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A Risk Assessment Study of Greek Population Dietary Chronic Exposure to Pesticide Residues in Fruits, Vegetables and Olive Oil

Ioannis N. Tsakiris³, Maria Toutoudaki¹, Manos Kokkinakis²,
Mitlianga Paraskevi³, and Aristides M. Tsatsakis¹,

¹Laboratory of Toxicology, Department of Medicine, University of Crete,
Voutes 71409, Heraklion

²Technological Education Institute (T.E.I) of Crete, Food Quality Laboratory,
K. Palama and I. Kakridi Str., 722 00 Ierapetra, Crete

³TEI of Western Macedonia, Florina Branch, Department of Agricultural
Products Management and Quality Control,
Terma Kontopoulou 53100 Florina
Greece

1. Introduction

The term Mediterranean diet refers to the diet regime adopted by people living around the Mediterranean Sea, and especially Greeks and Cretans. This diet regime allows the daily consumption of bread, cereals, pasta, rice, potatoes, pulses, nuts, vegetables, milk, cheese, yogurt, olives and olive oil. Consumption of eggs, chicken, fish and sweets is allowed a few times weekly, while consumption of red meat is allowed only a few times monthly. Moderate consumption of wine is allowed daily with the meals. Overall, the Mediterranean diet is characterized by low consumption of fats, especially saturated fats and a high consumption of carbohydrates that come from cereals, bread, rice, pasta, fruits and vegetables. Milk products are consumed regularly in small quantities.

One of the major diet components, especially in the summer, is grapes. They are characterized by high nutritional value as they supply several antioxidants and polyphenolic compounds to human organism. Many published papers report high concentrations of phenolic compounds such as flavonoids and resveratrol, especially in the red varieties (Dani et al., 2007).

The main source of fat is olive oil, which is rich in monounsaturated fatty acids. As already mentioned fruits and vegetables are major constituents of the Greek diet, and although high consumption of these components is thought to be beneficial for the human organism, it is also a source of exposure to the various pesticides used for the protection of the crops (Coxam & Puel, 2010) (Roche et al., 2000).

Many insects and pathogens (i.e. *Botrytis cinerea*, *Uncinula necator* and *Plasmopara viticola*, *Dacus olea*) affect the aforementioned cultivations and their occurrence demands the use of pesticides in order to eliminate economic losses. The key issues during crop protection planning are to use the pesticides at the right stage of crop (i.e flowering) and to keep the

levels of pesticides residues below the Maximum Residues Limits (MRLs) at harvest stage. Pesticide residues in fruits, vegetables and their processed products may also appear as a result of contaminated agro-inputs, drift from adjoining fields, as well as inappropriate or abusive treatments. Residual pesticides present in agricultural products may result to health hazards and affect the sensory quality of processed products. In the case of wine for example, they interfere with fermentative micro flora (Patil et al., 2009). It is therefore evident that it is necessary to monitor the levels of pesticide residues in specific agricultural products, in order to avoid risks for consumers.

Currently used pesticides differ from those used in previous decades. New groups of pesticides are developed and tested for plant protection, such as strobilurins (i.e. azoxystrobin and pyraclostrobin) and imidazolinones (i.e. fenamidone). Developed countries have established new laws in order to: 1) scale down the use of pesticides 2) protect the consumers (lower concentration limits in food) 3) protect farmers during application (reduced risk to humans) and 4) protect the environment (non target organisms and environmental resources). According to current tendency pesticides characterized by broad spectrum of action (fungicides), are more focused to target organisms (insecticides), and characterized by special penetration and redistribution properties. Additionally due to the withdrawal of many active ingredients as a result of the review process based on Council Directive 91/414/EEC, the use of remaining pesticides is more intensive compared to previous years.

Due to globalization, agricultural products with pesticides residues may travel all over the world. Thus consumers are increasingly conscious of the potential environmental and health problems associated with the build-up of toxic chemicals, particularly in food products. Exposure to pesticides through consumption of fruits, vegetables and olive oil is almost continuous, especially for Mediterranean people. In the recent years conventional cultivation of fruits is replaced by more controlled systems such as Integrated Crop Management (ICM) and biological (organic) cultivation in order to eliminate the exposure (Tsakiris et al., 2004) (Tsatsakis & Tsakiris, 2010).

Hereby, the status of pesticides residues in grapes, olive oil and vegetables (peppers, cucumbers, tomatoes and eggplants) is presented, focusing in organic (grapes, olive oil) and ICM cultivation (vegetables). Moreover monitoring results are used in order to estimate the dietary intake and cumulative risk from the detected pesticides in Greek people. Our data are based: 1) on the results reported by certification organizations in Greece and 2) on the unpublished results from monitoring programs of Toxicology Laboratory of the University of Crete.

2. Critical points for the determination of pesticides in agricultural products

Pesticide monitoring is performed by National and private laboratories, operating in each European country. National laboratories monitor pesticides and inform the European Union in order to publish specific pesticide reports. Private laboratories in each country perform routine analysis for major pesticide categories, with agricultural samples originating from independent farmers, farmer groups, super-markets or factories that export vegetables to other European countries. The majority of samples are analyzed as a prerequisite for certification purposes. Hence, when all agricultural products exported to other European countries are certified and the requirements of each certification scheme are strictly followed, public health is not jeopardized.

