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ISOTOPIC COMPOSITION INFLUENCE OF IRRIGATION WATER ON SOME AROMATIC PLANTS

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ABSTRACT. In this paper, three species of aromatic herbs (*Petroselinum crispum*, *Ocimum basilicum*, and *Origanum vulgare)* were investigated, by mean of stable isotopes (deuterium, oxygen and carbon) and total phenol content, in order to study the influence of irrigation water. The results revealed the fact that there is a strong correlation between the isotopic compositions of irrigation water (deuterium enriched water or tap water) and δD, $\delta^{18}O$, $\delta^{13}C$ values and total polyphenol content of studied plants. Multielemental content was subjected to analysis of variance (ANOVA). It was found that *Ocimum basilicum* plant was characterized by a higher level of As and Co as compared to other two species, while *Origanum vulgare* had the highest content of Cu. Also, a correlation between the irrigation water content and toxic metal uptake had shown that the Pb concentration is influenced by the water isotopic composition.

Keywords: *irrigation water, aromatic herbs, stable isotopes, total polyphenols, chemometrics.*

INTRODUCTION

Commonly found in edible as well as inedible plants, polyphenolic compounds have been reported to have numerous biological effects, such as antioxidant activity [1]. Herbs are used in many domains, including medicine, nutrition, flavoring, beverages, dyeing, repellents, fragrances, cosmetics [2]. Numerous species have been identified as having medicinal properties as well as

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a valuable impact on health, e.g. antioxidant activity, digestive stimulation action, anti-inflammatory, antimicrobial, hypolipidemic, antimutagenic effects and anticarcinogenic potential [3-4]. Raw extracts of herbs and spices, and other plant materials abundant in phenolics provide a high concern in the food industry due to the fact that they decelerate oxidative degradation of lipids and therefore enhance the quality and nutritional value of food.

Recently, medicinal plants have drawn an interest against oxidative stress. The existence of different natural antioxidants in herbs is known. Phenolic compounds, like flavonoids, can give away oxygen to the damaging free radicals to avoid the oxidative damage at the first initiation step. They are not roaming radicals, but constraining their genesis [5]. Parsley (*Petroselinum crispum*) is a widely known culinary plant and medicinal herb used in Europe since ancient times. Many biological activities are associated to its leaf and seed, and it is easy to grow. Consuming the leaf is beneficial to cardiovascular and diabetic diseases due to its anti-hyperglycemic, anti-inflammatory and anti-hyperlipidimic properties [6]. The conveniences are primarily related to the flavonoids and their antioxidant activity but the synergistic effect of all chemicals is important in the therapy [7-9]. Flavonoids are a varied group of polyphenolic compounds with diversified health effects.

On the other hand, it is of major interest to establish the levels of some metallic elements in common used plants, because at elevated levels, these metals could be toxic [10-11]. Determination of metals in aromatic plants is a part of quality control to establish their purity, safety and efficacy according to the World Health Organization (WHO). Although several attempts have been reported for determination of elemental content of aromatic plants from all over the world, but reports of aromatic plants irrigated with different type water (especially, tropical water) are scanty.

In this preliminary study three species of aromatic herbs, commonly used in cooking, were chosen as follows: *Petroselinum crispum, Ocimum basilicum* and *Origanum vulgare.*

Petroselinum crispum variety moss curled 2 (curly parsley) and *Petroselinum crispum classic* (parsley) – Parsley, including both leaf and root type, is a Mediterranean plant, member of the *Umbelliferae* family. *Ocimum basilicum* (basil), originating in tropical Asia is a classic culinary herb of Mediterranean and Southeast Asian cuisines, from *Lamiaceae* family. Many cultivars exist, selected for fragrance, flavor, color and size. *Origanum vulgare* (oregano) is an herb of the family *Lamiaceae*, too. Oregano is native to the mountainous parts of Mediterranean region and warm-temperate regions of Eurasia. All these plants are widely cultivated commercially and in kitchen gardens, having culinary and therapeutically properties.

The aim of this paper was the study of the irrigation water influence, having different isotopic content, on the isotopic composition (deuterium, oxygen and carbon), total polyphenol, essential nutrients, heavy metals and some rare earth content of the investigated aromatic herbs.

