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Can foliar-applied nutrients improve caraway (*Carum carvi* L.) seed oil composition?

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ABSTRACT

Caraway seeds contain between 0.5–7% essential oil, rich in monoterpenes that have a characteristic aroma and chemical properties. Caraway oil has several bioactive compounds that are of industrial importance, particularly for pharmaceutical and health care products. Carvone and limonene are the main terpenes present in caraway oil, which along with some unique fatty acids (i.e. petroselinic acid) determine caraway (*Carum carvi* L.) oil quality. Both terpenes are important raw materials for industrial applications and their concentration influences the price of caraway seed and oil, hence there is need for identifying management practices that may increase the concentration of these and other bioactive compounds to improve caraway seed oil quality. A field experiment with five treatments: a control and a series of foliar-applied micronutrients (either Cu, Mg, Mn or Zn was done to identify their potential to enhance caraway oil quality. Solid-phase microextraction and gas chromatography with a flame ionization detector were used to characterize oil quality. Our results indicate that while the micronutrient treatments have a significant effect on essential oil composition, both in carvone and limonene, such an effect was not found on all fatty acids but only in two of them—palmitoleic and vaccenic acid—, which were highest after the Mn treatment. Overall, the carvone content of the seeds decreased the least between years following Mn treatment. Mn treatment also caused an increase in limonene in the second year in contrast to the trend for all other treatments. The Mn foliar spray needs to be studied further to elucidate whether it could have a consistent positive effect on caraway oil seed quality upon adjusting dosage and spraying time.

1. Introduction

Seed oils are synthesized during seed development. Lipids stored in seeds are an excellent source of energy (giving twice the amount compared to carbohydrates) helping to maximize seed survival and germination, thus being a key characteristic for the ecological adaptation of plants (Zhang et al., 2015).

Seed oils are composed of long-chain hydrocarbons and stored in oil bodies in the mature seed tissue. On the other hand, essential oils are complex mixtures of low molecular weight compounds mostly terpenoids and phenylpropanoids, which depending on the plant species are stored in oil ducts, glands, glandular hairs and resin ducts (Raut and Karuppayil, 2014). Plant essential oils are valued to their wide range of bioactive use that include: herbicidal action on monocots, anti-inflammatory, antioxidant, antibacterial, anti-quorum sensing, anti-biofilm formation antifungal, antiviral, cytotoxic, cancer preventive, antimutagenic activities (Raut and Karuppayil, 2014; Camele et al., 2019; Elshafie et al., 2020; Grul'ová et al., 2020).

Caraway (*Carum carvi* L.) is an umbelliferous crop (*Apiaceae* family) native to Europe, Asia, and North Africa. Its fruit is a schizocarp (commonly called seeds) with characteristic flavor and aroma (Bowmeester et al., 1995, 1998; Iacobellis et al., 2005). The seeds have unique uses, such as inhibiting the sprouting of potatoes (Şanli, 2016; Şanli et al., 2010; Toxopeus et al., 1995), and they have allelopathic potential (Marichali et al., 2014; Shiwakoti et al., 2016). Caraway oil has distinct antifungal, antibacterial and antioxidant properties, thus having a wide range of uses in pharmaceutical, health care and cosmetics industry (Iacobellis et al., 2005; Laribi et al., 2009; Seidler-Łozykowska

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et al., 2013; Simic et al., 2008; Vallverdú-Queralt et al., 2015). Caraway oil is a valuable raw material for industrial use, which explain caraway being one of the most cultivated specialty crops (Seidler-Łozykowska et al., 2014; Wichtmann and Stahl-Biskup, 1987).

Caraway seeds contain between 0.47 and >7% total oil, depending on whether the crop is annual or biennial, the latter usually accumulating more oil (Bosko et al., 2016; Bouwmeester et al., 1998; Meshkatalsadat et al., 2012; Raal et al., 2012; Sedláková et al., 2003). In Finland and Canada the growing season is not suitable for producing a mature yield of annual caraway, and so the biennial type is preferred (Ferrie et al., 2011). Caraway essential oil is mainly made of the monoterpenes carvone and limonene, which make up to 95 % of the total seed oil (Acimovic et al., 2015; Bosko et al., 2016; Bouwmeester et al., 1998, 1999). Caraway seeds are also rich in several fatty acids: linoleic, oleic, palmitic, and petroselinic acid, the latter being a rare monounsaturated fatty acid (MUFA) of industrial importance (Laribi et al., 2009, 2013; Ngo-Duy et al., 2009).

In Finland, caraway has become an extremely popular crop that is cultivated in over 1600 farms covering 24,000 ha (Natural Resources Institute Finland, 2020). In Finland, the average yield per hectare of caraway has fluctuated considerably, being 310–930 kg/ha during the period 2007–2019; nevertheless its cultivated area continues to rise, with whole country production reaching a record 16.6 million kg in 2019 (Natural Resources Institute Finland, 2020).

Most of Finnish caraway is exported to about 40 countries, representing 20–30 % of the global market (Keskitalo, 2014). It is considered to be economically profitable if the average yield is over 750 kg/ha (Keskitalo, 2014).

There is a wealth of literature supporting the physiological role of nutrients on the yield formation and seed quality; said literature is largely available for secondary nutrients (macronutrients that are needed in less quantity than N, P, K) such as Mg and less so for micronutrients like Cu. Magnesium is well-known for playing a key role in plant photosynthesis and for being a cofactor or promoter of a series of enzymes involved in numerous cellular processes (e.g.,. carbon dioxide fixation, starch synthesis) (Maathuis and Padar, 2011). Zinc plays an important role in the activation of a wide range of enzymes (about 300 enzymes) which are involved in protein synthesis, carbohydrate metabolism, and pollen structure formation, among other key plant physiological processes (Sadeghzadeh and Rengel, 2011; Yang et al., 2009). The role of Cu and Mn in plant and soil biology is complex and less well understood, but it is known that both play a role in photosynthesis as well as in the reproductive growth of crops and thus seed yield losses may occur upon Cu and Mn deficiency (Brown and Bassil, 2011).

