

# The Assessment of Pesticides Residues in Some Organic Cultivated and Wild-Collected Medicinal Plants in Albania

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## 1. Abstract

Pesticide residues in environment are found in soil, water and plants due to the extensive use of pesticides for agricultural purposes. The residues of pesticides in medicinal plants are of high concern as they are toxic for human life since these plants are used for medicinal purposes. The objective of current study was to estimate the presence of pesticide residues in some organic cultivated and wild-collected medicinal plants in Albania during the years 2010–2013. The determination of pesticides residues in medicinal plants was achieved by using extraction of plant material with organic solvent, clean up procedure and followed by detection with chromatography techniques. Among the detected pesticide residues in the wild-collected plants as *Malva sylvestris*, *Fragaria vesca*, *Bellis perennis* were DDT, Dimethoat, Pirimiphos-methyl, Chlorpyrifos-ethyl, Carbendazim/Benomyl, Acetamiprid and Diphenylamine. Whereas in the cultivated medicinal plants as *Calendula officinalis*, *Centaurea cyani*, *Salvia officinalis*, *Sideritis raeseri*, the most common detected pesticide residues were Dimethoat, Chlorpyrifos, Pirimiphos-methyl, DDT and Carbendazim. The presence of pesticides in medicinal plant is related to the past use of pesticides as DDT and actual use of pesticides like Dimethoat, Pirimiphos-methyl, Chlorpyrifos, Acetamiprid, etc. Therefore, the quality of medicinal plants can be evaluated through estimation of pesticides residues in medicinal plants and comparison of the obtained values with acceptable limit values.

**Key words:** medicinal plant, organic production, pesticides, residues, MRLs

## 2. Introduction

Pesticides are used in agriculture to protect agricultural plants from pests in order to increase their yields and improve their quality. Due to the past and actual extensive use of pesticides, their residues can be found in different ecosystems as in soil, sediment, water, air and plant or animal organism, as well as in their products [1, 16, 17, 18, 27]. Pesticides are characterized from persistence in environment and often are subject to long transport from their place of application through air and water [2, 15, 16, 23]. Therefore, some of pesticides residues are found in areas or in plants with no history in pesticide application [15, 16, 23].

Unfortunately, pesticides have biocide effects not only for plant pests but they are also potentially harmful to other organisms and human beings [14, 19, 25]. World Health Organization (WHO) [26] estimates pesticide poisonings occurring every year between one and five million cases, resulting in

several thousands of fatalities [24, 26]. Due to their accumulation in the food chain and potential toxic effects to human life, the European Community has established directives and maximum residue levels (MRLs) of pesticides in food originated from animal and plant products [10, 11, 12, 13, 21] which are yearly up-dated.

Nowadays, the people who are becoming more and more aware of health issues, prefer products of “organic farming” in order to reduce the health risk from pesticides. Organic farming is defined under Regulation EEC 834/07 and others regulations or directives [3, 4, 8, 9], when the pesticide residue concentration must be lower than 10 µg/ kg product for any synthetic pesticide.

Medicinal and aromatic plants (MAPs) can be subject of pesticide contamination as a result of direct application of pesticides in plant growth or transport of pesticides from other contaminated places through air and/or water [1, 17, 18, 27]. The using of medicinal and aromatic plants (MAPs) for medical

purposes and foodstuff require control of their quality. Thus, the determination of pesticide residues in medicinal and aromatic plants (MAPs) is of high concern. Furthermore, their presence/absence has become a quality parameter of great importance, especially in the organic farming [4, 20].

An extensive use of pesticides was applied in the past in Albania, mainly organophosphorus and organochlorine pesticides [22]. Actually, the use of pesticides is applied in considerable amount in intensive agricultural farms [22].

In Albania, up to now, studies dealing with the detection of pesticide residues in medicinal and aromatic plants have been lacking. This study was conducted to assess the levels of contamination by pesticides in some organic cultivated and wild-collected medicinal and aromatic plants.

