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A STUDY ON CONTENTS OF NITRATE, VITAMIN C AND CRUDE FIBRE IN SOME SPECIES OF HORTICULTURAL PLANTS, AND OF ORGANIC CONTAMINANTS IN ALGERIAN AROMATIC HERBS AND SPICES. A STATISTICAL ANALYSIS

PhD Thesis of:

Dott. Alessandra Scinelli

Tutor:

Prof. Giuseppa Di Bella

Coordinator:

Prof. Concetta De Stefano

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INTRODUCTION

This thesis consists of two parts. The Part I is dedicated to the study of contents of Nitrate, vitamin C and crude fibre in some species of horticultural plants; the Part II is dealing with the study of organic contaminants in Algerian aromatic herbs and spices. A statistical analysis is done.

In Particular in the Part I a set of fresh horticultural plants, used in Mediterranean diet is considered. and a statistical analysis is done. The nitrate, the vitamin C and the crude fibre contents in these vegetables, measured in the laboratory, are taken into account and their frequency distributions, averages, variances and standard deviations are worked out, by statistical methods. Also some graphic representations are given. From the results it is shown the importance to follow a diet rich in vegetables in order to reach the recommended doses of vitamin C and crude fibre, to have health benefits, following the directives of nutrition national and international organizations.

Vitamin C (or ascorbic acid) is a water soluble vitamin having nutraceutical properties. It is an important antioxidant widely present in vegetables and fruits with functions to prevent several diseases in the human organism. It strengthens the immune system and offers several benefits. Vitamin C contrasts the negative influence of nitrates, that combined with amines, present in food or derived from protein degradation processes, occurring in the stomach, can produce nitrosamines, that are acknowledged as carcinogens. Crude fibre refers to the indigestible carbohydrate component, present in plant cell walls, having a fibrous structure. Crude fibre is the measure of the quantity of indigestible cellulose, pentosan, lignin and other components of this type present in foods. It increases the bulk and speeds up the passage of food through the digestive tract, reducing the absorbtion of toxic substances.

The nitrate contents, ingested by human organism by the consumption of the analyzed fruits and vegetables, does not constitute a risk for human health, when the assumption of these vegetables is limited, in agreement with the values recommended by the nutrition directives to prevent diseases.

The Part II is dealing with a statistical analysis of the content of 119 organic contaminants in some aromatic herbs and spices, purchased in markets of some Algerian cities. These aromatic herbs and spices are very important in the economy of Mediterranean countries for their production, export and import. Algeria is one of the major producers and exporters in UE market. From the measured values of the contents of the analyzed contaminants (ng/g), illustrated in Tables and by graphic representations, it is seen that this content (ng/g), ingested by human organism by the consumption of the analyzed herbs and species do not constitute a risk for the human health, when its assumption is limited, in agreement with the values recommended by the directives of international and national nutrition organizations. Aromatic herbs and spices are employed in several sectors like

medical sciences, cosmetics, and culinary science. Furthermore, they are anti inflammatory, anticancer, antimicrobial.

The organization of this thesis is the following. In the Chapter I we introduce a statistical variable, illustrating the measured nitrate contents in 26 fresh horticultural plants, working out its frequency distribution, its average, variance and standard deviation with some statistical graphic representations. Furthermore, the acceptable daily intake (ADI) of nitrate content of each fresh edible plant per 60 kg of body weight is calculated, discussing the results and the recommendations, given by international and national nutrition organizations. In the Chapter II the Mediterranean diet is introduced, emphasizing the motivations that have pushed the promotion of this diet in preventing diseases.

To this aim the contents of vitamin C and crude fibre in the horticultural plants, considered in Chapter I, are examined as two statistical variables, of which, knowing the frequency distribution, applying statistical methodologies, the average value and the standard deviation are calculated. The benefits of consuming vegetables containing vitamin C and crude fibre are discussed, according to the Mediterranean diet and the national and international nutritional guidelines.

The Chapter III is addressed to present the materials and methods used in order to analyze the samples of aromatic herbs and spices, purchased in different Algerian cities. In Chapters IV, V and VI the results, organized in Tables and Figures for the measured residues of organic contaminants (ng/g) in samples of aromatic herbs and spices purchased in the markets of Algerian cities Oran and Tlemcen, Constantine and Annaba, Algeri and Bijayad are worked out. The obtained results are discussed and it is seen that the values of the measured contaminants contents (ng/g) do not constitute a risk for the human health because their values do not exceed the maximum levels (MLs) permitted by the directives of international and national nutritional organizations. Finally, the Appendix A deals with the organic contaminants and their chemical classes, analyzed in the aromatic herbs and spices taken into account.

Part I

A STUDY ON CONTENTS OF NITRATE, VITAMIN C AND CRUDE FIBRE IN SOME SPECIES OF HORTICULTURAL PLANTS. A STATISTICAL ANALYSIS.

The studies presented in Chapter I and Chapter II of this Part I are contained, respectively, in the published articles:

1. G. Di Bella, N. Cicero, A. Scinelli, *A statistical study on Nitrate contents in a set of some horticultural plants used in Mediterranean diet*, Atti Accademia Peloritana dei Pericolanti, Vol. 97, No. S2, A24 (2019) DOI: 10.1478/AAPP.97S2A24.

2. G. Di Bella, N. Cicero, A. Scinelli, *A statistical approach to the study of vitamin C and crude fibre in some horticultural plants to introduce the Mediterranean diet,* Atti della Accademia Peloritana dei Pericolanti, ,Vol. 99, No. S1, A20 (2021) , DOI: 10.1478/AAPP.99S1A20

Chapter I

A statistical study on nitrate content in a set of some horticultural plants, used in the Mediterranean diet

In this Chapter we consider a set of fresh horticultural plants, used in Mediterranean diet, and we carry out a statistical analysis. In particular, we illustrate the nitrate contents in these vegetables, obtained in laboratory, as a sample variable and we study its frequency distribution, we compute its average, variance and standard variation and we work out some graphic representations. The derived results are more deepened with respect to those ones obtained in previous papers, where a classification in ordered classes of nitrate contents was taken into consideration. From the results it is seen that the average value of nitrate contents ingested by human organism by the consumption of the analyzed fruits and vegetables, does not constitute a risk for human health, when the assumption of these vegetables is limited, in agreement with the values recommended by the nutritional guidelines to prevent diseases. For this reason Mediterranean diet is recommended, because prescribes to eat many portions of fruits and vegetables to be in good health.

1.1 Introduction

In a previous contribution (see [1]) a statistical examination was given on nitrate contents in a set of 26 horticultural plants, following a classification in 5 ordered classes of this content (see [2] and also [3] - [6]) obtaining results very handy and practical to be applied in studying different vegetables. In this chapter the carried out results are more deepened and the statistical analysis conducted on the same plants is quantitative. The contents of nitrates (obtained in laboratory) are examined as a variable and correspond to the average of three measures estimated on each species of vegetable. Nitrates are salts of nitric acid and are an essential vegetal nutrient absorbed by the roots of plants from the soil. They originate from living matter as a result of degradation processes, mainly due to microorganisms, leading to the formation of simple compounds. Once absorbed, the nitrates are used for the synthesis of complex substances essential to the structures and functions of plants. The accumulation of nitrates in the foods can be influenced by several factors, including their level of concentration in the ground (closely related to the level of fertilization adopted, to its permeability and composition) and the light radiation, which, by acting on specific enzymes present in vegetables, can lead to a greater degradation rate of nitrates. Nitrates of potassium and sodium are used as food additives to promote the conservation of certain foods. Indeed,

in certain circumstances, nitrates may be transformed into nitrites. The excess of nitrates may constitute a risk for both environment and human health, but the biological cultivations reduce the content of nitrates in plants. Nitrate contents decrease in the following order depending on the following different parts of a plant: petiole, leaf, stem, root, inflorescence, tuber, bulb, fruit, seed. Furthermore, there are many factors that have as effect accumulation vary according the seasons and for open grown vegetables and of NO_3 in vegetable tissues coming from: genetic factor, environment (atmospheric humidity, temperature, irradiance, photoperiod), agricultural practices (use of herbicides, synthetic nitrogen fertilizers, nitrogen and other chemical nutrients). European Member states amended EC Regulations fixing limits for nitrate in vegetables, trying to harmonize the different national limits, that under glass grown vegetables (see [7]-[10]). In Section 2 we illustrate the materials and methods, used to measure the content of Nitrates in the considered vegetables. All the samples were analyzed in triplicate. In Section 3 we define the variable X_1, describing the 26 fresh horticultural plants taken into account. In Sections 4 we introduce the statistical variable X_2, illustrating the nitrate contents in the considered horticultural plants, working out its frequency distribution and its average, variance and standard deviation. Furthermore, the acceptable daily intake (ADI) of nitrate content of each fresh edible plant per 60 kg of body weight and the covered DIA (CDIA), expressed in %, are calculated, discussing the obtained results and the recommendations, given by international and national organizations for nutrition, as OMS (world health organization), FAO (food and agriculture organization), to avoid high content of nitrates to reduce the risk of several diseases. Finally, some graphic representations are given. They are colored in order to put in evidence with the same color equal values of nitrates contents and, then, their frequency distribution.

1.2 Materials and methods

1.2.1 Samples

Twenty-six horticultural plants were collected, marketing them in the same sicilian market. Coming from the same territory, where the manufacturers have utilized similar coltivation conditions. All chemicals were of HPLC grade and all reagents, eluent, standard and sample solutions used for the determination were prepared by ultrapure water with a specific conductivity less than 18 $mS\ cm^{-1}$ % purchased from Romil (Milan, Italy). The analytes, nitrite and nitrate ions were purchased from Dionex (Sunnyvale, CA, USA). In this study 3% acetic acid solution was used, prepared from ultrapure acetic acid (99.9 %) purchased from J. T. Baker (Deventer, the Netherlands). Mobile phase (9mM Na_2CO_3) was prepared from 0.5 M sodium carbonate obtained from Dionex.

1.2.2 Standard solution and sample preparation

Standard mixture concentrations ranged from 30 to 150 mgl^{-1} in ultrapure water (99.9 %). Standard solutions were prepared daily by serial dilution of the standard mixture prior to use. After homogenisation and agitation with a vortex, 10 gr of every sample were transferred into a 20ml volumetric flask, put in ultrasonic bath for 30 min and after they were centrifuged at 5000 rpm per 5 min, spiked with 2ml of 3% acetic acid and brought to volume by ultrapure water. A total of 1ml of this solution was diluted with ultrapure water again up to 50 ml.

1.2.3 Equipment

Analysis were performed by an ICS 1000 ion chromatography system (Dionex) equipped with an isocratic pump, a conductivity detector, a guard column (Dionex Ion Pac AG9-HC, 4 x 50 mm) to prevent potential fouling of the analytical column, a highcapacity anion exchange analytical column (Dionex Ion Pack AS9-HC, 4 x 250 mm, 9 μm), 25 μl sample loop, and an anion self-regenerating suppressor (ASRS 300, 4 mm). Data acquisition and instrument control were performed using Chromeleon software.

1.2.4 Ion exchange chromatography analysis

All experiments were performed at room temperature, with flow rate of 1.0 ml $min^{-1}$and 35^0 C flow cell temperature. Suppressor current was fixed at 45 mA. The isocratic elution was carried out using a 9mM sodium carbonate solution. The standard and sample solutions were filtered through 0.22 μm glass microfibre GMF Whatman chromatographic filter before entering the IEC system. Data collection was performed in triplicate. Ultrapure water was injected before the unknown samples.

1.2.5 Anions determination

The data showed that Na_2CO_3 concentration of 9mM permitted a fast separation of the two anions (about 15 min). The chromatographic peaks were well resolved and consequently the quantification steps were easy. Identification of analytes was carried out by comparing the retention times in the sample with those of the standard mixture. For quantification a calibration curve was obtained for each analyte by plotting peak areas versus their concentrations.

1.2.6 Validation of IEC analysis

The relative standard deviations (RSD %) on retention times and on peak area were determined by considering a mixture of standard anions at the concentration level of 2.5 (nitrite and nitrate). The measurements were performed, in the conditions reported above, within the same day (n=3). The highest RSD values

were 1.4 % and 2.2 % for T_R and 2.4 % and 3.7 % for areas. The linearity of the used method was assessed by analyzing seven standard solutions obtained from the standard mixture. Three replicate analyses were performed at each concentration level. Good linearity was observed in each concentration range, with linear correlation coefficients (R_2) > 0.9873. As per European Pharmacopoeia (2005), the limits of detection (LODs) and of quantification (LOQs) were experimentally calculated as a signal-to-noise ratio of 3 and 10, respectively. The accuracy of the method described for the determination of anions in the samples was evaluated at three spiking levels, with three replicates for each level. For the recovery test, a sample was previously analysed and then fortified with a known amount of standard anions. For the anions, the recoveries were around 88%. All RSDs< 2.8%, which shows the good precision of the method used for the determination of anions in horticultural plants.

1.3 Statistical analysis

In this Section we consider a sample of horticultural plants as a variable X_1, defined as follows

$$X_1: \mathrm{S} \longrightarrow T_1, \tag{1.1}$$

where the elements of the set S are the analyzed plants and the range T_1 contains the corresponding numbers, that order in increasing way the same plants: T_1 = {1, 2, ...26} (see Table 1.1).

Table 1.1 Statistical variable X_1: 26 fresh horticultural plants

S	T_1	
FAMILY	GENERA AND SPECIES	
Asteracae	*Cichorium endivia* L. var. *latifolium* Hegi	1
	Cichorium intybus L.	2
	Lactuca sativa L.	3
	Scorzonera hispanica L.	4
Liliaceae	*Allium cepa* L.	5
	Allium porrum L.	6
	Asparagus officinalis L.	7
Brassicaceae	*Brassica oleracea* var. *italica* Plenck	8
	Brassica oleracea L. var . *Sabauda* L.	9
	Brassica rapa L.	10
	Brassica rapa L. var. *rapa*	11
	Raphanus sativus	12
Cucurbitaceae	*Cucumis melo* L.	13
	Cucurbita moschata	14
	Cucumis sativus L.	15
Convolvulaceae	*Ipomoea batatas* L.	16
Graminaceae	*Zea mays* L. var. *saccharata* Körn	17
Leguminosae	*Phaseolus vulgaris* L.	18
	Pisum sativum L.	19
Polygonaceae	*Rhéum rhaponticum* L.	20
Solanaceae	*Capsicum annuum* L.	21
	Lycopersicon esculentum Mill.	22
	Solanum melongena L.	23
	Solanum tuberosum L.	24
Umbelliferae	*Apium graveolens* L. var. *dulce*	25
	Petroselinum crispum	26

1. 4 The variable X_2 describing the nitrate contents in horticultural plants, Tables and Figures

In this Section we give a statistical analysis of nitrate contents (expressed in mg/kg of fresh weight of edible plant) present in 26 analyzed horticultural plants, on the basis of obtained data in laboratory.

Then, we define the variable X_2 describing these nitrate contents as follows:

$$X_2: \mathrm{S} \longrightarrow T_2, \tag{1.2}$$

where the elements of the set S are the horticultural plants under consideration S = {1, 2, ..., 26} and the range T_2 contains the corresponding content of nitrates, obtained in laboratory, expressed in mg/kg of fresh weight of edible plant of the considered plants with own calculated standard deviation (see Table 1.2a). Such values correspond to the average of three measures estimated on each species of vegetable, purchased in the same sicilian market. Following some authors (see [2]) there exist a classification of the content of nitrates in 5 classes, i. e. : class 1 (indicating nitrates *very low* content (< 200 mg/kg)); class 2 (indicating nitrates *low* content (200 - 500 mg/kg); class 3 (indicating nitrates *medium* content (500 - 1000 mg/kg); class 4 (indicating nitrates *high* content (1000 - 2500 mg/kg) and class 5 (indicating nitrates *very high* content (> 2500 mg/kg). In [1] the nitrates content in the examined plants was studied statistically following the above classification.

Therefore, we define the frequency distribution $\mathrm{F}(X_2)$of the variable X_2, as follows:

$$\mathrm{F}(X_2): T_2 \longrightarrow W_2, \tag{1.3}$$

where T_2 contains the content of nitrates (expressed in mg/kg of fresh weight of edible plant) of the considered plants, and the elements of W_2 are the relative frequencies corresponding to the values of nitrates content (see Table 1.2 b). From the obtained data, presented in Table 1.2, we construct the graphic representations of X_2 and its frequency distribution $\mathrm{F}(X_2)$ (see Figures 1.1 and 1.2). Finally, we compute the average $\mathrm{M}(X_2)$:

$$\mathrm{M}(X_2)=\sum_{i=1}^{19} x_i f_i=732 \text{ mg/kg}, \tag{1.4}$$

where x_i (i = 1, 2,...,19) are the values of X_2 having relative frequencies f_i (i = 1, 2,...,19) (being $\sum_{i=1}^{19} f_i$ =1) and the variance V and the standard deviation σ having the expressions:

$$\mathrm{V} = \sum_{i=1}^{19}(x_i - M)^2 f_i = 819.523{,}48 \ (\mathrm{mg/Kg})^2, \tag{1.5}$$

$$\sigma = \sqrt{V} = 905{,}27 \ \mathrm{mg/kg}. \tag{1.6}$$

S	T_2
Cichorium endivia L. var. *latifolium* Hegi	1200 ± 0.34
Cichorium intybus L.	150 ± 0.15
Lactuca sativa L.	3000 ± 0.24
Scorzonera hispanica L.	250 ± 0.18
Allium cepa L.	250 ± 0.25
Allium porrum L.	1500 ± 0.12
Asparagus officinalis L.	190 ± 0.28
Brassica oleracea var. *italica* Plenck	400 ± 0.31
Brassica oleracea L. var. *Sabauda* L.	600 ± 0.27
Brassica rapa L.	600 ± 0.19
Brassica rapa L. var. *rapa*	350 ± 0.21
Raphanus sativus	2600 ± 0.26
Cucumis melo L.	93 ± 0.18
Cucurbita moschata	590 ± 0.28
Cucumis sativus L.	250 ± 0.15
Ipomoea batatas L.	150 ± 0.25
Zea mays L. var. *saccharata* Körn	30 ± 0.12
Phaseolus vulgaris L.	53 ± 0.22
Pisum sativum L.	53 ± 0.26
Rhéum rhaponticum L.	2400 ± 0.19
Capsicum annuum L.	25 ± 0.22
Lycopersicon esculentum Mill.	16 ± 0.16
Solanum melongena L.	460 ± 0.29
Solanum tuberosum L.	35 ± 0.31
Apium graveolens L. var. *dulce*	2600 ± 0.24
Petroselinum crispum	1200 ± 0.19

(a)

T_2	W_2
16	1/26
25	1/26
30	1/26
35	1/26
53	2/26
93	1/26
150	2/26
190	1/26
250	3/26
350	1/26
400	1/26
460	1/26
590	1/26
600	2/26
1200	2/26
1500	1/26
2400	1/26
2600	2/26
3000	1/26

(b)

Table 1.2: a) Variable X_2 (Content of nitrates mg/kg of fresh weight of edible plant) and b) its frequency distribution $F(X_2)$.

From these results it is seen that the average value 732,5 mg/kg of nitrates content in 26 analyzed horticultural plants indicates that eating fruits and vegetables of the considered set does not constitute risk for the human health, when the consumption of these vegetables is limited. In fact, scientific committee for food (SCF) established an acceptable daily intake (ADI) of nitrate content of 3,65 mg per kg of body weight/day.

Furthermore, the negative effects of nitrate contents are contrasted by the consumption of nutraceutical and antioxidant substances (carotenoides, vitamins C, E and other ones, selenium, crude fibre,
glucosinolates, isothiocyanates, flavonoids, phenols) contained in fruits and vegetables (see also [11] and [12]).

The ADI of nitrate content (in mg) per 60 kg of body weight/day is 219, 0 mg (ADI60). The ADI of fresh edible plant per 60 kg of body weight, expressed in Kg ($ADI60_{fp}$) is given in the set T_3 of Table 1.3, calculated by the expression:

$$\text{ADI60f p} = \frac{219{,}0mg}{nitrates\ in\ fresh\ plant\ mg} \times \text{Kg}$$

and represented in Fig. 1.3.

Finally, we calculate the covered DIA (CDIA), expressed in %, using the formula:

$$\text{XCDIA} = \frac{0{,}000219\ \text{Kg}}{ADI60_{fp}\ \text{Kg}} \times 100 \quad \%$$

(see the set T_4 in Table 1.4).

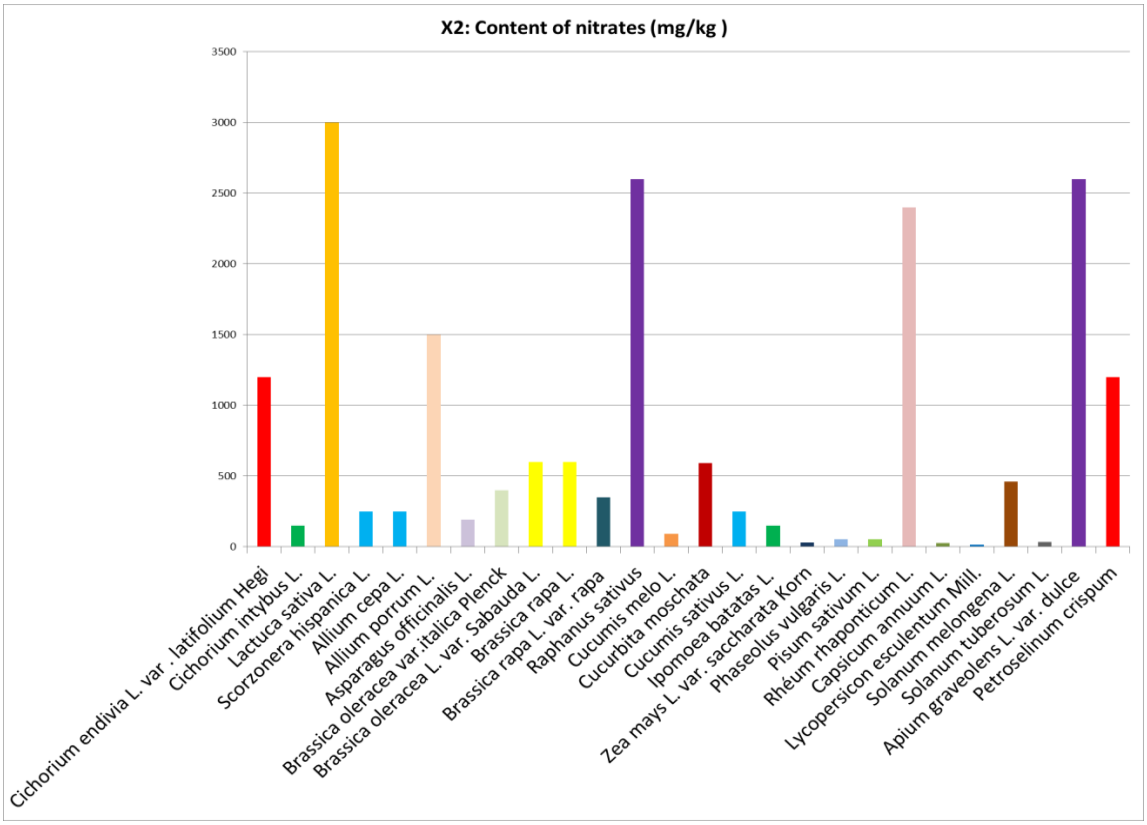

Figure 1.1: Diagram of the variable X_2

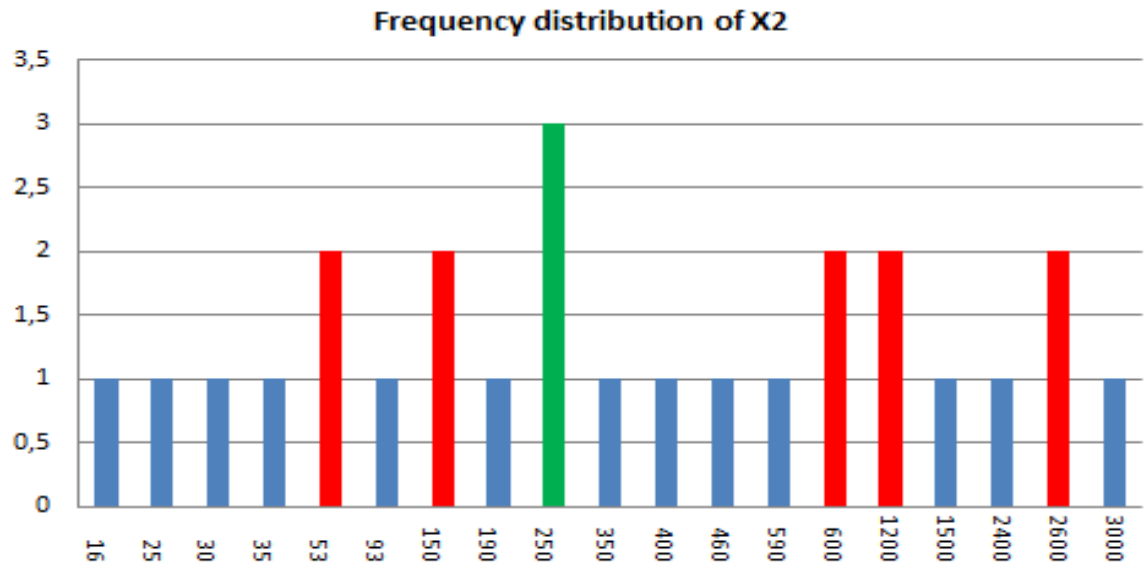

Figure 1.2: Diagram of the frequency distribution of X_2

ADI per 60 Kg of body weight of fresh edible plant (in Kg)

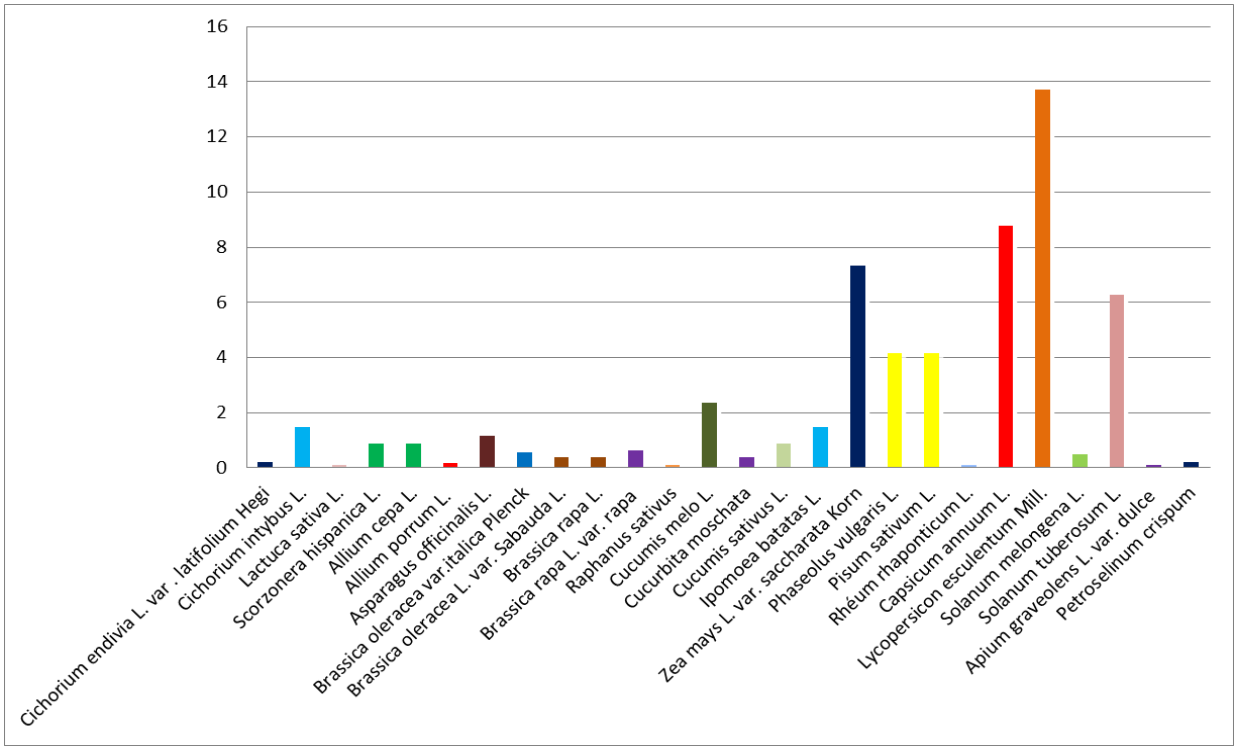

Figure 1.3: Diagram of ADI (acceptable daily intake) of fresh edible plant per 60 Kg of body weight ($ADI60_{fp}$) (in Kg).