Previously, few studies have evaluated the effect of different nutrients on the essential oil content of caraway, mostly evaluating the effect of macronutrients. In a study by El-Din Ezz et al. (2010), the application of nine different treatments combining N, as ammonium nitrate (NH_4NO_3) (33.5 %N) and K as potassium sulphate (K_2SO_4) (48.5 % potassium oxide) showed that N treatments increased oil content but K treatments did not. Although neither of the fertilizer treatments had a significant effect on carvone content, both fertilizer treatments did slightly increase the limonene content (El-Din Ezz et al., 2010).

There is evidence indicating that the application of different organic and synthetic fertilizers does not affect caraway yield (Acimovic, 2013) or its essential oil content (Aćimović et al., 2015). Kozera et al. (2013) evaluated the effect of three NPK fertilizer rates on the yield, essential oil content, and mineral composition of caraway. Their results show that although added fertilizer increased caraway yield, higher rates of NPK decreased the essential oil content and mineral composition, which were highest with the lowest NPK rate. In contrast, Valkovszki and Németh-Zambori (2011) found that K application increased the carvone content in oil from annual caraway; using 80 kg/ha as K_2SO_4 (50 % K).

A wide range of research shows that foliar application of Mg and micronutrients significantly enhances yield, oil content, and oil quality of several oil-producing plants, for example rapeseed (*Brassica napus* L.) (Yang et al., 2009; Bahrani and Pourreza, 2014), fenugreek (*Trigonella foenum-graecum* L.) (Boghdady, 2017), palmarosa (*Cymbopogon martinii* (Roxb.) Wats.) (Rao and Rajput, 2011), sunflower (*Helianthus annuus* L.) (Jabeen et al., 2013), and black cumin (*Nigella sativa* L.) (Rezaei-Chiyaneh et al., 2018). In contrast, micronutrient treatments in safflower (*Carthamus tinctorius* L.) resulted in small or no effect on oil content and fatty acid profile (Movahhedy-Dehnavy et al., 2009).

Clearly there is plenty of evidence indicating that the abovementioned nutrients play an important role in key physiological processes and in the quality of crop products, particularly that of essential oil content. However, such studies are not available for all nutrients or for caraway. To our knowledge, this is the first research evaluating the effect of Cu, Mg, Mn, and Zn foliar sprays on caraway yield formation and oil composition, of both volatile monoterpenes and fatty acids. The aim of this research is to determine whether foliar-applied nutrient sprays of Cu, Mg, Mn, and Zn are effective in improving caraway oil quality. Better quality caraway oil would be important for farmers, who would receive a premium price, and for industries whose processes would be more efficient by starting with a better raw material (i.e., higher quality seeds).

2. Materials and methods

2.1. Field experiment design

The field experiment was established at the Viikki Research Farm, University of Helsinki, Finland (60.219 °N, 25.031 °E, 2 m above sea level (m.a.s.l). Biennial caraway cv. 'Record' (Czech origin) was sown on 30 May 2016 and its cultivation continued until August 2018. The experimental set up was a randomized complete block design with four replicates, and the nutrient treatments were applied each year in a different area within the same 9.4 ha caraway field. Plot size was 1.5 m × 8 m in both years. The seed rate used at sowing was 15 kg/ha for a target density of 350 seedlings/m^2.

The experiment included four treatments of a flowable liquid fertilizer (referred as foliar spray across the manuscript) applied to a 15 cm tall plant stand and an untreated control. The foliar sprays used were YaraVita (Yara Oy, Espoo, Finland) products—COPTRAC (Cu 500 g/l, applied at 0.5 L/ha), MAGTRAC (Mg 300 g/l, applied at 4 L/ha), MANTRAC PRO (Manganese (Mn) 500 g/l, applied at 1 L/ha), or ZINTRAC (Zn 700 g/l, applied at 1 L/ha) —and an untreated control.

2.2. Field management and soil characteristics

The soil in the experimental site consists of a sandy loam topsoil and a clayey subsoil, which has stagnic properties (35.8 % clay, 56.1 % silt, and 8.1 % sand). The total carbon content is about 9.6 %, and it is assumed that all C in this slightly acidic soil is organic. Even though this particular soil has not been morphologically investigated, it can tentatively be classified according to the World Reference Base system as Eutric Gleyic Planosols (Drainic) and according to Soil Taxonomy as Aquic Haplocryolls. Comprehensive soil descriptions of nearby fields have been reported by Mokma et al. (2000), where the present soil most closely resembles the pedon 3. In terms of soil fertility, pH (H_2O) was 6.3 in 2017 and 2018, all minerals were at least at an adequate level, and deficiency of these nutrients cannot be expected, except for Mn, which was low in both years (Table 1).

In 2016, the establishment year, the field was fertilized with 20 kg/ha Yara CAN27 +Mg (N-P-K-Mg: 27-0-0-2.4, Yara, Espoo, Finland) and 20 m^3/ha cow manure, containing 1.5 kg/m^3 soluble N, 0.59 kg/m^3 P, and 1.7 kg/m^3 K. In 2017, plots were fertilized with 195 kg/ha Belor Standard Typpi (N-P-K-S [S = sulphur]: 38-0-0-8, Belor Agro, Salo, Finland). In 2018, plots were fertilized with 270 kg/ha YaraBela Suomensalpietari (N-P-K: 27-0-1, Yara Suomi Oy, Espoo, Finland).

