrothion	3, 7	2 = 1 (7)/NPC; 1 (3)/MRL = 10.0
Fenpropathrin	8, 9, 12, 13	84 = 2 (9)/NPC; 34 (13)/MRL = 0.2; 48 (8, 12)/MRL = 2.0
Fenthion	7	1 = MRL = 0.5
Fluazinam	12, 13	27 = 1 (13)/MRL = 1.0; 26 (12)/MRL = 2.0
Folpet	1, 9, 12, 13	23 = 19 (12, 13)/NPC; 3 (9)/MRL = 15.0; 1 (1)/MRL = 1.0
Alpha HCH	3, 13	3 = All NPC
Imidacloprid	8	1 = MRL = 3.0
Iprodione	3, 9, 12, 13	25 = 2 (9)/MRL = 1.0; 2 (13)/MRL = 4.0; 1 (3)/MRL = 0.5; 20 (12)/MRL = 2.0
Malathion	7, 9	2 = 1 (9)/MRL = 6.0; 1 (7)/MRL 4.0
Methamidophos	12, 13	4 = 1 (12)/NPC; 3 (13)/MRL = 0.5
Methidathion	7	6 = MRL = 2.0
Omethoate	9	2 = All NPC
Parathion methyl	7	1 = NPC
Permethrin	2, 10, 13	10 = 2 (2, 10)/NPC; 8 (13)/MRL = 0.3
Phenthoate	1, 10, 12, 13	5 = 3 (1, 10, 12)/NPC; 2 (13)/MRL 0.1
Phosalone	1, 10	4 = All NPC
Profenofos	13	3 = MRL = 1.0
Procymidone	3, 4, 5, 9, 11, 12, 13, 14	170 = 7 (9)/MRL = 5.0; 70 (12, 14)/MRL = 3.0; 1 (5)/MRL = 1.0; 2 (4)/NPC; 81 (11)/MRL = 0.5; 9 (13)/MRL = 2.0; 68 (12)/MRL = 3.0
Pyridaphenthion	9	17 = All NPC
Pyrimiphos methyl	14	1 = MRL = 10.0
Quintozene	13	1 = MRL = 0.1
Thiabendazole	8	8 = MRL = 6.0
Tetradifon	8, 9, 12, 13, 14	33 = 30 (9, 12, 14)/NPC; 1 (13) MRL = 1.0; 2 (8)/MRL = 0.05
Triazophos	13	1 = MRL = 0.5

1 Apple, *2* banana, *3* bean, *4* broccoli, *5* carrot, *6* chayote, *7* orange, *8* papaya, *9* peach, *10* pear, *11* potato, *12* strawberry, *13* tomato and *14* rice

NPC Not permitted for the crop

pyrethroids, insecticides and fungicides. It is important to detach that some commodities were frequently contaminated by pesticide residues, as strawberry (78.8%); pear (62.5%); peach (50.4%) and tomato (44%). In the study, chlorpyrifos and procymidone were the most frequently pesticides detected (9 and 8 commodities, respectively). The Table 1 shows the pesticides, the commodities and the total of findings.

According to Gebara et al. (2005a, b), positive results for vegetables and fruit correspond to 30% of analyzed samples, pesticide residues above the MRL were found in almost 1% of the samples and multiple findings corresponding to 30%–35% of the samples. The most frequent pesticides found were: captan and chlorothalonil.

Pesticides above the MRL were found in: one sample of bean (procymidone); one sample of apple (carbaryl); two samples of strawberry (iprodione, fluazinam) and three samples of tomato (chlorothalonil, cypermethrin, phenthoate). The pesticide not permitted for the pesticide/commodity combination is the most frequent identification.

The evaluation of the contribution of these substances to health risk were established using the data from IBGE (2004) for the adult consumption *per capita* and a basic diet for an infant and a child with some food items suggested by the nutritionists which correspond to 3 or 4 times an adult consumption.

In this study it was evaluated the TMDI applying the values obtained in the analysis, the national diet and body weighting 15 kg were considered to calculate the ingestion for infants and children.

The toxicological parameter (%ADI $>$ 100) were exceeded to the pesticides: carbaryl (103.6%), diazinon (258.5%), dimetenamide P (167.7%), fluazinam (357.3%) and methidathion (225%). Pesticides which the % ADI were among $<$100% and $>$10% were: acephate (15%), captan (59.8%), chlorpyrifos (21.3%), chlorothalonil (32.4%), dimethoate (24%), ethion (25%), folpet (18.7%), parathion ethyl (11.7%), phenthoate (22.2%), procymidone (17.5%) and triazophos (16%). The %ADI below 10%: azinphos ethyl (0.05%), bifenthrin (0.07%), carbendazim (3.9%), lambda cyhalothrin (0.2%), cypermethrin (0.4%), deltamethrin (0.1%), endosulfan (6.4%), fenitrothion (6%), fenpropathrin (9%), fenthion (0.7%)alpha HCH (0.6%), imidacloprid (0.1%), iprodione (9.3%), malathion (5.1%), methamidophos (5%), omethoate (0.01%), permethrin (0.7%), phosalone (3.5%), profenofos (1.6%), pyrimiphos methyl (6.6%), quintozene (1.3%) and thiabendazole (2.2%). Pesticides as amethryn, pyridaphenthion and tetradifon do not have ADI.

Multiple residues and pesticide from carbamates, organophosphorus and thiazols groups were observed by some authors as Gilbert-López et al. 2007 in juice and puree of fruits and have detected thiabendazol and imazalil in 40% of samples and 30% of samples were contaminated by multiple residues. Juice of apple was 50% contaminated by damidazone, chlorpyrifos was found in banana samples, and grape juice was contaminated by carbaryl; ethion and thiabendazole were found in orange juice. The work group also analyzed imported items and dimethoate, chlorpyrifos and captan were found in apple juice, thiabendazole in banana; dimethoate, malathion and ethion in orange juice.

Ciscato et al. (2006), found HCH and endosulfan as contaminants in milk samples 0.75% and 10.6%, respectively) analyzed during the period, the amount of such compounds combined with other results could increase the exposition.

Pesticide residues of fungicides and organophosphorus insecticides are the most important products found in food samples. The toxicological parameter of ADI was exceeded especially due to the fact that legislation does not use the ADI for children to establish the MRL. The great number of commodities with NPC corresponded to minor crops and there is a hard work on trying to establish or to contemplate these commodities with the extension of use. However, in this study it was not considered any processing of food or infant formula, which could present a different scene of the contamination of these compounds. The results show the necessity of continuous monitoring studies to avoid the health risk to the consumers and also the importance to considerate the childhood when establishing the MRL.

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