Table 1.3: ADI (acceptable daily intake) of fresh edible plant per 60 Kg of body weight ($ADI60_{fp}$) (in Kg).

S		T_3 (ADI)
FAMILY	GENERA AND SPECIES	
Asteracae	*Cichorium endivia* L. var. *latifolium* Hegi	0,182
	Cichorium intybus L.	1,46
	Lactuca sativa L.	0,073
	Scorzonera hispanica L.	0,876
Liliaceae	*Allium cepa* L.	0,876
	Allium porrum L.	0,146
	Asparagus officinalis L.	1,152
Brassicaceae	*Brassica oleracea* var. *italica* Plenck	0,547
	Brassica oleracea L. var . *Sabauda* L.	0,365
	Brassica rapa L.	0,365
	Brassica rapa L. var. *rapa*	0,625
	Raphanus sativus	0,084
Cucurbitaceae	*Cucumis melo* L.	2,354
	Cucurbita moschata	0,371
	Cucumis sativus L.	0,876
Convolvulaceae	*Ipomoea batatas* L.	1,46
Graminaceae	*Zea mays* L. var. *saccharata* Körn	7,3
Leguminosae	*Phaseolus vulgaris* L.	4,132
	Pisum sativum L.	4,132
Polygonaceae	*Rhéum rhaponticum* L.	0,091
Solanaceae	*Capsicum annuum* L.	8,76
	Lycopersicon esculentum Mill.	13,687
	Solanum melongena L.	0,476
	Solanum tuberosum L.	6,257
Umbelliferae	*Apium graveolens* L. var. *dulce*	0,084
	Petroselinum crispum	0,182

Table 1.4: Covered DIA (CDIA) in %

S		T_4 (CDIA)
FAMILY	GENERA AND SPECIES	
Asteracae	*Cichorium endivia* L. var. *latifolium* Hegi	0,120 %
	Cichorium intybus L.	0,015 %
	Lactuca sativa L.	0,300 %
	Scorzonera hispanica L.	0,025 %
Liliaceae	*Allium cepa* L.	0,025 %
	Allium porrum L.	0,150 %
	Asparagus officinalis L.	0,019 %
Brassicaceae	*Brassica oleracea* var. *italica* Plenck	0,040 %
	Brassica oleracea L. var . *Sabauda* L.	0,060 %
	Brassica rapa L.	0,060 %
	Brassica rapa L. var. *rapa*	0,035 %
	Raphanus sativus	0,260 %
Cucurbitaceae	*Cucumis melo* L.	0,009 %
	Cucurbita moschata	0,059 %
	Cucumis sativus L.	0,025 %
Convolvulaceae	*Ipomoea batatas* L.	0,015 %
Graminaceae	*Zea mays* L. var. *saccharata* Körn	0,003 %
Leguminosae	*Phaseolus vulgaris* L.	0,005 %
	Pisum sativum L.	0,005 %
Polygonaceae	*Rhéum rhaponticum* L.	0,240 %
Solanaceae	*Capsicum annuum* L.	0,003 %
	Lycopersicon esculentum Mill.	0,002 %
	Solanum melongena L.	0,046 %
	Solanum tuberosum L.	0,004 %
Umbelliferae	*Apium graveolens* L. var. *dulce*	0,260 %
	Petroselinum crispum	0,120 %

1.5 Conclusions

It is well known that high concentrations of nitrates are considered toxic. The conversion of nitrates to nitrites can occur in food during its preparation or within human body. In fact, when nitrates are combined with amines, present in foods or derived from protein degradation processes, occurring in stomach, then they can produce nitrosamines, recognized as carcinogens. There are many directives and recommendations from international and national organizations for nutrition, as WHO (World Health Organization), FAO (Food and Agriculture organization), EFSA (European Food Safety Authority), regarding the risk limits of nitrates content. Thus, the reduction of dietary nitrate is a advisable preventive measure. Nitrate levels in plants lower than nitrate threshold values indicate good practices in agriculture. In this Chapter, a statistical population of 26 horticultural plants was analyzed. The contents of nitrates (obtained in laboratory) were examined as a variable and correspond to the average of three measures estimated on each species of vegetable. It was seen that the average value of nitrate contents, intaken by human organisms by the consumption of the considered fruits and vegetables, does not constitute a risk when the assumption of vegetables is limited. Furthermore, the negative effects of nitrate contents in the Mediterranean diet are contrasted promoving a consumption of agrifood containing nutraceutical and antioxidant substances (carotenoides, vitamins C, E and other ones, selenium, crude fibre, glucosinolates, isothiocyanates, flavonoids, phenols). Vitamin C is capable of inhibiting conversion of nitrites to nitrosamines, transforming them into nitric oxide (see also [11], [12]), [13]).

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Chapter 2

A statistical approach to the study of vitamin C and crude fibre in some horticultural plants to introduce the Mediterranean diet

In this Chapter, using a statistical approach, we introduce the Mediterranean diet, recognized culturally as the patrimony of UNESCO, that promotes a consumption of agrifood, containing vitamin C and crude fibre, that have beneficial effects on the health. This contribution is based on previous papers [6], [7], where a set of 26 species of horticultural plants, used in Mediterranean diet, was examined from the statistical point of view, obtaining easily accessible and useful results. In particular, the recorded content of vitamin C and crude fibre of the considered plants, based on literature data, have been analyzed as two sample variables. Graphic representations and statistical studies are given for these two variables. From the average values found of crude fibre and vitamin C contents, ingested by the human organism through the consumption of the considered fruits and vegetables, it can be seen that it is necessary to follow a diet rich in vitamin C and crude fibre to prevent disease, in accordance with the directives coming from several national and international nutrition organizations, and thus to promote the Mediterranean diet, that represents the initial steps to the longevity and good health.

2.1 Introduction

United Nations Educational, Scientific and Cultural Organization (UNESCO), founded by the United Nations in 1946 to give courage to the nations to work together in the fields of education, science, culture and communication, recognized the Mediterranean diet as own patrimony to pretect [1], included in the list of oral and intangible heritages of humanity, in 2010. The Mediterranean Diet (MD) is a

modern food model introduced, and for the first time studied in a systematic way, by the physiologist, epidemiologist and nutritionist Ancel Benjamin Keys, coming from the United States, who investigated the effects of this diet on the epidemiological incidence of cardiovascular diseases in a famous study based on the research in seven countries [2], which pertains to Italy, Morocco, Spain, Greece, Cyprus, Croatia, Portugal. Keys understood the MD positive influence on disease prevention [3]. The results of Keys' studies have shown that populations of the Mediterranean basin had above average longevity and a very high protection from illnesses compared with populations of North

Europe and the United States. He correlated these features to the kind of Mediterranean food consumed by them, in which the horticultural plants play the main role.

In 1999 a research group from the Ministry of Health in Greece, starting from these epi- demiological studies, which demonstrate the efficacy of the Mediterranean diet on the longevity, elaborated a dietary scheme, published using the name "Pyramid of the Mediterranean Diet for Adults". The benefit derived from fruits and vegetables due to the high presence of the vitamin C and crude fibre contents (that among other things contrast the nitrates negative effects [4]) is one of the subjects studied on the topic of Mediterranean diet (see [5]).

The purpose of this chapter is to summarize and present in a didactic way a selection of results derived in previous papers (see [6] and [7]) by a statistical examination of selected literature data [8]-[12], regarding the vitamin C and crude fibre contents in 26 different species of agricultural plants, and to discuss how their consumption has benefits on the human health, in agreement with the recommendations of Mediterranean diet to live better, longer and in good health [13].

Vitamin C (or ascorbic acid) is a water soluble vitamin that has nutraceutical properties. It is an important antioxidant widely present in vegetables and fruits having important functions, that prevent several diseases in the human organism. It strengthens the immune system and offers a variety of health benefits.

Crude fibre refers to the indigestible carbohydrate component, that is present in plant cell walls. The name is derived from the fact that it has a fibrous structure. Crude fibre is the measure of the quantity of indigestible cellulose, pentosan, lignin and other components of this type present in foods. It increases the bulk and speeds up the passage of food through the digestive tract, and therefore reducing the absorption of toxic substances.

In Sections 2 and 3 we introduce the variables X_1 and X_2 illustrating the vitamin C and crude fibre contents, respectively, in 26 fresh horticultural plants. Then, we present graphic representations, the average *M,* the variance V and the standard deviation σ of these contents, calculated using the formula

$$\mathrm{M}=\sum_{i=1}^{n} x_i f_i, \qquad (2.1)$$

where x_i (i = 1, 2,...,n) are the measures of the values of the contents (of the vitamin C or the crude fibre) having relative frequencies f_i (i = 1, 2,...,n) (being $\sum_{i=1}^{n} f_i$ =1)

$$V = \sum_{i=1}^{n} (x_i - M)^2 f_i ,$$

$$\sigma = \sqrt{V} . \qquad (2.2)$$

Finally, we discuss the benefits of consuming vegetables containing vitamin C and crude fibre in reducing the risk of various diseases and on directing attention to the Mediterranean diet according to the nutritional guidelines of international and national organizations.

2. 2 Didactic method

In this didactic Chapter we introduce the Mediterranean diet using a statistical approach. This interdisciplinary method is one of the most recommended in education because it presents important current topics taking into account results obtained in correlated subjects, emphasizing the motivations that have pushed the promotion of the Mediterranean diet in preventing disease. The methods of univariate descriptive statistics are applied to analyze a set of fresh vegetables, by means of the construction of tables and graphs. More precisely, the vitamin C and crude fibre of the horticultural plants under consideration are examined one at a time and their values are considered like the values of two statistical variables, of which, knowing the frequency distribution, applying statistical methodologies, the average value and the standard deviation are calculated. The graphs of the vitamin ‘C and crude fibre have been colored in order to put in evidence with the same color equal values and, then, their frequency distribution. The average values obtained in the analysis of the two statistical variables are discussed, taking into account the values recommended by the Scientific Committee for Food (SCF), to show how following the educational rules of the Mediterranean diet can lead to a good health and to prevent several illnesses.

2.3 Vitamin C content in a set of horticultural plants

In this Section we summarize a selection of results obtained by a statistical examination of vitamin C content (expressed in mg/100g of fresh weight of edible plant) present in the 26 considered horticultural plants [7]), based on selected data obtained in literature [8]-[12], in order to show the benefit of consuming a diverse diet rich in vegetables in order to reach the recommended dose of vitamin C, to have health benefits, following the medical standard of nutrition national and international organizations. In fact, vitamin C contrasts the negative influence of nitrates, that have been shown to change into nitrites during the food preparation or within the human organism (see [4]). Nitrates combined with amines, present in food or derived from protein degradation processes, occurring in the stomach, can produce nitrosamines, that are acknowledged as carcinogens.

Vitamin C can inhibit the conversion of nitrites to nitrosamines, transforming them into nitric oxide. In fact, vitamin C is essential to stimulate the immune system, it allows the human body to oppose diseases, enclosing the various types and forms of cancer. Vitamin C (ascorbic acid) is a water soluble vitamin. The human organism needs vitamin C because it is not able to satisfy its vitamin requirement through the process of organic synthesis and, therefore, it depends on the dietary contribution. Vitamin C is widely present in vegetables and fruits. Studies have shown that the quantity of available vitamin C is greater in fresh fruits and vegetables and those stored correctly, protected against light and heat, but less in frozen fruits and vegetables. In food vitamin C deteriorates quickly by the transport, storage, cooking, bruising, and cutting of the plants or fruits.

Vitamin C facilitates the absorption of iron, contributes to production of red blood cells (thus it is useful in the treatment of anemia), it is necessary to the body to synthesize collagen (that reinforces bones, cartilage, muscles and blood vessels). It has an important antioxidant action and increases the effectiveness of the antioxidant vitamin E and the absorption of folic acid. It protects the brain and spinal cord from destruction by free radicals and helps the healing of wounds and bone fractures and maintains healthy teeth and gums.

Therefore, we define the sample variable X_1, describing the vitamin C contents corresponding to the 26 analyzed plants (see Table 2.1) and we give its graphic representation (see Figure 2.1).

From the values of vitamin C contents of Table 2.1, the average M_1 and the relative standard deviation σ_1, calculated using the formula (2.1) and (2.2), are:

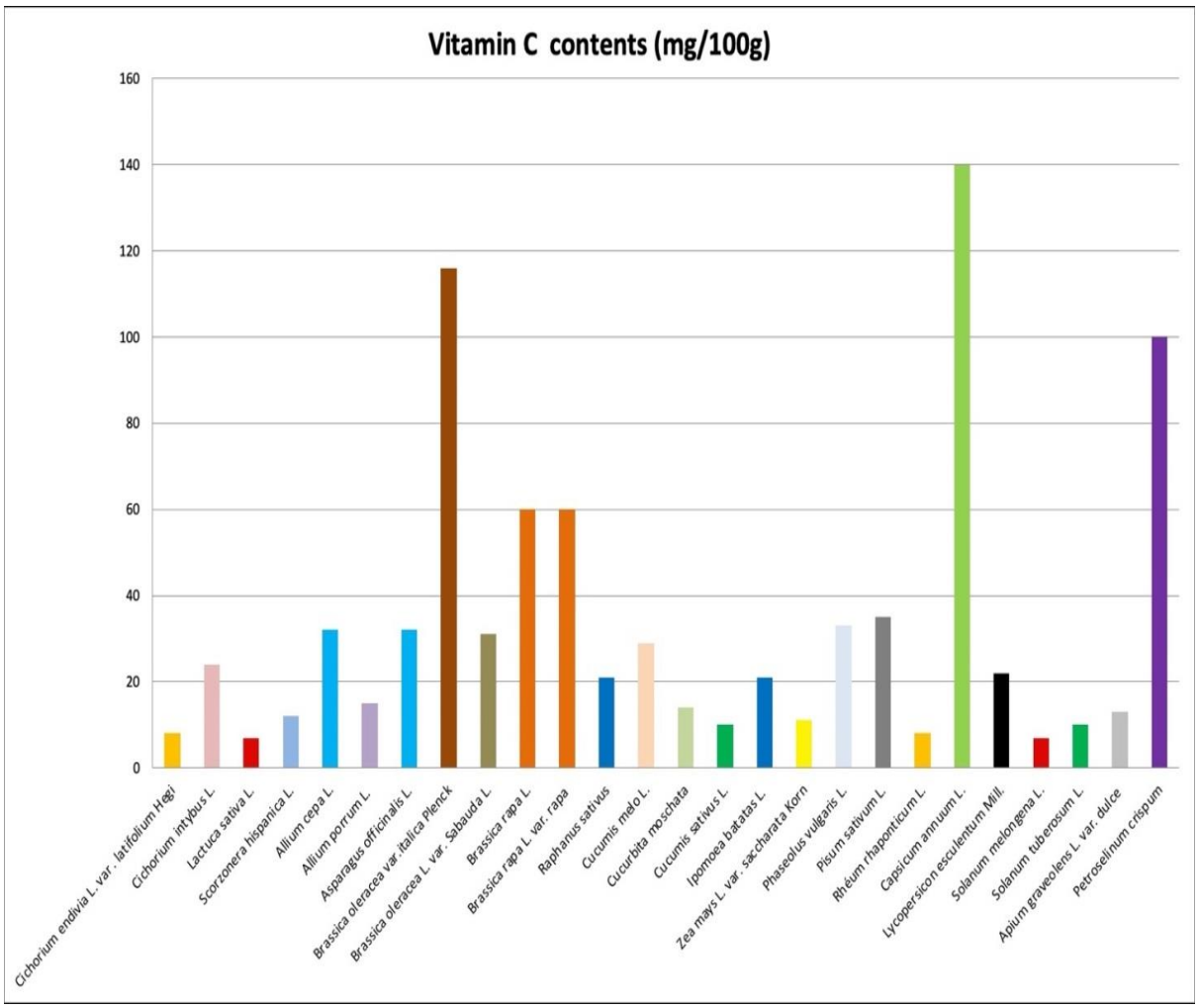
M_1 = 33, 50 mg/100g, σ_1 = 22, 14 mg/100g. (2.3)

Table 2. 1 Sample variable X_1. Content of vitamin C *mg*/100*g* of fresh weight of edible plant in 26 vegetables

	26 HORTICULTURAL PLANTS	**VITAMIN C CONTENT**
FAMILY	GENERA AND SPECIES	
Asteracae	*Cichorium endivia* L. var. *latifolium* Hegi	8
	Cichorium intybus L.	24
	Lactuca sativa L.	7
	Scorzonera hispanica L.	12
Liliaceae	*Allium cepa* L.	32
	Allium porrum L.	15
	Asparagus officinalis L.	32
Brassicaceae	*Brassica oleracea* var. *italica* Plenck	116
	Brassica oleracea L. var . *Sabauda* L.	31
	Brassica rapa L.	60
	Brassica rapa L. var. *rapa*	60
	Raphanus sativus	21
Cucurbitaceae	*Cucumis melo* L.	29
	Cucurbita moschata	14
	Cucumis sativus L.	10
Convolvulaceae	*Ipomoea batatas* L.	21
Graminaceae	*Zea mays* L. var. *saccharata* Körn	11
Leguminosae	*Phaseolus vulgaris* L.	33
	Pisum sativum L.	35
Polygonaceae	*Rhéum rhaponticum* L.	8
Solanaceae	*Capsicum annuum* L.	140
	Lycopersicon esculentum Mill.	22
	Solanum melongena L.	7
	Solanum tuberosum L.	10
Umbelliferae	*Apium graveolens* L. var. *dulce*	13
	Petroselinum crispum	100

From (2.3) it is seen that, being the average value of vitamin C in 26 analyzed plants 33,50 mg/100mg, it is necessary to consume diverse fruits and vegetables in order to obtain the recommended level of vitamin C which a body in good health must intake to satisfy its daily needs. The recommended daily allowance (RDA) for vitamin C ranges from 15-75 mg/day for children, 75 mg/day for adult women, 90 mg/day for adult men and 85-120 mg/day for pregnant and breastfeeding women, respectively. The Scientific Committee for Food (SCF) has established these RDAs in agreement with the national and international nutrion directives, to convey health benefits, thus the Mediterranean diet represents the initial steps to increase good health and longevity. It must be taken into consideration that, for smokers and pregnant women, vitamin C intake should be increased and, independently, for babies the amount of vitamin C will increase proportionally with increasing body weight. High doses of vitamin C are not recommended in patients with renal insufficiency.

Figure 2.1 Sample variable X_1.



2.4 Crude fibre content in a set of horticultural plants

In this Section we summarize a selection of results given in [6] (worked out by a statistical analysis of crude fiber content expressed in g/100g of fresh weight of edible plant) present in the 26 examined vegetables, based on selected data obtained in literature (see [8]-[12]), in order to show that it is necessary to consume different horticultural plants to rich the minimum value of crude fibre to have health benefits, following the recommendations of national and international nutrition organizations.

Table 2.2 Sample variable X_2. Content of fibre crude in g/100g of fresh weight of edible plant in 26 vegetables.

	26 HORTICULTURAL PLANTS	**FIBRE CRUDE CONTENT**
FAMILY	GENERA AND SPECIES	
Asteracae	*Cichorium endivia* L. var. *latifolium* Hegi	0,8
	Cichorium intybus L.	0,7
	Lactuca sativa L.	0,6
	Scorzonera hispanica L.	2,1
Liliaceae	*Allium cepa* L.	0,5
	Allium porrum L.	1,2
	Asparagus officinalis L.	0,8
Brassicaceae	*Brassica oleracea* var. *italica* Plenck	1,4
	Brassica oleracea L. var . *Sabauda* L.	1,2
	Brassica rapa L.	0,9
	Brassica rapa L. var. *rapa*	0,9
	Raphanus sativus	0,7
Cucurbitaceae	*Cucumis melo* L.	0,6
	Cucurbita moschata	1,4
	Cucumis sativus L.	0,5
Convolvulaceae	*Ipomoea batatas* L.	0,7
Graminaceae	*Zea mays* L. var. *saccharata* Körn	0,8
Leguminosae	*Phaseolus vulgaris* L.	1,1
	Pisum sativum L.	2,2
Polygonaceae	*Rhéum rhaponticum* L.	0,7
Solanaceae	*Capsicum annuum* L.	1,6
	Lycopersicon esculentum Mill.	0,6
	Solanum melongena L.	0,9
	Solanum tuberosum L.	0,7
Umbelliferae	*Apium graveolens* L. var. *dulce*	0,8
	Petroselinum crispum	1,6

Dietary fibre takes its name from its fibrous structure and refers to the indigestible carbohydrate component present in plants. It is not degraded by the enzymes of the digestive system and thus it can not be assimilated and used as a source of energy. Crude fibre accelerates the speed of intestinal transit, it is able to slow down the adsorption of carbohydrates and lipids, retaining bile salts, bile acids and cholesterol, and thus, in part, preventing undesired reabsorption and increasing the rate of elimination. Crude fibre comprehends different components, like hemicellulose, cellulose, lignin, pectins, gums, mucilages and galactomannans and others that are of minor quantitative importance. These substances are resistant to the action of digestive juices of the gastrointestinal tract. Hemicelluloses are partially degraded by intestinal bacteria. The cellulose is part of the support

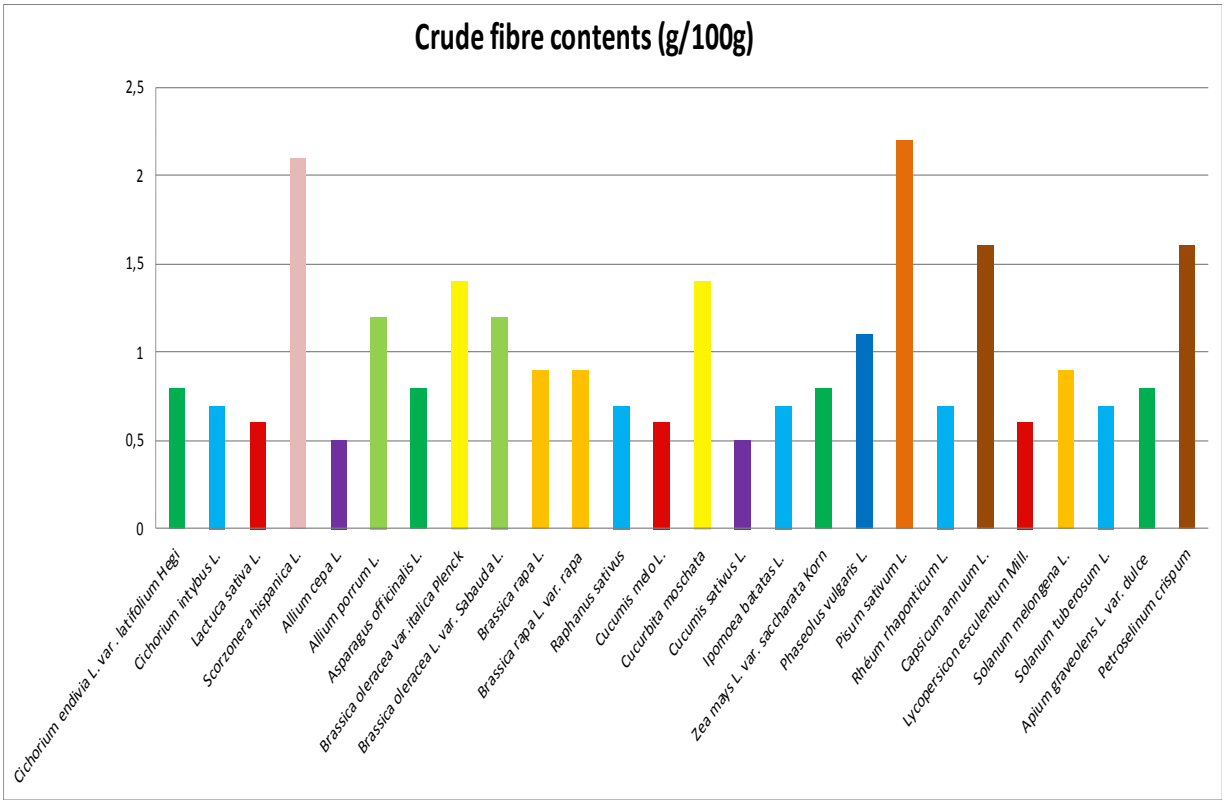


Figure 2.2 Sample variable X_2.

structures and of the cell walls of plants, it is hydrophilic and has a great power of adsorption and swells in presence of water and it is partially degraded by the intestinal flora. It is largely eliminated. Lignin is linked to cellulose. Pectins, constituents of plant cell walls, are the cementing substance of plant cells and tissue, have high hydrophilic properties and are completely degraded by intestinal bacteria. The most important features of pectin is retaining large amounts of water. Furthermore, it is important for vasodilation. Moreover, the recommendations to include an adequate content of fibre in the form of plant foods is justified by the fact that diets at high crude fibre content have the advantage to supply quantities of micronutrients with antioxidant properties, that reduce the risk of degenerative diseases. In addition, crude fibre has a satiety effect, inhibiting the hunger center (and therefore products rich in crude fibres can be referred to as adjuvants in diets), a mechanical effect on intestine and, therefore, it reduces the risk of diseases linked to the digestive system.