Table 1
Soil nutrients (mg/l) and pH at the experimental sites in 2017 and 2018.

Characteristic	Year	
	2017	2018
Boron	0.8	0.7
Calcium	3045.0	2925.0
Copper	37.7	21.2
Magnessium	310.0	306.3
Manganese	5.5	4.5
Sulfur	28.3	25.1
Phosphorus	11.7	12.0
Potassium	221.5	283.8
Zinc	9.4	5.2
pH	6.3	6.3

2.3. *Weather conditions*

The 2017 growing season was mild, while that of 2018 was considerably warm compared with the long-term temperature records particularly in May, July, and August (Table 2). Furthermore, the accumulated precipitation for May and July in both years was considerably low (compared with long-term precipitation records); thus both growing seasons had similar drought periods (Table 2). The climate of the experimental field site clearly falls within the boreal zone (Brandt, 2009) and thus the caraway was grown under conditions with day length fluctuating between approximately 11 and 18 h long (Helsingin yliopiston kalenteripalvelut Oy, 2020).

2.4. *Field measurements and seed chemical analysis*

2.4.1. *Plant and soil sampling*

At maturity, a subplot of 1 m^2 was harvested on 28 August 2017 and 17 August 17 2018 by cutting the plants at the soil surface by hand. They were then threshed and dried at 40 °C and stored at room temperature until further analysis. Before the chemical analyses, seed samples were milled to pass through a 0.5 mm sieve (Centrifugal Mill ZM200, Retsch, Haan, Germany). An additional ten plants were collected from each plot by hand on 23 August 2017 and 17 August 2018. From each plant, the number of lateral shoots and branches on the main stem was counted, the diameter of the secondary umbel and the main umbel was measured, and the number of umbellets in the main umbel and umbels per plant was counted. At maturity, all plots were harvested on 29 August 2017 and 17 August 2018, threshed, and seed yield and 1000 seed weight measured. Soil samples were collected from the topsoil (0–10 cm) across each of the plots in a "W'' pattern and pooled. Analysis of soil type, pH, and content of B, Ca, Cu, Mg, Mn, S, P, K, and Zn was conducted by Eurofins Expert Services Oy (Espoo, Finland).

Table 2
Monthly mean air temperature and total precipitation during the 2017 and 2018 growing seasons and long-term temperature (LTT) and precipitation (LTP) for the 30-year normal period 1981–2010 in Kaisaniemi, Helsinki, Finland (Pirinen et al., 2012).

	Air temperature (°C)		LTT	Precipitation (mm)		LTP
Month	2017	2018	(°C)	2017	2018	(mm)
May	9.3	14.4	10.2	12	6	37
June	13.3	14.9	14.6	66	47	57
July	15.6	20.6	17.8	26	26	63
August	15.9	18.2	16.3	83	54	80
September	11.7	13.5	11.5	54	42	56
Growing season record minimum	−2.1	−0.8				
Growing season record maximum	23.8	30.0				
Total				241	175	

LTT = long-term temperature.
LTP = long-term precipitation.

2.4.2. *Seed chemical analysis*

2.4.2.1. Fatty acid analysis. Oil was extracted from the milled caraway seed flour using the 'accelerated solvent extraction' (ASE) method, using acetone and an ASE instrument (Dionex ASE-200, Dionex Corporation, Sunnyvale, CA, USA). The ASE extraction, evaporation and methylation of caraway oil, was done with an internal standard as described in Lampi et al. (2015). The fatty acid composition was analyzed using gas chromatography with a flame ionization detector (GC-FID) on a gas chromatograph (GC-2010+, Shimadzu Corporation, Kyoto, Japan) equipped with a split injector set to a split ratio of 1:40 and an FID (Shimadzu Corporation, Kyoto, Japan) with a CP-Sil 88 column (100 m ×0.25 mm, 0.2 µm). The temperature program for the separation of the fatty acid methyl esters was the "column oven temperature": 4-min isothermal in the column oven at 70 °C, then 30 min at 170 °C, and followed by 60 min at 220 °C.

The sample volume injected was 1 µl. The injector temperature was 240 °C. Helium was used as a carrier gas at a pressure of 197.7 kPa. The data processing was performed with the GC Solution program running under Windows (Microsoft Corporation, Redmond, Washington, USA). The amount of fatty acids was expressed in mg/g. Methyl nonadecanoate and methyl petroselinate were used as internal standards (Nu-Chek-Prep, Minnesota, USA).

2.4.2.2. Volatile compound analysis. For characterizing the main volatile compounds carvone and limonene (commonly referred to as essential oils), approximately 0.2 g of caraway flour was weighed using three technical replicates per field replicate. Samples were analyzed by headspace solid-phase micro-extraction coupled to gas chromatography—mass spectrometry (HS-SPME-GC-MS). The SPME fiber used was divinylbenzene/carboxen/polydimethylsiloxane (DVB-CAR-PDMS; 50/30 µm). The incubation time was 20 min and the extraction time 30 min. The extraction temperature was set at 40 °C.

(R)-(+)-limonene and (+) – carvone analytical standards (Sigma Aldrich, St. Louis, MO, USA) were mixed with rapeseed oil to be used as standard mixtures at concentrations of 2–75 and 3–95 mg/g for limonene and carvone, respectively. Standard solutions of 0.2 g were prepared and run with each set of samples.

2.5. *Statistical analysis*

Results from all agronomic measurements and the oil quality analysis were analyzed using univariate analysis of variance, specifically a two-way ANOVA, which allowed accounting for two factors: treatment (foliar applied nutrient) and year of cultivation. Differences were considered significant as follows: *,**,*** when P values were <0.05, <0.01, <0.001 respectively. Correlation analysis was done on seed essential oil content concentrations and yield. All analyses were done using SPSS (Version 24, IBM, Armonk, NY, USA).