A great number of analytical methods for the determination of pesticide residues in agricultural products, especially in those that are extensively used by the Mediterranean diet, have been published up to now.

The analysed agricultural products may be divided into the three following categories: 1) Fresh fruits and vegetables 2) Alteration products of fruits and vegetables i.e. wine 3) Olive oil. Each category requires a different sample treatment process and presents a variable degree of difficulty in the analysis of residues.

Analytical methods for determining pesticide residues in two first categories involve several extraction and purification steps in order to remove the huge amount of potentially interfering compounds that are present at higher concentrations than the pesticides residues themselves. Many of them are characterized by laborious and time consuming sample preparation and also require non-environmentally friendly solvents. What's more, some of them demand expensive analytical instruments (i.e. LC-MS/MS) and this reduces their use for screening purposes.

For the detection of volatile and thermally stable pesticides gas chromatography (GC) in combination with appropriate detectors such as electron-capture (ECD), nitrogen-phosphorus (NPD) and mass spectrometry (MS) is most commonly used. On the other hand, for the detection of pesticides with low volatility and high polarity, methods based on liquid chromatography (LC) coupled to mass spectrometry are more common (Venkateswarlu et al., 2007).

The most widely used method for multi-class residues analysis is the QUECHERS method (Paula et al., 2007). The extraction procedure is based on liquid-liquid partitioning with acetonitrile followed by a cleanup step with dispersive-SPE. The great advantages of this method are the simplicity, the low cost of implementation and the short analysis time. A new method based on QUECHERS was developed for the evaluation of multiple pesticide residues in grapes, must and wine using the similar extraction procedures and low-pressure gas chromatography coupled to mass spectrometry (Cunhaa et al., 2009). Olive oil is a more difficult sample compared to the other products of this study, not only because of the relatively high amount of lipids that elute from the clean up system, but also because of the potential lipid interference at the GC determinate step (Lentza-Rizos, 1994). Another problem faced during olive oil analysis for pesticide residues is the fact that multiresidues analytical methods are highly desirable, although the different natures, classes and physicochemical properties of pesticides used in olive groves eventually hamper the development of such methodologies (Garcia-Reyes et al., 2007).

3. Pesticides residues in fruits, vegetables and olive oil

3.1 Monitoring data

Grapes peppers, tomatoes, cucumbers eggplants and olive oil were selected for pesticide monitoring and risk assessment since large amounts of these products are consumed daily in Mediterranean countries, especially during the summer period. The target of the study was not only to confirm that consumption of these products was safe for adults, but also for more sensitive population groups such as children. The first step of this study was to collect the raw data from pesticides residues analysis. Part of the results (olive oil and grapes) was obtained from Bio-Hellas monitoring program. Bio-Hellas is the biggest Control and Certification organism in Greece which supervises a great variety of agricultural products such grapes, olives, olive oil, fresh fruits, vegetables etc. Monitoring for grapes was

performed for 381 pesticides by GC/MS-MS and HPLC/MS-MS. During 2005-2009, some 234 samples were analyzed. Monitoring in olive oil from biological cultivation of olives was performed during 2008 - 2009 for the following, most frequently used pesticides in conventional cultivation: Chlorpyrifos, Cyfluthrin, α -Cypermethrin, Cyhalothrin, Deltamethrin, Diazinon, Dimethoate, Endosulfan (Endosulfan-a, Endosulfan-b, Endosulfan sulfate), Fenthion (Fenthion oxon, Fenthion sulfone, Fenthion sulfoxide, Fenthion o sulfone, Fenthion o sulfoxide), Malathion/Malaoxon, Methidathion, Methomyl, Parathion. The results for peppers (60 samples), tomatoes (45 samples), cucumbers (50 samples) and eggplants (45 samples) came from the monitoring program of Laboratory of Toxicology. Monitoring was performed for 175 pesticides by HPLC/MS-MS. The monitoring period for vegetables was 2008 - 2009 and the results are unpublished. All samples were analyzed in line with National Accreditation System SA ESYD laboratories (EN ISO/IEC 17025:2005) in accordance to standard official analytical methods.

As stated at 834/2007 EC biological products should be free of pesticides residues. Moreover according to 396/2005 EC the levels of detected pesticides residues should not exceed the MRLs. Thus the monitoring for pesticide residues is a crucial part of the inspection procedure in every cultivation system (biological cultivation, ICM and conventional cultivation). A very important stage of this procedure is the selection of the appropriate pesticides in the monitoring program. The available new analytical techniques allow the supervising agronomist to select multiresidue methods enabling simultaneous analysis of pesticides from different groups. This is very important because certification authorities are able to detect apart from the pesticides used in specific cultivations other pesticides used in wide spectrum of other crops. In this way contaminated samples (bad agricultural and industrial practice, drift etc) are more easily detected. Thus the reliability of the system is increased and the risk assessment studies are enhanced with a great amount of crucial data.

3.2 Monitoring results

A total of 815 samples from the selected agricultural products were analyzed during the monitoring period. The prevalence of positive samples of pesticide is shown in table 1. The percentage of residual pesticide detection was very low (4.62% was the maximum value) in samples from biological cultivations (grapes and olive oil) compared to vegetables (55.56% was the maximum value).

