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Risk Assessment of Organophosphorus Pesticide Dietary Intake for the Population of the City of Rome (Italy)

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Investigations on dietary intake of pesticide residues are particularly recommended by WHO (World Health Organization) in order to assess potential health risks from dietary exposure to pesticides.
In Italy the oldest systematic studies regarded chlorinated pesticides and were carried out since 1970 (, Del Vecchio et al. 1973a, Del Vecchio et al. 1973b, Del Vecchio and Leoni 1973, Leoni and D'Arca 1978, Leoni et al. 1989). As the increase of the amount of organophosphorous insecticides used in agriculture in the last years and the scarcity of data about organophosphorous dietary intake, the Italian Ministry of Health decided to sponsorize an investigation for the risk assessment of the organophosphorous pesticide dietary intake for the general Italian population. The work started in 1990, involving four Italian scientific structures operating in the North (Piacenza), in the Centre (Rome) and in the South (Naples and Catania).

This paper describes the results of the monitoring program carried out in the area of Rome. Some preliminary results have been previously published (Amodio Cocchieri et al. 1993). The investigation consisted in the collection of a significant number of the relevant raw commodities, representative of the average diet for the general population and the determination of 30 selected organophosphorous insecticide residues levels in food. The Estimated Daily Intake (EDI) was calculated by multipling the average residue level in each food for the amount of the average consumption of that food and summing the intakes from all commodities positive for the residue of the pesticide concerned. Then EDI was compared with the Acceptable Daily Intake (ADI) to assessing the risk connected with the organophosphorous residue dietary intake.

MATERIALS AND METHODS

The organophosphorous insecticides were selected on the basis of the most used products in Italy: acephate, azinphos-ethyl and azinphos-methyl, bromophos, chlorfenvinphos E and chlorfenvinphos Z, chlorpiriphos and chlorpiriphos-methyl, demeton, demeton-O and demeton-S-methyl-sulphone, diazinon, dimethoate, ethion, fenitrothion, heptenophos, malathion and malaoxon, methamidophos, methidathion, monocrotophos, omethoate, parathion and paraoxon,

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parathion-methyl and paraoxon-methyl, phosalone, pirimiphos-methyl, tetrachlorfenvinphos and vamidothion. The data on food consumption, obtained from a national household survey on food and nutrient intakes carried out by the National Institute of Nutrition in the years 1980-1984 (Cialfa et al. 1991) are listed in Table 1.

Table 1. Food consumption (net weight, g/man/day), considering at least the 1% of the standard daily food amount for general population in Italy (Data from National Institute of Nutrition, 1991).

Commodities	Consumption g/man/day
Wheat flour	19
Rice	15
Bread	158
Pasta	73
Grain products	***265***
Apples	72
Pears	22
Peach-apricots	24
Citrus	53
Other fresh fruit	38
Fruits	***209***
Legume (fresh and frozen)	14
Legume (dried and flour)	5
Tomato for salad	30
Tomato for sauce (fresh)	11
Tomato for sauce (canned)	57
Potatoes	54
Lettuce	34
Carrots, beets, celery, fennel	16
Cucumber and courgettes	12
Cabbage and broccoli	10
Pepper and egg-plants	15
Mixed vegetables (for soup)	13
Other vegetables	25
Vegetables	***296***
Olive oil	25
Wine	113
Milk	96
Fluids	***234***
Sugar	29
Other	***29***
Eggs	23
Butter	6
Veal and beef	42
Poultry	32
Sausages	24
Animal products	***127***

Foodstuffs (556 samples), produced in Italy, were collected from retail markets in the urban area of Rome. The majority of foodstuffs (470 samples) were vegetables and were generally collected proportionally to the average food consumption data. Fewer animal products samples (86) were collected and analysed. Sampling was carried out as recommended by Health Protection Branch of Canada (1986).
For an analytical purpose, the samples were divided into four classes, according to their content of water and fat; the most suitable procedures for extraction and purification were selected for each class. Determinations were generally performed on pools obtained by blending four unwashed samples of the same kind of foodstuff. An aliquot (25 g) of each homogenated pool was extracted, purified and analysed by gaschromatography with a photometric detector. As necessary, the identity of the compounds was confirmed by gaschromatography with a mass detector. The practical determination limit of the analytical method used is in the range 3-50 ppb for all commodities, except for the olive oil, that is ten times higher. The detailed analytical procedures, validated by recovery tests, are described in Leoni et al. (1992).

