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CONTENT OF SELECTED MINERAL COMPOUNDS, NITRATES III AND V, AND OXALATES IN SPINACH *(SPINACIA OLERACEA L.)* AND NEW ZEALAND SPINACH *(TETRAGONIA EXPANSA MURR.)* FROM SPRING AND AUTUMN GROWING SEASONS

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ABSTRACT

The alkalinity of ash, content of selected mineral compounds, nitrates III and V, and soluble and total oxalates were determined in spinach and New Zealand spinach grown in the spring or autumn period in the aspect of using these crops as a raw material for the food processing industry. In 100 g fresh weight of spinach the alkalinity of ash was 17.4-18.9 cm^3 1 M HCL. As for the analysed factors, the following values were determined: potassium 628-663 mg, phosphorus 34-59 mg, calcium 109-340 mg, magnesium 68-78 mg, sodium

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24-30 mg, iron 4, mg, nitrates 11.0-165.0 mg, nitrites 0.06-0.08 mg, soluble oxalates 347-563 mg, and total oxalates 370-938 mg. The mean alkalinity of ash in fresh weight of New Zealand spinach was 12% lower than in spinach. Also the content of potassium was 41% lower, of phosphorus 49%, of calcium 52%, of magnesium 38%, of iron 9%, of soluble oxalates 32%, of total oxalates 40%, and of nitrites 53%. The content of sodium was 222% and of nitrates 92% higher. In the two species changes in the level of magnesium, oxalates, and nitrates, in spinach of phosphorus, calcium, and nitrites, and in New Zealand spinach of potassium, sodium, and iron depended on the date of harvest.

Key words: spinach, New Zealand spinach, date of harvest, alkalinity of ash, minerals, nitrates, nitrites, oxalates

INTRODUCTION

The high biological value of leafy vegetables depends on the pronounced content of mineral compounds, especially magnesium and iron. In general these crops also contain significant amounts of beta-carotene, folic acid, and dietary fibre [3, 8, 10, 12, 15, 22, 24, 25, 26].

Of this group of vegetables most are seasonal crops with a limited value for processing. Spinach is particularly valuable owing not only to its very rich chemical composition but also to the prolonged harvest. In countries of the temperate zone spinach may be harvested for direct consumption from April to June and usually from mid-September to the end of October [6, 9]. This species is also highly valued in the processing industry and, owing to the good preservation of its sensoric qualities, it is commonly used for freezing [6, 13]. Similar values of sensory traits and utility for technological processing are characteristic of New Zealand spinach. In the temperate zone in contrast to spinach, New Zealand spinach may be grown for harvest in the period June-September, and therefore may supplement the former species on the market during hot weather. Also should be stressed that it gives very high and constant yields [8, 11]. On the other hand, contrary to the abundant data on the chemical composition of spinach, little information is available concerning the composition of New Zealand spinach.

The aim of the present work was to evaluate the content of selected mineral compounds, nitrates III and V, and oxalates in spinach and New Zealand spinach harvested in the spring and autumn seasons.

MATERIALS AND METHODS

The investigated material consisted of leaves of the spinach cultivar Markiza from the Plantico Golebiew plant breeding firm and of leaves with shoots of New Zealand spinach reproduced at the Dutch firm Topstar. The two species were grown in 1998 in the southwestern outskirts of the city of Cracow in brown soil originating from loess formations of the mechanical composition of silt loam, in the second year after farmyard manure. Everlasting pea was grown in the year preceding the spring cultivation of spinach. The autumn cultivation was preceded by broad bean harvested at the stage of milk maturity.

Mineral fertilization at the level of P_2O_5 60 kg ha^{-1} and K_2O 100 kg ha^{-1} was based on analyses of soil fertility and expected yields. Besides, nitrogen at a dose of 40 kg ha^{-1} was applied before sowing or in the case of New Zealand spinach before transplanting. As side-dressing doses of 20 kg N ha^{-1} were used. Additional doses of nitrogen were 30 kg ha^{-1} after each harvest of New Zealand spinach.