The levels of detected pesticides residues exceeded the MRLs only in the cases of dimethoate (1 grape sample), endosulfan (3 samples in olive oil), α -cypermethrin (2 samples in olive oil), chlorpyrifos (1 sample in olive oil), diazinon (1 sample in olive oil), in oxamyl (2 samples in peppers, 4 samples in tomatoes and 7 samples in cucumbers) and methamidophos (5 samples in cucumbers). According to these data only 3.06% of samples, from all food commodities, exceeded the MRLs.

In grapes dithiocarbamates and benzimidazoles (carbendazim and benomyl) were the most frequently detected pesticide categories. Fenthion and endosulfan were the most frequently detected pesticides in olive oil. Thiacloprid, spinosad, oxamyl and pyrimiphos methyl were detected in peppers, oxamyl, diethofencarb and carbendazims were detected in tomatoes, endosulfan, spinosad, azoxystrobin, metalaxyl and pyrimethanil in cucumbers and carbendazims and thiamethoxam in eggplants were the most frequently detected pesticides in the vegetable group of commodities.

Food commodity	Pesticide	Pos	%	Average concentration (mg/kg)	Max value (mg/kg)	MRLs (mg/kg)
Grapes (n=234)	Diothiocarbamates	8	3.42	0.274	0.84	5
	Carbendazim + Benomyl	4	1.71	0.055	0.1	0.3
	Iprovalicarb	2	0.85	0.032	0.04	2
	Myclobutanil	2	0.85	0.035	0.04	1
	Fenbutatin oxide	2	0.85	0.095	0.14	2
	Fenarimol	1	0.43	0.010	0.01	0.3
	Penconazole	1	0.43	0.020	0.02	0.2
	Pirimiphos methyl	1	0.43	0.010	0.01	0.05
	Deltamethrin	1	0.43	0.020	0.02	0.2
	Dimethomorph	1	0.43	0.050	0.05	3
	Dimethoate-omethoate	1	0.43	0.060	0.06	0.02
	Tetraconazole	1	0.43	0.010	0.01	0.1
	Boscalid	1	0.43	0.260	0.26	5
	Kresoxim methyl	1	0.43	0.010	0.01	1
	Tebuconazole	1	0.43	0.010	0.01	2
	Endosulfan sulfate	1	0.43	0.010	0.01	0.5
	Endosulfan a and b	1	0.43	0.020	0.02	0.5
Olive oil (n=381)	Fenthion	13	4.62	0.015	0.038	1
	Endosulfan sulfate	11	2.88	0.034	0.071	0.05
	Endosulfan-total	10	2.62	0.034	0.079	0.05
	Fenthion total	10	2.62	0.022	0.035	1
	a-Cypermethrin	7	1.83	0.055	0.200	0.05
	Chlorpyrifos	3	0.78	0.027	0.055	0.05
	Fenthion sulphoxide	2	0.52	0.022	0.022	1
	Fenthion o sulphoxide	2	0.52	0.022	0.022	1
	λ-cyhalothrin	1	0.26	0.050	0.050	0.5
	Diazinon	1	0.26	0.024	0.024	0.01
	Endosulfan-a	1	0.26	0.006	0.006	0.05
	Endosulfan-b	1	0.26	0.002	0.002	0.05
	Methidathion	1	0.26	0.021	0.021	1
Peppers (n=60)	Thiachloprid	31	51.67	0.026	0.04	1
	Spinosad A+D	16	26.67	0.310	0.61	2
	Oxamyl+Oxamyl-Oxine	10	16.67	0.018	0.09	0.02
	Pyrimiphos	10	16.67	0.020	0.020	1

Food commodity	Pesticide	Pos	%	Average concentration (mg/kg)	Max value (mg/kg)	MRLs (mg/kg)
	methyl					
	Pyriproxyfen	7	11.67	0.020	0.020	1
	Indoxacarb	5	8.33	0.020	0.020	0.3
	Pymetrozine	5	8.33	0.050	0.050	1
	Thiamethoxam	5	8.33	0.010	0.010	0.5
	Fenarimol	4	6.67	0.020	0.020	0.5
	Malathion	3	5.00	0.010	0.010	0.1
	Endosulfan a	2	3.33	0.010	0.010	1
	Endosulfan b	2	3.33	0.020	0.020	1
	Endosulfan sulfate	2	3.33	0.090	0.090	1
Tomatoes (n=45)	Oxamyl+Oxamyl-Oxine	25	55.56	0.009	0.12	0.02
	Diethofencarb	16	35.56	0.015	0.02	1
	Carbendazim + Benomyl	10	22.22	0.030	0.04	0.5
	Famoxadone	5	11.11	0.030	0.030	1
	Mepanipyrim	5	11.11	0.030	0.030	1
	Pyrimethanil	5	11.11	0.050	0.050	1
	Thiacloprid	3	6.67	0.020	0.020	0.5
Cucumbers (n=50)	Endosulfan sulfate	15	30.00	0.030	0.040	0.05
	Spinosad A+D	12	24.00	0.060	0.060	1
	Endosulfan b	11	22.00	0.010	0.010	0.05
	Azoxystrobin	10	20.00	0.010	0.010	1
	Diothiocarbamates	10	20.00	0.330	0.330	2
	Endosulfan a	10	20.00	0.010	0.010	0.05
	Metalaxyl	10	20.00	0.026	0.030	0.5
	Pyrimethanil	10	20.00	0.245	0.43	1
	Iprodione	8	16.00	0.050	0.050	2
	Carbendazim + Benomyl	7	14.00	0.020	0.020	0.1
	Oxamyl+Oxamyl-Oxine	7	14.00	0.04	0.040	0.02
	Bifenthrin	5	10.00	0.020	0.020	0.1
	Dimethomorph	5	10.00	0.020	0.020	1
	Methamidophos	5	10.00	0.020	0.020	0.01
	Tolyfluanid	3	6.00	0.001	0.010	2
Eggplants (n=45)	Carbendazim + Benomyl	11	24.44	0.030	0.030	0.5
	Thiamethoxam	10	22.22	0.010	0.010	0.2
	Thiacloprid	9	20.00	0.032	0.06	0.5
	Fludioxonil	6	13.33	0.030	0.030	1