Thus, we define the sample variable X_2 describing the crude fibre contents corresponding to the 26 analyzed vegetables (see Table 2.2) and we give its graphic representation (see Figure 2. 2).

From the values of crude fibre contents of Table 2.2 the average M_2 and the relative standard deviation σ_2 calculated using the formula (2.1) and (2.2), are

$$M_2=1{,}00 \text{ g/100g}, \qquad \sigma_2 =0{,}44 \text{ g/100g}. \tag{2.4}$$

From (2.4) it is seen that the average value of crude fibre in 26 analyzed plants is 1,00 g/100g, thus, it is necessary to follow a diet rich in fibre in agreement with the directives of the Scientific Committee for Food (SCF), that has established a recommended daily allowance (RDA) of 25 g/day, indicating the nutrient amount of crude fibre content that a person in good health must intake to satisfy their own daily needs. This recommendation is motivated by the fact that the crude fibre has the benefit to provide quantities of nutrients that decrease the danger of disease. Therefore, the Mediterranean diet, associated with a healthy lifestyle, takes the base level in the food pyramid, showing the crucial role of crude fibre in preventing disease.

2.5 Conclusions

In this Chapter, using an interdisciplinary method, by means of a statistical study of the vitamin C and crude fibre contents of a set of vegetables, we have put in evidence the importance of adhering to the educational guidelines defined in the Mediterranean diet in order to prevent diseases. Currently, there are many directives from international and national organizations for nutrition, like WHO (World Health Organization), FAO (Food and Agriculture Organization), EFSA (European Food Safety Authority), that recommend consumption of fruits and vegetables each day to ensure a balanced diet and to intake the indispensable content of nutrient feed to prevent diseases. In particular, Scientific Committee for Food (SCF) has established a recommended daily allowance (RDA) of 60 mg/day, as the amount of vitamin C content, and a RDA of 25 g/day as the amount of crude fibre content (both values referred to fresh weight of edible plant), that a person in good health must intake to supply their own daily requirement in order to be protected from illness.

The nutritionist Keys acknowledged that the MD, adopted by the populations of Mediterranean basin, acts against diseases and on longevity [3]. In this Chapter we have summarized a selection of the results obtained in previous papers [6] and [7]) regarding the vitamin C and crude fibre contents of fresh weight of 26 different edible plants, whose calculated averages are less than RDA fixed by the SFC to live in good health. Thus, it is necessary each day to ingest fruits and vegetables to ensure the indispensable nutrients to the human organism.

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PART II

ORGANIC CONTAMINANTS IN ALGERIAN AROMATIC HERBS AND SPICES. A STATISTICAL ANALYSIS

The studies presented in Chapter III of this Part II were presented as a contribution in the following Conference

G. Di Bella, M. Porretti, A. Scinelli, C. Faggio, *Environmental contaminants in Algerian aromatic herbs*. In Journal of Biological Research 2022, vol 95(s1), Pag. 25, 94rd National Congress of the Italian Society for Experimental Biology, 6-9 April 2022, Torino.

Part II Introduction

Contaminants are natural and/or chemical substances that have not been purposely added to food and feed, but can come from various causes: the different steps of production and working, the transport, or the environmental contamination, due to the human activity or unexpected natural disasters [1]. Contaminants represent a serious risk to human and animal health [2]. In this Part II we have analyzed 119 contaminants of different type, such as PAHs (polycyclic aromatic hydrocarbons), PCBs (polychlorinated biphenyls), OCPs (organochlorine pesticides), OPPs (organophosphorous pesticides), CAR (mecarbam), PYRs, (pyrethroid insecticides), IGRs (insect growth regulators), SYN (Piperonyl butoxides), Fs (fungicides), Hs (herbicides), in aromatic herbs and spices from Algeria, purchased in Algerian cities. These herbs and spices were tested in laboratory, because they can be contaminated during the various steps of the agricultural work processes of the land in which they are grown: the treatment of the soil through organic and chemical contaminants; its spraying using contaminated water; environmental pollution due to climate change; excessive urbanization of cities and physical contaminants [1], [2].

The aromatic herbs are horticultural plants, which can also grow spontaneously, of which the leaves are mainly used such as mint, rosemary, bay leaves and basil. They are mainly used fresh, often added to dishes, such as risottos or roast meats or particular fish preparations, in order to flavour, towards the end of cooking or when cooking is finished. They are fragrant plants and give a certain aroma to foods. They are called aromas. Spices come from different parts of plants: flowers, buds, rhizomes, roots, bark, seeds, drupes, etc. which are characterized by the high percentage of aromatic principles contained, mainly due to the presence of essential oils and resinous substances. Spices are predominantly of exotic origin. In fact they have particular geographical origins, such as pepper for example which is obtained from the berry of the plant of the same name which has the shape of a climbing shrub and is cultivated in tropical regions, its cultivation in a temperate climate or in a greenhouse would be very difficult.
If aromas flavor and aromatize without modifying the flavor of dishes, spices instead have more of the function of giving a certain taste to foods, of modifying the flavor of a dish, strengthening it or making it more pleasant to the palate.

Furthermore, aromatic herbs and spices play an important role like anticancer, antimicrobial, antioxidant, anti-inflammatory; they are used also in cosmetics, medical sciences, culinary science (contributing to the reduction of salt addition and improving the flavor of the dishes) and they can be employed in potential therapies for Coronaviruses (see [15]-[28]).

Nowadays these aromatic herbs and spices are very important in the economy of Mediterranean countries for their production, export and import.

Chapter III

Organic contaminants in Algerian aromatic herbs and spices, purchased at Oran and Tlemencen

In this Chapter samples of aromatic herbs (Mint, Verbena, Fennel, Laureal and Oregano) and spices (Black Pepper, Red Pepper, Garlic, Caraway and Coriander), purchased in Algeria in the cities of Oran and Tlemcen, are analyzed to measure in them residues of contaminants of organic kind In particular, we illustrate the values of the contaminants content, obtained in laboratory, by Tables and graphic representations for each aromatic herb and spice. From the results, it is seen that this content of contaminants (ng/g) ingested by human organism by the consumption of the analyzed herbs and species does not constitute a risk for the human health, when its assumption is limited, in agreement with the values recommended by the directives of international and national organizations nutrition, representing the maximum levels of contaminants (MLs) permitted in order to protect consumer health. Aromatic herbs and spices are employed in several sectors like medical sciences, cosmetics, and culinary science. Furthermore, they are anti inflammatory, anticancer, antimicrobial, antioxidant and can be employed in potential therapies for Coronaviruses.

3.1 Introduction

Nowadays the aromatic herbs and spices are very important in the economy of Mediterranean countries for their production, export and import. Contaminants come from various causes: the transport, the environmental contamination, different steps of production and other causes [1]. Contaminants represent a serious risk to human and animal health [2]. In [4] and previous contributions [5]-[14] of one of the authors (G. Di B.) culinary herbs and spices, presenting residues of various kinds of contaminants and coming from Mediterranean areas were studied.

In this Chapter we have analyzed 119 contaminants of organic kind (PAH, OCP, OPP, CAR, PYR, OPP/A, CAR/A, IGR, SYN, F, H) in aromatic herbs and spices purchased in Algeria in the cities of Oran and Tlemcen.

Aromatic herbs and spices are used also in culinary science, cosmetics, medical sciences, and they play an important role like antioxidant, anticancer, antimicrobial and other.

The chapter is organized in the following way. The Section 2 deals with the materials and methods used in order to analyze 43 samples of aromatic herbs (in particular 7 samples of Mint, 9 samples of Verbena, 9 samples of Fennel, 11 samples of Laurel and 7 samples of Oregano) and 42 samples of spices (in particular 9 samples of Black Pepper, 8 samples of Red Pepper, 7 samples of Garlic, 9 samples of Caraway and 9 samples of Coriander) purchased in Algerian local markets of Oran and Tlemcen cities. The Sections 3, 4 and 5 are addressed to present in the Tables 3.1- 3.4 and Graphics 3.1-3.10 the results obtained for the residues of the considered 119 contaminants found in the considered samples, and to discuss the results worked out in the Chapter. We have seen that the values of the measured contaminants contents (ng/g) do not constitute a risk

for the human health, because their values do not exceed the maximum levels (MLs) permitted by the directives of international and national nutrition organizations.

3.2 Materials and Methods

3.2.1 Samples and sample preparation

The investigation was performed on samples of aromatic herbs and of spices, purchased in local markets of the Algerian Oran and Tlemencen, cut into small pieces, selt dried and without a packaging. Every sample, cleaned from debris was reduced, using a mortar, in fine powder and stored to be analysed. To extract organic pollutants from aromatic herbs and spices the following simplified method (see [1]) was used, consisting in more steps: first 1 g of each sample was weighed, after was dissolved with 10 mL of ultrapure water and decanted into a 50 mL centrifuge tube, then 10 mL of a mixture hexane/ethyl acetate 9:1 and a salt packet of Q-sep QuEChERS were added. Furthemore, after shaking manually for about 1 minute, each sample, was centrifuged for 5 minutes at room temperature and 5000 rpm. Then, the organic phase was reduced to 1 mL in a rotary evaporator at 30 °C and, at the end, under a stream of nitrogen. Moreover, 1 mL of bromophos-methyl as internal standard (IS) was added, before instrumental analysis.

3.2.2 Chemicals and Standard solutions

Regarding chemicals (see [1]) PCBs (mixture of congeners n. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169 e 189 at the concentration of 2 μg/mL and mixture of congeners n. 28, 52, 101, 138, 153 e 180 at the concentration of 10 μg/mL), PAHs (mixture EPA 525 PAH Mix A at the concentration of 500 μg/mL) and triphenyl phosphate (TPP) were bought from Aldrich Chemical (Chicago, Il, USA), instead Q-sep QuEChERS extraction kit (4g $MgSO_4$ and 1g NaCl) was purchased from Restek Corporation (U.S., Bellefonte, PA).

The Absolute Standard Inc. Mix (Hamden, Connecticut, USA), consisting of α-HCH, β-HCH, γ-HCH, alachlor, aldrin, cis-chlordane, trans-chlordane, 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT, dieldrin, endrin and atrazine at the concentration of 100 μg/mL, was used; ethyl acetate, n-hexane, acetonitrile for organic residue analysis were purchased from Fluka Analytical (Milan, Italy); ultrapure water from WWR (Milan, Italy); acephate, ametryn, atrazine, azinphos ethyl, azoxystrobin, bendiocarb, boscalid, bromophos-methyl, bupirimate, buprofezin, captafol, captan, carbaryl, carbofuran, carbophenothion, chlorfenvinphos, chlorpyriphos-ethyl and methyl, coumaphos, λ-cyhalothrin, cypermethrin isomer I, II and III, cyproconazole isomer II, cyromazine, deltamethrin, diazinon, diclobutrazol, dicofol, diflufenican, dimethoate, diethofencarb, endosulfan α, β and sulphate, ethion, ethionfencarb, fenamiphos, fenarimol, fenchlorphos, fenhexamid, fenitrothion, fenthion, fenthion sulfone, fenthion sulfoxide, fluodioxonil, flusilazole, cis and trans-fluvalinate, furathiocarb, imazalil, indoxacarb, kresoxim-methyl, linuron, malathion, mecarbam, mepronil, metalaxyl-m, methabenzthiazuron, methidathion, methoxychlor, omethoate, oxyfluoren, parathion methyl, penconazole, cis and trans permethrin, phenoxycarb, phenthoate, phosalone, phosmet, phoxim, piperonyl butoxide, pirimicarb, pirimiphos-methyl, pyrimethanil,

pyriproxyfen, prochloraz, procymidone, propazine, propyzamide, quinalphos, quintozen, simazine, tebuconazole, terbuthilazine, tolchlophos-methyl, triadimafon, trifloxystrobin, trifluralin, and vinclozolin were bought from Dr. Ehrenstorfer (Augsburg, Germany).

Laboratory glassware was heated at 400 °C for at least 4 hours and was covered with aluminium foil prior to use. The contaminants analysed are reported in the Tables 1, 2, 3, 4. Stock standard solutions of individual standards were prepared by dissolving pure standard in n-hexane (approximately at 1000 mg/L); working standard solutions including all the examined compounds were set at 10, 50 e 100 ng/mL in n-hexane; calibration standard solutions were prepared at various concentrations in the range of 0.1-100 ng/mL in n-hexane. A standard solution of bromophos-methyl, used as internal standard (IS), was prepared at 50 ng/mL in n-hexane. All the solutions were stored in closed vials at 4 °C in a refrigerator

3.2.3 Equipment and analytical conditions

The equipment and the analytical conditions (see [1]) analyses were performed by a Thermo Scientific Trace GC Ultra coupled with a triple quadrupole mass spectrometer TSQ Quantum XLS equipped with an auto sampler TrisPlus RSH. The chromatographic separation was carried out on a column Supelco SLB-5ms 30 m x 0.25 mm, 0.25 μm of stationary phase film. The carrier gas was He with a constant flow of 1 mL/min, the column oven temperature was 60 °C for 1 min, 15 °C/min until 120 °C, 10 °C/min until 280 °C (15 min final isotherm). Programmable temperature vaporizing injector was set at 60 °C (0.05 min), 14.5 °C/sec until 250°C (1 min), and at the end a cleaning cycle at 320 °C for 4 min. Transfer-line temperature was 300 °C; injection volume was 1 μL; injection was in split less mode for 1 minute, after split 20 mL/min; source temperature (EI, 70 eV) was set at 250 °C. Each compound was characterized by its retention time (used for the quantification) and two SRM (selected reaction monitoring) transitions utilized as a confirmation. Variable collision energy experiments were worked out on each transition to determine the optimal one.

3.3 Tables for the analyzed aromatic herbs and spices

In this Section in Tables 3.1, 3.2 and Tables 3.3, 3.4 we have presented the results worked out for the content of the 119 organic contaminants, measured in the analyzed aromatic herbs and spices, respectively. The obtained values are illustrated in the Graphics 3.1-3.5 (for the aromatic herbs) and in the Graphics 3.6-3.10 (for the spices), wherein only the contaminants having considerable values have been taken into consideration. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in herbs. In [9] the maximum limits (MLs) for organic contaminants in herbs and spices established by different regulations were shown and it was seen that during the years, the European Commission has established and revised these MLs by numerous regulations and related amendments.

Table 3.1 Contaminants (ng/g) measured in aromatic herbs purchased at Oran and Tlemcen

CONTAMINANTS	**Mint** [n=7], N=1		**Verbena** [n=9], N=2		**Fennel** [n=9], N=2		**Laurel** [n=11], N=1		**Oregano** [n=7], N=2	
	Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen	
Acephate	**2**	0.24±0.1		-		-		-		-
Ethiofencarb		-		-		-		-		-
Acenaphthylene		-		-	**3**	2.8±0.1	**5**	7.52±0.2	**5**	6.04±0.5
Captafol		-		-		-	**3**	6.35±0.3		-
Carbaryl		-	**3**	6.12±0.3	**4**	4.8±0.2		-		-
Omethoate		-		-		-		-		-
Fluorene		-		-		-		-	**3**	7.72±0.3
Trifluarin	**3**	3.11±0.3	**5**	1.82±0.1		-		-		-
Bendiocarb		-		-		-	**2**	8.68±0.4		-
Methabenzthiazuron		-		-		-		-		-
Alpha-BHC		-	**2**	0.85±0.2	**2**	6.62±0.4		-		-
Dimethoate		-		-		-		-	**4**	8.11±0.4
Carbofuran	**5**	8.77±0.5		-		-		-		-
Simazine		-	**4**	1.22±0.1		-	**4**	9.74±0.2		-
Atrazine		-		-		-		-		-
Propazine	**1**	7.92± 0.6		-		-		-	**3**	9.65±0.6
Beta-BHC		-	**5**	7.76±0.3	**1**	7.21±0.3		-		-
Cyromazine		-		-		-		-		-
Quintozen		-		-		-		-	**2**	8.72±0.5
Terbuthilazine	**5**	0. 42±0.1		-	**3**	5.43±0.2	**6**	4.05±0.1		-
Propyzamide	**4**	9.66±0.2		-		-		-		-
Diazinon		-		-	**4**	8.52±0.5	**4**	2.76±0.1	**4**	6.63±0.2
Pyrimethanil		-	**3**	9.86±0.6		-		-		-
Phenanthrene	**1**	0. 81±0.1		-		-		-		-
Anthracene	**2**	2.03±0.2		-		-		-	**3**	9.12±0.2
Pirimicarb	**3**	4.98±0.5	**2**	0.28±0.1		-		-		-
Ethiofencarb		-		-	**3**	9.78±0.3		-	**2**	8.54±0.3
Chlorpyriphos_me		-		-	**2**	8.89±0.5		-		-
Vinclozolin		-	**1**	3.11±0.3		-	**2**	6.23±0.4		-
Parathion-methyl		-	**3**	6. 82±0.2	**2**	2.72±0.1		-		-
Tolchlophos_me	**2**	8.21±0.1		-		-		-		-
Alachlor		-		-	**4**	3.62±0.2	**1**	1.6±0.1	**4**	6.08±0.2
Metalaxyl-M		-		-	**5**	4.42±0.1	**4**	8.31±0.3		-
Ametryn	**1**	6.56±0.2	**2**	1.22±0.1	**3**	5.62±0.3		-		-
Fenchlorphos		-		-	**3**	9.52±0.4	**2**	9.18±0.5		-
Pirimiphos methyl	**4**	7.11±0.5		-		-		-	**4**	7.18±0.4
Fenitrothion		-		-		-	**2**	7.71±0.2		-
Malathion	**3**	0.47±0.1	**4**	7.02±0.3		-		-		-
Linuron		-		-		-	**3**	3.82±0.1		-
Diethofencarb		-	**1**	8.74±0.4	**2**	1.52±0.1		-		-
Chlorpyriphos		-		-		-	**4**	8.62±0.2	**3**	6.18±0.3
Fenthion		-	**2**	6.57±0.3		-		-		-
Triadimefon		-		-	**3**	9.86±0.2	**1**	9.71±0.3	**2**	9.12±0.2
Aldrin	**3**	8.45± 0.2		-		-		-		-
Dicofol	**4**	6.72±0.3		-		-		-		-
cis-Chlorfenvinphos	**2**	9.85±0.2	**3**	9.56±0.5	**2**	8.22±0.4		-		-
Penconazole		-		-		-	**3**	8.06±0.4		-
trans-Chlorfenvinphos		-		-		-		-	**4**	8.45±0.4
Mecarbam	**1**	0.65±0.2		-		-	**2**	6.06±0.2		-
Phenthoate		-	**2**	8.47± 0.6	**3**	2.14±0.1		-		-
Quinalphos	**2**	8.82±0.4		-		-		-	**3**	7.18±0.3
Procymidone		-		-	**5**	4.53±0.2		-		-
Captan	**1**	4.18±0.5		-	**3**	1.35±0.1	**3**	7.11±0.4		-
Methidathion		-		-		-		-	**4**	9.63±0.4
Cis-Chlordane		-		-		-		-		-
2,4' DDE	**4**	7.29±0.3		-	**5**	9.16±0.4	**4**	6.52±0.5		-
Endosulfan alfa		-	**3**	7.61±0.3		-		-		-
Fenamiphos		-		-	**3**	1.64±0.1		-		-
trans-Chlordane		-	**4**	8.13±0.4	**4**	7.32±0.2		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 3.2 Contaminants (ng/g) measured in aromatic herbs purchased at Oran and Tlemcen

CONTAMINANTS	**Mint** [n=7], N=1		**Verbena** [n=9], N=2		**Fennel** [n=9], N=2		**Laurel** [n=11], N=1		**Oregano** [n=7], N=2	
	Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen	
Pyrene		-	**2**	6.72±0.4			**2**	6.74±0.5		-
Imazalil	**1**	6.13±0.4		-	**5**	6.61±0.2		-	**3**	8.42±0.5
Fludioxonil		-		-		-		-		-
Oxyfluoren		-		-		-		-		-
Kresoxim methyl	**4**	0.81±0.1		-		-	**4**	7.02±0.2		-
4,4' DDE	**2**	8.71±0.3		-	**3**	7.54±0.3		-	**2**	6.32±0.3
Flusilazole		-	**3**	8.12±0.3	**2**	8.18±0.4		-		-
Bupirimate		-		-		-		-		-
Buprofezin		-		-	**2**	9.22±0.3		-		-
2,4' DDD	**3**	1.23±0.1	**4**	6.34±0.2		-		-	**3**	7.65±0.2
Diclobutrazol		-		-		-		-		-
Dieldrin		-		-		-		-		-
Cyproconazole isomer II	**2**	7.54±0.8		-		-		-	**4**	3.72±0.1
Fenthion Sulfoxide		-	**3**	3.08 ±0.1		-	**5**	8.56±0.3		-
Endrin	**3**	9.47±0.5.		-	**4**	8.12±0.5		-		-
Fenthion Sulfone				7.22±0.2		-		-		-
Ethion		-		-	**2**	7.21±0.1		-		-
Endosulfan beta		-		-		-	**4**	9.72±0.5		-
4,4' DDD	**2**	6.37±0.3	**4**	9.22±0.3		-		-	**3**	2.65±0.1
2,4' DDT	**3**	8.95±0.8	**3**	8.90±0.1		-		-		-
Mepronil		-		-		-		-		-
Trifloxystrobin		-		-		-	**3**	7.53±0.3		-
Carbophenothion	**4**	7.25±0.5		-	**3**	9.53±0.3		-		-
Endosulfan sulfate		-		-		-		-	**4**	8.14±0.3
Fenhexamid		-		-		-		-		-
4,4' DDT		-	**3**	7.65±0.3		-	**4**	9.62±0.4		-
Diflufenican	**3**	0.56±0.1	**2**	9.89±0.2	**4**	9.12±0.5		-		-
Tebuconazole		-		-		-		-		-
Piperonyl butoxide	**2**	9.87±0.4		-		-		-		-
Triphenyl phosphate		-		-	**2**	8.52±0.4		-		-
Phosmet		-		-		-		-		-
Phenoxycarb	**2**	7.54±0.2		-	**3**	7.61±0.3	**4**	7.89±0.1		-
Methoxychlor		-		-				-	**2**	9.12±0.4
Benzo[a]anthracene	**3**	6.53±0.3		-	**2**	2.42±0.1	**2**	9.32±0.2		-
Chrysene		-	**3**	6.18±0.1		-		-		-
Furathiocarb		-		-	**4**	1.52±0.1		-		-
Phosalone	**2**	9.11±0.2		-		-		-	**4**	2.42±0.1
Pyriproxyfen		-		-	**3**	6.18±0.5		-		-
Cyhalothrin		-	**4**	7.12±0.2		-		-		-
Fenarimol		-		-		-	**3**	6.12±0.6		-
Azinphos-ethyl		-		-		-		-	**3**	8.42±0.3
cis-Permethrin		-		-		-		-		-
trans-Permethrin		-		-		-		-		-
Coumaphos		-		-		-		-	**2**	7.52±0.2
Cypermethrin isomer III	**2**	0.98±0.1		-		-		-		-
Benzo[b]fluoranthene				-	**3**	9.32±0.6		-		-
Benzo[k]fluoranthene	**3**	6.52±0.3	**2**	6.23±0.3		-		-		-
Cypermethrin isomer I		-		-		-		-		-
Boscalid		-		-		-		-	**3**	9.42±0.2
Cypermethrin isomer II	**2**	8.38±0.3		-	**4**	7.18±0.3	**4**	7.26±0.4		-
Benzo[a]pyrene		-		-		-		-	**4**	7.81±0.1
cis-Fluvalinate		-		-		-		-		-
trans-Fluvalinate		-		-	**4**	6.33±0.4		-		-
(±)-Indoxacarb	**4**	3.63±0.2	**3**	8.57±0.4		-	**3**	9.34±0.5		-
Deltamethrin		-		-		-		-		-
Azoxystrobin		-		-		-		-		-
Benzo[ghi]perylene	**2**	6.13±0.5	**4**	7.86±0.3	**3**	8.71±0.5		-		-
Dibenz[a,h]anthracene		-	**3**	6.34±0.1		-		-	**3**	6.42±0.2
Indeno[1,2,3-cd]pyrene		-		-		-	**3**	8.42±0.2		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 3.3 Contaminants (ng/g) measured in spices purchased at Oran and Tlemcen in Algeria.