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The aim of the work was to obtain the investigated material in the shortest possible time span. New Zealand spinach was therefore grown both from transplants, yielding the material for analyses in spring, and from seeding to ensure the material in autumn. The plan was carried out fairly successfully, the yields of spinach and New Zealand spinach being obtained in spring on 1st June and 5th June, and in autumn on 23rd September and 25th September, respectively.

In the plots of the two species the cultivation measures were limited to mechanical weeding, side dressing with nitrogen in the form of ammonium nitrate, thinning to leave a suitable number of plants in an area unit, and if necessary applying sprinkler irrigation. Owing to the good sanitary condition of the plantation no protective measures against pests and diseases were used.

The edible parts of plants, i.e. leaves with petioles 4-5 cm in length of spinach and shoots 13-15 cm in length with leaves of New Zealand spinach were used in estimating their chemical composition. Chemical analyses were carried out directly after harvest. The evaluation was conducted in four replications, permitting statistical verification of the results. In determining the content of various mineral components the samples were mineralised in nitric and perchloric acids mixed at a 3:1 ratio. The analysed material was placed in test-tubes of the Tecator Kjeltec Plus II mineralization set and wetted with the acid mixture. The samples treated with acids were left until the next day and then subjected to full mineralization. The mineralized samples were diluted with distilled water and filtered to dry flasks. The content of potassium, calcium, magnesium, sodium, and iron in the solutions was determined using a Philips PU 9100X atomic absorption spectrophotometer. In the case of the remaining determinants the following methods were applied: ash alkalinity AOAC [1], 32.028, phosphorus AOAC [1], 3.098-3.100, total oxalates AOAC [1], 32.044, water-soluble oxalates Skorowska-Zieleniewska [20], and nitrates and nitrites ISO/6635 [7].

The results obtained were statistically verified using the Snedecor F and Student t tests, the least significant differences being calculated at the probability level $p=0.01$. Since in the literature the quoted results are calculated either in fresh or in dry matter, the obtained results were also referred both to fresh and dry weight.

RESULTS

In the group of vegetable crops leaf vegetables are among the most important sources of mineral compounds. Depending on the type of parsley, in dry matter of its leaves ash constituents amount to 12,0-14,8% [12], in celery 16,3% [26], in spinach 24,6% [26], and in New Zealand spinach even to 25,0% [11]. Unfortunately, these vegetables also contain nitrates undesirable in the diet [4, 6, 8, 12, 15, 17, 22, 25], and some of them also a considerable content of oxalates [4, 6, 22, 25, 26, 28].

Apart from genetic factors, the chemical composition of vegetables, including the content of compounds both beneficial and undesirable in the diet, is significantly affected by agrotechnical measures and especially by the pattern of weather conditions [6, 15, 16, 17, 22, 23, 25]. According to Pijanowski et al. [18], climatic conditions may effect changes in the chemical composition of horticultural plants measured by percentage deviation from the average content from –50 to +175%. In 1998 the weather conditions were typical of the region of spinach growing with regard to temperature: their sum from April to September was 2834^{o}C with a total rainfall of 419 cm. Rainfall was fairly small but it was uniformly