Food commodity	Pesticide	Pos	%	Average concentration (mg/kg)	Max value (mg/kg)	MRLs (mg/kg)
	Cypermethrin	5	11.11	0.020	0.020	0.5
	Iprodione	5	11.11	0.130	0.130	5
	Myclobutamil	5	11.11	0.020	0.020	0.3
	Cyprodinil	4	8.89	0.070	0.070	0.5

Table 1. Positive (pos) and %positive (%) detections of pesticide residues, average concentrations, max values and MRLs in grape samples from organic cultivations during 2005-2009, in olive oil samples from organic cultivations of olives and in vegetables (pepper, tomatoes, cucumbers and eggplants) from ICM cultivations during 2008-2009 (all samples are from Greece)

Table 2 presents the pesticides detected in two or more specific food commodities. Endosulfan was detected in all food items except tomatoes and eggplants. In biological cultivations it was detected only during 2008. Benzimidazoles represented by carbendazim and benomyl were detected in all food commodities except olive oil and peppers. The most frequently detected chemical categories, among all monitoring products, were organophosphates, organochorides, carbamates and pyrethrins.

4. Risk assessment

4.1 Dietary intake and cumulative risk assessment by Greek consumers

The results from monitoring program were used for the assessment of Greek consumers’ risk. The risk assessment was performed for the four most frequently detected chemical categories. The assessment of consumers’ exposure was based on Estimated Daily Intake (EDI) which was compared to Acceptable Daily Intake (ADI) and was expressed as a percentage of it (chronic dietary exposure). The calculation of EDI, expressed in mg/kg body weight/day, was based on the following equation:

$$EDI = R(\text{mean concentration of the residue in the food commodity in mg/kg}) * C(\text{daily consumption kg/person/day}) * EP(\text{edible portion, 0 to 1 values}) * PF(\text{Processing factor for the specific food commodity, 0 to 1 values}) / BW(\text{body weight, kg})$$

All calculations for the determination of EDI were according to international guidelines (Iñigo-Nuñez et al., 2010). Residue levels used were those derived from the mean of detected samples for each food commodity. The average daily intake used for grapes was 82.19 g, for olive oil was 43.56 g, for tomatoes 258.35, and for the cucumbers, peppers and eggplants 360.27g. These intakes were based on FAO foodbalance sheet for 2007 (<http://faostat.fao.org/site/368/DesktopDefault.aspx?PageID=368#ancor>, Accessed in 23/08/2010). The value of EP for all food commodities was 1 in order to represent the local practice in food consumption.

Moreover the effects of processing factors were not taken into account in any case (PF=1). The body weight used for all calculations was 60 kg. The ADI values for pesticides were taken from official EU Pesticides Database.

The Hazard Index (HI) method was used for risk assessment of the mixtures of the detected pesticides belonging to the same chemical group (organophosphates, organochoride, carbamate and pyrethrins). HI was calculated according to the following equation:

$$HI = EDI_1/ADI_1 + EDI_2/ADI_2 + + EDI_n/ADI_n = \sum_{i=1}^n \frac{EDI_i}{ADI_i}$$

EDI_i is the EDI of each active ingredient of each chemical group and ADI_i is the corresponding acceptable daily intake (Amvrazi & Albanis, 2009). If the hazard index exceeds 1, the mixture has exceeded the maximum acceptable level (e.g. ADI or ARfD) and there might thus be a risk. The fractions (EDI₁/ADI₁ etc.) are sometimes called the hazard quotients, HQ.

Based on the reported calculations, table 3 presents the cumulative risk assessment of the intake for the monitored food commodities. In the case of endosulfan where the MRLs were expressed as the sum of alpha- and beta-isomers and endosulfan-sulphate, the EDI was based on the average values of the reported values in table 1. The same practice was followed for fenthion and its metabolites (oxygen analogue, their sulfoxides and sulfone).

As can be seen in table 3 consumers exposure to pesticides do not exceeded the ADI in any of the reported cases. The hazard index of carbamates (cumulative risk) estimated for the adults (60kg) do not exceeded the value of 1 (0.38993) but because of the high value may constitute a risk for the consumers. The hazard index of organophosphorus pesticides estimated for the Greek adult population was 0,34361. The EDI/ADI values for organophosphorus pesticides ranged from 0.001 (fenthion) to 0,12 (methamidophos). Hazard indexes of organochlorine pesticides and pyrethrins were 0,08840 and 0,05288 respectively. Results indicate that there is a negligible risk associated with the exposure via the consumption of selected agricultural products for orgaclorines and pyrethrins. Special attention should be given to organophosphates and carbamates.