CONTAMINANTS	Black Pepper [n=9], N=2		Red Pepper [n=8], N=3		Garlic [n=7], N=4		Caraway [n=9], N=3		Coriander [n=9], N=4	
	Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen	
Acephate		-		-		-		-		-
Ethiofencarb	4	1.61±0.2		-	2	1.72±0.3		-	2	6.72±0.2
Acenaphthylene		-		-		-	3	1.16±0.1		-
Captafol		-		-		-		-		-
Carbaryl		-	3	6.23±0.3	1	6.63±0.2		-	3	1.51±0.1
Omethoate		-		-		-	2	7.51±0.2		-
Fluorene		-		-		-		-		-
Trifluarin		-		-	3	7.46±0.3		-		-
Bendiocarb	3	9.41±0.3	4	7.41±0.2		-		-		-
Methabenzthiazuron		-		-	1	9.54±0.6		-		-
alpha-BHC		-		-		-		-	4	7.89±0.3
Dimethoate		-		-		-	2	9.51±0.4		-
Carbofuran		-		-		-		-		-
Simazine		-		-	1	8.43±0.5		-		-
Atrazine		-	2	9.23±0.4		-		-		-
Propazine	2	2.68±0.1		-		-		-		-
beta-BHC		-		-	2	7.53±0.4		-		-
Cyromazine		-	1	7.82±0.5		-		-	3	2.42±0.1
Quintozen		-		-		-	3	6.23±0.2		-
Terbuthilazine		-		-	1	6.32±0.3		-		-
gamma-BHC		-		-		-	4	2.25±0.1		-
Propyzamide		-		-		-		-	4	8.43±0.2
Diazinon		-		-		-		-		-
Pyrimethanil	3	7.62±0.3		-	3	8.36±0.4	2	8.34±0.4		-
Phenanthrene		-		-		-	3	1.52±0.1	3	6.31±0.3
Anthracene		-		-		-		-		-
Pirimicarb		-	4	6.16±0.2	2	6.34±0.3		-		-
Ethiofencarb		-		-		-	4	9.12±0.5	3	8.42±0.1
Chlorpyriphos_me	2	8.12±0.4	2	8.16±0.4		-		-		-
Vinclozolin	4	6.32±0.1		-		-	2	2.72±0.1		-
Parathion-methyl		-		-		-		-		-
Tolchlophos_me		-		-	2	3.23±0.2	4	8.73±0.2		-
Alachlor		-		-		-		-	4	7.08±0.2
Metalaxyl-M	3	7.25±0.3		-		-		-		-
Ametryn		-	2	7.23±0.5	3	7.72±0.3		-		-
Fenchlorphos		-		-		-		-		-
Pirimiphos methyl	2	8.28±0.2		-		-		-	4	9.18±0.5
Fenitrothion		-		-		-	3	9.61±0.3		-
Malathion		-	3	6.34±0.4		-		-		-
Linuron		-		-	1	6.21±0.2	4	3.25±0.2		-
Diethofencarb		-		-		-		-		-
Chlorpyriphos		-		-	4	8.72±0.4		-	3	6.18±0.2
Fenthion	3	8.13±0.2		-		-		-		-
Triadimefon		-	3	9.16±0.3		-		-	2	8.12±0.5
Aldrin	2	2.12±0.1		-		-	2	7.24±0.4		-
Dicofol		-		-	2	1.71±0.1		-		-
cis-Chlorfenvinphos		-		-	4	9.41±0.4	4	8.23±0.6		-
Penconazole		-		-		-		-		-
trans-Chlorfenvinphos		-	4	8.61±0.1		-		-	4	9.45±0.4
Mecarbam	4	8.41±0.3	3	9.98±0.4	3	8.72±0.5	2	4.63±0.3		-
Phenthoate		-		-	2	6.12±0.7		-		-
Quinalphos		-		-		-		-	3	8.18±0.6
Captan		-		-	4	1.42±0.1	3	3.31±0.1		-
Methidathion	3	6.12±0.4		-		-		-	4	9.99±0.3
Cis-Chlordane		-	2	6.61±0.2		-		-		-
2,4' DDE	2	1.31±0.1		-	3	9.41±0.4	3	8.42±0.6		-
Endosulfan alfa		-	2	7.43±0.3		-		-		-
Fenamiphos	3	9.61±0.3		-	2	7.42±0.5	1	9.41±0.2		-
Trans-Chlordane		-		-		-		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 3.4 Contaminants (ng/g) measured in spices purchased at Oran and Tlemcen in Algeria.

CONTAMINANTS	Black Pepper [n=9], N=2		Red Pepper [n=8], N=3		Garlic [n=7], N=4		Caraway [n=9], N=3		Coriander [n=9], N=4	
	Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen		Oran, Tlemcen	
Pyrene		-		-	**3**	6.62±0.2		-		-
Imazalil		-		-	**3**	2.6±0.1	**4**	1.23±0.1		-
Fludioxonil		-	**3**	2.45±0.1		-		-	**3**	1.34±0.1
Oxyfluoren	**4**	7.51±0.5		-		-	**2**	6.42±0.3		-
Kresoxim methyl		-		-		-		-		-
4,4' DDE		-		-	**1**	4.62±0.2		-		-
Flusilazole	**3**	6.18±0.3		-		-	**3**	9.45±0.5		-
Bupirimate		-	**3**	7.28±0.4	**3**	8.71±0.5		-	**4**	7.34±0.3
Buprofezin		-		-		-	**2**	3.12±0.1	**2**	8.16±0.2
2,4' DDD		-		-	**3**	3.94±0.2		-		-
Diclobutrazol		-		-		-		-		-
Dieldrin		-		-		-		-		-
Cyproconazole isomer II		-	**3**	9.23±0.2		-		-		-
Fenthion Sulfoxide		-		-		-	**3**	2.34±0.1	**3**	7.14±0.2
Endrin		-		-		-		-	**2**	2.32±0.1
Fenthion Sulfone		-		-		-		8.05±0.4		-
Ethion	**4**	8.31±0.4		-	**4**	7.71±0.4		-		-
Endosulfan beta		-	**4**	6.12±0.3		-	**4**	7.32±0.5	**2**	3.22±0.1
4,4' DDD		-		-		-	**3**	9.23±0.3		-
2,4' DDT	**2**	6.45±0.2		-		-		-	**3**	8.23±0.3
Mepronil		-		-		-		-		-
Trifloxystrobin	**3**	9.23±0.5	**2**	9.12±0.4		-		-		-
Carbophenothion		-		-		-	**3**	8.63±0.3	**3**	7.31±0.4
Endosulfan sulfate		-		-		-	**2**	3.15±0.1		-
Fenhexamid	**2**	7.52±0.4	**3**	8.23±0.2	**2**	6.62±0.2		-		-
4,4'DDT		-		-	**3**	8.43±0.5		-	**4**	8.35±0.3
Diflufenican		-	**3**	6.23±0.4		-	**4**	2.16±0.1		-
Tebuconazole		-		-		-	**2**	7.23±0.2	**3**	3.32±0.1
Piperonyl butoxide		-		-		-		-		-
Triphenyl phosphate		-	**4**	9.81±0.5		-	**2**	-	**3**	6.32±0.2
Phosmet		-		-		-	**2**	6.72±0.4	**2**	9.56±0.3
Phenoxycarb		-	**3**	7.72±0.2	**3**	3.72±0.1		-		-
Methoxychlor		-		-		-	**3**	9.32±0.3		-
Benzo[a]anthracene	**2**	8.23±0.3		-		-		-		-
Chrysene		-		-	**2**	7.16±0.3		-		-
Furathiocarb	**2**	3.23±0.1		-		-	**2**	7.12±0.4		-
Phosalone		-	**2**	8.64±0.3		-		-	**5**	6.63±0.2
Pyriproxyfen	**2**	7.23±0.5		-		-		-	**3**	3.56±0.1
Cyhalothrin		-		-		-		-		-
Fenarimol		-	**4**	9.22±0.5	**3**	5.16±0.2		-		-
Azinphos-ethyl	**2**	6.17±0.4		-		-		-	**2**	8.12±0.3
cis-Permethrin	**4**	9.25±0.6		-		-		-		
trans-Permethrin		-		-		-		-		-
Coumaphos		-		-		-	**4**	4.12±0.2		-
Cypermethrin isomer III		-		-		-		-		-
Benzo[b]fluoranthene	**3**	6.23±0.1	**3**	7.35±0.6		-		-		-
Benzo[k]fluoranthene		-		-	**4**	8.12±0.6		-	**5**	7.62±0.2
Cypermethrin isomer I		-		-		-		-		-
Boscalid	**3**	8.37±0.1		-		-	**4**	7.99±0.1		-
Cypermethrin isomer II		-		-		-	**3**	6.72±0.2		-
Benzo[a]pyrene	**4**	7.54±0.2		-	**2**	6.16±0.2		-	**3**	8.34±0.3
cis-Fluvalinate		-		-		-				-
trans-Fluvalinate		-		-		-	**2**	9.45±0.3		-
(±)-Indoxacarb		-		-	**3**	7.24±0.3			**2**	9.43±0.4
Deltamethrin	**4**	9.52±0.3		-		-		-		-
Azoxystrobin		-	**4**	3.42±0.1		-		-		-
Benzo[ghi]perylene	**5**	4.42±0.5	**2**	9.51 ±0.4	**2**	9.42±0.2		-		-
Dibenz[a,h]anthracene		-	**1**	-		-		-		-
Indeno[1,2,3-cd]pyrene	**2**	8.23±0.6		7.48±0.2	**2**	8.23±0.1	**4**	8.58±0.2	**1**	7.23±0.2

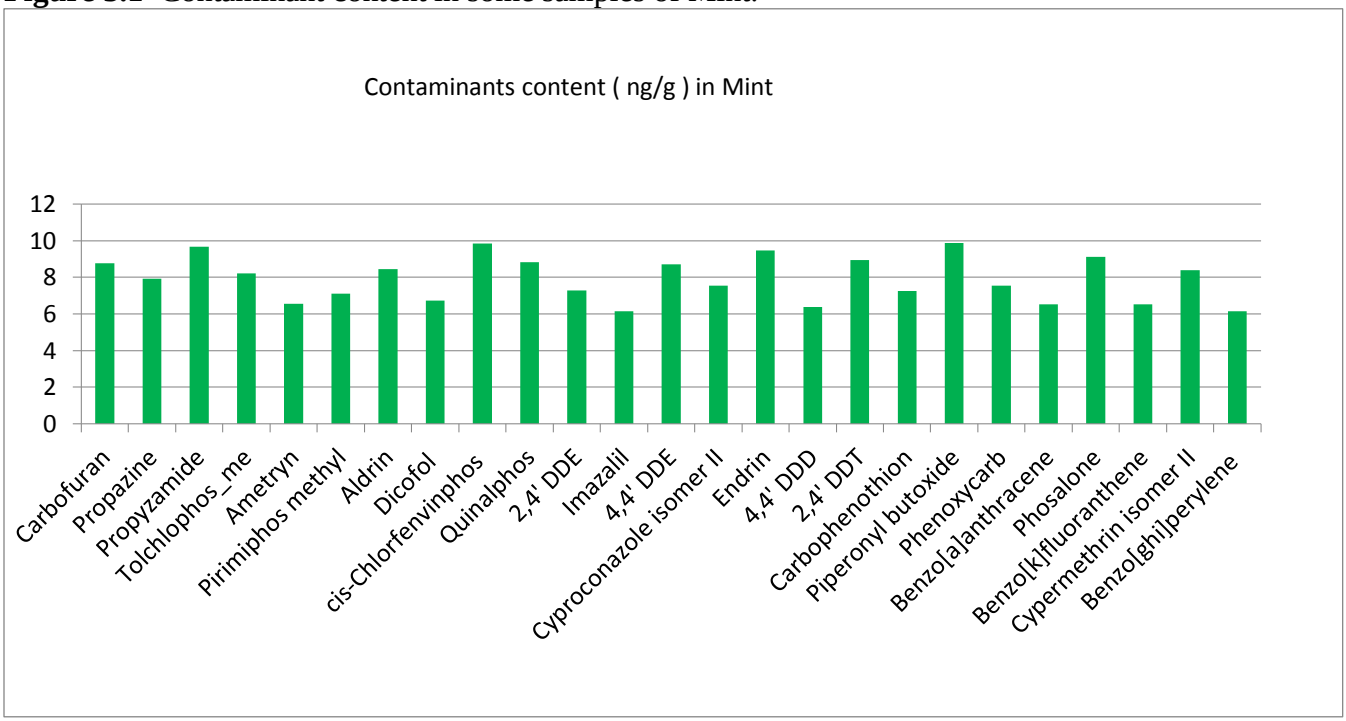
Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table

3. 4 Results regarding the samples of aromatic herbs

In Tables 3.1 and 3.2 the contents of contaminants in the samples of aromatic herbs taken into consideration are reported and in the Figures 3.1-3.5 the diagrams illustrating some relevant contents of contaminants in these aromatic herbs were performed. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in herbs. In [6] the maximum limits (MLs) for organic contaminants in herbs and spices established by different regulations were shown and it was seen that during the years, the European Commission has established and revised these MLs by numerous regulations and related amendments.

For the **Mint** samples we have derived the following graphic representation for the contents of contaminants

Figure 3.1 Contaminant content in some samples of Mint.



For the **Verbena** samples we have otained the following graphic representation for the contents of contaminants

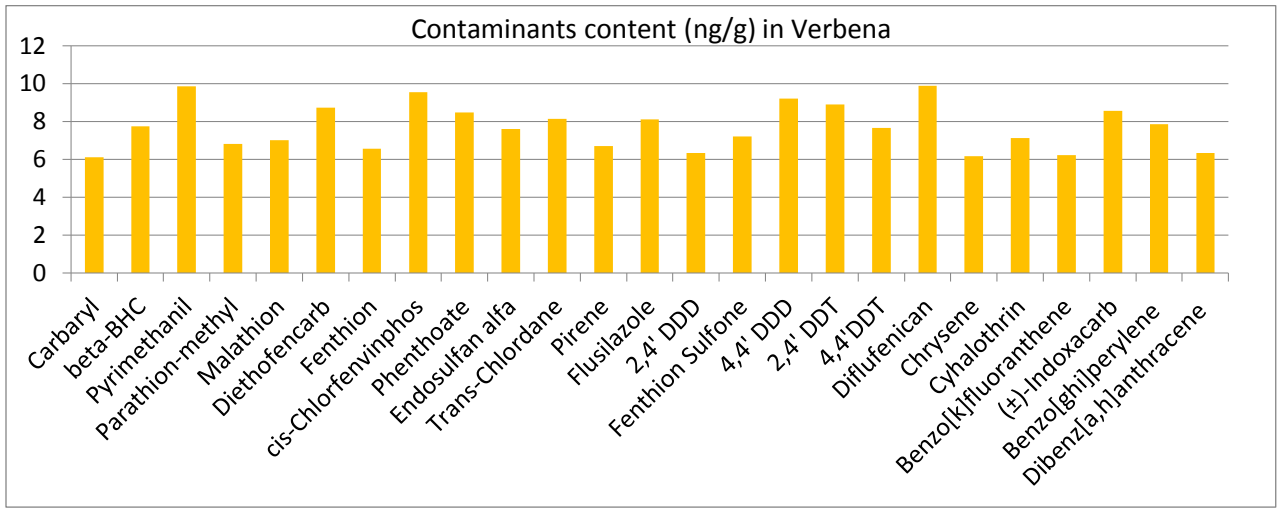
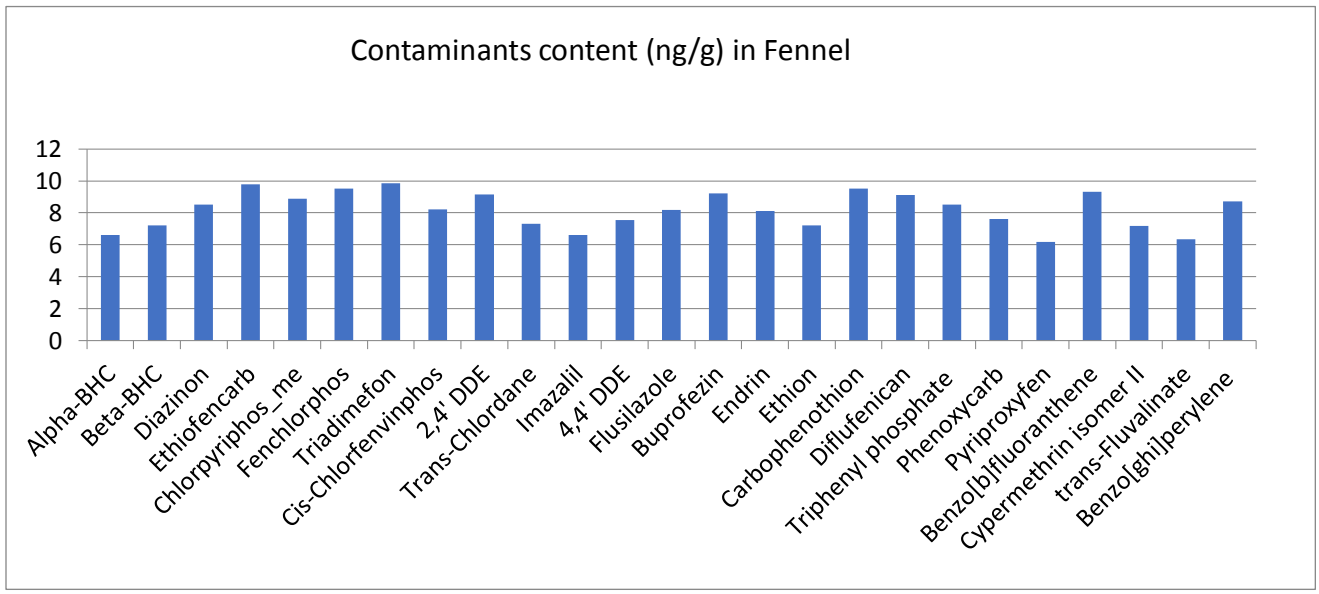


Figure 3.2 Contaminant content in some samples of Verbena

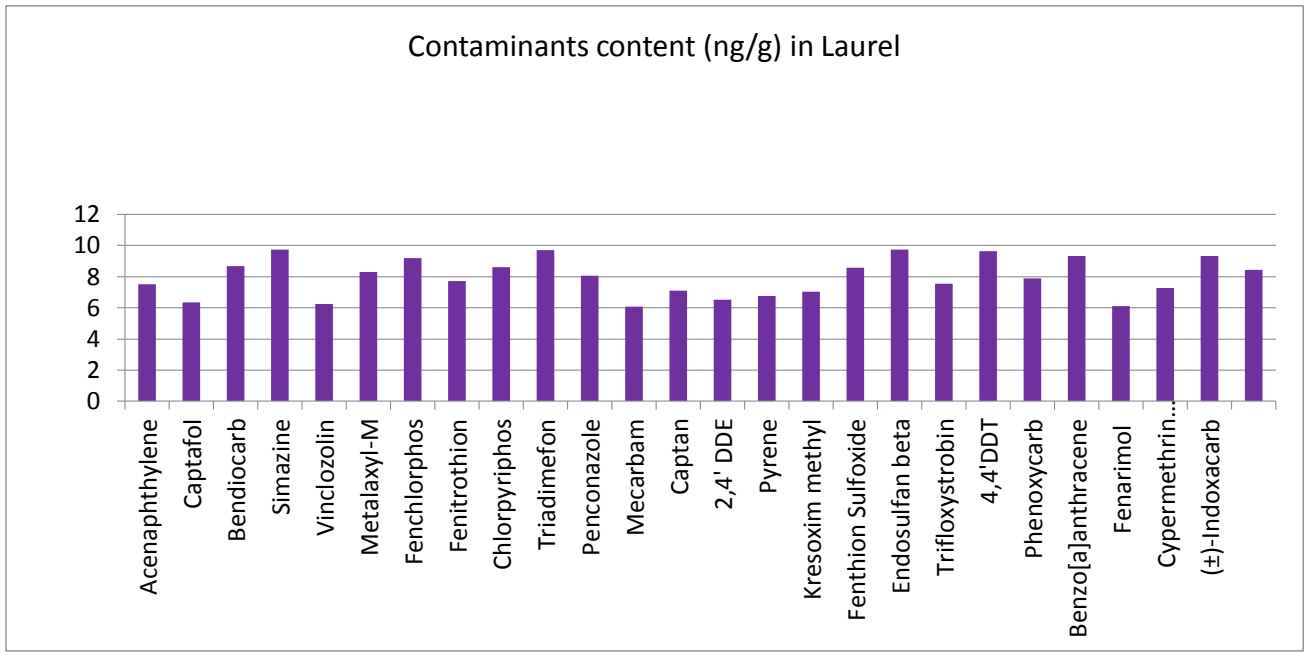
For the **Fennel** samples we have worked out the following graphic representation for the contents of contaminants

Figure 3.3 Contaminants content in some samples of Fennel



For the **Laurel** samples we have the following representation for the contents of contaminants

Figure 3.4. Contaminants content in some sam ples of Laurel.



For the **Oregano** samples we have the following representations for the contents of contaminants

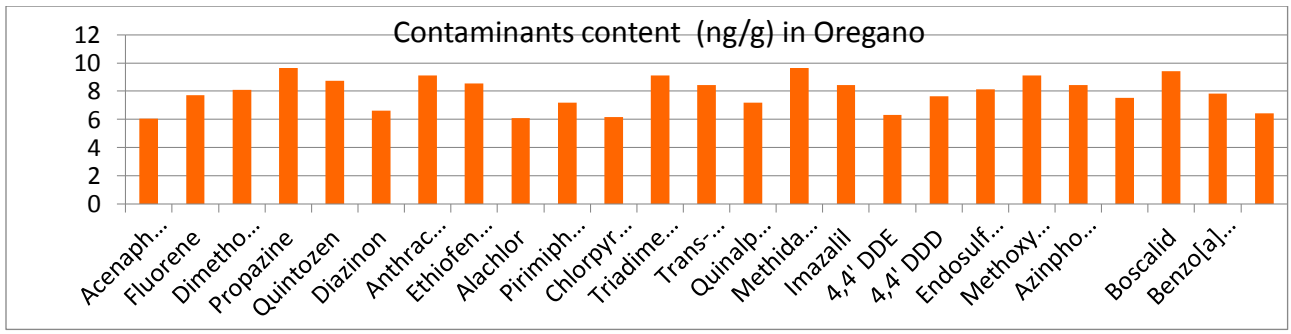


Figure 3. 5 Contaminants content in some samples of Oregano.

3.5 Results regarding the samples of spices

In Tables 3.3 and 3.4 the contents of contaminants in the samples of spices Black Pepper, Red Pepper, Garlic, Caraway and Coriander taken into account are reported and in the Figures 3.6 -3.10 the diagrams illustrating some relevant contents of contaminants in these spices were performed. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in spices (see in [9] the maximum limits (MLs) for organic contaminants in spices established by different regulations).

In particular, in the **Black Pepper** samples we have obtained the following contents of contaminants

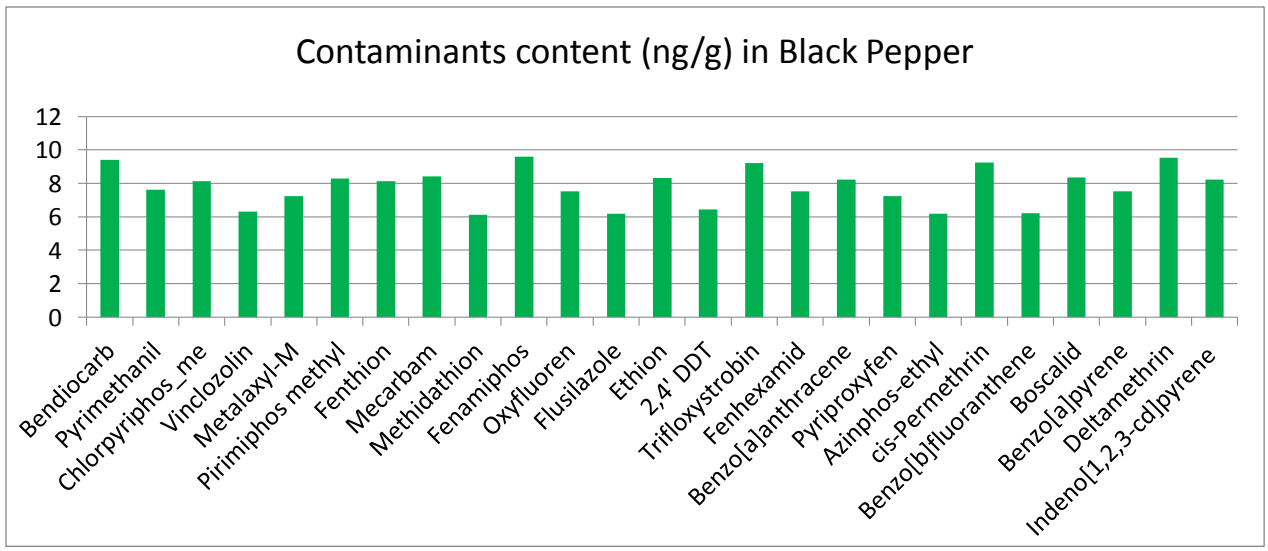


Figure 3.6 Contaminants content in some samples of Black Pepper

For the **Red Pepper** samples we have derived the following representations for the contents of contaminants

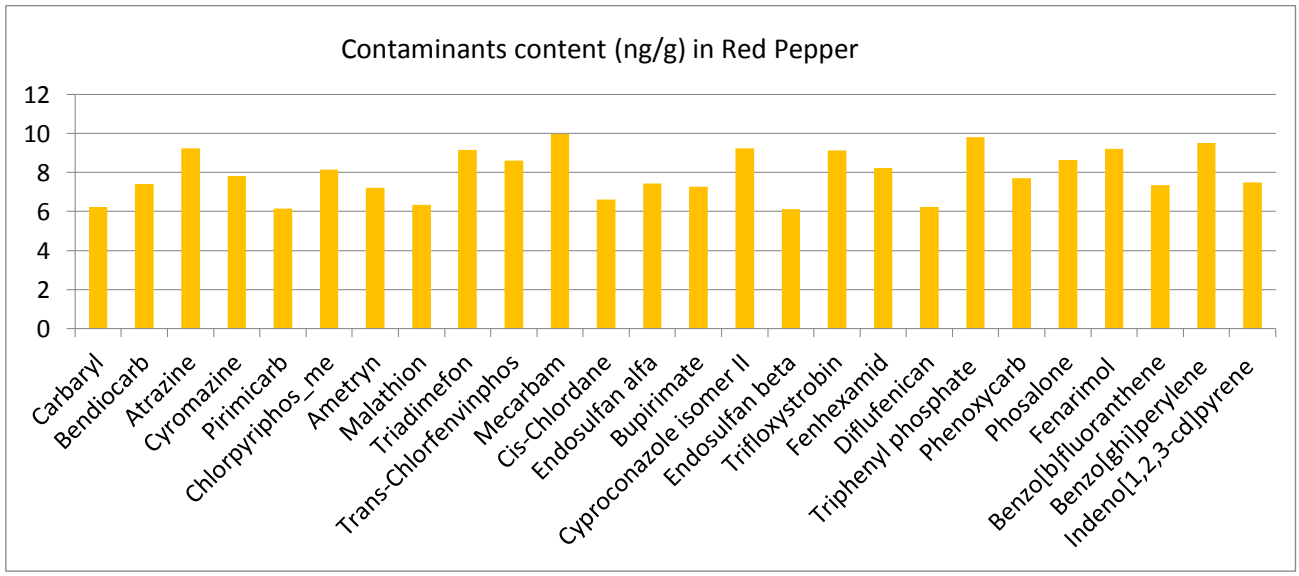
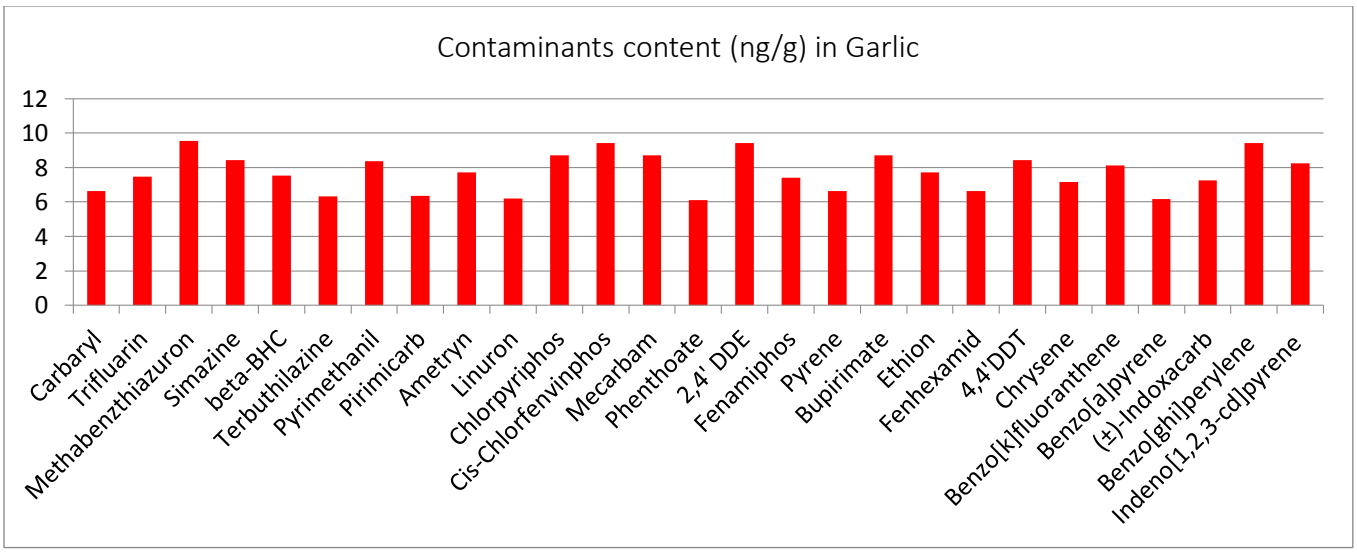