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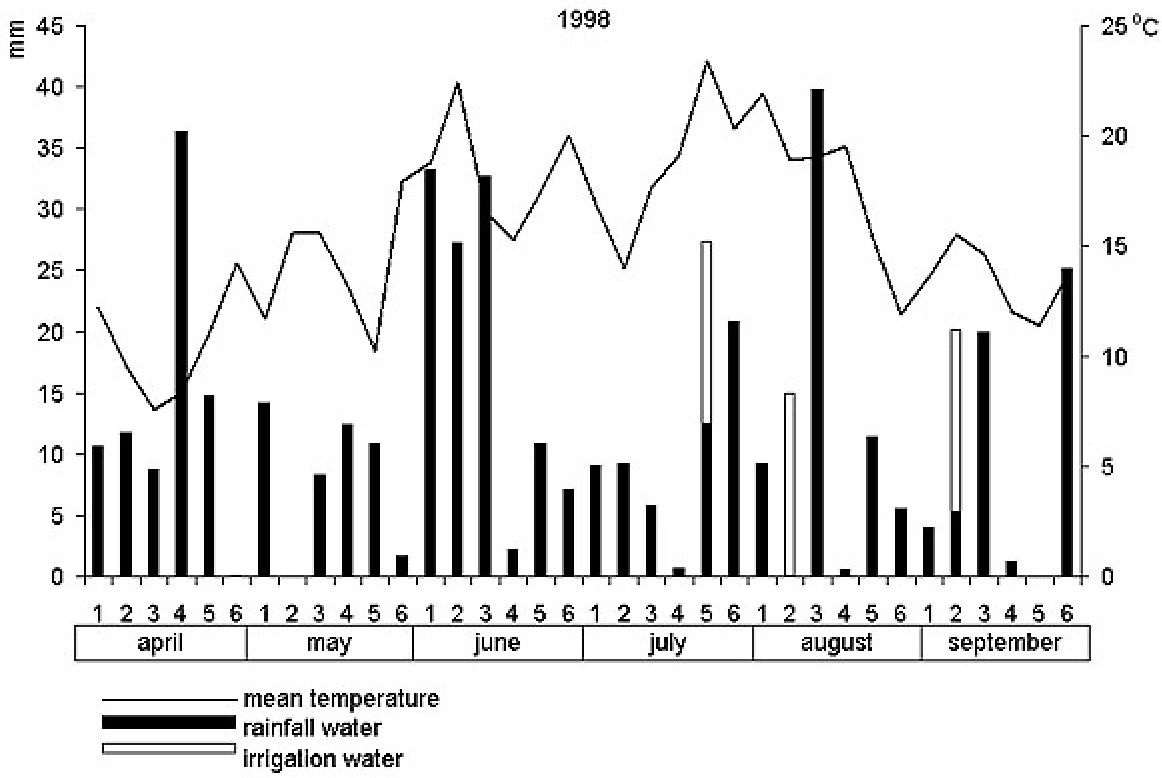
distributed and with 15 mm sprinkler irrigation applied three times no water deficiency was observed throughout the growing season. More precise information concerning the conditions of plant growth may be obtained from the average level of temperatures preceding each harvest than from the sum of temperatures in the whole period of growth (Fig.1). In spring from the emergence of spinach to its harvest (10th April - 1st June) the mean temperature was 12.7 °C. In the case of New Zealand spinach, from its transplanting to harvest (4th May - 5th June), the average temperature was 15.0 °C. In autumn from emergence to harvest of spinach (5th August - 23rd September) the average temperature reached 15.3 °C and from the penultimate cutting of New Zealand spinach to the harvest (17th August – 25th September) 14.1°C. The above data show that the thermal conditions were beneficial for spinach. For New Zealand spinach they were at least adequate, as evidenced by the height of the obtained yields [9].

Figure 1. Mean temperatures and total rainfall in the period of growth of spinach and New Zeland spinach (in peands)



From the point of view of dietetics, the alkalinity of ash is a very important subject. In 100 g fresh weight of the two investigated species the alkalinity ranged from 15.8-18.9 cm^3 1M HCl (Table 1). In spinach it was about 9% higher in the spring crop than in that from the autumn harvest. In New Zealand spinach no statistically significant differences were found between the two growing periods. On average, in fresh weight of spinach the alkalinity was 13% higher than in New Zealand spinach. In dry weight distinctly better parameters of New Zealand spinach were assessed, the differences in its favour reaching 63%. According to Pijanowski et al. [18], of 12 fruit and 14 vegetable species evaluated by Mc Cance and Windowson none was equal to spinach with regard to the alkalinity of ash. The only exception were potatoes with a level of 10 cm^3 1 M HCl/100 g. Kmiecik and Lisiewska [12] reported that the leaf blades of Hamburg and leaf-type parsley reached an average alkalinity level approximating to 20 cm^3 1M HCl from 10 harvests.