Previously studies regarding the influence of water isotopic content on living organisms were mainly related to the use of depleted water in cancer treatment. It was observed, that the use of deuterium depleted water in cancer treatment indicated a decrease of tumor sizes [12-13]. Also, the influence of depleted water and/or enriched water in studies regarding the plant growth indicated a direct relationship between isotopic composition of irrigated water and plant metabolic process [14-16].

RESULTS AND DISCUSSION

Stable isotope analysis

The δD and $\delta^{18}O$ values of leaf water were enriched in deuterium and oxygen-18 relative to the isotopic composition of irrigation water for both groups of aromatic herbs, (Table 1). Generally, the deuterium source for plants is irrigation water. This is taken through roots and moves upward in the xylem to the leaves. The transpiration process from plant leaves leads the fractionation of xylem water. As a result, leaf water is often considerably enriched in deuterium [20].

Table 1. Isotopic compositions of plants samples

Group no.	Plant leaf	$\delta D_{irrigation\ water}$ (‰)	$\delta^{18}O_{irrigation\ water}$ (‰)	δD (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)
I	*Petroselinum crispum* classic	-16.3	-1.2	1.5	11.1	-32.8
	Petroselinum crispum variety moss curled			1.1	10.8	-33.4
	Ocimum basilicum			5.3	13.8	-35.9
	Origanum vulgare			-1.5	6.3	-34.6
II	*Petroselinum crispum* classic	-70.6	-10.2	-22.0	2.3	-32.2
	Petroselinum crispum variety moss curled			-22.6	2.1	-33.2
	Ocimum basilicum			-13.2	5.9	-34.9
	Origanum vulgare			-25.1	1.3	-34.4

The differences observed between the two parsley varieties (*Petroselinum crispum classic* and *Petroselinum crispum* variety moss curled), within the same group, fit in experimental errors. Instead, isotopic differences were observed between the plants watered with water having different isotopic compositions, by nearly 20 ‰ for δD and 8 ‰ for $\delta^{18}O$, due to the used irrigation water.

The most important isotopic difference, caused by the irrigation water, was observed for the *Origanum vulgare* of nearly 23 ‰ for δD, and 8 ‰ for $\delta^{18}O$ for *Ocimum basilicum*, and the smallest isotopic difference was about 18 ‰ in the case of δD, for *Ocimum basilicum*, and of 5 ‰ in terms of $\delta^{18}O$ for *Origanum vulgare*.

The differences between the δD and $\delta^{18}O$ isotopic values of the irrigation water and the water extracted from the studied plants leaves are very well highlighted in both groups. Compared to the irrigation water, the most significant difference in the heavy isotopes of oxygen and hydrogen was recorded in group II for the *Ocimum basilicum* leaf, the isotopic enrichment being up to 57.4 ‰ for δD, and 12.7 ‰ for $\delta^{18}O$. For the first group, this enrichment of leaf water is about 21.6 ‰ for δD and 15 ‰ for $\delta^{18}O$. The smallest difference was recorded for the *Origanum vulgare* leaf in group II, having values of 45.5 ‰ for δD and 11.5 ‰ for $\delta^{18}O$, and 14.8 ‰ for δD and 7.5‰ for $\delta^{18}O$ in group I, respectively. These differences of the δD and $\delta^{18}O$ isotopic values between the irrigation water and the water extracted from the leaves are caused most likely by the morphology of the leaf.

The isotopic composition of carbon is not significantly influenced by the isotopic composition of the irrigation water, but is directly related to the studied plant species. Thus, the differences recorded for the same type of plant belonging to group I or II, the maximum difference recorded was 1 ‰, while between different species (parsley and basil) the difference may reach 3 ‰. This fact confirms that $\delta^{13}C$ is a better indicator for plant species, reflecting much less the isotopic composition of the irrigation water.

