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## Prospects of *Anthriscus*, *Chaerophyllum*, and *Myrrhoides* Species Utilization and Biofortification with Selenium

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**ABSTRACT:** Despite their remarkable content of biologically active compounds, highly valuable for human health, wild relatives of Umbelliferous plants show limited utilization. The aim of the present work was the evaluation of the antioxidant status of *Anthriscus*, *Chaerophyllum*, and *Myrrhoides* species gathered in different climatic zones (from Mediterranean to Arctic) and of their suitability to produce valuable functional food for optimizing the human Se status. Among the Crimean plants, *A. sylvestris*, *C. bulbosis*, and *M. nososa* showed the highest antioxidant status, while the lowest was recorded in *A. cerefolium* and *A. caucalis*, displaying a significant correlation between the antioxidant activity (AOA) and polyphenols (TP) ( $r = 0.93$ ;  $p < 0.001$ ). A positive correlation between the longitude and AOA, and TP was detected for *A. sylvestris* ( $r = 0.95$  and  $r = 0.93$ , respectively;  $p < 0.001$ ). The high adaptability and wide geographical distribution of the latter species, as well as its significant content in natural antioxidants, make it an interesting product for Se biofortification. Foliar supplementation of sodium selenate allowed to obtain a new functional food with high TP content ( $36.4 \text{ mg GAE g}^{-1} \text{ d.w.}$ ), ascorbic acid ( $42 \text{ mg } 100 \text{ g}^{-1} \text{ f.w.}$ ), and AOA ( $72 \text{ mg GAE g}^{-1} \text{ d.w.}$ ). Moreover, Se level exceeded  $3 \text{ mg kg}^{-1} \text{ d.w.}$ , which suggests the plant suitability for the human Se status optimization, especially in Se-deficient Arctic zone, particularly referring to Nikel settlement with relatively low levels of Se in human hair ( $377 \pm 13 \text{ } \mu\text{g kg}^{-1}$ ), bread ( $58 \pm 3 \text{ } \mu\text{g kg}^{-1}$ ), and freshwater fish ( $359 \pm 22 \text{ } \mu\text{g kg}^{-1}$ ). The high antioxidant status of *Myrrhoides nodosa* indicates the need for detailed investigation of plant biochemistry and the identification of its utilization prospects.

**KEYWORDS:** Wild Apiaceae relatives; nutritional value; *A. sylvestris*; selenium biofortification; human Se status optimization

### 1 Introduction

The need for new natural sources of antioxidants for the production of both biologically active food additives and raw material for the pharmaceutical industry suggests the need for underestimated edible wild plant species with interesting biochemical characteristics [1,2], capable of accumulating higher levels of vitamins, polyphenols, and other antioxidants, compared to the corresponding cultivated crops [3–5]. The mentioned approach is the basis for developing new functional foods along with medicinal drugs, generating



related product commercialization [6]. Furthermore, specific investigations indicate high prospects of wild edible plant biofortification with Se [7,8], an essential trace element to humans, showing remarkable synergism with natural antioxidants [9,10] and able to protect the organism against cardiovascular, oncological, and viral diseases [11]. This is especially important due to the high frequency of Se deficiency within the population of many countries worldwide, leading to decreased longevity, depressed brain activity, immunodeficiency, and, consequently, to significant economic losses [11].

Inside the plant kingdom. Apiaceae species and, particularly, the genera *Anthriscus*, *Chaerophyllum*, and *Myrrhoides* are of special interest due to the wide spectrum of biologically active compounds, including essential oils, polyphenols, polysaccharides, vitamins, and minerals [12]. The mentioned family includes about 3780 plant species, belonging to 434 genera, with the predominant distribution in the Mediterranean region and south-western Asia [13,14]. Cultivated Apiaceae species are highly valued in human nutrition and medicine, contrary to the corresponding wild relatives, whose utilization is significantly restricted to local communities. Indeed, residents in the Mediterranean countries consume less than 50% of native wild edible umbellifer species, among which *Anthriscus cerefolium* (L.) Hoffm., *Anthriscus sylvestris* (L.) Hoffm., and *Chaerophyllum bulbosum* L. are rather popular [15]. The utilization of these plants in human nutrition is extremely low and depends on the local culture. In this respect, while *Anthriscus sylvestris* L. Hoffm. is commonly used in Bulgaria, Armenia, and Crete, and is highly valued in traditional medicine in Romania [16], it is considered a disturbing weed in Russia.

*Anthriscus* genus combines 14 plant species, among which *A. cerefolium*, *A. caucasicus* M. Bieb., and *A. sylvestris* are the most widespread in the south of Russia. *A. cerefolium* is the only species widely cultivated in many countries in the world due to its unique biochemical composition determining aroma and taste, and application in traditional medicine [17]. Differently, the most typical peculiarity of *A. sylvestris* is its high environmental adaptability, allowing a wide distribution in Europe, Asia, Africa, New Zealand, and northern America, including Canada, Alaska [18], and the Island [19]. The antioxidant status and essential oil composition of *Anthriscus* species have been intensively studied, revealing their high medicinal and nutritional value [20]. The protection against bacterial infections, inflammation, and oncological diseases, along with immune-modulatory and cardio-protection effects [21,22], results in broad areas of their utilization. *A. caucasicus*, or burr-chervil, is a less studied plant inhabiting predominantly lowland European and Mediterranean areas, and as alien in some regions of Asia, North and South America, New Zealand, and Tasmania, where most of investigations were devoted to the essential oil whose main component is represented by cis-chrysanthenyl acetate in samples from Europe and North America, and sesquiterpene hydrocarbons in those from China [23].

*Chaerophyllum bulbosum*, or turnip chervil, is a not very diffused biannual plant cultivated for its tubers containing up to 76% of starch [24] and high levels of essential oil in leaves [25].

*Myrrhoides nodosa* (L.) Cannon (synonyms are *Physocaulis nodosus* (L.) W.D.J. Koch and *Chaerophyllum nodosum* (L.) Crantz plants are the least studied chervil relatives belonging to *Myrrhoides* Heist. ex Fabr. Genus, found in European and Mediterranean countries, Central Asia, Iran, Caucasus, and the Crimea. The latter plant was introduced to Great Britain and the non-Mediterranean areas of France, but has never been used for medicinal purposes, though its essential oil has been characterized [26,27].