Figure 3.7 Contaminants content in some samples of Red Pepper

In the **Garlic** samples we have obtained the following contents of contaminants

Figure 3.8 Contaminant contents in some samples of Garlic



For the **Caraway** samples we have worked out the following representation for the contents of contaminants

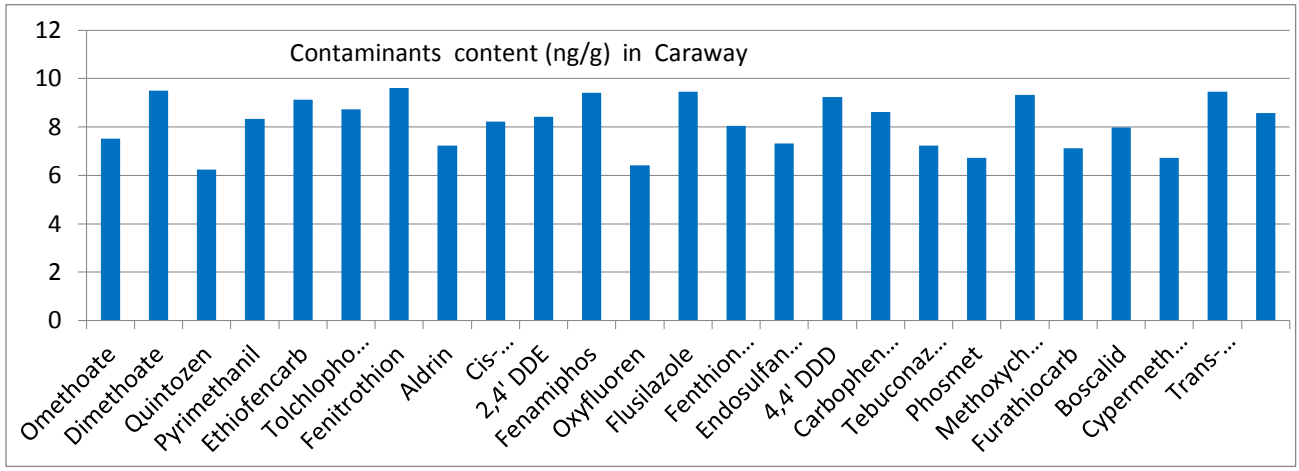


Figure 3.9 Contaminants content in some samples of Caraway

In the **Coriander** samples we have the following contents of contaminants

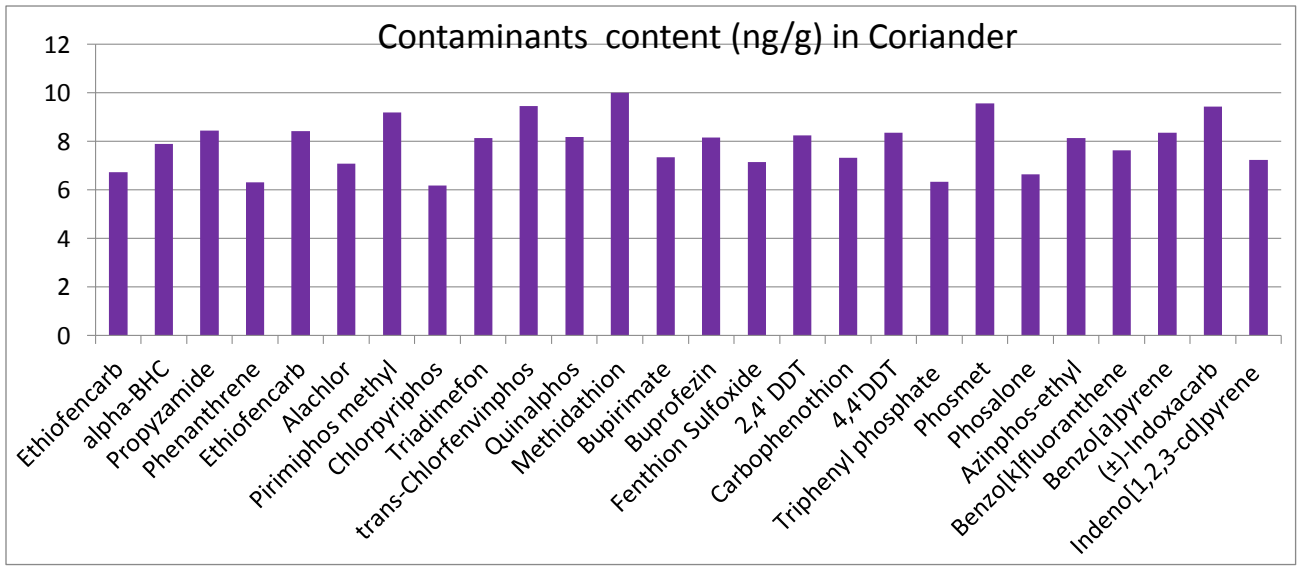


Figure 3.10 Contaminants content in some samples of Coriander

CHAPTER IV

Organic contaminants in Algerian aromatic herbs and spices, purchased at Constantine and Annaba

In this Chapter samples of aromatic herbs purchased in the Algerian cities Constantine and Annaba are analyzed to measure in them residues of organic contaminants. We illustrate the values of the contaminants content, obtained in laboratory, by Tables and graphic representations for each aromatic herb and spice. From the results, it is seen that this content of contaminants ingested by human organism by the consumption of the analyzed herbs and species does not constitute a risk for the human health, when its assumption is limited, in agreement with the values recommended by the directives the of international and national organizations.

4.1 Introduction

Contaminants are natural and/or chemical substances that can come from various causes: the different steps of production and working, the transport, or the environmental contamination, and other [1]. They represent a serious risk to human and animal health [2]. Aromatic herbs and spices play an important role such as anticancer, antimicrobial, antioxidant, anti-inflammatory. Also they they are used in cosmetics, medical sciences, culinary science and are very important in the economy of Mediterranean countries for their production, export and import.

In this Chapter 45 samples of aromatic herbs (8 of Rosemary, 8 of Sage, 9 of Thyme, 8 of Marjoram and 9 of Chives) and 42 spices (8 of Cloves, 9 of Nutmeg, 9 of Horseradish, 8 of Saffron) purchased in markets of the Algerian cities Constantine and Annaba are analyzed to measure in them residues of 119 contaminants of organic kind (PAHs, OCPs, OPPs, CARs, PYRs, OPP/As, CAR/A, IGRs, SYN, Fs, Hs). The Section 2 deals with the materials and methods used in order to analyze these 45 samples. The Sections 3, 4 and 5 are addressed to present in the Tables 4.1-4.4 and Graphics 4.1-4.10 the results obtained for the residues of the considered 119 contaminants found in the considered samples, and to discuss the results worked out in the Chapter. We have seen that the values of the measured contaminants contents (ng/g) do not constitute a risk

for the human health, when their values do not exceed the maximum levels (MLs) permitted by the guidelines of international and national nutrition organizations.

4.2 Materials and Methods

A simplified method was used for the extraction of organic pollutants without a purification step (see [1]); 1 g of each sample was weighed with 10 mL of ultrapure water. Extracted with 10 mL of 9: 1 hexane / ethyl acetate mixture 9:1 and a pack of Q-sep QuEChERS (salts of magnesium sulfate and sodium chloride 4:1)(stirred manually for 1 min and centrifuged for 5 min at room T ° at 5000 rpm). Dry with rotavapor at 30 ° C. Reconstituted in 1 mL with Internal Standard (IS) in hexane/ethylacetate 9: 1 and ignited by GC / MSMS. In particular, the samples and sample preparation, chemical and standard solutions, equipment and analytical conditions are reported in Chapter III. The measured values of these contaminants (ng/g) are illustrated in Tables and by graphic representations.

4.3 Tables for the analyzed aromatic herbs and spices

In this Section we have presented in Tables 4.1, 4.2 and Tables 4.3, 4.4 the results derived for the content of the 119 contaminants under consideration and measured within the aromatic herbs and spices, respectively, purchased in the Algerian cities Constantine and Annaba. The measured values of these contaminants (ng/g) are illustrated in the Figures 4.1-4.5 (for the aromatic herbs) and in the Figures 4.6-4.10 (for the spices), wherein only the contaminants having considerable values have been taken into account.

Table 4.1 Contaminants (ng/g) measured in aromatic herbs purchased at Constantine and Annaba in Algeria.

CONTAMINANTS	Rosemary[n=9], N=1		Sage [n=8], N=3		Thyme [n=9], N=2		Marjoram [n=8]N=2		Chives [n=9], N=1	
	Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba	
Acephate		-		-	3	1.45±0.1		-		-
Ethiofencarb	3	1.71±0.1		-		-		-	3	7.65±0.6
Acenaphthylene		-		-		-		-	2	8.56±0.2
Captafol		-	2	3.18±0.2		-		-		-
Carbaryl		-		-		-	2	6.41±0.6		-
Omethoate		-		-	2	6.78±0.2		-		-
Fluorene	2	3. 21±0.2		-		-		-		-
Trifluarin		-		-		-		-	4	4.34±0.3
Bendiocarb		-		-		-		-		-
Methabenzthiazurn		-	4	4.32±0.3		-	3	7.64±1.2		-
Alpha-BHC	1	7,81±0.3		-	3	4.64±0.3		-	2	6.32±0.4
Dimethoate		-		-		-		-		-
Carbofuran	4	9.72±0.5	2	6.48±0.4		-		-		-
Simazine		-			4	7.69±0.4		-		-
Atrazine	3	6.93±0.2		-		-		-		-
Propazine		-		-		-	3	3.67±0.4		-
Beta-BHC		-				-		-	2	5.85±0.3
Cyromazine		-	3	8.95±0.5		-		-		-
Quintozen	2	0.91±0.4		-	4	3.65±0.2		-		-
Terbuthilazine		-		-		-		-	3	9.56±0.2
Propyzamide		-		-		-	3	4.89±0.2		-
Diazinon		-	2	7.34±0.3		-		-		-
Pyrimethanil		-		-		-		-	2	4.67±0.3
Phenanthrene	2	1. 62±0.1		-	3	7.08±0.2		-		-
Anthracene		-	3	1.34±0.1		-	1	8.56±0.4		-
Pirimicarb	4	6.54±0.3			2	8.34±0.5		-		-
Ethiofencarb		-		-		-	2	9.45±0.3		
Chlorpyriphos_me		-		-		-		-	3	8.34±0.6
Vinclozolin		-	3	9.56±0.3		-		-		-
Parathion-methyl		-		-		-	4	0.97±0.1		-
Tolchlophos_me		-		-		-		-		-
Alachlor	3	8.92±0.4		-	2	9.74±0.4		-		-
Metalaxyl-M		-		-		-		-	3	6.77±0.4
Ametryn		-		-	1	4.16±0.2	3	7.24±0.5		-
Fenchlorphos		-	4	6.48±0.2		-		-		-
Pirimiphos methyl	2	7.12±0.5		-		-		-		-
Fenitrothion		-		-		-		-	2	4.78±0.3
Malathion		-		-	2	2.78±0.1	2	6.75±1.3		-
Linuron		-		-		-		-		-
Diethofencarb		-		-		-		-		-
Chlorpyriphos		-	2	8.45±0.6		-		-	3	8.94±0.2
Fenthion	2	6.96±0.3		-		-		-		-
Triadimefon		-		-			3	7.54±0.2		-
Aldrin		-		-	3	8.45±0.2		-		-
Dicofol	3	7.71±0.4		-		-		-	4	6.87±0.3
cis-Chlorfenvinphos		-		-		-		-		-
Penconazole		-		7.54±0.4		-		-		-
trans-Chlorfenvinphos	2	1.98±0.1		-	3	7.23±0.4	3	8.64±1.1		-
Mecarbam		-		-		-		-	3	9.56±0.4
Phenthoate		-	2	6.36± 0.2		-		-		-
Quinalphos		-		-		-	2	6.63±1.1		-
Procymidone	4	2.78±0.1		-		-		-		-
Captan	2	3.81±0.2		-	3	6.36±0.3		-		-
Methidathion		-		-		-		-		-
Cis-Chlordane		-	3	7.14±0.3		-		-		-
2,4' DDE		-		-		-		-		-
Endosulfan alfa	3	7.45±0.3	2	0.61±0.1		-	3	9.34±0.3		-
Fenamiphos		-		-	3	8.44±0.2		-		-
trans-Chlordane		-		-		-		-	3	4.85±0.2

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 4.2 Contaminants (ng/g) measured in aromatic herbs purchased at Constantine and Annaba.

CONTAMINANTS	Rosemary[n=9], N=1		Sage [n=8], N=3		Thyme [n=9], N=2		Marjoram [n=8]N=1		Chives [n=9], N=1	
	Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba	
Pyrene	4	6.21±0.3		-		-		-		-
Imazalil		-		-		-	4	3.65±0.1		-
Fludioxonil		-	3	7.29±0.6	4	1.06±0.1		-		-
Oxyfluoren	2	8.81±0.3		-		-		-	4	4.61±0.4
Kresoxim methyl		-		-		-		-		-
4,4' DDE		-		-		-		-		-
Flusilazole	3	6. 79±0.2		-		-	2	6.45±0.3		-
Bupirimate		-	2	5.42±0.3	3	6.77±0.2		-		-
Buprofezin		-		-		-		-	3	6.84±0.3
2,4' DDD		-		-		-		-		-
Diclobutrazol		-	3	9.34±0.4		-		-		-
Dieldrin	4	2. 63±0.1		-		-		-		-
Cyproconazole isomer II		-		-		-		-	4	2.86±0.2
Fenthion Sulfoxide		-		-		-	3	2.56±0.1		-
Endrin		-	4	3.56±0.1	2	4.63±0.3		-		-
Fenthion Sulfone				-		-		-		-
Ethion	2	7.11±0.3		-		-		-	3	8.54±0.5
Endosulfan beta		-	3	6.96±0.4		-		-		-
4,4' DDD		-		-	3	8.34±0.2		-		-
2,4' DDT		-		-		-	3	9.11±0.3		-
Mepronil	3	4.52±0.2		-		-		-	2	9.12±0.2
Trifloxystrobin		-	1	7.34±0.2	4	2.78±0.4		-		-
Carbophenothion		-		-		-		-		-
Endosulfan sulfate		-		-		-	4	3.67±0.2		-
Fenhexamid		-	3	1.32±0.1		-		-		-
4,4' DDT	2	9.23±0.4		-		-		-		-
Diflufenican		-		-		-		-	3	7.32±0.5
Tebuconazole		-		-	3	6.93±0.6		-		-
Piperonyl butoxide		-	2	7.12±0.5		-		-		-
Triphenyl phosphate		-		-		-	3	6.57±0.5		-
Phosmet	4	5.78±0.2		-		-		-	2	8.45±0.3
Phenoxycarb		-		-	2	9.41±0.2		-		-
Methoxychlor	2	7.82±0.3	3	6.23±0.6		-		-		-
Benzo[a]anthracene		-		-		-		-		-
Chrysene		-		-		-		-		-
Furathiocarb	3	8.11±0.4		-		-		-		-
Phosalone		-		-	3	8.36±0.6		-		-
Pyriproxyfen		-		-		-	4	4.36±0.4	3	6.34±0.4
Cyhalothrin		-	4	5.23±0.3		-		-		-
Fenarimol	4	2,78±0.1		-		-		-		-
Azinphos-ethyl		-		-		-		-		-
cis-Permethrin		-		-	3	4.67±0.2		-	2	9.38±0.2
trans-Permethrin		-		-		-		-		-
Coumaphos		-	3	6.45±0.2		-		-		-
Cypermethrin isomer III		-		-		-	3	7.65±0.2		-
Benzo[b]fluoranthene	2	4.67±0.2		-	4	6.56±0.3		-	3	6.78±0.5
Benzo[k]fluoranthene		-	4	1.21±0.1		-		-		-
Cypermethrin isomer I		-		-		-		-		-
Boscalid		-		-		-		-		-
Cypermethrin isomer II		-		-		-		-		-
Benzo[a]pyrene		-	2	0.99±0.1	3	3.87±0.1	3	4.78±0.3	2	8.71±0.4
cis-Fluvalinate		-		-		-		-		-
trans-Fluvalinate		-		-		-		-		-
(±)-Indoxacarb		-		-		-	2	9.34±0.4		-
Deltamethrin	3	7.98±0.4		-	2	8.45±0.3		-	3	7.45±0.3
Azoxystrobin		-	3	6.74±0.5		-	3	6.89±0.1		-
Benzo[ghi]perylene		-		-		-		-		-
Dibenz[a,h]anthracene		-		-		-		-		-
Indeno[1,2,3-cd]pyrene		-		-		-		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 4.3 Contaminants (ng/g) measured in spices purchased at Constantine and Annaba.

CONTAMINANTS	**Cloves** [n=8], N=3		**Nutmeg** [n=9], N=2		**Horseradish** [n=9], N=3		**Saffron** [n=8], N=1		**Ginger** [n=9], N=2	
	Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba	
Acephate		-		-		-		-		-
Ethiofencarb		-		-		-		-		-
Acenaphthylene		-		-		-	**2**	8.64±0.3	**2**	3.21±0.1
Captafol	**2**	3.67±0.1		-		-		-		-
Carbaryl		-	**3**	6.23±0.2		-		-		-
Omethoate		-		-	**2**	5,63±0.2		-		-
Fluorene	**3**	7.64±0.3		-		-		-	**3**	7.34±0.3
Trifluarin		-		-		6,71±0.3		-		-
Bendiocarb		-	**4**	7.41±0.3	**3**	-		-		-
Methabenzthiazuron		-		-		-	**3**	6.45±0.3		-
alpha-BHC		-		-		-		-	**2**	5.90±0.2
Dimethoate	**2**	8.34±0.4		-		-		-		-
Carbofuran		-		-		-	**3**	4.31±0.2		-
Simazine		-		-		-		-		-
Atrazine	**1**	6.54±0.5	**2**	9.23±0.4		-		-		-
Propazine		-		-	**2**	9.34±0.5		-		-
beta-BHC		-		-		-		-	**2**	9.42±0.3
Cyromazine	**2**	9. 32±0.4	**1**	7.82±0.3		-		-		-
Quintozen		-		-		-	**2**	7.54±0.4		-
Terbuthilazine		-		-	**4**	8.65±0.3		-		-
gamma-BHC		-		-		-		-	**4**	8.12±0.4
Propyzamide	**3**	2.67±0.1		-		-		-		-
Diazinon		-		-		-		-		-
Pyrimethanil		-		-		-		-		-
Phenanthrene		-		-	**3**	7.43±0.4		-		-
Anthracene		-		-		-	**1**	3.56±0.1		-
Pirimicarb		-	**4**	6.16±0.2		-		-	**3**	7.23±0.2
Ethiofencarb		-		-		-		-		-
Chlorpyriphos_me			**2**	8.16±0.4		-		-	**3**	4.52±0.3
Vinclozolin				-	**3**	3.41±0.1		-		-
Parathion-methyl		-		-		-	**3**	9.67±0.3		-
Tolchlophos_me		-		-		-		-	**1**	9.15±0.4
Alachlor	**1**	9.41±0.5		-		-		-		-
Metalaxyl-M		-		-	**2**	8.94±0.3		-		-
Ametryn		-	**2**	7.23±0.3		-		-	**3**	2.1±0.1
Fenchlorphos	**2**	3.78±0.1		-		-	**2**	1.32±0.1		-
Pirimiphos methyl		-		-	**3**	9.46±0.6		-		-
Fenitrothion		-		-		-		-		-
Malathion	**3**	6.45±0.2	**3**	6.34±0.2		-	**1**	2.35±0.1		-
Linuron		-		-		-		-	**2**	6.45±0.2
Diethofencarb		-		-	**4**	7.65±0.4		-		-
Chlorpyriphos		-		-		-		-		-
Fenthion		-		9.16±0.5		-		-	**3**	7.89±0.6
Triadimefon	**2**	8.82±0.4	**3**	-		-		-		-
Aldrin		-		-	**3**	4.56±0.2		-		-
Dicofol		-		-		-	**3**	7.64±0.4		-
cis-Chlorfenvinphos		-		-		-		-	**2**	4.52±0.3
Penconazole	**3**	6.89±0.3		-	**2**	6.45±0.3		-		-
trans-Chlorfenvinphos		-	**4**	8.61±0.2		-		-		-
Mecarbam		-	**3**	9.98±0.5		-		-		-
Phenthoate	**2**	4.32±0.2		-		-	**2**	9.51±0.3		-
Quinalphos		-		-	**3**	1.82±0.1		-		-
Captan		-		-		-		-	**3**	8.92±0.4
Methidathion		-		-		-		-		-
Cis-Chlordane		-	**2**	6.61±0.3		-	**1**	8.41±0.2		-
2,4' DDE		-		7.43±0.4	**3**	7.43±0.1		-		-
Endosulfan alfa	**3**	7.54±0.5	**2**	-		-		-		-
Fenamiphos		-		-		-		-		-
Trans-Chlordane		-		-		-		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 4.4 Contaminants (ng/g) measured in spices purchased at Constantine and Annaba

CONTAMINANTS	Cloves [n=8], N=3		Nutmeg [n=9], N=2		Horseradish [n=9], N=3		Saffron [n=8], N=1		Ginger [n=9], N=2	
	Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba		Constantine, Annaba	
Pyrene		-	1	3.46±0.1		-		-	2	2.41±0.1
Imazalil		-		-		-		-		-
Fludioxonil	2	3.23±0.1		-		-	1	2.72±0.1		-
Oxyfluoren		-		-		-		-		-
Kresoxim methyl	2	6.32±0.2		-		-	2	6.78±0.3		-
4,4' DDE		-		-	2	6.34±0.1		-		-
Flusilazole		-	3	8.56±0.5		-		-	3	8.72±0.6
Bupirimate		-		-		-		-	3	7.65±0.4
Buprofezin	3	4.53 ±0.3		-		-		-		-
2,4' DDD		-	2	7.54±0.2		-		-		-
Diclobutrazol		-		-	3	8.74±0.2		-		-
Dieldrin	-		1	6.89±0.1		-	3	9.31±0.4		-
Cyproconazole isomer II		-		-	3	6.95±0.3		-		-
Fenthion Sulfoxide		-		-		-		-	4	5.81±0.3
Endrin		-		-		-	1	2.31±0.2	1	-
Fenthion Sulfone	1	7.31±0.4	2	-		-		-		-
Ethion		-		9.34±0.4		-		-		-
Endosulfan beta		-		-		-	2	5.83±0.3		-
4,4' DDD		-		-		-		-		-
2,4' DDT		-		-		-		-	3	7.43±0.5
Mepronil	2	9.14±0.3		-		-		-	4	6.41±0.2
Trifloxystrobin		-		-	3	9.67±0.4		-		-
Carbophenothion		-	3	7.29±0.2		-		-		-
Endosulfan sulfate		-		-		-	3	7.18±0.5		-
Fenhexamid				-		-		-		-
4,4'DDT		-		-		-	3	6.89±0.4		-
Diflufenican	2	8.22±0.2		-		-		-	2	8.51±0.3
Tebuconazole		-	4	8.46±0.3		-		-		-
Piperonyl butoxide		-		-	2	3.24±0.1		-		-
Triphenyl phosphate		-		-		-		-		-
Phosmet		-		-		-			3	5.32±0.2
Phenoxycarb		-		-		-	2	8.54±0.6		-
Methoxychlor		-	2	3.42±0.1		-		-		-
Benzo[a]anthracene		-		-		-	3	9.41±0.5		-
Chrysene	3	2.16±0.1		-	3	9.06±0.4		-	2	6.75±0.5
Furathiocarb		-		-		-				-
Phosalone		-		-	2	6.58±0.2		-		-
Pyriproxyfen		-	3	5.94±0.2		-		-		-
Cyhalothrin	2	6.95±0.2		-		-		-	2	9.11±0.6
Fenarimol		-		-		-	4	2.41±0.1		-
Azinphos-ethyl		-	2	8.76±0.3		-		-		-
cis-Permethrin		-		-		-		-		
trans-Permethrin		-		-	3	7.52±0.3		-		-
Coumaphos	1	7.38±0.2		-		-		-	3	4.22±0.2
Cypermethrin isomer III		-		-		-		-		-
Benzo[b]fluoranthene		-		-		-		-		-
Benzo[k]fluoranthene		-		-		-		-		-
Cypermethrin isomer I		-		-		-	3	6.34±0.2		-
Boscalid		-	2	9.47±0.4		-		-	3	6.41±0.4
Cypermethrin isomer II		-		-		-		-		-
Benzo[a]pyrene	3	6.43±0.1		-		-		-	1	7.52±0.5
cis-Fluvalinate		-		-	2	8.24±0.2		-		-
trans-Fluvalinate		-		-		-		-		-
(±)-Indoxacarb		-		-	1	9.12±0.6		-		-
Deltamethrin	2	4.53±0.2		-		-		-	2	8.67±0.4
Azoxystrobin		-	3	5.52±0.2		-		-		-
Benzo[ghi]perylene		-		-		-	2	9.32±0.4		-
Dibenz[a,h]anthracene		-	1	2.34±0.1		-		-		-
Indeno[1,2,3-cd]pyrene	1	7.93±0.3		-	2	1.22±0.1		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table

4.4 Results regarding the samples of aromatic herbs purchased at Constantine and Annaba

In Tables 4.1 and 4.2 the contents of contaminants in the samples of aromatic herbs Rosemary, Sage, Thyme, Chivel and Chives taken into consideration are reported and in the Figures 4.1-4.5 the diagrams illustrating some relevant contents of contaminants in these aromatic herbs were performed. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in aromatic herbs.