Total polyphenols analysis

Total polyphenols content from the studied plants was analyzed by the conventional spectrophotometric Folin-Ciocalteu method. The content in polyphenolic compounds was proportional with the intensity of the blue color. The quantities of the total polyphenols (Figure 1), expressed as mg gallic acid/g fresh weight (FW) was calculated using the linear equation of the standard calibration curve:

$$y = 3.296\,x + 0.0137\ (R^2 = 0.9987) \qquad (1).$$

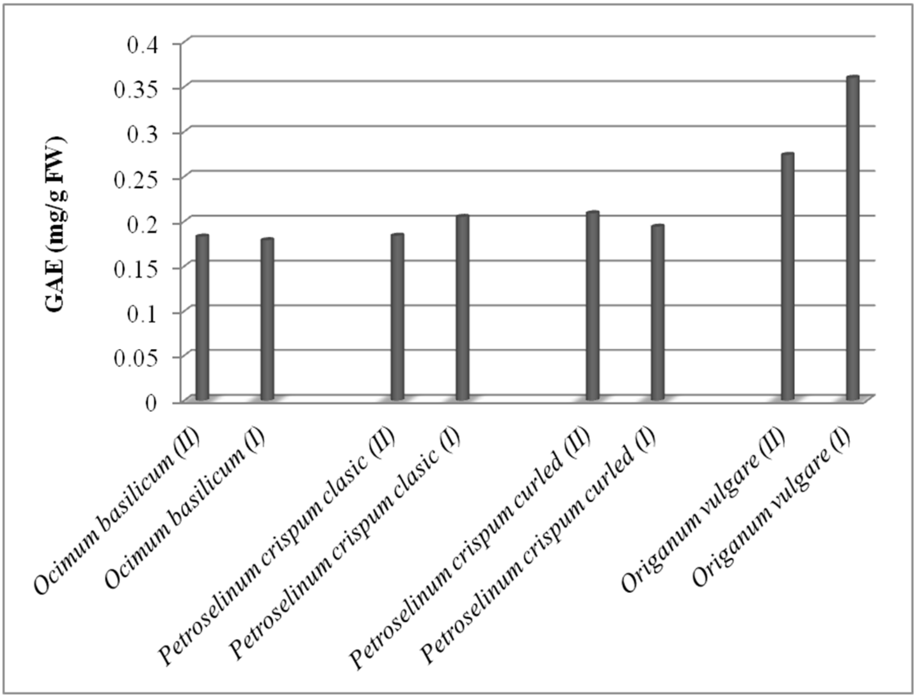

Figure 1. Total polyphenols content expressed as gallic acid equivalents in the studied plants.

It was observed that the amount of total polyphenols increases in some plants when they are watered with tropical water, while in other plants this quantity decreases. Thus, the amount of the total polyphenols increases in parsley and oregano and in the case of basil and curly parsley the amount of total polyphenols decreases in plant watered with tropical water compared with control plants group. The amount of polyphenols in irrigated plants with tropical water increased by 11.41 % in parsley, with 31.39 % in oregano, while in basil and curly parsley decreased by 2.02 %, respectively 1.95 % compared to control plants group.

ICP-MS analysis

The concentrations of some essential plant nutrients (P, K, Mg, Na, Fe, Mn, Cu, Zn) and toxic heavy metals (Co, Cd, Cr, Ni, Pb, As, Al, In) and some rare earth elements of plant species under investigation are presented in Table 2, 3 and 4, respectively. The obtained results are presented as mean ± standard deviation.