Up to date, no attempts have been made regarding the Se biofortification of *Anthriscus*, *Myrrhoides*, and *Chaerophyllum* species, many of which possess high antioxidant activity and a wide spectrum of biologically active antitumor, antimicrobial, and anti-inflammatory compounds [20,28–31]. The only exception is garden chervil *A. cerefolium*, which was recently the object of Se/I biofortification for obtaining the corresponding functional food product [7]. Theoretically, biofortification of the mentioned plants with Se, having similar

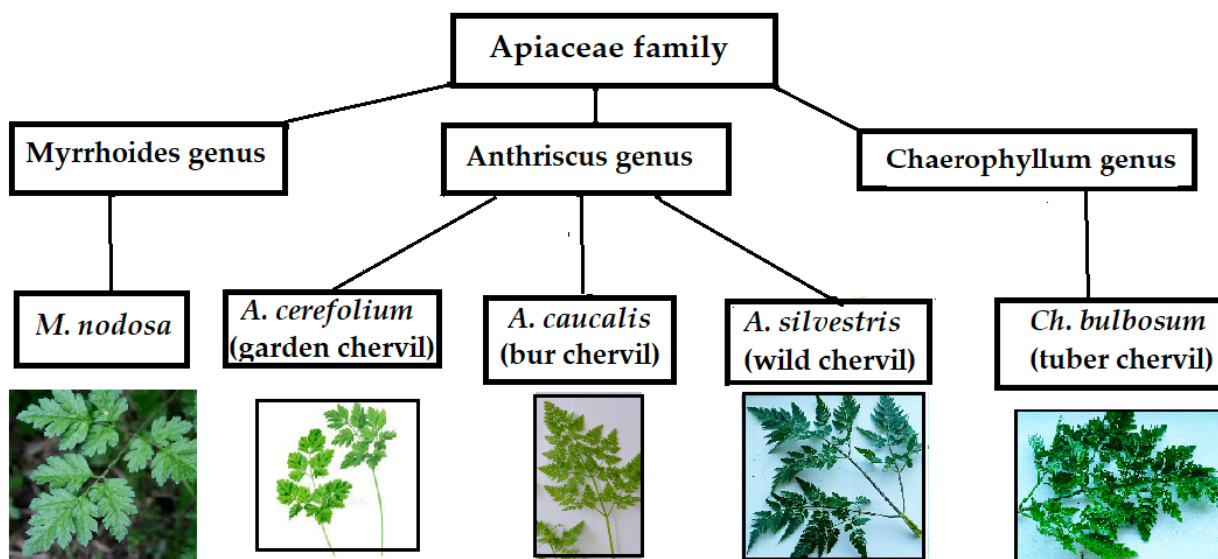
biological properties, can increase the medicinal and nutritional properties of the resulting products, creating a new group of Se-enriched functional foods.

The aim of the present research was (1) the evaluation of genetic and environmental effects on antioxidant properties of five Apiaceae species, *Anthriscus cerefolium*, *Anthriscus caucalis*, *Anthriscus sylvestris*, *Chaerophyllum bulbosum*, and *Myrrhoides nodosa*, cultivated or wildy grown in different climatic zones (the Southern Coast of Crimea, Karelia, Moscow, and Murmansk regions of Russia) and (2) the selection of the most promising species for the Se biofortification among the mentioned wild representatives, for manufacturing product with high antioxidant activity, essential for the human Se status optimization.

## 2 Material and Methods

### 2.1 Objects of Investigation

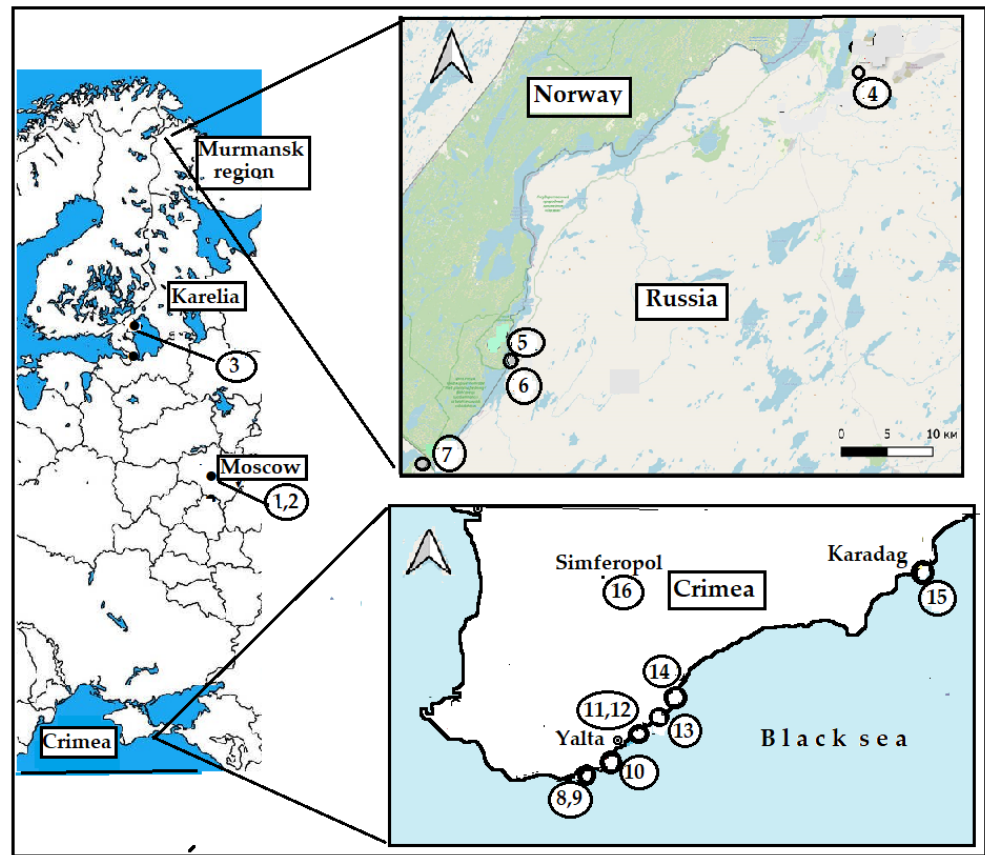
Three plant genera (*Anthriscus*, *Chaerophyllum*, and *Myrrhoides*) of the Apiaceae family with similar leaf architecture, including annual (*A. cerefolium*, *A. caucalis*, *M. nodosa*), biannual (*C. bulbosum*), and perennial (*A. sylvestris*) species were investigated (Fig. 1).