An acute dietary exposure assessment was also performed based on the monitoring results.

Food Commodity	Grapes	Olive Oil	Peppers	Tomatoes	Cucumbers	Eggplants
Pesticide						
Carbendazim + Benomyl	+	nd	nd	+	+	+
Endosulfan	+	+	+	nd	+	nd
Oxamyl	nd	nd	+	+	+	nd
Thiachloprid	nd	nd	+	+	nd	+
Dithiocarbamates	+	nd	nd	nd	+	nd
Iprodione	nd	nd	nd	nd	+	+
Pyrimethanil	nd	nd	nd	+	+	nd
Spinosad	nd	nd	+	nd	+	nd
Thiamethoxam	nd	nd	+	nd	nd	+

Table 2. Pesticides detected in more than two food commodities.
[n.d: not detected, +:detection]

In this case intake for each pesticide was compared to an acute reference dose (ARfD). The estimated short-term intake (ESTI) was used to estimate acute dietary exposure. For the calculation of intake the maximum reported values of residues for each pesticide (in mg/kg) were multiplied by previously reported food consumption for each food commodity and was divided by body weight (60 kg) as described by following equation (Tsoutsi et al., 2008):

$$\text{ESTI} = \frac{\text{HR}(\text{Highest residue value in mg/kg}) * \text{C}(\text{daily consumption kg/person/day})}{\text{BW}(\text{body weight, kg})}$$

The risk of exposure was considered as insignificant in the cases where the estimated exposure was equal or lower than to ARfD. Table 4 presents the estimated short term intake of pesticides residues by adults in Greece. In this table values for dithiocarbamates and benzimidazoles were not estimated due to the fact that the parent compound was not possible to be determined. In the case of metabolites the ARfD of mother compound was used. The ARfD values for pesticides were taken from official EU Pesticides Database.

In samples from biological cultivations (grapes and olive oil) the values of ESTI as a percentage of ARfD ranged from 0.01 up to 0.82 indicating a minimum acute risk from the detected pesticides. Despite the fact that the same values were estimated for vegetables, the reported values of ESTI as a percentage of ARfD for methamidophos in cucumbers and of oxamyl in peppers, tomatoes and cucumbers point out an acute risk for the consumers.

4.2 Case study: dietary exposure of Greek consumers to dithiocarbamates by consumption of grapes

The levels of dithiocarbamate residues in grapes, which are the most frequently detected class of pesticides, were used for further research and preliminary assessment of consumers risk resulting from exposure via grapes consumption. According to previously published papers, in order to evaluate the potential risk of dietary exposure to dithiocarbamates, the estimated intakes need to be compared to a toxicological reference value of one compound within the dithiocarbamate class or to a group of compounds with the same mechanism of toxicity, that are present in the analyzed food (Caldas et al., 2004) (Caldas et al., 2006).

The registered dithiocarbamates in Greece are mancozeb, maneb, metiram, propirined, thiram, ziram, and metam sodium. Ziram and metam sodium were not register for grapes.

Thiram is only registered for grapes used for the production of wine. Mancozeb, maneb and metiram belong to Ethylen bis-dithiocarbamate (EBDC) group, propineb in Propylene bis-dithiocarbamate and thiram in dimethyl dithiocarbamate.

According to local grape protection practice, the chemical groups of compounds and the toxicological profiles, the following exposure scenarios were visualized: The CS₂ detected in the samples was derived from the use of a) thiram or propineb alone, b) of at least one compound of mancozeb, maneb and metiram.

Residue levels used for the risk assessment were those derived from mean, median and 90th percentile in mg/kg. According to EFSA statement for the table grapes, the most critical European consumer was identified as a German child with body weight 16.15 Kg, eating in one occasion 211.5 g of table grapes (13.1 g table grapes per kg body weight) (<http://www.efsa.europa.eu/en/scdocs/doc/1590.pdf>, Accessed in 23/08/2010). In the same report it was also stated that for adult population the intake was less critical (maximum food intake for adults 6.35 g /Kg body weight, for a consumer with 63 kg body weight). Thus our exposure calculations were based on previously reported body weight and consumption data.

The risk assessment again was performed by the HI method. As can be seen in table 5, chronic dietary intake of dithiocarbamates by children and adult population did not overcome the ADI for any one of the suggested scenarios, except in the case of propineb in children population, with the EDI estimated as the 90th percentile value of pesticides residues levels.