3. Results and discussion

3.1. *Yield components, yield and 1000 seed weight*

The univariate analysis of variance indicated that cultivation year had a significant effect on most of the yield components measured, including diameter of secondary umbel, diameter of main umbel and number of branches ($P < 0.001$), on total number of umbels per plant ($P < 0.01$), and number of lateral shoots ($P < 0.05$). However, year did not affect the number of umbellets in the main umbel ($P > 0.05$), this trait was the most stable yield component, usually being around nine umbellets in the main umbel irrespective of year. The univariate analysis of variance also showed that the effect of nutrient foliar spray and the interaction of year × treatment did not have a significant effect on any of the yield components (Table 3).

In 2018, the plants had a noticeably higher number of branches holding axillary umbels and thus the total number of umbels per plant was also higher in that year (Table 3). Earlier, Seidler-Lozykowska and Bocianowski (2012) also found a positive correlation between number of branches on the main stem and number of umbels per plant.

Although in 2018 the number of branches and umbels was higher, this did not translate into a higher plot seed yield nor biomass. Year of cultivation had a significant effect on seed yield and biomass of caraway ($P > 0.001$), which was expected as this biennial caraway is known to yield less in the second yield-bearing year than in the first yield-bearing year (Keskitalo, 2014).

The foliar spray did not significantly affect caraway seed yield and biomass, nor did the interaction between year and treatment ($P > 0.05$). In the first year of harvest, the lowest yield, 248 g/m^2, was achieved with the Mn treatment, while the highest yield, 278 g/m^2, was achieved with both Cu and Mg treatments. In the second year of harvest, the lowest yield, 114 g/m^2, was achieved without nutrient treatment, while the highest yield, 160 g/m^2, was achieved with the Mg treatment (Fig. 1). Caraway yields are known to fluctuate markedly between years, which is due to the long biennial life cycle of the crop and the seed shattering risk of some cultivars (Bowmeester et al., 1995; Van Roon and Bleijenberg, 1964). In some cases, a second harvest year yield has been 75 % lower than the first harvest year yield (Hälvä et al., 1986). Although, it is known that in experimental plots the yield is usually higher than at farm level (Van Dijk et al., 2017), our results indicate that there is some potential in the Mg treatment to increase the yield during the second year harvest. Thus, it is worth testing its effect at a larger scale and in different soil types.

In Finland, Keskitalo (2014) showed that the yield of caraway in the first year fluctuates between 1771 and 2014 kg/ha, while in the second year it fluctuates between 280 and 509 kg/ha. The within-year fluctuations are mainly due to place of cultivation, N fertilizer application, and weed incidence (Keskitalo, 2014). Cultivar Record, the most commonly used in Finland, is reported to yield between 333 and 600 kg/ha in the second year of harvest (Keskitalo, 2014); thus the second year yields obtained and particularly those with the Mg treatment are well above the country average.

The foliar sprays did not have an influence on seed weight. The 1000 seed weight was within the range 2.07–3.29 g reported in other caraway studies (Acimovic et al., 2015; Bowmeester et al., 1995; Sedláková et al., 2018; Seidler-Lozykowska and Bocianowski, 2012)

3.2. Fatty acid composition

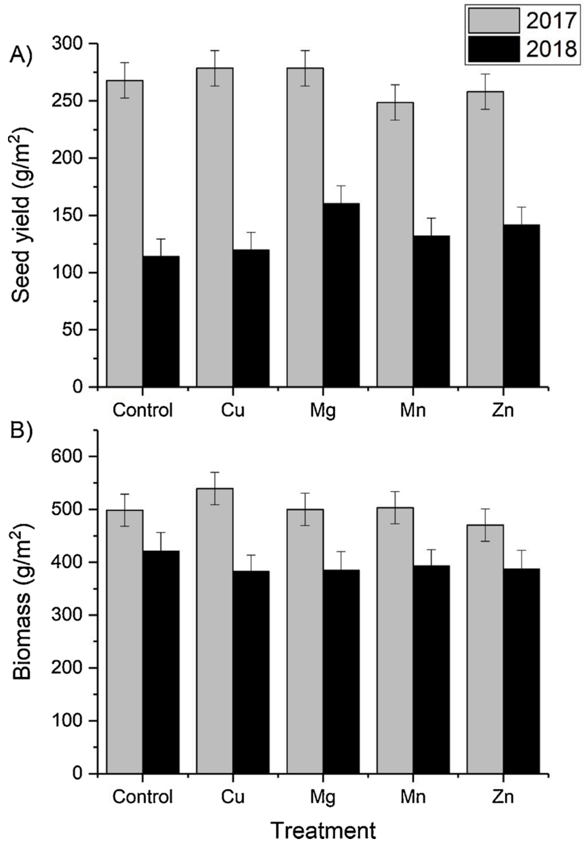

Fig. 1. A) Seed yield (g/m^2) and B) biomass (g/m^2) of caraway plants treated with different foliar-applied nutrients during years 2017 and 2018. Error bars show standard error. For seed yield values are means of four replicates (n = 4) and for biomass values of Control, Mg and Zn are the mean of three replicates (n = 3) due to plant lodging in some plots, and for Cu and Mn values are the mean of four replicates (n = 4).

The overall fatty acid profile of seeds from caraway plants treated with four different foliar sprays and the untreated control plants is given in Table 4. Across all treatments and cultivation years, 13 fatty acids were identified in caraway oil, and it is clear that the most abundant fatty acid is petroselinic acid, followed by linoleic and oleic acids (Fig. 2), which is in accordance with values reported for caraway cultivated in Tunisia, Germany, and Egypt (Laribi et al., 2010, 2013). Indeed, Ngo-Duy et al. (2009) reported petroselinic acid followed by linoleic acid as the two main fatty acids present in caraway and other plants from the Apiaceae family, including celery (*Apium graveolens* L.), carrot (*Daucus carota* L.), and parsley (*Petroselinum crispum* (Mill.)