**Figure 1:** Objects of investigation.

Samples of *Anthriscus cerefolium* wild relatives (*Anthriscus sylvestris*, *Chaerophyllum bulbosum*, *Anthriscus caucalis*, and *Myrrhoides nodosa*) were gathered in 2023–2024 at the territory of Moscow region and Crimea (Table 1), while cultivated species (*Anthriscus cerefolium*, cv. Ogorodnic, and *Chaerophyllum bulbosum* of Polish production) were produced in Moscow region at the experimental fields of Federal Scientific Vegetable Center (Table 1, Fig. 2).

To evaluate the effect of habitat on the antioxidant status of *A. sylvestris*, the latter was also gathered in Karelia and the Arctic region of European Russia (geographical coordinates of the sampling places are presented in Table 1).



**Figure 2:** Sampling places of Apiaceae species. The geographical coordinates and description of sampling places are indicated in Table 1.

**Table 1:** Objects of investigation and sampling places.

Species	Region	No.**	Location	Coordinates
<i>Anthriscus cerefolium</i>	Moscow*	1	Odintsovo	55°39'31" N, 37°12'23" E
	Moscow	2	Balashikha	55°48'34" N, 37°57'29" E
	Karelia	3	Kilpola island Ladoga lake	61°12'59" N, 29°55'56" E
<i>Anthriscus sylvestris</i>	Arctic	4	Nikel settlement	69°24'29" N, 30°13'14" E
		5	Pasvik Nature Reserve	69°08'16" N, 29°14'37" E
		6	Pasvik Nature Reserve	69°08'30" N, 29°14'57" E
		7	Rayakoski settlement	69°01'13" N, 29°00'21" E
	Crimea	10	Oreanda, Krestovaya mountain	44°27'30" N, 34°08'10" E
		11	Nikita	44°30'51" N, 34°14'07" E
		12	Nikita ash forest	44°30'56" N, 34°14'03" E
		16	Simpheropol	44°57'25" N, 34°06'38" E
<i>Anthriscus caucalis</i>	Crimea	8, 9	Alupka Vorontsov park	44°25'11" N, 34°02'35" E
		11	Nikita	44°30'51" N, 34°14'07" E
		14	Gurzuf	44°32'38" N, 34°16'25" E
<i>Chaerophyllum bulbosum</i>	Moscow*	2	Balashikha region	55°48'34" N, 37°57'29" E
	Crimea	15	Karadag Nature Reserve	44°56'10" N, 35°14'00" E
<i>Myrrhoides nodosa</i>	Crimea	13	Cape Martyan Nature Reserve	44°30'38" N, 34°15'25" E

\*Cultivated species; \*\*number on the map.

Leaves of all plants investigated were harvested at the end of June in Moscow region, Crimea, and Karelia, and in the middle of August at the Arctic.

## 2.2 Field Experiment

Garden and wild chervil plants (*A. cerefolium*, cultivar *Ogorodnik*, *C. bulbosum*, and *A. sylvestris*) were grown at the experimental fields of Federal Scientific Vegetable Center in 2023–2024 in clay-loam soil with pH 6.8, 2.1% organic matter, 1.32 mg-eq 100 g<sup>-1</sup> hydrolytic acidity; 18.5 mg kg<sup>-1</sup> mineral nitrogen; 21.3 mg kg<sup>-1</sup> ammonium nitrogen; 402 mg kg<sup>-1</sup> mobile phosphorous; 198 mg kg<sup>-1</sup> exchangeable potassium; sum of absorbed bases 93.6%; cation exchange capacity 15 mg-eq 100 g<sup>-1</sup> soil. No soil fertilization was practiced during the experiment, whereas the irrigation was activated when the soil humidity dropped to 75%.

*A. cerefolium* and *C. bulbosum* were sown on 10 May, while 2-year-old plants of wild *A. sylvestris* were transferred from the Balashikha park (55°48'34'' N 37°57'29'' E) to the experimental plot of 3 × 3 m<sup>2</sup> with a 40 cm distance between plants.

At the 15th day of seedling development, *A. cerefolium* and *A. sylvestris* plants were sprayed with a 25 mg L<sup>-1</sup> solution of sodium selenate, as in a previous investigation on *A. cerefolium* Se/I biofortification, which did not cause plant toxicity [7]. Foliar supply of Se was chosen as the most effective method of Se supply because of the significantly higher assimilation of this microelement compared to soil application [32]. Harvest was practiced 30 days after the vegetation beginning. Leaves were separated from plants, dried to constant weight in an oven at 70°C, and homogenized. The obtained powder was used for the determination of AOA and TP, while the ascorbic acid and photosynthetic pigments were determined on fresh homogenized leaves.

## 2.3 Biochemical Parameters

To determine the content of *photosynthetic pigments*, half a gram of dry samples was homogenized in a porcelain mortar with 10 mL of 96% ethanol. The homogenized sample mixture was quantitatively transferred to a volumetric flask, bringing the volume to 25 mL, and the mixture was filtered through filter paper. In the resulting solution, analyses of chlorophyll-a, chlorophyll-b, and carotene were performed through a spectrophotometer (Unico 2804 UV, USA). The calculation of chlorophyll and carotene concentrations was achieved using appropriate equations [33]:

$$\text{Ch-a} = 13.36A_{664} - 5.19A_{649};$$

$$\text{Ch-b} = 27.43A_{649} - 8.12A_{664};$$

$$\text{C c} = (1000A_{470} - 2.13 \text{ Ch-a} - 87.63 \text{ Ch-b})/209;$$

where A = Absorbance at the wave length of 664, 649, and 470 nm, Ch-a = Chlorophyll a, Ch-b = Chlorophyll b and C c = Carotene.