In particular, in the **Rosemary** samples we have the following contents of contaminants

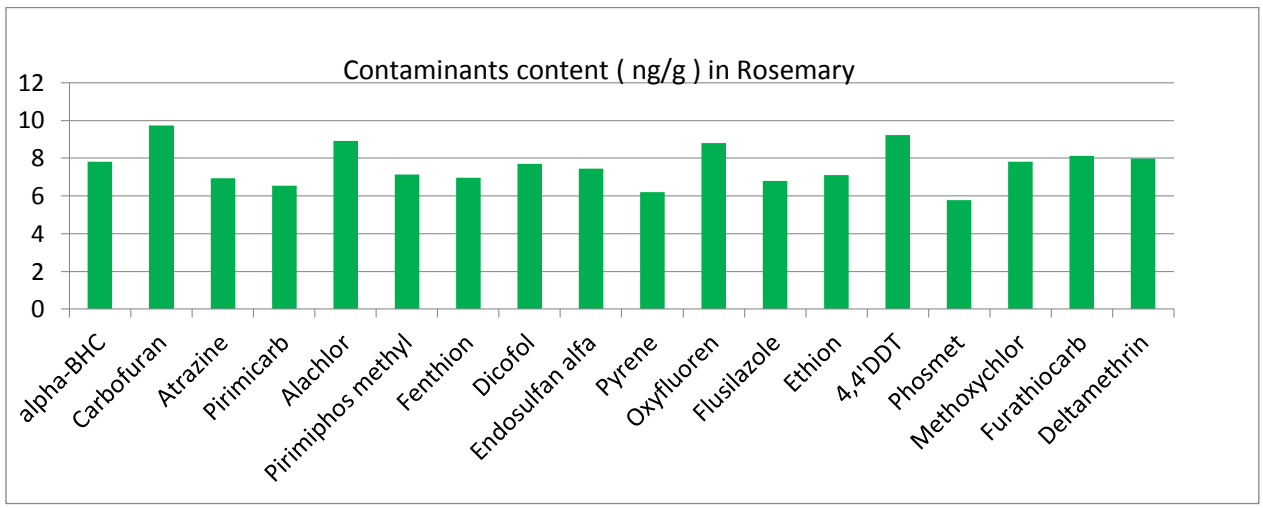


Figure 4.1 Contaminants content in some samples of Rosemary.

For the **Sage** samples we have the following representation for the contents of contaminants

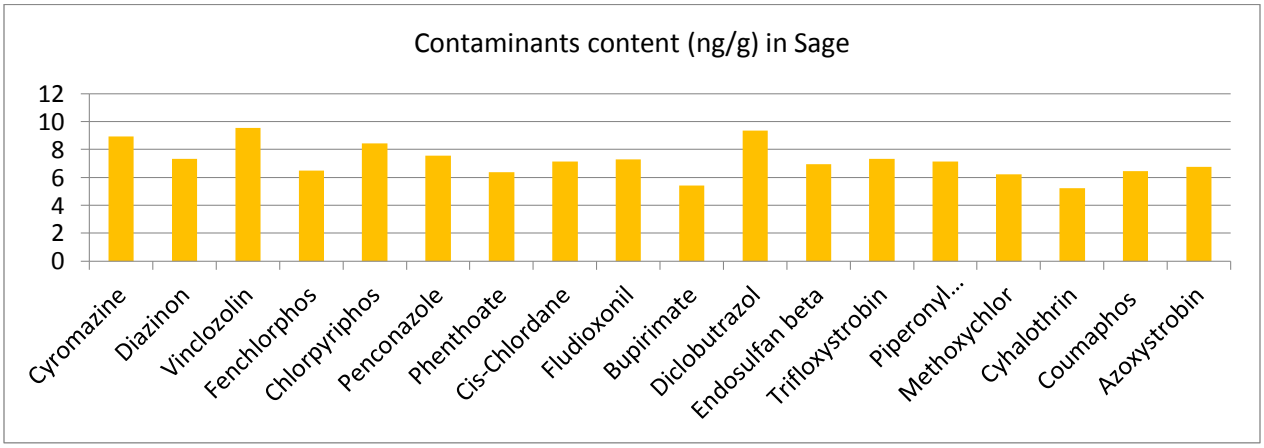


Figure 4.2 Contaminants content in some samples of Sage.

In the **Thyme** samples the contents of contaminants have the following representation

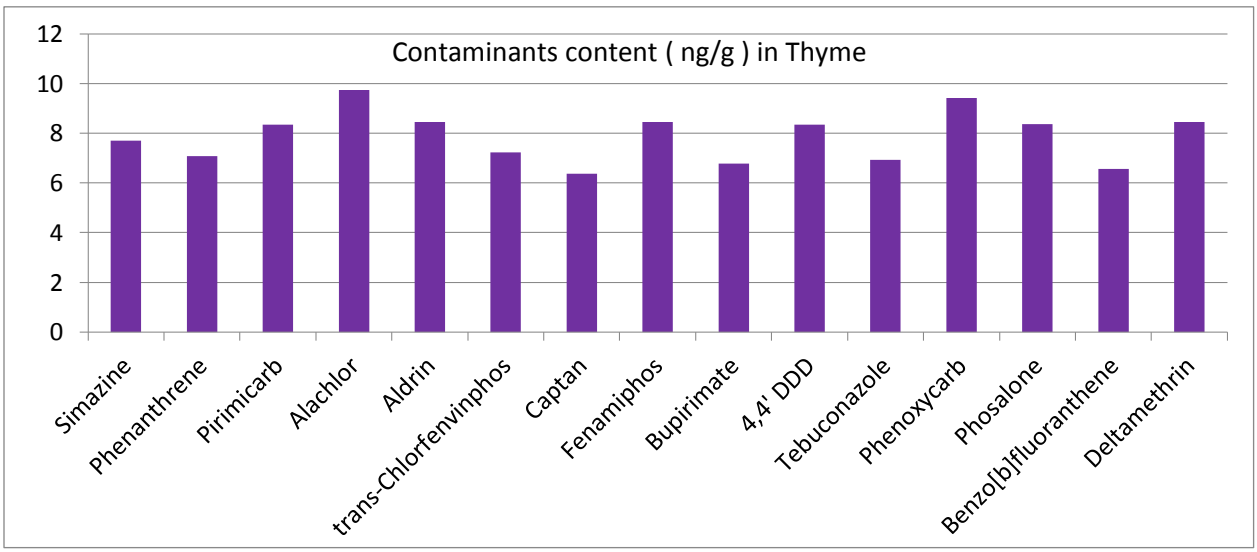


Figure 4.3 Contaminants content in some samples of Thyme.

In the **Marjoram** samples we have the following contents of contaminants

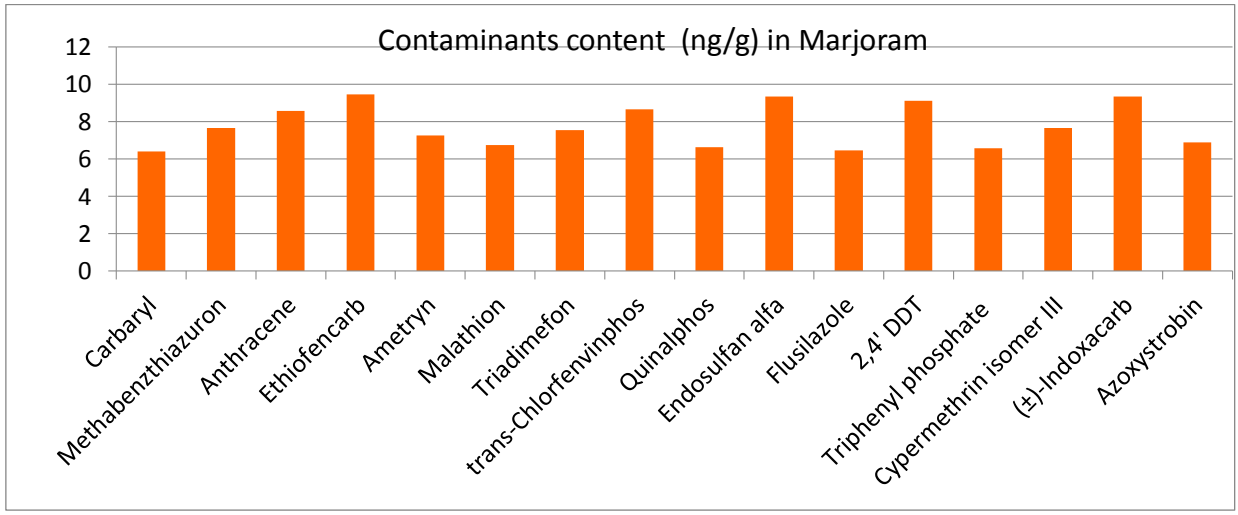
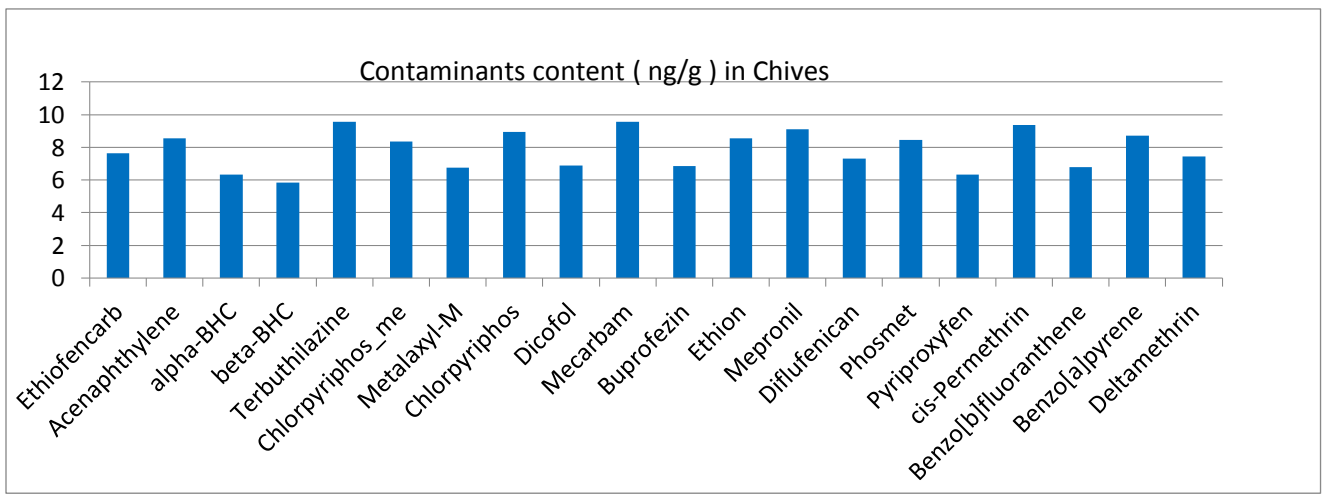


Figure 4.4. Contaminants content in some samples of Marjoram.

For the **Chives** samples we have obtained the following representation for the contents of contaminants

Figure 4.5 Contaminants content in some samples of Chives.



5. 3 Results regarding the samples of spices purchased at Constantine and Annaba

In Tables 4.3 and 4.4 the contents of contaminants in the samples of spices Cloves, Nutmeg, Horseradish, Saffron and Ginger taken into consideration are reported and in the Figures 4.6-4.10 the diagrams illustrating some contents of contaminants in these aromatic herbs were performed. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in herbs.

In particular, in the **Cloves** samples we have derived the following representation for the contents of contaminants

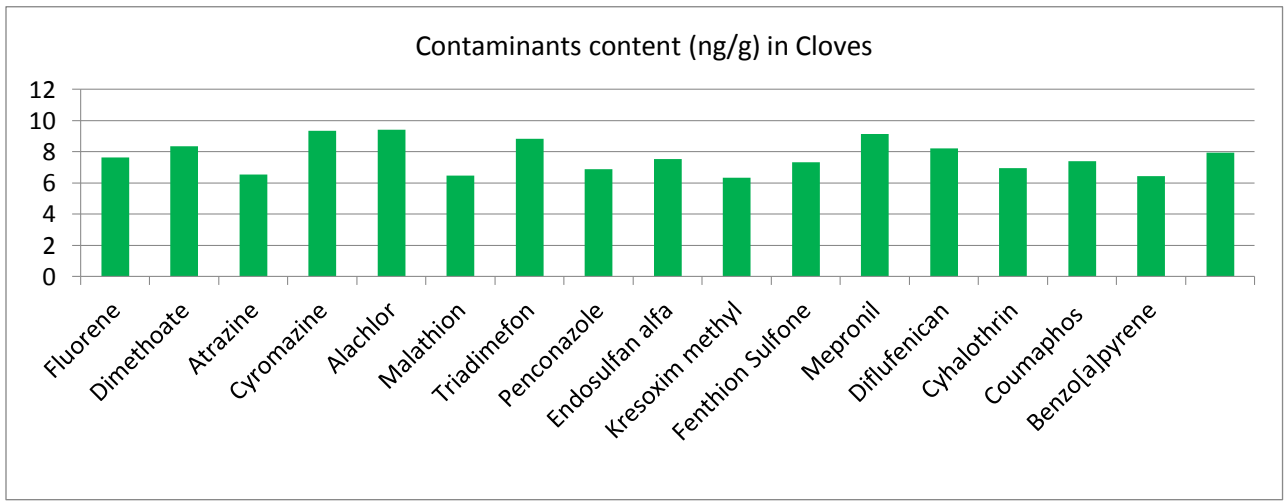
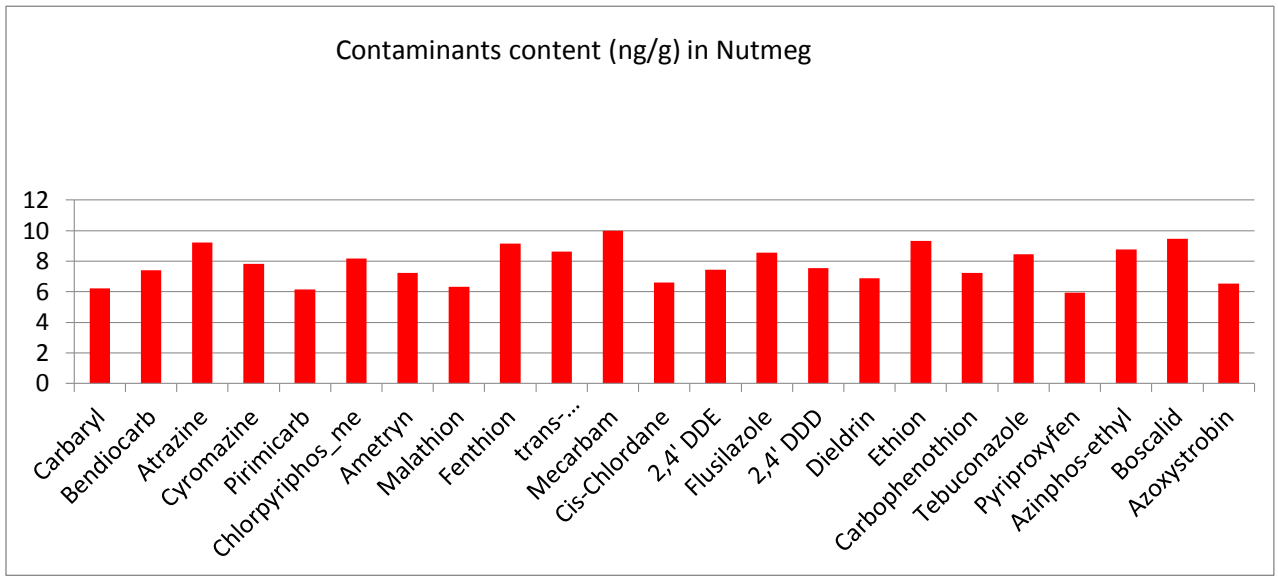


Figure 4.6. Contaminants content in some samples of Cloves.

For the **Nutmeg** samples we have worked out the following representation for the contents of contaminants

Figure 4.7 Contaminants content in some samples of Nutmeg.



In the **Horseradish** samples we have the following contents of contaminants.

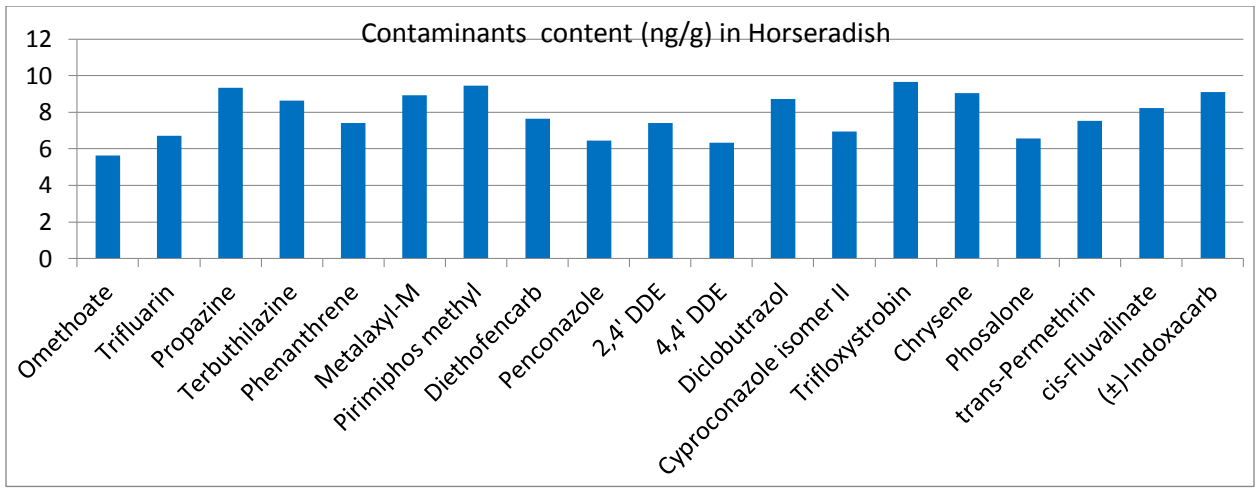


Figure 4.8 Contaminants content in some samples of Horseradish.

For the **Saffron** samples we have the following representation of the contents of contaminants

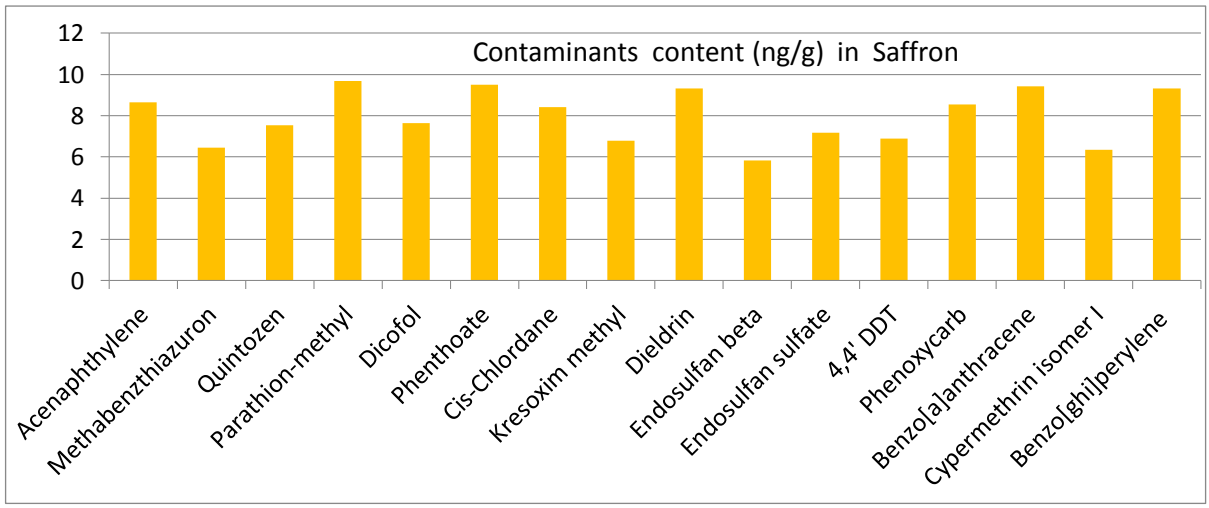


Figure 4.9 Contaminants content in some samples of Saffron.

For the **Ginger** samples we have the following representation for the contents of contaminants

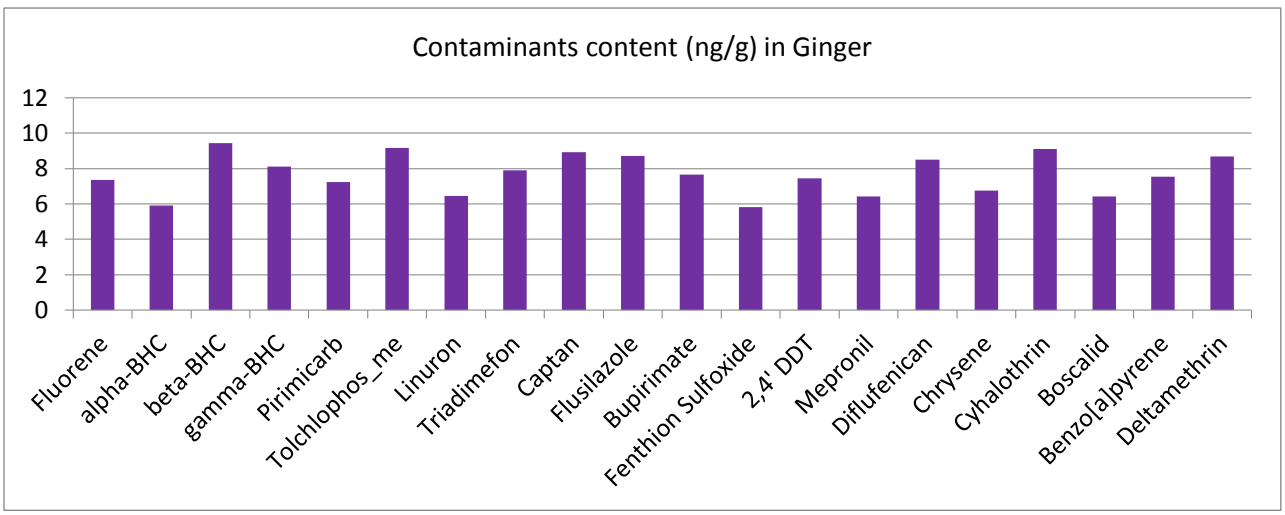


Figure 4.10. Contaminants content in some samples of Ginger.

CHAPTER V

Organic contaminants in aromatic herbs purchased at Algeri and Bijayad

In this Chapter residues of organic contaminants are measured in samples of aromatic herbs purchased in the Algerian cities Algeri and Bijayad Constantine. A statistical approach is applied. We illustrate the values of the contaminants content, obtained in laboratory, by Tables and graphic representations for each aromatic herb and spice. From the results, it is seen that this content of contaminants ingested by human organism by the consumption of the analyzed herbs and species does not constitute a risk for the human health, when its assumption is limited, in agreement with the values recommended by the international and national organizations.

5.1 Introduction

In this Chapter 45 samples of aromatic herbs (9 of Tarragon, 9 of Dill, 8 of Myrtle, 8 of Chervil and 9 of Rocket) and 42 spices (8 of Cardamom, 9 of Turmeric, 9 of Paprika, 9 of Cinnamon and 8 Juniper berries) purchased in markets of the Algerian cities Algeri and Bijayad, are analyzed
to measure in them residues of 119 contaminants of organic kind, PAHs, OCPs, OPPs, CARs, PYRs, OPP/As, CAR/A, IGRs, SYN, Fs, Hs, see Appendix. Indeed, aromatic herbs and spices can be contaminated during the various steps of the agricultural work processes of the land in which they are grown: the treatment of the soil through organic and chemical contaminants; its spraying using contaminated water; environmental pollution due to climate change; excessive urbanization of cities and physical contaminants [1], [2]. They represent a serious risk to human and animal health [2Aromatic herbs and spices play an important role in the medical sciences, in the culinary science and other fields. The Chapter is organized as follows. The Section 2 deals with the materials and methods used in order to analyze the 45 samples taken into account. The Sections 3, 4 and 5 are dedicated to the presentation, in the Tables 5.1-5.4 and the Figures 5.1-5.10, the results obtained for the residues of the contaminants found in the considered samples, and to discussion of the results. It is seen seen that the values of the measured contaminants contents (ng/g) do not constitute a risk for the human health, when their values do not exceed the maximum levels (MLs) permitted by the guidelines of international and national nutrition organizations.

5.2 Materials and Methods

A simplified method was used for the extraction of organic pollutants without a purification step (see[1]). In particular, the samples and sample preparation, chemical and standard solutions, equipment and analytical conditions are reported in Chapter III.

5. 3 Tables for the analyzed aromatic herbs and spices

In this Section we have presented in Tables 5.1, 5.2 and Tables 5.3, 5.4 the results derived for the content of the 119 contaminants under consideration and measured within the aromatic herbs and spices, respectively, purchased at Algeri and Bijayad. The measured values of these contaminants (ng/g) are illustrated in the Figures 5.1-5.5 (for the aromatic herbs) and in the Figures 5.6-5.10 (for the spices), wherein only the contaminants having considerable values have been taken into account.

Table 5.1 Contaminants (ng/g) measured in aromatic herbs purchased at Algeri and Bijayad.