Table 3
Yield components of caraway plants treated with different foliar-applied nutrients and a control. Measurements were taken during both yield-producing years 2017 and 2018. Data shown were calculated based on means of ten plants measured per experimental plot and four field replicates, n = 4.

Treatment	Lateral shoots, (number/plant)		Branches, (number/plant)		Total number of umbels/plant		Umbellets in main umbel (number)		Diameter of main umbel (cm)		Diameter of secondary umbel (cm)		1000 seed weight (g)	
	2017	2018	2017	2018	2017	2018	2017	2018	2017	2018	2017	2018	2017	2018
Control	0.13	0.15	5.98	7.25	11.68	20.53	9.68	9.65	9.91	7.16	7.63	5.94	2.80	3.10
Copper	0.43	0.00	5.78	6.50	12.03	14.75	9.53	9.20	10.08	6.64	7.78	6.18	2.67	3.11
Magnesium	0.45	0.03	5.13	7.10	12.33	17.58	9.08	9.40	9.74	7.35	7.79	6.24	2.73	3.12
Manganese	0.75	0.05	6.40	7.18	16.88	16.75	8.80	9.25	9.90	7.77	8.18	6.46	2.74	3.11
Zinc	0.53	0.00	6.03	6.70	12.75	15.75	9.68	9.68	9.90	6.91	7.80	6.14	2.76	2.98
Treatment	N.S.		N.S.		N.S.		N.S.		N.S.		N.S.		N.S.	
Year	*		***		**		N.S.		***		***		***	
Treatment × year	N.S.		N.S.		N.S.		N.S.		N.S.		N.S.		N.S.	

*,**,***: significant at $P < 0.05$, 0.01 and 0.001, respectively.
N.S. = not significant.

Table 4

Mean fatty acid concentration in seeds of caraway plants treated with different foliar applied nutrients. Total fatty acids is the sum of all fatty acids listed in the first column. Values shown are means of four field replicates (n = 4), for each of two years of harvest: 2017 and 2018.

Fatty acid / Nutrient treatment	Control				Copper				Magnesium				Manganese				Zinc				Significance of effects		
	2017		2018		2017		2018		2017		2018		2017		2018		2017		2018		Y	T	Y x T
	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.	mg/g	S.E.			
C16:0	4.51	0.50	4.52	0.44	3.88	0.44	4.13	0.44	3.90	0.44	3.67	0.44	3.79	0.50	5.44	0.44	3.89	0.50	4.43	0.44	N.S.	N.S.	N.S.
C16:1 (n-7)	0.11	0.01	0.08	0.01	0.09	0.01	0.08	0.01	0.09	0.01	0.08	0.01	0.09	0.01	0.11	0.01	0.09	0.01	0.09	0.01	N.S.	N.S.	N.S.
C16:1 (n-9)	0.07	0.02	0.16	0.01	0.06	0.01	0.16	0.01	0.06	0.01	0.12	0.01	0.06	0.02	0.22	0.01	0.06	0.02	0.16	0.01	***	*	*
C18:0	1.12	0.14	1.17	0.12	0.93	0.12	1.05	0.12	0.95	0.12	0.9	0.12	0.91	0.14	1.39	0.12	0.94	0.14	1.12	0.12	N.S.	N.S.	N.S.
C18:1 (n-7)	0.66	0.07	0.81	0.06	0.43	0.07	0.82	0.06	0.45	0.07	0.64	0.06	0.52	0.07	1.07	0.06	0.56	0.07	0.81	0.06	***	*	*
C18:1 (n-9)	11.75	1.73	13.68	1.50	9.74	1.50	12.55	1.50	9.77	1.50	10.72	1.50	9.28	1.73	17.68	1.50	9.68	1.73	13.8	1.50	**	N.S.	N.S.
C18:1 (n-12)	32.02	5.19	36.13	4.49	26.85	4.49	32.79	4.49	27.68	4.49	27.92	4.49	24.61	5.19	47.93	4.49	26.10	5.19	36.88	4.49	**	N.S.	N.S.
C18:2 (n-6)	29.42	4.02	31.73	3.48	25.04	3.48	29.2	3.48	25.35	3.48	25.21	3.48	23.71	4.02	40.35	3.48	24.65	4.02	32.26	3.48	*	N.S.	N.S.
C18:3 (n-3)	0.4	0.04	0.39	0.04	0.37	0.04	0.38	0.04	0.37	0.04	0.32	0.04	0.33	0.04	0.47	0.04	0.35	0.04	0.39	0.04	N.S.	N.S.	N.S.
C20:0	0.27	0.04	0.31	0.03	0.33	0.03	0.29	0.03	0.34	0.03	0.27	0.03	0.31	0.04	0.35	0.03	0.26	0.04	0.3	0.03	N.S.	N.S.	N.S.
C20:1	0.05	0.01	0.06	0.01	0.04	0.01	0.05	0.01	0.04	0.01	0.04	0.01	0.04	0.01	0.08	0.01	0.04	0.01	0.06	0.01	**	*	N.S.
C22:0	0.27	0.01	0.25	0.01	0.28	0.01	0.27	0.01	0.24	0.01	0.24	0.01	0.25	0.01	0.25	0.01	0.26	0.01	0.24	0.01	N.S.	N.S.	N.S.
C22:1 (n-9)	0.14	0.02	0.12	0.02	0.19	0.02	0.14	0.02	0.19	0.02	0.12	0.02	0.20	0.02	0.11	0.02	0.18	0.02	0.12	0.02	***	N.S.	N.S.
Total fatty acids	80.46	11.74	89.38	10.17	68.00	10.17	81.91	10.17	69.20	10.17	70.14	10.17	63.77	11.74	115.44	10.17	66.78	11.74	90.64	10.17	**	N.S.	N.S.