Chemical Group	Pesticide	ADI in mg/kg / bw/day	EDI in mg/kg / bw/day	EDI/ADI	Food Commodity
Carbamate	Oxamyl	0.001	0.00004	0.03875	Tomatoes
	Oxamyl	0.001	0.00111	0.10808	Peppers
	Oxamyl	0.001	0.00024	0.24018	Cucumbers
	Iprovalicarb	0.015	0.00004	0.00292	Grapes
$\sum \frac{EDI}{ADI} = HI$				0.38993	
Organophosphate	Methamidophos	0.001	0.00012	0.12009	Cucumbers
	Diazinon	0.0002	0.00002	0.08712	Olive Oil
	Dimethoate- omethoate	0.001	0.00008	0.08219	Grapes
	Pirimiphos methyl	0.004	0.00012	0.03002	Peppers
	Methidathion	0.001	0.00002	0.01525	Olive Oil
	Pirimiphos methyl	0.004	0.00001	0.00342	Grapes
	Malathion	0.03	0.00006	0.00200	Peppers
	Chlorpyrifos	0.01	0.00002	0.00196	Olive Oil
	Fenthion	0.007	0.00001	0.00156	Olive Oil
	$\sum \frac{EDI}{ADI} = HI$			0.34361	
Organochlorine	Endosulfan	0.006	0.00026	0.04253	Cucumbers
	Endosulfan	0.006	0.00024	0.04003	Peppers
	Endosulfan	0.006	0.00002	0.00342	Grapes
	Endosulfan	0.006	0.02000	0.00242	Olive oil
$\sum \frac{EDI}{ADI} = HI$				0.08840	
Pyrethrins	a-Cypermethrin	0.015	0.00040	0.02686	Olive oil
	Bifenthrin	0.015	0.00012	0.00801	Cucumber
	a-Cypermethrin	0.015	0.00012	0.00801	Eggplants
	λ-cyhalothrin	0.005	0.00004	0.00726	Olive oil
	Deltamethrin	0.010	0.00003	0.00274	Grapes
$\sum \frac{EDI}{ADI} = HI$				0.05288	

Table 3. Cumulative intake of carbamate, organophosphate, organochlorine and pyrethrins pesticides detected in all samples during monitoring period based on HI method.[n.a: not available, n.e: not estimated]

Food Commodity	Pesticide	ARfD in mg/kg/ bw/day	ESTI in mg/kg/ bw/day	ESTI as % of ADI
Grapes (n=234)	Dimethoate-omethoate	0.01	0.00008	0.82
	Deltamethrin	0.01	0.00003	0.27
	Endosulfan a and b	0.02	0.00003	0.14
	Fenarimol	0.02	0.00001	0.07
	Endosulfan sulfate	0.02	0.00001	0.07
	Tebuconazole	0.03	0.00001	0.05
	Tetraconazole	0.05	0.00001	0.03
	Penconazole	0.5	0.00003	0.01
	Pirimiphos methyl	0.15	0.00001	0.01
	Dimethomorph	0.6	0.00007	0.01
	Diothiocarbamates	n.a	0.00115	n.e
	Carbendazim + Benomyl	n.a	0.00014	n.e
	Iprovalicarb	n.a	0.00005	n.e
	Myclobutanyl	n.a	0.00005	n.e
	Fenbutatin oxide	n.a	0.00019	n.e
	Boscalid	n.a	0.00036	n.e
	Kresoxim methyl	n.a	0.00001	n.e
Olive oil (n=381)	λ-cyhalothrin	0.0075	0.00004	0.48
	α-Cypermethrin	0.04	0.00015	0.36
	Endosulfan-total	0.02	0.00006	0.29
	Fenthion	0.01	0.00003	0.28
	Endosulfan sulfate	0.02	0.00005	0.26
	Fenthion total	0.01	0.00003	0.25
	Fenthion sulphoxide	0.01	0.00002	0.16
	Fenthion o sulphoxide	0.01	0.00002	0.16
	Methidathion	0.01	0.00002	0.15
	Diazinon	0.025	0.00002	0.07
	Chlorpyrifos	0.1	0.00004	0.04
	Endosulfan-a	0.02	0.00000	0.02

Food Commodity	Pesticide	ARfD in mg/kg/ bw/day	ESTI in mg/kg/ bw/day	ESTI as % of ADI
	Endosulfan-b	0.02	0.00000	0.01
Peppers (n=60)	Oxamyl+Oxamyl-Oxine	0.001	0.00054	54.04
	Endosulfan sulfate	0.02	0.00054	2.70
	Thiachloprid	0.03	0.00024	0.80
	Fenarimol	0.02	0.00012	0.60
	Endosulfan b	0.02	0.00012	0.60
	Pymetrozine	0.1	0.00030	0.30
	Endosulfan a	0.02	0.00006	0.30
	Indoxacarb	0.125	0.00012	0.10
	Pyrimiphos methyl	0.15	0.00012	0.08
	Malathion	0.3	0.00006	0.02
	Thiamethoxam	0.5	0.00006	0.01
	Pyriproxyfen	10	0.00012	0.00
	Spinosad A+D	n.a	0.00366	n.e
Tomatoes (n=45)	Oxamyl+Oxamyl-Oxine	0.001	0.00052	51.67
	Carbendazim + Benomyl	0.02	0.00017	0.86
	Thiacloprid	0.03	0.00009	0.29
	Famoxadone	0.2	0.00013	0.06
	Diethofencarb	n.a	0.00009	n.e
	Mepanipyrim	n.a	0.00013	n.e
	Pyrimethanil	n.a	0.00022	n.e
Cucumbers (n=50)	Oxamyl+Oxamyl-Oxine	0.001	0.00024	24.02
	Methamidophos	0.003	0.00012	4.00
	Endosulfan sulfate	0.02	0.00024	1.20
	Carbendazim + Benomyl	0.02	0.00012	0.60
	Bifenthrin	0.03	0.00012	0.40
	Endosulfan b	0.02	0.00006	0.30
	Endosulfan a	0.02	0.00006	0.30