CONTAMINANTS	Tarragon [n=9], N=2		Dill [n=9], N=3		Myrtle[n=8], N=4		Watercress [n=8], N=3		Rocket [n=9], N=2	
	Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad	
Acephate		-		-		-		-		-
Ethiofencarb		-	2	9.26±0.5		-		-		-
Acenaphthylene		-		-		-		-		-
Captafol		-		-	2	9.12±0.4		-		-
Carbaryl		-		-		-	2	8.52±0.4		-
Omethoate	2	5.15±0.2		-		-		-	1	7.18±0.3
Fluorene		-	3	3.23±0.1		-		-		-
Trifluarin		-		-		-		-		-
Bendiocarb		-		-		-	3	6.02±0.2		-
Methabenzthiazuron		-		-		-		-		-
Alpha-BHC	3	0.89±0.1		-		-		-		-
Dimethoate		-	1	7.15±0.3		-		-	2	4.12±0.1
Carbofuran		-		-	4	0.97±0.1		-		-
Simazine		-		-		-		-		-
Atrazine	1	6.81±0.3		-		-		-		-
Propazine		-		-		-		-		-
Beta-BHC		-		-		-	2	6.67±0.3		-
Cyromazine		-		-		-		-		-
Quintozen		-	2	8.12±0.4		-		-	1	6.26±0.2
Terbuthilazine		-		-		-		-		-
Propyzamide	3	3.18±0.2		-		-		-		-
Diazinon		-		-		-	1	7.14±0.4		-
Pyrimethanil		-	3	4.18±0.2		-		-		-
Phenanthrene		-		-		-		-		-
Anthracene		-		-	1	8.75±0.4		-	3	8.16±0.3
Pirimicarb	2	7.25±0.3		-		-		-		-
Ethiofencarb		-		-		-		-		
Chlorpyriphos_me		-		-		-	1	9.24±0.3		-
Vinclozolin		-		-		-		-		-
Parathion-methyl		.		-		-		-		-
Tolchlophos_me		-	1	6.27±0.3		-		-		-
Alachlor	3	8.52±0.2		-		-		-	3	3.21±0.1
Metalaxyl-M		-		-	1	6.52±0.2		-		-
Ametryn		.		-		-		-		-
Fenchlorphos		-		-		-		-		-
Pirimiphos methyl		-		-		-	2	5.89±0.2		-
Fenitrothion		-	3	4.38±0.1		-		-		-
Malathion		-		-		-		-		-
Linuron		-		-		-		-	2	9.24±0.4
Diethofencarb	2	9.23±0.4		-		-		-		-
Chlorpyriphos		-		-		-		-		-
Fenthion		-		-	2	7.08±0.3		-		-
Triadimefon		-	2	7.48±0.2		-		-		-
Aldrin		-		-		-		-		-
Dicofol		-		-		-		-		-
cis-Chlorfenvinphos	3	2.25±0.1		-		-	2	2.78±0.1		-
Penconazole		-		-		-		-	1	6.45±0.3
trans-Chlorfenvinphos		-		-		-		-		-
Mecarbam		-	1	8.02±0.4		-		-		-
Phenthoate		-		-		-		-		-
Quinalphos		-		-	2	6.65±0.3		-		-
Procymidone		-		-		-		-		-
Captan		-		-		-		-		-
Methidathion	2	6.15±0.3		-		-		-	2	7.32±0.2
Cis-Chlordane		-		-	3	5.95±0.2		-		-
2,4' DDE		-	2	2.96±0.1		-		-		-
Endosulfan alfa		-		-		-		-		-
Fenamiphos	3	4.78±0.2		-		-	3	9.01±0.4		-
trans-Chlordane		-		-		-		-		-

Table 5.2 Contaminants (ng/g) measured in aromatic herbs purchased at Algeri and Bijayad

CONTAMINANTS	Tarragon [n=9], N=2		Dill [n=9], N=3		Myrtle [n=8], N=4		Watercress [n=8], N=3		Rocket [n=9], N=2	
	Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad	
Pyrene		-		-		-		-		-
Imazalil		-		-		-	3	-		-
Fludioxonil	2	7.36±0.2	3	-	2	-		-		8.35±0.3
Oxyfluoren		-		-		9.26±0.5		-	2	-
Kresoxim methyl		-		6.08±0.2		-		-		-
4,4' DDE		-		-		-		7.34±0.3		-
Flusilazole		-		-		-	2	-		-
Bupirimate	3	8.70±0.3	2	-	3	-		-		1.23±0.1
Buprofezin		-		-		-		-	3	-
2,4' DDD		-		-		4.18±0.1		-		-
Diclobutrazol		-	3	-		-		1.89±0.1		-
Dieldrin		-		-		-		-		-
Cyproconazole isomer II		-		-		-		-	2	-
Fenthion Sulfoxide		-		9.05±0.3		-	3	-		-
Endrin		-	2	-	2	-		-		9.08±0.4
Fenthion Sulfone	2	4.25±0.1		-		-		-		-
Ethion		-		-		7.38±0.2		-	3	-
Endosulfan beta		-	3	-		-		-		-
4,4' DDD		-		-		-		9.11±0.4		-
2,4' DDT		-		-		-	3	-		-
Mepronil		-		-		-		-	4	-
Trifloxystrobin		-	2	-	2	-		-		-
Carbophenothion	1	9.08±0.4		-		-		-		4.12±0.1
Endosulfan sulfate		-		-		8.42±0.4	3	-		-
Fenhexamid		-	3	-		-		-		-
4,4' DDT		-		7.65±0.2		-		-		-
Diflufenican		-		-		-		-	2	-
Tebuconazole		-		-	3	-		3.15±0.1		-
Piperonyl butoxide	2	2.92±0.1	4	-		-		-		-
Triphenyl phosphate		-		-		6.15±0.3	3	-		-
Phosmet		-		-		-		-	3	-
Phenoxycarb		-		-	2	-		-		-
Methoxychlor	2	-	3	-		-		-		6.73±0.2
Benzo[a]anthracene		-		1.55±0.1		-		-		-
Chrysene		-		-		7.12±0.2		-		-
Furathiocarb		6.52±0.2		-		-		6.84±0.2		-
Phosalone		-		-	3	-		-		-
Pyriproxyfen		-		-		-	3	-	3	-
Cyhalothrin		-	4	-		-		-		-
Fenarimol	1	-		6.71±0.2		-		-		-
Azinphos-ethyl		-		-		6.83±0.1		-		-
cis-Permethrin		7.43±0.3		-	2	-		-	3	-
trans-Permethrin		-		-		-		-		5.87±0.1
Coumaphos		-	3	-		-		8.14±0.4		-
Cypermethrin isomer III		-		-		-	4	-		-
Benzo[b]fluoranthene	2	-		-	3	-		-	2	-
Benzo[k]fluoranthene		-	2	-		7.53±0.2		-		-
Cypermethrin isomer I		-		8.14±0.3		-		-		-
Boscalid		-		-		-		-		7.31±0.2
Cypermethrin isomer II		-		-		-		-		-
Benzo[a]pyrene		-	2	-	3	-	3	-	4	-
cis-Fluvalinate		8.16±0.2		-		-		-		6.08±0.3
trans-Fluvalinate		-		-		-		7.54±0.3		-
(±)-Indoxacarb		-		-		-	2	-		-
Deltamethrin	3	6.68±0.1		8.36±0.4	2	-		-		-
Azoxystrobin		-	3	-		-	3	-		-
Benzo[ghi]perylene		-		-		-		6.68±0.2		-
Dibenz[a,h]anthracene		-		-		-		-		-
Indeno[1,2,3-cd]pyrene		-		-		-		-		-

Table 5.3 Contaminants (ng/g) measured in spices at Algeri and Bijayad.

CONTAMINANTS	Cardamom[n=8], N=2		Turmeric [n=9], N=3		Paprika [n=9], N=4		Cinnamon [n=9], N=3		Juniper berries [n=8], N=2	
	Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad	
Acephate		-		-		-		-		-
Ethiofencarb		-		-		-		-		-
Acenaphthylene		-		-	**3**	5.02±0.2		-		-
Captafol	**2**	6.41±0.2		-		-		-		-
Carbaryl		-	**1**	5.25±0.2		-		-	**1**	8.02±0.2
Omethoate		-		-		-	**2**	9.23±0.2		-
Fluorene		-		-	**1**	3.27±0.3		-		-
Trifluarin		-	**3**	2.57±0.1		-		-		-
Bendiocarb	**3**	2.87±0.1		-		-		-		-
Methabenzthiazuron		-			**2**	6.31±0.2		-		-
Alpha-BHC		-		-		-		-		-
Dimethoate	**2**	5.94±0.3		-		-	**3**	3.32±0.1		-
Carbofuran		-				-		-		-
Simazine		-				-		-	**3**	2.52±0.1
Atrazine		-	**2**	9.45±0.3		-		-		-
Propazine	**1**	3.72±0.1		-	**3**	2.01±0.3		-		-
Beta-BHC		-				-	**1**	6.42±0.2		-
Cyromazine		-				-		-		-
Quintozen		-		-		-		-	**2**	6.25±0.3
Terbuthilazine		-	**1**	0.85±0.1		-		-		-
Propyzamide		-		-	**3**	8.35±0.4		-		-
Diazinon	**2**	7.23±0.4				-	**4**	5.03±0.3		-
Pyrimethanil		-	**2**	3.56±0.2		-		-		-
Phenanthrene		-		-		-		-		-
Anthracene		-				-		-		-
Pirimicarb		-				-		-	**3**	4.16±0.2
Ethiofencarb	**4**	8.15±0.6		-		-	**3**	8.14±0.2		
Chlorpyriphos_me		-		-	**2**	9.26±0.2		-		-
Vinclozolin		-				-		-		-
Parathion-methyl	**2**	9.12±0.5		-		-		-		-
Tolchlophos_me		-	**3**	7.81±0.3		-		-	**2**	5.23±0.1
Alachlor		-		-		-	**3**	3.11±0.1		-
Metalaxyl-M		-		-	**2**	7.16±0.3		-		-
Ametryn	**3**	4.22±0.2		-		-		-		-
Fenchlorphos		-				-		-		-
Pirimiphos methyl		-		-		-		-	**2**	8.22±0.4
Fenitrothion		-	**1**	8.67±0.4		-		-		-
Malathion		-		-	**4**	5.12±0.1		-		-
Linuron		-		-		-		-		-
Diethofencarb		-	**3**	7.85±0.2		-	**1**	6.21±0.3		-
Chlorpyriphos		-				-		-		-
Fenthion		-		-	**1**	6.21±0.3		-	**3**	7.45±0.2
Triadimefon	**2**	6.46±0.2		-				-		-
Aldrin		-		-		-		-		-
Dicofol		-		-		-		-		-
cis-Chlorfenvinphos		-	**2**	6.25±0.3		-		-		-
Penconazole	**1**	7.08±0.3				-		-	**1**	4.16±0.3
trans-Chlorfenvinphos		.		-	**2**	7.43±0.2		-		-
Mecarbam		-		-		-		-		-
Phenthoate	**3**	5.16±0.1				-	**2**	7.12±0.2		-
Quinalphos		-		-		-		-		-
Procymidone		-	**1**	8.01±0.2		-		-		-
Captan		-		-		-	**3**	8,43±0.1		-
Methidathion	**2**	9.01±0.4		-		-		-		
Cis-Chlordane		-		-	**3**	8.01±0.4		-		-
2,4' DDE		-		-		-		-		-
Endosulfan alfa		-		-		-		-	**2**	9.11±0.3
Fenamiphos		-		-		-		-		-
trans-Chlordane		-		-		-		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of the table.

Table 5.4 Contaminants (ng/g) measured in spices purchased at Algeri and Bijayad.

CONTAMINANTS	Cardamom [n=8], N=2		Turmeric [n=9], N=3		Paprika [n=9], N=4		Cinnamon [n=9]N=3		Juniper berries [n=8], N=2	
	Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad		Algeri, Bijayad	
Pyrene		-		-		-		-		-
Imazalil		-		-		-	2	9.42±0.3		-
Fludioxonil	3	5.02±0.2		-		-		-		-
Oxyfluoren		-		-	1	0.88±0.2		-	1	-
Kresoxim methyl		-	2	9.13±0.4		-		-		6.36±0.2
4,4' DDE		-		-		-	1	0.75±0.1		-
Flusilazole		-		-		-		-		-
Bupirimate	1	6.20±0.4		-		-		-		-
Buprofezin		-	1	0,75 ±0.1		-		-	2	7.18±0.3
2,4' DDD		-		-	2	2.89±0.1		-		-
Diclobutrazol		-		-		-	4	3.18±0.3		-
Dieldrin		-		-		-		-	2	8.24±0.3
Cyproconazole isomer II		-	3	3.18±0.2		-		-		-
Fenthion Sulfoxide		-		-	3	9.16±0.3		-		-
Endrin	2	7.35±0.3		-		-		-		-
Fenthion Sulfone				-		-		-	3	9.42±0.4
Ethion		-		-		-	2	7.58±0.2		-
Endosulfan beta		-		-		-		-		-
4,4' DDD		-	2	7.25±0.3		-		-	1	0.87±0.1
2,4' DDT		-		-	3	5.62±0.2	3	-		-
Mepronil		-		-		-		-		-
Trifloxystrobin	2	8.41±0.5		-		-		-		-
Carbophenothion		-		-		-	1	6.82±0.4		-
Endosulfan sulfate		-		-		-		-	3	2.52±0.1
Fenhexamid		-	3	5.16±0.4		-		-		-
4,4' DDT		-		-		-		-		-
Diflufenican		-		-	1	8.82±0.3		-		-
Tebuconazole		-		-		-		-		-
Piperonyl butoxide		-		-		-		-	4	6.78±0.3
Triphenyl phosphate	3	2.38±0.1		-		-		-		-
Phosmet		-		-		-	2	5.11±0.2		-
Phenoxycarb		-	2	6.85±0.2	2	-		-		-
Methoxychlor		-		-		-		-		-
Benzo[a]anthracene		-		-		7.43±0.2		-		-
Chrysene		-		-		-		-	1	7.82±0.2
Furathiocarb	1	0.89±0.1		-		-		-		-
Phosalone		-		-		-	3	8.73±0.4		-
Pyriproxyfen		-	3	8.14±0.5		-		-		-
Cyhalothrin		-		-	3	6.12±0.3		-		-
Fenarimol		-		-		-		-	2	5.98±0.3
Azinphos-ethyl	3	7.02±0.4		-		-		-		-
cis-Permethrin		-	1	4.52±0.3		-	1	7.25±0.3		-
trans-Permethrin		-		-		-		-		-
Coumaphos		-		-		-		-	3	3.42±0.2
Cypermethrin isomer III		-		-	2	7.12±0.2		-		-
Benzo[b]fluoranthene		-		-		-		-		-
Benzo[k]fluoranthene		-		-		-	2	8.67±0.2		-
Cypermethrin isomer I	2	6.92±0.2		-		-		-	1	9.36±0.4
Boscalid		-	2	7.12±0.2		-		-		-
Cypermethrin isomer II		-		-	1	9.25±0.4		-		-
Benzo[a]pyrene		-		-		-		-		-
cis-Fluvalinate	3	2.18±0.2		-		-		-		-
trans-Fluvalinate		-		-		-	1	6.54±0.1		-
(±)-Indoxacarb		-		-	3	6.68±0.3		-		-
Deltamethrin		-		-		-		-		-
Azoxystrobin		-		-		-		-	2	6.15±0.2
Benzo[ghi]perylene	1	8.67±0.2		-		-		-		-
Dibenz[a,h]anthracene		-	3	8.55±0.4		-		-		-
Indeno[1,2,3-cd]pyrene		-		-		-		-		-

Legenda: The symbol " n " describes the *total number* of examined samples of each aromatic herb, the symbol " N" indicates the number of samples *without contamination*, the *number in blue color* in each column indicates the number of the *samples contamined* by the kind of contaminant present in the same row of theTable.

5.3 Results regarding the samples of aromatic herbs from Algeri and Bijayad

In Tables 5.1 and 5.2 the contents of contaminants in the samples of the aromatic herbs Tarragon, Dill, Myrtle, Watercress and Rocket purchased in markets of Algeri and Bijayad are reported and in the Figures 5.1-5.5 the diagrams describing some relevant contents of contaminants in these aromatic herbs were worked out. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in herbs. (MLs) for organic contaminants in herbs and spices established by different regulations were shown and it was seen that during the years, the European Commission has established and revised these MLs by numerous regulations and related amendments.

In particular, in the **Tarragon** samples we have obtained the following contents of contaminants

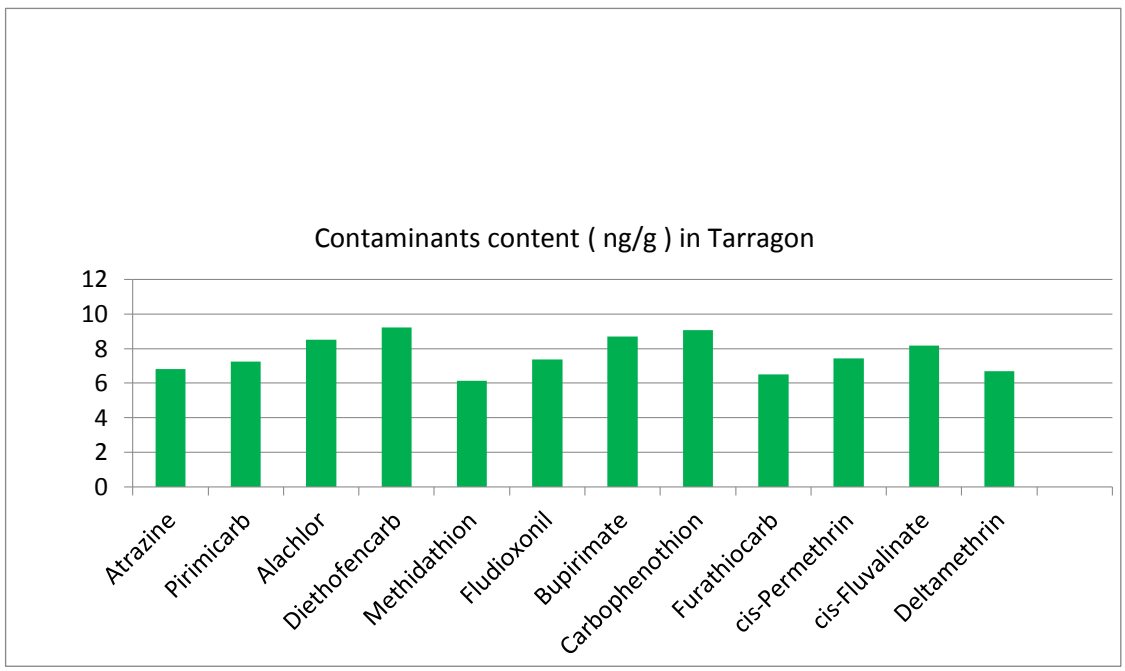


Figure 5.1 Contaminants content in some samples of Tarragon.

For the **Dill** samples we have derived the following representation for the contents of contaminants

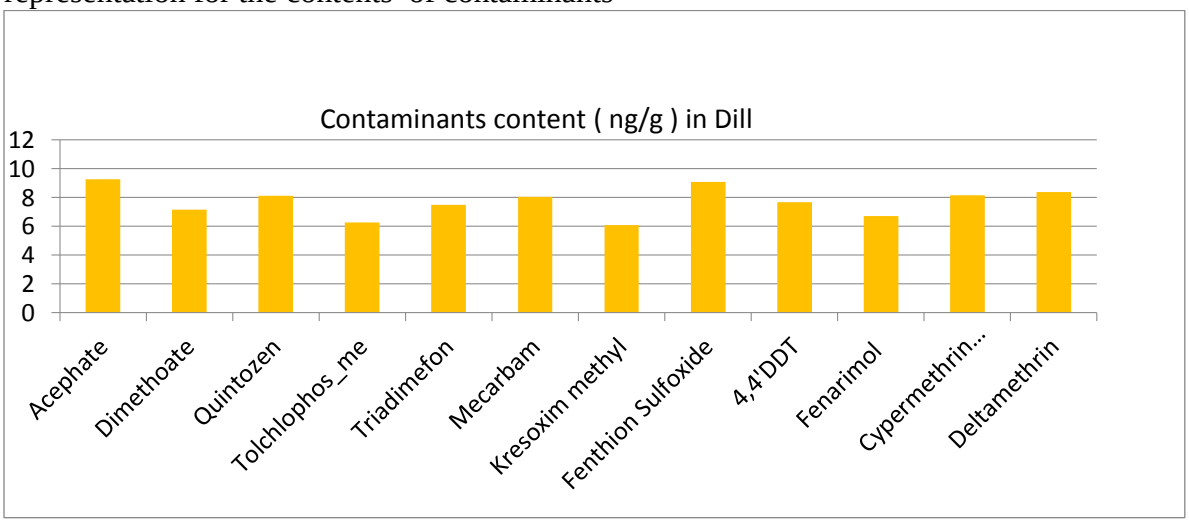


Figure 5.2. Contaminants content in some samples of Dill.

For the **Myrtle** samples we have obtained the following representation for the contents of contaminants

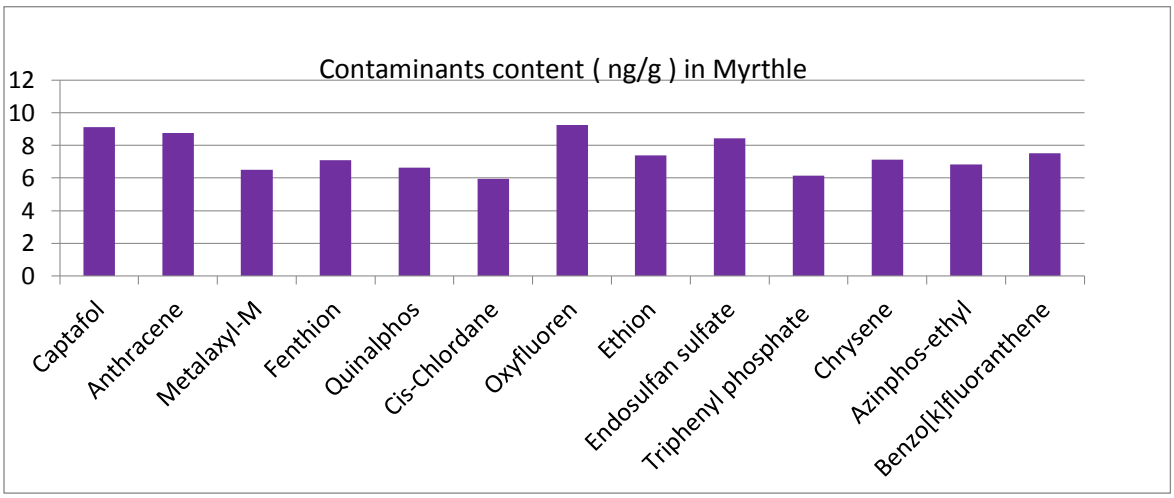


Figure 5.3 Contaminants content in some samples of Myrthle

For the **Watercress** samples we have derived the following representation for the contents of contaminants

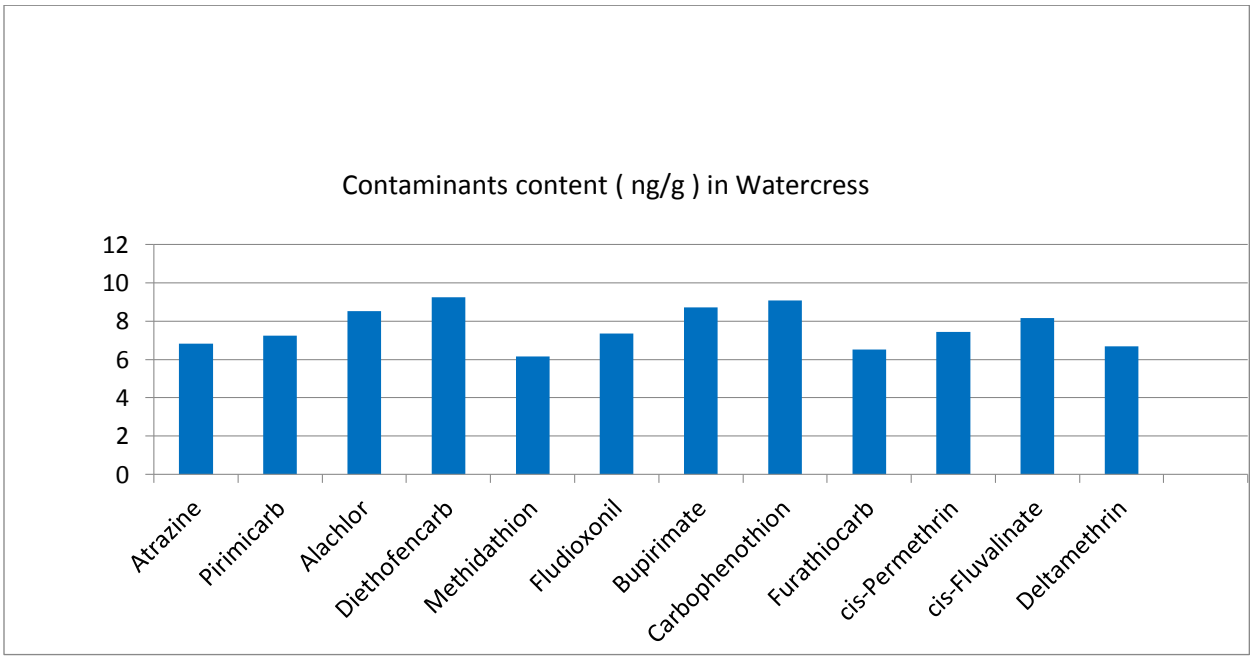


Figure 5.4 Contaminants content in some samples of Watercress.

For the **Rocket** samples we have obtained the following contents of contaminants

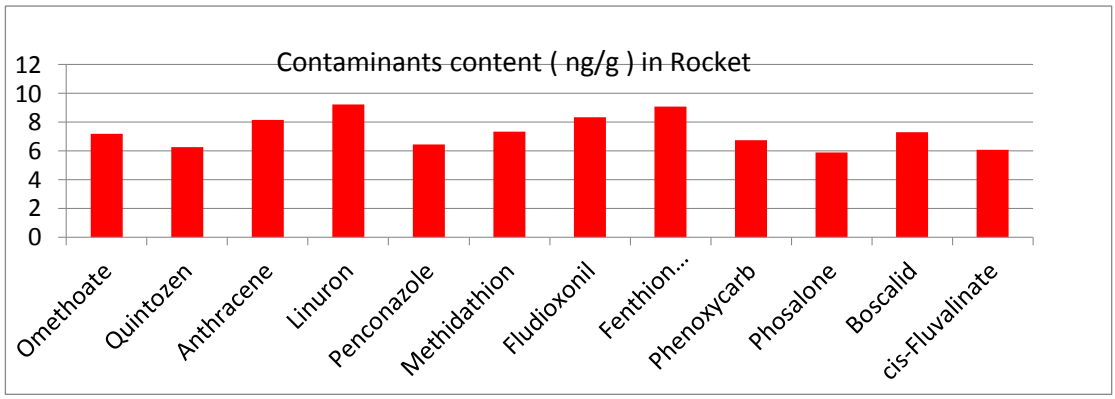


Figure 5.5 Contaminants content in some samples of Rocket.