S.E. = standard error.
Y = cultivation year.
T = nutrient foliar spray treatment.
Y × T= interaction of year by treatment.
*,**,***: significant at $P < 0.05$, 0.01 and 0.001, respectively.
N.S. = not significant.

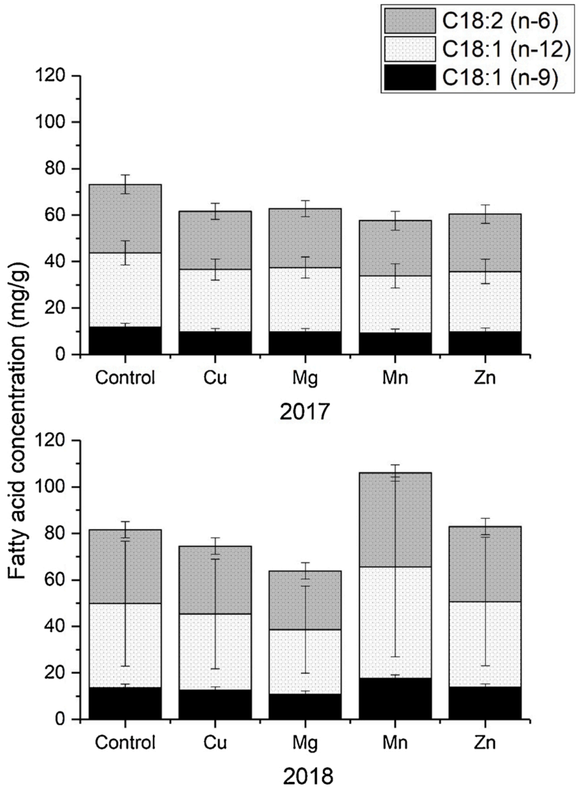

Fig. 2. Concentration of the main fatty acids in caraway oil—linoleic (C18:2 (n-6)), oleic (C18:1 (n-9)), and petroselinic (C18:1 (n-12)) acid (mg/g) —from caraway plants treated with different nutrient foliar sprays during years 2017 and 2018. Error bars show standard error. Values shown are means of four replicates (n = 4).

Nym.).

Year had a significant effect on the total fatty acid (TFA) concentration but not the foliar spray treatments. In 2017, the TFA concentration of caraway seed oil was highest in the untreated control plants with 80.5 mg/g. In contrast, in 2018 TFA concentration was highest after Mn with 115.4 mg/g (being almost twice the 63.7 mg/g from the previous year), followed by Zn with 90.6 mg/g and the control with 89.4 mg/g (Table 4). Since with all treatments the TFA concentration was highest in 2018, it is possible that the drier and warmer weather may have had an effect on the increased TFA concentration in that year.

In three Tunisian caraway ecotypes, petroselinic acid content ranged between 31.53 and 38.36 % (Laribi et al., 2010) while in German and Egyptian caraway it was 30.88 and 29.46 %, respectively (Laribi et al., 2013). In our study in Finland, petroselinic acid content ranged between 38.59 and 41.47 % (equivalent to between 24.61 and 47.93 mg/g in concentration) being highest with Mn treatment (Fig. 2). In contrast, oleic acid (C 18:1(n-9)) in our experiments was between 14 and 15 % (equivalent to between 9.2 and 17.6 mg/g in concentration), thus being considerably below the range reported in Germany and Egypt, i.e., between 21 and 27 %.

The effect of foliar spray was only significant on the concentration of palmitoleic acid (C16:1 (n-9)), vaccenic acid (C18:1 (n-7)), and eicosenoic acid (C 20:1); there was also a significant interaction of treatment by year for the former two fatty acids (Fig. 3). Since most fatty acids concentrations were highest in 2018 after the Mn treatment, except for behenic acid (C22:0) (which was highest with the Cu treatment) and erucic acid (which was highest in 2017 with Mn treatment), it could be argued that the Mn foliar spray is the most promising and apparently more effective when applied in the second year of harvest. Moreover, it seems to be the case that only erucic acid is sensitive to high temperatures and decreased precipitation, as it was the only fatty acid concentration to be lower in all treatments in 2018.