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Table 1. Alkalinity of ash and level of selected minerals in usable parts of spinach and New Zealand spinach

Index	Unit	Spinach		New Zealand spinach		LSD p=0.01	Mean for	
		spring	autumn	spring	autumn		spinach	New Zealand spinach
Alkalinity of ash	cm^3 1 M HCl/100 g f.w.	18.9	17.4	15.8	16.3	1.69	18.2	16.1
	cm^3 1 M HCl/100 g d.w.	176	197	300	307	26.0	186	304
Potassium	mg/100 g f.w.	628	663	484	272	57.4	646	378
	g/100 g d.w.	5.84	7.50	9.20	5.12	0.720	6.67	7.16
Phosphorus	mg/100 g f.w.	34	59	23	24	5.4	47	24
	g/100 g d.w.	0.32	0.67	0.44	0.45	0.074	0.50	0.45
Calcium	mg/100 g f.w.	340	109	107	106	74.5	225	107
	g/100 g d.w.	3.16	1.23	2.03	2.00	0.716	2.20	2.02
Magnesium	mg/100 g f.w.	68	78	33	57	6.0	73	45
	g/100 g d.w.	0.63	0.88	0.63	1.07	0.076	0.76	0.85
Sodium	mg/100 g f.w.	24	30	47	127	10.1	27	87
	g/100 g d.w.	0.22	0.34	0.89	2.39	0.178	0.28	1.64
Iron	mg/100 g f.w.	4.6	4.6	3.5	4.8	0.49	4.6	4.2
	g/100 g d.w.	0.04	0.05	0.07	0.09	0.009	0.05	0.08

f.w. – fresh weight
d.w. – dry weight

In spinach potassium constituted 33.8-35.2% of the total content of mineral components. In New Zealand spinach these values were 23.7-34.1%. In the former species the level of potassium in fresh weight did not statistically differ in the spring and autumn crops, reaching 646 mg/100 g on average (Table 1). This value may be compared with 570 mg/100g given by Wills et al. [26], 490 mg reported by Kimura and Itokawa [10], and 870-1300 mg determined by Oguchi et al. [15]. In New Zealand spinach the content of potassium in fresh weight was 78% higher in the crop from spring than that from the autumn growing season. The two harvest times being considered, spinach contained in fresh weight 71% more potassium on average and in dry weight 7% less than the New Zealand spinach.

In the two investigated species the level of phosphorus was from 23-59 mg/100 g of fresh weight, this corresponding with 1.8-3.1% of the total ash content in spinach and with 1.6-2.1% in New Zealand spinach. These contents approximate those evidenced in leaf-type beet and in soybeans [24, 27], exceeding the values reported for lettuce, sweet corn [27], red beet, carrot, cucumber, and tomato [18]. On the other hand, they are significantly lower than with pea, French bean, and asparagus [18]. Spinach from the autumn growing season contained 74% more phosphorus than that from the spring. In New Zealand spinach no

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statistically significant differences were found between the two growing seasons. In the case of average values found in the two seasons, spinach contained 96% more phosphorus in fresh weight than New Zealand spinach. If referred to dry weight, the results only differed by 11%.

Leaves of spinach and New Zealand spinach may be classed among vegetables with a very high level of calcium [18]. In fresh weight the content of calcium ranged from 109-340 mg/100 g and in dry weight from 1.23-3.16 g/100 g. Unfortunately, a significant part of this element occurs in the form of oxalates, limiting its utilization in the diet [5]. In spring spinach contained 212% more calcium than in the autumn crop. In September the content of 109 mg/100g did not significantly differ from that in New Zealand spinach from the two periods of cultivation. In general, the content of calcium in spinach and New Zealand spinach recorded in the present experiment approximated to or exceeded the data given in the literature. In New Zealand spinach Bakowski et al. [3] found 950-1045 mg/100 g in dry weight. In fresh weight of spinach Wills et al. [26] determined 53 mg/100 g, Oguchi et al. [15] 80-180 mg/100 g, and Scheffeldt et al. [19] 136.7 mg/100 g. Average values from the spring and autumn growing seasons being considered, spinach contained 110% more calcium in fresh weight than the other investigated species. In dry weight the difference was reduced to 9%.