RESULTS AND DISCUSSION

The collection and analysis of 556 food samples resulted in over 3500 determinations of organophosphorous pesticide residues. Table 2 shows the number of pools analysed for each commodity and the percentages of pools positive for organophosphorous residues. No presence of these compounds was found in animal products samples (eggs, poultry, beef, sausages and butter), except in a milk sample with azinphos-methyl at the high concentration of 1.7 mg/kg. This finding were considered anomalous since further analyses on several milk samples, collected in the same area, gave negative results. This data is reported in Tables 2 and 3 but excluded from the calculation of the total dietary intake. The majority of fresh vegetable commodities contained pesticide residues; there are no residues in dried legumes, potatoes, sugar and wine.

One or more organophosphorous pesticides have been found in about 55% of the analysed pools. Table 3 shows the organophosphorous residues found, the range of concentrations and the average concentration in each commodity. The lower limit of the ranges of concentration is the determination limit of the pesticide, when its concentration was lower than its limit. Samples with concentration of pesticides lower than the determination limit were considered negative in the calculation of the dietary intake. Average concentration values are lower than the maximum residue level (MRL) established by the Italian regulation (Italian Ministry Decree, July 18th 1990); absolute concentration values in each sample resulted lower than MRL too, except an olive oil sample positive for ethion (4 mg/kg). Considering as 20% the oil yield from olive, a value of 4 mg/kg of ethion in oil corresponds to 0.8 mg/kg in olive; this is a value over the corresponding MRL (0.1 mg/kg).

Malathion is the most commonly occurring pesticide (found in 16% of the pools), followed by pirimiphos-methyl (14%), omethoate and dimethoate (14% and 12% respectively), acephate (10%) and parathion (8%). These percentages, referred to analytical pools, might result as an

Table 2. Total number of pools analysed for each commodity and percentage of pools positive for organophosphorous residues.

Commodities	Total number of pools*	Pools positive (%)
Grain products		
Wheat flour	16**	69
Rice	1	100
Bread	9	100
Pasta	5	100
Fruits		
Apples	9	78
Pears	3	100
Peach-apricots	5	100
Citrus	7	71
Grapes	6	67
Vegetables		
Legumes, dried	1	0
Tomato for salad	3	100
Tomato for sauce, fresh	1	100
Tomato for sauce, canned	9	33
Potatoes	7	0
Lettuce	5	80
Carrots, beets, celery, fennel	2	50
Cucumber and courgettes	1	100
Cabbage and broccoli	1	100
Pepper and egg-plants	2	100
Mixed vegetables (for soup)	2	100
Other vegetables	2	100
Fluids		
Olive oil	11	27
Wine	11	0
Milk	14	7***
Other		
Sugar	3	0
Animal products		
Eggs	6	0
Butter	1	0
Poultry	3	0
Sausages	3	0
Beef	5	0

* Each pool is the sum of four samples.

** Number of samples, individually analysed.

*** 1 pool positive over 14 analysed; this finding was not confirmed by further analyses on other milk samples.

Table 3. Organophosphorous residues found, range of concentrations and average concentration in the commodities.