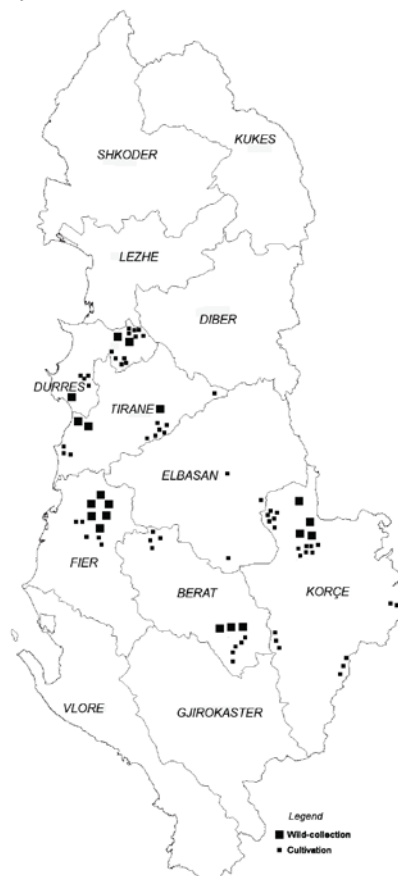
### 3. Material and methods

The determination of pesticide residues in medicinal plant was based on the multiresidues method DFG S19 which is published internationally under DIN EN 12393 (determination of pesticide residues in low-fat foods) [5, 6, 7]. Plant samples for analysis were collected randomly from the warehouses of various commercial companies either from wild collected or cultivated plant material. A total of 80 samples were collected, 19 from wild – collection and 61 from cultivation. All the products were certified organic and their origin was confirmed using the traceability system of the company. The sites of wild – collection or cultivation are shown in Figure 1. The samples were analyzed immediately to avoid possible degradation of the pesticides residues. If the analysis was not made immediately, the samples were stored in at a temperature of 4°C, protected from light.

An amount of sample up to 1 kg, was thoroughly mixed, sufficient for the analysis. Plant material was homogenized, chopped and powdered in a rotary chopper. 10 g prepared plant material was taken for the extraction procedure. 100 ml of acetone was added to the sample for the extraction step and was extracted for 15 min in an ultrasound bath, after that 30 min on a shaking device. Partitioning of the water and organic layers was made through filtering. The organic phase of samples was dewatered using sodium sulphate anhydrous ( $\text{Na}_2\text{SO}_4$ ) salt. Sodium sulphate salt was filtered from the organic layer on a folded filter in a rotary flask. Then, the organic phase was concentrated to dryness with rotary evaporator and was re-

dissolved in ethylacetate/cyclohexane (1:1, v/v). The organic phase was filtered through a membrane filter and was cleaned-up by using florisil column. The purified organic phase was concentrate to 1.5 ml with rotary evaporator and was evaporated to dryness under a gentle stream of nitrogen.

The residues of pesticides were re-dissolved in 500  $\mu\text{l}$  acetone/ethylacetate (1:1, v/v) for their analysis with GC-MS.



**Figure 1.** Sampling locations of wild collected and cultivated MAPs

### 4. Results and Discussion

Among the detected pesticide residues in the wild-collected MAPs as *Malva sylvestris*, *Fragaria vesca*, *Bellis perennis* were DDT, Dimethoat, Pirimiphos-methyl, Chlorpyrifos-methyl, Carbendazim/Benomyl, Acetamiprid, Diphenylamine (Table 1). Only 25 out of 80 samples resulted with contamination of one or several pesticides. The pesticide residues in the wild-collected MAPs could be due to the transport of pesticides from the application places to the natural growth place of the wild-collected MAPs. Also, persistence of pesticides leads to their occurrence in environment after many years of application, as can be explained the residues of DDT.

**Table 1.** Main pesticides found on wild-collected and cultivated medicinal and aromatic plants (MAPs) showing the range of values found (minimum and maximum) and limit values (mg/kg d.w.).

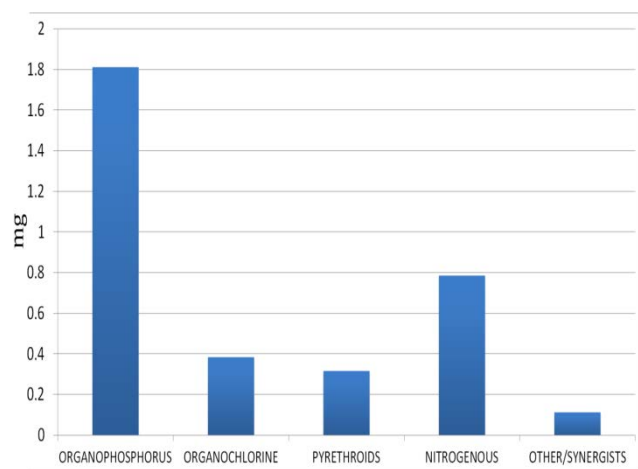
| Pesticides           | Wild-collected MAPs     |                       |                        | Cultivated medicinal MAPs    |                        |                           |                          | Limit value* |
|----------------------|-------------------------|-----------------------|------------------------|------------------------------|------------------------|---------------------------|--------------------------|--------------|
|                      | <i>Malva sylvestris</i> | <i>Fragaria vesca</i> | <i>Bellis perennis</i> | <i>Calendula officinalis</i> | <i>Centaurea cyani</i> | <i>Salvia officinalis</i> | <i>Sideritis raeseri</i> |              |
| DDT                  | ,001 - ,023             | n.d.**                | ,045                   | n.d.                         | ,014 - ,220            | ,012                      | ,053 - ,12               | 1            |
| Dimethoat            | ,024 - ,200             | ,011 - ,045           | ,013                   | ,022 - ,042                  | ,029                   | n.d.                      | n.d.                     | 0,1          |
| Pirimiphos- methyl   | n.d.                    | n.d.                  | ,012 - ,070            | ,011                         | ,005                   | n.d.                      | n.d.                     | 4            |
| Chlorpyrifos- methyl | n.d.                    | ,006 - ,240           | n.d.                   | n.d.                         | n.d.                   | n.d.                      | n.d.                     | 0,1          |
| Carbendazim          | n.d.                    | ,013                  | n.d.                   | n.d.                         | n.d.                   | ,012                      | n.d.                     | 0,1          |
| Acetamiprid          | ,016 - ,020             | ,020                  | n.d.                   | ,049                         | ,025                   | n.d.                      | n.d.                     | 0,05         |
| Diphenylamine        | ,027                    | ,024 - ,027           | n.d.                   | ,045                         | n.d.                   | n.d.                      | n.d.                     | 0,1          |
| Methomyl             | n.d.                    | n.d.                  | n.d.                   | ,020 - ,160                  | ,08                    | n.d.                      | n.d.                     | 0,1          |
| Chlorpyrifos         | n.d.                    | n.d.                  | ,032 - ,1              | ,022 - ,099                  | ,031                   | ,012 - ,026               | n.d.                     | 0,2          |