In general, magnesium is among deficient elements in the human diet while its daily consumption by adults should amount to 300-380 mg [29]. Compared with a number of fruit and vegetable species, both the spinach with 68-78 mg/100 g fresh weight and the New Zealand spinach accumulating 33-57 mg/100 g may be classed among crops with a pronounced content of this element [18]. As for spinach the amounts of magnesium determined in the present study were comparable with those quoted by Wills et al. [26] and Scheffeldt et al. [19]. They were higher than the values of 35 mg/100 g given by Kimura and Itokawa [10] and significantly lower than those found by Oguchi et al. [15], i.e.110-180 mg/100 g. The share of magnesium in the total content of ash components was 3.7-4.1% for spinach and 2.3-5.0% for New Zealand spinach. In the two species analysed a statistically higher magnesium content was recorded in autumn than in spring. The average content of magnesium in fresh weight of spinach was 62% higher than that in New Zealand spinach, while in dry weight it was 11% lower.

Currently no deficiency of sodium is observed in the human diet. Its level in the analysed vegetables ranged from 24 to 127 mg/100 g fresh weight, this corresponding to 1.3-11.0% of the total content of ash. In general, the level of sodium found in the present work was higher than that recorded by Scheffeldt et al. [19] and Wills et al. [26] in spinach, but distinctly lower than the values given by Pijanowski et al. [18] (123 mg/100 g fresh weight). Higher values were also reported by Visser and Burrows [24] for leaf-type beet, i.e. 140 mg/100 g in edible parts. The content of sodium in spinach did not depend to a significant degree on the time of harvest. On the other hand it was statistically lower than the content recorded for New Zealand spinach, which accumulated three times more sodium in autumn than in the spring growing season.

The daily requirement of iron for adults is estimated as 15-26 mg [29], this element frequently being deficient in the diet. In the two investigated species the content of iron was high, ranging from 3.5-4.8 mg/100 g fresh weight and 0.04-0.09 g/100 g dry weight. These values corresponded with 0.24-0.42% of the total content of ash constituents. Bakowski et al. [3] estimated the content of iron as 37-61 mg dry weight in New Zealand spinach, i.e. lower than the results obtained in the present work. Also in spinach the content of iron determined by

Kimura and Itokawa [10], Scheffeldt et al. [19], and Wills et al. [26] was slightly lower. In this species the content of iron was at an identical level in the two growing seasons while in New Zealand spinach a significantly higher content (37%) was assessed in the crop from the autumn growing season. Spinach contained on average 10% more iron in fresh weight than New Zealand spinach. The reverse was determined in dry weight, the latter species containing 60% more iron.

Table 2 contains information about the level of nitrates V and III and of oxalates. Abundant literature data are available concerning the content of nitrates (N-NO_3) in spinach [2, 4, 6, 15, 17, 22, 25], the extreme levels of the content varying in a very wide interval from 150 mg/1000 g fresh weight [15] to 5500 mg/1000 g fresh weight [4]. Scarce or even single data concern New Zealand spinach, the reported values being in the order of 1380-1990 mg/1000 g fresh weight [8]. The quoted authors, particularly Paschold [16, 17] stress the effect of such factors as cultivar, applied fertilizers, light conditions, temperature, soil humidity, and even the application of plant protection measures. It should be stressed that in the present investigation the same cultivars were used in spring and autumn cultivation, the vegetable being grown on the same site and with the application of identical nitrogen fertilization. Thus any effect of the above factors on the level of the analysed compounds should be excluded.

Table 2. Level of nitrates and oxalates in usable parts of spinach and New Zealand spinach