Commodities	**Residues found, range of concentrations [µg/kg] and average concentration** ***µg/kg***
Wheat flour	Cp-m [< 3.0 - 45] *5.9*; Mt [< 5.4 - 550] *136*; Pi-m [< 3.1 - 22] *2.0*
Rice	Pi-m [97] *97*
Bread	Cp-m [< 3.0 - 4.2] *1.7*; Mt [< 5.4 - 64] *22* ; Pi-m [9.0 - 138] *58*
Pasta	Ac [≤ 7.5] *3.0* ; Az-e [≤ 4.5] *0.9* ; Mt [< 5.4 - 23] *5.8*; Ma [≤ 5.3] *1.0* ; Pt[≤ 8.0] *1.8*; Pi-m [14 - 39] *30*
Apples	Ac [< 7.5 - 1836] *255.*; Az-m [≤ 13 - 92] *13* ; Dm [< 6.1 - 10] *1.9*; Fe [≤ 4.8] *0.5*; Om [< 3.0 - 10] *1.2*; Ph [< 9.1 - 110] *14*; Pt [≤ 8.0] *0.9*
Pears	Az-m [23 - 404] *174*; Cf-Z [< 5.4 - 23] *12* ; Cp [≤ 3.9] *1.3*
Peach-apricots	Ac [≤ 7.5] *1.5*; Az-m [≤ 13] *2.5* Dm [≤ 6.1] *1.2* ; Fe [≤ 4.8] *0.9*; Pt [≤ 8.0] *1.6*; Pt-m [≤ 3.2 - 4.5] *2.5*
Citrus	Dm [≤ 6.1] *0.8*; Om [< 3.0 - 16] *5.4*; Pt [≤ 8.0] *1.1*; Ph [≤ 9.1] *1.3*; Pi-m [< 3.1] *0.4*
Grapes	Ac [≤ 7.5] *1.2*; Cp [≤ 3.9] *0.6*; Dm [≤ 6.1 - 8.0] *2.7*; Mi [≤ 5.2] *0.9*; Om [≤ 3.0] *0.5*; Pt [< 8 - 16] *4.3*
Tomato for salad	Az-m [≤ 13] *4.5*; Dm [≤ 6.1] *2.0*; Ma [< 5.3 - 10] *3.3*; Om [< 3.0 - 17] *7.8*; Pt [≤ 8.0] *2.6*; Ph [≤ 9.1] *3.0*
Tomato for sauce, fresh	Om [≤ 3.0] *3.0*
Tomato for sauce, canned	Ac [≤ 7.5 - 10] *3.0*; Ma [< 5.3 - 6.0] *0.7*
Lettuce	Az-m [≤ 13.5 - 23] *4.6*; Cp [≤ 3.9] *0.7*; Dm [< 6.1 - 48] *9.6*; Om [< 3.0 - 23] *7.4*; Pt-m [< 3.2 - 18] *3.6*
Carrots	Cf-Z [< 5.4 - 9] *4.5*
Cucumber and courgettes	Cf-E [≤ 6.0] 6.0
Cabbage and broccoli	Ac [≤ 7.5] *7.5* ; Br [≤ 3.2] *3.2*; Mo [≤ 14] *14*
Pepper and egg-plants	Cp[< 3.9 - 10] *5.0*; Dm[≤ 6.1] *3.0*; Om[<3.0 - 5.0]*2.5*
Mixed vegetables (for vegetable soup)	Ac [27 - 40] *33*; Cf-Z [≤ 5.4] *2.6*; Cp-m [≤ 3.1] *1.5*; Ma [< 5.3 - 20] *10*; Mo [≤ 14] *7.0*; Om [< 3.0 - 5.0] *7.5*; Pt [≤ 8.0] *4.0*
Other vegetables	Ac [< 7.5 - 62] *31*; Cf-Z [≤ 5.4] *2.6*; Dm [≤ 6.1] *3.0*; Om [< 3.0 - 5.0] *2.5*
Olive oil	Az-m[< 135 - 600] 64; Et [< 42 - 4000] 374 ; Pt [< 80 - 110] 100
Milk	Az-m [< 13 - 1700] 121