The ascorbic acid content in leaves of *A. cerefolium*, *A. sylvestris*, and *C. bulbosum* plants was determined by visual titration of fresh leaf extracts in 3% trichloroacetic acid with Tillman's reagent [34]. Three grams of leaves were mixed with 5 mL of 3% trichloroacetic acid and quantitatively transferred to a measuring cylinder. The volume was brought to 60 mL using 3% trichloroacetic acid, and the mixture was filtered through a filter paper 15 min later. The concentration of the ascorbic acid was determined from the amount of Tillman's reagent that went into the titration of the sample.



*Total polyphenols* were determined in 70% ethanol extract using the Folin–Ciocalteu colorimetric method as previously described [35]. One gram of dry homogenates was extracted with 20 mL of 70% ethanol at 80°C for 1 h. The mixture was cooled down and quantitatively transferred to a volumetric flask, and the volume was adjusted to 25 mL. The mixture was filtered through filter paper, and 1 mL of the resulting solution was transferred to a 25 mL volumetric flask, to which 2.5 mL of saturated Na<sub>2</sub>CO<sub>3</sub> solution and 0.25 mL of diluted (1:1) Folin–Ciocalteu reagent were added. The volume was brought to 25 mL with distilled water. One hour later, the solutions were analyzed through a spectrophotometer (Unico 2804 UV, Suite E Dayton, NJ, USA), and the concentration of polyphenols was calculated according to the absorption of the reaction mixture at 730 nm. As an external standard, 0.02% gallic acid was used. The results were expressed as mg of Gallic Acid Equivalent per g of dry weight (mg GAE g<sup>-1</sup> d.w.).

The *antioxidant activity* of samples was assessed using a redox titration method [35] via titration of 0.01 N KMnO<sub>4</sub> solution with ethanolic extracts of dry samples, produced as described in the Section 2.2. The reduction of KMnO<sub>4</sub> to colorless Mn<sup>+2</sup> in this process reflects the quantity of antioxidants dissolvable in 70% ethanol. The values were expressed in mg Gallic Acid Equivalents (mg GAE g<sup>-1</sup> d.w.).

## 2.4 Selenium

Total Se content was analyzed using the microfluorimetric method [36]. Dried homogenized samples were digested via heating with a mixture of nitric and perchloric acids, subsequently selenate (Se + 6) was reduced to selenite (Se + 4) with a solution of 6 N HCl, and the resulting selenite was subjected to a complexation with 2,3-diaminonaphthalene to form piazoselenol. Calculation of the Se concentration was achieved by recording the piazoselenol fluorescence value in hexane at 519 nm-emission and 376 nm-excitation. Each determination was performed in triplicate. The precision of the results was verified using a reference standard of Se fortified mitsuba stem powder in each determination with a Se concentration of 1865 µg Kg<sup>-1</sup> d.w. (Federal Scientific Vegetable Center).

The appropriate determination of organic Se was achieved analogously after removal of inorganic Se species with distilled water rinsing and precipitation of water soluble proteins with trichloroacetic acid solution.

To evaluate the importance of Se-biofortified *A. sylvestris* utilization in the Arctic, the selenium status of Nikel residents (Murmansk region) was characterized by analyzing hair samples of 15 volunteers aged 30–46 (August 2024). Hair was washed with acetone to remove fat impurities, homogenized, and subjected to the Se analysis. Selenium concentrations were also determined in dried bread samples (n = 12) and muscles of fresh water whitefish (*Coregonus pidschian*) of the Paz River (n = 10).

## 2.5 Statistical Processing

The data were processed by the analysis of variance, and mean separations were performed through Duncan's multiple range test, with reference to a 0.05 probability level, using the SPSS software version 29 (Armonk, NY, USA). Data expressed as percentages were subjected to angular transformation before processing.

## 3 Results and Discussion

### 3.1 Antioxidant Status

#### 3.1.1 Genetic Peculiarities

The comparison of the polyphenol content (TP) and total antioxidant activity (AOA) between the examined species revealed great variations of the mentioned parameters depending on the genetic peculiarities and habitat (Table 2). Indeed, the AOA range indicated 5-time differences between the extreme

AOA values (20.0–99.9 mg GAE g<sup>-1</sup> d.w.), with the lowest level recorded in the Crimean *A. caucalis* and the highest in the Arctic *A. sylvestris*. A similar trend was shown by the polyphenol content, with an 8-time difference between the two mentioned species (4.4 to 36.6 mg GAE g<sup>-1</sup> d.w.), suggesting that the Arctic and Karelian *A. sylvestris* proved the best source of phenolics and *A. caucalus*, and *A. cerifolium* the least rich in these compounds.

The highest diversity of Apiaceae species at the southern Crimean sea shore was demonstrated by AOA decrease from 65.1–70.9 mg GAE g<sup>-1</sup> d.w. in *M. nodosa* and *C. bulbosum* to 30.0–63.1 mg GAE g<sup>-1</sup> d.w. in *A. sylvestris* (mean value 44.7 mg GAE g<sup>-1</sup> d.w.), and to 20.0–36.5 mg GAE g<sup>-1</sup> d.w. in *A. caucalis* (mean value 26.5 mg GAE g<sup>-1</sup> d.w.). The garden chervil *A. cerefolium* in the Moscow region was characterized by twice lower AOA, compared to *A. sylvestris*. The differences in antioxidant activity between the mentioned plants may relate to the corresponding annual/perennial growth cycle and half content of photosynthetic pigments in leaves of *A. cerefolium* [5]. Though *A. caucalis* is relatively abundant along the Crimean Sea shore, its antioxidant status was lower than that of the other species of the same genus.

**Table 2:** Total antioxidant activity (AOA) and total polyphenol content (TP) in cultivated chervil and its wild relatives.