Table 2. The concentrations of nutrients in the investigated plants

Nutrient element [mg/kg]	*Petroselinum crispum* classic	*Petroselinum crispum* variety moss curled 2	*Ocimum basilicum*	*Origanum vulgare*
	Group I			
Na	263.58±10.33	109.05±2.78	128.70±3.54	343.90±22.54
Mg	2689.96±95.63	919.13±32.25	2080.75±59.44	1657.03±58.09
P	6156.75±161.94	3586.04±72.89	3351.51±236.96	4599.10±163.30
K	31458.43±1648.80	33792.30±1724.57	38572.32±1368.98	16187.87±527.26
Mn	67.31±1.76	57.40±0.79	36.55±2.52	20.78±1.60
Fe	55.10±1.54	74.78±4.31	73.09±8.12	61.69±10.30
Cu	7.39±0.11	8.13±0.39	9.90±0.68	18.22±1.74
Zn	90.34±2.07	52.20±1.23	26.60±1.97	79.19±6.19
	Group II			
Na	286.85±9.54	117.35±11.60	14.80±0.21	24.39±1.79
Mg	1482.84±37.12	1398.83±39.96	1963.78±69.82	1478.55±48.13
P	858.86±24.50	5132.43±436.91	2663.12±70.05	5415.18±138.26
K	30655.50±967.73	34868.24±1552.47	32172.69±1460.95	20847.17±662.66
Mn	57.57±0.85	69.42±6.56	42.59±1.38	20.96±2.41
Fe	61.53±1.92	69.42±7.54	45.04±2.45	45.74±6.38
Cu	7.67±0.07	7.54±0.48	10.04±0.06	14.81±1.39
Zn	94.77±1.28	77.72±7.04	47.01±0.60	79.12±5.50

Table 3. The concentrations of toxic elements [mg/kg] in the investigated plants

Toxic elements	*Petroselinum crispum* classic	*Petroselinum crispum* variety moss curled 2	*Ocimum basilicum*	*Origanum vulgare*
	Group I			
Co	0.487±0.113	0.805±0.372	2.350±0.383	1.489±0.331
Cd	1.668±0.085	0.198±0.009	0.091±0.014	0.045±0.007
Cr	1.018±0.047	0.722±0.057	0.448±0.045	0.035±0.024
Ni	1.712±0.159	0.864±0.038	0.489±0.028	0.593±0.153
Pb	0.183±0.017	0.087±0.005	0.212±0.016	0.153±0.014
As	0.112±0.032	0.042±0.043	0.739±0.077	0.178±0.035
Al	9.410±0.759	14.841±1.691	8.287±0.945	30.063±2.264
In	0.0047±0.0005	0.0024±0.0013	0.0008±0.0003	0.0012±0.0014

	Group II			
Co	0.916±0.257	1.326±0.203	1.935±0.456	1.129±0.047
Cd	0.630±0.017	0.119±0.006	0.042±0.011	0.024±0.002
Cr	0.745±0.126	0.974±0.070	0.422±0.062	0.251±0.072
Ni	1.366±0.093	0.998±0.038	0.377±0.081	0.436±0.134
Pb	0.060±0.002	0.092±0.015	0.109±0.010	0.055±0.004
As	0.156±0.015	0.048±0.009	0.829±0.068	0.074±0.013
Al	9.539±0.376	4.933±0.489	4.744±0.223	6.367±0.385
In	0.0038±0.0013	0.0007±0.0003	0.0011±0.0005	0.0005±0.0000

Table 4. The concentrations of rare earth elements [mg/kg] in the investigated plants

Rare earth elements	*Petroselinum crispum* classic	*Petroselinum crispum* variety moss curled 2	*Ocimum basilicum*	*Origanum vulgare*
	Group I			
Y	0.0579±0.0444	0.0163±0.0026	0.0056±0.0008	0.0308±0.0037
La	0.0850±0.0031	0.0109±0.0025	0.0919±0.0204	0.0112±0.0020
Ce	0.1672±0.0188	0.0114±0.0013	0.1627±0.0073	0.0073±0.0036
Pr	0.0173±0.0047	0.0016±0.0003	0.0161±0.0014	0.0030±0.0007
Sm	0.0003±0.0005	0.0022±0.0031	ND	0.0003±0.0005
Eu	0.0071±0.0013	0.0025±0.0011	0.0020±0.0009	0.0012±0.0009
Gd	0.0017±0.0015	0.0027±0.0023	0.0013±0.0023	*ND
Dy	ND	ND	0.0003±0.0006	ND
Ho	ND	ND	ND	ND
Yb	ND	ND	ND	ND
	Group II			
Y	0.1193±0.0899	0.0745±0.0942	0.0103±0.0060	0.0090±0.0008
La	0.0152±0.0021	0.0160±0.0017	0.0151±0.0054	0.0031±0.0020
Ce	0.0292±0.0059	0.0217±0.0045	0.0112±0.0058	0.0005±0.0086
Pr	0.0032±0.0003	0.0028±0.0015	0.0011±0.0007	0.0008±0.0008
Sm	ND	ND	0.0008±0.0005	ND
Eu	0.0059±0.0011	0.0049±0.0015	0.0014±0.0008	ND
Gd	0.0004±0.0008	ND	ND	ND
Dy	0.0003±0.0005	ND	ND	ND
Ho	0.0003±0.0003	ND	ND	ND
Yb	0.0004±0.0008	ND	ND	ND