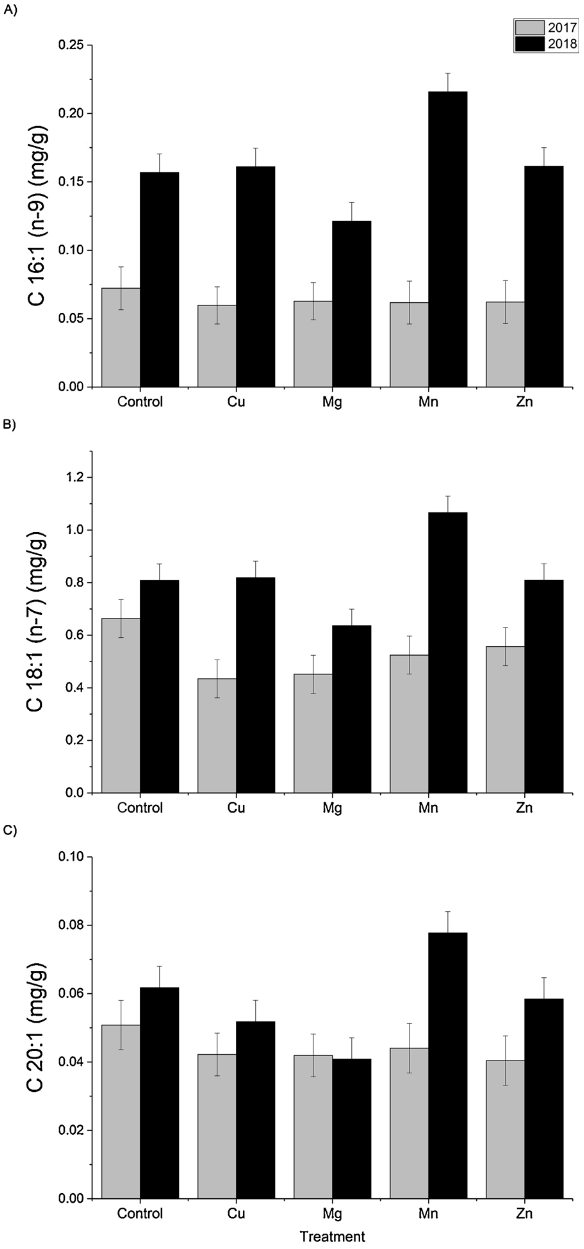

Fig. 3. Fatty acids in which there was a significant effect from year of cultivation and nutrient foliar spray: A) palmitoleic acid, B) vaccenic acid, and C) eicosenoic acid. Error bars show standard error. Values shown are means of four replicates (n = 4).

The effect of cultivation year on fatty acid concentration was significant for most fatty acids, except for C16:0, C16:1 (n-7), C18:0, C18:3 (n-3), C20:0, and C22:0 (Table 4). The concentration of palmitoleic acid (C16:1 (n-9)) and vaccenic acid (C18:1 (n-7)) was significantly higher in 2018 than in 2017 across all treatments, and for both fatty acids the highest concentration was achieved after the Mn treatment. A similar trend was observed for the eicosenoic acid (C20:1), with the exception that the concentrations obtained after the Mg treatment were slightly lower in 2018 (Fig. 3). Interestingly, in 2017, all treatments gave approximately the same concentration of palmitoleic acid (Fig. 3), but for vaccenic acid it was considerably higher in the untreated control, followed by Zn, Mn, Mg and Cu treatments. Thus, the interaction of year and treatment was more pronounced for the vaccenic acid than for the palmitoleic acid.

Higher mean air temperatures generally induce lower levels of polyunsaturated fatty acids (PUFAs) and higher levels of saturated fatty acids and MUFAs (Fila et al., 2020). For example, in seeds of canola (*Brassica napus* L. ssp. *oleifera* (Moench.) Metzg.), sunflower, soybean (*Glycine max* (L.) Merr.), and flax (*Linum usitatissimum* L.) found that increases in temperature from 10 to 40 °C decreased the content of linoleic (C18:2 (n-6)) and linolenic acid (C18:3 (n-3)), but increased that of oleic acid (C18:1) (Fila et al., 2020; Schulte et al., 2013; Singer et al., 2016). In contrast, the fatty acid profile of camelina (*Camelina sativa* (L.) Crantz) was considered to be temperature insensitive (Schulte et al., 2013).

MUFA content increased at higher temperatures in soybean and sunflower, and PUFA content decreased, while in canola and camelina such changes were minimal (Schulte et al., 2013). In our study, no specific trend between concentrations of MUFAs and PUFAs was observed in response to the warmer temperatures in 2018. The higher temperatures in 2018 did not decrease linoleic acid concentration in any of the treatments, while linolenic acid concentration only decreased in the control and Mg treatments, and as mentioned before erucic acid was the only fatty acid to be lower across all treatments that year (Table 4). Thus, it seems that caraway fatty acids show a minimal response to temperature changes, but studies under controlled conditions are still needed to test this at more extreme temperatures than those occurring in our field trials.

It is evident that the Mn treatment was the most promising to improve the fatty acid concentration in caraway oil, since in 2018 it considerably increased the content of palmitic, oleic, linoleic, and petroselinic acid by 1, 4, 8, and 10 mg/g, respectively, compared with the other treatments (Table 4). Such an increase is worth noting as while all four of these fatty acids are of industrial importance, petroselinic acid is of particular interest as it is relatively rare and can be cleaved to produce a mix of lauric acid and adipic acid (Bettaieb et al., 2011; Laribi et al., 2013).

Further field experimental research on the effect of a Mn foliar spray on the fatty acid composition of caraway seeds is needed to understand its effects with different soil types, dosages, and timing of application. However, field experiments are time-consuming since caraway is a biennial plant and thus the foliar spray treatments take 3 years to be completed, including the sowing year and the two subsequent harvest years.

3.3. *Essential oil composition*

The univariate analysis of variance showed that for both limonene and carvone the foliar spray ($P < 0.001$), year of cultivation ($P < 0.01$ and $P < 0.001$, respectively), and their interaction ($P < 0.001$), had a significant effect. However, the foliar sprays did not outperform the untreated control (Fig. 4). The interaction of foliar spray by year of cultivation was expected as it is known that both fertilization and growing conditions (i.e., temperature, radiation, and water availability, which vary from year to year) have an impact on essential oil content and composition (Balbino, 2017; Bouwmeester et al., 1995; Solberg et al., 2016).

The content of limonene in the control treatment was consistent during both years, being on average 28 mg/g. For most foliar sprays the content of limonene was higher in 2017, but not for the case of Mn, which performed better in 2018. The Cu treatment resulted in the lowest limonene content in 2018 with ~ 20 mg/g, while the highest was achieved in the same year by the Mn treatment with an average of 28.7 mg/g; while at the plot replicate level the Mn treatment achieved up to 31.8 mg/g.