\*Limit value of pesticides for organic product is 0,001 mg/kg d.w;

\*\* Not detected

Whereas in the cultivated MAPs as *Calendula officinalis*, *Centaurea cyani*, *Salvia officinalis*, *Sideritis raeseri*, the most common detected pesticide residues were Dimethoat, Methomyl, Chlorpyrifos, Pirimiphos-methyl, DDT and Carbendazim (Table 1). The presence of pesticides residues in the cultivated MAPs could be explained with their occurrence in agricultural soil because of past application in other cultivated agricultural plants and their persistence in soil environment.

The obtained results of pesticides residues in MAPs showed that the values were almost lower than MLRs (Maximum Residue Levels) set up for common production of MAPs [11, 13], but these values were higher than limit value of pesticide residues for organic products, therefore these product cannot be trade as organic products.

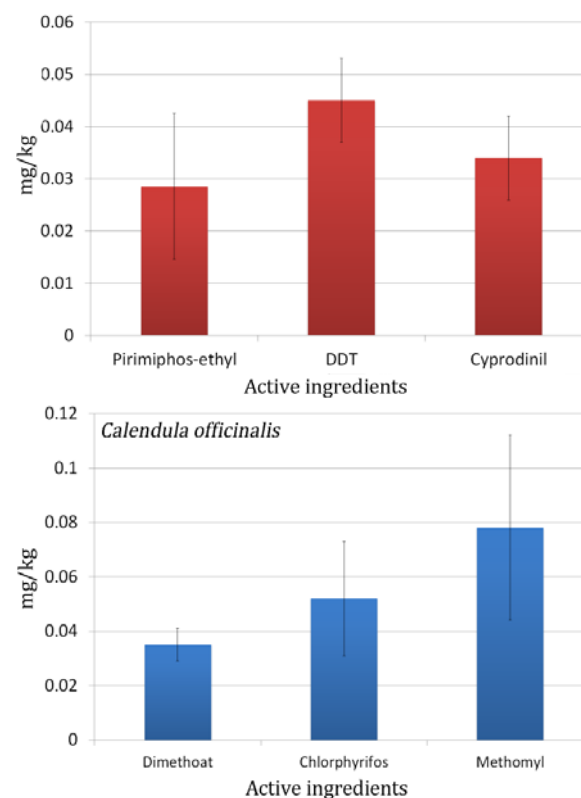


**Figure 2.** Pesticides groups by total weight of samples. Active ingredients found belong to these five large groups.

Among the groups of pesticides, the organophosphorous were the most common, followed by nitrogenous ones. Organochlorine and pyrethroids

were found in few cases (Figure 2 and Figure 3). Others, like 2,4-D were only found in one case. Dimethoat is found frequently in most of the samples. Its frequent presence could be due to its large use in field crops, especially maize.

Several insecticides found in cultivated MAPs samples were found close of fruit orchards, especially apple orchards in Korça area, when has an extensive use of pesticides.



**Figure 3.** Main pesticides found in two species, daisy (*Bellis perennis*), a wild – collected species (top) and marigold (*Calendula officinalis*), a cultivated species (bottom). Values represent the averages with error bars.

The particular case of DDT found in samples of both cultivated and wild collected is of particular concern considering its banned since 1990. It is an organochlorine pesticide with a long persistence in the soils used for actual organic cultivation of collected medicinal plants. Its persistence in environment leads to soil, water and air contamination therefore cultivated or wild plants can be contaminated.

## 5. Conclusions

The results of this study showed presence of pesticide residues in both cultivated and wild collected MAPs.

The presence of pesticides in MAPs is related to the past use of pesticides as DDT and actual use of pesticides like Dimethoat, Pirimiphos-methyl, Chlorpyrifos-methyl, Acetamiprid, etc.

The quality of medicinal plants can be evaluated through estimation of pesticides residues in medicinal plants and comparison of the obtained values with acceptable limit values or MLRs.

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