*ND – not detectable

The essential primary plant nutrients (P, K, Mg, and Na) are important for plant production and vital for growth and development of all living bodies. Some metals (such as Cr, Mn, Zn, Fe, Co, Cu, Ni) are essentials plant nutrients, but, they are phytotoxic at higher concentrations. Heavy metals are present in aromatic plants at different concentrations and the uptake of these by plants is influenced by various factors (i.e. type of plant, soil nature, climate, etc).

The biogeochemical behavior of rare earth elements (REEs) is not fully understood. Until recently, REEs were not characterized either as essential plant nutrients or as environmentally hazardous metals [21]. However, the last experimental studies demonstrated toxic effects of REEs for plants [22-23].

The obtained results indicated that the concentration of elements in investigated aromatic plants depends on the species of plant and irrigated water. For efficient processing of experimental data ANOVA test was employed.

For the first case, the matrix employed for statistical analysis was formed by all analyzed multielements in eight samples. For evidencing the elements that can separate the two investigated groups, according to irrigation water, ANOVA was applied. Only one element, namely Pb ($p < 0.05$) was found to be a good discriminator for these groups. It can be concluded that tropical water may facilitate the Pb intake by all analyzed herbs, except curly parsley, where the concentration is smaller.

For the second purpose, ANOVA was applied on the same matrix, this time having as independent variable, the species, and means of four groups were compared. The most important elements that can distinguish investigated aromatic group plants are: K (0.012), Cr (0.022), Mn (0.005), Co (0.037), Ni (0.005), Cu (0.005), Zn (0.034), As (0.001), In (0.027), Eu (0.018). *Ocimum basilicum* plant was characterized by the highest levels of As and Co, compared to other three plant types, while *Origanum vulgare* had the highest content of Cu and the lowest content of K. Other important parameters that can differentiate the above mentioned species was represented by total phenolic content ($p = 0.038$). Higher values for this parameter may be found in *Origanum vulgare* samples compared to *Ocimum basilicum* plant. The *Petroselinum crispum* classic had a high content of Ni, Zn, In and Eu, respectively. The highest concentrations for Cr and Mn were obtained for the *Petroselinum crispum* group, compared to *Origanum vulgare samples*.

CONCLUSIONS

This paper presents original data concerning the leaf isotopic content in two aromatic herbs groups, irrigated with water having two different isotopic compositions. The δD value of extracted leaf water for both groups was positively related to the δD value of irrigation water, and all leaf samples were enriched in deuterium and oxygen-18 relative to irrigation water.

Another important observation is that the value of the isotopic composition of the input water contributes to the modification of the content of total polyphenols, differently for the studied plants. So, for the parsley and oregano irrigated with water with isotopic composition specific to the tropical areas, the content of total polyphenols rises and for basil and curly parsley the content of total polyphenols decreases compared to the plants from the reference lot.

These preliminary results show that, by modifying the isotopic composition of the irrigation water, one can obtain plants with a larger contribution of total polyphenols, beneficial to the human body. Also, it is of interest that studies like these should be conducted on more species of herbs and other plants.

The isotopic content of irrigation water may have influence on Pb content assimilation by all studied plants. Regarding the comparison among investigated species, ANOVA highlighted the elements that differentiate the species. It was observed that parsley is characterized by the highest concentration of Ni, Zn, In and Eu. For both, parsley and curly parsley samples, the highest levels for Cr and Mn were founded as compared to oregano samples.