The content of carvone was consistently lower in the second year of harvest, being lowest in 2018 across all treatments. The untreated control had the highest carvone in both years, being 86.9 mg/g in the first year and 61 mg/g in the second year of harvest. Mg had the second highest carvone content in 2017 with ~79 mg/g and Mn in 2018 with 60 mg/g.

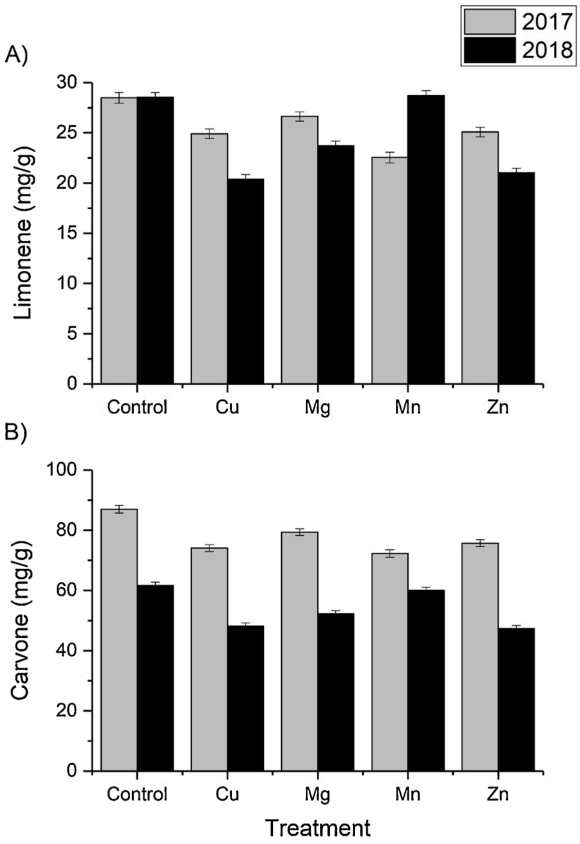

Fig. 4. A) Limonene and B) carvone concentration (mg/g) in seeds of caraway plants treated with different nutrient foliar sprays during years 2017 and 2018. Error bars show standard error. Values shown are means of four replicates (n = 4).

Overall, carvone content of the seeds decreased less between years following Mn treatment. Furthermore, Mn treatments also caused an increase in limonene in the second year in contrast to the trend for all other treatments. Thus, it is worth exploring this treatment further, as it is important to elucidate whether it could have a clearer positive effect on the essential oils if applied on the sowing year or on the first or second year of harvest.

Notwithstanding this increase in limonene in the second year with Mn treatment, the concentration of limonene did not fluctuate across years with the control treatment, while the carvone concentration was much lower in the second year of harvest. Across treatments, it is definitely clear that the reduction in carvone was markedly larger than that in limonene from the first to the second year of harvest. Nevertheless, in both years the carvone concentration was always much higher than the limonene concentration, meaning that the oil was of high quality as a larger carvone-to-limonene ratio is usually used as a standard to evaluate caraway oil quality (Galambosi, 1996).

Previously, Galambosi (1996) and Hälvä et al. (1986) reported carvone to represent 48–56 % of the oil in caraway cultivated in Finland. The carvone content of caraway seeds from Tunisia, Germany, and Egypt was about 76, 77, and 61 %, respectively (Laribi et al., 2013). In Poland, the carvone content of caraway accessions cultivated in botanical gardens ranged between 59 and 83 %, and cv. Record 64 %, indicating that the oil composition varies largely depending on the genotype (Seidler-Lozykowska et al., 2010). The carvone content in our caraway field trials is certainly within the range reported in the mentioned studies, and despite the lower values of 2018, overall carvone in all treatments was well above 50 % in both years (Fig. 4).

In contrast, Solberg et al. (2016) reported considerably lower values of carvone—14 % in Iceland and 13 % in Sweden—in two commercial cultivars and two wild populations of caraway. This is in disagreement with earlier reports by Galambosi (1996) who found a more even ratio between carvone (50–55 %) and limonene (42–49 %) in wild and cultivated caraway in Fennoscandia.

Our experiments were done in a field that had a high level of Cu, good levels of both Mg and Zn, and low but not limiting levels of Mn (Table 1). The low Mn value in the research farm site is expected, as topsoils in the North of Europe have a much lower Mn content than elsewhere in Europe (Natural Resources Institute Finland, 2021; Tóth et al., 2016). As with other crops, for caraway cultivation, the usual management practice is to focus on NPK fertilization, while secondary nutrients (e.g. Mg) and other micronutrients (Cu, Mn, Zn) are rarely included in the fertilization plan. Our results show that it is important to supply both Mg and Mn in the second year of harvest, to aim for a higher content of fatty acids and higher seed yield. The effect of the foliar nutrient treatments was not as clear on the main terpenes, but Mn appears to be conducive to higher terpene concentration in the second year, while all other treatments performed worse than the control.

4. Conclusion

Our results indicate that Mg and Mn foliar spray treatments are the most promising ones to improve caraway seed yield and oil quality. The Mg foliar spray increased the seed yield in the second year of harvest, which is key as in the second year the yield is considerably lower in biennial caraway. The Mn foliar spray increased the fatty acid content and the limonene content in the second year of harvest. Although carvone is the main component of interest in caraway, limonene is also of industrial importance, so it is useful to have achieved this increase for use in different industrial products. Further research is underway to expand the understanding of how to customize the Mg and Mn management to improve caraway oil quality. However, oil quality is also dependent on other factors such as genotype and environmental factors; thus additional research testing all factors is needed.

CRediT authorship contribution statement

Clara I. Lizarazo: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - original draft, Visualization, Project administration, Funding acquisition. **Anna-Maija Lampi:** Methodology, Investigation, Resources, Writing - review & editing. **Pirjo S.A. Mäkelä:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors report no declarations of interest.

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