Species	Region	No on the Map	AOA		TP
			mg GAE g <sup>-1</sup> d.w.		% from the AOA
<i>Anthriscus cerefolium</i>	Moscow	1	34.1 ± 3.1 <sup>cd</sup>	10.5 ± 1.0 <sup>f</sup>	30.8
	Moscow	2	66.3 ± 6.2 <sup>b</sup>	25.2 ± 2.4 <sup>c</sup>	38.0
	Karelia	3	93.6 ± 0.7 <sup>a</sup>	36.6 ± 1.9 <sup>a</sup>	39.1
<i>Anthriscus sylvestris</i>	Arctic	4	88.3 ± 6.5 <sup>a</sup>	31.6 ± 1.9 <sup>ab</sup>	35.8
		5	99.9 ± 7.1 <sup>a</sup>	35.3 ± 2.0 <sup>a</sup>	35.3
		6	86.3 ± 6.8 <sup>a</sup>	33.4 ± 1.9 <sup>a</sup>	38.7
		7	99.6 ± 7.0 <sup>a</sup>	29.0 ± 1.8 <sup>b</sup>	29.2
	Crimea	10	30.0 ± 1.3 <sup>d</sup>	15.0 ± 0.6 <sup>e</sup>	50.0
		11	63.1 ± 6.0 <sup>b</sup>	25.8 ± 2.5 <sup>c</sup>	40.9
		12	41.7 ± 2.0 <sup>c</sup>	23.2 ± 1.1 <sup>d</sup>	55.6
		16	43.8 ± 4.1 <sup>c</sup>	18.6 ± 1.8 <sup>d</sup>	42.5
<i>Anthriscus caucalis</i>	Crimea	8	20.0 ± 1.1 <sup>f</sup>	4.4 ± 0.1 <sup>h</sup>	22.0
		9	23.0 ± 2.0 <sup>ef</sup>	7.1 ± 0.2 <sup>g</sup>	30.9
		11	36.5 ± 3.5 <sup>c</sup>	13.4 ± 1.3 <sup>e</sup>	36.9
		14	26.4 ± 2.5 <sup>de</sup>	9.8 ± 0.9 <sup>f</sup>	37.1
<i>Chaerophyllum bulbosum</i>	Moscow	2	67.8 ± 6.4 <sup>b</sup>	18.4 ± 1.8 <sup>d</sup>	27.1
	Crimea	15	70.9 ± 6.9 <sup>b</sup>	25.5 ± 2.5 <sup>c</sup>	36.0
<i>Myrrhoides nodosus</i>	Crimea	13	65.1 ± 6.4 <sup>b</sup>	28.9 ± 2.7 <sup>bc</sup>	44.4

Moscow region: (1) Odintsovo; (2) Balashikha. Karelia: (3) Ladoga lake. Arctic: (4) Nikel settlement; (5, 6) Pasvik Nature Reserve; (7) Rayakoski settlement. Crimea: (8, 9) Alupka; (10) Oreanda; (11, 12) Nikita; (13) Cape Martyan; (14) Gurzuf; (15) Karadag; (16) Simpheropol. AOA—total antioxidant activity; TP—total polyphenols; within each column, values with the same letters do not differ statistically according to Duncan test at  $p < 0.05$ .

Contrary, the high antioxidant status of *M. nodosa* in the Mediterranean zone, compared to *A. caucalis* and *A. sylvestris*, entails the importance of further investigations of this species nutritional and medicinal value aimed at widening the list of powerful antioxidant sources and improving the plant utilization. Notably, close values of antioxidant status were recorded in wild (Crimea) and cultivated (Moscow region) *C. bulbosum*. At present, the bulbs of the latter plant are rarely used in human nutrition [2], while the leaves have never been considered as a possible component of the human diet.

### 3.1.2 Environmental Factors

The wide spectrum of climatic differences between the chosen sampling places and the ubiquitous character of *A. sylvestris* distribution allowed us to reveal the effect of the environmental factors on the antioxidant status of plants. Indeed, the latitude range between 44°25' to 69°42' combines both the zone of Mediterranean climate (the Southern shore of Crimea with dark chestnut saline on Meikop clays), moderate continental climate of Moscow region (with sod-podzolic loamy soils), Karelia (with podzolic soils), and subarctic zone of Murmansk region (with tundra bog soils), i.e., regions greatly differing in terms of soil pH, mean annual temperature and precipitation, annual amount of total solar radiation (Table 3). According to the available data, the mean values of *A. sylvestris* total antioxidant activity were more than double in the Arctic region, compared to the Southern one (Table 2), in agreement with the above mentioned environmental characteristics. The measured parameters ranged in these regions from 4.3 to 8.0 (pH), 250 to 713 mm (precipitation), −3.1 to +13.5°C (mean annual temperature), and 70 to 118.3 kJ cm<sup>−2</sup> (annual amount of total solar radiation) (Table 3). The neutral pH favourable for *A. sylvestris* growth [17] led to the tallest plants in the Moscow region (about 100 cm), while the mean height of wild chervil in the Arctic zone was about 30 cm (Pasvik Nature Research). The correlation coefficients between AOA, TP, and climate characteristics confirmed a powerful regulation effect of the environment on *A. sylvestris* antioxidant status and the existence of intensive oxidant stress in Arctic conditions, promoting the antioxidant biosynthesis in plants [3,37].