Ac = acephate; Az-e = azinphos-ethyl; Az-m = azinphos-methyl; Br = bromophos; Cf-Z = chlorfenvinphos Z; Cf-E = chlorfenvinphos E; Cp = chlorpyriphos; Cp-m = chlorpyriphos-methyl; Dm = dimethoate; Et = ethion; Fe = fenitrothion; Mt = malathion; Ma = methamidophos; Mi = methidathion; Mo = monocrotophos; Om = omethoate; Pt = parathion; Pt-m = parathion-methyl; Ph = phosalone; Pi-m = pirimiphos-methyl.

Table 4. Dietary intake of organophosphorous pesticides and comparison with their ADI (FAO/WHO).

Pesticides	**EDI** **µg/man/day**	**ADI** **µg/man/day**	**% ADI** **ingested**
Acephate	24.34	1800	1.3
Azinphos-ethyl	0.03	**	-
Azinphos-methyl	8.32	150	5.5
Bromophos	0.02	2400	<0.1
Chlorfenvinphos E	0.05	120	<0.1
Chlorfenvinphos Z	0.46	120	0.4
Chlorpiriphos	0.12	600	<0.1
Chlorpiriphos-methyl	0.40	600	<0.1
Demeton	*	18	-
Demeton-O	*	18	-
Demeton-S-methyl-sulphone	*	18	-
Diazinon	*	120	-
Dimethoate	0.72	600	0.1
Ethion	9.52	360	2.6
Fenitrothion	0.08	300	<0.1
Heptenophos	*	**	-
Malaoxon	*	**	-
Malathion	6.46	1200	0.5
Methamidophos	0.24	36	0.7
Methidathion	0.03	300	<0.1
Monocrotophos	0.12	36	0.3
Omethoate	0.90	18	5.0
Paraoxon	*	**	-
Paraoxon-methyl	*	**	-
Parathion	0.76	300	0.2
Parathion-methyl	0.15	1200	<0.1
Phosalone	1.37	360	0.4
Pirimiphos-methyl	12.81	600	2.1
Tetrachlorvinphos	*	**	-
Vamidothion	*	480	-

* Lower than determination limits of the used analytical method. The determination limit of the pesticides are: 2.8 ng/g for demeton-O, 3.6 ng/g for Demeton-S-methyl, 47 ng/g for Demeton-S-methyl-sulphone, 3.6 ng/g for Heptenophos, 12 ng/g for Malaoxon, 6.0 ng/g for Paraoxon, 8.4 ng/g for Paraoxon-methyl, 8.0 ng/g for Tetrachlorvinphos, 52 ng/g for Vamidothion.
** ADI not established

overestimate of the findings; the detected compounds could be present just in one out of the four food samples composing the pool.

The calculated EDI and the comparison with the ADI, expressed by the percentage of the % ADI ingested (% ADI) are shown in Table 4. The % ADI ingested is quite low for all the compounds, ranging from < 0.1 to 5.5. The sum of the percentages of ingested ADI is about 20%. To confirm the validity of these results, 14 compounds out of the 30 studied were selected on the basis of the organophosphorous pesticides considered in another monitoring, carried out on some thousands of raw food samples in Italy in the period 1986-1987 (Camoni et al. 1994). The sum of the % ingested ADI resulted in the same range (about 13%) in both of the studies.

In conclusion, considering that our monitoring analysed all the most used organophosphorous compounds in Italy and a considerable number of the relevant commodities, the overall value of 20% of ADI ingested can be regarded as a reasonably accurate estimate. From a sanitary point of view, the value of 20% of total ADI ingested shows a relatively safe use of these compounds; besides, data were obtained from raw commodities without considering the effect of preparation, processing and cooking of food that cause a decrease of organophosphorous levels (UNEP/FAO/WHO 1988, Ishikura et al. 1984).

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