5.2. Results regarding the samples of spices from Algeri and Bijayad

In Tables 5.3 and 5.4 the contents of contaminants in the samples of the spices Cardamom, Turmeric, Paprika, Cinnamon, Juniper berries taken into consideration are reported and in the Figures 5.6-5.10 the diagrams illustrating some relevant contents of contaminants in these aromatic herbs were performed. From the obtained results it is seen that they do not constitute a risk for the human organisms being the values of these contents less then the respective maximum limits MLs fixed in EU by the Food safety authorities for organic contaminants in herbs [6].

In particular, for the **Cardamom** samples we have obtained the following representation for the contents of contaminants

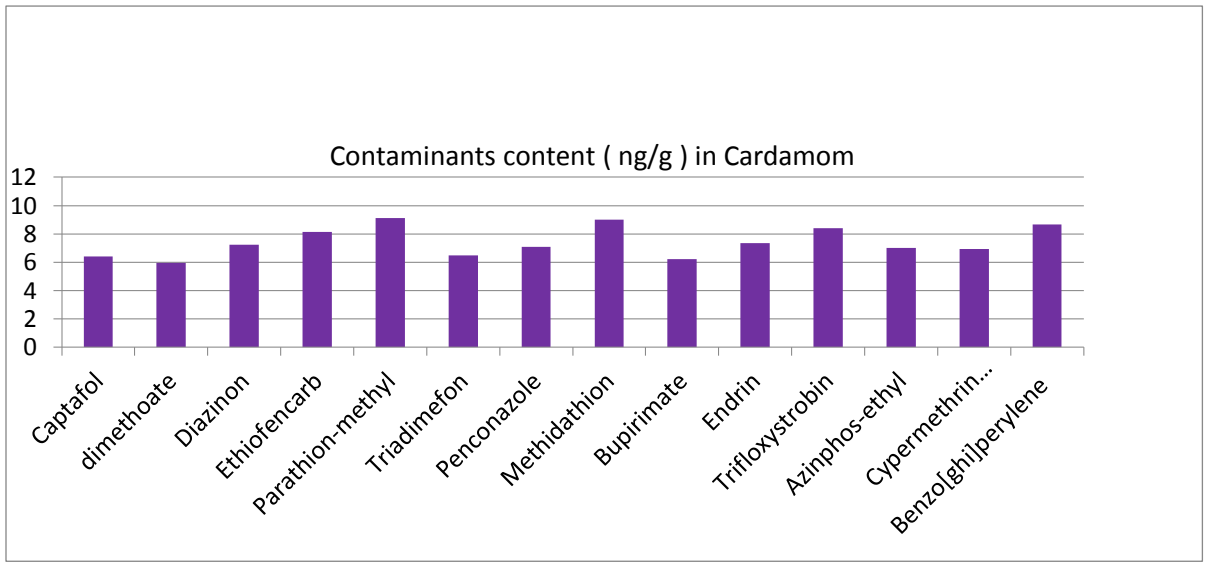


Figure 5.6 Contaminants content in some samples of Cardamom.

In the **Turmeric** samples we have derived the following representation for the contents of contaminants

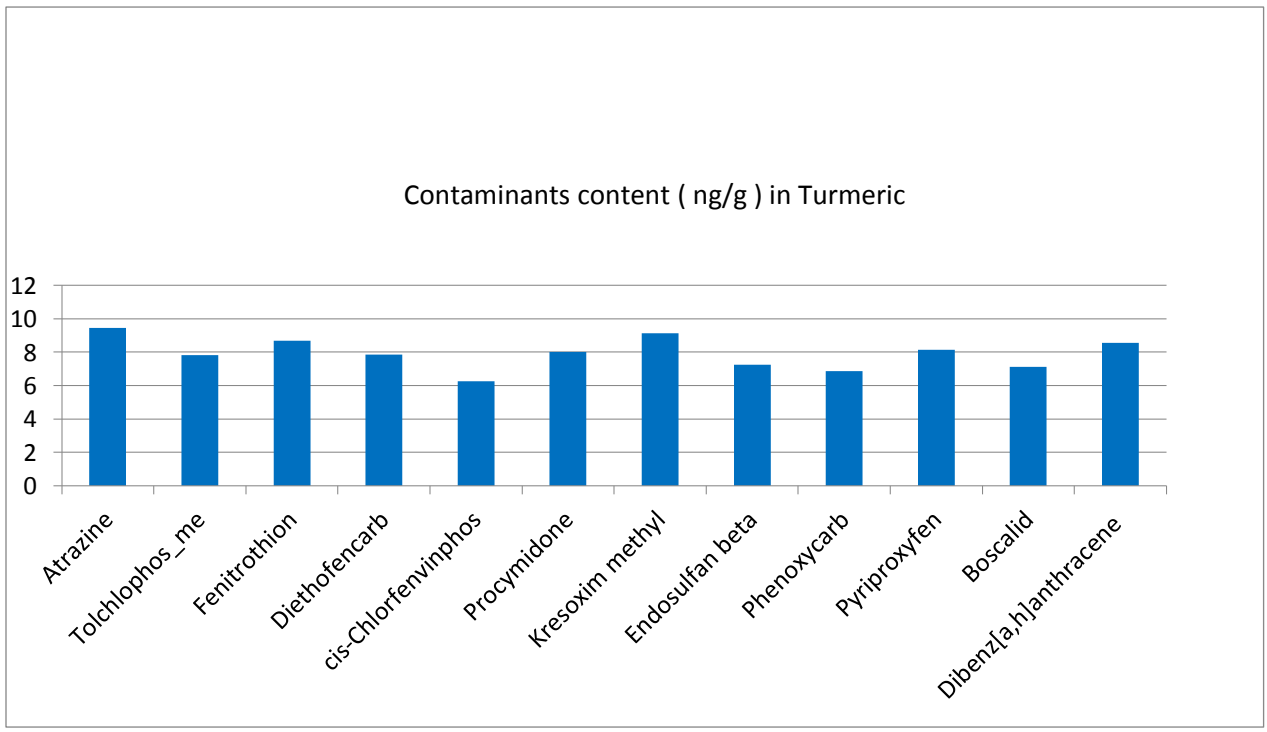


Figure 5.7 Contaminants content in some samples of Turmeric

For the **Paprika** samples we have obtained the following representation for the contents of contaminants

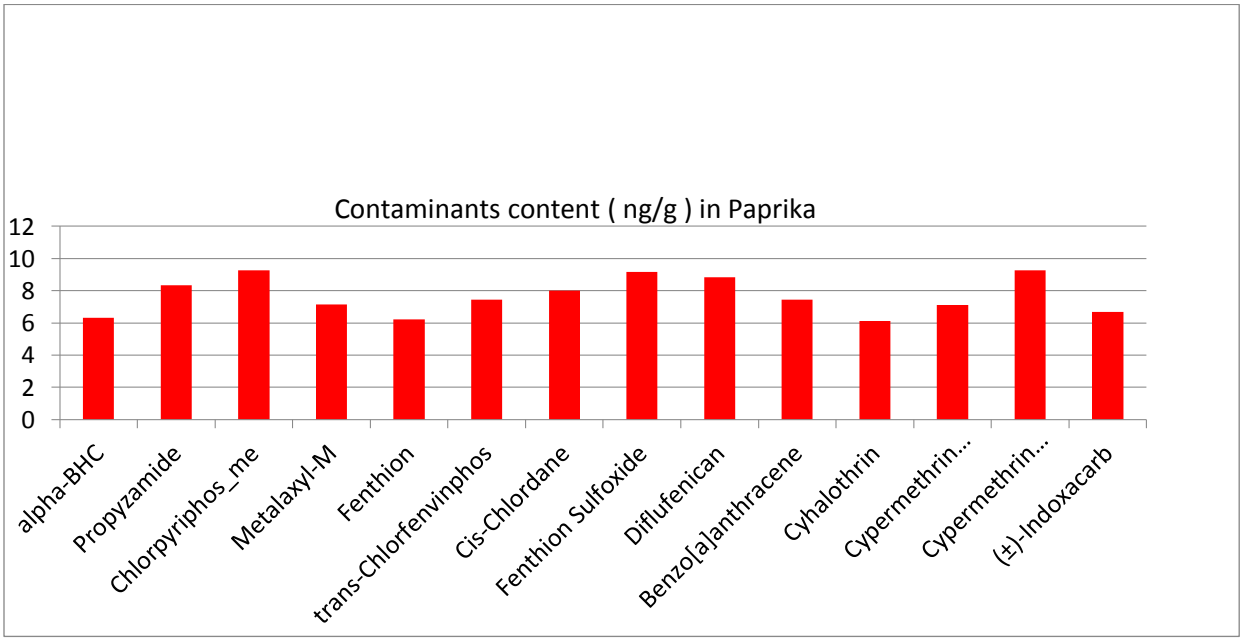


Figure 5. 8 Contaminants content in some samples of Paprika

For the **Cinnamon** samples we have derived the following representation for the contents of contaminants

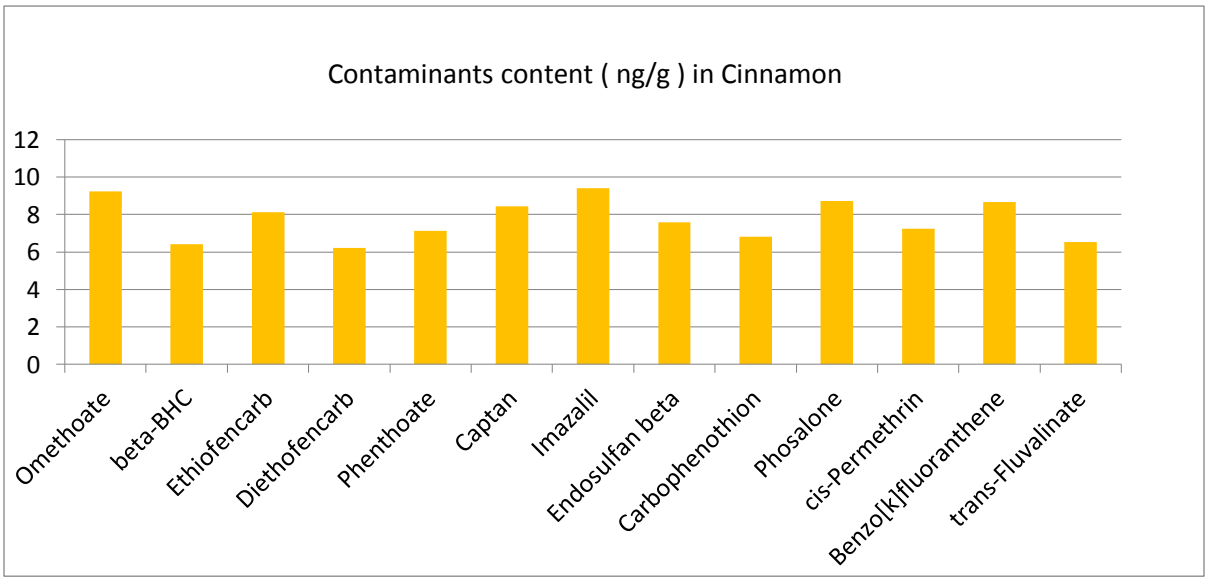


Figure 5.9 Contaminants content in some samples of Cinnamon.

For the **Juniper berries** samples we have the following representation for the contents of contaminants

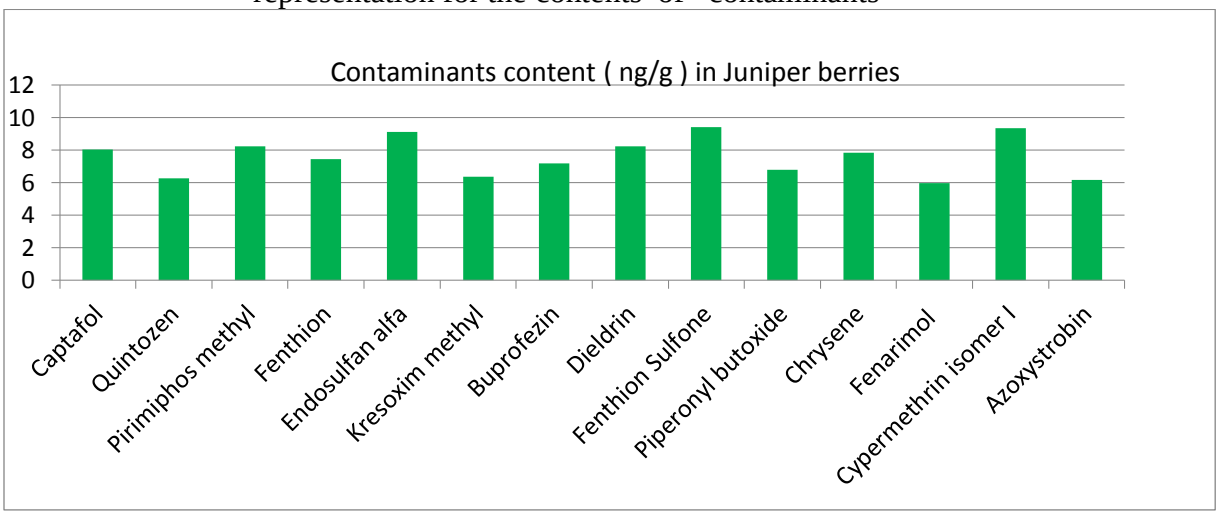


Figure 5.10 Contaminants content in some samples of Juniper berries.

Conclusions of Part II

Algeria is one of the major producers and exporters, in UE market of the countries of Mediterranean areas, of spices and aromatic herbs, that have a crucial role in several fields as medical sciences, cosmetics, culinary science. They are used against the cancer, the inflammation, the diabetes, the metabolic syndrome, they are also antimicrobial, and antioxidant and nowadays scientists and researchers from divergent medical fields are studying them for their applicability as antiviral drugs against viruses, such as the COVID-19 [15]-[28]. In particular, in [20] spices are seen as functional foods, in [21] aromatic herbs are studied as sources of bioactive compounds, in [22] the role played by herbs and spices in diseases, in longevity and to live better and in good health is treated and in [23] they are investigated as an integral part of the daily diet.

Thus, human consumption of herbs and spices requires a quality control to protect human health. To this aim in this Part II of this thesis we have investigate in aromatic herbs and spices, purchased in Algerian cities, the possible presence of 119 contaminants. Tables and graphic representations were worked out. It was seen that their consumption by human organisms does not constitute a risk because the contents of these contaminants are less then their MRLs fixed in EU by the Food safety authorities responsible for checking the legal limits of their presence. Because of there are much differences among the legislations and MLs fixed in UE the major challenge in the trade of aromatic herbs and spices is having a harmonization of the European Commission on common guidelines and regulatory measures.

In particular, in 2003 the European Food Safety Authority (EFSA) was created, that has set up an Emerging Risk Unit (EMRISK), in order to manage future scenarios based on available evidence. Risk management belongs to both the European Commission and the Member States, which can take appropriate measures to protect public health. For reasons of free trade and respect for the rules of the WTO (World Trade Organization) in the world the rules of the "Codex Alimentarius" " (World Health Organization and the Food and Agriculture Organization of the United Nations, Understanding the Codex Alimentarius, Third Edition 2006) [3] are applied by the organism JEFCA (Joint FAO/WHO Expert Committee on Food Additives), that is constitued by an international expert scientific committee, administered jointly by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO). Maximum limits (MLs) for organic contaminants in herbs and spices are set by various regulations. It has been seen that over the years the European Commission has established and revised, with numerous Regulations and related amendments, these MLs. Due to the many differences between the legislations and the MLs established in the EU, the main challenge in the trade of aromatic herbs and spices is the harmonization of the European Commission on guidelines and regulatory measures. In [7] and [8]-[17] culinary herbs and spices, presenting residues of various kinds of contaminants and coming from Mediterranean areas were studied.

APPENDIX A

Organic contaminants and their chemical classes analyzed in aromatic herbs and spices

Contaminants represent a serious risk to human and animal health [2]. Food contaminants are natural and/or chemical substances not added to food but which can derive from various causes: the different phases of the agricultural work processes of the land in which they are cultivated (the treatment of the soil through organic and chemical contaminants, its spraying using contaminated water); the production process; the packaging; transport. Furthermore, environmental pollution and physical contaminants should not be underestimated.

In this Appendix we introduce the organic contaminants anlayzed in Algerian aromatic herbs and spices: PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; OCPs, organochlorine pesticides; OPPs, organophosphorus pesticides; CARs, carbamate; PYRs, pyrethroid; A, acaricide; IGRs, insect growth regulator; SYNs, synergist; Fs, fungicide; Hs, herbicide.

A.1 PAHs (polycyclic aromatic hydrocarbons)

Polycyclic Aromatic Hydrocarbons (PAHs) are chemical compounds present in the atmosphere in both gaseous and particulate form. Benzo [a] pyrene B [a] P is the compound best known for its harmful effects. PAHs are formed during the incomplete combustion processes of organic matter. The main sources include: emissions of industries, vehicles on the roads, waste treatment and combustion of natural and agricultural biomass, domestic heating boilers.

The material that contains these compounds can have harmful effects on the health of exposed people. Exposure to PAHs has been associated with genetic mutations with cell damage, cancer and an increased risk of cardiopulmonary mortality.

Legislation: Directive 2004/107 / EC requires each member state to monitor PAHs relevant to health. This Directive proposed a limit of 1ng / m3 for the total B [a] P content in the PM10 fraction of the particulate matter averaged over one year.

PAH very known are:

Pyrene, Anthracene, Phenanthrene, Fluorene, Acenaphthylene, Indeno[1,2,3-cd]pyrene, Benzo[g,h,i]perylene, Dibenzo[a,h]anthracene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Benzo[a]anthracene, Chrysene.

A.2 PCBs (polychlorinated biphenyls)

The polychlorinated biphenyls (PCBs) are a class of organic compounds whose structure is similar to that of biphenyl whose hydrogen atoms are replaced by one to ten chlorine atoms. They are considered persistent pollutants by toxicity in some cases such as that of dioxin. Most PCBs come in the form of colorless crystalline solids, while industrial mixes are viscous liquids. All PCBs are characterized by low solubility in water, high solubility in oils and fats and low volatility. They have high chemical stability, and can only be destroyed by incineration or through catalytic processes. PCBs were also used as additives in pesticides, copying papers, adhesives, sealants, flame retardants and microscope fixers. They are chemical compounds with toxic properties for humans, which propagate in the air, water and soil and, due to their chemical stability, remain in the environment for a long time. These are substances which, due to their strong stability and marked lipophilicity, are significantly involved in the mechanisms of bioaccumulation in organisms. Following accidents, PCB production was first banned in Japan in 1972, then banned in the United States starting in 1977, and in Italy starting in 1983.
PCBs very known are:
PCB 28, PCB 52, PCB 77, PCB 81, PCB 101, PCB 105, PCB 114, PCB 118, PCB 123, PCB 126, PCB 138, PCB 153, PCB 156, PCB 157, PCB 167, PCB 169, PCB 180, PCB 189.

A.3 OCPs (organochlorine pesticides)

Organochlorine pesticides are a group of organic compounds with a chemical structure that share one or more chlorine atoms in the molecule. The use of these pesticides has played an important role in the prevention and control of pests and the consequent improvement of agricultural yields. They are remarkably stable in the environment and characterized by very low degradability. These molecules are extremely effective as insecticides (they are absorbed through the chitinous cuticle of insects), but they have an environmental impact. In fact, they remain in the soil for over 10 years and are easily absorbed by the roots of plants even years after the last treatment. Furthermore, small amounts of these substances dissolved in water over the years are concentrated in aquatic plants, plankton and fish, resulting in high concentrations in fish and piscivorous birds living in contaminated areas. Many organochlorines are known, or suspected, also to have carcinogenic effects in humans and animals. The use of these pesticides has been drastically reduced. In Europe today only a few organochlorines with low environmental persistence are permitted, because they are highly fat-soluble they produce accumulation phenomena in adipose tissue, nervous tissue, liver. Furthermore, in birds, especially birds of prey or with fish-based feedings, these pesticides have negative effects on their fertility. In fact, it has been observed that some organochlorines are able to alter the reproductive cycles of birds.
OCPs very known are:
Alachlor, Methoxychlor, a-HCH, b-HCH, c-HCH, cis-Chlordane, trans-Chlordane, Aldrin, Dieldrin, Endrin, 2,4’-DDD, 2,4’-DDE, 2,4’-DDT, 4,4’-DDD, 4,4’-DDE, 2,4’-DDT, Endosulfan a, Endosulfan b, Endosulfan sulfate, Dicofol.

A.4 OPPs (organophosphorus pesticides)

Organophosphorus pesticides are a group of organic compounds with a chemical structure that contains atoms of phosphorus in the molecule.
Organophosphorus are chemical compounds born from nerve gas studies during World War II. They have been and still are widely used both as insecticides in agriculture and as pesticides on animals. The degradation of these molecules in the environment by light, bacteria and humidity is fast. In fact, most of these molecules degrade in a few weeks, other molecules degrade in several months. Some organophosphorus preparations are microencapsulated, so as to be slow-release, so that the molecule increases the duration of its effects and has less toxicity. The toxicity of organophosphorus varies greatly: a few milligrams of can cause the death of an animal, while for other animals it takes hundreds of milligrams to produce intoxication. Furthermore, the toxicity of these compounds depends on the storage mode. Many products prepared long before actual use show a more toxic action than the starting compound. In addition to the toxicity related to the type of organophosphorus and the dose in which it is taken, other factors that influence intoxication are the route of entry (oral, inhalation or skin) into the animal and the conditions and type of animal.
OPPs very known are:
Acephate, Ethion, Methidathion, Fenthion, Fenthion Sulfone, Fenthion Sulfoxide, Malathion, Parathion-methyl, Chlorpyriphos, Chlorpyriphos methyl, Coumaphos, cis-chlorfenvinphos, trans-chlorfenvinphos,Phosmet, Diazinon, Quinalphos, Phosalone, Omethoate, Dimethoate, Phenthoate, Azinphos-ethyl, Fenchlorphos, Fenitrothion, Phoxim, Triphenyl phosphate, Fenamiphos.

A.5 CARs (carbamate)

Carbamates are used as insecticides, herbicides and fungicides. They interfere with the metabolism of target insects by inhibiting acetylcholinesterase. Carbamic pesticides are preferred to organochlorines as not being very stable they can be hydrolyzed into simpler compounds having a lower toxicity.

CARs very known are:
Bendiocarb, Carbaryl, Ethiofencarb, Diethofencarb, Carbofuran,
(±)-Indocarb, Furathiocarb, Phenoxycarb, Pirimicarb, Diethofencar Mecarbam, Carbophenothion

A.6 PYRs (pyretroid)

Pyrethroids are a class of synthetic insecticides and acaricides.
They are the synthetic analogues of pyrethrins, natural constituents of the flowers of Tanacetum cinerariifolium. By virtue of the similarity of the molecule, in fact, they act in the same way as the correspondents of natural origin, however overcoming the main limitation of pyrethrins consisting in their photoleability.
In this way, much more persistent active ingredients are available.
The first pyrethroid, allethrin, was synthesized in 1949.

Due to the photoleability and therefore the short persistence, the first pyrethroids did not find use in the defense of crops but only in the civil field, mostly against flies and mosquitoes. In 1973 a new generation of pyrethroids, called photostable,
found use in agriculture.
The mechanism of action consists in alterations of the nerve transmission of the insect and the action occurs by contact or ingestion. In agriculture, they are exclusively "cover" insecticides, that is, they are unable to penetrate plants to systemically defend them from insect attacks.
Pyrethroids are widespread in anti-mosquito nebulization systems and in general in all diffusers designed to fight mosquitoes, flies and other insects.
PYRs very known are:
cis-Permethrin, trans-Permethrin, Cypermethrin isomer I, Cypermethrin isomer II, Cypermethrin isomer III, Deltamethrin, K-Cyhalothrin, cis-Fluvalinate, trans-Fluvalinate.

A.7 IGR (insect growth regulator)

They are insect growth regulators. They control the life cycle of several insects, as cockroaches, mosquitoes, ticks, fleas, flies. Insects that do not mature into adults cannot reproduce. They inhibit the metamorphosis of mature larvae, blocking their evolution towards more advanced stages with their consequent death. Furthermore, their activity on recently fertilized eggs is also relevant, because the formation of the embryo is inhibited. The IGRs are agent only in the stages of the insect as the newly fertilized embryo and the larva in the last stage
IGR very known are: Cyromazine, Pyriproxyfen, Buprofezin.

A.8 OPP/A (acaricide)

Acaricides are substances capable of inhibiting the development of mites, destroying them or repelling them. OPP/A very known are: Pirimiphos-methyl, Carbophenthion.

A.9 CAR/A (carbamate)

Carbamates are substances used as insecticides, acaricides or molluscicides. Their toxicity of varies greatly from substance to substance.
A CAR/A very known is Mecarbam.

A.10 SYN (synergist)

Synthesis gas (also called syngas) denotes a mixture of gas, essentially carbon monoxide (CO) and hydrogen (H2), with presence in different quantities of methane (CH4) and anhydride carbon dioxide (CO2). CO/H2 mixtures and nitrogen (N2) and hydrogen mixtures are indicated by different terms, for instance: air gas, water gas, crack gas, oxo gas, town gas and methanol synthesis gas.
Very known Piperonyl butoxide.

A.11 F (Fungicide)

They are substances (sulfur, inorganic copper derivatives, organic and metallorganic compounds) having the property of destroying fungi and their spores, or inhibiting their growth. They are used in agriculture and, in industry (to protect products and artifacts).

Fungicide very known are:

Flusilazole, Bupirimate, Tebuconazole Penconazole, Diclobutrazol, Trifloxystrobin, Mepronil, Quintozen, Captafol, Pyrimethanil , Fluodioxonil, Kresoxim-methyl, Cyproconazable isomer II, Imazalil, Captan, Triadimefon, Fenarimol, Prochloraz, Fenhexamid, Vinclozolin, Tolchlophos_methyl, Metalaxyl-M, Procymidone, Boscalid, Prochloraz, Azoxystrobin.

A.12 H (Herbicide)

Herbicides are substances used to control the development or destruction of weeds. The most common herbicides are synthetic chemical compounds, often xenobionts, i.e. chemically unrelated to compounds present in living beings. The environmental impact of the use of herbicides in agriculture is very relevant. Herbicides are used for civil use but even for military use.

Herbicide very known are: Simazine, Atrazine, Propazine, Diflufenican, Trifluralin, Oxyfluoren,

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