**Table 3:** Effect of climate parameter differences between the territories investigated.

Region and Correlations	pH	Precipitation (mm)	Annual Air Temperature (°C)	Annual Amount of Total Solar Radiation (kJ cm <sup>−2</sup> )
Southern shore of Crimea [38]	7.8–8.0	596	13.5	118.3
Moscow region [7]	6.8–7.0	713	6.3	90
Southern part of Karelia [39]	4.5–5.5	611	2–3	80
Arctic [40]	4.3–4.5	350–428	−3.1	70
AOA correlation	−0.929 <sup>a</sup>	−0.666 <sup>c</sup>	−0.919 <sup>b</sup>	−0.925 <sup>a</sup>
TP correlation	−0.854 <sup>a</sup>	−0.621 <sup>d</sup>	−0.837 <sup>a</sup>	−0.655 <sup>c</sup>

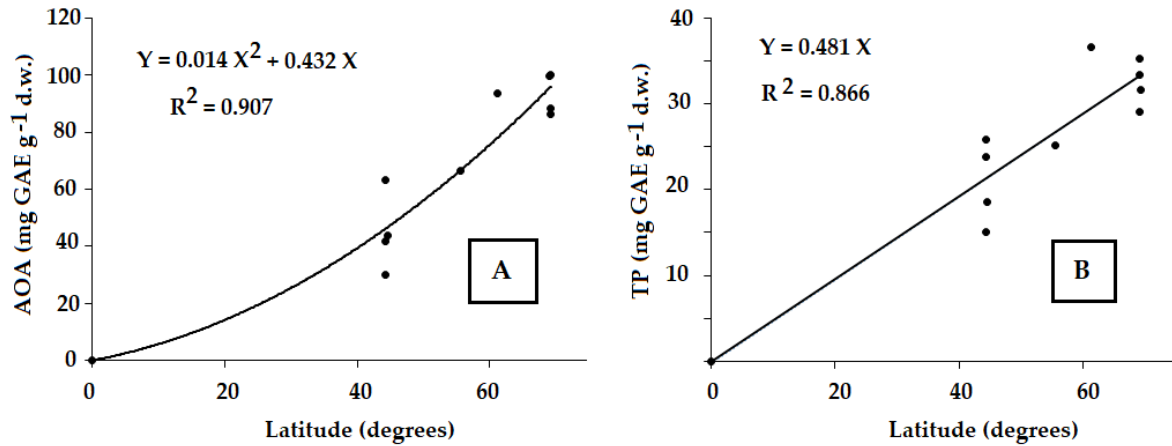
Significance of correlations (n = 10): <sup>a</sup>*p* < 0.001; <sup>b</sup>*p* < 0.002; <sup>c</sup>*p* < 0.02; <sup>d</sup>*p* < 0.05.

In this respect, latitude may be considered as an integral parameter governing climate and showing significant correlations with the wild chervil antioxidant status (Fig. 3A,B).

The revealed positive correlations between antioxidant status parameters (AOA and TP) of *A. sylvestris* leaves and the latitude (Fig. 3A,B) were in accordance with previous observations regarding the AOA and TP activation under the environmental stress applied [3,37,41,42]. The ubiquitous character of the revealed phenomenon entails high prospects of Arctic *A. sylvestris* utilization as a powerful source of natural antioxidants.

As far as the Crimean samples are concerned, the plants grown at the Nikita settlement (*A. caucalis* and *A. sylvestris*) demonstrated significantly higher local AOA and TP values, compared to those of other seashore habitats, which may relate to a local anthropogenic influence.

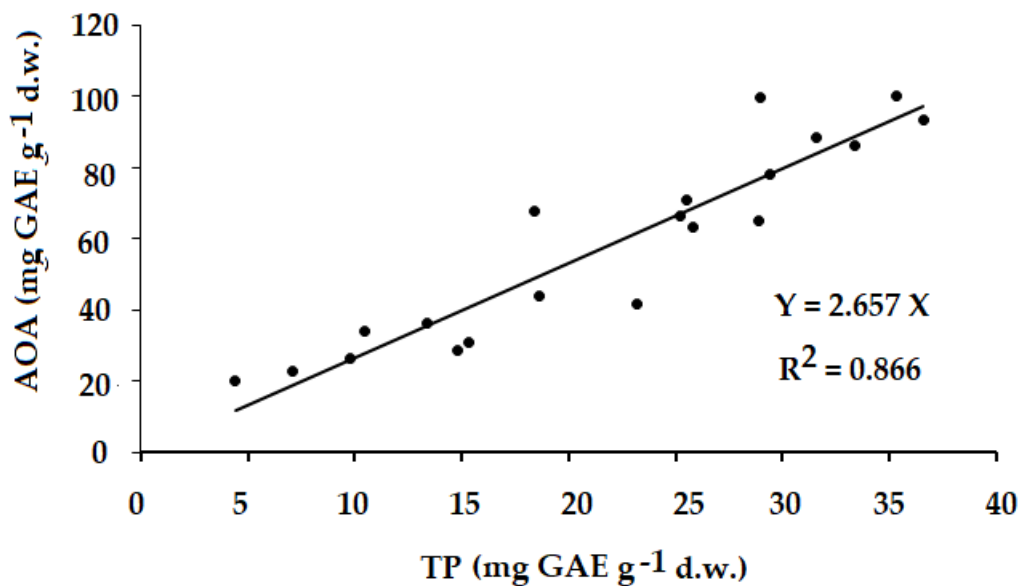




**Figure 3:** Relationship between the antioxidant activity (A) and polyphenol content (B) in *A. sylvestris* leaves and place of habitat ( $r = +0.952$  and  $r = +0.931$ , respectively,  $p < 0.001$ ;  $n = 10$ ).

### 3.1.3 General Patterns of Antioxidant Accumulation

The results of the present research show the significant positive correlation between the total antioxidant activity (AOA) and polyphenol content in all the Apiaceae species examined (Fig. 4), consistently with previous reports [42].



**Figure 4:** Relationship between AOA and TP in leaves of all the Apiaceae species examined ( $r = 0.931$ ;  $p < 0.001$ ).

The same relationship has been recorded in other plant species: tree and shrub bark from 5 distinct geographical regions of Russia [42], *Allium* representatives [43], and mushrooms [40].

### 3.2 Selenium Biofortification

For the perspective of new functional food creation, the topic regarding the peculiarities and expediency of Se biofortification of edible wild plants arises [44]. Previous investigations indicated high prospects of Se-biofortified *Allium ursinum* [45], *Azolla caroliniana* [46], *Portulaca oleracea* [47], *Taraxacum officinale* [48], *Plantago* [47,49], and *Rumex acetosa* [47], etc. Contrary, wild *A. sylvestris*, *A. caucalis*, *M.*

*nodosa*, and *C. bulbosum* have never been used for these purposes. In this respect, among the plants studied *A. sylvestris* was chosen for Se foliar biofortification due to the chance to predict its antioxidant status in different geographical zones, as well as its high adaptability, wide habitat, and remarkable nutritional and medicinal value.