Food Commodity	Pesticide	ARfD in mg/kg/ bw/day	ESTI in mg/kg/ bw/day	ESTI as % of ADI
	Metalaxyl	0.5	0.00018	0.04
	Dimethomorph	0.6	0.00012	0.02
	Tolyfluanid	0.25	0.00006	0.02
	Spinosad A+D	n.a	0.00036	n.e
	Azoxystrobin	n.a	0.00006	n.e
	CS2	n.a	0.00000	n.e
	Pyrimethanil	n.a	0.00258	n.e
	Iprodione	n.a	0.00030	n.e
Eggplants (n=45)	Thiacloprid	0.03	0.00036	1.20
	Carbendazim + Benomyl	0.02	0.00018	0.90
	Cypermethrin	0.04	0.00012	0.30
	Thiamethoxam	0.5	0.00006	0.01
	Fludioxonil	n.a	0.00018	n.e
	Iprodione	n.a	0.00078	n.e
	Myclobutamil	n.a	0.00012	n.e
	Cyprodinil	n.a	0.00042	n.e

Table 4. Estimated short term intake of residual pesticides by Greek adults (60 kg bw) expressed as percentage of ARfD

The lowest value of EDI% of ADI was obtained when median value of pesticides residues levels was used in the calculation and increased when the mean value was used. The highest value was observed when 90th percentile was used. The exposure of children population was always higher than that of an adult.

5. Conclusions

- Only 3.06% of total samples (815) exceeded the MRLs. The problem occurred in the case of dimethoate (1 grape sample), endosulfan (3 samples in olive oil), a-cypermethrin (2 samples in olive oil), chlorpyrifos (1 sample in olive oil), diazinon (1 sample in olive oil), in oxamyl (2 samples in peppers, 4 samples in tomatoes and 7 samples in cucumbers) and methamidophos (5 samples in cucumbers).
- The most frequently detected pesticides for each food commodity were dithiocarbamates for grapes (3.42%), fenthion in olive oil (4.62%), thiacloprid in peppers (51.67%), oxamyl in tomatoes (55.56%), endosulfan sulfate in cucumbers (30%), and carbendazim group in eggplants (24.44%).
- The most frequently detected chemical categories, among all monitored products, were organophosphates, organochlorine, carbamate and pyrethrins.

Risk assessment parameters		Dithiocarbamate		
		EBDC	Propineb	Thiram
ADI (in CS ₂ mg/kg / bw/day)		0.0169	0.0036	0.0063
Child	EDI ^{median}	0.0025		
	EDI ^{median} % of ADI	15.07	69.32	40.35
Adult	EDI ^{median}	0.0012		
	EDI ^{median} % of ADI	7.30	33.60	19.56
Child	EDI ^{mean}	0.0035		
	EDI ^{mean} % of ADI	21.09	97.04	56.49
Adult	EDI ^{mean}	0.0017		
	EDI ^{mean} % of ADI	10.22	47.04	27.38
Child	EDI ^{90th}	0.0061		
	EDI ^{90th} % of ADI	36.24	166.71	80.82
Adult	EDI ^{90th}	0.0029		
	EDI ^{90th} % of ADI	17.56	80.82	47.04

Table 5. Risk assessment of exposure of child (16.15 Kg body weight) and adult (63 Kg body weight) population to the dithiocarbamate pesticides (mean, median and 90th percentile value of pesticides residues values) in EDI% of ADI based on 211.5 g and 400g consumption respectively, of table grapes originate from biological cultivations. [The transform of ADI of each dithiocarbamate to CS_s was based on molecular weight factor reported in E.D Caldas et. al 2004., CS₂: Carbon disulfide, EDI^{mean,mediam,90th}:Estimated Daily Intake in CS_s (mg/ kg / bw / day) based on mean, median and 90th percentile value of pesticides residues levels respectively.]

- According to selected parameters for the risk assessment (food commodities, consumption, body weight,) pyrethrins (HI value 0.05288) and organochlorine (HI value 0.08740) present a negligible hazard for the consumers. Organophoshates with estimated HI value of 0.34361 and carbamates with estimated HI value 0.38993, which were also far below 1, do not expect to constitute a risk but further attention should be given. A long term monitoring program from different areas and different times of sampling is necessary in order to reach more accurate conclusions.
- All samples from biological cultivations (grapes and olive oil) presented a minimum acute risk from detected pesticides.
- The acute risk from methamidophos in cucumbers (ESTI was 4% of ARfD) and especially from oxamyl in peppers(ESTI was 54.04% of ARfD)and in tomatoes (ESTI 51.67% of ARfD) is high.
- The chronic dietary intakes of dithiocarbamates by adult and children through the consumption of grapes originating from organic cultivations did not overcome the toxicologically acceptable levels.

- Grapes originating from organic cultivation may consist a reliable choice for the consumers and especially for the most sensitive groups such as children.
- A wide spectrum of pesticides should be included in monitoring programs in order to eliminate the possibility of contaminated samples to reach the markets store. The usage of multiresidue methods characterized by simultaneous analysis of pesticides from different groups could enhance the risk assessment studies with a great amount of crucial data.