Component	Unit	Spinach		New Zealand spinach		LSD	Mean for	
		spring	autumn	spring	autumn	p=0.01	spinach	New Zealand spinach
Nitrates V (N-NO_3)	mg/1 kg f.w.	110	1650	1634	1750	13.8	880	1692
	g/1 kg d.w.	1.02	18.67	31.06	32.96	0.245	9.84	32.01
Nitrates III (N-NO_2)	mg/1 kg f.w.	0.84	0.55	0.27	0.38	0.174	0.70	0.33
	g/1 kg d.w.	0.008	0.006	0.005	0.007	0.0018	0.007	0.006
Soluble oxalates	mg/100 g f.w.	563	347	407	214	22.3	455	311
	g/100 g d.w.	5.24	3.93	7.74	4.03	0.313	4.59	5.89
Total oxalates	mg/100 g f.w.	938	370	505	276	44.0	654	391
	g/100 g d.w.	8.73	4.19	9.60	5.20	0.474	6.46	7.40

f.w. – fresh weight
d.w. – dry weight

In the investigated vegetables the content of nitrates (N-NO_3) ranged from 110-1750 mg/1000 g fresh weight. In spinach harvested in autumn the content of nitrates was 15 times greater than that in the June harvest. Bakowski et al. [2] and Paschold [16, 17] also showed that in the material harvested in autumn the level of nitrates was higher than in that from the spring cultivation. In New Zealand spinach the level of nitrates was similar to that determined in

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spinach from the autumn harvest. Also in this case the content of nitrates was statistically higher, though only 7%, in the autumn crop.

The determined content of nitrites was statistically differentiated, but it did not exceed the limit of 1 mg $N\text{-}NO_2$/1000 g fresh weight in any of the investigated samples. This value is regarded as normal, resulting from physiological changes of nitrogen compounds [14].

Oxalates take part in the changes of nitrogen compounds occurring in the plant [21]. They are regarded as undesirable constituents of the diet, reducing the assimilation of calcium and favouring the formation of renal calculi [5, 23]. Oxalates occurring in the form of potassium and sodium salts are classed as water-soluble, while the calcium, magnesium, and zinc salts are insoluble [5]. The literature gives the limit values of oxalate content in spinach as within 250 mg/100 g fresh weight [15] and 1760 mg/100 g fresh weight [28]. In New Zealand spinach the average level of these compounds is 894 mg/100 g fresh weight [28].

In the present work the total content of oxalates was 276-938 mg/100 g fresh weight. Statistically significant differences were found among all the samples, the content of these compounds being 154% higher in the spinach from spring harvest than in that from the autumn one. In New Zealand spinach it was greater by 83%. The content of total oxalates in fresh weight was 67% higher in spinach than in New Zealand spinach, and in dry weight 13% lower. In the case of results calculated into fresh weight water-soluble oxalates constituted 60-94% of total oxalates in spinach and 78-81% in New Zealand spinach. Also Watanabe et al. [25] determined a considerable share (80-87%) of soluble oxalates in their total content. According to data given by other authors [22, 28], this share may be lower, amounting to 54-68%.

CONCLUSIONS

Practically no literature data are available concerning New Zealand spinach against the background of detailed studies on the chemical composition of spinach. The present work permits a precise description of the ability of accumulating the investigated compounds by New Zealand spinach in the spring and autumn growing seasons. It was found that if the results were referred to fresh weight spinach was a distinctly better source of all the analysed mineral compounds with the exception of sodium. Moreover, especially in the spring growing season, this species accumulates smaller amounts of nitrates but with the unfortunately higher ability to accumulate oxalates. This significant difference in favour of spinach distinctly diminishes if the results are referred to dry weight. In this case New Zealand spinach manifests more favourable traits in the alkalinity of ash, content of potassium, magnesium, and iron. This superiority may be explained by the distinctly lower content of dry matter in New Zealand spinach compared with spinach. The respective values for spring and autumn harvest are 5.26 and 5.31 g/100 g, and 10.75 and 8.84 g/100 g, with the average high content of ash of 24.4 g/100 g dry weight of New Zealand spinach.

In autumn, when the two species because of economic and organisational aspects are most frequently preserved in the form of frozen products

- spinach contains in fresh weight statistically more phosphorus, magnesium, and nitrates and less calcium and oxalates than in spring. No differences were found in the alkalinity of ash and in the content of potassium, sodium, and iron,

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- analogous data for New Zealand spinach show greater amounts of magnesium, sodium, and iron, a slightly higher content of nitrates, and less potassium and oxalates. In the alkalinity of ash and the content of calcium no differences were noted.

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