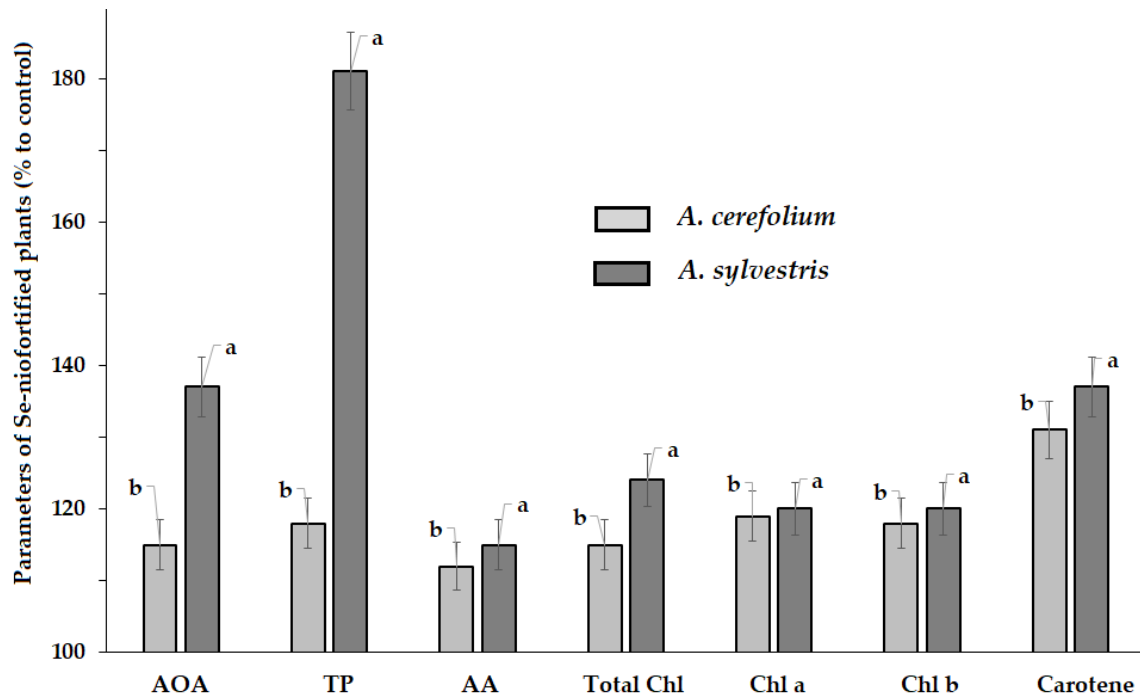
The production of functional food via plant biofortification with Se is one of the most interesting approaches for protecting human health and preventing hunger [39,46]. In this respect, wild relatives of agricultural crops are especially interesting due to their higher levels of adaptability and antioxidants [50]. Indeed, wild chervil (*A. sylvestris*) demonstrated unexpectedly great concentrations of total phenolics, ascorbic acid, and chlorophyll content, compared to garden chervil (*A. cerefolium*) (Table 4).

The comparison of foliar Se biofortification effect on wild *A. sylvestris* and cultivated *A. cerefolium* showed that, despite the higher initial antioxidant characteristics of *A. sylvestris*, compared to *A. cerefolium*, the mentioned plants displayed similar levels of resistance to Se treatment and increase of chlorophyll a, b, carotene, ascorbic acid, and Se biofortification (Table 4, Fig. 5). A beneficial effect of Se on the biosynthesis of plant antioxidants was recorded in many agricultural crops, suggesting the high prospect of Se biofortification [8,51]. Notably, in our research a significantly higher increase in the total antioxidant activity and polyphenol content was recorded in wild chervil under Se supplementation, compared to *A. cerefolium*, with values of 72.0 and 36.4 mg GAE g<sup>-1</sup> d.w., respectively (Fig. 5). The data presented in Table 4 indicate that the consumption of 10 g of Se-fortified wild chervil powder may provide up to 60% of the Recommended Dietary Allowance for Se equal to 55 µg per day, not exceeding the Tolerable Upper Intake Level (UL) for adults of 400 µg [52]. Furthermore, the amount of organic Se in Se fortified plants was as high as 81.2% for Se biofortified *A. sylvestris* and 77.9% for *A. cerefolium*. These results are in accordance with the known ability of plants to use the external Se to synthesize various organic Se compounds, such as Se containing amino acids (selenomethionine, selenocysteine), the corresponding peptides, polysaccharides, etc., using the chemical similarity of Se and S [44]. As an essential microelement for human health, Se in the form of amino acids is incorporated into different enzymes, providing the antioxidant activity of glutathione peroxidases and thioredoxin reductase, participating in thyroid hormone metabolism in triiodothyronine deiodinases, ensuring Se transport in the form of selenoprotein P, regulating the inflammation processes in the form of selenoprotein S [10].