EXPERIMENTAL SECTION

Sampling and stable isotope analysis

Three species of aromatic herbs, consisting of 8 samples, were grown during twelve weeks. The samples were divided into two groups, depending on the irrigation water. Thus, the plants from first group (I) were watered with deuterium - enriched water (tropical water). This water has a similar isotopic composition of rainwater in the tropics (δD = -16.3 ‰, $\delta^{18}O$ = -1.2 ‰). The second group (II), for control, was irrigated with drinking water from the public network (δD = -70.6 ‰, $\delta^{18}O$ = -10.2 ‰). In this experiment, for both plant groups, the same soil type (commercial soil) was used.

Water from plant parts (leaf) was extracted without any isotopic fractionation by cryogenic distillation. The $\delta^{18}O$ and δD values in water extracted from leaf were determined by using a liquid-water isotope analyzer (DLT – 100, Los Gatos Research). For $\delta^{13}C$ analysis, the plant samples were dried at 55 ^{0}C. Carbon isotope analyses were performed using a Delta V Advantage mass spectrometer (Thermo Scientific) operated in dual inlet mode [17-18]

The stable isotope values were express in delta (δ) notation:

$$\delta X = \left(\frac{R_{sample}}{R_{std}} - 1\right) \times 1000 \qquad (2)$$

where X is the heavy isotope (D, ^{13}C, ^{18}O), δ is in parts per thousand (‰) deviation relative to a standard gas, and R_{sample} and $R_{standard}$ are the ratios of the heavy to the light isotopes for sample and standard, respectively. The isotopic compositions were expressed relative to standard V-SMOW for D and ^{18}O measurements, and V-PDB for ^{13}C measurements, respectively. The limit of uncertainty of the isotopic analysis was ± 0.2 ‰ for $\delta^{13}C$ and $\delta^{18}O$ and ± 1.0 ‰ for δD.

Preparation of plant extracts and determination of total polyphenols content

One gram of fresh leaves was ground and fin pulverized by adding liquid nitrogen. 1 g of the fresh plant material with 2 mL 60 % ethanol was subjected to sonication for 30 minutes using an ultrasound device (Elmasonic S 15H, 37 kHz). After extraction, the sample was filtered by nylon syringe filter (0.45 µm), after which, the final volume was adjusted to 2 mL with the same solvent mixture used for extraction. Each extract was performed in three parallel samples.

The Folin-Ciocalteu reagent was used for total polyphenols content determination, according to the Slinkard method [19]. According to this method 5 mL of distilled water and 0.5 mL Folin-Ciocalteu reagent were added to 1 mL of extract. After 3 min, 1.5 mL of sodium carbonate (5 g/L) was added to the mixture and distilled water up to 10 mL. The sample was kept in a water bath at 50 °C for 16 min and after cooling, the absorbance was read at 765 nm against distilled water as the blank, using a Shimadzu UV-160A spectrophotometer (Kyoto, Japan). The total polyphenols were expressed as mg/g gallic acid equivalents, concentration of gallic acid ranging from 0.001 to 0.40 mg/mL. All measurements were taken in triplicates and mean values were calculated.

Determination of essential plant nutrients and heavy metals concentrations

For ICP-MS method from each dried samples, 0.1 g was weighed and transferred to a Teflon receptacle. Afterward, 2.5 mL of concentrated ultrapure nitric acid (65 %) was added and were subjected to mineralization by oven at 180 °C for 12 hours. Then clear solutions were transferred quantitatively into the volumetric flasks (50 mL) and made up with ultrapure water. Plant nutrient elements and heavy metal concentrations were determined with ELAN DRC (e) instrument. Calibration standards solutions and internal standards were prepared by successive dilution of a high-purity ICP multielement calibration standard 10 μg/mL of Al, As, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs Cu, Fe, Ga, In, K, Li, Mg, Mn, Ni, Pb, Rb, Se, Na, Ag, Sr, Ti, V, U, Zn (Perkin Elmer Life and Analytical Sciences).

Statistical approach

Many analytical techniques provide large amount of experimental data, which might became difficult to interpret or to extract the most meaningful conclusions. In this case, ANOVA was applied on multielemental concentrations obtained from ICP-MS, having two important purposes: i) to evidence elements that may distinguish two plants groups weathered with water having different isotopic content and ii) to highlight the elements that can differentiate the four investigated plant types (curly parsley, parsley, basil, oregano). All statistical analysis was made using specific software.

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