6. Acknowledgment

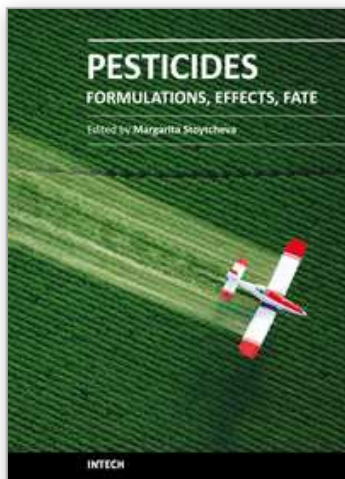
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7. References

- Amvrazi, E.G & Albanis T.A. (2009). Pesticide residue assessment in different types of olive oil and preliminary exposure assessment of Greek consumers to the pesticide residues detected. *Food Chemistry*. 113, 253-261
- Caldas, E.D.; Boon P.E. & Tressou, J. (2006). Probabilistic assessment of the cumulative acute exposure to organophosphorus and carbamate insecticides in the Brazilian diet. *Toxicology*. 222, 132-142
- Caldas, E.D.; Miranda, M.C.C.; Conceicao, M.H. & de Souza L.C.K.R. (2004) Dithiocarbamates residues in Brazilian food and the potential risk for consumers. *Food and Chemical Toxicology*. 42, 1877-1883
- Coxam, V.; Puel, C. & Davicco, M.J. (2010). *Olives and Olive Oil in the Prevention of Osteoporosis*, In: *Olives and Olive Oil in Health and Disease Prevention*. Eds. V. R. Preedy, R.R. Watson, 1195-1203, Oxford Academic Press
- Cunhaa, S.C.; Fernandesa, J.O.; Alvesb A.P. & Oliveiraa, M.B.P.P. (2009). Fast low-pressure gas chromatography-mass spectrometry method for the determination of multiple pesticides in grapes, musts and wines. *Journal of Chromatography A*. 1216, 119-126
- Dani, C.; Oliboni, L.S.; Vanderlinde, R.; Bonatto, D.; Salvador, M. & Henriques, J.A.P. (2007). Phenolic content and antioxidant activities of white and purple juices manufactured with organically or conventionally produced grapes. *Food and Chemical Toxicology*, 45, 2574-2580
- Garcia-Reyes, J.F.; Ferres, C.; Gomez-Ramos, M.J.; Molina-Diaz, A. & Fernandez-Alba, A.R. (2007). Determination of pesticide residues in olive oil and olives. *Trends in Analytical Chemistry*. 26 (3), 239-251
- Iñigo-Nuñez, S.; Herreros, M.A.; Encinas, T. & Gonzales-Bulnes, A. (2010) Estimated daily intake of pesticides and xenoestrogenic exposure by fruit consumption in the female population from a Mediterranean country (Spain). *Food Control*. 21, 417-477
- Lentza-Rizos, Ch. (1994). Monitoring of pesticide residues in olive products: Organophosphorus insecticides in olives and oil. *Journal of Association of Official Analytical Chemists International*. 77, 5
- Patil, S.H.; Banerjee, K.; Dasgupta, S.; Oulkar, D.P.; Patil, S.B.; Jadhav, M.R.; Savant, R.H.; Adsule, P.G. & Deshmukh, M.B. (2009). Multiresidue analysis of 83 pesticides and

- 12 dioxin-like polychlorinated biphenyls in wine by gas chromatography–time-of-flight mass spectrometry. *Journal of Chromatography A*, 1216, 2307-2319
- Payá, P.; Anastassiades, M.; Mack, D.; Sigalova, I.; Tasdelen, B.; Oliva, J. & Barda, A. (2007). Analysis of pesticide residues using the Quick Easy Cheap Effective Rugged and Safe (QuEChERS) pesticide multiresidue method in combination with gas and liquid chromatography and tandem mass spectrometric detection. *Analytical and Bioanalytical Chemistry*. 389, 1697-1714
- Roche, M.H.; Gibney, M.J.; Kafatos, A.; Zampelas, A. & Williams C. M. (2000). Beneficial properties of olive oil. *Food Research International*, Volume 33, Issues 3-4, Pages 227-231
- Tsakiris, I.N.; Danis, T.G.; Stratis, I.A.; Nikitovic D.; Dialyna I.A.; Alegakis A.K. & Tsatsakis A.M. (2004). Monitoring of pesticide residues in fresh peaches produced under conventional and integrated crop management cultivation. *Food Additives & Contaminants*. 21(7), Jul, 670-7
- Tsatsakis A.M. & Tsakiris I.N. *Fenthion Dimethoate and Other Pesticides in Olive Oils of Organic and Conventional Cultivation*. In: *Olives and Olive Oil in Health and Disease Prevention*. Eds V. R. Preedy, R. R. Watson, 415-424 Oxford Academic Press
- Tsoutsis, C.S.; Konstantinou, I.K. & Hela, D.G. (2008). Organophosphorus pesticide residues in Greek virgin olive oil: levels, dietary intake and risk assessment. *Food Additives and Contaminants*. Vol.25, No. 10, October, 1225-1236
- Venkateswarlu P.; Mohan K.R.; Kumar C.R. & Seshaiiah, K. (2007). Monitoring of multi-class pesticide residues in fresh grape samples using liquid chromatography with electrospray tandem mass spectrometry. *Food Chemistry*, 105, 1760-1766

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
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InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

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