**Table 4:** Biochemical characteristics of control and Se biofortified *A. sylvestris* and *A. cerefolium* leaves.

Parameter	<i>A. sylvestris</i>		<i>A. cerefolium</i> *	
	Control	Se	Control	Se
Dry matter (%)	21.5 ± 1.6 <sup>a</sup>	24.4 ± 1.7 <sup>a</sup>	10.9 ± 0.9 <sup>b</sup>	11.1 ± 1.0 <sup>b</sup>
Chlorophyll (mg g <sup>-1</sup> f.w.)	4.37 ± 0.39 <sup>b</sup>	5.44 ± 0.51 <sup>a</sup>	2.24 ± 0.20 <sup>c</sup>	2.58 ± 0.21 <sup>c</sup>
Chlorophyll a (mg g <sup>-1</sup> f.w.)	2.73 ± 0.21 <sup>b</sup>	3.38 ± 0.30 <sup>a</sup>	1.58 ± 0.15 <sup>d</sup>	1.88 ± 0.19 <sup>c</sup>
Chlorophyll b (mg g <sup>-1</sup> f.w.)	1.64 ± 0.13 <sup>b</sup>	2.06 ± 0.18 <sup>a</sup>	0.66 ± 0.06 <sup>c</sup>	0.78 ± 0.08 <sup>c</sup>
Carotene (mg g <sup>-1</sup> f.w.)	0.43 ± 0.03 <sup>c</sup>	0.59 ± 0.04 <sup>b</sup>	0.59 ± 0.03 <sup>b</sup>	0.77 ± 0.04 <sup>a</sup>
Ascorbic acid (mg 100 g <sup>-1</sup> f.w.)	38.0 ± 2.5 <sup>a</sup>	42.0 ± 3.1 <sup>a</sup>	28.0 ± 2.0 <sup>b</sup>	31.0 ± 2.1 <sup>b</sup>
AOA (mg GAE g <sup>-1</sup> d.w.)	52.5 ± 4.5 <sup>b</sup>	72.0 ± 6.0 <sup>a</sup>	35.7 ± 3.0 <sup>d</sup>	40.9 ± 3.8 <sup>c</sup>
TP (mg GAE g <sup>-1</sup> d.w.)	20.0 ± 1.7 <sup>b</sup>	36.4 ± 3.2 <sup>a</sup>	10.8 ± 0.9 <sup>c</sup>	12.7 ± 1.1 <sup>c</sup>
Se (µg kg <sup>-1</sup> d.w.)	59 ± 5 <sup>d</sup>	3288 ± 191 <sup>b</sup>	110 ± 9 <sup>c</sup>	5150 ± 321 <sup>a</sup>

AOA: total antioxidant activity; TP: total polyphenols cultivar; \*cultivar Ogorodnik. Along each line, values with the same letters do not differ statistically according to Duncan test at  $p < 0.05$ .



**Figure 5:** Antioxidant and chlorophyll differences between Se biofortified *A. cerefolium* and *A. sylvestris* and control. AOA: total antioxidant activity; TP: total polyphenol content; AA: ascorbic acid; Chl: chlorophyll. Values with the same letters do not differ statistically according to Duncan test at  $p < 0.05$ .

### 3.3 The Possible Role of Se-Fortified *A. sylvestris* for Human Health Protection in Arctic

From a practical point of view, the new Se-biofortified product shows the highest values of the AOA and TP content in plants from the Moscow region, similar to those recorded in the Arctic *A. sylvestris*. Future investigations may provide additional data, as the effect of altitude on the efficiency of Se biofortification in *A. sylvestris* in Arctic conditions has never been investigated previously. Supposedly, Se supply will further enhance plant tolerance to severe northern climate due to the antioxidant properties of Se, allowing to protect plants against all forms of oxidant stresses [8,51]. Moreover, rather high levels of Se may become significant for the northern zones of selenium deficient soil and low human Se status [53].

Indeed, epidemiological investigations in Nikel settlement indicated rather low Se levels in human hair:  $377 \pm 13 \mu\text{g kg}^{-1}$  d.w. on average ( $358\text{--}394 \mu\text{g kg}^{-1}$  d.w.;  $n = 15$ ), along with low Se content in bread ( $58 \pm 3 \mu\text{g kg}^{-1}$  d.w. on average;  $54\text{--}63$ ;  $n = 9$ ) produced from grain of the neighboring Se-deficient regions and in whitefish muscles (*Coregonus pidschian*) of the Paz river ( $359 \pm 22 \mu\text{g kg}^{-1}$  f.w.;  $n = 12$ ). These results confirm the low Se status of the mentioned region and are in agreement with the previous investigations carried out in Syktyvkar, Komi republic (human serum Se concentration range of  $54\text{--}91 \mu\text{g L}^{-1}$ ) [53] and the evaluation of Se content in whitefish from Arkhangelsk region ( $340 \mu\text{g kg}^{-1}$  f.w.; Pechora river; Narian-Mar;  $67^{\circ}38'16''$  N.;  $53^{\circ}00'24''$  E) [54].

*A. sylvestris* is widespread in the territory of the Pechenga district of Murmansk region, where the Nikel settlement is situated. According to our observation, this plant grows especially at unpolluted territories, with the exception of Nikel settlement, where imported soil has been used after the closure of Pechenganikel Cu/Ni smelting plant, which entails the possibility of *A. sylvestris* Se biofortified production in the Murmansk region, for the human Se status optimization. Unfortunately, no attempts have been made to assess the efficiency of plant Se biofortification in the Arctic zone, where severe climate may hamper

plant growth and, therefore, the results may significantly differ from those obtained in the Moscow region; however, the latter hypothesis needs experimental confirmation.

The production of Se biofortified *A. sylvestris* plants may become important for the residents of other Se-deficient areas in Russia and other countries, due to the significant levels of antioxidants, sufficient Se levels predominantly in organic form, and low-cost technology of this new functional food. At present, *A. sylvestris* is used in salads, pastry, and soups [4,16], while the present results provide some new aspects of Se-enriched plant utilization as a spice and biologically active food additive.

#### 4 Conclusion

A comparative assessment of the antioxidant status in *Anthriscus*, *Chaerophyllum*, and *Myrrhoides* species, grown in different climatic zones, revealed high prospects of *A. sylvestris* utilization to produce functional food beneficial for optimizing the human Se status and protection against oxidant stresses. The ubiquitous character of *A. sylvestris* distribution across different geographical zones, its high levels of adaptability, antioxidants, and efficiency of Se biofortification confirm the importance of this plant in human nutrition and health maintenance, especially in zones with remarkable oxidative stress and Se deficiency. A positive correlation between the antioxidant activity of wild chervil leaves and the habitat latitude shows its importance in the Arctic zone characterized by an increased environmental stress and low soil Se. Among the wild Apiaceae species from the Mediterranean zone, *Myrrhoides nodosa* may become another functional food ingredient due to its high antioxidant content, which suggests the need to deepen the investigation of this plant's biochemistry and exploitation prospects.

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